

# Adhesives from Renewable Resources

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# Foreword

The ACS SYMPOSIUM SERIES was founded in 1974 to provide a medium for publishing symposia quickly in book form. The format of the Series parallels that of the continuing ADVANCES IN CHEMISTRY SERIES except that, in order to save time, the papers are not typeset but are reproduced as they are submitted by the authors in camera-ready form. Papers are reviewed under the supervision of the Editors with the assistance of the Series Advisory Board and are selected to maintain the integrity of the symposia; however, verbatim reproductions of previously published papers are not accepted. Both reviews and reports of research are acceptable, because symposia may embrace both types of presentation.

# Preface

**T**HE OBJECTIVE OF THIS SYMPOSIUM was to include research on a broad range of natural products directed to a wide variety of bonding applications. The speakers described research on adhesive polymers derived from lignins, tannins, carbohydrates, terpenes, and proteins for applications as diverse as tire-cord bonding and eye surgery.

Byproducts of the forest products industry are potentially primary sources of natural resource-based adhesives. Because this industry is both a producer of huge tonnages of residues and a major consumer of adhesives, this book focuses on adhesives from renewable resources derived from trees. Composites made from wood will remain the primary materials used for the construction of homes and their furnishings for the foreseeable future.

The date of the symposium on which this book is based marked the 15th anniversary of the severe petroleum shortage of 1973–1974. Much of the research presented in this volume was begun in the early 1970s in response to shortages of petroleum-based adhesives for the forest products industry when the nation was in the midst of a record-setting demand for housing materials. Left with this indelible memory, the forest products industry has supported the development of adhesives from renewable resources.

The chapters presented in this book show that new alternatives based on renewable resources will be available should supplies of resins derived from petrochemicals become inadequate again. Outstanding opportunities for the development of high-value specialty polymers are highlighted by work presented here on polymers derived from mollusks.

This book is the product of the efforts of chemists from around the world. Our thanks go first to the authors who so kindly contributed papers and patiently responded to our requests. We thank the American Chemical Society for providing a venue for the symposium that made this book possible. We also thank the clerical support staff of the U.S. Department of Agriculture, Forest Service at both the Southern Forest Experiment Station and the Forest Products Laboratory, who tirelessly worked to make this a meaningful enterprise.

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# Chapter 1

## Adhesives from Renewable Resources

### Historical Perspective and Wood Industry Needs

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The wood products industry has a long and successful history of utilizing adhesives based on renewable resources. Their performance was adequate to see us through World War II and beyond. But the tremendous postwar expansion in the petrochemical industry provided compounds for synthetic resin adhesives so inexpensively, they steadily displaced natural adhesives. When embargo threatened key petrochemicals in 1973, their availability dropped and prices increased abruptly. Industry reacted with an immediate partial return to natural adhesives. As oil's availability improved and prices became more competitive, synthetic resin adhesives again became the industry standard. With over 70% of all wood products now bonded, industry is concerned about future sources of adhesives in the event that oil supplies are again disrupted by world events. There is strong support for research into adhesives based on renewable resources with emphasis on: 1) Phenol, methanol, urea, and resorcinol-acting compounds; 2) copolymeric adhesives involving synthetic resins and natural polymers; 3) new adhesive mechanisms and substrate treatments; 4) greater exterior durability for animal and vegetable protein adhesives.

From the days of early Egyptian artisans until the relatively recent past, the woodworking industry was entirely dependent on natural adhesives for all forms of bonded joinery. These applications were then largely preempted by low-cost, durable synthetic adhesive polymers developed from petrochemicals. Since the volume and utility of bonded wood products have greatly expanded and the continuing availability of synthetic adhesives is now somewhat uncertain, more

thorough research into natural adhesive performance and resources is clearly indicated. This overview chapter attempts to project wood industry needs and suggests appropriate areas for investigation.

## History

There is a 58-year-old reference that gives a fairly clear picture of the wood-working industry's adhesive choices from, say, the Industrial Revolution in the mid-1700's until about 1930. The 1929 U.S. Department of Agriculture Bulletin by T. R. Truax entitled "The Gluing of Wood" lists the five classes of adhesives used most in woodworking during that long timespan. These included animal glues, liquid glues, casein and vegetable protein glues, starch glues, and blood albumin glues. Liquid glues were described as a lower strength variety of fish or animal glue that had been stabilized with acid for long-term storage in ready-to-use form. Passing reference was also made to a number of other "adhesive substances" such as sodium silicate, mucilage, pastes, rubber cements, phenol-aldehyde compounds, asphalts, gums, and shellacs that were used occasionally for wood bonding at the time.

Since there were really no other options, the chemistry and application of these naturally derived polymers evolved to a fine art that was summarized occasionally in such publications as the one mentioned. Fully exterior durable adhesives simply did not exist at that time. However, certain natural glues such as alkaline-dispersed casein and blood adhesives did develop a significant degree of water resistance. With adequate surface protection, they could be made to serve exterior purposes on an intermittent basis. This was the state of adhesive technology going into World War I. It was at that point that an urgent need arose for durable wood glues to bond wood laminations into aircraft propeller stock and other wooden elements into the panels and frames of the planes themselves. In the absence of better alternatives, both blood and casein glues were further improved in durability by the alteration of their proteins with various chemical denaturants and by the application of heat during cure. In this form, protein glues served the Allied war effort extremely well, while laying the groundwork for the advanced blood and casein glue technology of later years.

The Second World War saw the extensive use of alkaline-dispersed soybean and blood glues in plywood for all kinds of construction, packaging, and transportation uses. Thus, both vegetable and animal protein glues contributed heavily to wartime logistic successes. During this crisis, with petroleum in critically short supply, a truly exterior blood-based adhesive was developed involving the reaction of alkaline-dispersed soluble blood with cresylic acids. Plywood bonded with this adhesive was still performing well in unprotected outside locations a generation after it was made.

From about 1930 to the present, casein glues have been used successfully for bonding high-strength softwood lumber into glued laminated beams and arches for interior or covered exterior service. Even earlier, until perhaps 1900, casein

glues were used to laminate simpler structural members. Because of their very tolerant assembly properties and strong, gap-filling gluelines, these glues were particularly well suited to this heavy structural application and also to the end grain joinery of millwork.

Animal and starch glues, especially because of their low color and ease of application on complex joint surfaces, were the adhesives of choice in the furniture and cabinet industries from colonial days until the advent of synthetic emulsion adhesives after World War II. Service conditions were limited to dry interior applications, of course. Leaving a chair out in the rain meant dismantling and regluing.

These are just a few of the examples that can be cited with respect to the historical and comparatively recent uses of natural adhesives by the woodworking industry, hence, their familiarity.

### **Advent of Synthetics**

As a result of successfully meeting the challenge of World War II, large oil-refining and petrochemical industries were in place, each with substantial idle capacity, just after the war. The economic pressure to develop new outlets for this productive capacity was tremendous. The synthetic resin and plastics industries as we know them today appear to have been actually created at that time by this pressure. True, resorcinol-formaldehyde resins for bonding white oak into minesweeper frames and birch veneer into helicopter blades were developed during the war to meet national emergencies, but on the basis that cost was no object. It's also true that phenol-formaldehyde resins, initially as dried films on paper and later as liquid resin syrups for adhesive formulating, had been known since the early 1930's. However, the cost of the chemical raw materials to make these synthetic resins was sufficiently high during that period to effectively limit their uses to specialty or military applications.

This situation changed abruptly with the postwar availability of relatively low-cost, high-volume petrochemicals. It was already known that phenolic resin adhesives set a standard of performance for exterior durability that could not be reasonably matched with natural adhesives of any existing type. This fact represented a strong stimulus for commercial research to optimize the performance and extend the applications of phenolic resins. It only remained for the prices of phenol, resorcinol, and formaldehyde to become low enough for phenolic and phenol-resorcinol resins to take over large segments of the bonded wood market. This occurred between 1945 and about 1950. The accompanying Table I of resin production volumes from 1942 through 1959, adapted from the 1962 edition of Irving Skeist's "Handbook of Adhesives," illustrates this rapid growth clearly. By 1978, the annual consumption of phenolic, urea, and vinyl adhesives for all purposes had each passed the billion-pound level.

Initially, only the exterior-bonded product markets fell to the synthetics. Glued products of interior or intermediate durability continued to be largely



the domain of natural adhesives (mainly soybean, casein, and blood) on the basis of their very fast hot-press times or cold-press capability until the early 1960's. At that point, the prices of commodity petrochemicals became so low under worldwide competitive pressures that a compelling case could be made for using exterior synthetic resin adhesives to bond essentially all structural wood products, both exterior and interior. For example, it became cheaper and simpler to purchase additional hot presses in order to reach the plywood production capacity offered until then only by the faster curing protein glues. With this change, the conversion to synthetic resin adhesives was nearly complete.

Table I. Principal Synthetic Resins Produced for Adhesives,  
1942-1959<sup>1</sup>  
(millions of pounds)

Year	Phenolics	Vinyls	Urea and Melamine Types	Total
1942	2.6	1.5	—	4.1
1943	12.7	10.0	—	22.7
1944	26.3	15.0	27.1	68.4
1945	22.0	13.0	30.4	65.4
1946	22.3	16.9	37.5	76.7
1947	31.9	10.0	45.6	87.5
1948	22.3	10.0	50.0	82.3
1949	28.6	11.9	40.8	81.3
1950	31.5	15.5	85.6	132.6
1951	41.9	22.8	78.7	143.4
1952	42.4	17.8	79.8	140.0
1953	106.6	26.9	63.5	197.0
1954	109.6	29.0	86.2	224.8
1955	166.7	37.7	106.7	311.1
1956	169.1	43.9	115.2	328.2
1957	183.4	46.7	107.8	337.9
1958	162.0	52.1	113.2	327.0
1959 (Prelim.)	209.6	59.5	134.1	403.2

<sup>1</sup>Excludes laminating. Source: U.S. Tariff Commission statistics.

A similar story of technical development, raw material cost reduction, and adhesive optimization can also be told for the amino resins, the urea and melamine polymers. Especially because of their versatile hot- and cold-curing capabilities, this development also led to the widespread replacement of natural adhesives. The rapid postwar growth of amino resins, along with phenolics

and vinyls, shows plainly in the Tariff Commission figures for annual resin production. Since the initial use of urea adhesives for plywood in 1937, entire new industries have arisen. The commodity manufacture of particleboard and medium density fiberboard is a familiar example.

Thus, the picture emerges of a multifaceted wood products industry founded largely on natural adhesives but successfully weaned onto synthetic resins by a combination of low material costs and formerly unattainable performance properties. As a result of this improved performance, the development of other useful bonded wood products was heavily stimulated.

### Threat to Supply

The woodworking industry, now converted almost wholly to synthetics, grew and prospered for a decade between 1963 to 1973. Then, the worldwide crude oil crisis abruptly forced petrochemical suppliers to place their products on allocation. Whether the shortage was real or contrived, this interruption of access to low-cost, seemingly endless raw material supplies for synthetic resin adhesives deeply shocked the woodworking industry. This was especially significant because by 1973 about 70% of all wood products required gluing in one form or another. Thus, the threat to existing markets was very real and very large. Wood product manufacturers reacted to this crisis by seeking immediate alternatives wherever possible. In many cases, the older natural adhesives were still available, were still approved by certifying agencies, and were again pressed into service. In other cases, such as the structural flakeboard, waferboard, and strandboard industries, no workable prior alternatives existed. For them, it was phenolic, isocyanate, or possibly amino resins, or nothing. The choices were to operate as efficiently as possible on a reduced basis or simply shut down, as a number of commodity woodworking plants did at that time.

The oil crisis of 1973 is long gone, of course, but the memory of it is indelibly stamped on the woodworking industry. What if there were another oil embargo or a sudden regional war? (Current events in the Middle East make this a distinct possibility.) Or simply, what is going to happen as world oil reserves become increasingly limited in the not-too-distant future, and the transportation/energy industries preempt the remaining supply? There are reassurances, to be sure, such as this recent statement from the April 1987 issue of *Business Month*:

Forget OPEC's \$18-a-barrel goal. European analysts say the price of oil will remain far below that for at least the next five years because of sluggish demand in the industrialized economies and the discovery of vast new reserves in South America, Western Europe and the Far East. "I'm talking about \$15 oil in the first half of the 1990's," says Rotterdam Analyst Walter Ten Brinck. Economists at the Paris-based International Energy Agency agree. Says one, "I can't see oil

above \$15 for a sustained period unless there's a major international crisis. And if that happens, we'll all have more to worry about than the price of oil."

Such indications of continuing oil supply and price allow us to believe that we can look forward to business as usual in the near-term future. However, both from the standpoint of interruptability and also eventual price and supply, the woodworking industry strongly favors current research into renewable raw materials and practical adhesive systems based upon them. This can be seen in the annual review of the USDA Forest Service's research budgets and projects by the National Forest Products Association's Committee on Research Evaluation. For the last 9 years this industry group has strongly and consistently recommended research into alternative wood-bonding systems based on renewable resources. Likewise, groups of woodworking companies have helped support academic research into new adhesive concepts and renewable raw material sources.

### Suggested Research

The research emphasized by industry falls roughly into four categories. First, the recovery or production of today's synthetic resin raw materials directly from renewable resources or as byproducts in waste streams from industries that utilize renewable resources themselves, such as pulp and paper. Examples would be:

1. The recovery of phenol, cresols, and guaiacol by extraction from kraft pulping process black liquor.
2. The steam pyrolysis of kraft black liquor to yield specific phenolic compounds by thermal decomposition.
3. The extraction and possible chemical modification of resorcinol-acting compounds from a variety of tree barks, nut shells, and other natural residues which are high in appropriate tannins.
4. The production of methanol via selective fermentation or direct hydrogenation of carbon monoxide.
5. The oxidation of methane from a variety of natural sources to formaldehyde. (The world's atmosphere is gaining in methane content at the rate of 1% a year.)
6. The bulk extraction of hemicelluloses and pentosans from woody biomass and their conversion to furan compounds.
7. The direct fixation of atmospheric nitrogen and its conversion into ammonia, then urea, then melamine.

Some of these are existing –even classical– processes, but they all share a basis of renewable resource derivation. The list could go on. As a common denominator, the output in this research category is specific organic compounds for reaction into the synthetic adhesive polymers we know and use today. It is understood that the prices of chemical compounds derived from these sources will be substantially higher in most cases. However, organic chemical prices in general will be equally higher due to global limitations on access or supply of crude oil and natural gas.

The second category of industry-favored adhesive research involves synthetic resins of recognizable performance based on partial or total replacement of a critical petrochemical constituent such as phenol with a functional organic compound or residue derived from renewable sources. Examples here include:

1. The institution of fractionated or chemically modified lignin for part or all of the phenol in the synthesis of phenol-formaldehyde resins. This would particularly include the newer forms of lignin recovered with minimum structural alteration and also those representing virtually complete depolymerization to phenylpropane units.
2. The substitution of selected and possibly modified carbohydrates for part or all of the phenol in the synthesis of phenol-formaldehyde resins.
3. The reaction of isolated and probably functionalized tannins from natural sources with formaldehyde to yield low temperature-curing thermoset adhesives. These resins may be suitable for use alone or in combination with conventional resorcinol-formaldehyde or phenol-resorcinol-formaldehyde resins.
4. The incorporation of animal or vegetable protein constituents into phenolic resins to form exterior durable adhesives of fast-curing or special properties.
5. The creation of difunctional or multifunctional isocyanate molecules entirely based on renewable resource chemistry.
6. The development of useful adhesive compositions based on the interaction of isocyanate resins with natural polymers such as lignin, proteins, and carbohydrates.

The third category of adhesive research that is particularly interesting to the woodworking industry relates to the development of entirely new adhesive concepts, including pretreatments of wood surfaces to enhance the bonding capabilities of conventional adhesives. This would even include the unlikely but tempting possibility of autoadhesion of wood to itself. Examples here are fewer but tantalizing:

1. The adhesion or "welding" of wood surfaces to each other on the basis of a chemical pretreatment of the surfaces and probably heat activation.
2. The recovery and reactivation of natural adhesive or living structure polymers into crosslinkers for raw or treated wood surfaces. Examples of these would be:
  - activated lignins
  - carbohydrates converted *in situ* to crude yet functional furan resins
  - solubilized chitin
  - recovered marine bioadhesives activated to bond wood
  - the conversion of cellulose itself or cellulose derivatives into durable adhesives for wood

The fourth research category mentioned in the NFPA review relates to enhancing the performance of established natural adhesives for wood bonding to provide durability equivalent to that of the synthetics. This is especially desirable where natural adhesives presently offer significant performance advantages over synthetics in terms of fast hot-press times, short-cycle cold cure, or improved gap-filling properties. Specific examples would include:

1. Blood glues with permanently boil-proof and mold-resistant bonds. (Both hot- and cold-setting formulations would be desirable.)
2. Soybean-based, quick-clamping cold-press glues of exterior durability and mold resistance.
3. Weatherproof and permanently mold-resistant casein-based laminating glues. (This would include both low-staining formulations for door and millwork assembly and more highly alkaline lumber-laminating adhesives.)
4. Quick-setting collagen-based adhesives for furniture and cabinet assembly that would become permanently insolubilized against the effects of high humidity if not actual wetting after normal cold cure.
5. Sprayable exterior adhesives of competitive performance for structural panels such as flakeboards, waferboards, and strandboards based on renewable resources. (A blood-lignin adhesive for oriented strandboard or waferboard would be an example.)

It should be pointed out that some natural adhesives and constituents remain in general use today, mostly because the properties they contribute are not yet provided by synthetic adhesives, or at as favorable a price. Such current uses include:

1. Alkaline-dispersed amylaceous materials in phenolic plywood adhesives for improved assembly time tolerance and prepress tack.
2. Partially insolubilized animal blood as a very efficient foaming agent in air-extended phenolic plywood glues. The blood solids are also considered active exterior adhesive solids.
3. Casein-soybean adhesives for assembling flush doors in short, room-temperature-curing cycles.
4. Fully soluble animal blood in urea resin glues for hardwood plywood to improve water resistance.
5. Straight casein lumber laminating adhesives for their superior open and closed beam assembly time tolerance and gap-filling properties.

In view of these suggestions and examples, it is evident that the wood products industry retains its faith in natural adhesives and their capabilities even in this era of synthetics. It is likely that the industry will continue to turn to them without restraint as their price or performance dictates. The desire, of course, is to keep the various wood-bonding operations functioning as efficiently as free market conditions and competitive innovation will permit.

### **Industry Priorities**

In a restrictive situation where petrochemicals are no longer freely available, essential priorities emerge. The first priority, of course, is to maintain the performance of any given wood product as near normal as possible and adequate for the intended public use. Our current liability and implied warranty laws prevent the industry from doing otherwise. As a second priority, woodworking companies will consider paying whatever amount is necessary to obtain adhesives that permit the manufacture of on-grade products at normal production rates and costs. The assumption is that the entire competing industry will have to incur this same increased adhesive cost, so the product price structure will remain uniform but at a higher level.

The third priority, that of changing plant process or reducing plant capacity, will only be implemented after all reasonable alternatives have been exhausted. These reductions may take the form of longer press times, more complex or limited assembly procedures, or restrictive handling requirements dictated by the operating characteristics of available adhesives. Loss of productive capacity

for any of these reasons means higher unit costs that can quickly reverse the modest profit margins on commodity wood products. The remaining choice, of course, is shutdown.

Since shutdown represents a clear loss both to the producer and the public, there is an expressed willingness within the wood products industry to accept (even if reluctantly) considerable production change in the interests of continued operation. From this industry position, the message to adhesive scientists seems clear and supportive although perhaps indirect. Namely:

1. The woodworking industry sees a considerable part of its future in glued products of increasing volume and sophistication.
2. Especially because of its vulnerability to interruption in petrochemical adhesive raw material supplies, the woodworking industry strongly endorses research into production adhesives based on renewable resources.
3. The fact that adhesives based on renewable resources may not be fully competitive in price or performance with today's production adhesives should not be a deterrent to their development and optimization.
4. More importantly, it should be understood that failure by industry to immediately adopt and utilize an adhesive based on renewable resources is in no way a reflection on its performance or value. As far as the woodworking industry is concerned, it represents vital reserve technology that will be implemented as circumstances require.
5. Finally, for those adhesive developments based on renewable resources that are immediately competitive and/or unique in performance, the wood products industry will do its share to assist with their evaluation and use. Commercial guidance toward this end will be freely provided.

## Conclusion

These thoughts and suggestions are industrially oriented, to be sure. They arise from practical need and reflect concern for future adhesive supply. Collectively, the various forms of wood utilization represent an extremely large and diverse market for adhesives, probably the largest in the world today. Thus, industrial comments seem appropriate. Apart from identified needs, however, the wood products industry recognizes the value of research into the chemical structure and adhesive mechanisms of natural polymers unrelated to current problems. The next echelon of technical development can be expected to arise from this research. It is also acknowledged that certain of the adhesive performance characteristics requested cannot be accomplished with the current level of scientific information. Finally, it is the wood products industry's view that natural adhesives and resources will inevitably play an important part in its future. Thus, they represent a significant and potentially productive area for current adhesive research.

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# Chapter 2

## Lignin in Adhesives

### Introduction and Historical Perspective

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Lignins, complex organic polymers produced by all vascular terrestrial plants and second in abundance only to cellulose, are the substances holding plant fibers together. They are recovered mainly as byproducts from woodpulp operations with about 75 million tons produced annually worldwide. Over the last hundred years or so, there has been an enormous effort to develop lignin-based adhesives, but this has met with no real commercial success principally due to product variability, dark color, and lack of chemical reactivity. Lignin-based adhesives normally require excessively long curing times and high curing temperatures during composite board production. However, they can be employed as extenders in diverse wood-composite resins with no significant deterioration in the mechanical properties of the board products. This is particularly true if the lignins are activated chemically (e.g., by methylation). Several recent reports have been directed toward improving even further the lignin chemical reactivity (e.g., in the synthesis of soda bagasse lignin-formaldehyde-resorcinol and lignin-isocyanate resins). Apparently, these developments surmount previous difficulties and allow for some cautious optimism for the future.

Terrestrial vascular plants have evolved with a unique capacity to synthesize lignin, whose main physiological functions are to provide rigidity and strength to plant cell walls and to act as a barrier to infection (1). Next to cellulose, lignin is nature's second most abundant organic material and is often described as the material binding plant fibers together (2).

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In gymnosperms, lignin is formed from *p*-coumaryl (1) and coniferyl (2) alcohols, whereas, in angiosperms, sinapyl alcohol (3) is also involved (3). Lignification is generally viewed to occur exclusively via the random, dehydrogenative polymerization of monolignols (1) - (3) (4), a reaction requiring both H<sub>2</sub>O<sub>2</sub> and peroxidase (5) (Figure 1).

It is also well known that the ratio of monolignols (1) - (3) involved in the lignification process is species (6), time (7), light (8) and morphological origin (9,10) dependent. Lignification can apparently also be influenced by gravitational forces experienced by plants during growth (11-19).

The following conclusions can be made with regard to current knowledge of the lignification process: 1) strict enzymatic control leading to the final product apparently does not occur and 2) both regulatory processes controlling its deposition and structure *in situ* are poorly understood.

Lignin formation in plants of many families of Angiospermae, particularly those in Commelinidae of Cronquist (20) (i.e., grasses), suffers from an additional complication due to the presence of cell-wall-bound hydroxycinnamic acids, such as *p*-coumaric (4) (21), ferulic (5) (22,23), 5-hydroxyferulic (6) (24), diferulic (7) (23,25,26), and 4,4'-dihydroxytruxillic (8) acids (27) (Figure 2). These acids have long been speculated to be involved directly in lignification, and this is only now being clarified. This clarification was achieved by administering specifically <sup>13</sup>C-labelled forms of ferulic acid (5) to wheat (*Triticum aestivum* L.). Subsequent analysis of the plant tissue (28) and isolated lignins (29) by solid and solution state <sup>13</sup>C-NMR, respectively, revealed that these acids were covalently bonded to lignin.

### Lignin and Papermaking

The discovery of lignin and its subsequent use in adhesive formulations are intertwined with technological developments in the pulp and paper industry. Surprisingly, it is not generally appreciated that the massive worldwide production of pulp and paper, using wood as a resource, only began about 1850 or so. This is in spite of the fact that formation of paper from wood (e.g., by treatment of mulberry bark with lye) had been developed by Ts'ai Lun in 105 A.D. in China (30) and perhaps even earlier by others (31). However, by the time this technology reached the Western Hemisphere via the Middle East, wood had long been replaced by other plant materials of higher cellulosic content (e.g., cotton, linen, flax). Wood remained forgotten as a source of paper until Rene A.F. de Reamur (1683-1757) noted that wasps produced a paperlike nest from wood (30).

In 1839, Payen discovered that wood was not homogeneous but contained cellulose and an "incrusting material" (32-34) for which Schultze coined the term lignin in 1865 (35). As shown in Table I, chemical woodpulp processes were developed to dissolve away lignin, hemicelluloses, and extractives (30). These represent the major woodpulp processes in operation today.

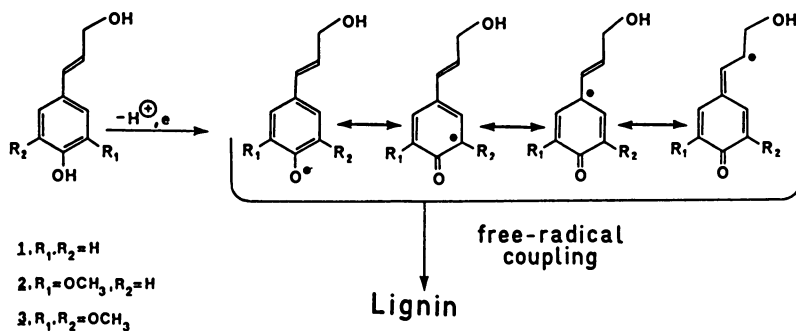


Figure 1. Lignin formation from monolignols (1) - (3).

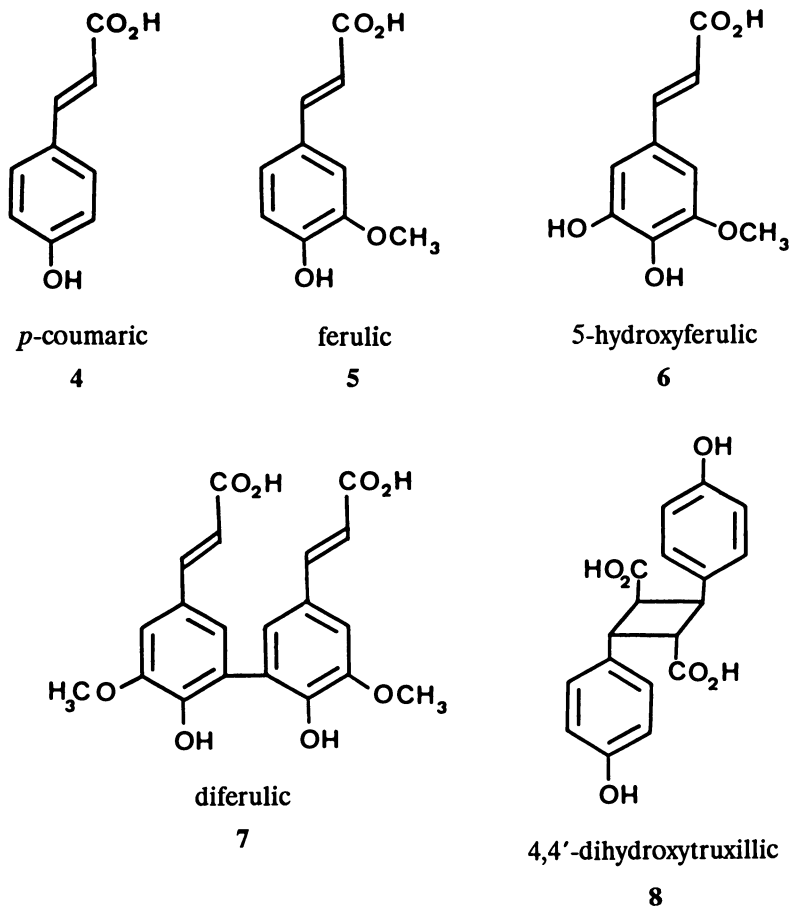


Figure 2. Cell-wall-bound hydroxycinnamic acids.

Table I. Major Chemical Pulping Processes

Type	Developer(s)
Soda	Burgess and Watt (1854)
Sulphite	Tilghman (1857)
Kraft	Dahl (1884)

### Sources of Lignin

Essentially all of the lignin commercially available is isolated as byproducts from either the sulphite or the kraft process. Table II gives a very conservative idea of annual lignin production in the United States (2) and worldwide (36).

Table II. Estimated Annual Production of Lignin  
(millions of tons)

Type	United States	Worldwide
Kraft lignin	20	75
Lignosulphonates (Sulphite pulping)	1.5	15

In addition to kraft or sulphite lignins, there are a number of other processes whereby lignin could potentially be recovered (e.g., by acidolysis, steam-explosion, organosolv, biological treatment, etc). The existing and potential processes for lignin recovery are described briefly in the following sections.

**Kraft Pulping.** This is the major woodpulping process and potentially represents the primary source of technical lignin. During pulping, cellulosic fibers are obtained from wood by treatment with solutions of sodium hydroxide and sulphide at elevated temperatures, pressure and high pH. The hemicelluloses (and some cellulose) are degraded to give mainly isosaccharinic acids, the chemistry of which has been adequately described elsewhere (37). On the other hand, the lignin released from the cell wall during pulping increases in molecular size as delignification proceeds (38) and is highly polydisperse (39). Kraft spent pulping liquors thus consist of lignin ( $\approx 47\%$ ), hydroxy acids ( $\approx 28\%$ , e.g., isosaccharinic acid), inorganics, and small quantities of other organics (37). Lignin can be isolated from these spent pulping liquors as a precipitate by acidification. Almost all kraft lignin is burned for energy recovery; however, about 35,000 tons are produced annually in the United States for various chemical byproducts (2).

**Sulphite Pulping.** This is a generic term used to describe various sulphite chemical woodpulping processes carried out at different pH's and pulp yields (37). (The term yield refers to the quantity of fiber recovered from the original wood.)

In the acid sulphite low-yield pulping process, wood is treated with solutions of ammonium, sodium, calcium, or magnesium sulphite/bisulphite at low pH ( $\approx 1-2$ ) and at elevated temperatures and pressures. During this treatment, essentially all of the lignins, hemicelluloses, and extractives are "dissolved" away, leaving behind a fiber of very high cellulosic content. The hemicelluloses undergo severe hydrolysis, affording mainly water-soluble monosaccharides in the spent sulphite liquor (SSL). The sulphonated lignin fragments released initially during delignification ( $\approx 30-40\%$  lignin removal) are mainly monomeric compounds containing either mono-, di-, or tri-sulphonic acids (3,40). However, as delignification proceeds, the lignin released from the cell wall is of increasing molecular size and highly polydisperse (40). Consequently, low-yield spent sulphite liquors (SSL) recovered after woodpulping largely consist of lignosulphonates ( $\approx 55\%$ ), wood sugars ( $\approx 25-30\%$ , e.g., glucose, mannose, etc.), inorganics, and other organics in smaller amounts (37). Depending upon the pulping process employed, lignosulphonates can be recovered as either ammonium, calcium, sodium, or magnesium salts (35). Currently, only about 20% of all SSL materials produced are used as chemical products (e.g., as inexpensive binders for animal feed and dirt roads, and as dispersants in oil-well drilling and cement/concrete admixtures).

**Acidolysis.** Acidolysis lignins are recovered from processes whereby plant material (e.g., wood) is saccharified by treatment with mineral acids, such as sulphuric or hydrochloric acids (41). The lignin is recovered primarily as an insoluble residue. This process has been used in Europe in the past, but is not commercially important in the Western Hemisphere.

**Steam Explosion.** Steam-explosion lignins are obtained from wood (or some other plant material) that has been subjected briefly to high temperatures and pressures followed by rapid decompression (42). This process is used to a limited extent today particularly for the processing of low-quality hardwoods. The lignins recovered are of relatively low molecular weight ( $M_n \approx 700$ ) and soluble in either alkali or certain organic solvents (42,43).

**Organosolv.** Organosolv lignins are obtained as relatively low-molecular-weight entities by treatment of plant tissue with aqueous solutions of organic solvents, normally containing trace amounts of mineral acids (44). Solvents include ethanol, methanol, butanol, acetic acid, ethyl acetate, phenol, etc. To date, this approach has not been commercialized due to the quantities of organic solvents consumed and the low quality of the pulp fiber obtained.

**Enzymatic Liberation.** This is a process whereby lignin-rich residues are obtained by treatment of plant material with cellulases/hemicellulases/pectinases, etc. These lignin preparations may more closely resemble "native" lignin due to the very mild processing conditions employed.

### Lignin in Wood-Composite Adhesives

It is worthwhile to review the U.S. market size for the four principal resins currently used in wood-panel products today (45). These are phenol-formaldehyde (PF), urea-formaldehyde (UF), melamine-formaldehyde (MF), and resorcinol-formaldehyde (RF) (Table III). When these production figures are compared to the quantities of lignin potentially available (Table II), it is immediately obvious that all wood adhesives could be replaced by only a very small fraction of the lignin produced annually during chemical woodpulping processes.

Table III. U.S. Production of Thermosetting Resins (1983) in Metric Tons ( $\times 10^3$ )

Resin <sup>1</sup>	Total	Wood Products
RF	15.5	1.5
UF	586.0	440.0
MF	90.0	5.0
PF	660.0	297.0
<b>Totals</b>	<b>1,351.5</b>	<b>743.5</b>

<sup>1</sup>RF = resorcinol-formaldehyde

UF = urea-formaldehyde

MF = melamine-formaldehyde

PF = phenol-formaldehyde

There have been many attempts to replace these resins with lignin derivatives for wood composite adhesives suitable for plywood, particleboard and waferboard. Most of these studies have been empirical in nature, and few have achieved further consideration for industrial application. As wood binders, technical lignins are variable in quality and poorly reactive in comparison to conventional resin systems such as phenol-formaldehyde (PF) resins. Consequently, they are not utilized on their own. Indeed, if they were, this would adversely affect production quality and times, and necessitate equipment changes. In the wood composite industry, resins having such deleterious effects are not likely to be used *even if savings could be made in terms of material costs*.

Progress toward producing industrially acceptable lignin adhesives can be broken down into two main categories as either 1) lignin-based binders (by themselves as such or in chemically modified form), or 2) as copolymers (with other reactant adhesives).

**Lignosulphonates.** Crude SSL can be obtained as a brownish, spray-dried powder or as a viscous, hygroscopic, dark-colored liquid. SSL and the lignosulphonates present in it have been the focus of numerous efforts to produce an

industrially useful adhesive. Essentially, there are two methods of curing SSL-based adhesives, namely, by thermosetting or by free-radical polymerization.

With respect to thermosetting, it has been well documented that crude Ca-based SSL can be used as a particleboard adhesive (46). This application has been evaluated on a mill-scale basis in Denmark, Finland, and Switzerland, but has not been adopted on a commercial scale. This is because resin curing required both high press and autoclave temperatures as well as long heating times. While this development was a "technical" success, it was – according to Nimz (36) – never commercialized due to the frequency of fires experienced during mill-scale trials.

Subsequent attempts to improve the properties (i.e., reactivity) of SSL adhesives have essentially employed either acidification of Ca-based SSL or membrane filtration of the crude pulping liquors. Acidification of Ca-SSL with concentrated  $H_2SO_4$  gave an adhesive suitable for particleboard applications (47). However, processing parameters still required high press temperature ( $\approx 204^\circ C$ ), press times (5-7 min), and pressure (400 psi). The very low pH ( $< 1$ ) of the resin used may also have a longterm corrosive effect on nails, staples, etc., and engender wood deterioration. Membrane filtration of SSL shows somewhat greater promise. This approach was first reported by Forss et al. (48,49) in the development of KARATEX, a PF/lignin adhesive binder containing either lignosulphonates or kraft lignins of nominal molecular weight  $> 5000$  as determined by passage through a membrane. Applying this approach, Shen and Calve (50) examined the waferboard binding properties of an ammonium-based SSL that had been subjected to membrane filtration. Board pressing conditions were still excessive (e.g., 8 min at  $210^\circ C$  for 11-mm-thick waferboard). Best board properties were obtained with the low-molecular weight permeate ostensibly of  $< 5,000$  molecular weight and containing sulphonated lignins and monosaccharides. On the other hand, the lignosulphonate retentate ( $> 5,000$  mol wt) gave boards of unacceptable mechanical properties.

It should be recognized at this point that 1) the lignosulphonates ( $< 5,000$  mol wt) largely consist of the monomers containing mono-, di- or tri-sulphonic acids as previously described (3,40), and 2) the mechanical properties of the waferboards were determined largely by monosaccharide, rather than lignosulphonate, content (51). It was subsequently proven, under controlled laboratory conditions, that the rate of thermosetting of both high and low molecular weight lignosulphonates can be improved by increasing the monosaccharide content of the adhesive (52). In an analogous manner, formaldehyde was shown to be capable of slightly increasing the rate of thermosetting, presumably by increasing the rate of crosslinking.

However, while the use of fractionated  $NH_4$ -SSL remains a "technical success," the thermosetting rates are still very low in comparison to PF resins. Therefore, the likelihood of producing a commercially acceptable thermosetting lignosulphonate-based resin is still very far from reality.

Lignosulphonates in crude SSL can also be oxidatively polymerized by either chemical (36,59) or biochemical (54) means. In the former process, oxidants such as hydrogen peroxide, catalyzed by sulphur dioxide (or potassium ferricyanide), can be used to cure fermented Ca-based SSL. This was found to be suitable as an adhesive for medium-density interior-grade particleboard (36,59). Optimum bonding conditions used 20% of a technical SSL (54%), 9% of a 35% H<sub>2</sub>O<sub>2</sub> solution, 4% ammonium chloride and 0.6% SO<sub>2</sub> for bonding particleboard at 120 °C with a press time of 5 min. Difficulties experienced previously in controlling the exothermic nature of this curing reaction have apparently been resolved. Whether this development will receive commercial endorsement remains to be seen.

Another approach to curing SSL by oxidative polymerization employs the use of enzymes (54). In that study, SSL was treated with the white-rot fungus *Fomes annosus* and a laccase-inducing phenoloxidase until the solution reached a "honeylike" consistency. This viscous liquid was then subsequently used to bond wood particles together at a pressure of 0.03 kg cm<sup>-2</sup>. It now needs to be established whether the mechanical properties of these boards survive accelerated aging tests.

The application of lignosulphonates as an extender or co-reactant in PF or UF resins has been well studied, industrially applied, and extensively documented in a recent comprehensive review (36). Since that study, waferboards have been produced with excellent mechanical properties after being bonded at 204 °C, 4 to 5 min, 3375 kPa with a lignosulphonate-PF resin (55). The phenolic resin was modified by use of K<sub>3</sub>Fe(CN)<sub>6</sub> stabilized lignosulphonates; both phenol and the lignosulphonates were used in approximately equal proportions.

With regard to potential lignin utilization, perhaps some of the best reported results have been enunciated by Forss et al. (48,49). As described previously, spent sulphite liquor (SSL) was subjected to membrane filtration, and the lignosulphonate retentate (> 5,000 nominal molecular weight cutoff) was used to replace from 40 to 70% of PF resin with no significant deterioration in mechanical board properties. Particleboard, plywood, and fiberboard were then produced in Finland using resins containing high molecular weight lignosulphonates and PF in mill-scale trials under normal processing conditions, and this use was apparently successful (48,49). A widely stated advantage of this ultrafiltration approach is that lignin derivatives can be commercially produced with less product variability. However, it does not appear that this methodology is currently being used commercially to produce lignin-based adhesives.

The use of SSL or lignosulphonates in other polymeric adhesive systems has also been examined [e.g., with polyacrylamide, proteins/aldehydes, polyethylene oxide, polyethylene imine, epoxides, melamine, styrene oxide, polyisocyanates (36)]. So far, these procedures, for different reasons, have not led to any major practical application (36). It would, however, be interesting to reexamine some of these processes using not crude spent sulphite liquors, but instead those purified by membrane filtration.

**Kraft Lignins.** Kraft lignins are normally obtained as brown powders having very broad molecular weight distributions and variable properties. Both color and product variability are disadvantages that do not lend themselves to easy acceptance by resin manufacturers. They are mainly unsuitable as thermosetting adhesives since press times required are too long, press temperatures too high, and board/panel mechanical properties poor. This poor resin reactivity is readily explainable; the phenolic content of kraft lignin is low, there are normally substituents *ortho* and *para* to any phenolic hydroxyl functionalities, and its molecular size may prevent efficient crosslinking reactions due to steric constraints.

Kraft lignins are essentially acid-insoluble, but up to 35% by weight of lignin in solution can be achieved under alkaline conditions. However, as such, these solutions are too viscous to be of any practical use in liquid adhesive formulations. One means to reduce viscosity difficulties has been to obtain high solids ( $\approx 40\%$ ), low-viscosity lignin solutions by employing phenol-H<sub>2</sub>O or phenol:H<sub>2</sub>O:NaOH (or NH<sub>3</sub>) as solvents (56). This approach was used to give a plywood adhesive with excellent board properties (57). The adhesive was prepared in a two-step process by partially condensing phenol and formaldehyde together under alkaline conditions. The resulting condensate was then reacted with a lignin concentrate and formaldehyde in the presence of alkali to produce a resin of 37.2% solids content, pH 11.4, and a viscosity of 460 cP.

Like lignosulphonates, the use of kraft lignin as extenders or co-reactants in PF and UF resins has been well explored and occasionally implemented (36,58-60). Referring again to the work by Forss (48,49), some of the best results claimed, as regards PF replacement, were obtained using high molecular weight kraft lignins. Indeed, properties appeared superior to those using lignosulphonates.

In real terms, though, the problems that kraft (and other lignins) face are those of poor reactivity, product variability, and discoloration. In order for more reactive kraft lignin adhesives to be made, they must be chemically modified in some manner. This can be done by a variety of means (e.g., introduction of reactive crosslinking sites onto the lignin molecules by means of hydroxymethylation, epoxidation, isocyanation, and the like).

Hydroxymethylation (methylolation) was first reported as a means of activating kraft lignins for crosslinking reactions with PF resins (61-63). In these studies, it was demonstrated that base-catalyzed condensation of formaldehyde with softwood kraft lignin introduced CH<sub>2</sub>OH groups mainly at C-5 of the aromatic ring and, to a lesser extent at C <sub>$\beta$</sub>  (Figure 3). These authors (61-63) indicated that of all the C-5 and C <sub>$\beta$</sub>  positions in softwood lignin, only 0.33 and 0.03, respectively, were available for condensation with formaldehyde. The C <sub>$\beta$</sub>  positions require activation for condensation by either an adjacent C <sub>$\alpha$</sub> -carbonyl or by the presence of a C <sub>$\alpha,\beta$</sub> -double bond. These findings were unambiguously confirmed in a recent investigation by Chen and Gratzl (64). However, even with the introduction of these additional crosslinking sites, the rate of con-



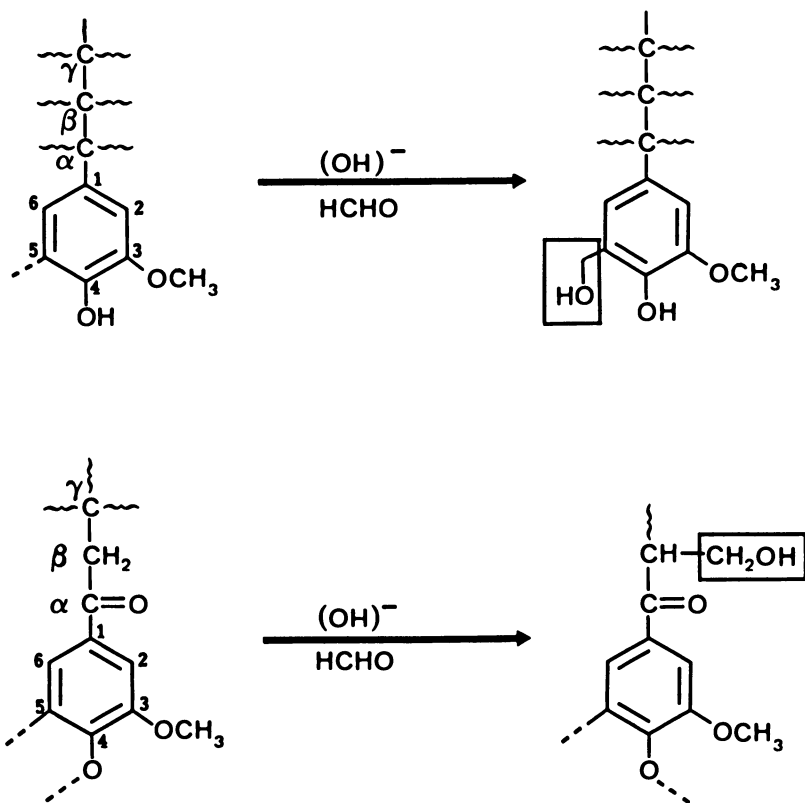


Figure 3. Proposed hydroxymethylation reactions of lignin (61-64).

densation of methylolated kraft lignins is still far less than that for PF resins (65). Consequently, they are not used on their own and need to be applied in combination with PF resins (65-71).

Interestingly, soda bagasse lignin is much more reactive toward formaldehyde than other lignins, a feature attributable to fewer substituents at C-3 and C-5 (72). This material, after methylation, resorcinol grafting, and mixing with phenolic resin, produces cold-setting wood adhesives suitable for structural fingerjoints and glulam.

**Epoxy Resins.** The use of lignin in organic polyisocyanate-liquid aromatic epoxide binders has also been evaluated (73). According to the authors, the lignin served only as a diluent, although fairly high levels of substitution ( $\approx 35\%$ ) by lignin were achieved.

**Lignin Isocyanates.** In the very near future, isocyanate adhesives are likely to grow in importance in the wood panel industry. In this regard, a number of investigations have attempted to improve the wood-bonding properties of lignin by reaction with isocyanates, or by inclusion of isocyanate functionalities into the lignin polymer. For example, Gamo (74) was able to prepare an adhesive suitable for producing 3-ply plywood with acceptable mechanical properties. This was achieved by reacting 20 parts of isocyanate solution (methylene diisocyanate:toluene, 3:1) with 100 parts kraft lignin-formaldehyde resin. Other approaches involve reaction of kraft lignin with propylene oxide to afford hydroxypropyl lignins that can then be reacted with polymethylene-polyphenylene isocyanate or hexamethylene diisocyanate (75). In a somewhat similar manner, lignin-modified polyurethane adhesives have been prepared from 4,4'-diphenylmethane-diisocyanate-lignin-maleic anhydride-propylene oxide copolymers (76,77).

The use of lignin, essentially as a diluent (extender), has also been investigated (78). In this case, di- or polyisocyanates were reacted with ethylene or propylene carbonates in a solution containing lignin. These mixed ethylene and propylene carbonate-containing organic polyisocyanates were suitable as particleboard adhesives.

**Steam-Explosion, Acidolysis, Organosolv, and Cellulase Lignins.** Steam-explosion lignins have received some attention as adhesives mainly because this process offers some potential for utilizing low-quality hardwoods. Like kraft lignin, these preparations also require activation [e.g., by hydroxymethylation (79), isocyanation (75,80)] to achieve any type of acceptable wood composite adhesive properties.

Acidolysis lignins, organosolv, and cellulase lignins are presently laboratory curiosities due to a lack of commercialization. Whether these lignins will offer any advantages at all with respect to resin adhesives currently used remains to be established. Preliminary experiments [e.g., with acidolysis lignins (81)] have not demonstrated any superior qualities to date.

## Conclusions

Considerable research activity has been directed toward producing wood composite adhesives from lignin, and this has been accompanied by very little practical success in terms of commercial implementation. By themselves, and regardless of source, lignins offer no advantages in terms of chemical reactivity, product quality, or color when compared to conventional wood composite adhesives. At low replacement levels (10 to 30%), lignins can and will continue to be employed as extenders for UF and PF resins. When they are used as extenders, best results are obtained when chemically activated (e.g., by methylation).

However, lignin may find application as a suitable wood-composite adhesive in adhesive formulations if chemically modified in some manner. In this respect, the recent developments with soda bagasse lignin-resorcinol-formaldehyde and lignin-isocyanate adhesives allow for some cautious optimism for the future.

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# Chapter 3

## Search for Lignin Condensation Reactions with Modern NMR Techniques

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A common feature of lignin condensation reactions and phenol/resorcinol formaldehyde curing reactions is the formation of methylene bridges between aryl units. Although this reaction is necessary for resin curing, it may be a detriment to efficient delignification in pulping systems. This condensation reaction of lignin was investigated by treatment of loblolly pine milled-wood lignin with alkali in the presence of formaldehyde or lignin model compounds. By the use of a  $^{13}\text{C}$ -label, it was established that formaldehyde liberated from a lignin model ultimately resulted in methylene bridges between lignin aryl units. Formaldehyde liberation from lignin and model compounds, by reverse-aldol reaction, also resulted in the formation of vinyl ether structures. With modern NMR techniques, it was demonstrated that alkaline treatment of milled-wood lignin at 140 °C resulted in the formation of vinyl ether structures, whereas, after 50 °C treatments, no vinyl ether was detected.

Lignin condensation reactions have been studied for many years, mainly because they possibly interfere with efficient delignification of wood. Numerous model compound studies established the various types of condensation reactions that may occur between lignin fragments (1-5) or between lignin and carbohydrates (1,2,6,7) during alkaline pulping. An important class of condensation reactions involves formaldehyde.

Forty years ago, it was discovered that formaldehyde is released from isolated lignins by either acid or alkaline treatment. It was concluded that the

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formaldehyde came from the primary alcohol groups ( $\gamma$ -hydroxymethyl) of the propyl side chain (8). About 20 years later, it was recognized that the formaldehyde that is continuously released during pulping may react with lignin in accordance with the well-known reactions between phenol and formaldehyde (9). Since then, many investigators have published results of studies on model compounds, which are consistent with the elimination of formaldehyde from a quinone methide (II; Figure 1), generated from a phenyl propane unit with a free C-4 phenolic group (I) by a reverse aldol reaction and formation of a vinyl ether (III) (10). Subsequent addition of formaldehyde to free phenolic units (usually at the 5-position) may then occur to give structure V (Figure 2). Ultimately, the new hydroxymethyl groups condense with elimination of water and formaldehyde or condense at a free C-5 position with elimination of water, resulting in formation of a methylene bridge structure (VI) (10,11). One of the most noteworthy studies utilized VII as a model compound (Figure 3) with a  $^{13}\text{C}$ -label in the  $\gamma$ -hydroxymethyl group. Alkaline treatment of this model compound resulted in a complex mixture.  $^{13}\text{C}$ -NMR spectroscopy of the mixture showed that much of the label ended up in methylene bridges between aryl units (12).

Clearly, phenol-formaldehyde type reactions form a common bond between pulping chemistry and adhesives chemistry. In fact, the reactions of added formaldehyde to lignins and the utilization of the phenolic nature of lignin to produce PF resins have been studied extensively (13-15). Although for adhesives PF-condensation reactions are important, they are a nuisance during pulping. The impetus for a more complete understanding of lignin condensation reactions is the hope of increasing the efficiency of delignification by preventing or minimizing condensation reactions during pulping as well as controlling and manipulating them for practical and uniform adhesives. Because of the complexity of lignin, the type and extent of condensation reactions that occur during alkaline pulping are still not well understood. Most of the information regarding these reactions is speculation based on studies with model compounds.

This study was a preliminary effort to detect and characterize structures in the lignin polymer that result from condensation reactions during alkaline treatment. The only method capable of observing this complex polymer with the necessary detail on an atomic scale is  $^{13}\text{C}$ -NMR spectroscopy. Enormous progress has been made in the capabilities of NMR especially in the last few years, and very few of the modern techniques have yet been applied to lignin.

In order to facilitate the detection of condensation structures, lignin was treated with alkali in the presence of  $^{13}\text{C}$ -labeled formaldehyde or model compounds (Figure 3) enriched with  $^{13}\text{C}$  at the  $\gamma$ -position on the side chain. In this manner, the detection of cross condensations between the model and the lignin was facilitated. Conventional and modern NMR experiments were then utilized to examine the treated lignins.

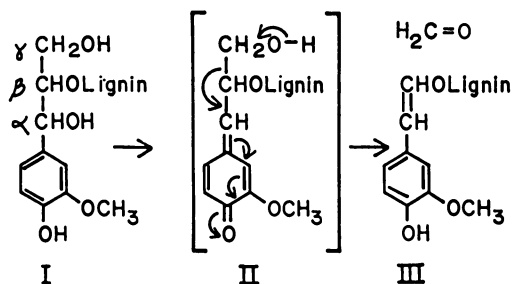


Figure 1. Quinone methide and vinyl ether formation from free-phenolic lignin units.

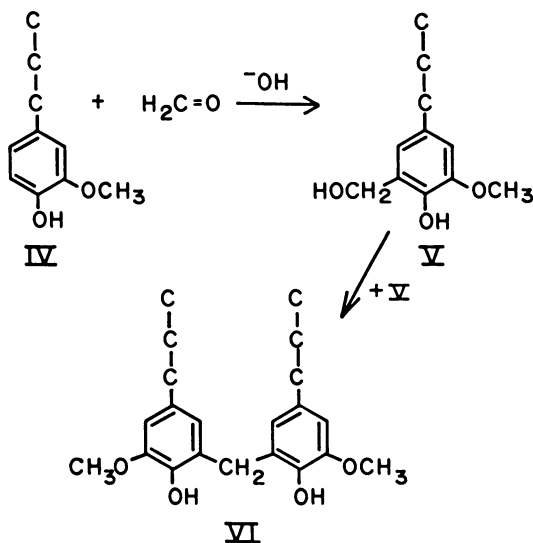


Figure 2. Condensation of formaldehyde with lignin free-phenolic units.

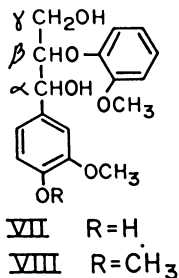


Figure 3. Lignin model compounds.



## Experimental Methodology

**Lignin.** Milled-wood lignin (MWL) from loblolly pine was obtained by 95% dioxane/water extraction of extractive-free vibratory ball-milled wood. The yield was about 20% based on the lignin in the wood.

**Lignin Models.** *1-(4-Hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)propan-1,3-diol (VII)*. The 4-benzyloxy- $\alpha$ -keto precursor to VII was prepared as previously described (16). Treatment of this compound (70 mg, 0.17 mmole) in THF(2 mL)/H<sub>2</sub>O(0.1 mL) with 10% Pd/C under H<sub>2</sub> (balloon), with stirring, for 3 hours gave a colorless oil (49 mg, 91%) which was shown to be VII by comparison (TLC and NMR) with authentic material. A 70:30 *erythro:threo* ratio was indicated by <sup>13</sup>C-NMR. The <sup>1</sup>H and <sup>13</sup>C-chemical shifts (CDCl<sub>3</sub>) have been previously published (17). Compound VII enriched with <sup>13</sup>C at C $_{\alpha}$  was prepared from labeled acetovanillone, which was prepared from guaiacol and acetic acid-1-<sup>13</sup>C by a procedure analogous with that described previously (16). The  $\gamma$ -<sup>13</sup>C enriched compound was made by simply utilizing <sup>13</sup>C-formaldehyde in the synthesis.

*1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)propan-1,3-diol (VIII)*. Procedures analogous with those described above gave a 94% yield of a 70:30 *erythro:threo* product as a colorless oil.

**Lignin Treatments.** The MWL (100 mg, 0.5 mmole C<sub>9</sub> units) in 0.5M NaOH (3 mL) was placed in a 5 mL stainless steel bomb along with the lignin model compound (10 mg, 0.03 mmole) or formaldehyde (1.7 or 17% soln, 0.03-6 mmoles), and heated in an oil bath at 50 °C or 140 °C. All of the model/lignin runs were at 140 °C.

**Chromatographic Method.** The acetylated reaction product was applied on a 93 cm x 2.4 cm column of Bio-Beads S-X2 (Bio-Rad), which was then eluted with CHCl<sub>3</sub>.

**NMR Procedures.** All spectra were obtained at 30 °C with a Bruker WM-250 (62.9 MHz <sup>13</sup>C-spectrometer controlled by an Aspect 2000A minicomputer. Solutions of lignin product (70-80 mg) in CDCl<sub>3</sub> (0.3 mL) containing tetramethylsilane as internal reference were used. For conventional noise-decoupled <sup>13</sup>C-spectra, a Bruker power-gated sequence (POWGATE) was utilized with Waltz-16 decoupling (18). Other Bruker standard microprograms were used for the DEPT and QUAT experiments. Generally, 30,000-60,000 free-induction decays (FID's) of 8K data points were accumulated over a spectral width of 15,000 Hz. For optimum resolution and S/N, the FID's were zero-filled to 16K points and a 6 Hz line-broadening function was applied prior to Fourier transformation. Resolution-enhanced spectra were obtained by applying a 6 Hz Lorentzian-to-Gaussian function.

## Results and Discussion

**Direct Formaldehyde Addition.** In initial attempts to characterize formaldehyde-promoted condensation reactions, loblolly pine milled-wood lignin was treated with alkali at 50 °C in the presence of either unlabeled or  $^{13}\text{C}$ -labeled formaldehyde. The  $^{13}\text{C}$ -spectra of the acetylated products are illustrated in Figure 4. The control was a 50 °C alkaline treatment in the absence of formaldehyde. With unlabeled formaldehyde, 10 moles were added per mole lignin ( $\text{C}_9$  unit basis). This is actually about a fiftyfold excess, if it is assumed that only about one-fifth of the C-5 positions are activated by a free phenolic group in the milled-wood lignin (19). Even with this enormous excess, it is difficult to detect an appreciable amount of aryl- $\text{CH}_2$ -aryl resonances (Figure 4b), possibly due to a relatively large chemical shift spread (30-40 ppm) among the various types. However, new resonances at 61.3 and 63.3 ppm are clearly seen. Also, an expected increase in primary alcohol groups is seen at 170.5 ppm due to the carbonyls of the alcohol acetates. In addition, the missing resonances at 121-123 ppm (Figure 4a expansion) were assigned to tertiary C-5s in guaiacyl units, based on the expected conversion of most of the available tertiary C-5s to quaternary C-5s (replacement of hydrogen with a hydroxymethyl group) and on previous assignments in 9:1 acetone- $\text{d}_6/\text{D}_2\text{O}$  (19). The addition of a large excess of formaldehyde may be appropriate for adhesive research, but certainly is not representative of what occurs during alkaline pulping. However, this extreme case assisted in the assignment of some resonances.

In another experiment,  $^{13}\text{C}$ -labeled (98%) formaldehyde was used, but in a much smaller quantity (0.4 mole/ $\text{C}_9$  unit) than with the unlabeled (1% natural abundance)  $^{13}\text{C}$ -material. The result was an enormous increase in intensity of the formaldehyde, derived resonances (Figure 4c), particularly those centered around 35 ppm that were barely detectable before (Figure 4b). A broad "envelope" of overlapping resonances in this region was also observed with the alkaline treatment of VII in the presence of  $\text{H}_2^{13}\text{C}=\text{O}$  (12). The observation that considerable resonances are still present in the 121-124 ppm region indicates that, with the smaller amount of formaldehyde, there are still many unsubstituted C-5 positions.

All of the new resonances are due to methylene carbons, as shown by a DEPT (Distortionless Enhancement by Polarization Transfer) pulse sequence (20) (Figure 5). This modern NMR experiment distinguishes among carbon types. It is a polarization-transfer experiment in which the  $^{13}\text{C}$ -signals are enhanced by transfer of magnetization from attached protons. In this particular version of DEPT, the methyls and methines are positive, methylenes are negative, and quaternaries are not observed. The unusually low field methylenes at 93.3 to 94.1 ppm were assigned to  $\beta$ - or  $\gamma$ -carbons of hemiformal chains, which arise because commercial formalin is a mixture of oxymethylene and hemiformal oligomers (21). The new resonances in the 60-70 ppm region are assigned to the  $\alpha$ -carbons of these hemiformal chains, along with the hydroxymethyl carbons.

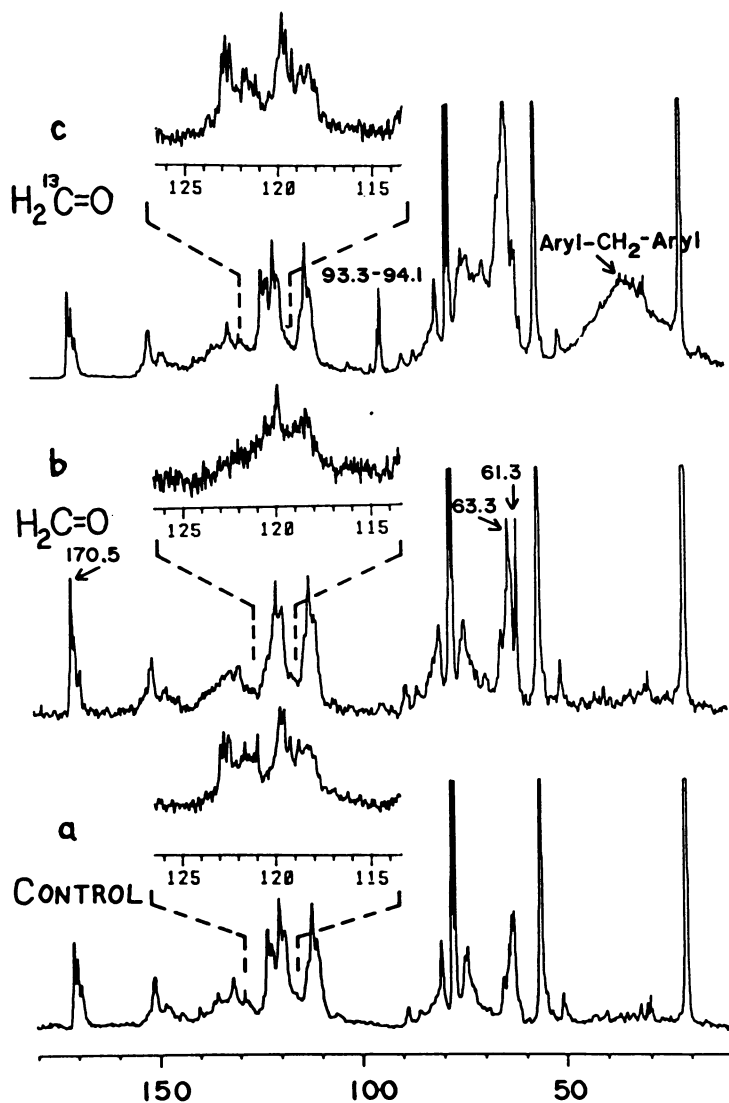


Figure 4. Alkaline treatments of loblolly pine MWL at 50 °C for 20 hours: a. control; b. unlabeled formaldehyde (10/1); c. labeled formaldehyde (0.4/1).

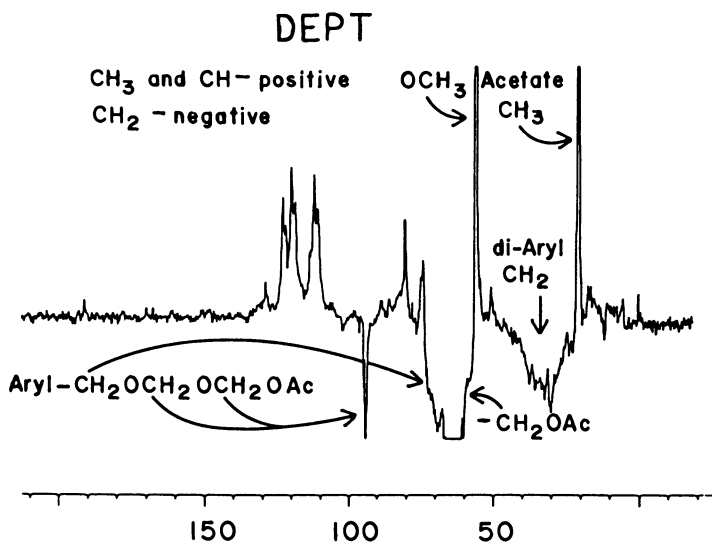


Figure 5. DEPT spectrum of labeled formaldehyde/lignin product.

Substitution of the acetate group in the hemiformal structures by a second aryl group is also feasible, since the chemical shift of the  $\alpha$ -carbon will be little affected (21).

An apparent discrepancy in the intensity of the resonance at 61.3 ppm between Figures 4b (unlabeled) and 4c (labeled) might be explained by differences in the proportions and types of structures due to the large difference in formaldehyde concentration between the two treatments. Further reduction of the formaldehyde level to only 0.05 moles  $\text{H}_2^{13}\text{C}=\text{O}$ /mole  $\text{C}_9$  still resulted in appreciable methylene signals (Figure 6). Even after 1 hour at 50 °C, there was a significant methylene bridge content (Figure 6b). The gradual reduction of the 5-hydroxymethyl resonance at 59.9 ppm and the hemiformal resonance at 93.3 ppm with time and temperature is readily apparent from the series of spectra in Figure 6.

Although the NMR spectra were not run under quantitative conditions, a very crude estimate, based on peak areas relative to the methoxyl peak, indicated that the large excess of unlabeled formaldehyde (Figure 4b) resulted in the substitution of about 20 C-5 positions per 100  $\text{C}_9$  units with  $\text{CH}_2$  bridges per hydroxymethyl group in a ratio of 1/3. The smaller amount of labeled formaldehyde (Figure 4c) resulted in considerably less substitution, but there appear to be roughly equal amounts of  $\text{CH}_2$  bridges and hydroxymethyl groups.

**Lignin Treatment in the Presence of Models.** Loblolly pine milled-wood lignin was treated with alkali at 140 °C for 1 hour in the presence of guaiacyl or veratryl lignin models VII or VIII (Figure 3), representing free and etherified  $\beta$ -O-4-phenylpropane units. In some treatments, models enriched with  $^{13}\text{C}$  at the  $\gamma$ -carbon (98%) were used. After the treatment, the reaction mixtures were acetylated and then fractionated on a polystyrene gel to remove low molecular weight byproducts and unreacted model. Typical chromatograms are illustrated in Figure 7. The high molecular weight (MW) portion (fraction A) accounted for over 85% of the material applied on the column. Fraction B, which was 7-8% of the total, was not investigated. Fraction C is the monomeric portion.

Condensation involving formaldehyde liberated from the  $\gamma$ -hydroxymethyl of the added guaiacyl model is confirmed by the series of partial spectra of the high MW portions (fraction A), illustrated in Figure 8. Although a small difference can be seen between the control (no model compound added) and the unlabeled guaiacyl model/lignin spectra in the diarylmethylene region, the major effect is that of the label (difference between Figures 8b and 8c). In contrast, with the veratryl model (Figure 8d), the diarylmethylene region (about 35 ppm) is very similar to the control (Figure 8a). This is consistent with the observation that when the phenol is blocked, quinone methide formation is prevented, and liberation of formaldehyde, according to the scheme in Figure 1, does not occur (10,22). The lowest MW fraction (fraction C, Figure 7) in the guaiacyl model/lignin runs was found to be mainly composed of the  $\beta$ -guaiacyl vinyl ether, generated from the free-phenolic model analogous to the scheme illustrated in Figure 1, and accounted for 7 to 9% of the total. As

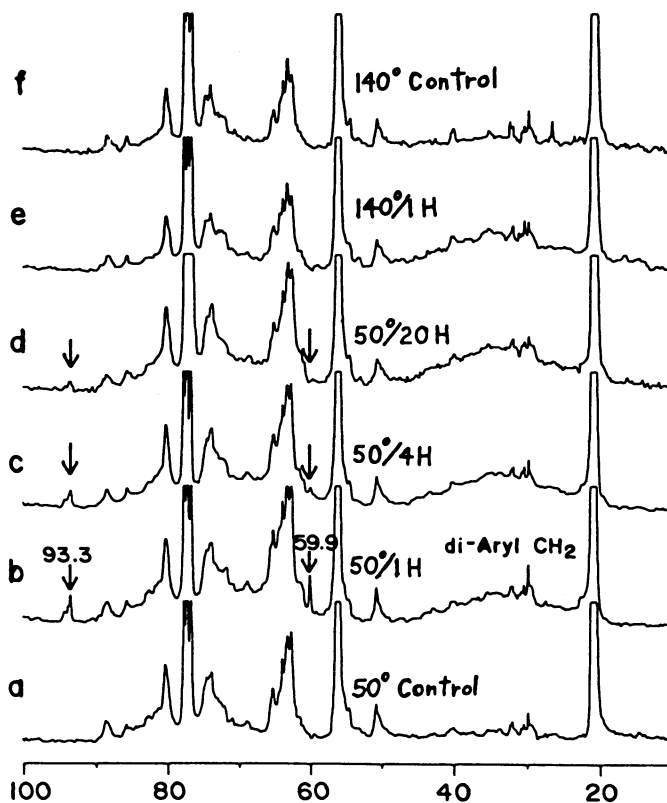


Figure 6. Partial spectra of labeled formaldehyde/lignin runs (0.05/1): a. 50 °C/1 hour control; b. 50 °C/1 hour; c. 50 °C/4 hour; d. 50 °C/20 hour; e. 140 °C/1 hour; f. 140 °C/1 hour control.

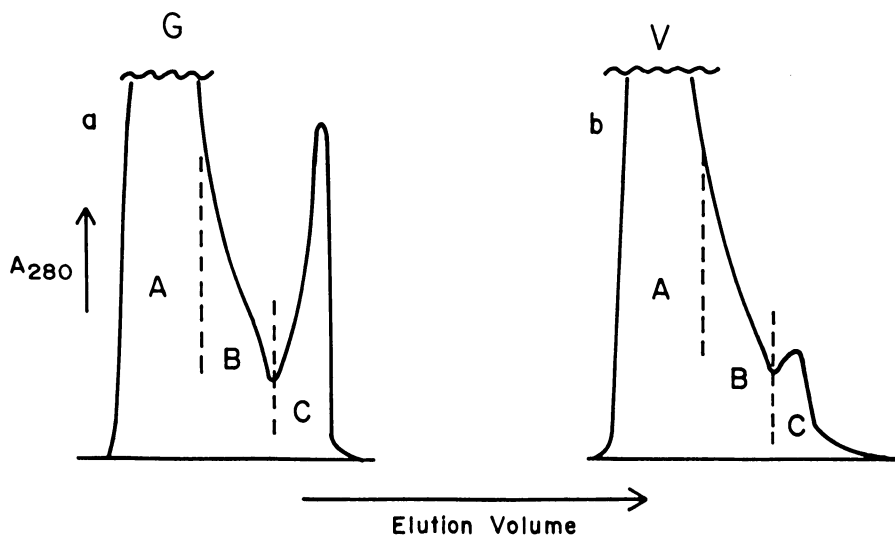


Figure 7. Typical gel chromatograms from: a. guaiacyl model/ lignin; b. control or veratryl model/lignin.

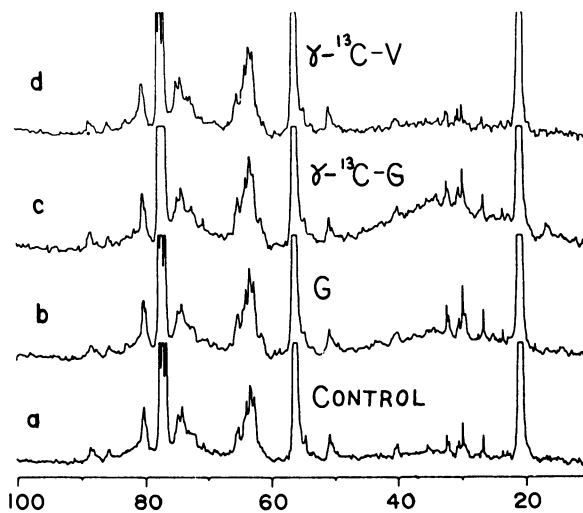


Figure 8. Partial spectra of high MW fractions of 140 °C lignin treatments in the presence of: a. control; b. unlabeled guaiacyl model VII; c.  $\gamma$ -labeled guaiacyl model VII; d.  $\gamma$ -labeled veratryl model VIII.



expected, there was no evidence of vinyl ether in fraction C of either the control or veratryl model/lignin runs. It is presumed that unreacted veratryl model and its degradation products were present in fraction B, since many sharp resonances present in the spectrum of unfractionated reaction product were absent in both the high MW fraction A and the lowest MW fraction C. Vanillyl acetate was detected in fraction C in both the control and veratryl model/lignin runs by mass spectroscopy. Fraction C in these runs accounted for 1-3% of the total material.

Since vinyl ether formation does not result in ether cleavage and a reduction in molecular weight, the lignin vinyl ether's corresponding to structures III (Figure 1) would be expected to remain in the high MW fraction. The presence of vinyl ether structures in alkali treated lignins is illustrated in Figure 9. Spectrum "a" is a mixture of *cis* and *trans* acetylated  $\beta$ -guaiacyl vinyl ether models corresponding to structure III in Figure 1. The resonances of interest are the  $\beta$ -carbons at 142.6 (*cis*) and 145.2 (*trans*) ppm. In the 140 °C control spectrum "b", the corresponding lignin vinyl ether  $\beta$ -carbons can be seen, but are partly obscured by overlapping quaternary carbons. These  $\beta$ -carbons are highly deshielded relative to most of the other protonated carbons of lignin and appear in the quaternary carbon region. This fact becomes an asset when a pulse sequence such as DEPT is utilized. Since this technique does not detect quaternary carbons, the interfering peaks are removed and the deshielded protonated carbons are revealed. For example, the vinyl ether  $\beta$ -carbon resonances can now be cleanly assigned at 142.1 (*cis*) and 145.0 (*trans*) ppm in the DEPT spectrum "c". Spectrum "d" is the product from a guaiacyl model/lignin treatment prior to chromatographic separation. Interestingly, both the lignin vinyl ether and the model vinyl ether resonances (sharp) are observed. The small difference in chemical shift is presumably due to the substitution in the 4' position in the lignin vinyl ether. Finally, in the 50 °C control spectrum "e", the absence of vinyl ether resonances can be explained by the fact that quinone methide formation (Figure 1) is too slow at this temperature (1).

Tentative assignments of  $\beta$ -carbon vinyl ether resonances in acetylated kraft lignin preparations have previously been made (23). Values of 144.3-144.4 ppm (*trans*) and 141.5-142.0 ppm (*cis*) in CDCl<sub>3</sub> were reported. However, a rather low-field (20 MHz) instrument was used along with the conventional proton noise-decoupled technique, so extreme overlap with quaternary carbons was unavoidable.

Along with the DEPT pulse sequence, a useful complement is the QUAT sequence, which detects only quaternary carbons (24). As illustrated in Figure 10, a QUAT spectrum of a 140 °C control lignin does not detect the protonated  $\beta$ -vinyl ether carbons that are present in both the DEPT and conventional spectra. However, some quaternary resonances do appear in the QUAT spectrum in the same position as does the *trans* vinyl ether resonance visible in the DEPT spectrum. Thus, it is generally not possible to accurately assign the *trans* resonance by conventional NMR spectroscopy. A disadvantage of the

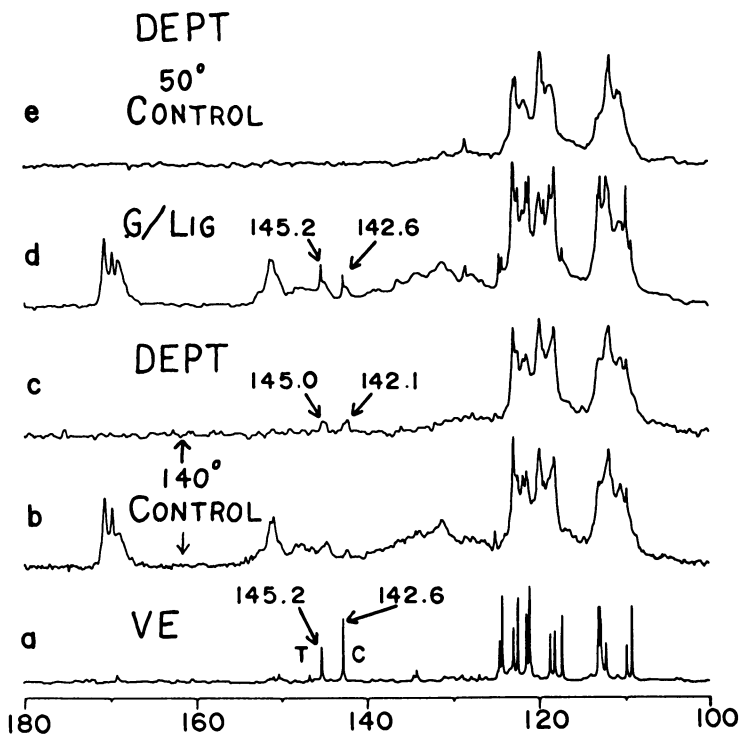


Figure 9. Partial spectra illustrating vinyl ether formation in lignin: a. acetylated  $\beta$ -guaiacyl vinyl ether III; b. 140 °C control; c. DEPT spectrum of 140 °C control; d. guaiacyl model/lignin product prior to chromatographic separation; e. DEPT spectrum of 50 °C control.

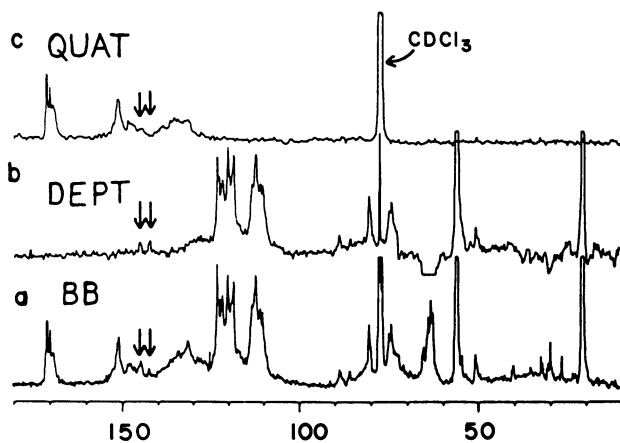


Figure 10. Spectra of lignin product from 140 °C/1 hour treatment: a. conventional broadband (BB) decoupled; b. DEPT; c. QUAT.

QUAT experiment is that long recovery times are necessary for optimum acquisition of the slowly relaxing quaternary carbons.

### Conclusions

Applying modern NMR techniques facilitated the examination of lignin products resulting from alkaline treatment of loblolly pine MWL in the presence of formaldehyde or lignin model compounds. It was determined that  $^{13}\text{C}$ -labeled formaldehyde liberated from a free-phenolic lignin model compound condensed at the C-5 position of the guaiacyl  $\text{C}_9$  units. The resulting hydroxymethyl substituted lignin was relatively unstable in base, even at  $50^\circ\text{C}$ , and underwent further condensation leading to labeled methylene bridges between aryl units. As a result of formaldehyde liberation by a reverse-Aldol reaction, relatively stable vinyl ether structures were formed. It was clearly established by the use of the modern NMR pulse sequences, DEPT and QUAT, that vinyl ether structures were present in the lignin macromolecule following  $140^\circ\text{C}$  alkaline treatments and absent in the lignin from corresponding  $50^\circ\text{C}$  treatments.

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# Chapter 4

## Cross-linking Options for Lignins

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For isolated lignins to become the primary backbone component of a network polymer, a reaction with a bifunctional or multifunctional crosslinking agent must be performed that is sufficiently reactive as well as compatible with lignin in either solvent-free or highly concentrated form. Since the essential prerequisites of compatibility and miscibility often are not met by isolated lignins, improvements may require chemical modification prior to crosslinking. Opportunities exist for preparing lignins by chemical derivative formation for incorporation into polymer networks. Modification reactions include sulfonation, methylation, phenolation, alkoxylation, acrylation, and many others. These prepare lignins for incorporation into phenolics, epoxies, urethanes, acrylics, and several other types of thermosetting materials.

The macromolecular, multifunctional nature of isolated lignins invites applications in which lignin serves as the principal component of thermosetting network polymers (1). Most prominent (in terms of market volume) of the thermosetting materials are phenolics, and these are joined by polyurethanes, unsaturated polyesters, polyamines, and epoxies with smaller market volumes (2). Although most efforts to incorporate lignin into thermosets by crosslinking with other resin components have concentrated on phenolics (3), other options exist as well. This paper briefly reviews alternatives for crosslinking lignins in a variety of thermosetting network polymer systems.

### Gillham's TTT Diagram

The extent to which lignin becomes a component of a polymer network may be constrained either by reactivity or by solubility. The contribution of lignins to phenolic resins is known to be limited by the number of available uncondensed

phenolic guaiacyl units (i.e., reactivity), and this may be improved by modification prior to crosslinking (3,4). By contrast, poor solubility in and miscibility with the components of a liquid network forming resin were held responsible for the creation of inhomogeneous (i.e., phase separated) cured polyurethanes (5,6). The process of gelation is best illustrated by the time-temperature-transformation (TTT) cure diagram of Gillham (7). This is illustrated in Figure 1 in simplified form. The diagram illustrates the various transformations a resin undergoes during isothermal cure in relation to time. At low temperature and short time, the resin remains a homogeneous (fluid) mixture that experiences demixing (or phase separation) as a result of reaction advancement if either time or temperature increases. Gelation, which according to Flory (8), corresponds to the formation of a molecule with infinite molecular weight, is seen to occur at a later point in time during isothermal cure. The fact that cure follows demixing implies that an inhomogeneous material is formed, since phase separation limits the ability of molecules to undergo crosslinking and network formation. The process of phase separation, in turn, is governed by the Gibbs free energy equation:

$$\Delta G_{mixing} = \Delta H_{mixing} - T\Delta S_{mixing}$$

Phase separation occurs when  $\Delta G$  rises above 0. This may be triggered by a rise in enthalpy (i.e.,  $\Delta H$ ) or a decline in entropy (i.e.,  $\Delta S$ ). To allow for the formation of a uniform network polymer, phase separation must be delayed until crosslinking is well enough advanced to prevent individual molecules from demixing. This delay is achieved by either reducing  $\Delta H$  or by raising  $\Delta S$  (in concert with  $T$ ). The enthalpy factor ( $\Delta H$ ) is controlled by the difference in Hildebrand's solubility parameter ( $\delta$ ) between the various reacting components, since

$$\Delta H = \phi_1\phi_2(\delta_1 - \delta_2)^2$$

where  $\phi$  is volume fraction; and  $\Delta S$  declines with increasing molecular weight according to Flory and Huggins (9). Both approaches have been employed with lignin-based network polymers. The lower molecular weight fractions of kraft lignin have been used successfully for the formulation of homogeneous solution cast polyurethane films (10-12), and the solubility of lignin has been increased by chemical modification prior to crosslinking. The following discussion illustrates examples of how chemical modification made crosslinking possible by limiting phase separation.

**Chemical Modifications.** Unmodified lignin is well known for its poor solubility characteristics and its high glass transition temperature. Methods for improving the solubility (and/or reactivity) of lignin prior to crosslinking in specific network forming systems are summarized in Table I. Such systems may be based on aqueous solutions at pH below or above neutral or on solutions in polar or nonpolar solvents. Typical modifications that enhance the solubility of

lignin in aqueous solvent systems of pH <7 involve sulfonation, carboxylation (by oxidation), and grafting with a substituent that produces a water-soluble polymer chain. Solubility in aqueous solutions of pH >7 typically concentrates on the introduction of ionizable functional groups. Sulfonation, phenolation, and carboxylation (by reaction with anhydrides or chloroacetic acid) belong to this group. Organic solvent solubility may be enhanced by reducing the hydrogen-bonding capacity of lignin through etherification and/or through the introduction of substituents with low polarity. The list in Table I provides evidence for the observation that isolated (polymeric) lignin, in the majority of cases, needs to be chemically modified prior to network formation. (As mentioned above, phase separation prior to gelation may, however, also be controlled and delayed by the use of low molecular weight lignin fractions.)

**Crosslinking Reactions in Water at pH <7.** Lignin derivatives soluble in acidic aqueous medium can be crosslinked by acid condensation (Figure 2) or oxidative coupling reactions. This has been reviewed by Nimz (3) in the context of lignin-based phenolic resins.

**Crosslinking in Water at pH >7.** Resin cure in aqueous alkali is common practice for phenolics (44). Although most isolated lignins have satisfactory solubility in aqueous alkali, phenolation has been found to enhance the tolerance of phenolic resins to the addition of macromolecular fractions of lignin (4,45-47). Improved miscibility and reactivity both account for this phenomenon.

The crosslinking of lignin derivatives in aqueous alkaline medium has been achieved with several additional crosslinking agents. Nimz et al. employed bifunctional bis-diazonium salts in an effort to produce a novel type of azo resin from lignin sulfonates (24) (Figure 3). This technique was adopted by Psotta et al. (25) who found that, although sulfonated wattle extracts crosslinked well and formed useful network polymers, sulfonated lignin derivatives posed problems attributed to frothing (due to reagent decomposition) and loss of control over cure rate.

Bifunctional acid chlorides were useful in crosslinking sulfonated lignin model compounds in aqueous alkali (Figure 4), but they behaved poorly during intermolecular crosslinking of polymeric lignins (26).

Cyanuric chloride was described as a potent trifunctional crosslinking agent for both model compounds and sulfonated lignins (27) (Figure 5). A healthy incorporation of triazine functionality produced homogeneous network gels.

Introduction of carboxylic acid groups enhances surface active properties (17) of lignins as well as their reactivity with propylene oxide (39). (A more highly propoxylated lignin has superior solubility and reactivity with diisocyanates.) Carboxylated lignins have, however, not been the target of network-forming reactions.

**Crosslinking in Organic Solvents.** The solubility of most isolated lignins in (polar) organic solvents is poor. It needs to be improved before uniform network polymers can be produced by crosslinking. This may be achieved through



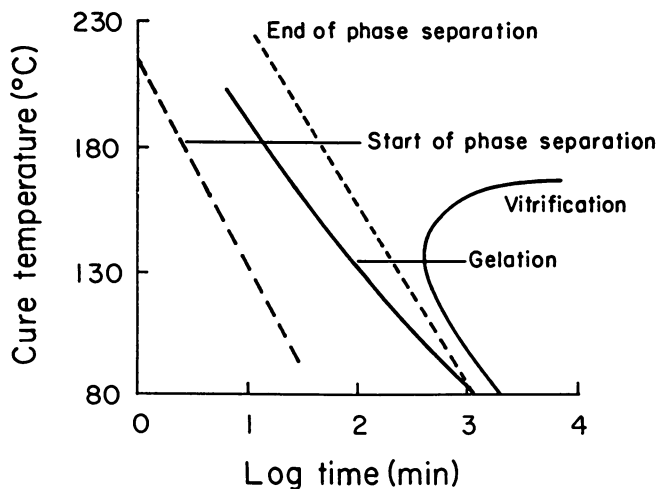


Figure 1. Time-temperature-transformation cure diagram by Gillham [adapted from (7)].

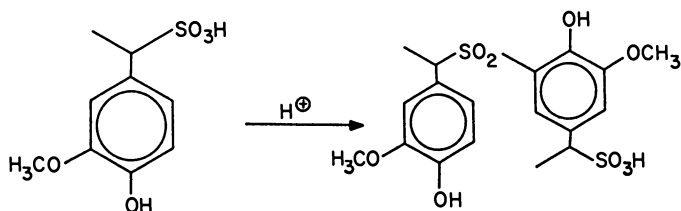


Figure 2. Condensation reaction of liginosulfonates at pH < 7 [adapted from (9)].

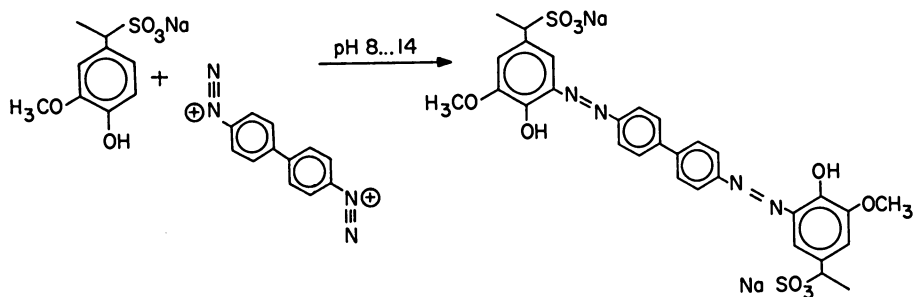


Figure 3. Reaction of liginosulfonates with bis-diazonium salts [adapted from (24, 25)].

Table I. A Non-comprehensive List of Crosslinking Reactions and Pretreatment Methods for Improving Solubility and/or Reactivity

Principal Solvent	Method <sup>1</sup>	Principal Crosslinking Agent <sup>2</sup>	Network Type <sup>3</sup>	Reference
Water (pH ≤ 7)	S	H <sup>+</sup> (C)	PR	13,14
	S	H <sub>2</sub> O <sub>2</sub> (OC)	PR	15
	M	PF	PR	16
	MO	NA	NA	17
	G	NA	NA	18
Water (pH > 7)	S,M,P	PF	PR	4,19 <sup>4</sup> ,20 <sup>5</sup> , 21 - 23
	S	BD	AZR	24,25
	S	AAC	PE	26
	S	CC	Resins	27
	CM	NA	NA	28
	MAC	NA	NA	29
	MCR	NA	NA	17,30
Organic solvents	E	NEH	ER	31,32
	A	DI	PU	33 - 40
	M+EP	NEH	ER	41,42
	MA	MEA	AR	43

<sup>1</sup>S = sulfonation, M = methylolation, MO = miscellaneous oxidation, G = grafting, P = phenolation, CM = carboxymethylation, MAC = maleic anhydride copolymerization, MCR = miscellaneous carboxylation reactions, E = epichlorohydrin (also in conjunction with phenolated lignin), A = alkoxylation (i.e., ethylene, propylene, and butylene oxides), M+EP = modification with compounds containing unsaturated end groups ("divalent hydrocarbons") followed by epoxidation with peroxide, MA = methacrylic acid.

<sup>2</sup>C = condensation, OC = oxidative coupling, PF = phenol formaldehyde, NA = crosslinking not performed—modification was aimed at network formation, BD = bis-diazonium salts, AAC = aryl acid chlorides, CC = cyanuric chloride, NEH = normal epoxy hardeners, MEA = methacrylate.

<sup>3</sup>PR = phenolic resin, AZR = azo resin, PE = polyester, ER = epoxy resin, PU = polyurethanes, AR = acrylic resin.

<sup>4</sup>Based on high-molecular-weight fraction of ultra-filtered spent sulfite or kraft liquor.

<sup>5</sup>Based on alkali-soluble methylolated kraft lignin which was precipitated by acidification and blended with an acid-curing phenolic resin.

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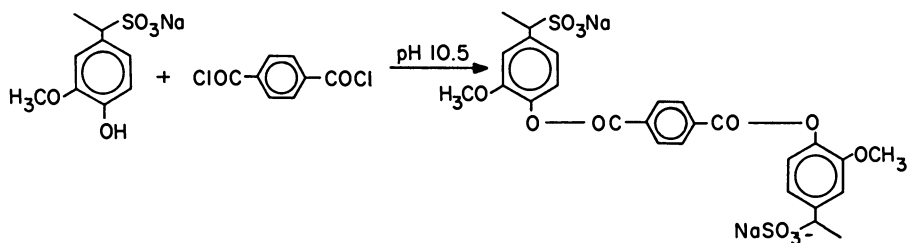


Figure 4. Reaction of lignosulfonates with acid chlorides [adapted from (26)].

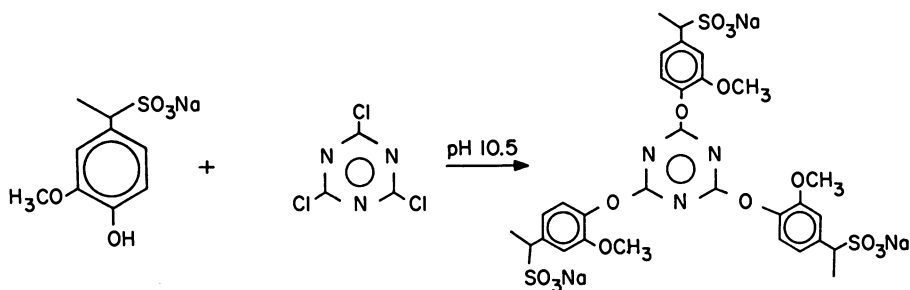


Figure 5. Reaction of lignosulfonates with cyanuric chloride [adapted from (27)].

etherification with ethylene, propylene, or butylene oxide (35,48) to form a variety of hydroxyalkyl lignin derivatives. These have greatly improved solubility in polar organic solvents; they have dramatically reduced glass transition temperatures; and they form the basis for homogeneous polyurethane thermosets (39,49) (Figure 6). The formulation of polyols from lignin for the production of rigid and semirigid polyurethanes by crosslinking with diisocyanates has been the subject of numerous studies. Clear, homogeneous films were cast with aromatic and aliphatic diisocyanates from methyl-ethyl ketone solution, and phase separation was not noted when polyethylene glycol of molecular weights up to 4000 Daltons was added to the uncured resin as a soft segment (50).

Hydroxyalkyl lignin derivatives were crosslinked with diisocyanates or with melamine in both solvent and aqueous emulsion-based adhesive formulations for wood products (51) (Figure 7). Adhesive performance was found to be related to component solubility and compatibility (51). The use of kraft lignin in aqueous alkali and that of lignin sulfonates in water has been explored in combination with emulsifiable diisocyanates (52) in wood adhesives. Satisfactory strength properties were reported.

The introduction of oxirane (epoxide) functionality in lignin has been achieved both by epoxidation of olefin groups with peracids, and by reaction with epichlorohydrin (41,42). The introduction of unsaturated functionality into lignin by modification with a wide range of chemical reagents prior to reaction with peroxides was patented in 1981 (42). This was reported as a convenient pretreatment for converting lignin into a multifunctional epoxide suitable for crosslinking with diamines and triamines (42).

An alternative reaction route to epoxides has involved the modification of lignin with various alcohols, phenols, carboxylic acids, and dialkyl sulfates with the objective of preparing a more soluble lignin derivative suitable for reacting with epichlorohydrin. Lignin-glycidyl ether derivatives were reported by Tai et al. (31,32) in 1967. Kraft lignin, phenolated kraft lignin, and several other kraft lignin derivatives (including bisguaiacyl lignin) were employed as raw materials for reactions with epichlorohydrin (Figure 8). The resulting lignin-based glycidylethers had satisfactory functionality (i.e., phenolated lignin produced a maximum degree of epoxidation of 0.28 eq/100 g, and other derivatives were in the range of 0.16-0.19 eq/100 g), but all suffered from poor solubility characteristics. Phenolated lignin was reported to be the most useful lignin derivative for conversion into epoxy resins. The introduction of nonpolar substituents, such as hydrocarbon group containing compounds, was found to raise the solvent solubility of lignin. These types of derivatives were used in the reaction with epichlorohydrin by D'Alelio (41). Useful epoxy resins that could be crosslinked with diamine hardeners were reported.

The introduction of vinyl functionality by acrylation has been reported by Naveau (43). Methacrylyl chloride and methacrylic anhydride were used to introduce 10 to 20% methacrylate groups into lignin (Figure 9). Acrylated

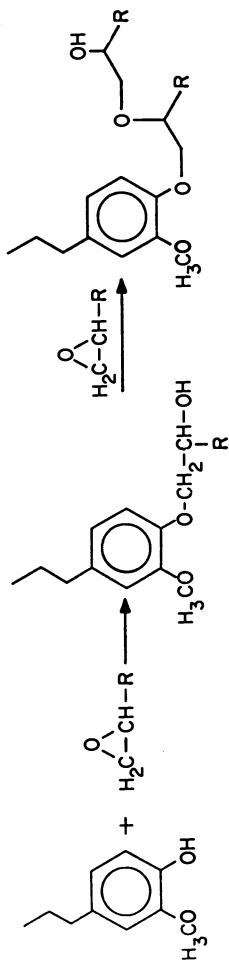


Figure 6. Reaction of lignin with alkylene oxide [adapted from (95)].

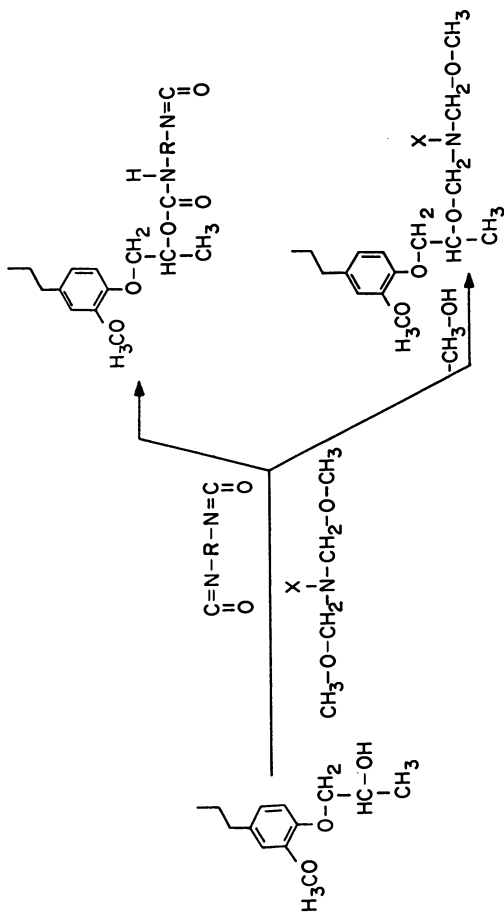


Figure 7. Reaction of hydroxypropyl lignin with an isocyanate and an amine (X is a melamine) [adapted from (51)].

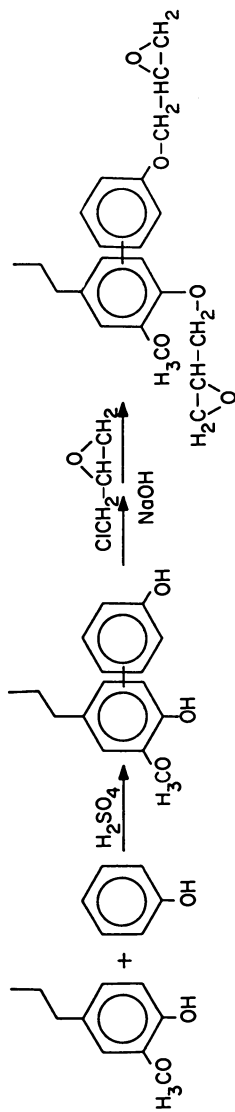


Figure 8. Reaction of phenolated lignin with epichlorohydrin [adapted from (31)].

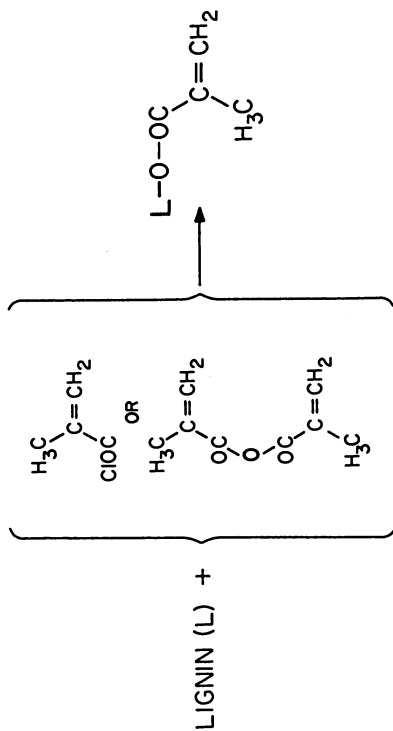


Figure 9. Reaction of lignin with methacrylyl chloride and methacrylic anhydride [adapted from (43)].

lignin derivative was copolymerized with methylmethacrylate to yield highly crosslinked, hard, and glassy acrylic copolymers.

This represents a selection of examples showing how lignin was crosslinked following some sort of chemical modification. The question of whether a particular crosslinking reaction has produced a uniform and homogeneous network polymer—that is, one without significant phase separation prior to gelation—is often difficult to answer with lignin-based materials that are nontransparent owing to their dark color. It has recently been illustrated that a mathematical model by Chan et al. (59) could be applied to judge network uniformity of polyurethanes based on lignin (6). This model relates the rise in glass transition temperature to network density. Network density is thereby expressed as average molecular weight between junction points ( $M_c$ ). The model considers both effects on  $T_g$ , that of chemical modification and that of network formation. Compliance with the model was seen as an indication for network uniformity, whereas, failure to comply with the model was attributed to phase separation and nonuniform gelation.

## Conclusions

The formation of uniform network polymers from lignin requires that phase separation prior to gel formation remain limited. The process of component demixing is controlled by both an enthalpic and an entropic contribution to Gibbs free energy. Whereas, the entropic factor requires the use of low molecular weight fractions for uniform gel formation, the enthalpic parameter necessitates chemical modification. The type of modification needed depends on the medium in which gel formation is performed. Examples of improving the solubility and compatibility with various reaction media are cited.

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# Chapter 5

## Modification of Lignins for Use in Phenolic Resins

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The high temperature phenolysis of a commercially available, spray-dried, spent ammonium sulfite liquor from the pulping of softwood has been investigated under both batch and continuous regimes as a route to a phenol substitute for use in phenol-formaldehyde resins. During the phenolysis reaction, the ammonium ion content of the lignin sulfonate rapidly decreased, and up to 0.9 mol of phenol per mol of lignin C<sub>9</sub> repeating units could be chemically attached to the lignin by reaction at 246 °C for 2 hours. Phenolation also reduced the water solubility and the molecular weight of the lignin sulfonate. The kinetics of phenolysis under autogeneous pressure are second order with respect to phenol and lignin concentrations and the rate constant between 150 and 250 °C is  $-4.7 (\pm 0.7) \times 10^7 \exp(-22,000 \pm 600 \text{ cal/RT}) \text{ L/mol min}$ .

Large volumes of wood composites are bonded with phenol-formaldehyde adhesives. The U.S. output of phenol in 1987 will likely set a record of more than 3 billion pounds, and approximately 40% of this will be used as a comonomer with formaldehyde in adhesive applications (1).

The partial replacement of some of this phenol with lignins has long represented an apparently attractive market opportunity because the phenol used in wood adhesives is worth about \$528 MM per year when phenol is 44 cents a pound, which was the August 1987 bulk price of phenol with all allowances taken into account (2).

Realistically, however, it would be unlikely that more than 25% of the total of this adhesive phenol could be replaced. This assumption decreases the value of the potential market opportunity to \$132 MM per year. Since the phenol

substitute will have to sell for less than phenol itself (say by 25%), the estimate of the size of the financial opportunity will have to be still further reduced to \$100 MM per year.

The final definition of the magnitude of the possible financial gain ultimately depends, of course, upon the difference between the cost of the phenol and the cost of the replacement lignins. For each cent that the cost of the lignin substitute is below that of the replaced phenol, the gain would be \$3 MM per year. This number is independent of the market price of phenol.

These calculations show that if renewable resources such as lignins are to find use as substitutes for phenol in wood adhesives, the cost differential between these materials must be maximized to attract investment capital. Clearly, the pulp lignins already being produced are likely to be the lowest cost renewable resource available for this purpose. Those generated in the kraft process are already recycled for their fuel value in the recovery furnace and are not easily accessible. There is only one U.S. company selling kraft lignin, and its lowest bulk price is 40 cents a pound (3).

In contrast, the lignins from the sulfite pulping processes are readily available in commercial quantities from several pulp producers in different countries. More than enough is available annually to replace the entire output of synthetic phenol. In aqueous solution, the price of these lignin sulfonates can be as low as 3 cents a pound on a dry basis. The spray-dried forms sell for about 15 cents a pound (4). Clearly, the process of spray drying is not inexpensive.

Why then are these lignin sulfonates not used as a partial replacement for phenol in phenol-formaldehyde-based wood adhesives? The first reason is that the presence of the sulfonate groups confers a water sensitivity to the adhesive. This sensitivity is exacerbated by the presence of water-soluble carbohydrates. A second reason is the low reactivity of the lignin sulfonates with formaldehyde and the consequent low level of crosslink density achieved in the final adhesive. A third reason is the molecular size of some of the lignin sulfonates. Large molecular weight material cannot penetrate the cell walls of the wood to form an adhesive continuum between contiguous wood particles.

Before lignin sulfonates can be usefully incorporated into phenolic wood adhesives, these shortcomings must be remedied in a cost-effective way relative to the price of phenol. The remedial approach selected in this work has been to investigate the phenolysis of commercial lignin sulfonates with commercial grade phenol.

## Experimental Procedures and Results

**Selection of Lignin Substrate.** The lignin sulfonate chosen for the initial experiments was an ammonium salt rather than the corresponding calcium, magnesium, or sodium counterparts, which are the other commercial forms available. This selection was made on the basis that ammonium lignin sulfonates actually differ significantly in physical and chemical properties from the

superficially analogous metal salts. Perhaps the most striking difference is that ammonium lignin sulfonates are soluble in a variety of organic solvents, whereas, the calcium, magnesium, and sodium salts are only soluble in water.

This solubility difference implies that the ammonium salts may have chemical properties quite distinct from the other members of the lignin sulfonate clan. Certainly, during the pulping process, many of the lignin fragments detached from the wood must react with the ammonia present, since carbonyl functions exist in all lignins, and these groups readily combine with ammonia. The existence of this reaction is evidenced by the fact that only a portion of the nitrogen content of the ammonium lignin sulfonates can be distilled off as ammonia under alkaline conditions. Ammonium salts and amides, of course, are quantitatively converted to ammonia under these conditions; amines and imines are not. These observations would also apply to carbohydrate material admixed with the ammonium lignin sulfonates.

The nature of the covalently bound nitrogen in ammonium lignin sulfonates or the associated carbohydrates has not yet been reported, but if it is present as a primary or secondary amine, the reactivity toward formaldehyde would likely be increased (5) and the crosslink density of the resultant adhesive thereby augmented.

**Choice of the Lignin Modification Reaction.** The phenolysis reaction was selected as a means of modifying the structure and reactivity of the ammonium lignin sulfonate for three main practical reasons. First, because this lignin derivative is soluble in (and will ultimately be used in conjunction with) liquid phenol itself; second, because unreacted phenol, unlike other reaction solvents, would not have to be removed from the phenolated product after reaction and before conversion to the adhesive resin; and third, because lignins and carbohydrates are known to react with phenols under acidic conditions (6, 7).

A discussion of the various possible facets of the chemistry of the interactions of lignins and carbohydrates with phenol lies beyond the scope of this article. However, in a general way, it can be stated that, because of the excess of phenol in the reaction mixture, the combination with either lignin or carbohydrates is most likely to involve only one of the three reactive positions on the aromatic ring of the phenol. Consequently, the reactivity of the modified lignins and carbohydrates to formaldehyde ought to be enhanced relative to the prephenolyzed material because, for every reactive position lost by combination, two new reactive positions are created by the added phenol moiety.

**Phenolysis Reaction Procedure.** To explore the concept of phenolation, mixtures of a commercial spray-dried softwood ammonium lignin sulfonate (10 g, Orzan A, 60% ammonium lignin sulfonate ( $MW_o = 228$ ), 28% sugars, 6.2% sulfur, 2.5% ash, ITT-Rayonier, Shelton, Washington available in bulk at 17 cents a pound (8) and commercial grade phenol (15 mL, Reichhold Chemicals Inc., Tacoma, Washington) contained in small pressure bombs (30 mL, Parr Instrument Company, Moline, Illinois) were heated by suspension in a hydraulic

fluid heating bath maintained at  $200 \pm 3$  °C for various periods of time. After being heated and before being opened, the sealed bombs were cooled for 5 minutes in an ice bath.

**Fate of Ammonium Ion During Lignin Phenolation.** Aliquots (1-5 g) of the reaction products were then diluted with water (200 mL) and analyzed for their ammonium ion content. The procedure comprised treatment with an aqueous solution of NaOH (20% w/v, 100 mL), distillation with collection of the distillate (175 mL) in an aqueous solution of boric acid (4% w/v, 50 mL), and titration with a standard solution of sulfuric acid. The results obtained are compiled in Table I.

Table I. Effect of Duration of Heating on the Ammonium Ion Content of a Mixture of Ammonium Lignin Sulfonate and Phenol (61.5%)

Duration of Heating (min)	Ammonium Ion Content (%)
0	3.63
10	2.43
20	1.84
30	1.95
40	1.81
50	1.76
60	1.74
75	2.01
80	2.01
120	1.81
134	1.70

The data in the table demonstrate that about half of the water-soluble ammonium ion content is converted into some new form of nitrogen, the nature of which has yet to be determined. Concurrent total nitrogen analyses by the use of a modified Kjeldahl procedure (9) capable of cleaving heterocyclic structures confirmed that no detectable amount of nitrogen had been lost from the phenolysis reaction system.

It is also evident from the results in Table I that the transformation of the ammonium ion is essentially complete within a 20-minute reaction period. This is an important finding in terms of the sizing and operation of a continuous reactor, details of which (10) will be reported elsewhere.

**Phenolysis Pressures in Larger Batch Reactor.** Because of the difficulties of working with small amounts of material, the foregoing experiments were repeated in a larger capacity (500 mL) stirred batch reactor. This enabled

measurement of the pressures generated during phenolysis. The pressure data collected are shown in Table II.

Table II. Comparison of Total Pressure Generated by Heated Phenol and a Phenol-Ammonium Lignin Sulfonate (38.5%) Mixture in a Stirred Batch Reactor

Duration of Heating (min)	Gauge Pressure (kN/m <sup>2</sup> ) <sup>1</sup> Generated by	
	Phenol	Phenol-Ammonium Lignin Sulfonate
0	0	0
2	14	-
4	41	-
6	83	14
7	103	-
8	110	-
10	-	41
11	131	-
14	-	145
15	152	-
18	-	207
20	164	234
25	165	289
30	166	289
40	166	-
50	166	289
55	-	310
60	-	310
70	-	310

<sup>1</sup>Multiply by 0.145 to convert to psi.

From the data in Table II, it seems that the pressures involved in carrying out the phenolysis modification do not pose any special engineering problems since the maximum encountered is only 45 psi. Subsequently, however, in another set of experiments that were carried out for longer heating periods, the pressures observed rose to much higher levels (cf. Table VIII). This may be due to the presence of water generated by dehydration reactions.

The conversion of ammonium ions achieved in this larger stirred reactor was very similar to that accomplished in the smaller Parr bombs. However, because of the heat capacity of the larger reactor, the time necessary to raise the temperature to secure an equivalent extent of reaction was lengthened to 70 minutes.

**Solubility of Phenolated Lignin Sulfonates.** Since the presence of ammonium sulfonate moieties tends to confer water solubility, their disappearance should be reflected in a reduction of this characteristic. The extent of this effect was assessed by measuring the solubility of a stirred aliquot (1-4 g) of the 200 °C phenolysis product in water (200 mL). The resultant suspension was filtered and the residue dried for about 2 days at 22 °C to constant weight. The results obtained under a variety of reaction conditions are summarized in Table III.

Table III. Effect of Duration of Heating on Ammonium Ion Content and Water-Solubility of a Mixture of Phenol (61.5%) and Ammonium Lignin Sulfonate

Duration of Heating (min)	Ammonium Ion Content (%)	Yield of Water-Insolubles <sup>1</sup> (%)
0	3.62	0.0
20	2.30	0.8
30	2.21	21.0
40	2.08	—
50	—	23.4
60	—	27.5
70	1.86	28.8

<sup>1</sup>Expressed in terms of the ammonium lignin sulfonate feed.

Another related set of experiments was also carried out to determine the effect of temperature on the insolubilization of the ammonium lignin sulfonate by phenolysis for a period of 2 hours. The results obtained, which are summarized in Table IV, show that more than one-third of the commercial product can be made water-insoluble by this procedure.

For subsequent adhesive production, it is important to note that all the reaction mixtures were completely soluble in 0.1% and 1% aqueous sodium hydroxide solution. The solubilities in 0.1N and 1N aqueous sulfuric acid solutions were 81.9 and 75.4%, respectively.

**Phenolysis of Carbohydrates.** The carbohydrates are also modified by reaction with phenol under comparable conditions as has been demonstrated by Mathur (11). Among the products identified were levulinic acid, furfural, and hydroxymethylfurfural. All are capable of forming carbon-carbon bonds with phenol.

**Degradation of Lignin Molecular Weight.** In addition to these transformations of the water-sensitive carbohydrates, the phenolysis reaction also affects

the molecular weight of the lignin sulfonate. This is evidenced by comparison of the viscosity of the phenolysis mixture after reaction at two different mean residence times in a continuous tube reactor. The viscosity was measured in a Brookfield viscometer (Brookfield Engineering Company, Stoughton, Massachusetts, Model No. RVF) fitted with a No. 3 spindle rotating at 20 rpm and calibrated with glycerol. When the residence times were 9.7 and 20.0 minutes, the viscosities measured were 1770 and 1170 centipoise, respectively.

Table IV. Effect of Reaction Temperature on Extent of Phenolysis and Degree of Water Insolubility Conferred upon a Commercial Ammonium Lignin Sulfonate Admixed with Phenol (61.5%) and Heated for 2 Hours

Reaction Temperature (°C)	Yield of Water Insolubles <sup>1</sup> (%)	Recoverable Phenol (%)	Combined Phenol per Lignin Unit (mol)
134	2.4	95.9	0.15
135	—	95.3	0.19
139	—	95.9	0.15
150	5.2	98.2	0.01
162	10.2	96.3	0.13
170	14.2	93.0	0.34
181	19.4	89.8	0.54
196	23.6	90.6	0.49
212	31.0	89.3	0.57
224	32.8	85.4	0.82
246	36.1	85.7	0.80

<sup>1</sup>Expressed in terms of the ammonium lignin sulfonate feed.

Collaborative chemical evidence for the breakdown of the lignin sulfonates was the discovery that the steam distillate of phenolysis mixtures, batch-reacted at 224 °C, contained guaiacol, methylguaiacol, and catechol. These are typical fragments resulting from the high-energy degradation of lignins (12). Further data showing the extent of degradation of the lignin sulfonates during phenolysis have been gathered by the use of gel filtration chromatography (13) and will be reported elsewhere.

**Kinetic Study of the Phenolysis Reaction.** With the demonstration that all of the already outlined deficiencies of ammonium lignin sulfonates as a phenol replacement can be reduced by phenolysis, attention was turned to consideration of the construction of a pilot plant scale continuous tube reactor. This is needed in order to prepare the large amounts of phenolyzed lignin sulfonates required for resin synthesis and testing under plywood production conditions.



Such testing, to be reported in detail later, showed that the phenolyzed product can be successfully used in adhesive formulations for plywood (14).

As a prelude to the design of the tube reactor (10), a kinetic study of the phenolysis procedure as a function of temperature was carried out on a larger scale. The equipment used was a stainless steel pressure reactor (Model 4501, Parr Instrument Company, Moline, Illinois). This reactor is fitted with an internal stirrer, an external electric heater, and a continuous sampling device. A mixture of the commercial ammonium lignin sulfonate (668 g) and molten phenol (1000 mL) was sealed into the reactor and heated to the designated temperatures. Approximately 3 hours were needed to heat the reactor from room temperature to 200 °C. A similar period of time was required to cool the reactor and its contents back to 22 °C after completion of a run. After a reaction period nominally lasting 2 hours, the unreacted phenol was steam distilled from the reaction mixture and the amount measured by comparative UV spectroscopy. The results obtained and summarized in Table IV show that a substantial amount of phenol becomes chemically combined with the renewable resource feedstock.

The effect of heating time on the extent of phenolysis in this larger reactor was also studied at 220 °C, and the resulting data secured are summarized in Table V. It was necessary to use a heating time correction because the exothermicity of the phenolysis reaction at 200 °C increased the temperature of the reactants as the time of reaction progressed.

Table V. Effect of Time-Corrected Duration of Heating at 220 °C on Extent of Phenolysis of a Commercial Ammonium Lignin Sulfonate Admixed with Phenol (61.5%)

Time-Corrected Duration of Heating (min)	Combined Phenol per Lignin Unit (mol)
5	0.08
10	0.13
16	0.19
22	0.23
48	0.40

**Analysis of Kinetic Data.** To gather the data necessary for this type of analysis, yet another set of phenolysis experiments was carried out; this time in a small Parr bomb that was immersed in an oil bath maintained at 220 °C for relatively short periods of time. The data collected and summarized in Table VI were correlated for zero, first, and second order kinetic models by the use

of an integral method (15). The correlation coefficients for the fit with these orders of reaction kinetics were 0.93, 0.875, and 0.975, respectively.

With this demonstration that the kinetics of the phenolysis reaction are second order in nature, an Arrhenius rate constant model

$$k = k_o \exp(-E_o/RT) \quad (1)$$

was applied (15) to the temperature and time data in Table VII for temperatures between 150 and 246 °C. The calculated activation energy,  $E_o$ , determined by this procedure was 23,075 cal/mol K.

Table VI. Kinetic Data for the Phenolysis of Ammonium Lignin Sulfonate in Phenol (61.5%)

Time of Immersion Heating (min)	Concentration of Phenol [P] (mol/liter)	Concentration of Lignin Units [L] (mol/liter)	$\ln [P]/[L]$
0	7.71	1.20	1.86
5	7.54	1.03	1.99
10	7.44	0.93	2.07
15	7.33	0.82	2.19
20	7.34	0.83	2.17
30	7.26	0.75	2.27
60	6.90	0.42	2.80

This value, together with the heating and cooling times of the reactor that are summarized in Table VIII, was used to correct the rate constant data in Table VII. This correction is based on the recognition that for second order kinetics

$$\frac{dC_a}{dt} = -kC_aC_b \quad (2)$$

where  $C_a$  and  $C_b$  denote the concentrations of species A and B, respectively, at time  $t$  while  $k$  represents the rate constant of the reaction.

By substitution of equation (1) into (2) and integration, equation (3) is obtained where the original concentrations are designated as  $C_{a_o}$  and  $C_{b_o}$ .

$$\ln(C_aC_{b_o}/C_bC_{a_o}) = (C_{b_o} - C_{a_o})k_o \exp(-E_o/RT)t \quad (3)$$

Table VII. Data for Calculation of Activation Energy of the Phenolysis of Ammonium Lignin Sulfonate in Phenol (61.5%) using the Arrhenius Rate Constant Model (15)

Phenolysis Temperature (°C)	Amount of Phenol Combined mmol/kg Reactants	Concentration <sup>1</sup> of Phenol <sup>2</sup>		Rate of Lignin Unit Combination <sup>4</sup> (mmol/L min)	Phenolysis Rate Constant (L/mol min)
		mmol/L	(mmol/L)		
130	154	7406	1068	1.52	1.92
135	155	7402	1064	1.52	1.93
139	154	7406	1068	1.52	1.92
150	104	7465	1127	1.03	1.22
162	239	7305	968	2.35	3.33
170	328	7201	863	3.22	5.18
181	527	6966	629	5.18	11.82
196	707	6753	415	6.96	24.80
212	835	6602	265	8.21	46.98
224	1005	6402	64	9.89	241.38
246	995	6414	76	9.78	200.63

<sup>1</sup>The density of the initial reaction mixture was 1.18 g/mL.

<sup>2</sup>The initial concentration of phenol was 7590 mmol/L.

<sup>3</sup>The initial concentration of lignin units was 1250 mmol/L.

<sup>4</sup>Measured after a period of phenolysis of 120 min.

Table VIII. Temperature and Pressure Variation in the Phenolysis Reactor as a Function of Heating Time

Duration of Heating (min)	Temperature in Reactor (°C)	Gauge Pressure of Reactor (kN/m <sup>2</sup> )
0	43	0
25	50	69
35	63	76
50	83	76
70	102	83
90	122	90
142	140	103
160	157	166
178	177	248
200	205	1028
250	208	1559
292	208	2014
326 <sup>1</sup>	208	2379
340	0	855

<sup>1</sup>After this heating period, the reactor was cooled by immersion in ice water.

When two identical sets of reactants are maintained at different temperatures, the extent of reaction of each is also identical only when the products of the rate constants and reaction times ( $t_a$  and  $t_b$ ) are equal, so that

$$t_a k_o \exp(E_o/RT_a) = t_b k_o \exp(E_o/RT_b) \quad (4)$$

$$\frac{t_a}{t_b} = \frac{\exp(E_o)}{(1/RT_a - 1/RT_b)} \quad (5)$$

Equation (5) was used to correct the heating times in Table VII, and new reaction rate constants were then calculated. Thereafter, a new activation energy was obtained by a second Arrhenius fit of the corrected data. This procedure was repeated until the difference in the calculated activation energy from two successive iterations was less than the standard deviation of the error of the fit of the data. The final activation energy value obtained was  $22,182 \pm 612$  cal/mol K, and the correlation coefficient was then 0.996.

This value of the activation energy, together with the corrected rate constants for each temperature, was employed to evaluate the pre-exponential constant,  $k_o$ , in the Arrhenius rate constant model. The value thus derived was

$$k_o = -4.7 (\pm 0.7) \times 10^7 \text{ L/mol min}$$

where the error is the standard deviation from the mean value.

The final corrected value for the activation energy was also used to adjust for the exothermic heating observed in the small bomb runs, which modified the initial kinetic data. The adjusted time values were 4.60, 8.31, 14.53, 20.18, 25.08 and 31.77 minutes, corresponding to the values 5, 10, 15, 20, 30 and 60 listed in Table VI.

As an example of the consequence of this time adjustment, the value of the rate constant for the phenolation reaction at 220 °C becomes

$$k = -4.5 (\pm 0.3) \times 10^{-3} \text{ L/mol min}$$

The correlation coefficient, after elimination of the data points at 20 and 25 nominal minutes by invoking Chauvenet's criterion (16), was found to be 0.986.

## Conclusions

Given all the foregoing information, it is clear that the phenolysis of ammonium lignin sulfonates ameliorates the several shortcomings of this renewable resource as a component of phenol-formaldehyde adhesives. Moreover, the simplicity of the phenolysis process suggests that it is a feasible route to an economically attractive and marketable replacement for phenol. The kinetic data established will enable a large-scale continuous tube reactor to be designed to convert a mixture of commercial grade ammonium lignin sulfonates (40%) in phenol (60%) into a mobile black oil suitable for use in adhesive formulations.

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# Chapter 6

## Adhesive Feedstocks from Lignin

### Mechanistic Studies on the Oxidative-Cleavage Reaction of Some Lignin Model Compounds

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Many attempts have been made to utilize lignin as a phenolic substitute in adhesives. Unfortunately, the structure of lignin restricts its reactivity and thus limits the industrial usefulness of lignin-based resins. One process for activating it would be to oxidatively cleave lignin to low molecular weight phenolic benzaldehydes. These benzaldehydes could then be reduced to condensable methylol phenols or alternately used as a feedstock for other polymeric products. Mechanistic, kinetic, and structure-activity studies of the oxidative cleavage reaction of lignin model compounds using different oxidants showed that the reaction is probably homolytic and involves the benzylic hydroxyl group. No evidence was obtained that supported a quinone methide intermediate. Oxidations with CAN showed that electron abstraction occurred at the benzylic oxyanion rather than at the aromatic ring. It is believed that several reagents oxidatively cleave lignin via a common mechanism. A proposed mechanism has been suggested based on our experimental results.

Despite extensive research, the commercial utilization of lignin in phenolic resins is negligible. The major problem is that the structure of lignin restricts its re-

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activity, where reactivity is defined as the extent to which a lignin can condense with formaldehyde (T. Sellers and W. Nearn, Mississippi State University, personal communication, 1987). (See Chapters 2 and 3 for a discussion of the various active sites of lignin.)

A proposed scheme for increasing the reactivity of lignin and thus enhancing its usefulness as an alternative adhesive feedstock is presented in Figure 1. The first step is to perform an oxidative-cleavage reaction to form phenolic benzaldehyde compounds.

These benzaldehydes could then be directly used as a feedstock for various polymeric products or reduced to form phenolic benzylic alcohol derivatives; (i.e., *p*-methylol groups). The *p*-methylol groups would thus be active sites, whereas in unmodified lignins, the C-1 site is blocked and unreactive. In addition, the oxidative-cleavage step will hydrolyze a portion of the lignin interunit ether bonds, and thus increase the total fraction of free phenolic units to further enhance the reactivity. Other possible benefits are that the lignin would be extensively depolymerized and would form a more uniform feedstock material; both conditions would give a product that is easier to handle.

The second step in Figure 1 involves the reduction of the newly formed benzaldehydes. This reaction is performed commercially using either catalytic hydrogenation or reagents such as sodium borohydride. The reduction mechanisms are well understood. The oxidative-cleavage reaction of lignin using reagents such as nitrobenzene or copper(II), however, is not well understood.

The objective of this research was to gain a better understanding of the oxidative-cleavage pathway. If this mechanism could be comprehended, it is possible that a relatively low-cost and environmentally safe process could be developed for producing a durable, commercially acceptable, lignin-based adhesive.

## Experimental Methodology

The details of the reaction conditions used in this study have been described elsewhere (Dershem, S. M., et al., *Holzforschung*; Fisher, T. H., et al., *J. Org. Chem.*, in press). To test the importance of a *p*-hydroxyl substituent, the kinetics of oxidation of three benzyl alcohols: *p*-hydroxybenzyl alcohol, (1), *m*-hydroxybenzyl alcohol, (2), and 4-hydroxy-3-methoxybenzyl alcohol, (3), were examined under alkaline nitrobenzene oxidation conditions. Some 1-(4-hydroxyphenyl)-2-(4'-substituted phenyl)ethanols, (4), were synthesized as  $\beta$ -1 lignin model compounds and subjected to alkaline nitrobenzene oxidation at 120 °C to study substituent effects. For controls, some of these compounds were reacted with or without nitrobenzene, alkaline catalyst, or water. In an effort to determine the effects of substituents on the oxidative-cleavage reaction of 4-hydroxystilbenes (5), a series of competitive rate experiments using both nitrobenzene and copper(II) as the oxidants in 2*N* NaOH was performed (Dershem, S. M., et al., *Holzforschung*, in press).



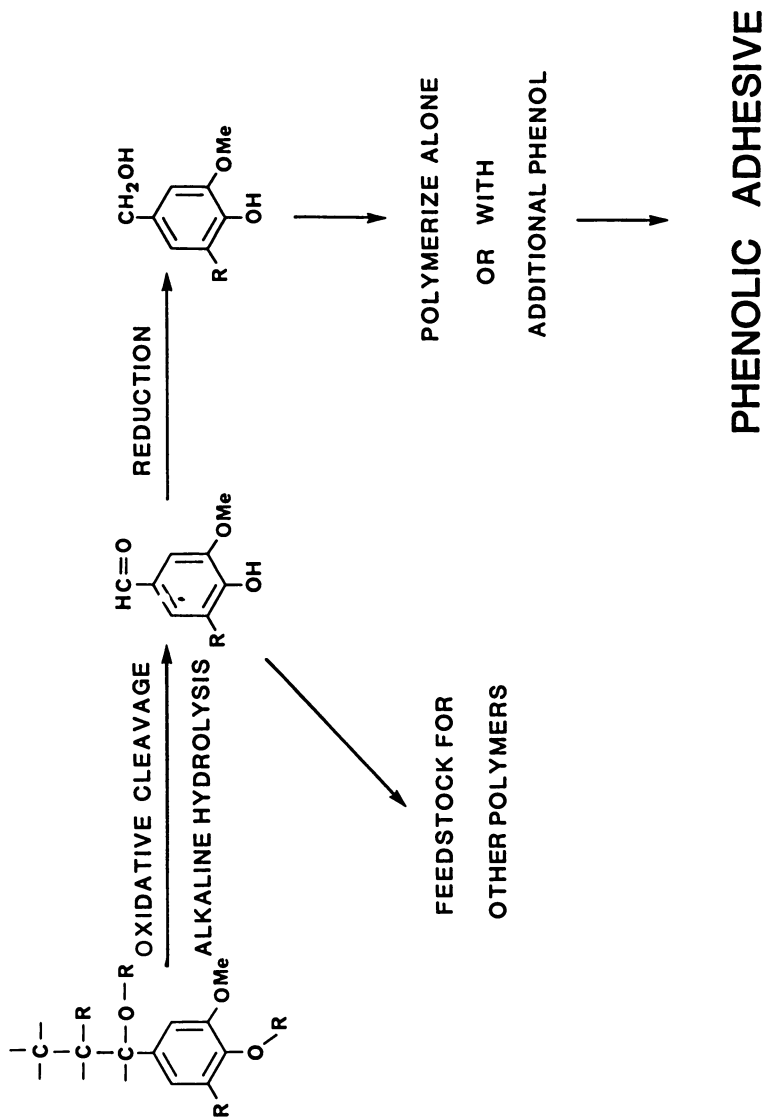


Figure 1. Proposed scheme to activate lignin for use in phenolic resins and as a feedstock for other polymeric products.

Oxidations of 1-(4-methoxyphenyl)-2-(4-substituted phenyl)ethanols, (6), [identical to alcohols (4a) to (4e) except for methylation of the 4-OH group] were also studied with cerium(IV) as the catalyst (Fisher, T. H., et al., *J. Org. Chem.*, in press). To determine if oxidation occurs by electron abstraction from the benzylic hydroxyl or the aromatic ring, a competitive oxidation procedure was examined on the diaryl ethanol 6a and its methyl ether analog, 1-methoxy-1-(4-methoxyphenyl)-2-phenylethane, (7), (Fisher, T. H., et al., *J. Org. Chem.*, in press).

## Results and Discussion

A number of early researchers have conducted studies on lignin oxidations using nitrobenzene and copper(II) reagents. A comprehensive review has been summarized by Chang and Allan (1). Based on their review, Chang and Allan proposed a mechanism for the nitrobenzene oxidation reaction. They noted that free phenolic groups were necessary to: 1) ensure adequate solubility in base, 2) protect the aldehyde products from further oxidation via the Cannizzaro reaction, and 3) form a quinone methide, which was believed to be a key reaction intermediate. The initial reaction was presumed to be alkaline hydrolysis of the lignin. The nitrobenzene oxidation reaction was proposed to be a two-electron (heterolytic/ionic) pathway. Compounds with an  $\alpha$ -carbonyl function, such as guaiacyl propanone, were thought to first undergo enol/keto tautomerism followed by formation of a quinone methide. It was suggested that a nonenolic oxidation would give benzoic acids derivatives.

Chang and Allan also reviewed the available publications on cupric ion (copper(II)) oxidations and proposed a mechanism for this reaction. They reported that the copper(II) oxidation products and yields were similar to those obtained from a nitrobenzene oxidation. Their proposed mechanisms for the two reagents (copper(II) and nitrobenzene) were different, however. The proposed copper(II) mechanism involved a quinone methide intermediate, which was formally identical to the intermediate proposed in the key nitrobenzene step. The differences between the two reagents, however, included the observation that copper(II) is a well-known one-electron oxidant (2), and that a phenoxy radical was first formed.

Although Chang and Allan (1) reviewed essentially all the available lignin oxidation work, they observed that most of the research was not mechanistic in nature. Thus, they noted that their proposed mechanisms were based on limited data and were presumed to require possible further modifications.

**Role of the *p*-Hydroxyl Group.** Preliminary nitrobenzene oxidation experiments were conducted on several benzylic hydroxyl compounds, both with and without a *p*-hydroxyl group (3). Contrary to what was expected from the literature, some compounds without a *p*-hydroxyl group formed benzaldehyde products.

Methylation experiments by Leopold (4) have been cited (1) as proof of the necessity for a quinone methide intermediate during a nitrobenzene oxidation. However, a critical reexamination of Leopold's paper showed that he actually suggested that methylation of the benzylic hydroxyl groups was the cause of the low vanillin yield from methylated lignins, rather than methylation of the phenolic groups as suggested by Chang and Allan (1). Furthermore, two references were found where nitrobenzene was used to oxidize nonphenolic toluene and benzylic alcohol derivatives (5,6). An experiment was conducted to critically test the necessity of a *p*-hydroxyl group in its presumed role of acting as a precursor for the formation of a quinone methide intermediate during nitrobenzene oxidations (7). Three benzyl alcohols were oxidized under alkaline nitrobenzene conditions: *p*-hydroxybenzyl alcohol, (1); *m*-hydroxybenzyl alcohol, (2); and 4-hydroxy-3-methoxybenzyl alcohol, (3). The pseudo first-order rate constants (Table I) for the nitrobenzene oxidation of 1 (with a *p*-OH) and 2 (with a *m*-OH) were similar. The minor differences in the rate constants are of the magnitude expected from substituent effects. The reaction rate of 1 was about twice that of 2, and the value for 3 was about twice that of 1. The activation parameters  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  (Table I) for 1 and 2 are the same within experimental error. The similarity of products, rate constants, and activation parameter data for 1 and 2 strongly suggested that the nitrobenzene oxidation of both compounds must proceed through a common mechanism. This mechanism cannot involve a quinone methide intermediate because such an intermediate is not possible from compound 2.

Table I. Pseudo First-Order Rate Constants and Activation Parameters for the Nitrobenzene Oxidation of Selected Compounds (7)

Benzyl Alcohol	$10^5 k \text{ (sec}^{-1}\text{)}$			$\Delta H^\ddagger$ (kcal/mol)	$\Delta S^\ddagger$ (eu)
	120 °C	135 °C	150 °C		
1 4-OH	4.74	18.1	35.4	$21.4 \pm 2.5$	$-24 \pm 6$
2 3-OH	1.92	5.2	16.6	$22.8 \pm 1.6$	$-23 \pm 2$
3 4-OH, 3-OMe	6.86	27.8	78.2	$26.1 \pm 1.2$	$-12 \pm 3$

Phenolic groups are important, however, to ensure that the lignin fragments have adequate alkali solubility. Furthermore, a *p*-hydroxyl group is necessary to protect the aldehyde products from reacting further via the Cannizzaro reaction.

**Oxidation of Hydroxystilbene Derivatives with Nitrobenzene and Copper(II).** To serve as  $\beta$ -1 lignin model compounds, some 1-(4-hydroxyphenyl)-2-(4'-substituted phenyl)ethanols, (4), (Figure 2) were synthesized (8). The  $\beta$ -1 lignin model was chosen, since it is the only common lignin unit structurally suitable for substituent-reactivity studies on oxidation rates. In an effort to study

substituent effects, the various alcohols were subjected to alkaline nitrobenzene oxidation at 120 °C. The major reaction that occurred was dehydration to give the stilbenes **5** (Figure 2). However, some *p*-hydroxybenzaldehyde was formed from the chloroalcohol **4b** in addition to the major chlorostilbene product **5b**. A control experiment on the chlorostilbene **5b** using the identical reaction condition (120 °C) formed no benzaldehyde product. However, at 155 °C, equivalent amounts of benzaldehyde were formed from both the chloroalcohol **4b** and the chlorostilbene **5b** (Dershem, S. M., et al., *Holzforschung*, in press).

Another control experiment was done to determine the importance of water in this oxidative cleavage reaction. Water was found to be a necessary reagent for the reaction to occur since no *p*-hydroxybenzaldehyde was obtained when the sodium salt of chlorostilbene **5b** was heated in neat nitrobenzene with or without solid sodium hydroxide and a crown ether phase transfer catalyst. Another set of controls was done to evaluate the formation of *p*-hydroxybenzaldehyde by a nonoxidative reaction, such as the loss of X-Ph-CH<sub>2</sub> in a retrograde-type Aldol reaction. No *p*-hydroxybenzaldehyde was formed when the chlorostilbene **5b** was heated at 155 °C for 5 hours in the presence of 2*N* NaOH but without the presence of nitrobenzene and atmospheric oxygen. Finally, in all of the above control experiments, no oxidized cleavage products were observed from the nonphenolic side of the alcohols **4** or stilbenes **5** (Dershem, S. M., et al., *Holzforschung*, in press).

All of these control experiments are consistent with a mechanism in which the stilbenes **5** are in dynamic equilibrium with the equivalent benzylic alcohols **4** and the oxidative-cleavage reaction occurs on the latter. This equilibrium explains: 1) the observed requirement for water for the stilbene oxidations; 2) the unsymmetrical product distribution from both the alcohols and stilbenes; and 3) the enhanced reaction rate of the chlorobenzyl alcohol **4b** as compared to the stilbene analogue **5b** at 120 °C.

A series of competitive rate experiments using both nitrobenzene and copper(II) as the oxidants in 2*N* NaOH to determine the effects of substituents on the oxidative-cleavage reaction of 4-hydroxystilbenes **5**, were made (Dershem, S. M., et al., *Holzforschung*, in press). The relative rate measurements, shown in Table II, were determined by following the loss of substituted stilbenes **5b-d** versus the unsubstituted stilbene **5a**, since all stilbenes gave the same product: *p*-hydroxybenzaldehyde. The relative rate of copper(II) oxidation of methyl stilbene **5c** appears to be anomalously high, even though it is reproducible. The probable source of this anomaly is that copper(II) is also a known oxidant of arenes (9), and the methyl group undergoes oxidation along with the C = C group. This competing oxidation produces an exaggerated value of  $k_X/k_H$  for the methyl stilbene **5c**.

The relative rate data of Table II were subjected to Hammett plots of  $\log k_X/k_H$  versus  $\sigma$  and  $\sigma^+$ . In the nitrobenzene oxidations, a better correlation was found with  $\sigma^+$  ( $\rho^+ = -0.48$ ,  $r = -0.994$ ). The preferred dependence on  $\sigma^+$  was also found in the copper(II) oxidations when the kinetic point for the methyl

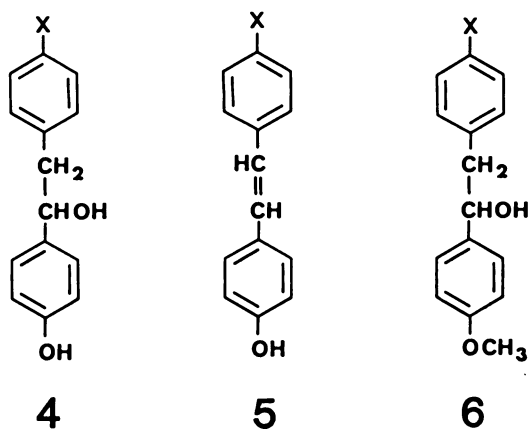


Figure 2. Compounds used to determine structure–reactivity correlations:  
(a)  $\text{X} = \text{H}$ , (b)  $\text{X} = \text{Cl}$ , (c)  $\text{X} = \text{Me}$ , (d)  $\text{X} = \text{OMe}$ , (e)  $\text{X} = \text{NO}_2$ .

derivative was ignored for the above-mentioned reason. The values obtained were  $\rho^+ = -0.45$  ( $r = -0.990$ ). When all four points were used for copper(II), the Hammett constant was  $\rho^+ = -0.48$  ( $r = -0.854$ ).

The small magnitudes of  $\rho^+$  found are consistent with a free-radical process since homolytic reactions usually give smaller  $\rho^+$  values than comparable heterolytic reactions (10,11). The negative  $\rho^+$  value and the excellent correlation with  $\sigma^+$ , however, imply that some positive charge is centered upon the incipient benzyl carbon during the oxidative-cleavage step.

Table II. Relative Rates of Nitrobenzene and Copper(II) Oxidations of 4-Hydroxystilbenes **5** in 2N NaOH at 155 °C<sup>1</sup>

Stilbene	$k_X/k_H$ for PhNO <sub>2</sub> <sup>2,3</sup>	$k_X/k_H$ for copper(II) <sup>2,4</sup>
<b>5b</b> Cl	0.93 ± 0.07	0.78 ± 0.12
<b>5a</b> H	1.00	1.00
<b>5c</b> Me	1.58 ± 0.14	2.17 ± 0.27
<b>5d</b> OMe	2.44 ± 0.04	2.06 ± 0.22

<sup>1</sup>Dershem, S. M., et al., *Holtzforschung*, in press.

<sup>2</sup>Average of six or more replications.

<sup>3</sup>Identical results under nitrogen or air.

<sup>4</sup>Done under air.

Since copper(II) is a known homolytic oxidant and since nitrobenzene gives an essentially identical reaction constant ( $\rho^+$  of -0.45 versus -0.48), the logical implication is that nitrobenzene also acts as a homolytic oxidant under these conditions.

**Oxidation of 1-(4-methoxyphenyl)-2-(4'-substituted phenyl)ethanols, **6**, by Cerium(IV).** Dehydration prevented the oxidative-cleavage study of 1-(4-hydroxyphenyl)-2-(4'-substituted phenyl)ethanols, **4**, (**8**). As an alternative study, the oxidation of these phenolic compounds using the homolytic oxidant ceric ammonium nitrate (CAN) in an acidic environment was initiated. However, preliminary oxidations of these compounds were unsuccessful due to the apparent formation of complexes of cerium(IV) with the phenolic hydroxyl groups.

The oxidations of 1-(4-methoxyphenyl)-2-(4'-substituted phenyl)ethanols, (**6**, Figure 2), which were identical to alcohols **4** except for methylation of the 4-OH group, were successful with cerium(IV) (Fisher, T. H., et al., *J. Org. Chem.*, in

press). The reactions between CAN and these compounds were essentially instantaneous at room temperature with *p*-anisaldehyde being the cleavage product. No reaction products were found from the 2-aryl ring of alcohols **6**, despite the fact that all of the alcohols had a methoxy group on ring-1, and **6d** had a methoxy group on both aryl rings-1 and -2. The average relative rates for the four substituted alcohols **6b-e** against the unsubstituted compound **6a** are presented in Table III. The Hammett plot of the log of these values against  $\sigma^+$  and  $\sigma$  gave a superior fit with  $\sigma$  ( $\rho = -1.24$ ;  $r = -0.997$ ). Nave and Trahanovsky's (12,13) results for the competitive oxidation of 2-aryl-1-phenylethanols with CAN, by contrast, correlated best with  $\sigma^+$  and gave a  $\rho^+$  of -2.00. Their results for the homolytic oxidation of the same alcohols with chromium(IV), however, gave a better fit with  $\sigma$  ( $\rho^+ = -1.0$ ).

Table III. Relative Rate Results  
for the CAN Oxidation of  
Alcohols **6a-6e**

Compound	$k_X/k_H$
<b>6e</b> NO <sub>2</sub>	0.11 ± 0.01
<b>6b</b> Cl	0.61 ± 0.03
<b>6a</b> H	1.00
<b>6c</b> Me	1.58 ± 0.03
<b>6d</b> OMe	2.37 ± 0.10

<sup>1</sup>Fisher, T. H., et al., *J. Org. Chem.*, in press

The obvious implication of the kinetic results from these methoxy benzylic alcohols **6** is that no significant positive charge is centered on the benzylic carbon in the transition state. The difference between this result and that reported by Nave and Trahanovsky (12,13) for cerium(IV) oxidation of 1,2-diarylethanols must, therefore, reflect the influence of the *p*-methoxyl substituent in the ring alpha to the alcohol function. Trahanovsky's original argument for the observed correlation with  $\sigma^+$  was based on the presumed ability of the complexed cerium(III) ion to polarize the electron distribution in the transition state. The presence of the strong electron donating *p*-methoxyl substituent for alcohols **6** would be expected to partially counterbalance this polarization. The positive charge on the nonhydroxyl-containing benzylic carbon should thus be correspondingly diminished.

The conditions required for Trahanovsky's oxidation of 1,2-diarylethanols by cerium(IV) were considerably more rigorous than those needed in this study (i.e., 20 min at steam bath temperatures versus seconds at room temperature).

Thus, the *p*-methoxyl group also caused the oxidation rates of the alcohols 6 to be strongly accelerated. A final area of investigation examined whether the initial oxidation (electron abstraction) occurs at the benzylic hydroxyl group or at the aromatic ring. If the CAN oxidation involves alkoxy radicals, then methylation of the benzylic hydroxyl group should inhibit the oxidative-cleavage reaction. However, if aryl radical cations (12,14-16), not alkoxy radicals, are intermediates in this mechanism, then the oxidative-cleavage reaction should still be possible with benzyl ethers. A competitive oxidation procedure was used on the diaryl ethanol 6a and its methyl ether analog, 1-methoxy-1-(4-methoxyphenyl)-2-phenylethane, (7), to differentiate between these two possible mechanisms (Fisher, T. H., et al., *J. Org. Chem.*, in press). The results from several competitive runs were near quantitative recovery of the benzylic ether 7 while as much as 50% of the benzylic alcohol 6a was oxidatively cleaved. The ether 7 was also reacted with CAN in the absence of the benzylic alcohol 6a. Again, essentially all of the ether 7 was recovered unchanged. This clearly shows that the benzylic hydroxyl group is necessary for the CAN oxidation of compounds 6 to occur, and that alkoxy radicals, not aryl cation radicals, are the intermediates in the oxidative-cleavage reaction of alcohols 6.

It is also important to note that none of the methoxylated benzylic alcohols 6 were capable of forming a quinone methide structure, since the phenolic positions of each compound had been methylated.

**Heterolytic Versus Homolytic Pathway.** Chang and Allan (1) proposed that nitrobenzene functions as a heterolytic (2-electron or ionic) oxidant during the oxidative depolymerization of lignin. Studies on nitrobenzene, however, report that nitrobenzene easily forms radical anions in alkaline solutions (17,18). The apparent ease with which nitrobenzene can form a radical anion makes a homolytic mechanism appear more attractive than a heterolytic mechanism for the nitrobenzene reaction in alkali. A homolytic pathway has also been suggested based on the observation that ESR spectra of kraft lignin heated in aqueous alkali showed only minor amounts of radical species; whereas, kraft lignin plus nitrobenzene showed a large concentration of radicals (9). As mentioned earlier, the structure-reactivity correlations of stilbenes 5 provided further proof for a homolytic pathway (Dershem, S. M., et al., *Holzforschung*, in press). This evidence included: 1) the low values of  $\rho^+$  for both copper(II) and nitrobenzene, which is characteristic of homolytic reactions (10,11); 2) the similarities of the  $\rho^+$  values obtained; and 3) the fact that copper(II) is widely accepted as a one-electron oxidant (2). Our conclusion is that nitrobenzene acts in the same manner as the homolytic reagent copper(II).

The homolytic evidence is further strengthened by the product distribution obtained from lignin. Both copper(II) and nitrobenzene give substantial and similar yields of aldehyde products (19). Benzoic acids rather than benzaldehydes, however, are the expected terminal oxidation products from the action of heterolytic oxidants. If vanillin is produced from lignin via heterolytic oxidation by nitrobenzene, then the high survivability of an aldehyde in the presence of an



excess of a heterolytic oxidant is an extraordinary occurrence. Finally, it should be noted that Trahanovsky (20) reported that there are no clearly documented cases where a heterolytic oxidant yielded benzaldehyde cleavage products from a secondary alcohol substrate.

**Proposed Oxidative-Cleavage Mechanism.** Results from the mechanistic studies discussed earlier lead us to propose that the mechanism shown in Figure 3 occurs during the oxidative-cleavage reaction of benzylic alcohols by CAN, nitrobenzene, and copper(II). This pathway is similar to a CAN mechanism proposed by Trahanovsky (20). The steps of this mechanism are:

1. The homolytic oxidative reagent, nitrobenzene, either abstracts an electron from a hydroxide ion as reported by Ashby and coworkers (21,22) (Scheme 1 of Figure 3) or from the benzylic hydroxyl group (Scheme 2 of Figure 3).
2. The nitrobenzene radical anion (17,18) then abstracts either a proton (Scheme 2) or a hydrogen atom (Scheme 1) to form a benzylic alkyloxy radical.
3. In a homolytic, nonoxidative elimination step, the  $C_{\alpha}$ - $C_{\beta}$  bond is cleaved to form a benzaldehyde and a separate alkyl radical.

The evidence that supports this oxidative-cleavage pathway includes: 1) prior mechanistic studies, especially the work by Trahanovsky and coworkers (20); 2) the nonspecific nature of the reaction: i.e., similar products obtained (benzaldehydes) when a wide variety of model compounds and lignin substructures are treated; 3) the necessity of a benzylic hydroxyl group; 4) the lack of reactivity of ketone derivatives (9); 5) the apparent noninvolvement of a quinone methide intermediate; 6) evidence that strongly suggests a homolytic rather than a heterolytic pathway; 7) similarities in the structure-reactivity correlations when two different reagents were used; 8) the lack of a significant isotope effect for compounds with  $^2\text{H}$ -labeled benzylic hydrogens (9); and 9) the absence of aryl radical cation intermediates in the CAN oxidation of benzylic alcohols 6.

The reaction depicted in Figure 3 can also be applied to the copper(II) oxidative-cleavage of lignin. In this case, copper(II) is reduced to copper(I) as the lignin is oxidized. Interestingly, copper(I) can be reoxidized to copper(II) by air (23). This autoxidation of copper(I) could explain why air was necessary for the copper(II) oxidation of stilbenes; whereas, when nitrobenzene was used, identical experimental results were obtained under either an air or nitrogen atmosphere (Table II).

The mechanism proposed in Figure 3 can easily be applied to the oxidative depolymerization of the lignin macromolecule by nitrobenzene or copper(II) in aqueous alkali. A recent model of softwood lignin (24) contains 27% free benzylic hydroxyl groups and 12% aromatic ring-conjugated double bonds (stilbene

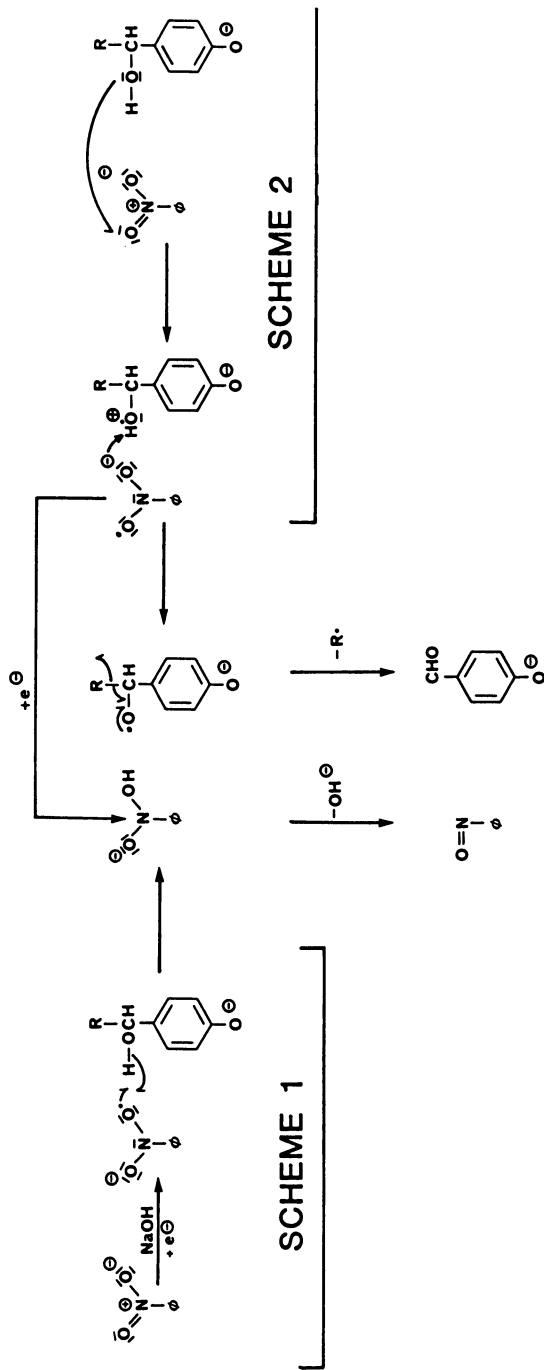


Figure 3. Proposed mechanism for the nitrobenzene oxidative-cleavage of lignin.

derivatives). Numerous additional benzylic hydroxyl groups are also formed when lignin is exposed to hot aqueous alkali. If the oxidative-cleavage reaction is mainly dependent on the availability of a benzylic hydroxyl group, with the other lignin functional groups and structures having little or no effect, then it is expected that only one major product (vanillin) would be formed from a softwood lignin. The abstraction of an electron from a phenolate anion does not seem to occur with nitrobenzene (3) or with copper(II) since no dimerization or polymerization products were observed. Thus, the competitive oxidative-coupling reaction of phenoxy radicals discussed by Chang and Allan (1) for copper(II) oxidations was not found in our copper(II) oxidations. However, phenolic oxidative-coupling reactions can occur with some oxidative reagents, such as potassium ferricyanide or ferric chloride (25).

Alkaline hydrolysis of lignin increases the number of reactive benzylic hydroxyl groups and may also be important in further depolymerizing the lignin once the oxidative-cleavage reaction has occurred. The formation of a *p*-electron-withdrawing -CHO substituent on aryl lignin units should increase the rate of hydrolysis of the ether bonds (26). Hydrolysis also forms *p*-phenylate ions, which then protect the benzaldehyde from further reaction via the Cannizzaro reaction, as mentioned earlier.

## Conclusions

Marton and coworkers (27) estimated that only about 0.30 reactive aromatic sites are available for formaldehyde condensation per every C<sub>9</sub> lignin unit of a softwood kraft lignin. Since this is only one-tenth as many available reactive sites as on phenol, it is not surprising that the utilization of lignin for commercial phenolic adhesives is extremely limited.

The reactivity of a lignin can be enhanced via the scheme presented in Figure 1 of this paper, both by the activation of the C-1 sites and by hydrolysis of the remaining ether bonds. In addition, formation of a more uniform, depolymerized material (28) than the starting lignin will give a product that may be easier to handle industrially. The authors hope that a better understanding of the oxidative-cleavage reaction will eventually lead to a reactive lignin-derived feedstock that is worth the additional processing costs. For example, an oxidative reagent which could be continuously regenerated by atmospheric oxygen, such as copper(II) (29), could significantly lower the costs.

## Acknowledgments

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# Chapter 7

## Soda Bagasse Lignin Adhesives for Particleboard

### Preliminary Results

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The development and application of low-cost adhesives for interior-grade particleboard and for exterior-grade structural glulam derived from soda bagasse lignin are very advanced. Laboratory results and optimum conditions of application of these adhesives for particleboard manufacture have been evaluated. The results satisfy the requirements of the relevant standard specifications. This research project is now at the pilot-plant stage, and initial tests indicate that considerable potential exists for commercial utilization of these types of grass lignins.

Many examples of lignin-based wood adhesives have been presented in the scientific literature in the last few decades (1). While undoubtedly many interesting adhesive formulations and uses have been devised, the lignin-based adhesives that have been proposed or even industrially used for limited periods of time have always suffered from some serious drawbacks, sometimes technical, sometimes economical.

Certainly, the most widely investigated avenue is the utilization of lignin in phenol-formaldehyde (PF) wood adhesives. However, to date no industrial lignin has found application in these products in such a manner that the lignin could substitute for the major portion of the synthetic resin. This is due to the low number of sites on the lignin fragments that are reactive to formaldehyde under alkaline-catalyzed conditions. This constraint has led to a number of innovations to increase the number of reactive sites on the lignin fragments. Demethylation of the methoxy groups of the lignin, for example, affords 3,4-

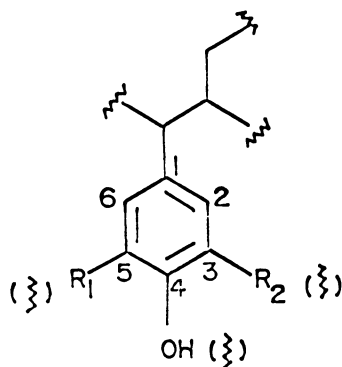
dihydroxyphenylpropanoid structures (see Figure 1). The 2- and 6-positions on these units are situated *ortho* and *para* to the newly introduced aromatic 3-hydroxyl group and thus yield the required reactivity (2). Alternatively, lignin fragments of a high molecular mass can be separated from those of low molecular mass by ultrafiltration (3). These modifications again have some drawbacks, such as cost or the fact that only part of the lignin source is utilized.

Recently, however, an industrial lignin was described that shows a much larger number of sites reactive to formaldehyde than the average industrial lignin (4). This lignin is obtained from the soda pulping of sugarcane bagasse. The industrial pulping of bagasse is done at the relatively mild conditions of 170 °C for only 15 minutes (typically also employed for other grassy materials such as straw). The bagasse lignin is consequently not extensively condensed and contains a high number of unsubstituted 5-positions (Figure 1) that can react with formaldehyde. In Table I, the molecular formula and number of unsubstituted 5-positions on phenolic phenylpropanoid units of soda bagasse lignin are compared with those of a typical kraft lignin and an extensively condensed soda/AQ hardwood lignin.

Table I. Different Lignin Molecular Formulae (4)

Lignin	Molecular Formulae	Reactive Points Per C <sub>9</sub>
Soda/ AQ	$C_9H_{2.10}^{Ar}H_{2.96}^R O_{0.56}(OH)_{0.77}^{Ar}(OH)_{0.54}^R (OMe)_{1.29}$	0.1
Soda bagasse	$C_9H_{3.05}^{Ar}H_{3.36}^R O_{0.63}(OH)_{0.63}^{Ar}(OH)_{0.76}^R (OMe)_{0.85}$	0.7
Kraft pine	$C_9H_{2.48}^{Ar}H_{3.75}^R O_{0.39}(OH)_{0.62}^{Ar}(OH)_{0.99}^R (OMe)_{0.86}S_{0.05}$	0.3

The unique high reactivity of the industrial bagasse lignin was subsequently utilized in the development of cold-curing adhesives (5). Both cold-setting and fast-setting wood adhesives were developed and are currently being evaluated on pilot plant scale. A summary of the strength properties of some of the cold-setting bagasse lignin adhesives is listed in Table II. The ability of this lignin to substitute for three-quarters of the solids in the cold-setting adhesives clearly underlines the compatibility of the reactive bagasse lignin with PF resins.



$R_1, R_2 = H$

⌋ and ⌋ = Possible linkage to other phenyl propanoid units

Figure 1. Phenyl propanoid units of lignin.

In this chapter, the development of a thermosetting adhesive from soda bagasse lignin is described. The research has concentrated on the development of interior-grade adhesives for particleboard. The local market for exterior boards is smaller than that for the interior panels, and adhesives for exterior boards are already covered by an excellent range of tannin-based adhesives.

Table II. Strength of Cold-Setting Wood Adhesives Prepared from Industrial Bagasse Lignin (5)

Adhesive	Dry Test		24-hour Cold Soak		6-hour Boil	
	Strength (N)	Wood Failure (%)	Strength (N)	Wood Failure (%)	Strength (N)	Wood Failure (%)
Cold set <sup>1</sup>	3,338	33	2,473	95	1,870	80
BS <sup>2</sup>	–	–	2,200	75	1,500	75
Finger-joint <sup>3</sup>	2,250	100	2,343	100	2,237	100
SABS <sup>4</sup>	–	–	1,400 2,800	90-100 30-40	1,400 2,800	90-100 30-40

<sup>1</sup>Lignin-based cold-setting adhesives evaluated on beech strips (74% lignin; 26% resorcinol).

<sup>2</sup>BS 1204-1965, part 2 specification for synthetic adhesives for marine-grade wood.

<sup>3</sup>Lignin-based fast-set as component B and commercial PRF as component A (1:1); evaluated by finger-joint.

<sup>4</sup>SABS 970-1976 finger-joint requirement.

## Experimental Methodology

Lignin was obtained from an industrial soda bagasse spent liquor as before (5). The lignin was initially evaluated as a thermosetting adhesive by the beech strip test. Prior to its application as adhesive, the lignin was reacted with formaldehyde in alkali at temperatures below 60 °C to afford a hydroxymethylated lignin (6). The hydroxymethylation reaction was done at pH 12 and 13, and samples of the reaction mixtures were evaluated on beech strips with overlaps of 25 x 25 mm, cured for 4 hours at 90 °C and 12% equilibrium moisture content.

One-layer particleboards were prepared from Eucalyptus chips with a resin content of 10 percent on dry chips. The boards were formed 12-mm thick on a laboratory press with the press platens at 170 °C for press times of 15 minutes.



The final density of the boards was approximately  $700 \text{ kg/m}^3$ . Different ratios of commercial PF and UF resins were added to hydroxymethylated lignin.

## Results and Discussion

The results presented in Figure 2 clearly indicated that the bagasse lignin can be used to prepare a thermosetting adhesive of high strength. The strength of the adhesive increased with increasing hydroxymethylation times, which were as long as 15 hours.

Improvement of the performance of the lignin adhesive was subsequently attempted by the addition of several crosslinking agents. These materials are capable of further improving the degree of crosslinking of the lignin adhesive (Table III). The addition of phenol (Table III, entries 1-3) resulted only in small increases in the dry strength results.

The addition of a PF resol resin to fixed-time hydroxymethylated bagasse lignin resulted in a substantial improvement in the adhesive performance (Table III, entries 13-18), whereas, addition of phenol to the PF resin/lignin combination did not improve the dry strength of the bonded joints over the control. The strength of the adhesive obtained by the addition of 33% resol resin by mass (entry 15) practically complies with requirements of the South African and British Standard specifications for interior type synthetic adhesives for wood, and it is not too far from the exterior-grade requirements. The addition of a resol resin to hydroxymethylated bagasse lignin therefore constitutes a versatile adhesive preparation. Employing more resol resin in the adhesive mixture, on the other hand, results in a thermosetting adhesive that marginally complies with the South African and British specification for exterior-grade resins.

The addition of the nitrogen-containing crosslinking agents, melamine, urea, and urea-formaldehyde (UF) resin, resulted in a substantial increase in strength (Table III, entries 7-12). The best results were obtained by the melamine-crosslinked adhesives. The addition of 33% melamine resulted in an adhesive with strength values well within exterior-grade adhesive specifications.

Further optimization of the lignin adhesive was attempted by mixing different proportions of a commercial PF resin with hydroxymethylated soda bagasse lignin and paraformaldehyde as hardener. It must be pointed out that a commercial PF resin has not been engineered to function as a lignin adhesive fortifier but to cure by itself. It is thus not an ideal fortifying resin. The results presented in Figure 3 indicated that optimum strength was obtained at 60:40 PF:lignin. This is, however, not ideal as an economic proposition. Economic considerations dictated that a lower level of commercial PF fortification had to be employed for the screening work.

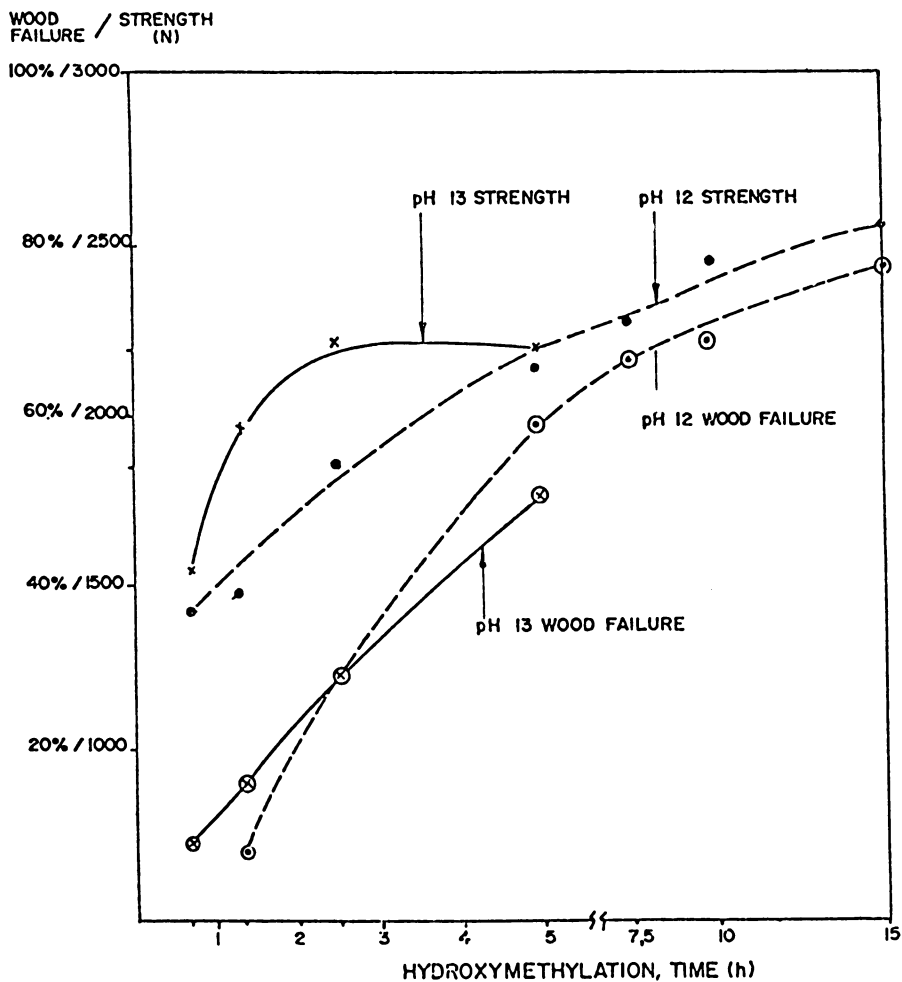


Figure 2. Strength and wood failures obtained on beech strips glued with lignin hydroxymethylated for different times at pH 13 or 12.

Table III. Beech Strip Strengths of Hydroxymethylated Bagasse Lignin Adhesives Crosslinked with Various Fortifiers

Entry	Fortifier	Percentage Fortifier On Resin Solids (%)	Adhesive Strength (% Wood Failure)		
			Dry	Soak	Boil
1	Phenol	8	2,480 ( 96)	1,020 ( 5)	1,160 ( 0)
2		15	2,290 ( 76)	1,040 ( 5)	0 ( 0)
3		25	2,300 ( 81)	820 ( 5)	0 ( 0)
4	Melamine	11	2,970 (100)	2,250 ( 98)	670 ( 2)
5		20	3,150 (100)	2,170 (100)	1,070 (15)
6		33	2,700 (100)	2,730 ( 93)	1,450 (28)
7	Urea	5	2,510 ( 56)	1,180 ( 17)	130 ( 0)
8		10	2,570 ( 60)	1,270 ( 22)	0 ( 0)
9		16	2,680 ( 90)	1,370 ( 48)	0 ( 0)
10	UF resin	11	2,550 ( 85)	1,480 ( 2)	0 ( 0)
11		20	2,830 (100)	1,620 ( 35)	0 ( 0)
12		33	2,620 (100)	140 ( 97)	0 ( 0)
13	PF resol resin	20	2,970 ( 86)	1,780 ( 32)	1,259 (66)
14		25	2,720 ( 99)	1,920 ( 64)	1,350 (24)
15		33	2,930 (100)	2,090 ( 83)	1,490 (75)

Table III (cont.). Beech Strip Strengths of Hydroxymethylated Bagasse Lignin Adhesives Crosslinked with Various Fortifiers

Entry	Fortifier	Percentage Fortifier On Resin Solids (%)	Adhesive Strength (% Wood Failure)		
			Dry	Soak	Boil
16	PF resol resin	10	2,190 ( 89)	990 ( 7)	710 ( 2)
17	+15% phenol	15	1,960 ( 53)	1,180 ( 12)	1,120 (11)
18		25	2,230 ( 61)	1,320 ( 16)	1,410 (25)
19	Hydroxy- methylated lignin control with no fortifier	0	2,110 ( 58)	130 ( 0)	0 ( 0)
20	National specifi- cation (for exterior applications)		2,500 ( 75)	2,200 ( 75)	1,500 (75)
21	British specifi- cation (for exterior applications)		- ( -)	2,200 ( -)	1,450 ( -)

The bagasse lignin adhesives were subsequently evaluated as particleboard adhesives. The results listed in Table IV clearly indicate that the lignin-based adhesives do provide proper bonding of particleboard. The larger proportion of lignin used with the PF resin, however, showed a decrease in internal bond strength (Table IV, entries 1 and 2). The reverse was evident for the UF lignin adhesives. The poor performance of the adhesive mixture containing the largest proportion of UF resin can probably be attributed to degradation of the UF component due to the long press times of 15 minutes.

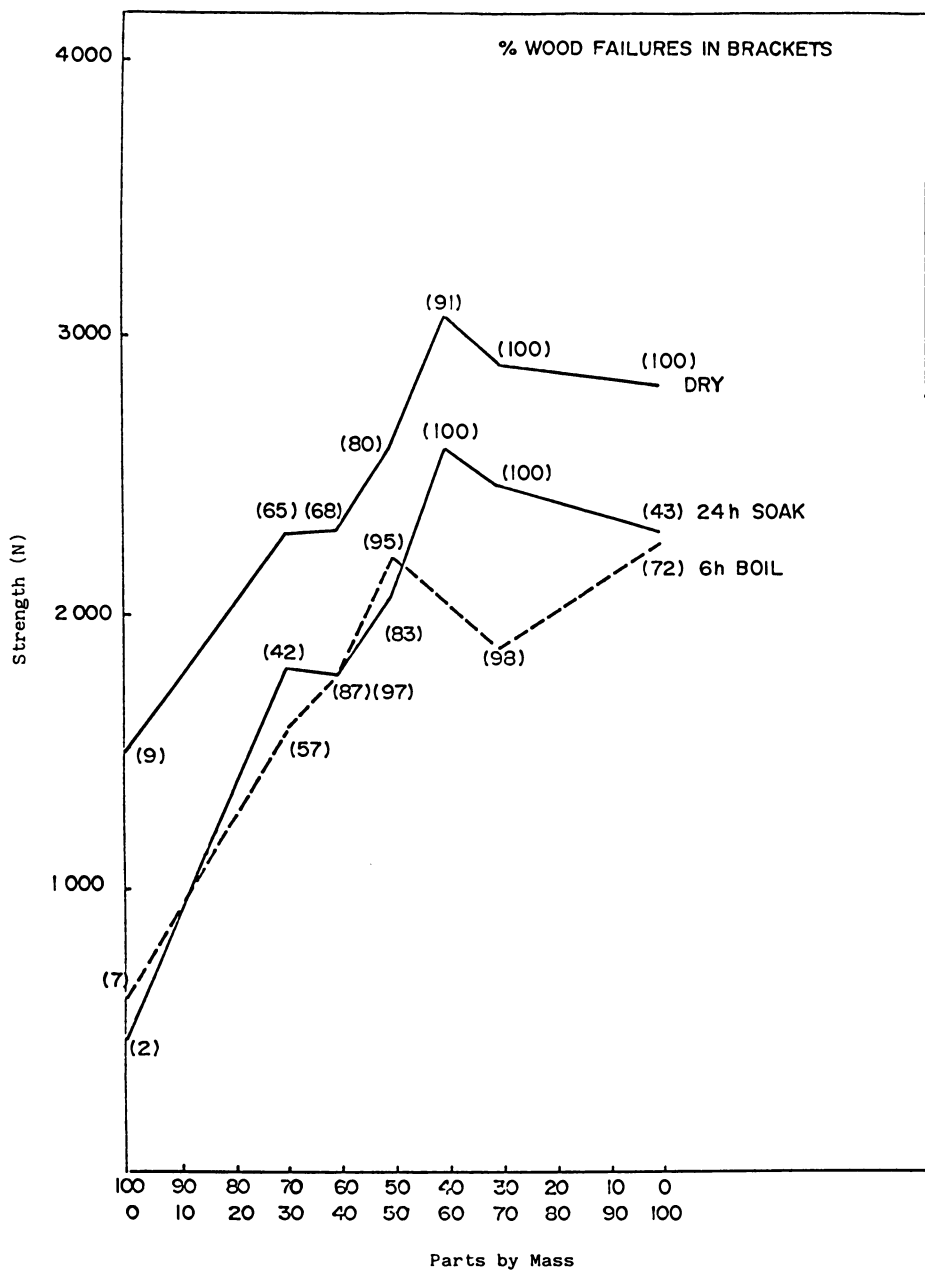


Figure 3. Strength and wood failures of beech strips glued with hydroxymethylated lignin and PF resin in different ratios cured at 90 °C for 4 hours.

Table IV. Internal Bond Strength of Particleboard, 12-mm-Thick, Prepared from Soda Bagasse Lignin Adhesives (10% on Dry Chips) After Pressing at 170 °C for 15 Minutes

Entry	Adhesive	Dry Internal Bond (MPa)
1	Hydroxymethylated lignin : PF (50 : 50)	0.80
2	Hydroxymethylated lignin : PF (67 : 33)	0.63
3	Hydroxymethylated lignin : UF (67 : 33)	0.35
4	Hydroxymethylated lignin : UF (80 : 20)	0.62

The moisture dependence of the two PF-extended lignin adhesives was subsequently determined. Single-layer boards were prepared with the resinated chips at different moisture contents. The adhesive content (10%) and press conditions (170 °C, 15 min.) were kept constant. The results presented in Figure 4 indicate the deleterious effect of high moisture contents of the chips on the strength of the boards. The application of the lignin particleboard adhesive thus clearly requires strict control of the moisture content of the chips.

The 67:33 lignin:PF adhesive was subsequently evaluated as an adhesive for a three-layer board. A ratio of 25% surface and 75% core chips was used. The pressing times were varied from 15 to 5 minutes. The internal bond strengths of the boards, presented in Figure 5, show that much shorter times than the previously employed 15 minutes can produce acceptable boards. A press time of only 5 minutes was, however, too short. The bagasse lignin:PF (67:33) adhesive also was used for the preparation of one-layer board from bagasse fiber instead of wood chips. For this material, 2-1/2-minute press times were long enough to produce acceptable dry internal bond strengths for 5-mm-thick board and a 5-1/2-minute pressing time for 12-mm-thick board (Figure 6).

## Conclusion

Soda bagasse lignin used after hydroxymethylation as a thermosetting adhesive gave acceptable adhesion of beech strips and particleboard. The lignin-based particleboard adhesive used was supplemented with a commercial PF resin to levels of only 33% synthetic resin (i.e., 66% lignin). For three-layer particleboard prepared from wood chips, a press time of 7-1/2 minutes was required. When bagasse fiber was used, a press time of 5-1/2 minutes was sufficient for a one-layer 12-mm board. Extraction of the lignin is currently being evaluated on a pilot plant scale; this will enable the evaluation of the lignin particleboard adhesive on an industrial scale.

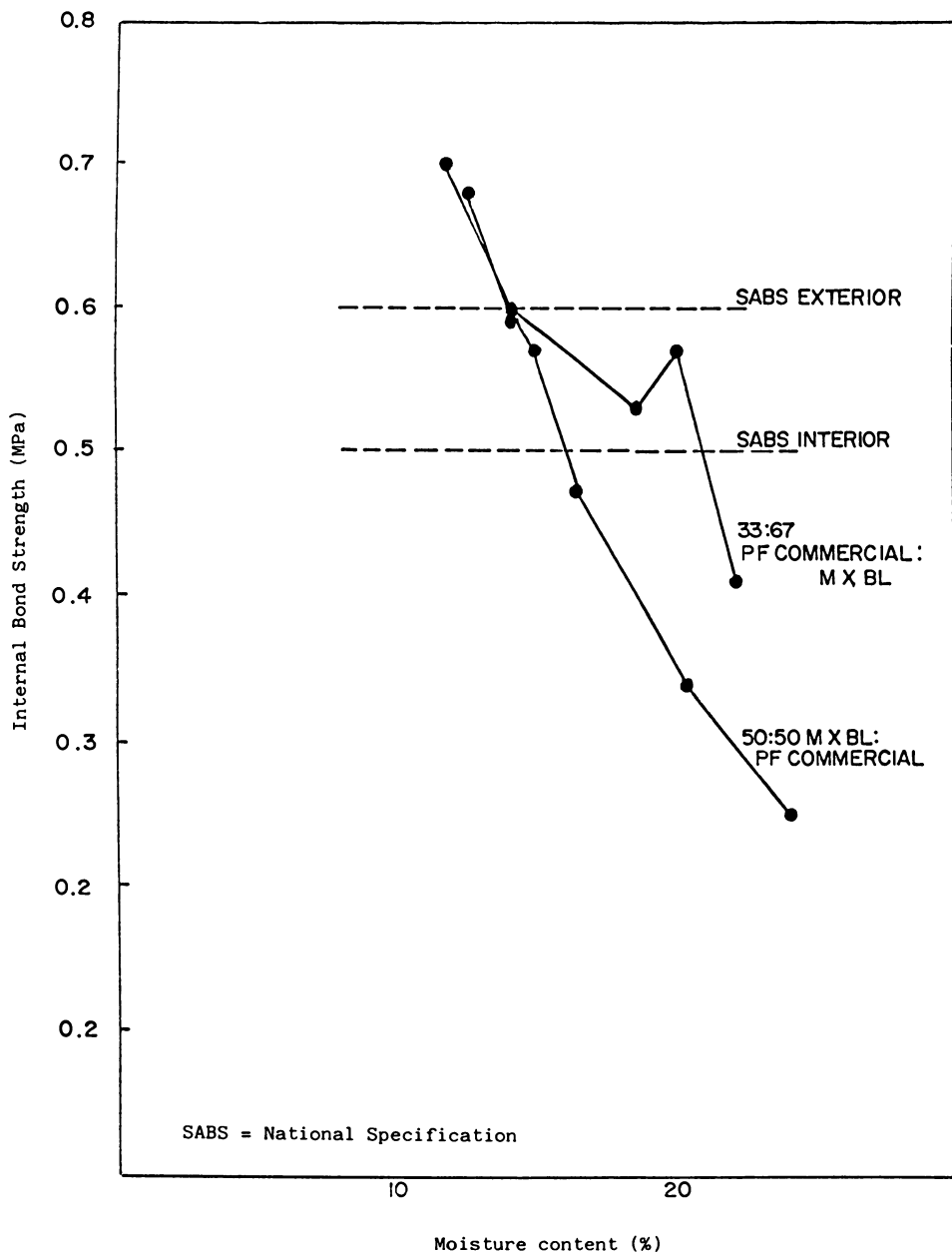


Figure 4. Dependence of strength on moisture content of 12-mm one-layer board glued with a mixture of hydroxymethylated lignin and commercial PF (67:33) pressed at 170 °C for 15 minutes.

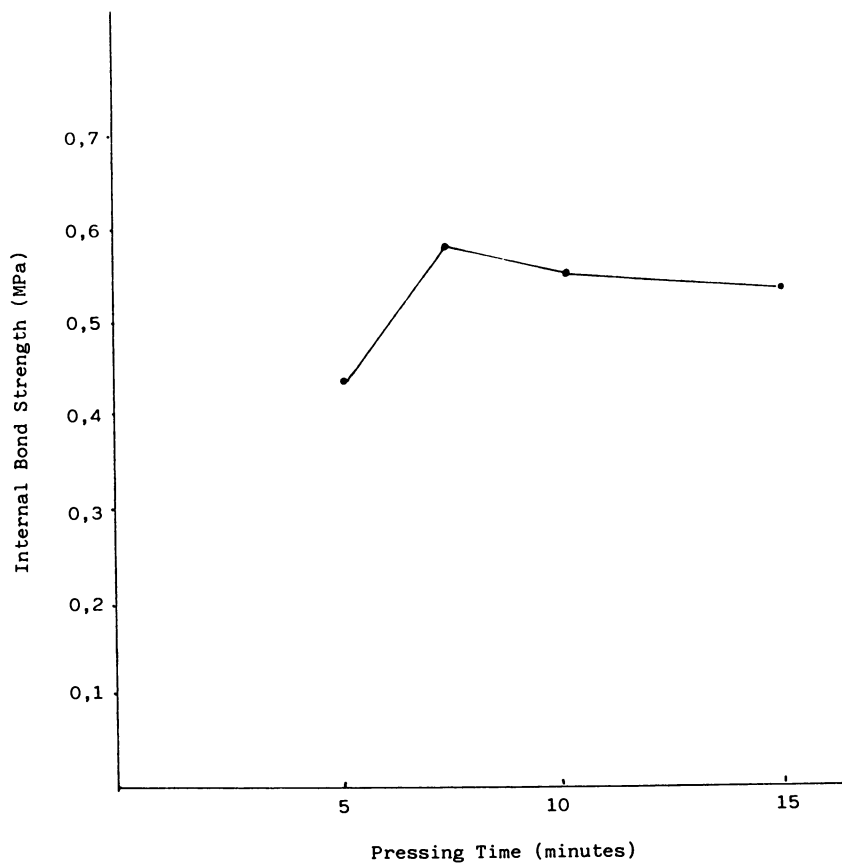


Figure 5. Strength of three-layer particleboard (20% surface chips) glued with hydroxymethylated bagasse lignin/commercial PF resin (67:33) and pressed at 170 to 180 °C for different times, 12% chip moisture content, final density 680 kg/m<sup>3</sup>.



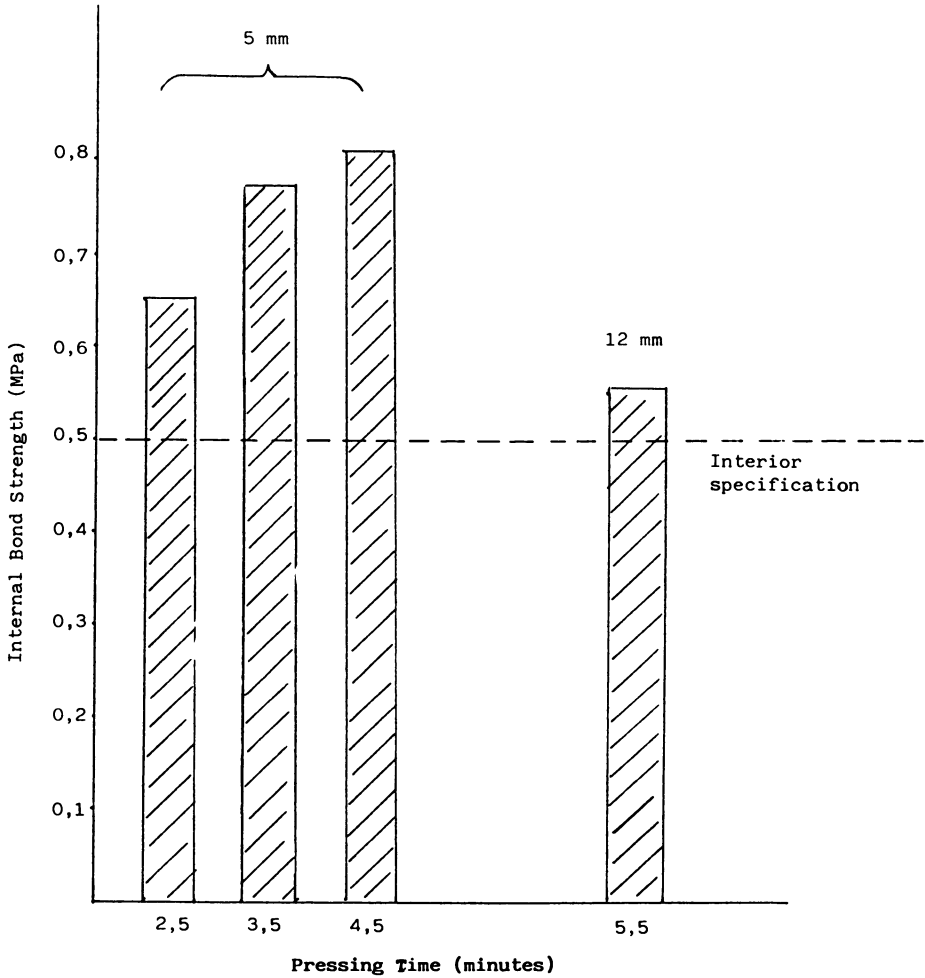


Figure 6. Strength of boards prepared from bagasse fiber and glued with hydroxymethylated lignin: commercial PF (67:33) and pressed at 170 °C for different times.

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# Chapter 8

## Effects of Phenol-Formaldehyde Copolymer on Gluebond Performance of Lignin-Phenolic Resin Systems

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A series of experiments was conducted to optimize 1) molar ratio of formaldehyde/phenol, 2) sodium hydroxide catalyst, and 3) reactant concentration of phenolic copolymer to lignin in terms of providing the best performance of lignin-phenolic resin systems for structural flakeboard panels. At 25/75 (w/w) mixture of phenolic/lignin, a methylolated lignin blended with phenolic resin synthesized with a formaldehyde/phenol ratio of 3 consistently resulted in higher bond strength, lower thickness swell, and smaller linear expansion of structural flakeboard. Gluebond performance improved as the NaOH/phenol ratio increased from 0.2 to 0.7. Further increases in sodium hydroxide adversely affected gluebond performance. Panel strength properties decreased with increasing resin solids content. Adhesives formulated with 75% of methylolated lignins as substitutes for phenolic resins can be used to make structural flakeboards with acceptable properties.

Incorporation of lignin into phenol-formaldehyde resins has been one of the primary areas of research in lignin utilization. When lignin is used directly as a replacement for phenol, the maximum acceptable level of replacement is about 20% (1). However, a higher degree of replacement can be achieved using modified lignin (2-7). Of all lignin modification treatments, those that increase chemical reactivity or reactive sites, such as phenolation or methylation, seem to be the most promising.

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In formulating lignin-phenolic resin adhesives for fabrication of wood composites, the importance of the compatibility of a phenol-formaldehyde copolymer for lignin often has not been fully recognized. Recently, Calve and Shields (8) indicated that lignin copolymerized with an acid-cured phenolic showed the best potential in waferboard production; whereas, lignin copolymerized with an alkaline-curing phenolic was most suitable for plywood. However, no comprehensive studies have been published on the effect of resin variables on the properties and bond performances of lignin-phenolic resin systems. The experiments reported here provide information on strength properties of structural flakeboards bonded with lignin-phenolic resin adhesives as affected by 1) the molar ratio of formaldehyde/phenol, 2) the amount of sodium hydroxide catalyst, and 3) the solids content of phenolic resins. The objective of the research was to optimize lignin-phenolic copolymer resin systems.

### Experimental Methodology

The bond performances of lignin-phenolic resin systems were studied through a series of experiments, each designed to elucidate a facet of the problem. The resin preparation and panel fabrication procedures were, however, maintained as uniformly as possible. Thus, unless otherwise specified, the experimental procedures described below were used in the study.

**Resin Preparation.** All phenolic resins were prepared in the laboratory. Resin preparations were replicated one time. To prepare each resin, all phenol and water were placed in a reaction kettle. The formaldehyde was added in three steps: 1) total formaldehyde less 1 mole of formaldehyde was added at the beginning; 2) the balance was divided into two equal parts (i.e., 0.5 mole each), one of which was added 1 hour after the reaction began; and 3) the remainder of formaldehyde was added 20 minutes later. The sodium hydroxide was added as catalyst in four steps (i.e., four equal parts at 10-minute intervals). To initiate the reaction, the mixture was heated and maintained at 75 °C. All reactions were terminated at the end of 100 minutes. Gel time, pH, viscosity, solid content, and specific gravity were determined. The general conditions for resin preparation were:

NaOH/phenol ratio - 0.3  
Solids content - 42%  
Reaction temperature - 75 °C  
Reaction time - 100 minutes

**Gel-Permeation Chromatography.** A Water Associates HPLC with four Shodex GPC-AD-802S columns was used with dimethylformamide at a flow rate of 1 mL/minute. The gel is polystyrene-divinyl benzene copolymer and has exclusion limit of 8,000 by polystyrene molecular weight. Sample injection

volume was 100  $\mu\text{L}$  at a concentration of 1% (wt/v), if not specified. Columns were calibrated with standard molecular weight polyethylene glycols (i.e., 3,000, 1,500, 1,000, 600, 400, and 300), 2,2'- and 4,4'-dihydroxyphenyl methane, 2- and 4-hydroxymethylphenol, and phenol. Mathematical approximation of the GPC calibration curve was made by exponential fit of molecular weight vs. elution volumes of the standards. The number and weight average molecular weight were calculated by the method described by Navas (9).

**Methylation of Kraft Lignin.** Southern pine kraft lignin was obtained from the Westvaco Corporation. The acidified lignin (approximately 97% solids and ash content of less than 1%) was Indulin AT. Methylation was performed according to the method developed in a previous study (10). Briefly, the lignin was dissolved in dilute sodium hydroxide solution and allowed to mix for 75 minutes at 80 °C. The resulting solution was adjusted to pH 12.0. The temperature was then adjusted to 50 °C, and formaldehyde solution (50%) was added slowly to the lignin solution. The methylation reaction was allowed to proceed for an hour with continuous stirring. The molar ratio of formaldehyde to lignin (molecular weight of lignin was assumed to be 180) was 1/1, and the ingredients in parts by weight were:

Water - 1,200  
Kraft lignin (97%) - 600  
Formaldehyde (50%) - 192  
Sodium hydroxide (50%) - 185

**Blending of Lignin-Phenolic Resin System.** The methylolated lignin was blended with the phenolic resins at a solid weight ratio of 75/25 and at room temperature. The mixture was mechanically stirred for 15 minutes. The gel time, pH, and solids content were determined for each resin system.

**Evaluation of Gluebond Quality.** Structural flakeboard panels were prepared in the laboratory with sweetgum flakes 3 inches long, 0.015 inches thick, and variable widths. General conditions for panel preparation were:

Panel size - 1/2 by 22 by 24 in.  
Panel density - 43 lbs per cu. ft.  
Resin content - 5% of oven-dry weight of wood  
Hot press temperature - 193 °C  
Press closing time - 45 sec.  
Hot press time - 6 min.

To prepare each panel, wood furnish was weighed out and placed in a rotating blender. The required amount of resin was then weighed and applied to the wood particles by air-atomizing nozzles. The blended particles were then carefully felted into the final mat with a forming box. The mat was transferred

immediately to a single opening hot press heated at 193 °C. All panels were conditioned at room temperature for 24 hours. After conditioning, each panel was trimmed and cut into 2-inch wide strips. A bending specimen and two IB blocks were cut from each strip. Three bending specimens were selected at random for determination of dry MOR and MOE and three specimens were selected from each panel for determination of bond durability. Ten IB specimens were selected at random from each panel. Bending and internal bond tests were performed in accordance with ASTM standards for evaluating properties of wood-based fiber and particle panel materials (D 1037-72). The bond durability was evaluated by a vacuum-pressure soak test (ODVPS) under the following constraints: 1) specimens were dried at 102 °C for 24 hours; 2) they were placed in pressure cylinder and flooded with tap water; 3) the system was subjected to a vacuum  $27 \pm 2$  inches of mercury for 1 hour and then pressure  $> 90 \pm 10$  psi for 2 hours. This procedure was developed by the American Plywood Association and designated as APA Test Method P-1. Linear expansion (LE) and thickness swell (TS) values are based on the change from the oven-dry condition to the end of the ODVPS cycle. Bending and IB of ODVPS specimens received the additional treatment of drying in an oven for 24 hours followed by at least 48 hours of conditioning at 50% relative humidity before evaluation.

*Experiment 1. Effect of Molar Ratio of Formaldehyde/Phenol on Strength Properties of Lignin-Phenolic Resin System.* Phenolic resins, with formaldehyde in excess of 2 moles per 1 mole phenol, have proved to be most useful for gluing plywood and flakeboard. In general, additional formaldehyde (i.e., higher molar ratios) will not react effectively, and thus contributes little to resin performance. When the ratio of formaldehyde to phenol is less than 2 moles, the reactivity or gelation time of the resin is lengthened. However, in lignin-phenolic resin systems, the optimum ratio of formaldehyde to phenol has not been clearly defined. This experiment was designed to optimize the formaldehyde/phenol ratio of the resin system. The variables were four levels of formaldehyde/phenol ratios—2.0, 2.5, 3.0, and 3.5.

*Experiment 2. Effect of Molar Ratio of Sodium Hydroxide to Phenol of Phenolic Resin on Strength Properties of Lignin-Phenolic Resin Adhesives.* Sodium hydroxide has been the predominant chemical used as a catalyst in resol resin technology. Through variation in the amounts of the catalyst and the method of catalyst addition, a wide variety of resin systems can be formulated. This experiment examined the properties of phenolic resins formulated with various sodium hydroxide/phenol ratios and their effects on the bond properties of structural flakeboards made with lignin-phenolic resin adhesive systems. Variables for resin preparation were four molar ratios of sodium hydroxide/phenol (i.e., 0.2, 0.45, 0.7, and 0.95). The formaldehyde/phenol ratio and solids content were fixed at 3/1 and 42%, respectively.

*Experiment 3. Effect of Phenolic Resin Solid Content on Strength Properties of Lignin-Phenolic Resin System.* Past experience has shown that the optimum solids content of typical phenolic resin formulations is between 40% to 50%.

The most popular is the 40% solids content family, since it seems to give a little better cost/performance relationship. This experiment examined the effect of phenolic resin solids on the properties of structural flakeboards bonded with the lignin-phenolic resin system. The variables were three levels of phenolic resin solids content – 39%, 46%, and 54%. The formaldehyde/phenol ratio and NaOH/phenol ratio were 3/1 and 0.7/1, respectively.

## Results and Discussion

**Characteristics of Methylolated Kraft Lignin.** The basic properties of methylolated kraft lignin are summarized as follows:

pH-12

Viscosity-216 cps as determined on a Brookfield viscometer  
with spindle No. 2 at 25 °C and 20 rpm

Specific gravity-1.2

Free formaldehyde-1.8% with formaldehyde/lignin ratio of  
1/1 after reaction for 1 hour at 50 °C,

and

0.46% with formaldehyde/lignin ratio of  
0.5/1 after reaction for 1 hour at 50 °C

**Phenolic Resin Properties.** Average physical and chemical properties of phenolic resins as affected by molar ratio of formaldehyde/phenol are summarized as follows:

CH <sub>2</sub> O/Phenol Ratio	pH	Viscosity (cps)	Solids Content (%)	Specific Gravity (g/cc)	Gel Time (min)
2.0/1	9.64	18	43	1.16	62
2.5/1	9.86	20	41	1.16	38
3.0/1	9.78	20	40	1.16	27
3.5/1	9.78	23	39	1.17	26

As expected, the gel time decreased consistently as formaldehyde/phenol ratio increased to 3.0/1; thereafter, further increase in formaldehyde/phenol ratio had little effect on the gel time. The effects of formaldehyde/phenol ratio on pH, viscosity, solid content, and specific gravity were not significant.

Figure 1 shows the GPC chromatograms of phenolic resins reacted at different formaldehyde/phenol ratios. In general, the chromatogram is divided into

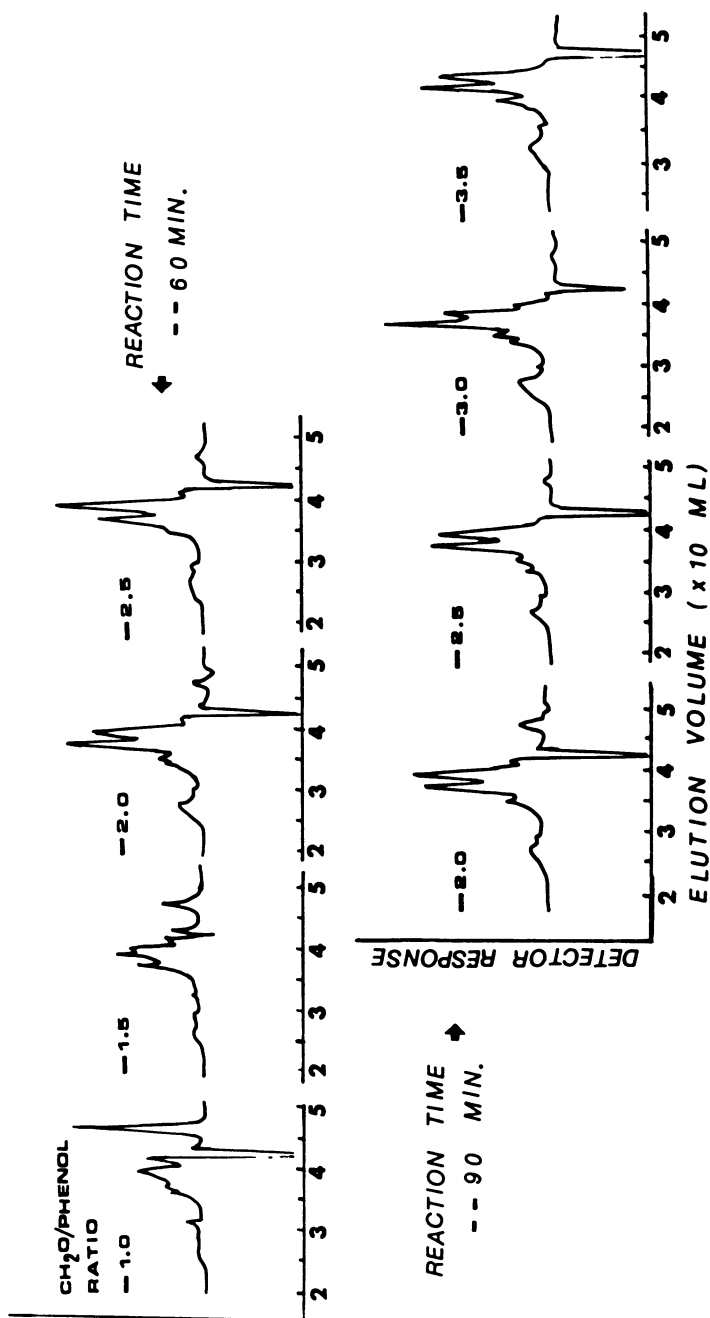


Figure 1. GPC chromatograms of phenolic resins reacted at different phenol/formaldehyde ratios.



two groups of peaks. At an early stage of reaction several peaks are observed. The peak between 45 and 50 mL elution volume is that of phenol, and the negative peak between 40 and 45 mL is due to formaldehyde and water in the sample. These identifications were made by comparing GPC chromatograms of phenolic resins before and after addition of phenol and formaldehyde to the sample. The assignments agree with those of previous workers (10-19). Other peaks evident at early stages of the reaction (i.e., those between elution volumes 32 and 45 mL) may be monomers and dimers of polymethylolphenol. These peaks can be integrated together (Group A) as an estimate of low molecular weight products. In later stages of the cook peaks develop at lower retention volumes that can be integrated together (Group B) to represent a measure of the higher molecular weight products obtained by condensation reactions.

It is noted that, at the same reaction time, the free phenol content decreased as the formaldehyde/phenol ratio increased. As expected, only a small amount of high molecular weight fraction (Group B) formed at formaldehyde/phenol ratios below 2/1 (Figure 1). The result indicated that there was not enough formaldehyde to promote the condensation reaction of the resin. The number average molecular weight increased slightly as the mole ratio increased from 2.0 to 3.0 with high molecular weight fraction dropping slightly at the 3.5 ratio (Figure 2). The result indicates that the excess formaldehyde was not effective in promoting condensation of the resin.

**Formaldehyde to Phenol Ratio.** The effect of formaldehyde/phenol ratio on pH, viscosity, and gel time of the lignin-phenolic resin system is summarized as follows:

CH <sub>2</sub> O/Phenol Ratio	Methylolated		Viscosity (cps)	pH	Gel Time (min)
	Lignin/Phenolic Resin Ratio				
2.0/1.0	75/25		120	11.15	64
2.5/1.0	75/25		112	10.95	45
3.0/1.0	75/25		112	10.95	32
3.5/1.0	75/25		114	11.15	30

It is noted that the gel time decreased as the formaldehyde/phenol ratio of the phenolic resin in the system increased. Furthermore, the gel time curve of the lignin-phenolic system was, in general, similar to that of phenolic resins measured in the previous section. The similarity of the gel time curves (Figure 3) may indicate that the phenolic resin plays the major role in affecting the cure speed of the lignin-phenolic resin system even though the phenolic resin consisted of only 25% by weight in the system.

Average physical and mechanical properties of the flakeboards are summarized in Table I. On the average, panels bonded with the lignin/phenolic resin

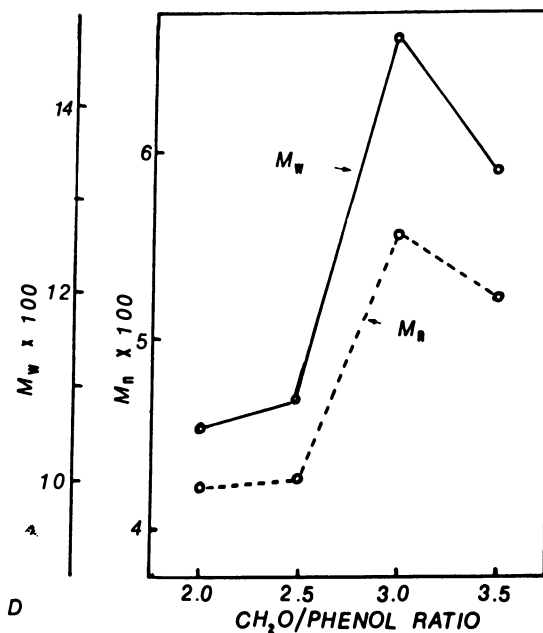


Figure 2. Effect of formaldehyde/phenol ratio on number ( $M_n$ ) and weight ( $M_w$ ) average molecular weight of phenolic resins.

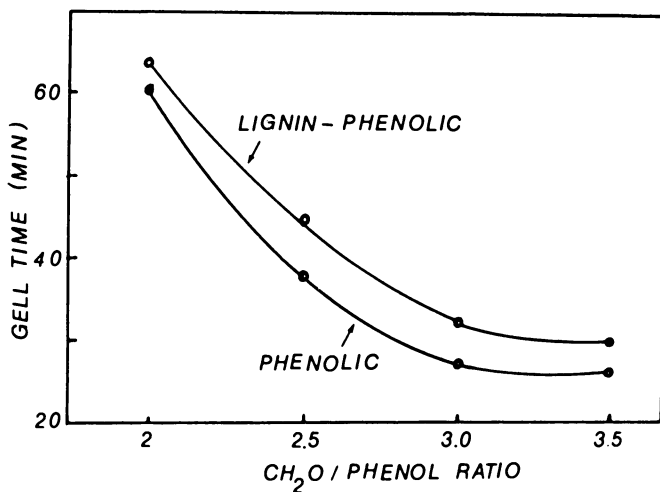


Figure 3. Gel time curves of phenolic and lignin-phenolic resins as affected by formaldehyde/phenol ratio.

slightly higher strength properties before and after the ODVPS treatment. The ODVPS treatment resulted in an average of more than 66% reduction in MOE, 39% in MOR, and 22% in IB. Similar to the strength properties, the panels bonded with the P/F ratio 3:1 resins also were superior in dimensional stability and exhibited less water absorption (WA, Table I). Based on these evaluations, the P/F ratio 3:1 seems to provide consistently better performance and was chosen for the second phase, the experiment on optimizing the NaOH/phenol ratio.

Table I. Average Physical and Mechanical Properties of Flakeboards

CH <sub>2</sub> / Phenol Ratio	Lignin Phenolic Resin Ratio	After ODVPS Treatment								
		IB (psi)	MOR (psi)	MOE (10 <sup>3</sup> psi)	IB (psi)	MOR (psi)	MOE (10 <sup>3</sup> psi)	LE (%)	TS (%)	WA (%)
2.0/1	75/25	66	6475	875	48	3726	373	0.19	37	106
2.5/1	75/25	72	5167	798	60	3078	345	0.27	44	107
3.0/1	75/25	80	7318	915	60	4211	437	0.23	33	99
3.5/1	75/25	69	6133	814	55	4212	412	0.27	34	104

**Molar Ratios of Sodium Hydroxide/Phenol.** Table II summarizes the effect of varying molar ratios of NaOH/phenol on pH, viscosity, solid content, specific gravity, gel time, and molecular weight of the resins. The GPC chromatograms of the phenolic resins reacted at different NaOH/phenol ratios are given in Figure 4.

Table II. Effect of Molar Ratio of NaOH/Phenol on Physical and Chemical Properties of Phenolic Resins

Molar Ratio NaOH/Phenol	Gel Time (min)	pH	Viscosity (cps)	Specific Solid Content (%)	Gravity (g/cm <sup>3</sup> )
0.20/1	39	9.41	20	40	1.15
0.45/1	25	10.06	22	40	1.18
0.70/1	24	10.38	24	39	1.19
0.95/1	92	10.70	26	42	1.20

The significant effect of NaOH/phenol ratio on gel time is plotted in Figure 5. The fastest gelation rate occurred between NaOH/phenol molar ratios

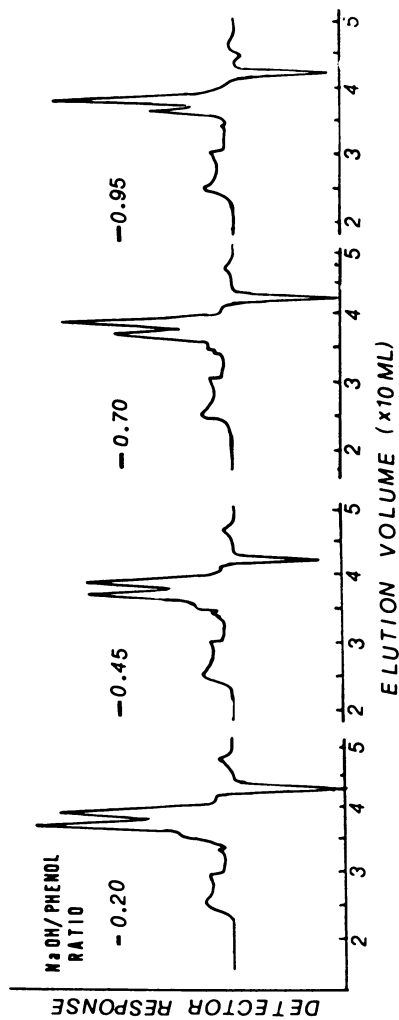


Figure 4. GPC chromatograms of phenolic resins reacted at various NaOH/phenol ratios.

of 0.45 and 0.70; and the gel time increased sharply at both extremes of the NaOH/phenol ratios. The GPC chromatogram showed two distinct molecular weight fractions (i.e., a high molecular weight fraction between elution volumes of 20 and 30 mL and a low molecular weight fraction between elution volumes of 35 and 45 mL). The low NaOH content of 0.2 resulted in significantly lower percentage of high molecular weight fraction (Table III, column 2). This result may indicate insufficient catalyst to effectively promote condensation.

The high NaOH content of 0.95 resulted in a substantially lower average molecular weight (Table III, columns 3 and 4). The effect of high caustic content on average molecular weight may be attributed to the Cannizzaro reaction as shown in a previous study (15). The formaldehyde deficiency may have limited methylol groups to sufficiently prolong the condensation, resulting in lower average molecular weight.

Average physical and mechanical properties of the flakeboards are summarized in Table IV. The caustic content level of 0.2 consistently resulted in the smallest strength (i.e., IB, MOR, and MOE), whereas, that of 0.45 resulted in slightly higher MOR, 0.7 gave the highest IB, and 0.95 the highest MOE. As expected, the ODVPS treatment reduced all strength values substantially. Nevertheless, the differences among the various NaOH contents were not significant. The effect of caustic content on stability of the panels shows the ratio of 0.7 resulted in most stable panels with less linear expansion (LE) and thickness swell (TS). Based on this experiment, it was concluded that the molar ratio of NaOH/phenol at 0.7 should be chosen for the subsequent experiment.

Table III. Effect of NaOH Content on Content of High Molecular Weight Fraction and Average Molecular Weight

NaOH/ Phenol	Content of High Molecular Weight	After ODVPS	
		Weight Average	Number Average
0.20	19	1488	488
0.45	25	1688	508
0.70	26	1685	491
0.95	26	845	294

**Resin Solids Content.** Average physical and chemical properties of the resins are summarized in Table V. The effect of resin solids content on pH and specific gravity was not significant. However, the gel time decreased and viscosity increased as the resin solids content increased.

Figure 6 shows the GPC chromatograms of the phenolic resins. Other than the phenolic resin at 46%, resin solid content resulted in slightly higher molecular weight (Table V), the effect of resin solid content on molecular weight distribution was not significant.

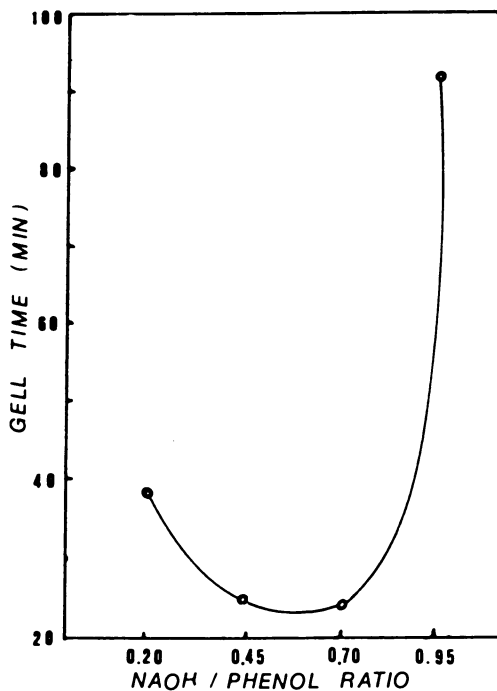


Figure 5. Effect of NaOH/phenol ratio on gel time of phenolic resins.

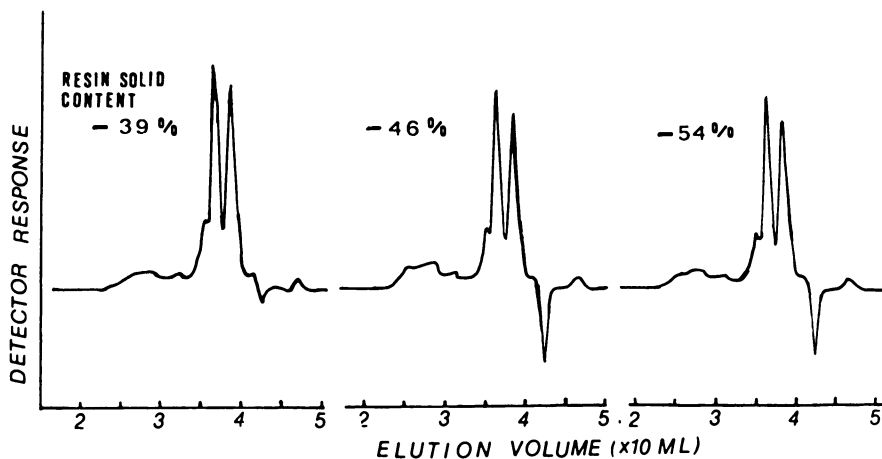


Figure 6. GPC chromatograms of phenolic resins at various resin solid contents.

Physical and mechanical properties of the flakeboards are summarized in Table VI. On average, all strength properties decreased as the phenolic resin solids increased, with one exception (i.e., MOE at 46% resin solids). The effect of phenolic resin solid on the stability of the flakeboard was not significant (Table VI).

Table IV. Effect of Caustic Content on Physical and Mechanical Properties of Flakeboards

NaOH/ Phenol Ratio	Lignin/ Phenolic Resin	IB	MOR	MOE	After ODVPS Treatment					
					IB	MOR	MOE	LE	TS	WA
		(psi)	(psi)	(10 <sup>3</sup> psi)	(psi)	(psi)	(10 <sup>3</sup> psi)	(%)	(%)	(%)
0.20/1	75/25	58	5081	746	50	3503	338	0.33	38	110
0.45/1	75/25	72	6706	794	52	3874	399	0.31	37	109
0.70/1	75/25	77	5680	762	54	3580	396	0.28	34	106
0.95/1	75/25	70	5918	821	53	3275	405	0.32	34	103

Table V. Effect of Resin Solids Content on Physical and Mechanical Properties of Phenolic Resins

Resin Solid Content	pH	Specific Gravity	Gel Time	Viscosity	Molecular Weight	
(%)		(g/cc)	(min)	(cps)	M <sub>n</sub>	M <sub>w</sub>
39	10.6	1.17	26.5	24	468	972
46	10.7	1.20	21.5	40	491	1293
54	10.8	1.24	18.5	84	469	1086

Table VI. Physical and Mechanical Properties of Flakeboard

Phenolic Resin Solids Content	Lignin/ Phenolic Resin Ratio	IB	MOR	MOE	After ODVPS Treatment					
					IB	MOR	MOE	LE	TS	WA
		(psi)	(psi)	(10 <sup>3</sup> psi)	(psi)	(psi)	(10 <sup>3</sup> psi)	(%)	(%)	(%)
39	75/25	72	6849	817	60	3867	436	0.29	36	105
46	75/25	66	6413	853	57	3594	415	0.29	36	105
54	75/25	57	5639	723	49	3592	392	0.29	35	110

## Conclusions

Performance of lignin-phenolic resin bonded flakeboard is related to molar ratio of formaldehyde to phenol, amount of sodium hydroxide catalyst, and the solids content of the blended phenolic resins. At a 25/75 (w/w) mixture of phenolic resin/methylolated lignin, the blends formulated with a phenol/formaldehyde ratio of 1:3 consistently resulted in higher bond strength, lower thickness swell, and smaller linear expansion. Gluebond performance improved as the phenol/NaOH ratio increased from 1:0.2 to 1:0.7. Further increases in sodium hydroxide adversely affected panel properties. The bond strength decreased slightly as the resin solids content increased. Structural flakeboard panels with acceptable strength and durability can be made using methylolated lignin as 75 percent replacement for phenolic resins.

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# Chapter 9

## Durable Wood Adhesives from Kraft Lignin

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Kraft lignin having a high reactivity with formaldehyde is the basis for two new durable wood adhesives. Bonds formed under moderate acid-catalysis of a dispersion of hydroxymethylated lignin had high strength and were water resistant. However, they required longer press times than those needed for bonding with conventional phenolic adhesives at comparable temperatures. An alternative formulation involved the dispersed hydroxymethylated lignin reacting with a blocked diisocyanate. This formulation required less energy for bonding and yielded high-quality bonds. These formulations use little or no petrochemicals and produce energy efficient bonding. Further work on formulation variables and bonding conditions should result in commercial adhesive systems for flakeboard, oriented strandboard, and plywood manufacture.

It has been demonstrated (1) that at least one kraft lignin possessed sufficient formaldehyde reactivity to yield a cured adhesive with high insolubility in both dilute acids and bases. This lignin, after hydroxymethylation and curing by acid catalysis, produced wood bonds having high water resistance without requiring copolymerization with phenol. A satisfactory level of acidity for catalysis could be attained using organic acids at pH levels similar to those found in natural wood. The incorporation of polyhydroxy compounds to suppress condensation reactions during hydroxymethylation permitted an element of control over adhesive working properties and bond performance. The adhesive could be readily applied to wood surfaces, possessed good storage stability, and had wide latitude in working properties. It was readily cleaned from operating equipment, created minimal waste, and posed no special problems with waste disposal. While

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these results were quite encouraging, it was recognized that additional research was required to: 1) optimize formulation and bonding conditions, 2) elucidate the reaction mechanisms involved, 3) develop satisfactory quality-control procedures, 4) assess the cost of bonding in comparison with that required for phenolic adhesives, 5) evaluate the longterm performance properties, and 6) determine the applicability of the lignin system for bonding flakeboards, oriented strandboards, and plywood from both softwood and hardwood species. As a step toward fulfilling these needs, this chapter describes the evaluation of formulation variables to help define the useful range of ingredient concentrations, practical conditions for achieving the hydroxymethylation reaction, and the acidification conditions required for producing good working properties in the adhesive so that reproducible high-quality bonds could be formed.

### Background Information

The earlier report just referred to described how lignin materials were evaluated for formaldehyde reactivity and for their ability to form solids that were insoluble in dilute acids and bases—a requirement that must be met by an adhesive if high performance in exterior environments is to be expected. A lignin material that yielded encouraging results under the conditions used was a purified kraft lignin available commercially in reproducible quality, Indulin AT. It was reported to have an ash content of 1% and a carbohydrate content of less than 1%. It was found that one-half a mole of formaldehyde reacted with each mole of lignin, assuming a molecular weight of 180 for lignin. This is roughly the weight of an average C<sub>9</sub> unit, the basic repeating structure in lignin. Only every other C<sub>9</sub> unit, on the average, was able to react with formaldehyde.

This lignin proved capable of forming waterproof bonds with wood after hydroxymethylation, precipitation at pH 5.5, catalysis with oxalic acid, and hot pressing for 10 minutes at 150 psi and 150 °C. The formulation consisted of 1) reacting (7 days, room temperature) the following molar quantities of materials: lignin 1.0, formaldehyde 2.0, water 20.0, triethylene glycol (TEG) 0.5, sodium hydroxide 0.5; followed by 2) the additional molar quantities of materials: acetic acid 0.5, and oxalic acid 0.4. This formulation evolved by trial and error with the deliberate use of formaldehyde in large excess during hydroxymethylation.

One of the problems that arose during the previous experimentation concerned the character of the solid produced by the acetic acid addition after hydroxymethylation. Dolenko and Clarke (2) described the physical changes that took place upon acidification of hydroxymethylated kraft black liquor as starting with a homogeneous black solution at high pH and changing upon a reduction in pH to a black, semisolid mixture difficult to stir, then to a precipitate visible as a chocolate-brown dispersion, and finally at acid pH to a tan-colored, fine particle size thixotropic dispersion. The purified lignin evaluated here also went through much the same kind of changes, with the character of the acidi-

fied dispersion depending upon the lignin-to-water ratio, temperature, and rate of acidification. Room temperature acidification at slow rates of addition often led to dispersions that required dilutions to as low as 20% solids before a brushable consistency was obtained. There are material-handling problems associated with the precipitation of solids by acidification of kraft black liquor whether or not it has been hydroxymethylated. In cases where the objective was to produce a filterable solid, Merewether (3) found that acidification at elevated temperatures was effective, while Whalen (4) found acidification in the presence of organic liquids such as chloroform or methylene chloride resulted in a granular form of solid easily filtered, washed, and dried. A solution to this problem was needed so that an adhesive of reasonably high total solids could be prepared that retained a brushable or sprayable consistency.

Conditions for hydroxymethylation of lignin have been reported by other investigators. However, these results are often difficult to interpret because the lignin-starting materials lack definition, particularly from a stoichiometric standpoint. The work at the Canadian Laboratory in Ottawa, as described by Dolenko and Clarke (2), Clarke and Dolenko (5), and Calve and Shields (6), involved crude kraft black liquor as did the work of Enkvist (7). The starting materials could be described by such parameters as percent solids content, specific gravity, pH, and percent of free formaldehyde in the liquor. The mole ratio of reactants could not be determined in some of these cases. However, in reports where the concentration of reactants could be determined, mole ratios were calculated with the assumed molecular weight of lignin as 180. Representative data are summarized in Table I.

Table I. Conditions for Hydroxymethylation of Lignin

Lignin	Moles of Reactants			Reaction		Reference
	HCHO	NaOH	H <sub>2</sub> O	Temperature	Time	
1.0	2.1	0.5	30.5	Room	3 days	(5)
1.0	1.26	0.9	33.3	80 °C	1 hour	(8)
1.0	2.16	0.9	48.0	70 °C	20 hours	(9)
1.0	2.16	0.9	48.0	Room	3 days	(9)

The hydroxymethylation conditions used in the research reported here involved efforts to define practical ranges rather than optimize conditions.

### Experimental Methodology

The hydroxymethylation reaction was carried out under several time-temperature conditions using different mole ratios of reactants in a search for conditions that would maximize the extent of hydroxymethylation. The hydroxymethylated lignin (HML) reaction product was then evaluated for its ability to form

wood bonds of high quality with regard to strength and water resistance. A detailed description of example adhesive formulations is given in Table II.

Table II. Adhesive Formulations

Moles	Molecular Weight	Ingredient	Total (g)	Solids (g)	Volatiles (g)
Basic components:					
1.0	180	Indulin AT (95%)	189.5	180.0	9.5
0.5	40	NaOH (50%)	40.0	20.0	20.0
1.0	30	Formalin (37%)	81.1	12.0	69.1 <sup>1</sup>
0.5	150	TEG	75.0	75.0	—
20.0	18	Water	261.4	—	261.4
0.5	60	Acetic acid	30.0	21.0	9.0 <sup>2</sup>
Additional component:					
ALTERNATIVE 1 <sup>3</sup>					
0.4	126	Oxalic acid	50.4	36.0	14.4 <sup>4</sup>
ALTERNATIVE 2 <sup>5</sup>					
—	—	Isoset CX-11 <sup>6</sup> crosslinking agent	67.7	67.7	—

<sup>1</sup> Assuming 40% of formaldehyde added to lignin with remainder volatilizing in one form or another—an estimate for calculation purposes only.

<sup>2</sup> Reaction with sodium hydroxide forming sodium acetate and water.

<sup>3</sup> Total solids = 47.3%. Lignin is 52.3% of the solids.

<sup>4</sup> Due to 2 moles of water of crystallization.

<sup>5</sup> Total solids = 50.4%. Lignin is 47.9% of the solids.

<sup>6</sup> Ashland Oil, Inc.

The hydroxymethylation reaction was carried out by combining water, triethylene glycol, and formalin, and dispersing the Indulin AT powder in the liquid mixture with mechanical stirring at room temperature. The sodium hydroxide solution was then added with additional stirring until the dispersed solid dissolved. The mixture was then heated for a specified time at a selected temperature. The reaction was terminated upon the addition of the glacial acetic acid with the mixture at 50 to 80 °C and the precipitation of the reaction product. After cooling, the oxalic acid powder was added and the dispersion homogenized to a smooth, brushable consistency.

**Differential Scanning Calorimetry.** Thermograms of samples were obtained with a Perkin-Elmer DSC-2 differential scanning calorimeter. Stainless steel capsules sealed with Viton O-rings allowed routine operations to 200 °C. Indium was used to establish temperature calibrations. Baselines were established by cooling capsules and rescanning the temperature range after obtaining the initial thermogram.

Specimen preparation and testing are described in detail in the earlier report (1). In general, the adhesive was used to bond yellow birch rotary-cut veneers in panels with two-ply laminations with grain parallel. Bonding was carried out by hot pressing at 150 psi, 150 °C for either 5, 10, or 15 minutes. Miniature specimens were cut 15 mm wide with 10-mm overlap. Specimens were tested for shear strength in the dry condition and in the wet condition after either a vacuum-pressure soak procedure or after boiling in water for 4 hours. The shear strength values reported are the average of five specimens tested, rounded to the closest 5 psi.

## Results and Discussion

**Control of Precipitate Formation.** The problem with the character of the precipitated HML proved to be easily resolved with the particular lignin under study. When the addition of the glacial acetic acid was carried out at temperatures only as high as 50 °C, the reaction product was granular and did not retain large quantities of water in a semisolid mass. However, this condition required a redispersion of the solid after the oxalic acid catalyst had been added. This could be accomplished with mixers designed to homogenize and disperse materials in liquids.

**Effect of Formulation and Processing Variations on Shear Strength.** The conditions studied for the hydroxymethylation reaction included 23 °C, 50 °C, and 80 °C. The criterion used for determining the extent of the reaction was the ability of the reacted lignin to develop high-quality bonds with wood—in this case, bonds with wet shear strength of 900 psi or greater. The development of shear strength as a function of time at each of the three temperatures is shown in Figures 1, 2, and 3. Figure 1 shows results for room temperature reactions involving mole ratios of lignin 1.0, sodium hydroxide 0.5, formaldehyde 1.25, triethylene glycol 0.5, and water 20.0. It is apparent from Figure 1 that data from wet testing show bond-quality differences much better than do the values from dry testing. Also, 5-minute press time does not provide adequate cure, while 10- and 15-minute press times developed wet shear strength greater than 900 psi at all times after 2 days of hydroxymethylation reaction. There was a suggested trend of increasing wet shear strength development from 2 to 19 days' reaction, but the increase was slight. Thus, hydroxymethylation at room temperature yielded high-quality bonds with reaction times ranging from 2 to 19 days.

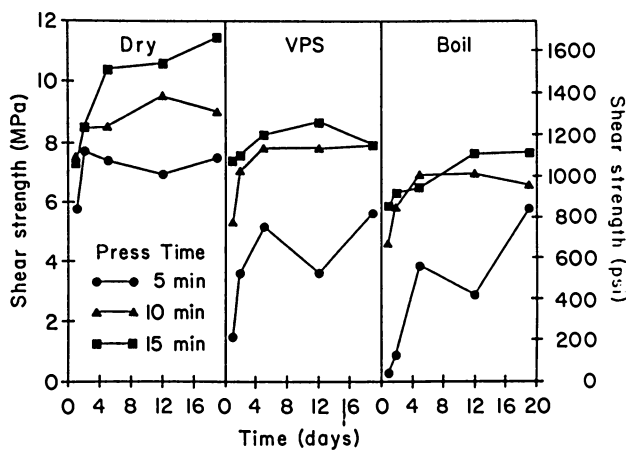


Figure 1. The effect of hydroxymethylation time at 23 °C on shear strength development.

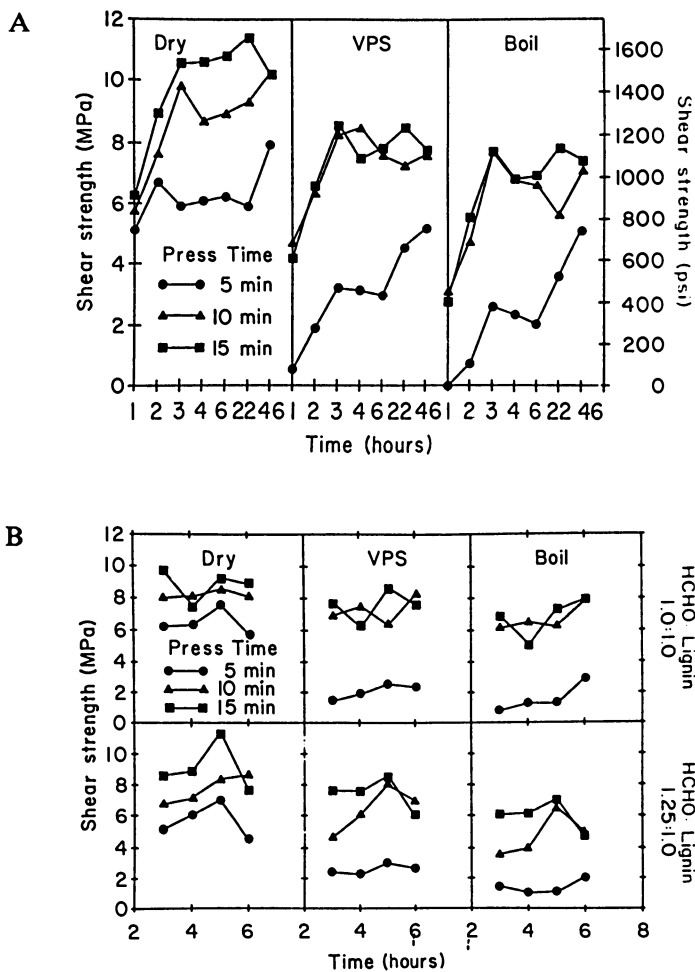


Figure 2A and 2B. The effect of hydroxymethylation time at 50 °C on shear strength development.

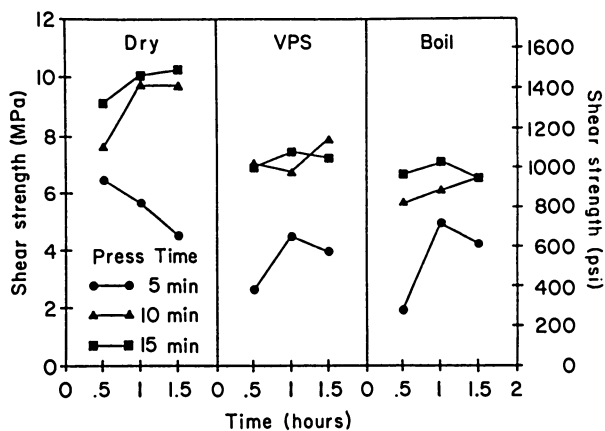


Figure 3. The effect of hydroxymethylation time at 80 °C on shear strength development.



Hydroxymethylation at 50 °C took place in a matter of hours with the same formulation. Data covering the time span from 1 to 46 hours are shown in Figure 2A with wet shear strength above 900 psi developing after 3 hours' reaction. Again, there was a long reaction period during which adequate wet shear strength was developed. Additional data were obtained at 3, 4, 5, and 6 hours of reaction time, which is shown in Figure 2B for two formaldehyde-to-lignin mole ratios, 1.0 and 1.25 to 1.0. In this case, the 1:1 mole ratio of formaldehyde to lignin appeared to develop higher wet shear strength than did the 1.25:1. Again, 10- to 15-minute press times were required for adequate cure. The data suggest that a reaction time of at least 5 hours at 50 °C should provide high-quality bonds.

The data obtained with reaction at 80 °C are shown in Figure 3 for a formulation with a formaldehyde-to-lignin ratio of 1:1. These data show that a reaction time of 1 hour provided high wet shear strength.

The effect of varying the sodium hydroxide-to-lignin ratio is shown in Figure 4A where the ratio evaluated was 0.25, 0.5, 0.75, and 1.0 to 1.0. The conditions used for hydroxymethylation were those found earlier to produce a complete reaction (when 0.5 mole of sodium hydroxide and 1.15 moles of formaldehyde had been used). Only two press times were evaluated, 10 and 15 minutes, since shorter times had proved to be inadequate for full cure. The lowest and highest concentrations of sodium hydroxide yielded poor bond quality, while the 0.5 and 0.75 levels produced high wet shear strength. Additional data were obtained at ratios of 0.4, 0.5, and 0.6 to 1.0 as shown in Figure 4B with two formaldehyde-to-lignin ratios, 1.0 and 1.25 to 1.0. High-quality bonds, both wet and dry, were produced by all three sodium hydroxide concentrations and little, if any, difference resulted from reducing the formaldehyde content by only 0.25 mole per mole of lignin.

It would be most desirable to use as little formaldehyde as possible and still achieve complete hydroxymethylation under reasonable time-temperature conditions for reaction. Some losses would be expected by the Cannizaro reaction. The ratio of formaldehyde to lignin would need to be greater than 0.5 to 1.0. When the ratio was increased to 1.0, 1.5, and 2.0 to 1.0, the shear strength data shown in Figure 5 were obtained. With hydroxymethylation taking place at room temperature for 7 days, high wet and dry shear strengths were obtained at all three ratios. When the hydroxymethylation was carried out for 3 hours at 50 °C, shear strength appeared to increase with increasing formaldehyde content, suggesting that the reaction time may have been insufficient for complete reaction except when a large excess of formaldehyde was present to advance the extent of reaction by mass action. These data indicate that a formaldehyde-to-lignin ratio of 1:1 would be satisfactory, providing the reaction time was adequate for complete reaction to occur.

The fact that a 10-minute press time at 150 °C and 150 psi was required before high wet strength was obtained indicated the need for more energy to cure the lignin adhesive than was required for cure of a phenolic adhesive. The

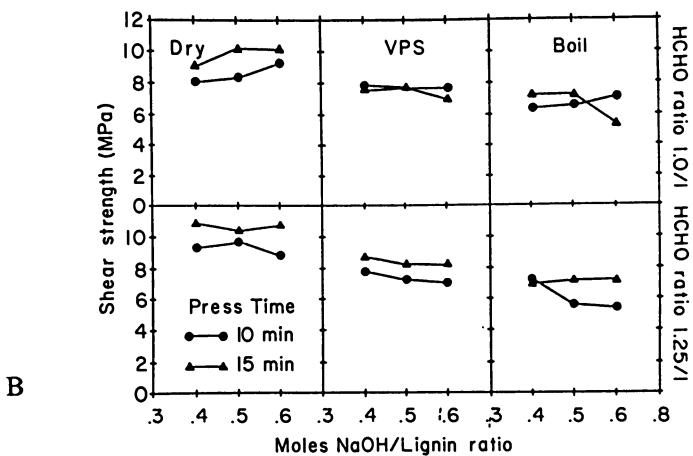
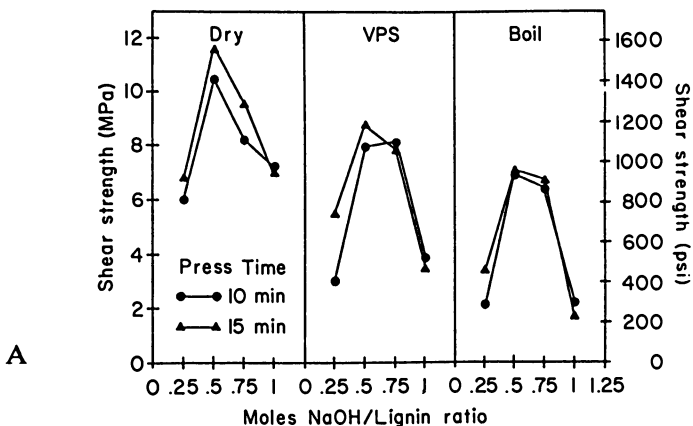


Figure 4A and 4B. The effect of changing sodium hydroxide to lignin ratio on shear strength development.

wet shear strengths obtained after the 4-hour boil were in most cases slightly lower than those resulting from the vacuum-pressure soak. This indicated that the degrading effect of the boiling treatment was more severe than the soaking treatment. This also showed that the boiling treatment did not supply extra heat energy to advance the cure of the lignin adhesive, which is in contrast to its influence on undercured phenol-formaldehyde (PF) resin adhesives.

I also evaluated the shelf life or pot life of the adhesive with room temperature storage after the oxalic acid had been added. The results shown in Figure 6 indicate satisfactory use after more than 120 days of storage.

**Differential Scanning Calorimetry.** The thermal behavior of the lignin-based adhesives was compared with that reported by Christiansen and Gollob (10) on PF resins used for wood bonding. Their results are summarized in Figure 7 and were obtained with liquid resins in sealed capsules to suppress water and formaldehyde vaporization endotherms. Resins that produced scans a, b, and c varied in formaldehyde-to-phenol ratio and the manner in which the sodium hydroxide catalyst had been added. The free formaldehyde content in the resins evaluated was 3.1, 1.2, and 0% for a, b, and c, respectively. In general, a sharp exothermic peak in the temperature range of 98 to 129 °C was attributed to addition reactions of free formaldehyde with phenol, while a broader, higher temperature peak in the range of 139 to 151 °C was attributed to chain-building condensation reactions involving hydroxymethyl groups.

The lignin adhesives were also evaluated in sealed capsules, but after air drying to reduce water and free formaldehyde to low levels. The series of adhesives having variations in sodium hydroxide contents (shear strength data in Figure 4A) yielded the scans shown in Figure 8 for different sodium hydroxide-to-lignin ratios. These scans represent different levels of formaldehyde addition and chain-condensation reactions. When only 0.25 mole of sodium hydroxide was used (scan d), an apparent endotherm at 150 °C splits the exotherm, resulting in peaks at 140 and 167 °C. Under stronger catalysis (0.5 mole of sodium hydroxide in scan c), the endotherm almost disappears with a major exotherm peak at 157 °C, and with 0.75 mole a predominant exotherm peaks at 177 °C. With sodium hydroxide of 1.0 mole (which is in excess for the conditions used for the reaction conditions reported here), there is a broad exotherm starting early with a maximum at about 140 °C. This suggests that poor bond results as condensation reactions advance too fast. In contrast, the adhesive with 0.25 mole of sodium hydroxide also produced poor bond quality, most likely due to inadequate hydroxymethylation of available reactive sites. Increased time or temperature of reaction with 0.25 mole of sodium hydroxide would be expected to develop reaction levels closer to those shown for scans b and c of Figure 8, which resulted from formulations that yielded high-quality bonds with wood.

The temperature for exotherms representing condensation reactions with the lignin adhesive ranged from about 157 to 177 °C, in contrast to values for PF resins of 139 to 151 reported by Christiansen and Gollob (10). These differences

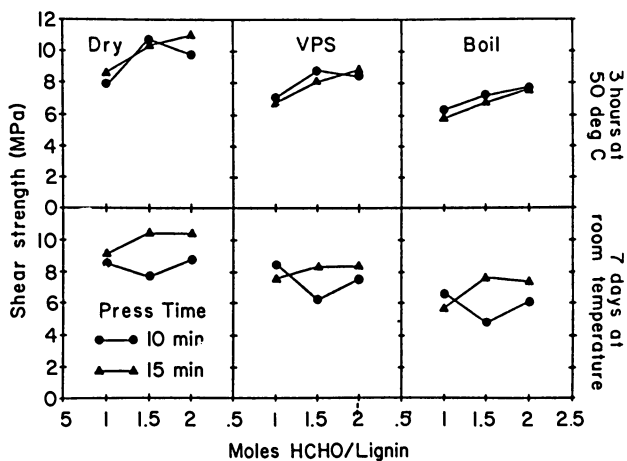


Figure 5. The effect of changing formaldehyde to lignin ratio on shear strength development.

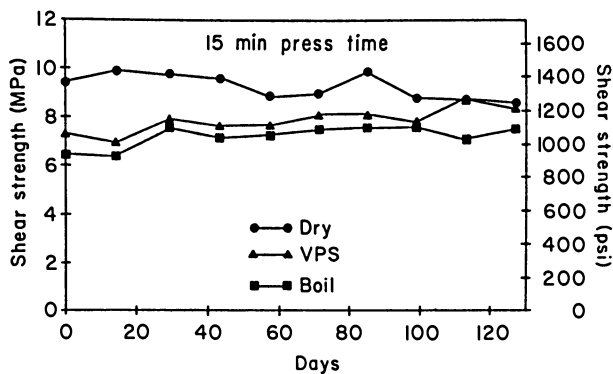


Figure 6. Storage life of oxalic acid-catalyzed HML at room temperature.

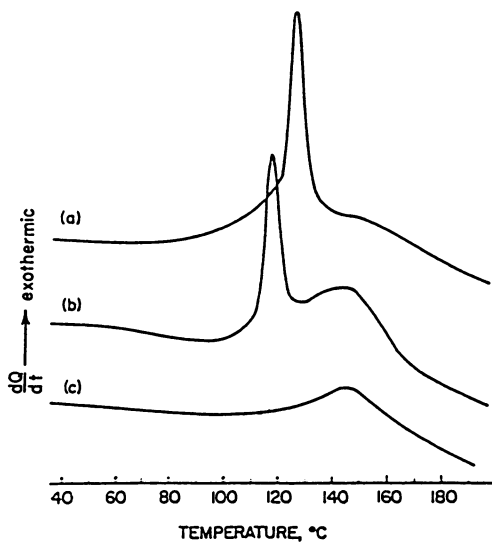


Figure 7. DSC thermograms of a phenolic resin (10).

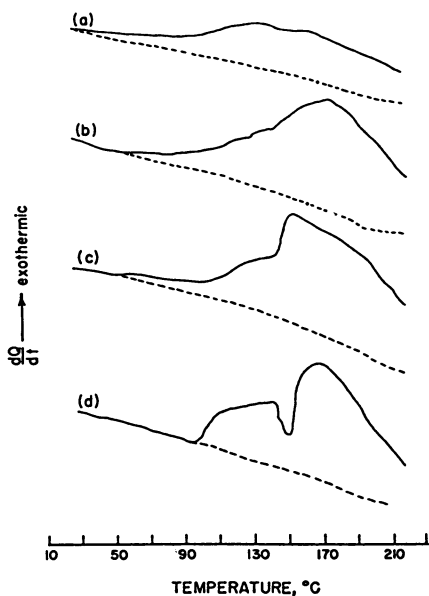


Figure 8. DSC thermograms of lignin hydroxymethylated under different sodium to lignin ratios: a) 1.0, b) 0.75, c) 0.5, and d) 0.25.

emphasize that extended press times are required to cure the lignin adhesives compared to PF adhesives.

### Reduction in Energy Demand for Curing Hydroxymethylated Lignin.

One method of reducing the energy requirements for crosslinking of methylolated lignins would be to incorporate a difunctional material having much greater reactivity with methylol groups than they have for themselves and would, therefore, function as a crosslinking agent. Diisocyanates are such materials and they are available with blocking groups that allow their use in water systems without premature reaction with water, alcohols, acids, or other reactive materials. An example is Isoset CX-11. This was added at different stages in formulating the lignin adhesive at either 10 or 20% of the total mixture weight, and two-ply birch panels were bonded for shear strength tests. The HML was prepared with the following mole ratios: Indulin AT 1.0, formalin 1.0, sodium hydroxide 0.5, triethylene glycol (TEG) 0.5, water 20.0, and acetic acid 0.5. The shear strength results are shown in Table III.

Table III. Shear Strength of Diisocyanate-Modified Lignin Adhesive

Formulation	Storage Time Prior to CX-11 Addition	Storage Time After CX-11 Addition	Press Time at 150 °C (min)	Shear Strength		
				Vaccum Pressure Dry (psi)	4-Hour Soak (psi)	Boil (psi)
<b>HML</b>						
+ oxalic						
+ 10% CX-11	25 days	18 hr	5	880	620	755
			10	1,020	930	760
<b>HML</b>						
+ 10% CX-11	3 hr	1 hr	5	1,325	965	900
			10	1,710	1,155	1,135
<b>HML</b>						
+ 10% CX-11	3 hr	20 hr	5	1,065	545	665
<b>HML</b>						
+ 20% CX-11	3 hr	1 hr	5	1,325	880	815
			10	1,655	1,140	1,090
<b>HML</b>						
+ 20% CX-11	3 hr	20 hr	5	965	360	410

An exploratory experiment to determine compatibility and working properties consisted of adding the crosslinking agent to a formulated adhesive that had been stored at room temperature after its use to obtain the data shown in Figure 3. The liquid crosslinking agent was easily incorporated by slow addition to the adhesive with stirring and without any noticeable exotherm. After standing overnight, the mixture appeared foamy, indicating some reaction between the diisocyanate and oxalic acid or water generating carbon dioxide. The wet shear strength obtained with this formulation was encouraging even when pressing for only 5 minutes at 150 °C and 150 psi, as compared with results without diisocyanate addition.

Since the diisocyanate addition to HML would not require oxalic acid (its presence might even be detrimental to the desired reaction), additional formulations were prepared from HML after precipitation by acetic acid to a pH of approximately 5.5. The crosslinking agent was added at 10% to the mixture weight in one case and at 20% in another. Birch panels were bonded with each formulation approximately 1 hour after the addition of the crosslinking agent at 5- and 10-minute press times. The formulations were stored at room temperature overnight, and panels were then bonded with 5-minute press times. The data in Table III show that at 10% addition of crosslinking agent, high wet shear strength developed even at a press time of 5 minutes. The 20% addition did not produce as high wet shear strength as was developed by the 10% addition. The highest shear strength was obtained soon after mixing the crosslinking agent into the mixture, and overnight storage at room temperature was decidedly detrimental. While the optimum concentrations and working properties of this system remain to be defined, the results obtained to date indicate that blocked diisocyanates can provide increased reactivity for curing HML. High wet strength bonds can be obtained under conditions that appear to approximate those currently used in commercial practice with phenolic adhesives, but additional research will be required to substantiate this expectation.

## Summary and Conclusions

A wood adhesive producing high shear strength and water resistance was prepared from a purified kraft lignin material without the need for copolymerization with phenol. The lignin was hydroxymethylated by reaction with formaldehyde in alkaline medium, precipitated by acidification to a pH of approximately 5.5, catalyzed with oxalic acid, and homogenized to a smooth brushable consistency. A satisfactory formulation consisted of the following molar quantities, with lignin assigned a molecular weight of 180: lignin 1.0, sodium hydroxide 0.5, formaldehyde 1.0, triethylene glycol 0.5, water 20.0, acetic acid 0.5, and oxalic acid 0.4. High-quality bonds with high wet strength were developed when hydroxymethylation was carried out for at least 2 days at room temperature, or 5 hours at 50 °C, or 1 hour at 80 °C. Under the best component concentrations and reaction conditions evaluated, high wet strength bonds required 10- to 15-

minute press times at 150 °C and 150 psi, which is longer than normally required for a phenolic adhesive. With the addition of a blocked diisocyanate to the HML, high wet strength bonds were obtained at shorter press times, indicating that the sluggish reactivity of HML in condensation reactions may be overcome by such crosslinking agents.

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# Chapter 10

## Room-Temperature Curing Adhesives Based on Lignin and Phenoloxidas

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An effective adhesive for wood materials, e.g. particleboards, consists of spray-dried lignin, particularly liginosulfonate, and a phenoloxidase containing culture fluid of filamentous fungi grown on dilute lignin solutions in the presence of cheap C and N sources in a fermenter. Wood laminates bonded with this two-component room-temperature curing adhesive had tensile strengths above 2.0 MPa. The underlying reaction mechanism is the crosslinking of lignin via oxidative polymerization catalyzed by the phenoloxidase. The production of this adhesive includes the total utilization of waste lignins a) directly as one component of the binding system and b) indirectly as nutrient source of the phenoloxidase-producing fungi.

The pulping industry releases about 40 million tons of lignin annually, which are still far from being utilized effectively. Indeed, only 20% of this vast potential is used for various industrial purposes, the rest being burnt. Irrespective of SO<sub>2</sub> emission during the burning of waste pulping effluents, the process represents an enormous dissipation of a renewable raw material that could be better utilized. Among the many considerations regarding lignin utilization, two seem to be very important to any increase in lignin's market value:

1. Applications should make use of the polymeric structure of lignin.
2. The market has to be large enough to absorb enormous quantities of lignin.

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The already large tonnage of lignins produced in pulping wood will further increase because of the increasing need for high-value chemical pulp and because the main use today—the food industry—will need much less low-value lignin as a pelletizing agent.

In this respect, the most important future application of lignin will be as a natural plastic in the field of general polymer applications, especially as adhesives for wood composites.

The adhesive properties of lignin, its reactivity with formaldehyde, and its structural similarity with phenolic adhesives invited investigation of the applicability of lignin in adhesive resin systems. Therefore, during the past several years, numerous attempts have been made to replace the expensive petrochemical resins totally or partially with the renewable raw material lignin (1).

However, the polydisperse character and the accompanying impurities created significant problems for the utilization of technical byproduct lignins (from spent sulfite liquor and kraft black liquor) as extenders for petrochemical resins. Phenolic resins, for example, react primarily with the low molecular weight lignosulfonates so that the percentage of phenolics that could be replaced remained rather low. This disadvantage was circumvented by the "Karatex" adhesive developed by Forss and coworkers (2). Even in this advanced process (which produces annually nearly 4,000 tons of adhesive), the high molecular weight lignin fraction, obtained by ultrafiltration, can replace only  $\approx 40\%$  of phenolic resins. Another problem for the utilization of lignosulfonate as an adhesive is the high content of sulfonate groups, which causes a hygroscopic character and thus prevents their conversion to a water-resistant polymer. Kraft lignin seems to be better suited because of its water insolubility. However, from the estimated annual production of  $2 \times 10^7$  tons, only 0.1% is isolated and marketed (3). Many of the mills burning black liquor for recovery of the chemicals are already operating above recovery furnace capacity, so a use for this lignin would help to unburden their operations.

Finally, it should be stated that the processes that use lignin alone as thermosetting resin in particleboards (4-6) did not find industrial application, whereas, the processes using lignin in combination with synthetic resins (2, 7) are economically feasible though the remaining proportion of synthetic resin is still relatively high (60%).

One reason for the limited opportunities for replacing phenolic resins with lignin is the rather low content of phenolic groups (0.6 and 0.3 phenolic OH-groups per monomer in Kraft and sulfite lignin, respectively (8)). Therefore, new developments focus on the "activation" of the lignin molecule, for example, by the synthesis of hydroxyalkyl derivatives for use in combination with melamine or isocyanate (9). Other new and interesting investigations into the use of more "active" lignin in combination with synthetic resins, in addition to our chapter, are reported elsewhere in this book.

## Experimental Methodology

The approach we used to make lignin a suitable "partner" in an adhesive formulation is based on the following considerations. Our idea was to use the lignin not merely as filling material, where it is obviously inferior to the more active phenolic resins because of the few phenolic groups and condensed structure of lignin. Rather, we thought that liginosulfonate itself could be a good binding agent even without addition of synthetic resins, if new active sites were introduced. "Active sites" means, for example, the disintegration of the condensed structure, the addition of phenolic hydroxyls, the splitting of methyl ethers so that new phenolic groups are formed, the introduction of new functional groups (for example, carboxyl groups), and last but not least, the formation of radicals that then could react to form an oxidative polymerizate.

Both the activation of lignin and its crosslinking to form a binder for wood material could be performed by a single biotechnological process based on the observation that enzymes are often much more powerful catalysts in the conversion of naturally occurring polymer molecules than manmade chemicals can ever be.

The binding capacity of the lignin-based enzymatic adhesive is based on the following reactions (10-12). The enzyme used is a phenoloxidase, also called "laccase", classified by IUPAC as monophenol, dihydroxy-L-phenylalanine: oxygen oxido-reductase (E.C. 1.14.18.1). This relatively unspecific copper-containing enzyme catalyzes the one-electron oxidation of aromatic substrates (e.g., phenols) by coupling to the four-electron reduction of molecular oxygen to water. In our case, the phenolic substrate is lignin. The initial one-electron oxidation of lignin by phenoloxidase, peroxidase and oxygenase yields radical cation intermediates that can react in two ways:

1. They react with water to form new phenolic groups (e.g.), via demethylation. This reaction represents the "activation" of the lignin molecule because new active phenolic groups, which can be further oxidized, are formed (13).
2. They react with each other to form an oxidative polymerizate. This reaction represents the crosslinking, and thus the actual gluing process.

Thus, the activation and crosslinking of the lignin are performed in one step. In this way, the apparent average molecular weight of liginosulfonate is increased up to  $1 \times 10^6$  Daltons (Figure 1). We measured this by Sepharose GPC and calibrated the column by molecular weight determinations of several fractions in an analytical ultracentrifuge (14). The curve with the broad distribution in Figure 1 shows native liginosulfonate; the sharp peak is the same liginosulfonate after enzymatic polymerization. This polymerizate was still water-soluble because

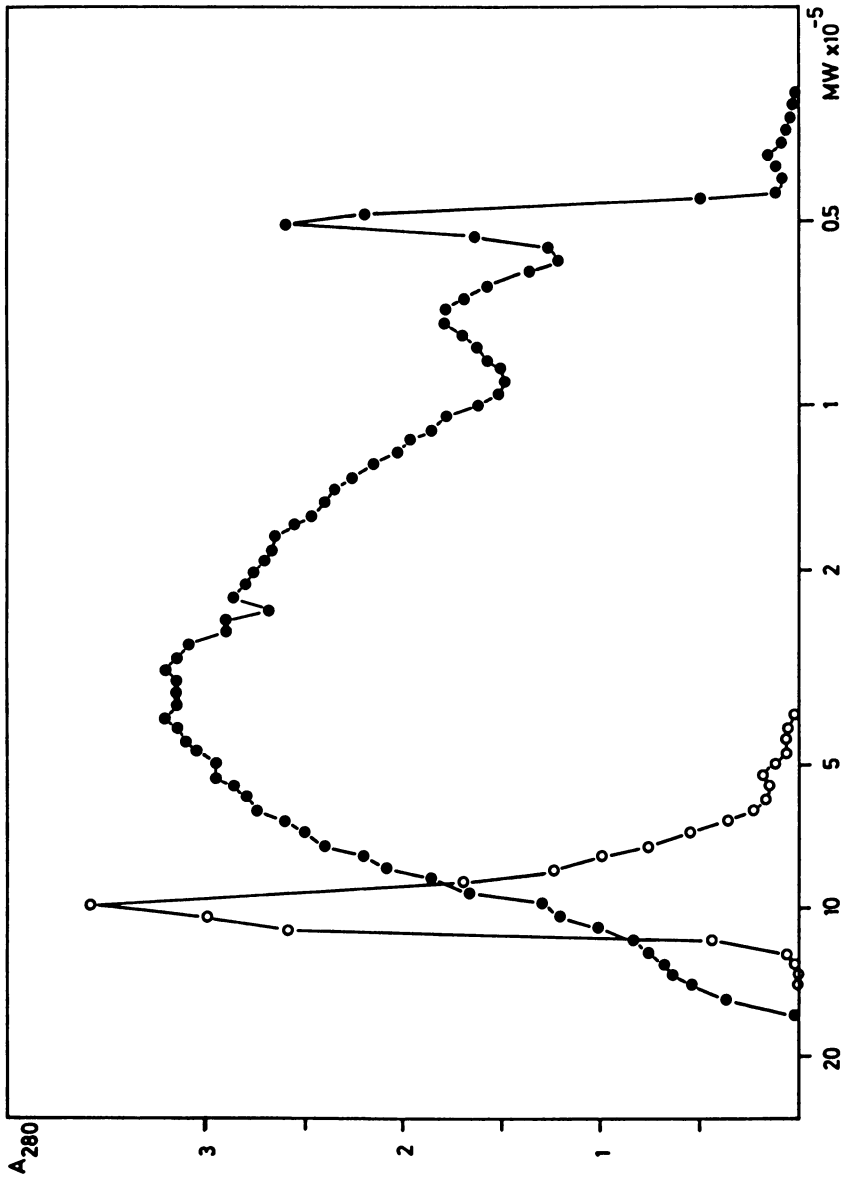


Figure 1. Molecular weight distribution (determined by Sepharose CL6B GPC) of lignosulfonate before (open circles) and after (filled circles) incubation with phenoloxidase.

of the sulfonate groups. However, water-soluble organosolv lignin fractions became water-insoluble after enzymatic polymerization, and this is important for a water-resistant adhesive (11).

Of course, an enzyme applied to a technical process in such a dimension as adhesives for wood materials has to have certain properties. It must be:

1. Producing in large quantities on cheap nutrients.
2. Highly reactive with technical lignins.
3. Stable at room temperature.
4. More thermotolerant than enzymes usually are.
5. Applicable as a crude preparation without further purification.

We found that all these conditions were fulfilled by extracellular phenoloxi-dases produced by a group of filamentous fungi called white-rot basidiomycetes (15). Among the many species and strains tested, the fungus *Trametes versicolor*, a frequent inhabitant of the woods of the Northern Hemisphere, showed the most active enzyme production. It was an especially good candidate for our purposes because it could be adapted to very cheap nutrient sources. The sulfite liquor itself, consisting mainly of lignosulfonate and sugars, was suitable in dilute form for growth of the fungus and for inducing phenoloxidase production.

The enzyme activity was determined using 2,6-dimethoxyphenol as the substrate (16). The phenoloxidase activity obtained when this fungus was grown on dilute sulfite liquor was 12 to 15 U/mL, which was a multiple of the production on sole carbohydrate without lignin (11,17). For use as an adhesive component, this enzyme solution has to be further concentrated, by ultrafiltration or evaporation. To save energy, it was desirable to increase the enzyme production of the fungus. We tested many phenols and lignins and found that lignins obtained by an organosolv pulping process had a nearly tenfold capacity for enzyme induction (12). These results were obtained in 500-mL shaking cultures. The next step was to transfer the enzyme production to a larger scale. We were able to grow the fungus *Trametes versicolor* in a 30-L fermenter scale on 0.1% organosolv lignin in the presence of a cheap additional C-source producing 70 U/mL of extracellular phenoloxidase. After removal of the mycelium by filtration and subsequent sterile filtration of the enzyme-containing nutrient broth, this preparation was stable at room temperature for at least a month and could be used without further purification as a component in the lignin-based adhesive. The thermostability of the phenoloxidase was unusually high compared to most enzymes; even heating up to 65 °C did not destroy the activity. Considering that lignosulfonate contains 0.3 phenolic OH-groups per monomer and that the  $K_m$  value of phenoloxidase toward phenols lies between  $10^{-2}$  and  $10^{-4}$  M, an enzyme concentration of 400 U/mL in the aqueous solution of 45 to 50% lignin should be sufficient to cause the activation and crosslinking within a reasonable time, so that a sufficient binding capacity is obtained (Table I).

The enzyme solution represents one component of the two-component wood adhesive system. The second component is merely spray-dried sulfite liquor. The adhesive preparation was as follows. The biocomponent is mixed with the spray-dried sulfite liquor at a ratio of approximately 2 parts of sulfite liquor and approximately 1 part of aqueous enzyme solution, so that the dry matter content of the adhesive is between 50 and 60%. This mixture is homogenized and heated up to 50 °C to reduce its viscosity. The test boards were produced by mixing 150 g of adhesive with 1 kg of wood chips and pressing the mat at a temperature of 190 °C for 5 minutes at 30 kg/cm<sup>2</sup>. It has to be kept in mind that the heating process is *not* necessary for gluing with this phenoloxidase-lignin adhesive. Of course, the polymerization is carried out at room temperature. The heating serves only to remove the water within a short time. We bonded boards at 24 °C, and they had the same tensile strength as urea-formaldehyde and phenol-formaldehyde bonded boards that must be pressed at about 200 °C to obtain polymerization (Table I).

Table I. Tensile Strengths of Lignin-Based Two-Component Wood Bonding Systems Compared to Synthetic Resins

Type of Resin	Versal Tensile Strength <sup>1</sup> (MPa)	Temperature (°C)
a. Synthetic resins:		
Urea-formaldehyde	0.52 <sup>2</sup>	190
Phenol-formaldehyde	0.62	190
b. Controls (only one component):		
Spray-dried sulfite liquor SA <sub>1</sub> <sup>3</sup>	0.25	24
Lyophilized enzyme (320 U/mL)	0	24
Spray-dried SA <sub>1</sub> + denaturated enzyme	0.25	24
c. Lignin-phenoloxidase resins:		
SA <sub>1</sub> + 320 U/mL (CA <sup>++</sup> )	0.64	24
SA <sub>2</sub> + 320 U/mL (CA <sup>++</sup> /Mg <sup>++</sup> )	0.51	24
SA <sub>3</sub> + 320 U/mL (Mg <sup>++</sup> )	0.60	24
SA <sub>1</sub> + organosolv lignin + 320 U/mL	0.05	24

<sup>1</sup>The minimum standard requirement for 19-mm V20 particleboards is 0.35 MPa.

<sup>2</sup>Mean values of 10 replicates tested by DIN 52365.

<sup>3</sup>SA = sulfite liquor.

## Results and Discussion

In all cases, the minimum German standard requirement of 0.35 MPa is exceeded by lignin-phenoloxidase resins (Table I). In most cases, the break occurred in the wood and not in the glue line. As can be seen in Section B of the table, no component alone, whether the enzyme or the sulfite liquor, is capable of meeting standard requirements. A synergistic effect is obtained if the components are mixed. The cation of the sulfite liquor has no significant effect on the tensile strength; comparable results were obtained both with magnesium and calcium sulfite liquors.

Though the contact area between adhesive and wood is much larger in particleboards than in wood laminates, only 75% of the tensile strength was obtained when the lignin-based adhesive was applied as thermosetting system in particleboards (Table II). The following reasons may be applicable:

1. The curing time at room temperature under pressure was much longer (8 h) in the cold-setting system than in the particleboard production (Table II). Indeed, the tensile strength could be increased when the particleboard was pressed at room temperature for some hours. However, this procedure is of course not applicable in a technical process.
2. Besides the shorter curing time, the spraying procedure also plays a role in determining tensile strength. The relatively high viscosity of the adhesive caused some problems that can, however, easily be overcome in a technical process.

Table II. Versal Tensile Strength of Lignin-Based Adhesive<sup>1</sup> Used to Bond Pairs of Wood Laminates and Wood Chips (Particleboard)

Procedure and Properties	Wood Laminates	Wood Chips
1) Mixing procedure of the adhesive: time and temperature	10 min-22°C	30 min-22°C
2) Pressing procedure: time and temperature	8 h-22°C	5 min-190°C
3) Tensile strength	0.55 MPa	0.22 MPa

<sup>1</sup>Composition of the adhesive: One part spray-dried, milled sulfite liquor containing ca. 20% sugar and 1.5 parts concentrated culture filtrate of *Trametes versicolor* (grown on 0.1% organosolv lignin in a 25 L fermenter), containing 420 U/mL phenoloxidase activity.

A problem that still has to be solved is the deficiency of water resistance. The sulfonate groups are so polar that the polymerizate is still water-soluble. As was mentioned before, water-soluble fractions of organosolv lignins became insoluble in water after enzymic polymerization (11). Therefore, we hoped that an addition of phenol-rich organosolv lignin would improve the water resistance. However, as can be seen in the last line of Table I, this is not the case.

The enzyme concentration was not the rate-limiting factor in the system, because an increase of activity up to 1,000 U/mL did not lead to a higher tensile strength or a better water resistance. Currently, we are investigating several mixtures of less polar lignosulfonates and kraft lignins. Because these studies are being conducted cooperatively with an industrial partner, the results must be considered confidential at this time.

## Conclusions

Fungal phenoloxidase enzymes produced on waste lignin containing effluents were suitable biocomponents in cold-setting and thermosetting lignin-based adhesives. The phenoloxidase-lignin bio-adhesive will be suitable as thermosetting glue in particleboard production if the water resistance of the boards can be increased. Results in this area have already been obtained. The properties of lignin-phenoloxidase-bonded particleboards revealed several advantages compared to synthetic resins:

1. The lignin phenoloxidase adhesive implies the total utilization of waste lignin, directly as one component of the adhesive and indirectly as nutrient of the phenoloxidase-producing fungus.
2. The production of enzyme-lignin-bonded particleboard is much less hazardous than the production of isocyanate-bonded particleboard, for example.
3. The bio-adhesive consists of renewable raw material, so the production does not depend on the oil market.
4. The phenoloxidase-lignin-bonded particleboards are free of any emission.
5. The phenoloxidase-lignin adhesive is not only applicable as thermosetting adhesive but also as a cold-curing system.

## Acknowledgments

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# Chapter 11

## Biomass Pyrolysis Oil Feedstocks for Phenolic Adhesives

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Fast pyrolysis of pine sawdust in a small vortex reactor operating at 10 to 20 kg/h and 480 to 520 °C produces high yields of primary pyrolysis oils (over 55% by weight on a dry basis). The vortex reactor transmits very high heat fluxes to the sawdust, causing primarily depolymerization of the constituent polymers into monomers and oligomers. A preliminary scheme separates the raw oils into a carbohydrate-derived aqueous fraction and a phenolic-rich ethyl acetate (EA) soluble fraction. The EA fraction is washed with water and with aqueous sodium bicarbonate to remove acids yielding 20% to 25% of the feed as phenols and neutrals (P/N) in the EA solution. After EA evaporation, a novolak formulation with 50% phenol and 50% of the P/N fraction was successfully prepared. Gel times for the P/N fractions suitably prepared are intermediate between resorcinol and traditional phenol-formaldehyde resins. Preliminary projected amortized production costs for the P/N fraction are 10(16) cents per pound for a 1,000(250) tons per day plant (\$10/dry ton feedstock, 15% interest with 20-year amortization).

Pyrolysis of biomass is known to produce a complex mixture of phenolic compounds, which are derived primarily from the lignin fraction of the biomass (1-4). Elder and Soltes (5, 6) have investigated a phenolic fraction obtained from pyrolysis oils made in an updraft gasifier by TECH AIR as a source of phenolic adhesives; a phenolics fraction was separated by solubility differences of oil fractions based on solubility of acids in aqueous bicarbonate solutions and

solubility of the phenolics fraction in aqueous alkali solution. Adhesive formulations were preliminarily tested, and the effect of a few metal ions (such as barium) on the gel times of adhesives was measured. The formulations tested met with limited success. These results suggested that these oils would have to be chemically modified to be a full replacement for phenol or could be considered as simple extenders for petroleum-derived phenol. Russell and Reinmath (7) have employed a similar fractionation method on oils from high-pressure biomass liquefaction (8). A limited amount of adhesive testing was carried out, and a few bonded wood specimens were shown to have tensile strengths superior to the adhesive bond of a commercial birch veneer (9).

This chapter describes the initial results of converting waste sawdust into phenolics through fast pyrolysis employing a vortex reactor and a very fast heat transfer to depolymerize biomass into monomeric and oligomeric components. The pyrolysis method and the chemical fractionation employed to isolate the phenolic-rich fraction used in the subsequent adhesive gel testing are described. Results of an economic evaluation of the process are presented as well as the characterization of the phenolic-rich material. A novolak and a resol were successfully prepared with these compounds.

## Experimental Methodology

**Primary Pyrolysis Vapor Generation in the Vortex Reactor (10).** The pyrolysis reactor used to generate the pyrolysis oils is shown schematically in Figure 1. Coarse softwood sawdust (<5 mm) was metered by a screw feeder into the entrained solids/gas flow from the exit of the recycle loop. The ID of the 300 series stainless steel recycle loop was 11 mm. Nitrogen was used as the carrier gas rather than steam. The entrained particles flowed to the nitrogen ejector where they were accelerated by the supersonic jet to velocities over 100 m/s. The fast-moving entrained solids flow then entered tangentially into the vortex reactor. Inside the vortex reactor, the biomass particles were centrifuged to the wall and were forced into an abnormally tight helical path through the reactor. As the particles slid and bounced on the wall, they were in excellent thermal contact with the externally heated wall maintained at 625 °C. Under these conditions, the particle surface is very rapidly heated to about 450 °C, where pyrolysis to oils is favored. The diameter of the vortex tube reactor was 13 cm, and its length was 70 cm. A 5-cm-diameter, axial exit tube protruded into the aft end of the vortex reactor, which served to encourage partially pyrolyzed feedstock and large char particles to enter the recycle loop. The feedstock was recycled until it was fully pyrolyzed, which allowed a decoupling of the time required to pyrolyze the feedstock particles and the gaseous residence time. The ability of the carrier gas ejector to create a pressure differential across the recycle loop determined the rate of gas flow in the recycle loop. The pressure of the system was adjusted to maintain the feed hopper at about 250 Pa above atmospheric pressure (2.5-cm water column) by restricting the flow out of the system. The

char was removed in a hot cyclone. Typical throughput for this reactor is 10 to 20 kg of sawdust per hour with 1- to 2-kg carrier gas per kilogram of sawdust.

**Oil Collection.** The pyrolysis oils were collected in a series of condensers followed by a coalescing filter to remove residual aerosols, as shown in Figure 2. The first condenser was a cyclonic condenser 37 cm in diameter with a 45-cm-high cylindrical section. The tangential entry was a round 5-cm tube. This cyclone was wrapped with copper tubing, through which chilled water circulated at about 20 °C. The cooling coils were externally irrigated with water to transfer the heat from the cyclone wall to the cooling water. Inside and outside the axial outlet of the cyclone condenser were additional cooling coils. The pipe connecting the first and second condenser was also wrapped with a chilled water cooling coil and a drain was provided for condensate. The second condenser consisted of a vertical vortex tube having a 7.5-cm diameter with a rectangular entrance made from a 1.7-cm ID tube and with the axial outlet near the tangential entrance. The vortex tube condenser was cooled by refrigerated glycol at 2 °C, which was circulated through a copper tube wrapped around the OD. The third condenser was a 20-L glass carboy immersed in a dry ice and propanol bath. The entering gases were tangentially directed onto the ID of the carboy. The gas and aerosol stream then passed to the coalescing filter to remove the aerosols. Except for the glass carboy, the oil collection system was stainless steel, since the oils have been shown to be corrosive to iron and zinc (galvanized iron).

**Fractionation of Pyrolysis Oils.** Pyrolysis oil obtained from the vortex reactor was fractionated according to the scheme shown in Figure 3. Whole oil (1 kg) was dissolved in ethyl acetate (EA) on a 1:1 (w/w) basis. The oil was then vacuum filtered through filter paper to remove fine char. Upon standing, the EA/pyrolysis oil separated into two phases—an organic rich, EA-soluble phase and an EA-insoluble phase. Most of the water formed during pyrolysis is contained in the EA-insoluble phase. The EA-soluble portion of the oil was washed with water (2 x 75 mL) to remove the remaining water-soluble derived products.

The EA-soluble phase was then extracted with NaHCO<sub>3</sub> (5% w/w, 10 x 200 mL) and the aqueous layer saved for isolation of the organic acids fraction. The solvent was removed from the remaining EA-soluble fraction, which contained the phenolic and neutrals (P/N) fractions, on a rotoevaporator until no EA distilled over. The EA was not dried prior to evaporation, but rather, water was azeotroped during the distillation. Final water contents of each fraction were 0.5 to 1.0% by weight.

The organic acids fraction was isolated by acidifying the aqueous layer (pH 2) with 50% H<sub>3</sub>PO<sub>4</sub>, saturating the solution with NaCl, and extracting the organic layer with fresh EA. Solvent was removed by rotoevaporation. The water-soluble and EA-insoluble fractions were also isolated by rotoevaporation.

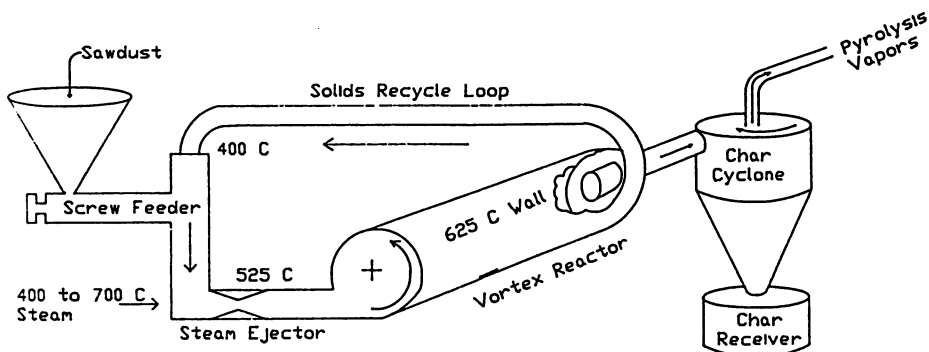


Figure 1. Schematic of vortex reactor for fast pyrolysis.

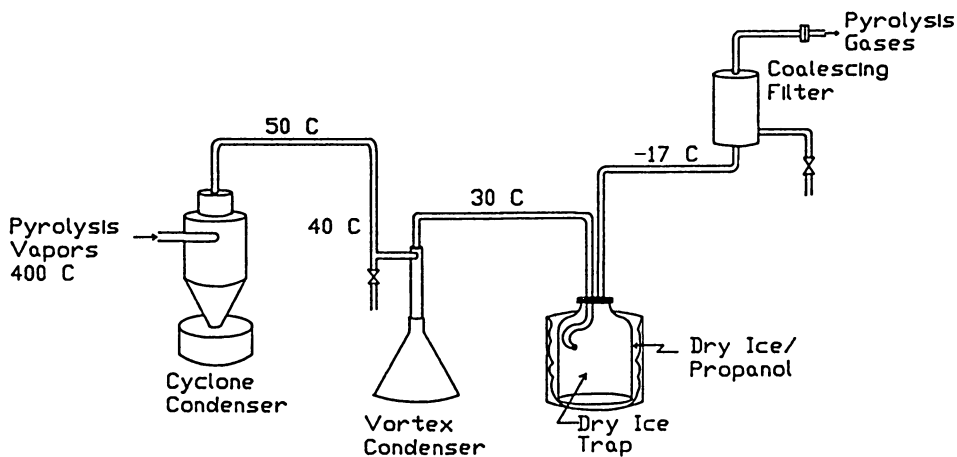


Figure 2. Schematic of pyrolysis oil condensation train.

**Methods of Analysis. Water Content of Fractions.** A chromatographic method was employed using a glass column (6 ft x 0.2 mm ID) packed with Porapak QS. The chromatographs used were a Varian 3700 or a Hewlett Packard 5880. Water contents were also determined by the Karl Fisher method by Huffman Laboratories, Golden, Colorado.

**Total Carboxyl and Phenolic Hydroxyl Content.** Conductimetric titrations employed were modifications of the procedure described by Sarkanen and Schuerch (11) for lignin total phenolic content. Spectroscopic determinations on the phenolics and neutrals fractions were carried out using the JEOL FX-900 Fourier Transform NMR spectrometer and the Nicolet 5SXC Fourier Transform Infrared Spectrometer. In addition, the solid state CP/MAS  $^{13}\text{C}$ -NMR spectra were obtained by the Regional NMR Center at Colorado State University using conditions described in Bryson et al. (12).

**High Performance Size Exclusion Chromatography.** The Hewlett-Packard 1090 liquid chromatograph was used with the HP 1040 diode array or HP 1037A refractive index (and HP 3392 integrator) detectors. A fifty Å (5 mm, 300 x 7 mm) Polymer Laboratories PL gel (polystyrene-divinylbenzene copolymer gel) column was used and standards were as described in Chum et al. (13). Tetrahydrofuran solutions of oil and oil fractions were analyzed.

**Molecular-Beam Mass-Spectrometry.** This procedure was carried out on equipment described by Evans and Milne (14). Pyrolysis of the oils (or fractions) was performed under controlled conditions and followed in real time by a free-jet, molecular beam MS. Pyrolysis products and fragmentation ions were detected.

**Adhesive Testing.** All gel times of the adhesive resins were determined using a stirring apparatus, which consisted of a 150-mm long, 25-mm OD disposable borosilicate test tube to which a total of 5.0-g of resin plus any additional component was added. The volume in the test tube was such that approximately 15 mm above the outside bottom end was filled with material. A 6-mm glass rod with a fire-polished, circular tip was fastened to be parallel to a second 6-mm glass rod using two miniature (8-mm wide) worm-drive hose clamps. The second glass rod was inserted into the chuck of a low torque stirring motor. With this arrangement, a thick cylindrical path was stirred that averaged only 2.5 mm from the test tube wall, with the result that the stirring rod did not form a hole in the gelling resin. Once the stirring was begun, a preheated, magnetically stirred molten wax bath was raised rapidly such that the lower 40 mm of the test tube was submerged. Gel times were from initial submergence of the test tube into the wax bath until the stirring was stopped by the gelling resin. The stirrer power setting was kept constant, and all resin gel times were compared with that for fresh Cascophen 313 (Borden Chemicals liquid phenol-formaldehyde resol with 40% solid fillers used with 2.5% NaOH to have a pH of 11) determined at the same bath temperature. Gel times at the same bath temperature were reproducible within 10% of each other and were often much closer together. When the gel time was less than 6 minutes, it was redetermined

at a lower temperature because there were indications that, at very short gel times, the rate of heat transfer became the determining factor.

Novolaks were prepared using a phenol-to-formaldehyde molar ratio of 4:1 with 5 mole percent of  $\text{H}_2\text{SO}_4$  added as a catalyst. Typically, 47 g liquid phenol (91.7% assay), 3 g paraformaldehyde, and 30 mL water plus the required acid catalyst were added to a three-neck, 250-mL round bottom flask. The flask was fitted with a reflux condenser and stirrer. The mixture was refluxed for 2 to 4 hours with the oil bath at 115 °C; then, the mixture was neutralized with 50% (w/w) NaOH and the excess phenol removed by steam distillation for 5 to 6 hours. The remaining viscous oily residue was washed repeatedly with boiling water. A novolak with the P/N fraction was prepared as described above with 1:1 by volume phenol and P/N fraction and half of the amount of formaldehyde. Initial wood-gluing testing with this novolak indicates wood failure rather than glueline failure.

To prepare material for gel testing, 2 moles of paraformaldehyde were added per mole of phenolic hydroxyl. The pH was varied by adding aqueous 50% (w/w) NaOH dropwise with rapid stirring. All of this was done in the disposable borosilicate test tube. Total amount of all resin formulation in the test tube was always adjusted to 5.0 g. The pyrolysis oils were usually solubilized first by adding sufficient NaOH.

## Results and Discussion

**Fast Pyrolysis Global Reactions.** The pyrolysis of biomass occurs through a large number of reactions that can be grouped into: 1) dehydration reactions that form char, water, and a small amount of carbon oxides; and 2) depolymerization reactions that form monomer fragments, monomers, and oligomers, which are of interest for phenolic adhesive production. However, as shown in Figure 4, the polymer fragments are very reactive, and they quite readily undergo secondary reactions to form gases and more stable organic compounds (e.g., polycyclic aromatic tars). At low temperatures, the dehydration reactions that favor char formation are faster than the depolymerization reactions that form primary pyrolysis oil vapors. However, the depolymerization reactions are strongly favored at elevated temperatures. Consequently, it is necessary to quickly heat the biomass particles to elevated temperatures (>400 °C) to maximize the pyrolysis oil yields and then to rapidly cool the product vapors. This rapid heating requires a large heat flux be provided to the biomass surface, which conventionally would be achieved by using very high temperatures. However, the presence of the high temperatures has the undesirable effect of excessively heating the oil vapors to cause some of them to decompose to gases (15). An alternate method of supplying the large heat fluxes is to use a heat transfer mechanism that has a relatively large heat transfer coefficient. For achieving these heat transfer phenomena in a chemical reactor, an externally heated vortex tube was selected (16). The advantage of this reactor system

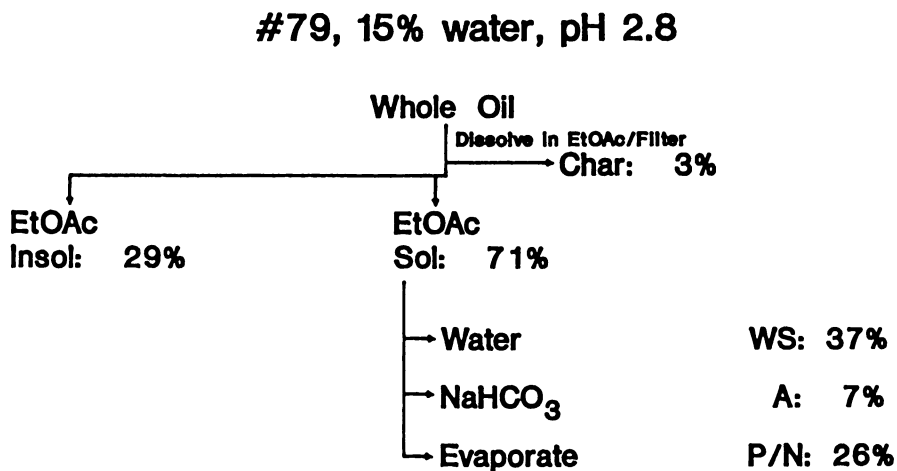


Figure 3. Pine sawdust pyrolysis oil fractionation scheme. Yields are on a dry basis.

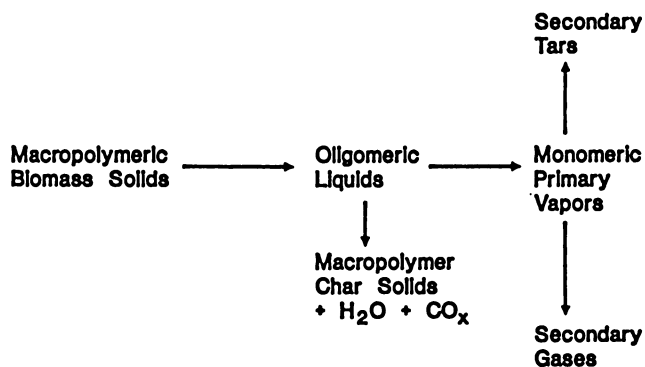


Figure 4. Biomass pyrolysis global mechanism.



is the high yields of pyrolysis oils and the high heat transfer possible from the wall to the biomass, which translates to a relatively small reactor with a high throughput (10).

**Oil Collection.** Table I shows the temperature of the process stream as it passed through the heat exchangers, as well as the amount and moisture content of condensate collected at each location. For Run 83, this oil collection train demonstrated a wet oil recovery of 67% of the dry feedstock for a mass closure of 94%. The wet oil contained an average of 18% water of pyrolysis for a recovered yield of 55% dry pyrolysis oil.

Table I. Primary Oil Collection Train (Run 83)

	Exit Temperature °C	Weight Percent of Dry Oil	H <sub>2</sub> O Weight Percent in Wet Oil
15-Inch-diameter cyclonic condenser	50	50	20
1-Inch-diameter transfer line HXR	40	21	10
3-Inch-diameter vortex condenser	30	23	8
Dry-ice trap	-17	11	30
Coalescing filter	-17	5	31
<b>Total</b>		<b>100</b>	<b>18</b>

The collection of the pyrolysis oils is difficult due to their tendency to form aerosols and also due to the volatile nature of many of the oil constituents. As the aerosols agglomerate into larger droplets, they can be removed by cyclonic separators. However, the submicron aerosols cannot be efficiently collected by cyclonic or inertial techniques, and collection by impact of the aerosols due to their Brownian or random motion must be utilized. A coalescing filter is relatively porous, but it contains a large surface area for the aerosol particles to impact by Brownian motion as they are swept through by the pyrolysis gases. Once the aerosol droplets impact the filter fibers, they are captured and coalesce into large drops that can flow down the fibers and be collected.

**Pyrolysis Yields.** Before the present collection system had been developed, mass and elemental balances showed that the yields of oxygenated pyrolysis oils generated in the vortex reactor must be very high and that the observed large lack of mass balance closure could not be due to large water yields. Based on elemental analysis of the char, oil, and gases, a char yield of 12.7% corresponds to calculated yields of 69% oil vapors, 14% water, and 4.3% gases. Without the recycle loop, gas yields have been observed to be in the 3 to 4% range of the pyrolyzed feedstock. However, with the recycle loop installed, the gas yields

were seen to increase to about 14% due to an increase in the cracking of the oil vapors to a characteristically different slate of permanent gases (15). Minor changes in the operation of the vortex reactor are expected to reduce the gas yields in the future and to result in enhanced pyrolysis oil yields.

**Phenolics/Neutrals for Adhesives.** The fractionation scheme described in Figure 3 allowed the isolation of 21% to 31% of the starting oil as a P/N fraction, as shown in Table II. This fraction consists of 73% phenolics, extractable by aqueous sodium hydroxide solution from an ethyl acetate solution, and 27% neutrals. The total yield of the P/N fraction was reproducible (cf. runs 79 and 83 in Table II). Isolation of the P/N fraction from oils condensed from the cyclone and transfer-line heat exchanger indicates that the P/N fraction predominates in the transfer-line heat exchanger condensate. Experiment 78 was collected from the cyclonic condenser, and thus, the results compare well with those from experiment 81A.

Table II. Fractionation of Sawdust Pyrolysis Oils  
Yields (% on dry oil basis)

Experiment No.	Ethyl		Acids	Phenols/ Neutrals
	Acetate Insoluble	Water Soluble		
78	43	25	6	21
79	29	37	7	26
81	23	39	7	31
81A - cyclone	45	26	5	23
81B - heat exchanger	20	28	9	47

The typical whole oil contained about 6.2% and 0.4% phenolic hydroxy and carboxylic acid contents, respectively. The P/N fraction contained 6.6% phenolic hydroxy and no carboxylic acid content, whereas, the acids fraction contained 9.2% and 0.9% of phenolic hydroxy and carboxylic acid contents, respectively.

The apparent molecular weight distributions of selected fractions of isolated oil components are shown in Figure 5. The phenols fraction contained the highest apparent molecular weight components, and their absorption spectra in the UV region resembled that of low-molecular-weight lignins.

From the molecular beam MS of the pyrolysis products of the P/N fractions, a number of phenolic compounds were detected: guaiacol (2-methoxyphenol) ( $m/z$  124), catechols ( $m/z$  110), isomers of substituted 2-methoxyphenols with alkyl groups such as methyl ( $m/z$  138), vinyl ( $m/z$  150), 3-hydroxy-propen(1)-yl ( $m/z$  180), allyl ( $m/z$  164), hydroxyethyl ( $m/z$  168), and ethyl (152), most likely in the *para* position. In addition, a few carbohydrate-derived components are also present in this fraction such as furfuryl alcohol and other furfural derivatives.

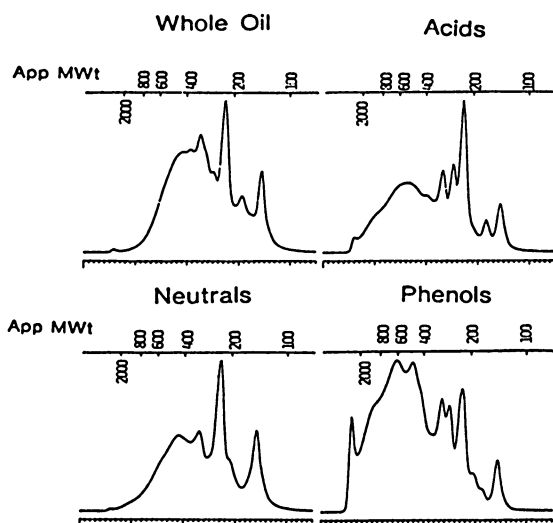


Figure 5. High-performance size exclusion chromatograms of pine sawdust pyrolysis oils and fractions of acids, phenols, and neutrals contained in the ethyl acetate soluble oil.

From the proton NMR of the P/N fraction, of the total proton intensity, the aromatic protons (6.5 to 10 ppm) constitute 52%, the aliphatic (1.5 to 3.5 ppm) about 20%, and the methoxy region (3.0 to 4.2 ppm) 30%, which is in agreement with the proposed compounds obtained from the molecular beam MS pyrolysis experiment. The  $^{13}\text{C}$ -NMR spectra of the P/N fraction also indicated mixtures of compounds with aromatic carbons in the 110 to 148 ppm region, a very pronounced methoxy peak at 55.6 ppm, and aliphatic carbons.

**Preliminary Adhesive Testing Results.** Phenol at a pH of 11 with twice the molar amount of formaldehyde was compared with Cascophen 313 (commercial softwood plywood resin by Borden Chemicals). At 124 °C, Cascophen 313 took 12.2 minutes to gel, whereas, the phenol with added paraformaldehyde did not gel even after 30 minutes. Table III.

Table III. Gel Times for Cascophen and Phenolics/Neutrals from Pyrolysis Oils

pH	Temperature °C	Gel Time, Minutes	Equivalent Cascophen Time	Percent Equivalent Time
Cascophen <sup>1</sup>				
	118	15.3		
	125	12.2		
	130	9.7		
Phenols/Neutrals <sup>2</sup>				
9.0 <sup>3</sup>	127	12.0	11.1	—
9.5 <sup>4</sup>	127	5.2	11.1	—
9.5	124	3.7	12.6	29
9.5	112	6.2	18.2	34
9.5	101	10.8	23.4	46
9.5	89	24.5	29.0	—

<sup>1</sup>5 g Cascophen + 0.2 mL of 50% NaOH, pH 11.5.

<sup>2</sup>4g Phenol/neutrals from sawdust pyrolysis oils reacted with 1 g paraformaldehyde and 0.5 mL of 50% NaOH.

<sup>3</sup>0.2 mL of 50% NaOH.

<sup>4</sup>0.4 mL of 50% NaOH.

Of the various fractions of pyrolysis oil, only the P/N fraction gave a positive gel test under these conditions. In preliminary gel testing of the P/N extract, arbitrarily 1 g of paraformaldehyde was added to 4 g of the extract. The pH of

the extract was adjusted by adding 0.2 to 0.8 mL of 50% (w/w) NaOH. There appeared to be a strong buffering of the pH by the extract at a pH of 9.5. Cascophen 313 was used for comparison. The information obtained is presented in Table III. At 0.5 mL of added NaOH, the gel time of the P/N fraction was much shorter than that of the Cascophen, with a gel time of only 29% that of Cascophen at 124 °C, at 112 °C, it was 34%; and at 101 °C it was 46% that of Cascophen. At the original pH of 3 of the P/N fraction, there was no gelling of the mixture even at 132 °C with the same amount of added paraformaldehyde.

The novolaks prepared were characterized by solid-state  $^{13}\text{C}$ -NMR spectra. The peaks in the  $^{13}\text{C}$ -NMR spectra obtained in this study were assigned on the basis of comparisons with solution- and solid-state  $^{13}\text{C}$ -NMR of novolaks (12) and solution-state lignin NMR spectra (17, 18). The spectra of a phenol-formaldehyde novolak and similar novolak in which 50% by volume of the phenol was replaced by the P/N fraction from the fast pyrolysis of pine sawdust are compared in Figure 6. The authentic novolak (Figure 6a) produced main peaks (from deconvolution) at 150, 130, and 120 ppm corresponding to hydroxy-substituted aromatic carbons, unsubstituted *meta*-aromatic carbons, and unsubstituted *para*-aromatic carbons, respectively; and in the aliphatic region, the main peaks are at 35 and 40 ppm, assigned to *ortho-para* methylene bridges and *para-para* methylene bridges, respectively. The presence and intensity of such peaks correspond to the formation of random novolaks as discussed by Bryson et al. (12). On substitution of phenol with the P/N fraction (Figure 6b), the key peaks of the random novolak remain, but peaks characteristic of the types of phenolic compounds present also appear such as at 155 ppm (*meta*-aromatic carbons attached to methoxy groups), 55 ppm (methoxy groups), and 20 ppm (aliphatic groups). Key differences between the authentic novolak and the P/N-substituted novolak are in relative peak intensities. While the ratio of unsubstituted *meta*-aromatic carbons to *ortho-para* methylene bridges (130 to 35 ppm) in the authentic sample is roughly 7:1, the ratio in the P/N novolak is approximately 4:1 (60% of the original value). Such a difference is expected, since the P/N novolak contains a number of *meta*-substituted methoxy compounds. The phenol-formaldehyde novolak has a higher ratio of hydroxy-substituted aromatic carbons (150 ppm) to unsubstituted *meta*-aromatic carbons (130 ppm) than the P/N novolak (40% versus 30%).

A few preliminary resols have also been made with a 50% replacement of phenol by the P/N fraction of the wood oil. Tests have shown these adhesives to have shear strengths and wood failure comparable to that obtained with Borden's Cascophen 313. This work is in progress.

**Technoeconomic Assessment.** Although the use of fractionated pyrolysis oils as adhesives is still in the early phases of development, a technological assessment of the process was made using the best projections available for the yields and operating conditions. A detailed process flowsheet was made with mass and energy balances around each major piece of equipment. The equipment was sized and then valued using data from the literature. The costs

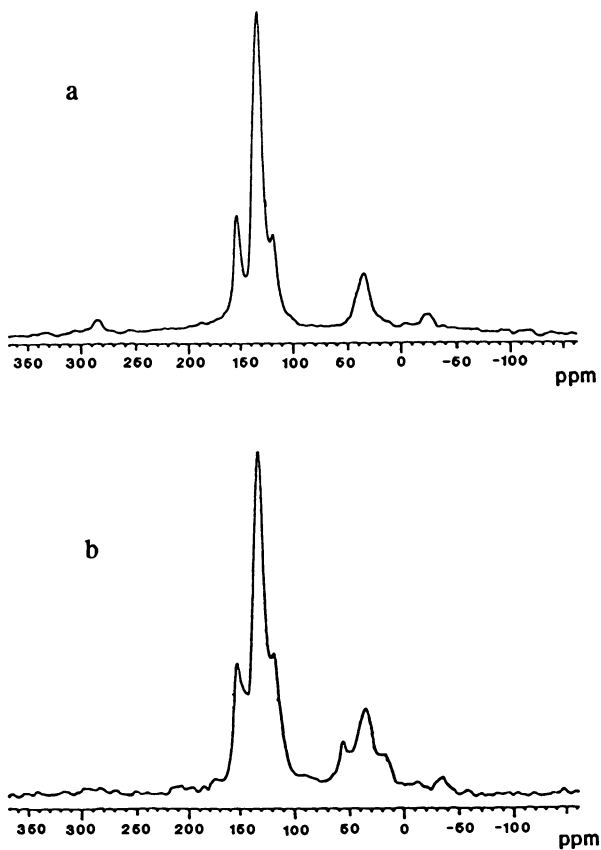


Figure 6. CP/MAS  $^{13}\text{C}$ -NMR of novolaks: a) phenol-formaldehyde; b) phenol:phenols/neutrals (1:1) pine sawdust pyrolysis oil fraction and formaldehyde.

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for installed equipment were calculated using standard cost factors (19). All costs were updated to fourth quarter 1986 dollars using the CE cost index. The process flowsheet included a feedstock drying step using waste process heat. The drying step has a significant cost, but any moisture in the feedstock would be evaporated first in the pyrolysis step and then accumulated in the process where it would have to be evaporated again with premium heat in the incineration section of the furnace. Steam was used as the carrier gas at a weight ratio of 1.33 times that of the feedstock. The energy for the drying step would be obtained from the cooling and condensation of the pyrolysis process stream. The extraction of the P/N fraction was assumed to be by the use of EA as the solvent. The EA soluble acids were removed by an aqueous sodium carbonate wash. The aqueous phase was first heated to boil off the EA, which has a significant solubility in water. The water-soluble organics were then concentrated in triple-effect evaporators prior to their incineration in the convection section of the pyrolysis furnace. The economics of the production of the P/N fraction were evaluated for a 15% interest rate over a 20-year amortization period. The production costs were shown to be a strong function of plant size and feedstock costs as shown in Figure 7. The cost to produce the P/N fraction was projected to be about \$0.10 per pound in a plant consuming 1,000 TPD feedstock costing \$10 per dry ton. Production in a small 250 TPD plant would add about \$0.06 per pound. Increasing the feedstock cost to \$40 per dry ton would add \$0.07 per pound of P/N. If the plant were to be integrated with an existing forest products mill, some of the costs related to feedstock preparation would be considerably reduced. It was concluded that this process has considerable economic potential if it is developed properly and the assumptions made are verified through additional research and development.

## Conclusions

Fast pyrolysis of biomass provides a method for the production of phenolics that has the potential to replace at least 50% or more of the phenol in phenol-formaldehyde thermosetting resins. The gel tests indicate that the P/N fractions from pine sawdust pyrolysis with paraformaldehyde have shorter gel times than commercial plywood resins such as Cascophen 313, even without prepolymer formation. A novolak formulation has been prepared using 1:1 by volume of phenol and P/N fraction and about half of the amount of formaldehyde that would be used than if phenol alone were employed. Very promising resols have also been made with a similar substitution of the P/N fraction for phenol. Wood testing and resin formulation development are ongoing activities. The projected economics suggest that additional research and development of this process are fully warranted.

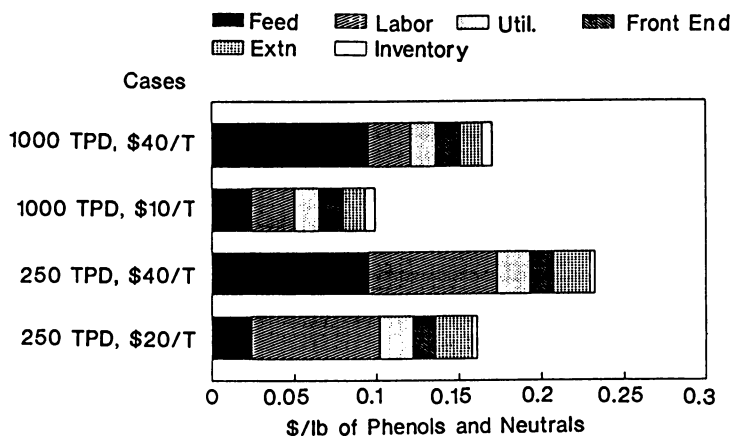


Figure 7. Amortized costs of phenolics and neutrals fraction from pine sawdust pyrolysis calculated as a function of feedstock cost and plant size. Note that the calculations include costs associated with all feedstock preparation as if this were an independent plant.



## Acknowledgments

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# Chapter 12

## Condensed Tannins in Adhesives

### Introduction and Historical Perspectives

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Sequential extraction of the bark of most species of conifers and deciduous trees, using water or polar organic solvents followed by aqueous alkali, yields two fractions of polymeric polyphenols, respectively referred to as condensed tannins and phenolic acids. These materials react with formaldehyde or phenol-formaldehyde prepolymers to make suitable resins for cold-setting waterproof adhesives for wood lamination or thermosets for exterior-grade plywood. Commercial production of bark extracts from western hemlock, Douglas-fir, and redwood in North America found limited application for adhesives during the period 1955-1975. Wattle (*Acacia mearnsii*) bark tannins, produced in South Africa, are currently used in adhesive formulations. The availability of large quantities of pine bark residues from pulping operations in the Americas, Australia, and New Zealand located near waferboard, plywood, and wood-laminating producers who consume substantial amounts of phenolic adhesives suggests that the time is ripe for production of bark-based adhesives. Lower cost, higher yield isolation techniques, in particular, may still be needed for this objective to become a commercial reality.

The conversion of animal hides into leather by treatment with water-soluble plant extractives has been practiced since antiquity. This process became known as tanning and obviously involved the reaction of a naturally occurring extractive, tannin, with the protein in the hide. We now know, of course, that tannins comprise a whole spectrum of chemical compounds, but generally they are polyphenolic and polymeric. Tannins have been isolated from a wide variety of raw materials, including insect galls, fruit skins, seed hulls, leaves, bark, and heartwood. Indeed, tannins are of nearly ubiquitous occurrence in higher orders

of the plant kingdom. Since they occur in highest concentrations in those tissues of a plant exposed to air, it is generally agreed that their function in a plant is to help it resist the invasion of pathogens.

During the early and middle stages of the industrial revolution, rapidly increasing quantities of leather were required for factories and transportation as well as for food production to supply the exploding populations spawned by this upheaval. By the beginning of the twentieth century, leather tanning was one of the major industries in North America. Since the industry required relatively concentrated sources of tannins, much technical attention was devoted to analyses of plant materials for tannin content. Only the bark and heartwood of a limited number of wood species were found to contain sufficient quantities of water-soluble tannins to make them attractive for commercial extraction. In the United States, the bark of eastern hemlock and some oak species was the main source of tannins at the turn of the century (1). Subsequently, chestnut wood became the main source of tannin until it largely disappeared because of chestnut blight. Imported extracts from quebracho and, to a lesser extent from mimosa (*Acacia Sp.*), gradually displaced domestic tannin production.

The rapid growth of the pulp and paper industry following World War II coupled with a renewed scientific interest in utilization of bark and wood residues led to investigative programs on bark and wood tannins. The leather industry was continuing to decline in importance, so other alternatives were needed. One of these was replacement of phenol in whole or in part in phenol-formaldehyde adhesive formulations. This work progressed to the point where commercial quantities of polyphenolic extractives were made and sold for adhesive application. Excessive capacity and low petrochemically derived phenol prices in the 1960's led to the demise of this effort in the United States (2,3).

More recently, there has been a renewed recognition of the potential of bark-derived polyphenols for adhesives as a result of improved understanding of the chemical structure of these materials (4,5), new types of formulations (6), and the fact that tannins are being commercially used in adhesives in South Africa (7), thus serving as a prototype for utilization in other parts of the world. In order to properly assess the current developments in this field, this overview will provide a historical perspective on adhesives based on tannins as well as a summary of the extraction techniques and chemical structures. Finally, areas where additional work could be fruitful will be suggested.

## Raw Materials

Tannins generally can be classified into two broad categories: hydrolyzable and condensed. The hydrolyzable tannins consist of many individual compounds and oligomers; but all are based on combinations of gallic acid or its derivatives and simple sugars such as glucose or rhamnose. Hydrolysis with dilute mineral acid or enzymes results in degradation to gallic or ellagic acid (a dimer formed from gallic acid) and the sugar component, hence the name, hydrolyzable tannins.

For example, coralagin (1), a component of eucalyptus tannins, yields gallic acid (2), ellagic acid (3) and glucose when hydrolyzed in dilute sulfuric acid (Figure 1). Most of the characterization studies have been done on those tannins isolated from fruits, leaves, or galls. Very little is known about the hydrolyzable tannins from the wood and bark of hardwoods except for eucalyptus, oak, and maple (4,8). Although the studies have not been extensive, it seems quite likely that hydrolyzable tannins do not occur in conifers, but they often co-occur with condensed tannins in hardwoods. There are no literature references that suggest utility for hydrolyzable tannins in adhesive formulations, so no further mention will be made of them in this overview.

Condensed tannins, on the other hand, occur in the bark of all conifers and hardwoods examined to date, and they are frequently present in the wood. They are primarily responsible for the tan to brown color of wood after it is exposed to air. In their purest form, condensed tannins are colorless, but they become colored very readily once isolated because of their propensity to oxidize to quinones. The primary characteristic of the water-soluble condensed tannins (4) is dehydration/oxidation to intensely colored anthocyanidin pigments (5) when refluxed in butanol and hydrochloric acid (Figure 2). For this reason, there has been a tendency to refer to these compounds as "proanthocyanidins" in the last few years. Prior to that, they were referred to as "leucoanthocyanidins" (i.e., the colorless chemical form of anthocyanidins). All references earlier than the late 1950's, when the structure of these substances was just beginning to be understood, used the term "condensed" tannin.

Another characteristic of the condensed tannins was usually observed during leather tannage with these materials. Aqueous suspensions of tannin that were acidic from the tanning process gradually precipitated insoluble materials known as "tanner's reds" or phlobaphenes. These substances, derived from the tannin, were no longer soluble in water, but they could be dissolved in polar solvents such as ethanol or acetone or in aqueous base. Since most species of bark contain an extractive fraction that physically resembles the tanner's reds, they are referred to as phlobaphenes in the literature. Very little characterization work has been done on this fraction, and there is substantial reason to believe that the bark phlobaphene fraction contains a variety of water-insoluble polymers, some of them totally unrelated to the condensed tannin family.

In addition to the water-soluble and insoluble members of the condensed tannin family, both of which are soluble in polar organic solvents, there is a third related fraction, usually called a "phenolic acid." This material can only be isolated by extraction with aqueous alkaline solutions or with sodium sulfite or bisulfite solution at elevated temperatures and pressures. Since the tannins and phlobaphenes are also soluble in aqueous base, they will be coextracted from bark along with the phenolic acids when bark is extracted with base. This is important to remember in the subsequent discussion on bark-based adhesives.

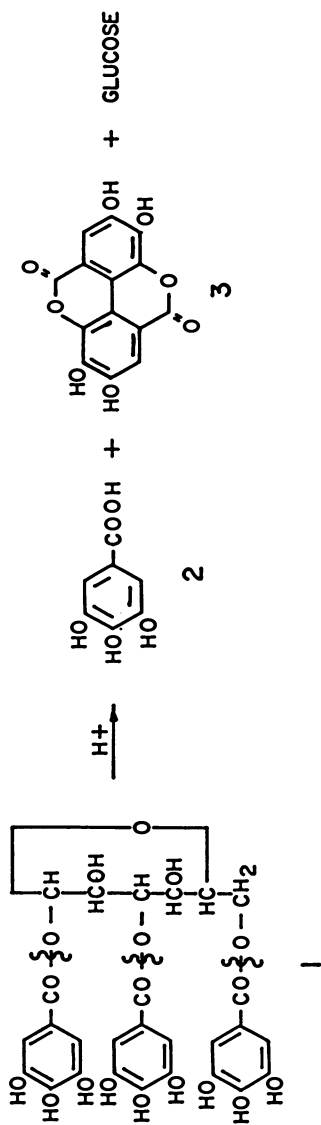


Figure 1. Conversion of hydrolysable tannin to gallic acid, ellagic acid, and glucose.

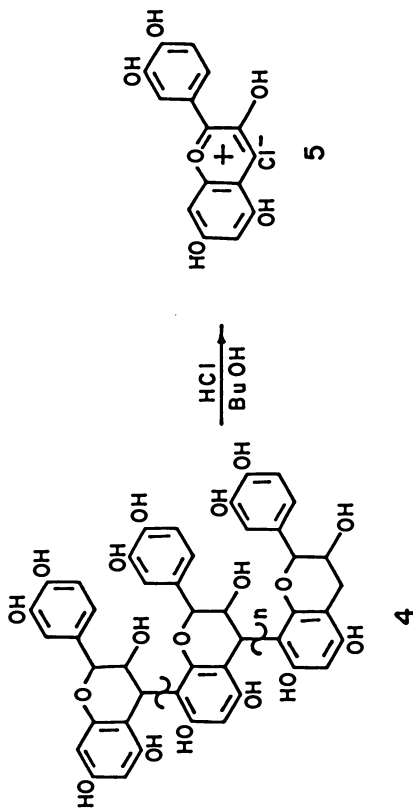


Figure 2. Conversion of proanthocyanidins to cyanidin by mineral acid treatment in butanol.

### Isolation of Condensed Tannins

Bark or heartwood, the primary raw materials for tannin production, contain many extraneous substances. The broad categories of compounds are listed in Table I, and, as can be seen, no single category is isolatable by simple solvent extraction. Most work on the use of tannins for adhesives has involved a hot water or mild alkaline extract. The reason for this is quite simple: the value of the product for the intended end use could not support the cost of subsequent refractionation or purification. Carbohydrate impurities are particularly undesirable, so investigators over the years have usually expended much effort in trying to find a particular plant species that would yield an extract high in tannin content and low in the offending carbohydrate "contaminants." Insofar as chemical structure studies are concerned, progress was slow until chromatographic techniques were devised in the last decade (9-11) for separation of the dimeric and trimeric proanthocyanidins from the higher polymers, sugars, etc., present in an extract. This permitted indirect deduction of the structure of the higher polymeric fractions (e.g., the true tannins).

Table I. Materials Extractable from Bark or Heartwood with Various Types of Solvents

Type of Extractive	Solvent				
	Petroleum Ether	Ethyl Ether	Ethanol	Hot Water	Aqueous Alkali
Wax, fats, terpenes	X	X	X		X
Flavones		X	X		X
Flavanols		X	X	X	X
Stilbenes		X	X	X	X
Proanthocyanidins			X	X	X
Solvent-soluble lignin			X		X
Simple sugars			X	X	X
Pectins				X	X
Arabinogalactans				X	X
Xylans					X
Ash (oxalates, etc.)				X	X
"Polyphenolic acids"					X
"Lignin"					X



## Chemical Structure of Condensed Tannins

Through an impressive array of experiments conducted over the last 15 years, it has been shown that the aqueous extracts contain a series of compounds based on a substituted flavonoid structure. For purposes of this overview, it does not appear to be appropriate to go into a lot of detail. Mainly, it is important to keep in mind that: 1) the flavonoid substitution pattern seems to be characteristic for a given species; 2) stereochemistry can vary at the 2, 3, and 4 positions in the C-ring (Figure 3); 3) the B-ring can have a variable pattern of one, two or three hydroxyl groups; 4) the bond joining the monomeric units extends from the 4 position in the C-ring to the 6 or 8 position of the A-ring; and 5) the terminating unit may differ in substitution pattern or stereochemistry from all the other units in the chain.

Water solubility seems to be primarily a function of chain length. In the procyanidin polymers (Figure 3, 6), chains with a DP greater than about 8 are not soluble in water. This suggests that the "phlobaphene" fraction may simply be a higher molecular weight version of the water-soluble tannins, while the so-called phenolic acids are of even higher molecular weight, crosslinked, or tightly complexed to cell wall carbohydrates through an alkali-labile linkage. Mimosa (Figure 3, 7) and quebracho tannins (Figure 3, 8) differ from the conifer bark tannins in that the A-ring is based on resorcinol rather than phloroglucinol. These tannins also tend to have a higher degree of water solubility and less likelihood of rearranging to highly colored byproducts, thus making them more attractive for leather tanning.

Generally, the hot-water extract of a bark or heartwood source of tannin will comprise about 60 to 65% tannin polymers as measured by a standard hide powder absorption test. The remainder will be a mixture of sugars, pectin, hemicellulose, and lower molecular weight ( $\leq 300$ ) polyphenols. Cold-water extraction will yield a somewhat higher purity tannin extract, but overall yields based on the weight of starting material will be lower. Quebracho wood and mimosa bark are unusual in that their water extract has a measured "purity" up to 75 to 80%. The "tannins" in each case consist of a series of oligomers with a DP of 2 to about 7 to 9, depending upon extraction conditions.

## Cleavage Reactions and Rearrangement

To better understand the reactivity of the condensed tannins in adhesive formulations, it is important to recognize molecular changes accompanying extraction of the tannins when sulfites or alkali are used to enhance yield. A model compound study on catechin (Figure 4, 11) (27) showed that treatment with sodium bisulfite solution at 170 °C for 30 min opened the flavan ring with formation of a sulfonate group on the 2 position (12). This was believed to explain the formation of tannin sulfonates during a commercial process involving bisulfite extraction of western hemlock bark (3,19). More recently, it has been found

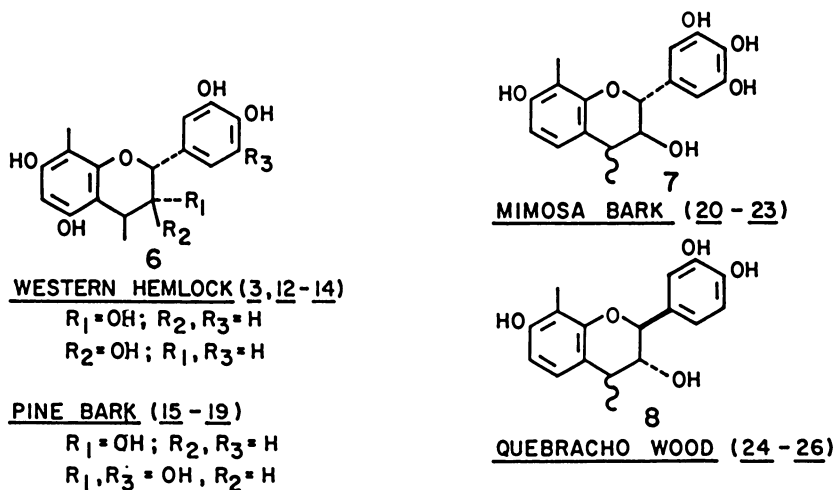


Figure 3. Proanthocyanidins extractable from bark or heartwood with various types of solvents.

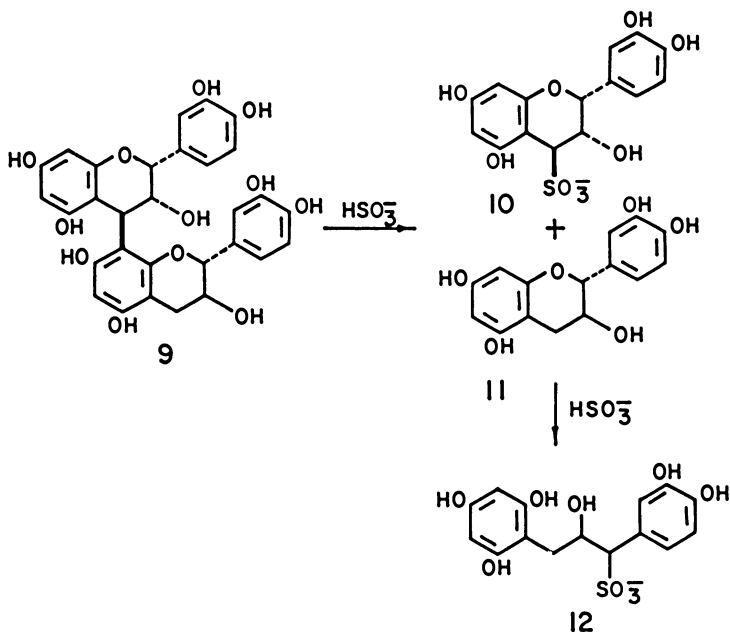


Figure 4. Sulfonation reactions of condensed tannins.

(28) that the interflavonoid bond is much more likely to be cleaved than the pyran ring. The 4 → 6 or 4 → 8 bonds are broken with concomitant sulfonation at the 4 position (10). When the tannin does not have a hydroxyl group in the 5-position, as is the case with mimosa and quebracho tannins, the interflavonoid bond is much more stable. In this instance, sulfonation primarily leads to the formation of substitution at the C-2 atom (29). Even though the precise details of these sulfonation reactions need further clarification, it seems reasonable to conclude that water-insoluble tannins can be converted to lower molecular weight fractions with solubilizing sulfonate groups in the 2 and/or 4 positions by treatment with sodium sulfite or bisulfite at elevated temperatures. This reaction is suitable, therefore, for extraction of phlobaphenes and "phenolic acids" from bark as well as the water-soluble tannins.

During early phases of structural studies on bark polyphenols (15), it was noted that alkali treatment of isolated tannin polymers resulted in the formation of an acidic group, presumed to be a carboxyl, and the loss of formaldehyde reactivity. It was surmised that the so-called bark phenolic acids were, in fact, higher molecular weight tannins that underwent rearrangement during isolation. Support for this idea was greatly strengthened by elucidation of the alkaline rearrangement of catechin to catechinic acid (13) → (14) (Figure 5) by Sears, *et al.* (30). Laks and Hemingway (31) have continued to study the reactions of tannins with alkali using phloroglucinol or phenylmethanethiol as a nucleophile. This work clearly shows opening of the pyran ring, formation of a reactive site in the 2 position, cleavage of interflavonoid bonds, and formation of carbonyl groups in the A-ring. It is not at all surprising that earlier workers had great difficulties in trying to determine bark tannin structure when they used alkaline extraction methods. Furthermore, the rearrangement of the A-ring with consequent loss of formaldehyde reactivity should be kept in mind when adhesive formulations are made up from alkaline extracts.

### Preparation of Tannin-Based Adhesives

Interest in use of condensed tannins as components of adhesive formulations began about three decades ago. While research studies have been carried out in widely scattered laboratories around the world, three major areas of activity can be distinguished. These are: 1) development of bark extracts and commercial production facilities on the west coast of North America, 1953 to 1975; 2) application of tannins in adhesive formulations in South Africa based on indigenously produced mimosa (wattle) tannin, early 1970's to the present; and 3) a resurgence of interest in pine bark as raw material for tannin-based adhesives, beginning in the middle 1970's. Each of these activities has been characterized by parallel efforts on structural identification of the tannins and development of unique methods for incorporating the isolated tannins into adhesives.

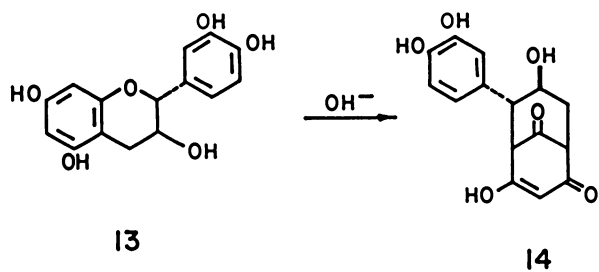


Figure 5. Alkaline rearrangement reactions of (+)-catechin.

### Western Conifer Bark Polyphenols

Following World War II, extensive investigative effort was initiated to find new uses for the mountains of bark generated as byproducts of the West Coast forest products industry in the United States and Canada. This work was carried out at the Institute of Paper Chemistry (sponsored by the Pacific Lumber Company of Scotia, California), the Oregon Forest Products Laboratory, Rayonier Incorporated, the Weyerhaeuser Company, and the Forest Products Laboratory on the University of British Columbia campus.

Western hemlock bark was considered to be an attractive material for tannin production (32), since its chemical composition was thought to closely parallel that of eastern hemlock bark, the major raw material for tanning in the United States at the beginning of the century. Much of the hemlock bark in the West was recovered from seawater-floated logs and/or the use of hydraulic debarkers that diminished the yield of water-soluble tannins. Nevertheless, such tannin as could be obtained was found to be useful as an oil well-drilling dispersant or as an adhesive when mixed with formaldehyde, according to the British Columbia research team (33). Subsequent work showed that much higher yields of polyphenolic extracts could be obtained by elevated temperature extractions with sodium bisulfite, sodium hydroxide, or ammonia (34-36). Rayonier built two commercial plants for the production of such extracts, one at Hoquiam, Washington, and the other at Vancouver, British Columbia (19).

Attempts to make adhesive formulations by direct reaction of formaldehyde or its equivalent resulted in products that were excessively viscous, and the working time was too short for commercial application (37). It was concluded that formaldehyde, although readily reactive with the tannin molecule, provided much too short linkages to connect the bulky tannin molecules. This problem was circumvented by the preparation of a polymethylolphenol reagent that, when put in solution with the bark extract, formed a combination that was stable for several weeks at room temperature. When heated, the polymethylolphenol and bark extract reacted rapidly to form an infusible resin. Commercial trials were made to produce exterior-grade Douglas-fir plywood. Widespread use of the extracts for this purpose, however, was inhibited by a drop in the price of phenol below what the bark extracts could be manufactured for. (The best extract for adhesive purposes was an ammonia extract of hemlock bark converted to a sodium derivative prior to spray drying, a more costly extraction procedure than simple sodium hydroxide extraction of bark.)

Subsequent work was, therefore, directed to substitution of resorcinol, a much more expensive phenol, in cold-setting, waterproof adhesives (38). Formulations based on 30 to 60% of extract mixed with a resorcinol-formaldehyde condensate and additional formaldehyde met pot-life and assembly time requirements for timber lamination. Test bonds passed requirements of the major performance standards in the United States, but competition from lower cost, phenol-modified resorcinol resins and the lack of longterm commercial perfor-

mance records prevented significant acceptance of the products. Sales of 300 tons per year did not justify continued production, so the effort was terminated in 1972. Bark extraction by Rayonier (now ITT Rayonier) was stopped in 1976. Parts of the extraction plant at Hoquium were subsequently used for making products from lignin.

About the same time Rayonier began marketing bark extracts from western hemlock, the Pacific Lumber Company at Scotia, California, built an extraction plant to produce alkaline extracts from redwood bark. The products were called Palcotan and Sodium Palconate. They mainly found uses in oil well drilling. Attempts to use the product in adhesive formulations do not seem to have been successful, mostly because of viscosity problems associated with carbohydrates coextracted from the bark along with the polyphenols. Weyerhaeuser produced alkaline extracts of Douglas-fir bark during the 1960's. They were said to be applicable in adhesive formulations, but there are no literature references attesting to their commercial success. The most recent attempt at this market was the preparation of finely divided Douglas-fir bark, which had been preextracted with nonpolar solvents to remove wax, as a reactive extender for phenol-formaldehyde adhesives. The Bohemia Lumber Company's plant for such products shut down in the early 1980's.

Attempts were made to revive interest in western hemlock bark polyphenols through a research program at the Western Forest Products Laboratory, Forintek Canada Corp. In this work, it was concluded (39) that the phenolic acid fraction of the bark, when isolated by alkaline extraction, was insufficiently reactive with formaldehyde to be of commercial value. This investigation suggested ethanol extraction as the preferred route to tannins for adhesive application. Since environmental restrictions in the United States have largely eliminated water storage of hemlock logs and hydraulic debarking during the last decade, quantities of hemlock bark are now available that have not been water leached. The bark is used as fuel, but it may be timely to reconsider extraction of polyphenols prior to the burning process as a higher form of utilization than simple combustion.

### Mimosa Tannin Adhesives

The only tannins in the world currently being commercially exploited for adhesive applications are those isolated by hot- (or cold-) water extraction of *Acacia mearnsii* bark in the province of Natal, South Africa. Approximately 100,000 tons of mimosa tannin were being produced annually as reported in 1980, the latest year for which production figures were available (41). Of this amount, about 10,000 tons were used in adhesive applications mainly in South Africa, Australia, and New Zealand. While this number is not large in light of the 300,000 to 400,000 tons of phenol used annually in resins, it does provide evidence that bark tannins can be economically used for adhesives. This application is facilitated by the relatively high cost of phenol and resorcinol in

South Africa and the political strategy to reduce or eliminate imports of strategic materials such as petrochemicals as much as possible.

Earliest application of mimosa tannins for adhesives came in the field of plywood and chipboards (41). Exterior plywood adhesives were based on condensation of wattle tannin with urea formaldehyde crosslinking agents, a phenol-formaldehyde resol, or a phenol-resorcinol-formaldehyde polymer to which paraformaldehyde was added to provide crosslinking between the resorcinol and the A-ring of the tannin. Fast-curing rates and good tolerance to high moisture content veneers characterize these systems. Metal catalysts such as zinc acetate have been found to be useful for speeding the cure rate. Problems with viscosity can be ameliorated by cold-water extraction of the bark to reduce polymeric carbohydrate content in the extract or by mild sulfonation of the tannins. The literature does not indicate whether these two procedures are currently being practiced in mimosa tannin production.

Early attempts to use mimosa tannin in particleboard adhesives involved high-temperature alkaline treatment of the extract to reduce viscosity of the 40% solids level needed (42,44). Subsequent improvements followed the same course as with plywood, namely the use of phenol-formaldehyde or phenol-resorcinol-formaldehyde as crosslinking agents (45) and the use of catalysts or mix modifications to reduce press temperature requirements and to extend pot life. Recent work (46) has shown that exterior chipboard adhesives can also be prepared by crosslinking of mimosa tannins with 4,4'-diphenylmethane diisocyanate.

Applications for cold-setting, wood-laminating adhesives initially followed the same approach (47) used for laminating resins from western hemlock (38) (i.e., reaction of tannin with phenol-resorcinol-formaldehyde prepolymers). Improvements resulted through the application of Kreibich's "Honeymoon" technique (48) wherein one side of the material to be bonded is treated with resin and the other with catalyst. One of the preferred systems (49) was phenol-resorcinol-formaldehyde or tannin-resorcinol-formaldehyde at pH 8 with extra paraformaldehyde on the A-side and tannin at 53% solids or tannin-resorcinol-formaldehyde at pH 12 on the B-side. Such resin systems are currently used to laminate eucalyptus or pine in most South African timber-laminating plants.

### **Pine Bark Tannin Adhesive Formulations**

Interest in pine bark as a source of adhesive components began to accelerate following the oil crisis of 1973. Sodium hydroxide extracts of southern pine bark were successfully used in replacing up to 40% of the phenolic resin for bonding of particleboards, oriented strandboards, and composites with a flakeboard core and veneer facing (50,51). Similar results were obtained with extracts from patula pine (52). Encouraged by results of this type, the New Zealand Forest Products Ltd. Corporation expanded their radiata pine bark tannin pilot plant to full-scale operation in 1981 to produce an extract trademarked Tannaphen. This material was crosslinked with paraformaldehyde and used as an adhesive

for chipboard panels marketed primarily as flooring material in New Zealand. The extraction plant and adhesive formulation were discontinued recently without explanation. Boards made with Tannaphen were known to be marginally deficient in moisture durability. Boards meeting exterior-quality standards can be formulated, however, using pine bark extracts combined with isocyanate resins (52). Satisfactory exterior plywood adhesive formulations have also been prepared by combining bark extracts with phenol-formaldehyde prepolymers followed by the addition of paraformaldehyde.

Recent efforts to develop cold-setting phenolic resins from pine bark have followed paths similar to those used for wattle tannins. One of these has involved the acid-catalyzed cleavage of southern pine bark using resorcinol as a nucleophile (53). A second approach has been to purify tannins of co-occurring carbohydrate and use them as resorcinol replacements in the Honeymoon system (48). One surface was spread with commercial phenol-resorcinol-formaldehyde-laminating adhesive with added formaldehyde, and the other was spread with pine tannin in sodium hydroxide solution. The most recent (and the most economical to date) approach involves resorcinol replacement by using bark tannins extracted with sodium sulfite. Molecular weights are reduced during the course of the extraction, and the sulfonate function is a good leaving group under conditions of lamination. The sulfite extracts can be applied as mixed system adhesives, wherein they are combined with conventional phenol-resorcinol-formaldehyde resins, or in the Honeymoon system. Up to 50% replacement of synthetic resin by sulfonated bark tannins is envisioned by this process (54).

### Future Outlook

A number of quite satisfactory adhesive formulation techniques incorporating bark tannins have been developed, especially during the last decade. Unfortunately, in many instances, they introduce degrees of complexity into the board or laminate production line not otherwise experienced when 100% phenol or resorcinol-based adhesives are used. Inducement of the board manufacturer to switch to bark-based adhesives must involve significant economic incentives (e.g., the use of bark-based adhesives must be substantially cheaper than the corresponding phenol-based formulation). Thus, it seems additional attention needs to be paid to finding lower cost, higher yield isolation techniques. Pine bark, in particular, has the potential to give higher yield extracts than are reported in most of the experiments mentioned in this review. Possibly, sulfonation is the answer, but more work is required to establish this approach. In the meantime, R & D and capital commitments are needed in North America and other pine-growing areas from a consortium of potential extract producers and users such as exists in South Africa. This could well lead to a major new business activity during the next decade.



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# Chapter 13

## Viscosity and Formaldehyde Consumption of Procyanidin Solutions

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The last decade has seen quite remarkable advances in our knowledge of the structure and properties of the proanthocyanidins. Viscosity measurements were made of solutions of procyanidins isolated from *Theobroma cacao* and *Chaenomeles speciosa* with number-average degrees of polymerization of 6.1 and 11.8, respectively, in water and 1% sodium hydroxide at 25 °C. Procyanidins are apparently completely crosslinked by formaldehyde up to a chain length of 6 units, but few units are crosslinked in polymeric procyanidins. The second order rate constants observed for the formaldehyde reaction with catechin or epicatechin are approximately six times higher than that observed for the *C. speciosa* polymer.

Proanthocyanidins are plant phenolic biopolymers that consist of flavanoid monomer units. Two major classes of proanthocyanidins occur: those that possess a resorcinol-pattern A-ring (Figure 1) and those that possess a phloroglucinol-pattern A-ring. The latter are by far the most common, occurring in a high proportion of monocotyledonous and dicotyledonous plants (1,2). The resorcinol-pattern proanthocyanidins are confined to a few genera of tropical or subtropical hardwoods and associated shrubby species (2), but are economically important, since the internationally commercially predominant wattle (3,4) and quebracho (5) tannins are of this type. Together, they constitute approximately two-thirds (i.e., approximately 300,000 tons) of the world production of vegetable tannins (6).

The resorcinol-pattern proanthocyanidins are widely used not only for leather tanning, but also for a range of other commercial products, particularly as adhesives for plywood and fiberboard (6,7). Wattle tannin is produced from sustained-yield forests of *Acacia mearnsii*, largely in southern Africa (6,8). Some of the impetus at least to develop other uses for wattle tannin, apart from

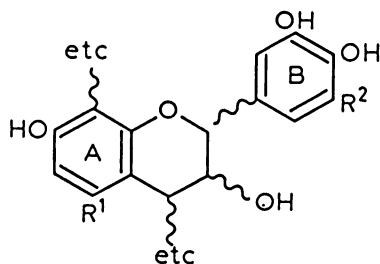


Figure 1. Structure and nomenclature of proanthocyanidins.

Phloroglucinol-pattern A-ring proanthocyanidins:

$R^1 = OH$ ;  $R^2 = H$ . Procyanidins.

$R^1 = R^2 = OH$ . Prodelphinidins.

Resorcinol-pattern A-ring proanthocyanidins:

$R^1 = R^2 = H$ . Profisetinidins.

$R^1 = H$ ;  $R^2 = OH$ . Prorobinetinidins.

leather tanning, grew out of a worldwide trend away from vegetable tannins in favor of synthetic and chrome tanning methods.

Potentially, the phloroglucinol-pattern proanthocyanidins, the procyanidins, and prodelphinidins (Figure 1) represent an enormous resource of renewable industrial phenolics. They occur in high concentration in the bark and needles of most conifers, and also in the majority of Temperate Zone hardwoods (2). Large quantities of this type of tannin are still used in the leather industry – especially in China and Russia (Sun Dawang, personal communication) and India (9). Although actual tonnages are difficult to ascertain, the quantities used for leather tanning in these countries are about half those of the total production of wattle and quebracho tannins combined. Attempts to use procyanidins as wood adhesives and other products, particularly those derived from Douglas-fir, western hemlock, and *Pinus radiata* (10,11), date back to the 1950's; but so far, no truly successful industrial process has been developed, largely because of a number of problems associated with their high chemical reactivity and relative instability in solution.

Much of the problem in finding successful industrial applications has revolved around a lack of basic understanding of the structure and chemistry of phloroglucinol-pattern proanthocyanidins. Whereas, South African workers (especially Roux and his colleagues) mounted a concerted and successful campaign beginning in the 1950's to understand the chemistry of wattle and quebracho proanthocyanidins (4,5), similar advances in our knowledge of the phloroglucinol-pattern proanthocyanidins had to wait for the improved chemical technology of the last decade.

These advances started with isolation of procyanidin oligomers as the free phenols using dextran gels (12) and elaboration of their properties and the subsequent unequivocal demonstration that polymeric procyanidins and prodelphinidins consist of extended chains of flavan-3-ol units (13), the commonest type being based on epicatechin units (Figure 2). Subsequent to these studies, rapid advances have been made in our understanding of the reactions of procyanidins in acidic or basic solutions and their reaction with sulfite, thiols, and other phenols. Advances in these areas up to the present have been considered in some detail by Hemingway and his colleagues (14-17) and will not be further discussed, except in context.

The current study seeks to extend our knowledge of the behavior of procyanidins in two areas important to their industrial utilization: 1) the viscosity of procyanidin polymers in aqueous solutions, and 2) the stoichiometry and rate of reaction of procyanidins with formaldehyde.

## Experimental Methodology

**Procyanidins.** Catechin (Fluka) and epicatechin (ex. cacao beans) were recrystallized and dried before use. The oligomers epicatechin-(4 $\beta$ →8)-epicatechin and [epicatechin-(4 $\beta$ →8)]<sub>3</sub>-epicatechin were obtained from the ethyl acetate sol-

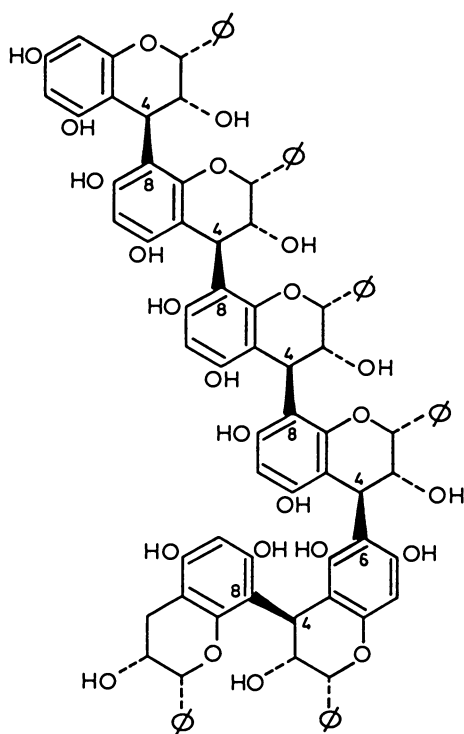


Figure 2. An example of a hexameric homo-oligomer of epicatechin, containing one ( $4\beta\rightarrow 6$ ) and four ( $4\beta\rightarrow 8$ ) interflavanoid linkages.  $\phi = 3,4$ -dihydroxyphenyl.

uble fraction of cacao bean procyanidin<sup>r</sup> by chromatography on Ser. adex LH-20 and MCI-gel and identified by comparison of their properties with published data (18,19). The pentameric and hexameric procyanidin fractions were obtained from the cacao bean polymer fraction (see below) by chromatography on Fractogel HW-40 in methanol (20). The molecular weight of all oligomers was checked by negative ion FAB mass spectroscopy using a glycerol matrix (21).

The procyanidin polymers were isolated by acetone-water extraction and Sephadex LH-20 chromatography as described elsewhere (19). The polymers had the following properties: (1) cacao bean (*Theobroma cacao*):  $[\alpha]_{578}^{20} = +155^\circ$  (*c* 0.2, water). *Analysis*. Calcd. for  $C_{15}H_{12}O_6 \cdot 2H_2O$ : C, 55.4; H, 5.0. Found: C, 55.4; H, 4.6. Number-average molecular weight determined by vapor pressure osmometry in methanol: 1,970; (2) japonica fruits (*Chaenomeles speciosa*) polymer:  $[\alpha]_{578}^{20} = +149$  (1 0.2, water). *Analysis*. Calcd. for  $C_{15}H_{12}O_6 \cdot 3H_2O$ : C, 52.6; H, 5.3. Found: C, 52.9; H, 5.5. Number-average molecular weight determined by vapor pressure osmometry in methanol: 4,035.

**Viscosity Measurements.** These were carried out on solutions of the procyanidin polymers using a Ferranti-Shirley cone viscometer at  $25.0 \pm 0.1^\circ C$  with a 3.5-cm-radius cone. This viscosity was measured at several rotation rates to check for shear dependence. The results were constant over the ranges used (20 to 500 revolutions per minute, depending on the viscosity), and the resulting viscosity values were averaged to obtain the results in the test.

**Formaldehyde Reaction Rate and Consumption Experiments.** Solutions of approximately 1% w/v formaldehyde were prepared by suitable dilution of a 38% w/v formalin solution (BDH) and were standardized by the chromotropic acid method (22).

The kinetic and reaction stoichiometry experiments were carried out in a magnetically stirred, water-jacketed, 70 mL-capacity closed glass beaker equipped with four ports for a condenser, combined glass and calomel electrode, nitrogen inlet, and sample withdrawal. The latter three were all sealed with septa. The kinetic runs were carried out by transferring an appropriate amount of accurately weighed flavanoid to the vessel together with 50 mL of pH 8.0 borate/hydrochloric acid (Merck) buffer. The vessel was assembled and allowed to come to temperature (30 °C maintained via water circulated from a thermostated waterbath) under a slow stream of nitrogen. The flavanoid caused a downward shift of buffer pH, and this was carefully readjusted to pH 8.0 by dropwise addition of 0.1M sodium hydroxide. Then, the reaction was immediately initiated by addition of 0.5 mL of 1% formaldehyde solution, and the residual formaldehyde concentration was measured by removal at timed intervals of 0.5 mL aliquots, dilution of these aliquots to 5.0 mL with pH 6.0 citrate-sodium hydroxide (Merck) buffer, and transfer of two 1.0 mL samples of the diluted solution to 8 mL-capacity screw-top glass vials equipped with teflon-lined lids. A 3.0 mL aliquot of a solution of 1 mL of acetylacetone and 0.6 mL of glacial acetic acid in 100 mL of 2M ammonium acetate was added to each vial, which were



capped and the contents agitated on a vortex mixer; the vials were then heated at 60 °C for 40 minutes. The formaldehyde concentration was then measured spectrophotometrically from the intensity of the absorption band at 412 nm by reference to a standard curve (23).

The total consumption of formaldehyde for each reaction was estimated by removing two 7 mL aliquots of the reaction mixture and heating these at 60 °C for 2 hours in screw-top glass vials and analyzing residual formaldehyde by the above method.

## Results and Discussion

**Viscosity Measurements.** The viscosity results obtained for the two procyanidin polymers were as follows, the percentage values being the solution concentrations (w/w):

Polymer	Viscosities (mPa·s)			
	20%	30%	40%	40% (NaOH)
<i>Theobroma cacao</i>	4.5	18.0	159	192
<i>Chaenomeles speciosa</i>	6.4	45.7	441	897

The lower viscosities observed for the *T. cacao* polymer are expected as its number-average degree of polymerization is about half that of the *C. speciosa* polymer, the values being 6.1 and 11.8, respectively. The degrees of polymerization were calculated by dividing the number-average molecular weights by the hydrated monomer molecular weight as indicated by microanalysis (24).

These results may be compared with viscosities obtained in a similar way from conifer bark extracts which, while heterogeneous, contain polymeric procyanidins or mixed polymeric procyanidins and prodelfinidins as their predominant components (2). For example, Weissman (25) reported a viscosity of 65 mPa·s for a 30% solution of the water extract from *Pinus oocarpa* bark, and Dix and Marutsky (26) obtained a value of 31 mPa·s for a similar solution from *Picea abies* bark. These viscosities are similar to those observed for the 30% procyanidin polymer solutions. They indicate that the viscosities of these bark extract solutions are dominated by the proanthocyanidins and that there is little influence from any accompanying polysaccharides—as already suggested by Weissmann (25)—in contrast to wattle extracts where gums play an important role in determining solution viscosities (7).

Ayla (27) reported a viscosity of 65 mPa·s for a 40% solution of the bark extract from *Pinus brutia*. This is very much lower than that obtained for the *T. cacao* procyanidin polymer, even though Ayla's (27) estimate of 7-8 for the number-average degree of polymerization was apparently higher than the value of 6.1 obtained for the *T. cacao* polymer. However, it has recently been shown that the *P. brutia* polymer is actually a procyanidin-*O*-glucoside (28). When

allowance is made for this, the degree of polymerization of the *P. brutia* polymer is reduced to 4 to 5, which probably accounts for the lower viscosity.

In contrast, Yazaki and Hillis (29) obtained a viscosity of 8,500 mPa·s for a 45% solution of the aqueous extract from *Pinus radiata* bark. This is almost an order of magnitude higher than that expected on the basis of the procyanidin polymer results. Viscosities of the methanol-soluble portion and the ultrafiltered portions of this extract were 500 and 90 mPa·s, respectively. The former value is about that expected for a proanthocyanidin polymer, but the latter indicates that most of the polymer has been excluded by the filter, and it further implies that molecular sizes of proanthocyanidins based on ultrafiltration measurements are often misleading.

When *P. radiata* bark is extracted by sulfite-carbonate, the solution viscosities are much lower. For example, Woo (30) reported a viscosity of 1,600 mPa·s for a 45% solution of "Tannaphen," a commercial tannin extract from *P. radiata* bark that contains approximately 70% proanthocyanidins. When extracted with sulfite-carbonate, the proanthocyanidins will be partly depolymerized (31), which will cause a fall in viscosity. Whether the very high viscosities observed for aqueous extracts by Yazaki and Hillis (29) are due to the *P. radiata* proanthocyanidins being of much higher molecular weight than other conifer tannins or due to complexation of the proanthocyanidins with the polysaccharide fraction (32) remains to be shown.

The viscosity measurements in alkaline solution are more difficult to interpret. Hemingway and his colleagues (15,17) have shown that, in strongly alkaline solutions, procyanidin polymers are rapidly converted at ambient temperatures to species where most monomers contain a rearranged A-ring, such as shown in Figure 3. On this basis, procyanidins are converted to chains with a greater degree of rigidity than the original polymer. It is possible that this may explain the increased viscosity (33).

However, the procyanidin results are very different from those obtained by Weissmann (25) for alkaline extracts from *Pinus oocarpa* bark. On the basis of 30% w/w solutions at 25 °C, the water-soluble material was found to have a viscosity of 65 mPa·s, whereas, the material soluble in 1% sodium hydroxide had a viscosity of 1,294 mPa·s. In light of the results of the current study, this observation is only explicable if the viscosity of the sodium hydroxide extract is due to nontannin components.

**Reaction of Procyanidins with Formaldehyde.** Our knowledge of the kinetics and stoichiometry of the reaction of proanthocyanidin polymers with formaldehyde to produce crosslinked resins is based mainly on three studies of the reaction of model phenols or catechin with formaldehyde (34-36). These studies showed that, at lower temperatures and pH values between 2 and 9, the stoichiometry of the reaction was near equimolar in catechin and formaldehyde.

Kiatgrajai et al. (36) studied the kinetics of the reaction of catechin with formaldehyde over a range of stoichiometries, pH values, and temperatures, and obtained the activation energies for the reaction. They interpreted their data in

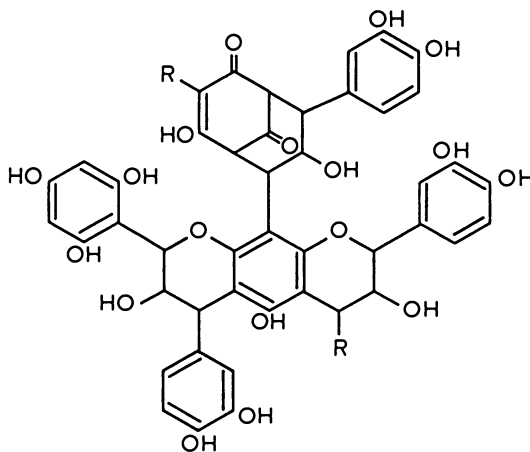


Figure 3. Representation of the general structure of a procyanidin polymer chain that has undergone alkaline rearrangement. R = H, or a continuation of the same type of structure [after reference (15)].

terms of first-order kinetics, which was stated to be observed over the first half of the reaction, followed by a slower rate process. This was explained by assuming different reactivity of C-6 and C-8 toward formaldehyde. These observations were a little surprising in view of the fact that McGraw and Hemingway (37) had observed that electrophilic substitution at C-6 or C-8 lacked regioselectivity for a small attacking species—such as formaldehyde. The reaction kinetics were reinvestigated, therefore, for catechin, epicatechin, and two procyanidins.

The progress of the reaction was followed by monitoring the decrease in formaldehyde concentration with time. Previous studies used the hydroxylamine hydrochloride method of analysis (34-36), but this was avoided in the current study as it requires tedious pH titrations. Instead, a colorimetric method was used that was first developed by Nash (29), involving formation of 3,5-diacetyl-1,4-dihydrolutidine, by reaction of formaldehyde with ammonia and acetylacetone at neutral pH. The cyclic product absorbs at 412 nm with a molar extinction coefficient of 8,000 (29). Other colorimetric methods cannot be used as they all involve very strongly acidic or basic media (22), which would force the phenol-formaldehyde reaction to completion.

The reactions were carried out in a borate-hydrochloric acid buffer at pH 8.0, the pH being readjusted, if necessary, by addition of 1M sodium hydroxide solution after the addition of procyanidin. The above pH was chosen to obtain a convenient reaction rate while minimizing catechinic acid formation (36). It was found that, if water rather than buffer was used for the reaction, and the pH was simply adjusted to pH 8.0 as described by Kiatgrajai et al. (36), the observed pH was unstable and subject to drift.

The experimental values for the kinetics and stoichiometry of formaldehyde consumption are summarized in Table I. The experimental values for reaction stoichiometry illustrate that, at least up to a hexamer, procyanidins form completely crosslinked products in dilute solution, whereas, very little crosslinking occurs for the *C. speciosa* procyanidin polymer. If the values of X for the hexamer and the *T. cacao* polymer are compared, it may be seen that, although they have similar degrees of polymerization, the hexamer obeys the crosslinked model well, whereas, the polymer consumes more formaldehyde than predicted by this model. The difference is apparently due to the presence of longer chain length species in the polydisperse (24) *T. cacao* procyanidin polymer (which contains oligomers from trimers to greater than heptamers as indicated by chromatography-FAB mass spectrometry). This result implies that the ability of procyanidin oligomers to form substantially crosslinked products must start to fail at somewhere around a chain length of 8 or 9 units.

These results support the thesis that to achieve high degrees of crosslinking in proanthocyanidin chains, bridging species larger than formaldehyde must be used to span the increased intermolecular distances due to unfavorable steric dispositions (7). However, the above results show that formaldehyde is able to achieve substantial crosslinking at a surprisingly high degree of polymerization. These results also explain the success of utilizing *P. brutia* bark extracts for wood

Table I. Stoichiometry and Kinetics of the Reaction  
Between Formaldehyde and Some Flavan-3-ols  
(pH 8.0 and 30 °C)

(a) Stoichiometry			
Compound	X (observed) <sup>1</sup>	X (predicted) <sup>2</sup>	
		0.5 model	1.0 model
Epicatechin	1.0	1.0	2.00
Dimer <sup>3</sup>	0.79	0.75	1.50
Tetramer <sup>4</sup>	0.70	0.62	1.25
Pentamer <sup>5</sup>	0.54	0.60	1.20
Hexamer <sup>5</sup>	0.59	0.58	1.17
<i>Theobroma cacao</i> polymer	0.73	0.58	1.17
<i>Chaenomeles speciosa</i> polymer	0.96	0.54	1.08

(b) Kinetics<sup>6</sup>

Compound	$k_2$ (M <sup>-1</sup> sec <sup>-1</sup> )
Catechin	0.23
Epicatechin	0.22
Dimer <sup>3</sup>	0.095
<i>Chaenomeles speciosa</i> polymer	0.036

<sup>1</sup> X = moles of formaldehyde consumed per epicatechin unit.

<sup>2</sup> Predicted values of X assuming either 0.5 or 1.0 molecules of formaldehyde reacts with each A-ring site. If the 0.5 model is obeyed, then all hydroxymethylene groups will have crosslinked.

<sup>3</sup> Epicatechin-(4 $\beta$ →8)-epicatechin.

<sup>4</sup> [Epicatechin-(4 $\beta$ →8)]<sub>3</sub>-epicatechin.

<sup>5</sup> Unfractionated mixtures of epicatechin pentamers or hexamers obtained chromatographically from the *T. cacao* polymer.

<sup>6</sup> Concentration of formaldehyde was 3.6 x 10<sup>-3</sup> molar and the ratio of formaldehyde per A-ring reaction site was 0.5 in each run.

adhesives (27) since, with a degree of polymerization of 4 to 5, they are obviously well within the established range for substantial crosslinking. Alternatively, a procyanidin polymer with a high degree of polymerization must be cleaved with reagents such as sulfite of resorcinol to reduce the average chain lengths prior to reaction with formaldehyde (38,39).

**Kinetics.** Data were collected for catechin, epicatechin, epicatechin-(4 $\beta$ →8)-epicatechin and the *C. speciosa* polymer. The ratio of reactants was chosen so that the concentration of formaldehyde and reaction sites was equimolar, assuming complete crosslinking (i.e., 0.5 molecule of formaldehyde per reaction site converts to one molecule per reaction site after crosslinking, as each formaldehyde molecule reacts with two sites). The concentration of formaldehyde was kept the same for each compound so as to provide a consistent basis for comparison.

Plots of (absorbance)<sup>-1</sup> versus time were linear for greater than 90% of the reaction for each system studied. These observations may be interpreted in terms of the reaction obeying second-order kinetics where the reactants are equimolar (40). Second-order or more complex kinetics are typical of phenol-formaldehyde condensations under alkaline conditions (7).

As expected,  $k_2$  for catechin and epicatechin are the same, since the reaction rate would be expected to be independent of C-ring stereochemistry. The comparatively smaller rate constants observed for the two procyanidins could be explained by the fact that they possess fewer reaction sites per monomer unit than catechin or epicatechin and also by steric effects.

## Conclusions

The current study confirms that formaldehyde is too small a bridging group to substantially crosslink extended proanthocyanidin chains, extensive crosslinking apparently starting to fail at chain lengths of greater than 6 units. The study also defines the viscosity range characteristic of procyanidin polymers and illustrates that the viscosity of aqueous extracts from some conifer barks is dominated by proanthocyanidins, whereas, high viscosities characteristic of nontannins or tannin-polysaccharide complexes are characteristic of the aqueous extracts in other cases.

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# Chapter 14

## Reactions of Tannin Model Compounds with Methylphenols

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Most formulations of tannin-based adhesives employ phenol-formaldehyde prepolymer as crosslinking agents. These condensations were modeled by reacting equimolar proportions of *o*- and *p*-hydroxybenzyl alcohols with resorcinol, phloroglucinol, or (+)-catechin in various combinations over a pH range of 3.0 to 11.0 at 100 °C. The <sup>1</sup>H- and <sup>13</sup>C-NMR spectra of peracetate derivatives of reaction products show that: 1) similarities in rates of condensation of *o*- and *p*-hydroxybenzyl alcohols with resorcinol, phloroglucinol, or (+)-catechin suggest that the stabilities of carbocations/quinone methides rather than the nucleophilicity of the phenol are rate controlling; 2) the nucleophilicity of the phenol is significant in determining product ratios when the phenols are competing for the same electrophile; 3) that condensations are selective, favoring those of *p*-hydroxybenzyl alcohol; 4) because of the dominance of condensation with *p*-hydroxybenzyl alcohol, there is little regioselectivity in the condensations at the C-6 or C-8 positions of (+)-catechin; 5) rearrangements are important in the reaction of (+)-catechin at alkaline pH, epimerization to (+)-epicatechin being prominent at pH ≤ 9.0, and formation of catechinic acid being dominant in reactions at pH 10.0 or 11.0; 6) because of the slow rate of condensation of hydroxybenzyl alcohols with phloroglucinol or (+)-catechin and rearrangement at alkaline pH, practical applications of these reactions in development of tannin-based adhesives are limited.

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MacLean and Gardner (1) first demonstrated the importance of crosslinking condensed tannins with polymethylol phenols rather than with formaldehyde in the formulation of plywood adhesives based on conifer bark extracts. The need to use polymethylol phenols arose because of the extremely rapid condensation rate of conifer bark tannins when reacted with formaldehyde over a wide range of reaction pH conditions. Herrick and Bock (2) were able to successfully develop exterior plywood glues based on western hemlock bark tannins by crosslinking them with specially formulated polymethylol phenols. Since their work, most of the attempts to develop plywood or particleboard adhesives based on condensed tannins have involved their reactions with phenol-formaldehyde prepolymers (3). Improved properties of the cured polymers are thought to arise from a higher frequency of more flexible crosslinks (4) when using these phenol-formaldehyde resins.

Surprisingly little is known about the reactions of condensed tannins with phenol-formaldehyde prepolymers despite widespread attempts to use these condensations in formulation of tannin-based adhesives. McGraw and Hemingway (5,6) first examined the reactions of (+)-catechin with either *o*- or *p*-hydroxybenzyl alcohol to model the condensation of phenol-formaldehyde resins with condensed tannins. In reactions of catechin with *p*-hydroxybenzyl alcohol, substitution occurred at the C-6 and C-8 positions of the phloroglucinol rings in approximately equal proportions. However, significant regioselectivity was seen in the reactions of catechin with *o*-hydroxybenzyl alcohol. Substitution at the C-8 position was preferred over that at C-6 by a factor of about 2.5 to 1. The rate of condensation of either *o*- or *p*-hydroxybenzyl alcohol with (+)-catechin was slow in comparison with the reactions of formaldehyde with phloroglucinol or (+)-catechin. Recent work on the use of condensed tannins for the formulation of cold-setting phenolic adhesives (7,8) has pointed out the need for understanding more about the reactions of condensed tannins with polymethylol phenols under a variety of conditions. Therefore, either resorcinol, phloroglucinol, or (+)-catechin was reacted with equimolar amounts of *o*- and *p*-hydroxybenzyl alcohols at 100 °C over a pH range of 3.0 to 11.0.

## Experimental Methodology

**Reaction Conditions.** Equimolar quantities of *o*-hydroxybenzyl alcohol, *p*-hydroxybenzyl alcohol and either resorcinol, phloroglucinol, or (+)-catechin were dissolved in *p*-dioxane-water (1:2, v/v) and the solution pH adjusted to 3.0, 5.0, 7.0, 9.0, 10.0, or 11.0 by addition of acetic acid or 5.0M NaOH. An aliquot was freeze-dried immediately (0-Time), and the remainder was divided and added to a series of sealed vials, flushed with N<sub>2</sub>, and heated for time period of 1, 2, or 6 hours in a boiling water bath. After the appropriate reaction period, the samples were transferred to round-bottomed flasks and freeze-dried. In a similar manner, equimolar quantities of two competing phenols were reacted with one equivalent of either *o*- or *p*-hydroxybenzyl alcohol.

The freeze-dried residues were acetylated with acetic anhydride-pyridine (1:1, v/v) at ambient temperature overnight. The samples were then added to water in a separatory funnel and the peracetates extracted into dichloromethane. The dichloromethane-soluble fraction was dried over anhydrous sodium sulfate and then evaporated to an oil on a rotary evaporator at  $\leq 40$  °C. Toluene was added and evaporated repeatedly (four or five times) until no odor of pyridine was detectable. The samples were then dried under high vacuum at ambient temperature for 1 hour.

The reaction with resorcinol at pH 11 was run in solvent systems containing 50%, 67%, and 100% water. The degree of substitution was measured as described below to determine the effect of dioxane on the condensation. After 6 hours at 100 °C, the degree of substitution was 16% lower in dioxane-water (1:1) and only 2% lower in dioxane-water (1:2) than in water.

**Interpretation of Spectra.** Spectra of the peracetate derivatives in deuteriochloroform were recorded at 80 MHz for protons and 20 MHz for carbons using a Varian FT80A spectrometer. Assignments for the  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra of the resorcinol, phloroglucinol, and catechin reaction products, summarized in Tables I and II, respectively, are largely drawn from previously reported results (5,9-12).

Acetylated products of the competitive reactions of equimolar proportions of *o*- and *p*-hydroxybenzyl alcohols with resorcinol were examined by  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR in deuteriochloroform.  $^1\text{H}$ -NMR spectra were normalized using the relationship:

$$14 \text{ H} = \text{Ar-H} + \text{Mo}/2 + \text{Mb}$$

where Ar-H is the number of aromatic protons (i.e., 12 protons when equimolar proportions are added and no reaction has occurred), Mo is the number of methylol protons (i.e., 4 protons when equimolar proportions of the *o*- and *p*-hydroxybenzyl alcohols are added and no reaction takes place), and Mb is the number of methylene bridge protons.  $^1\text{H}$ -NMR spectra of the products of the reaction of phloroglucinol with equimolar proportions of *o*- and *p*-hydroxybenzyl alcohols were normalized similarly using the relationship:

$$13 \text{ H} = \text{Ar-H} + \text{Mo}/2 + \text{Mb}$$

Dibenzyl ether linkages were only observed early in the reaction of *p*-hydroxybenzyl alcohol with phloroglucinol and resorcinol at a pH of 3.0.

The spectra of 0-Time samples generally contained only about 80% of the expected methylol protons, probably due to more hydration of the benzyl alcohols than the resorcinol or phloroglucinol. Also, some samples showed the presence of small amounts of methylene linkages due to some self-condensation of the hydroxybenzyl alcohols prior to their reaction with either resorcinol or phloroglucinol. Therefore, calculations of the number of methylols lost and

Table I. Selected  $^1\text{H-NMR}$  Assignments for Peracetate Derivatives of Model Products

$\delta$ from TMS	Assignment
2.67-2.85	H-4 in heterocyclic ring of (+)-catechin.
3.71	<i>o-o</i> methylene $\text{CH}_2$ in di-( <i>o</i> -hydroxybenzyl) resorcinol.
3.78	<i>o-o</i> methylene $\text{CH}_2$ in <i>o</i> -hydroxybenzyl resorcinol.
3.82	<i>o-p</i> methylene $\text{CH}_2$ in di-( <i>p</i> -hydroxybenzyl) resorcinol.
3.85	<i>o-p</i> methylene $\text{CH}_2$ in <i>p</i> -hydroxybenzyl resorcinol.
3.74	<i>o-o</i> methylene $\text{CH}_2$ in <i>o</i> -hydroxybenzyl phloroglucinol.
	<i>o-o</i> methylene $\text{CH}_2$ in di-( <i>o</i> -hydroxybenzyl) phloroglucinol.
3.80	<i>o-p</i> methylene $\text{CH}_2$ in <i>p</i> -hydroxybenzyl phloroglucinol.
	<i>o-p</i> methylene $\text{CH}_2$ in di-( <i>p</i> -hydroxybenzyl) phloroglucinol.
3.80	<i>o-o</i> methylene $\text{CH}_2$ in di( <i>p</i> -hydroxybenzyl) phloroglucinol
3.85	<i>o-p</i> methylene $\text{CH}_2$ in di( <i>p</i> -hydroxybenzyl) phloroglucinol
3.91	<i>p-p</i> methylene $\text{CH}_2$ in self-condensation products.
3.64	methylene $\text{CH}_2$ in 6-( <i>o</i> -hydroxybenzyl) catechin.
3.74	methylene $\text{CH}_2$ in 6-( <i>p</i> -hydroxybenzyl) catechin.
3.62 + 3.74	methylene $\text{CH}_2$ in 6,8-di-( <i>o</i> -hydroxybenzyl) catechin.
3.80	methylene $\text{CH}_2$ in 8-( <i>o</i> -hydroxybenzyl) catechin.
3.84	methylene $\text{CH}_2$ in 8-( <i>p</i> -hydroxybenzyl) catechin.
3.74 + 3.80	methylene $\text{CH}_2$ in 6,8-di-( <i>o</i> -hydroxybenzyl) catechin.
5.04	$\text{CH}_2$ of <i>o</i> - and <i>p</i> -hydroxybenzyl alcohol.
5.00-5.40	H-2 and H-3 of heterocyclic ring in (+)-catechin.
6.55-6.75	ArH of <i>A</i> -ring of (+)-catechin.
6.75-7.45	ArH of benzyl alcohols, resorcinol, phloroglucinol and <i>B</i> -ring of (+)-catechin.

Table II. Selected  $^{13}\text{C}$ -NMR Spectral Assignments for Peracetates of Product Models

$\delta$ from TMS	Assignment
24.0	C-4 in catechin
26.1	C-4 in epicatechin
29.9	methylene in <i>p</i> -hydroxybenzyl phloroglucinol
30.7	methylene in di-( <i>p</i> -hydroxybenzyl) phloroglucinol
30.3	methylene in <i>o</i> -hydroxybenzyl resorcinol
30.5	methylene in 2,2-dihydroxydiphenyl methane
30.9	methylene in di-( <i>o</i> -hydroxybenzyl) resorcinol
35.4	methylene in di-( <i>p</i> -hydroxybenzyl) resorcinol
35.3	methylene in 2,4-dihydroxydiphenyl methane
40.0	methylene in 4,4-dihydroxydiphenyl methane
37.8 or 37.7	C-8 in catechinic acid as phenol or salt
54.8 or 45.6	C-6 in catechinic acid as phenol or salt
59.5 or 50.7	C-5 in catechinic acid as phenol or salt
67.6 or 61.5	C-1 in catechinic acid as phenol or salt
68.0 or 71.2	C-7 in catechinic acid as phenol or salt
61.0	benzyl $\text{CH}_2$ in <i>o</i> -hydroxybenzyl alcohol
65.3	benzyl $\text{CH}_2$ in <i>p</i> -hydroxybenzyl alcohol
66.7	C-3 in epicatechin
68.4	C-3 in catechin
76.7	C-2 in epicatechin
77.8	C-2 in catechin
107.7	C-8 in catechin
109.1	C-8 in 6-( <i>o</i> -hydroxybenzyl) catechin
109.3	C-6 in 8-( <i>o</i> -hydroxybenzyl) catechin
108.8	C-6 in catechin
112.5	C-2 in phloroglucinol
114.0	C-4 and C-6 in <i>p</i> -hydroxybenzyl phloroglucinol
115.7	C-6 in di-( <i>p</i> -hydroxybenzyl) phloroglucinol
115.3	C-2 in resorcinol
116.0	C-2 in <i>o</i> -hydroxybenzyl resorcinol
117.1	C-2 in di-( <i>p</i> -hydroxybenzyl) resorcinol
117.3	C-2 in di-( <i>o</i> -hydroxybenzyl) resorcinol
117.4	C-8 in 8-( <i>o</i> -hydroxybenzyl) catechin
117.6	C-6 in 6-( <i>o</i> -hydroxybenzyl) catechin
117.9	C-6 in 6,8-di-( <i>o</i> -hydroxybenzyl) catechin
118.4	C-8 in 6,8-di-( <i>o</i> -hydroxybenzyl) catechin
119.0	C-6 in 4-( <i>o</i> -hydroxybenzyl) resorcinol
128.0	C-4 and C-6 in 4,6-di-( <i>o</i> -hydroxybenzyl) resorcinol

methylenes gained were based upon changes in the number of protons actually found between 0- and X-Time of reaction.

Assignments for the  $^1\text{H-NMR}$  spectra of (+)-catechin derivatives are given in Table I. These data are based on results published earlier (5,12). The  $^1\text{H-NMR}$  spectra of the catechin reaction products were normalized by assigning 11 protons to the broad band of signals at 6.75 to 7.50 ppm.

The carbon spectra were obtained using a  $45^\circ$  pulse and an 0.8 second acquisition time with no pulse delay. A comparison of these spectra with those obtained by quantitative methods (i.e., a  $45^\circ$  pulse, nOe suppressed, and a 14 - second pulse delay) (13) indicated that accurate estimates of the ratios of *o*- or *p*-methylols, the ratios of *o*- and *p*-methylenes, and the unsubstituted, mono-substituted, and disubstituted resorcinol or phloroglucinol C-2 carbons could be obtained using a fast pulse sequence. The  $^{13}\text{C-NMR}$  spectra were, therefore, used to compute: 1) the relative amounts of residual *o*- and *p*-methylols; 2) the relative amounts of *o-o*, *o-p*, and *p-p* methylenes that may have been produced by self-condensation of the benzyl alcohols; 3) the relative amounts of *o*- and *p*-methylenes formed by reaction with resorcinol, phloroglucinol, or catechin, and 4) the relative proportions of unsubstituted, monosubstituted, and disubstituted resorcinol or phloroglucinol derivatives. The ratio of *p*- to *o*-methylol carbon signals averaged 0.87 to 1.0, respectively, in samples at 0-Time using these NMR parameters. It is possible that the differences observed in the intensity of these carbon signals were due to differences in the extent of hydration of the two benzyl alcohols used for the reactions. On average, 91.4% of the loss of *p*-methylol was accounted for by an increase in the intensity of the *p-o-o* methylene carbon signals, and 85.6% of the loss of *o*-methylol was accounted for by increases in the *o-o-o* methylene bridge carbon signals in reactions with phloroglucinol. Similar results were obtained in reactions with resorcinol and with (+)-catechin in reactions at acidic to neutral pH.

Assignments for the  $^{13}\text{C-NMR}$  spectra of (+)-catechin derivatives are given in Table II. Most of these assignments were previously published (5,12). When a  $45^\circ$  pulse and an 0.8 second acquisition time are used, the signals for C - 6 and C-8 of the catechin *A*-ring, as well as those for the C-2, C-3 and C-4 of the heterocyclic ring, are all of approximately equal area. The signals for the *o*- and *p*-hydroxybenzyl  $\text{CH}_2$  are approximately 50% of the intensity of the catechin C-2 and C-3 carbons. Therefore, the  $^{13}\text{C-NMR}$  spectra were interpreted through reference to the average of the catechin heterocyclic C-2 and C-3 carbon signals. The proportions of *A*-ring carbons lost and methylene carbons gained were computed directly from the relative intensity of these peaks. The estimates for the number of *o*- or *p*-methylol carbons lost were obtained by multiplying the changes in signal intensity by a factor of 2. Results obtained in this way were reasonably consistent with those obtained from the  $^1\text{H-NMR}$  spectra but usually indicated a higher degree of condensation.

## Results and Discussion

***o*- and *p*-Hydroxybenzyl Alcohols with Resorcinol.** The condensation of equimolar proportions of *o*- and *p*-hydroxybenzyl alcohols with resorcinol was most rapid at pH 3.0. At this pH, condensation was about 50% complete after 1 hour and over 75% complete after 6 hours at 100 °C. The reactions were much slower at pH 5.0 and pH 7.0 and somewhat slower at pH 9.0, 10.0, and 11.0. There were only small differences in the extent of condensation in reactions made at initial pH conditions of pH 9.0, 10.0, and 11.0. At these pH values, initial rates of condensation were less than half that obtained at pH 3.0 (Figure 1). Estimates of the degree of condensation obtained by measuring the loss of methylols or the gain in methylenes from <sup>1</sup>H-NMR spectra and from the proportion of unsubstituted, monosubstituted, and disubstituted resorcinol from the <sup>13</sup>C-NMR spectra usually gave similar results (Table III).

Comparisons of the ratios of *o*- to *p*-methylol signal intensities in <sup>13</sup>C-NMR spectra indicated strong selectivity in the condensation of the *p*-methylols at either extreme of reaction pH (i.e., initial pH of 3.0 or 11.0). However, as the reaction pH approached neutrality, there was significantly less difference in the rates of loss of *o*- and *p*-methylols (Figure 2). Selectivity in condensation with *p*-methylols was also evident from comparisons of the intensities of *o-p* and *o-o* methylene signals in the <sup>13</sup>C-NMR spectra. At more acidic or more alkaline pH, the *o-p* methylenes dominated early in the reaction (Table III). As the degree of condensation increased, the *o-o* methylenes increased in relative proportion as would be expected because of low residual concentrations of *p*-methylols. In reactions at pH 7.0, the *o-p* methylene signals were more dominant than would have been expected from the change in *o*- and *p*-methylols, but the relative proportions of the *o-p* and *o-o* methylenes did not change much after longer reaction times. This also would be expected because of the comparatively larger amounts of residual *p*-methylols.

***o*- and *p*-Hydroxybenzyl Alcohols with Phloroglucinol.** These results closely parallel those from reaction of these alcohols with resorcinol. The overall rates of condensation with phloroglucinol were also sensitive to initial reaction pH. At pH 3.0, condensation was over 70% complete after 6 hours of heating at 100 °C. The degree of substitution decreased with increasing initial reaction pH to a minimum at pH of 9.0 where only about 40% of the total methylol had reacted after 6 hours at 100 °C. The rates of condensation increased at more alkaline pH where approximately 60% and 55% of the methylol reacted after 6 hours at 100 °C, at pH 10.0 and pH 11.0, respectively. Estimates of the relative proportions of unsubstituted, monosubstituted, and disubstituted phloroglucinol derivatives, obtained by integration of the C-2 phloroglucinol carbon signals at 112.5, 114.0, and 115.7 ppm, respectively, were reasonably consistent with results obtained from integration of the methylol and methylene signals in the <sup>1</sup>H-NMR spectra (Table IV).

As was observed in reactions with resorcinol, the <sup>13</sup>C-NMR spectra showed

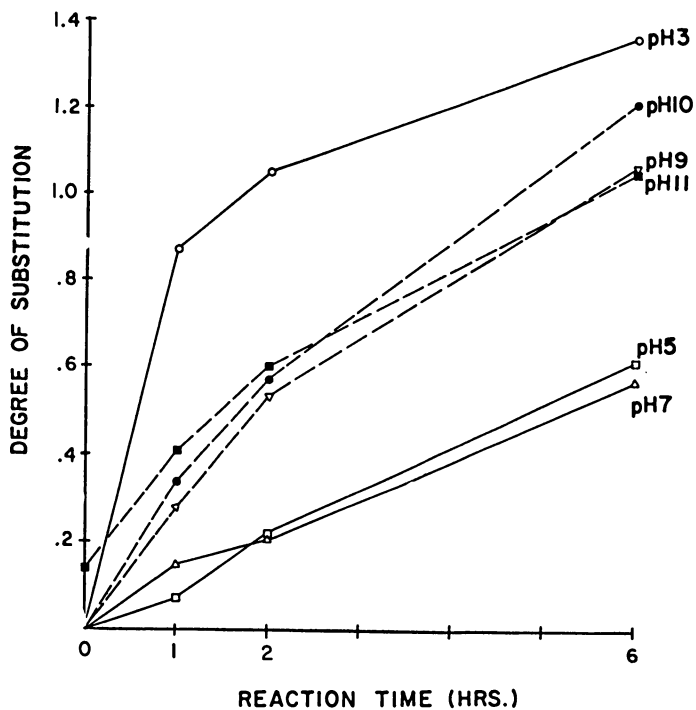
RESORCINOL + Q- + P- HYDROXYBENZYL ALCOHOLS

Figure 1. Degree of substitution onto resorcinol at various pH values plotted against reaction time.



Table III. Methylol, Methylene, and Degree of Substitution per Mole of Resorcinol after Reaction with *o*- and *p*-Hydroxybenzyl Alcohols

Reaction Time (Hrs)	Methylols		Methylenes		Substitution		
	<i>p</i>	<i>o</i>	<i>o-p</i>	<i>o-o</i>	unsub	mono	disub
<b>pH 3.0</b>							
0	0.82	0.86	-	-	1.00	-	-
1	0.20	0.70	0.60	0.12	0.33	0.39	0.28
2	0.04	0.63	0.75	0.24	0.21	0.42	0.37
6	0.00	0.30	0.79	0.50	0.14	0.32	0.54
<b>pH 5.0</b>							
0	0.77	0.83	-	-	1.00	-	-
1	0.71	0.87	nm	nm	0.81	0.19	-
2	0.62	0.82	0.12	0.06	0.74	0.19	0.07
6	0.40	0.62	0.34	0.17	0.46	0.34	0.20
<b>pH 7.0</b>							
0	0.74	0.81	-	-	1.00	-	-
1	0.73	0.79	0.11	0.04	0.72	0.28	-
2	0.61	0.81	0.15	0.09	0.73	0.27	-
6	0.43	0.59	0.29	0.16	0.45	0.35	0.19
<b>pH 9.0</b>							
0	0.79	0.83	-	-	1.00	-	-
1	0.61	0.81	0.21	0.07	0.63	0.37	-
2	0.51	0.77	0.32	0.14	0.35	0.51	0.14
6	0.30	0.47	0.52	0.46	0.17	0.32	0.52
<b>pH 10.0</b>							
0	0.85	0.87	-	-	1.00	-	-
1	0.56	0.87	0.27	0.09	0.63	0.37	-
2	0.42	0.72	0.44	0.18	0.35	0.51	-
6	0.13	0.43	0.64	0.46	0.17	0.32	0.52
<b>pH 11.0</b>							
0	0.69	0.78	0.19	-	0.87	0.13	-
1	0.48	0.80	0.23	0.09	0.48	0.43	0.10
2	0.28	0.70	0.37	0.16	0.32	0.45	0.23
6	0.11	0.53	0.66	0.33	0.19	0.37	0.43

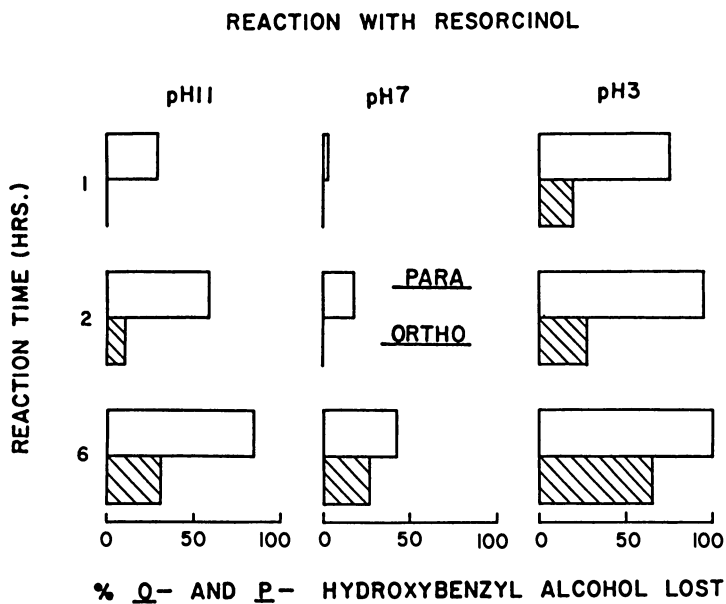


Figure 2. Percent of *o*- and *p*-hydroxybenzyl alcohol reacting with resorcinol as a function of time.

Table IV. Comparison of Methylol Loss, Methylene Formation, and Phenol Substitution as Percentage of Methylol Consumed after 6 Hours and 100 °C at Various pH

Initial pH	Methylol Lost <sup>1</sup>	Methylene Gained <sup>1</sup>	Phenol Substitution <sup>2</sup>	Average
Resorcinol				
3.0	82.5	76.0	70.0	76.2
5.0	35.7	31.2	37.0	34.7
7.0	33.5	28.4	36.5	32.8
9.0	52.5	55.6	59.3	55.8
10.0	67.4	65.7	79.1	70.7
11.0	56.5	67.3	83.7	69.2
Phloroglucinol				
3.0	82.0	67.0	67.5	72.2
5.0	58.7	39.0	50.0	49.2
7.0	49.7	32.0	44.5	42.1
9.0	48.7	37.5	34.9	40.4
10.0	58.3	56.3	67.5	60.7
11.0	49.6	49.6	68.5	55.9

<sup>1</sup>Based on <sup>1</sup>H-NMR data and number of methylols at 0-time.

<sup>2</sup>Based on <sup>13</sup>C-NMR data and assuming equimolar proportions. Does not account for possible trisubstituted product.

that the extent of selectivity in reactions of *o*- and *p*-methylols was highly dependent on initial reaction pH. Condensation of the *p*-methylol dominated in reactions at pH 3.0, pH 10.0, and pH 11.0, but there was less selectivity in reactions made at initial pH of 7.0 to 9.0 (Table V). This same preference for condensation with *p*-hydroxybenzyl alcohol was evident in the high proportion of *p*-methylenes in reaction products obtained at acidic pH.

***o*- and *p*-Hydroxybenzyl Alcohols with (+)-Catechin.** The <sup>1</sup>H-NMR spectra of products of the reaction of catechin with approximately equimolar proportions of *o*- and *p*-hydroxybenzyl alcohols indicated that (+)-catechin reacts with these phenols at rates similar to those found for resorcinol and phloroglucinol. In reactions at pH 3.0, about 50% of the catechin *A*-ring protons were lost due to substitution after 1 hour. Only about 15% of the *A*-ring protons remained after 6 hours of reaction at pH 3.0 and 100 °C. As was observed in the reactions with phloroglucinol, the rates of condensation of *o*- and *p*-hydroxybenzyl alcohols with (+)-catechin are dependent on the initial reaction pH. The condensation rate decreases with an increase in reaction pH to a minimum at pH 7.0.

In reactions at pH 9.0, there is significant epimerization of (+)-catechin to (+)-epicatechin. This was best seen in the <sup>13</sup>C-NMR spectra where there are large differences in the chemical shifts of the C-2 and C-3 carbon signals (Table II). Reductions in the intensity of *A*-ring protons, losses of methylol protons, and gains in methylene protons were reasonably consistent, suggesting that the major reaction was condensation with the hydroxybenzyl alcohols in addition to this epimerization. After 1 hour at 100 °C and pH 9.0, the ratio of catechin to epicatechin was 3 to 1 (Figure 3). The loss of *A*-ring carbons was slightly higher than the loss of methylols or the increase in methylene carbons, suggesting that about 10% of the flavan-3-ols may have been lost by base-catalyzed rearrangement to catechinic acid.

In reactions at initial pH of 10.0 or 11.0, there is significant loss of the phloroglucinol *A*-ring functionality through rearrangement of catechin to catechinic acid (14-16). This was evident in the large loss of *A*-ring proton signals in comparison with the much smaller increase in the methylene or loss of methylol protons. Rearrangement of catechin to catechinic acid dominates over condensation with hydroxybenzyl alcohols when reactions are made at pH of 10.0, since only about half of the *A*-ring carbons lost could be accounted for by losses in methylol or gains in methylene bridge carbons. The <sup>13</sup>C-NMR spectra of peracetates recovered from reactions at pH 10.0 and 11.0 for 1 hour showed intense signals at chemical shifts expected for a mixture of *o*- and *p*-hydroxybenzyl alcohol. Much smaller signals occurred at chemical shifts found for catechin. Although a number of other small signals was evident, none of these could be readily assigned to catechinic acid or other logical products of (+)-catechin.

In reactions at pH 11.0, no phloroglucinol *A*-ring can be detected after only 1 hour at 100 °C, and there is little change in the amount of methylol or formation of methylene bridge after 6 hours of heating. The methylene signals that are

Table V. Methylol, Methylene, and Degree of Substitution per Mole of Phloroglucinol after Reaction with *o*- and *p*-Hydroxybenzyl Alcohols

Reaction Time (Hrs)	Methylols		Methylenes			Substitution		
	<i>p</i>	<i>o</i>	<i>o-p</i>	<i>o-o</i>	<i>o-o-o</i>	unsub.	mono	di
<b>pH 3.0</b>								
0	0.88	0.78	-	-	-	1.00	-	-
1	0.16	0.70	0.05	0.58	0.12	0.32	0.37	0.31
2	0.08	0.52	0.08	0.69	0.26	0.22	0.36	0.42
6	0.00	0.30	0.04	0.70	0.44	0.16	0.33	0.51
<b>pH 5.0</b>								
0	0.77	0.87	-	-	-	1.00	-	-
1	0.64	0.75	0.04	0.13	0.04	0.62	0.28	0.10
2	0.48	0.78	0.04	0.19	0.09	0.56	0.35	0.10
6	0.18	0.50	0.05	0.50	0.23	0.32	0.38	0.31
<b>pH 7.0</b>								
0	0.78	0.84	-	-	-	1.00	-	-
1	0.59	0.81	0.24	0.51	0.24	0.79	0.21	.00
	0.40	0.73	0.03	0.22	0.12	0.55	0.34	0.11
6	0.28	0.53	0.06	0.40	0.17	0.37	0.37	0.26
<b>pH 9.0</b>								
0	0.78	0.74	-	-	-	1.00	-	-
1	0.62	0.76	-	0.17	-	0.87	0.13	-
2	0.59	0.67	-	0.17	0.06	0.68	0.29	0.03
6	0.27	0.51	0.04	0.33	0.20	0.57	0.33	0.10
<b>pH 10.0</b>								
0	0.65	0.81	-	0.05	-	0.92	0.08	-
1	0.65	0.80	0.08	0.06	0.03	0.76	0.24	-
2	0.46	0.69	0.09	0.19	0.08	0.62	0.32	0.06
6	0.08	0.55	0.07	0.55	0.23	0.23	0.52	0.25
<b>pH 11.0</b>								
0	0.69	0.72	-	0.02	-	0.98	0.02	-
1	0.53	0.74	0.04	0.20	0.07	0.68	0.28	0.04
2	0.41	0.61	0.06	0.34	0.09	0.54	0.36	0.10
6	0.12	0.60	0.06	0.49	0.16	0.28	0.46	0.26

seen after 6 hours of heating at pH 11.0 are predominantly at  $\delta$  3.80 to 3.90 ppm, suggesting that the condensation that does occur is primarily due to self-condensation of the hydroxybenzyl alcohols.

It was suspected that the catechinic acid formed by rearrangement was not recovered after acetylation. Therefore, products of these base-catalyzed reactions were examined by  $^{13}\text{C}$ -NMR in the free phenolic form (Figure 4). Comparison of the spectrum to the  $^{13}\text{C}$ -NMR chemical shifts given in Table II indicate that the major product, isolated from the reaction of catechin with equimolar proportions of *o*- and *p*-hydroxybenzyl alcohol at pH 10 or 11, was the sodium salt of catechinic acid. In this reaction product, there are no signals apparent for the C-6 and C-8 of catechin (95.5 to 96.0 ppm in the phenol), yet the catechol ring resonances are prominent as are those for the hydroxybenzyl alcohols. If retaining some of the phloroglucinol reactivity of the tannin for subsequent reaction with aldehydes in cold-setting adhesive applications (7,8) is desired, it is important that the initial condensation with phenol-formaldehyde prepolymers be carried out under acidic pH conditions.

The high degree of selectivity in reaction of (+)-catechin with *p*-hydroxybenzyl alcohol is readily seen in the  $^{13}\text{C}$ -NMR spectra. All of the *p*-methylol had reacted after only 1 hour at pH 3.0 and 100 °C. At this same time, the ratio of *p*- to *o*-methylenes formed was about 2 to 1. In reactions at pH 5.0, the average ratio of *p*- to *o*-methylols lost and methylenes formed was about 1.8 to 1. As was observed in reactions with phloroglucinol, the selectivity in reactions of the *p*-hydroxybenzyl alcohol decreased with an increase in reaction pH. The average ratio of *p*- to *o*-methylols lost and methylenes gained decreased to about 1.4 to 1 in reactions made at pH 7.0. Because of the preference for reaction with *p*-hydroxybenzyl alcohol, there was no evidence for selectivity in the substitution at C-8 over that at C-6. This result is in agreement with earlier work that showed no significant regioselectivity in the reactions of (+)-catechin with *p*-hydroxybenzyl alcohol (5,6).

***o*- or *p*-Hydroxybenzyl Alcohol with Resorcinol and Phloroglucinol.** Resorcinol and phloroglucinol were reacted with either *o*- or *p*-hydroxybenzyl alcohol at pH 3.0 and pH 11.0. Condensation proceeded most rapidly at pH 3.0 with the *p*-hydroxybenzyl alcohol. Less than 65% of the *o*-hydroxybenzyl alcohol was condensed after 6 hours at 100 °C and pH 3.0, while less than 35% reacted under similar conditions at pH 11.0. In contrast, the *p*-isomer was almost 90% reacted after 6 hours at 100 °C and pH 11.0 and was completely consumed before 2 hours of reaction time at pH 3.0.

In all of the reactions, most of the condensation took place with phloroglucinol, yielding four to six times more of that condensation product. A somewhat higher ratio of phloroglucinol versus resorcinol condensation obtained with the *p*-hydroxybenzyl alcohol compared to the *o*-isomer seems to indicate that steric factors do influence the product ratios, but not significantly. Although the overall reaction rates of resorcinol or phloroglucinol with the hydroxybenzyl alcohols

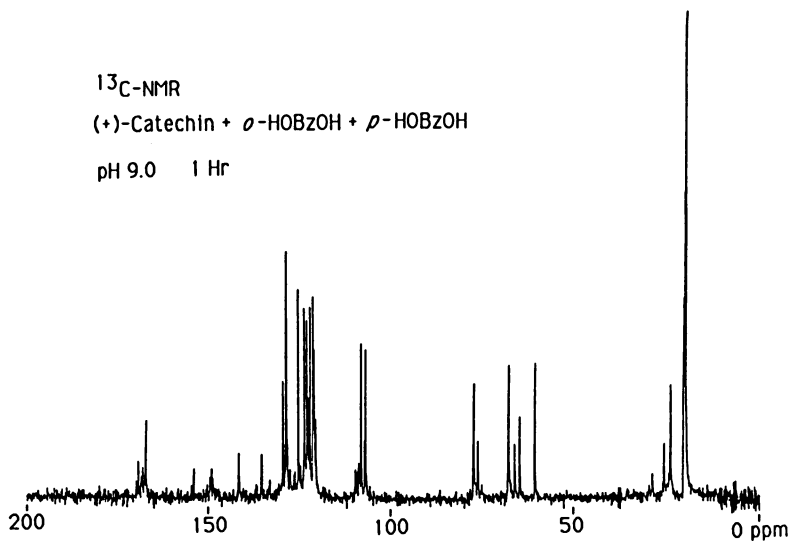


Figure 3.  $^{13}\text{C}$ -NMR of reaction products of (+)-catechin with *o*- and *p*-hydroxybenzyl alcohol at pH 9 and 100 °C for 1 hour.

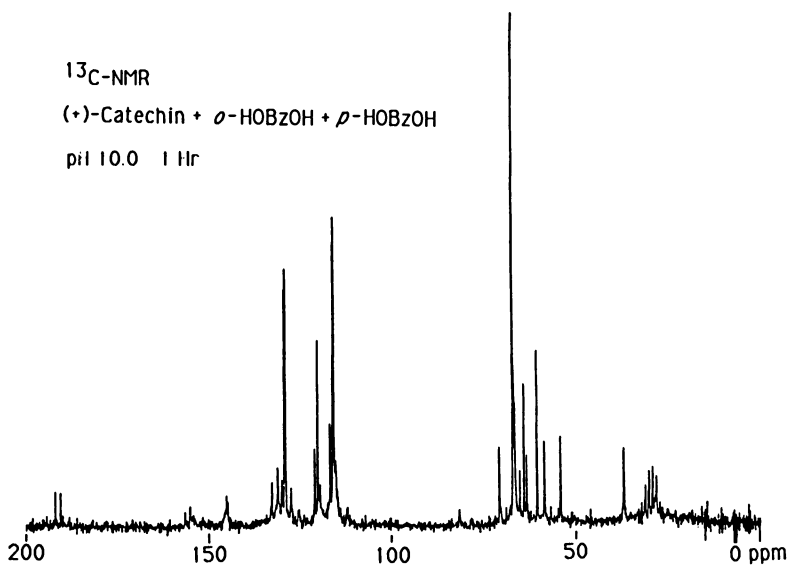


Figure 4.  $^{13}\text{C}$ -NMR of free phenol reaction products of (+)-catechin with *o*- and *p*-hydroxybenzyl alcohol at pH 10 and 100 °C for 1 hour.

are similar, there is significant selectivity for the phloroglucinol when the two ring systems are competing for the same electrophile.

***o*- or *p*-Hydroxybenzyl Alcohol with Resorcinol and (+)-Catechin.** The *p*-hydroxybenzyl alcohol was completely consumed before 2 hours at pH 3.0 and 100 °C with 84% of the condensation occurring on (+)-catechin. After 6 hours reaction time, only 85% of the *o*-hydroxybenzyl alcohol had condensed. Of the condensation that had occurred, 88% took place with (+)-catechin and only 12% with resorcinol. The results are very similar to those obtained when phloroglucinol and resorcinol were reacted and yield the same conclusions regarding the influence that steric factors and nucleophilicity of the phenolic rings have on the condensation reactions.

***o*- or *p*-Hydroxybenzyl Alcohol with Phloroglucinol and (+)-Catechin.** As before, the *p*-hydroxybenzyl alcohol was more reactive than the *o*-isomer with the former being completely condensed before 2 hours of reaction time elapsed, while a small amount of the *o*-hydroxybenzyl alcohol remained unreacted after 6 hours at 100 °C and pH 3.0. Both hydroxybenzyl alcohols reacted much more readily with phloroglucinol early in the reaction, but when condensation was complete, only slightly more condensation had occurred on phloroglucinol than on (+)-catechin - 55% condensation on phloroglucinol with *p*-hydroxybenzyl alcohol and 51% condensation on phloroglucinol with *o*-hydroxybenzyl alcohol. Since the number of substitution sites and ring reactivity favor condensation with phloroglucinol, steric factors apparently have some influence on product ratio.

## Conclusions

A comparison of the <sup>1</sup>H- and <sup>13</sup>C-NMR data for the reactions of *o*- and *p*-hydroxybenzyl alcohols with resorcinol, phloroglucinol, and (+)-catechin shows no significant difference in overall rates of condensation dependent on the structure of the phenol. This suggests that it is the formation of the quinone methide/carbocation from the benzyl alcohol that determines rate and not the attack on the aromatic ring. Thus, the nucleophilicity of the phenol does not significantly affect the rate of reaction. However, the nucleophilicity of the phenol is significant in determining the rate at which the quinone methide/carbocation condenses with the ring and thus influences product ratios when nucleophiles compete for the same electrophile.

Generally, there is substantial selectivity in these condensation reactions for the *p*-hydroxybenzyl alcohol. Earlier work (5,6) had shown that the *o*-isomer reacted preferentially at the C-8 of (+)-catechin, whereas, there was little regioselectivity in reactions with the *p*-isomer. One might suspect that phloroglucinol and (+)-catechin would preferentially react with the *p*-isomer because of less steric hindrance. The results support that, but they also show that resorcinol exhibits this same preference for reaction with the *p*-isomer. Because of the dominance of the *p*-isomer in these reactions, there is little regioselectivity in



the condensation at the C-6 or C-8 positions of (+)-catechin. When phenolic nucleophiles compete for the same electrophile, steric factors resulting from differing hydroxylation patterns apparently do influence the product ratio, but that influence is minor compared to the effect the hydroxylation pattern has on the nucleophilicity of the phenols.

In addition to the effect pH has on the overall reaction rate, it is also important to note the effect of pH on rearrangement reactions of (+)-catechin. At alkaline pH, these secondary rearrangement reactions dominate. Epimerization of (+)-catechin to (+)-epicatechin is a prominent reaction at pH 9.0. This is not serious in terms of adhesive formulation because it does not alter the reactivity of the aromatic nucleus toward condensation with benzyl alcohols. However, in reactions at pH 10.0 or 11.0, the intramolecular rearrangement to catechinic acid dominates and results in loss of the phloroglucinol functionality.

If polymeric procyanidins extractable from conifer tree barks are to be used in adhesive formulations requiring condensation with phenol-formaldehyde prepolymers, these reactions must be performed at acidic pH conditions, and because of solubility limitations, this will probably require the use of sulfonate derivatives.

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# Chapter 15

## Tannin-Based Adhesives for Finger-Jointing Wood

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Recent advances in formulating adhesives using tannin sulfonates from conifer bark suggest that these extracts can substitute for half the resorcinol now in general use in end-jointing adhesives. Tannin sulfonates used as one component of a honeymoon system have good potential for materially reducing adhesive costs. The tannin extracts were obtained from southern pine bark by digestion of bark at 100 °C with an aqueous solution of 4.0% sodium sulfite and 0.4% sodium carbonate based on dry bark weight. These extracts were used as 50% substitutes for PRF (phenol-resorcinol-formaldehyde) adhesives in bonding of structural end-joints by conventional honeymoon gluing. Lodgepole pine or Douglas-fir end-joints with exterior structural quality were obtained using tannin sulfonate plus sodium hydroxide solution as component A and phenol-resorcinol resin plus paraformaldehyde solution as component B. Approximately 5 to 10 minutes at ambient temperature was required to develop sufficient strength to permit gentle handling (500 psi), and about 20 minutes was required for the tensile strength to build to 50% of ultimate bond strength. Several adhesive formulations gave ultimate tensile strength values exceeding 5,000 psi when tested dry, after vacuum-pressure water soak, or after 2 hours of immersion in boiling water.

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Declining tree quality has increased the use of adhesives in the manufacture of large, strong, structural materials from wood. Because laminated beams are produced in lengths up to 150 feet, it is necessary to end-joint lumber to provide plies up to that length with gluebonds that do not fail when exposed to moisture over longterm loading conditions. This is especially critical for the plies that will be under tensile stress for the lifetime of the structural beam. Industry practice in North America is to fabricate end-jointed plies using resorcinol-formaldehyde or melamine-urea-formaldehyde resins and cure the bonds using radio-frequency.

In South Africa, however, end-jointed lumber for laminated beam manufacture is generally bonded with adhesives containing wattle tannins that are formulated in a "honeymoon" system (1-3). Pizzi and coworkers (2) have described three honeymoon systems for cold-setting end-jointing adhesives where A:B components are PRF:PRF, PRF:TRF and PRF:tannin extract. The PRF resins are conventional phenol-resorcinol-formaldehyde resins, the TRF is a tannin-resorcinol-formaldehyde resin and tannin extracts are obtained from wattle bark. The PRF/wattle tannin system has been used commercially in South Africa since the middle of 1985. One system developed by Pizzi employs a sodium hydroxide extract from pine bark (2). Our experience in working with extracts from the bark of southern pines suggests that condensed tannins of the procyanidin type, as found in extracts from bark of pine trees, are labile to alkaline rearrangement reactions that lead to substantial reductions in reactivity with aldehydes (4,5). Therefore, we have attempted to minimize the exposure of tannins to alkaline conditions in formulating cold-setting adhesives.

Because of differences in the structure and molecular weight of wattle and conifer bark tannins (6,7), our approach to formulation of end-jointing adhesives using pine bark extracts has been different from that of Pizzi and coworkers (2). Recent advances in the formulation of cold-setting adhesives using tannin sulfonates from southern pine bark as substitutes for 50% of the phenol-resorcinol-formaldehyde resin (8) have suggested that fast-curing, face-laminating adhesives could be formulated in either mixed adhesives or honeymoon systems. The tannin sulfonate derivative (9) was simply produced in the process of extraction of finely ground bark with 4.0% sodium sulfite and 0.4% sodium carbonate on the basis of bark dry weight at 100 °C for 2-3 hours. Sulfonation greatly reduces the extract viscosity and increases water-solubility but, because the sulfonic acid functions in these derivatives are very good leaving groups (10), condensation products with formaldehyde at alkaline pH are not soluble in water (8).

Although preliminary studies suggest that face-laminations can be obtained using adhesives made from condensed tannins that pass the standards of the American Institute of Timber Construction (8), less is known about how to formulate adhesives using these materials for end-jointing of wood. This study, funded by the USDA Small Business Innovation Research Program, was undertaken to develop adhesive formulations containing 50% of sulfite extracts obtained from the bark of southern pine trees and demonstrate their use in

end-jointing of lumber. Additional details are provided in a final report to Grant No. 86-SBIR-8-0-126 (11).

If this method proves to be commercially feasible, a renewable and abundant waste product of forest products manufacture could replace expensive petrochemicals. Additionally, use of an inexpensive waste product from processing of forest products could materially reduce adhesive costs and expand opportunities for manufacture of structural materials from low-quality wood. This benefit is particularly important since the difficulty in producing large, strong, structural members from timber resources of declining quality is growing exponentially with time. The cost-benefit ratios of replacing PRF resins with extracts from conifer barks are, therefore, quite favorable in a honeymoon system.

### Experimental Methodology

**Adhesives.** A description of the honeymoon system of wood gluing was first published in 1974 (1). It is, in principle, a system in which two different adhesive compositions are applied to the two surfaces to be mated. Since wood adhesives penetrate the wood surface (and have to do so in order to provide a good bond), it is important that both individual components of the system ultimately cure to form a solid durable polymer. This can be achieved either by designing the components such that each will fully cure by itself or by providing ingredients in the two components that react after mutual diffusion takes place; ultimately, all layers of the glue line must reach the fully cured state.

In order to establish control values for the adhesives formulated using tannins, the initial work was done with phenol-resorcinol-formaldehyde (PRF) or resorcinol-formaldehyde (RF) resins on both surfaces, but modified for the honeymoon principle. The PRF resin chosen for this work was Borden's resin LT-75 with Borden's hardener FM-260. The RF resin used for a comparison was Chembond's RF-900. These resins have been used for wood gluing in the United States for more than two decades, especially for the manufacture of structural laminated timbers.

The pilot plant-scale extract used in this study was made from bark obtained from old trees decked at a plywood plant. When 4.0% sodium sulfite and 0.4% sodium carbonate (on dry bark weight basis) were used to extract this finely ground bark for 2 hours at 100 °C, extract yields were only 18% of dry bark weight. The extract had a Stiasny polyphenol number of only 0.52; it gave a total of 18% sugars after hydrolysis, and contained 5.8% sodium and 3.8% sulfur. When bark from pulpwood-aged trees is extracted under similar conditions, extract yields typically vary between 20 and 24% and Stiasny polyphenol numbers are typically 0.60 to 0.75. The extract used for this work was also dried by a hot-pan evaporation method rather than being spray dried. So, the extract used represented a near "worst-case" example.

The tannin side (component A) was made alkaline by addition of NaOH at various levels (Table I). No formaldehyde source was added to the tannin

solution. Otherwise, the tannin component, under highly alkaline conditions, would have reacted with the paraformaldehyde very quickly and rendered the tannin component unuseable within just a few seconds. The viscosity (and, therefore, the penetration) of component A was adjusted by addition of various amounts of Methocel. The entire amount of paraformaldehyde was added to the near-neutral PRF resin side. The phenol-resorcinol-formaldehyde resin used as the PRF component B of the system was Borden's LT-75 resin with Borden's FM-260 hardener with additional paraformaldehyde.

**Test Unit for Tensile Strength Development.** It has been, and still is, customary to judge the suitability of adhesives for end-joint applications on their performance under standard block-shear test conditions (ASTM 2559). For decades, the development work on end-joint adhesives was done using this test procedure. The need to approach the development of structural end-joint adhesives more directly led to the concept, design, and building of a test unit specifically for finger-joint adhesive evaluation. The unit receives two profiled members, registers their position, pulls the dry joint apart, swings the two profiled ends free for adhesive application, swings the members back into the mating position, compresses the joint under a specified load, and allows for variable compression times. It then pulls the joint in tension while measuring the tensile force needed to break the joint.

Table I. Adhesive Formulations Using Tannins in Component A

Resin	Component A				Component B		
	Tannin	Water	NaOH	Methocel	LT-75	FM-260	Para
D	45.0	55.0	10.59	0.00	40.0	4.0	8.0
F-A	42.0	58.0	10.64	0.05	40.0	4.0	8.0
F-B	42.0	58.0	10.50	0.10	40.0	4.0	8.0
F-C	42.0	58.0	10.50	0.20	40.0	4.0	8.0
F-D	44.0	56.6	7.58	0.23	40.0	4.0	8.0
F-E	44.0	56.3	5.00	0.21	40.0	4.0	8.0
F-F	44.0	56.0	2.26	0.21	40.0	4.0	8.0
F-G	44.0	56.0	1.27	0.05	40.0	4.0	8.0
M-A	44.1	56.3	7.54	0.25	40.0	4.0	8.0
M-B	44.0	56.0	1.25	0.05	40.0	4.0	8.0

At the time the end-joint test unit was being built, the industry used both horizontal and vertical end-joint profiles. This question/dilemma was eliminated by designing the unit for a lumber cross-section of 1.5 x 1.5 inches. Restriction to this dimension was also necessary to keep the power requirements within reasonable limits. At present, the unit is limited to approximately 3,000 psi in tension, at which point the hydraulically-driven grips begin to slip. The unit thus allows one to determine the strength development in the joint during the

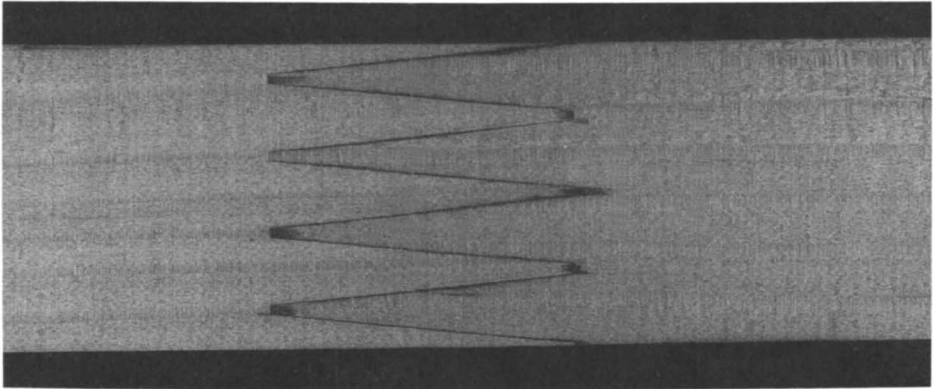
few minutes when fast-cure adhesives begin to gel and cure. It also allows one to conveniently compare the tensile strength development for different adhesives. Although the unit is coupled with a radio-frequency (RF) generator, for the purposes of the work reported here, the RF source was moved out of the way, and all bonding was done at ambient temperature using the honeymoon system. Gluing experiments were made on both lodgepole pine and Douglas-fir.

**Selection of the End-Joint Profile.** Because the purpose of this work was to determine whether a portion of the phenol-resorcinol-formaldehyde adhesive used in structural end-joints could be replaced by tannin extracts from southern pine bark, it was necessary to use a structural end-joint profile design. The profile chosen was the design used by many U.S. plants for the manufacture of structural end-joints. A reproduction in natural size with a drawing showing the exact dimensions is shown in Figure 1.

**Testing of Bond Quality.** In most cases, each honeymoon adhesive formulation, consisting of a tannin-sodium hydroxide component A on one side and a PRF-paraformaldehyde component B on the other side, was evaluated by bonding parallel laminates of 5.5 x 7.5 inches as well as a number of end-joints. For the parallel laminates, vertical grain Douglas-fir was used (1 x 6 inch nominal). After being glued and reconditioned, each laminate was cut to yield six shear block specimens of 1.5 x 2 inches in glueline dimension (ASTM 2559). Two blocks were sheared dry (AITC 107), two were sheared after being subjected to vacuum-pressure water soak cycle (AITC 110), and two were sheared after 2 hours of immersion in boiling water.

End-joint strength development was measured using the test unit described above. The specimens were 1.5- x 1.5-inch finger-profiled blanks of either lodgepole pine or Douglas-fir. Some of the end-joints were pulled in tension in the test machine immediately after the prescribed press time had elapsed, whereas, others were removed from the test unit without destruction of the joint. The latter were allowed to cure for several days at room temperature and edge-trimmed to 1-inch width to remove some of the edge effect. They were then cut from the other face into 0.25-inch thickness strips. Each end-joint gave four specimens for testing after full cure. These were tested to destruction in tension using an Instron testing machine. In each case, one of the four strips was tested dry (AITC 107), two were tested after exposure to the normal vacuum-pressure water immersion cycle (AITC 110), and one was tested in tension after having been submersed in boiling water for 2 hours.

The shear and tension tests after submersion of specimens in boiling water for 2 hours are not tests accepted or specified by any regulatory or testing society or agency. Gluing experience over many years, however, has shown that important conclusions with respect to reasons for adhesive failure, as well as important pointers for adhesive development, can be obtained by careful interpretation of the comparison of test results after boil with those from dry and vacuum-pressure testing.



**ACTUAL END-JOINT**

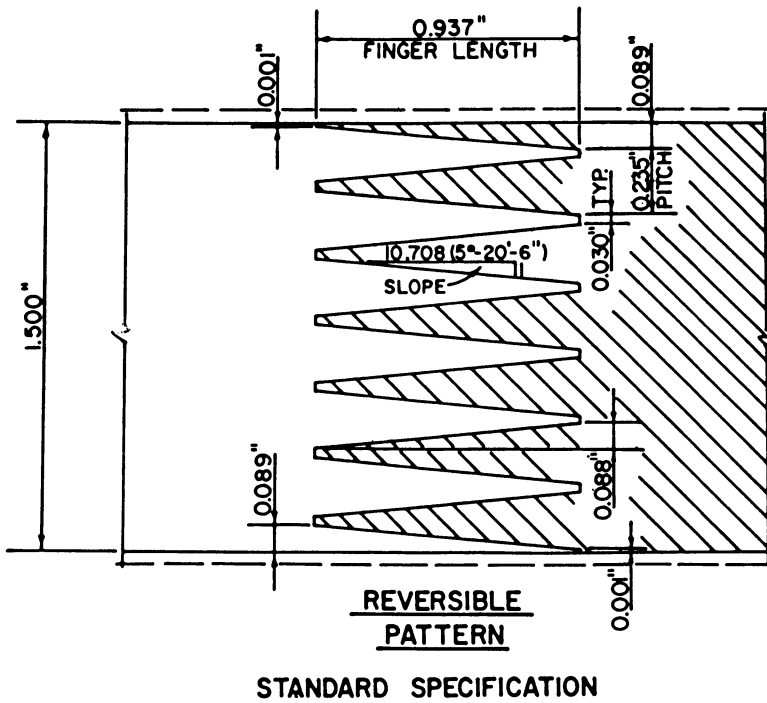


Figure 1. Specifications for structural end-joint design.



## Results and Discussion

**Tensile Strength Development in RF/RF and PRF/PRF Honeymoon Systems.** For comparison, commercially available resorcinol-formaldehyde (Chembond's RF-900) and phenol-resorcinol-formaldehyde (Borden's LT-75 with FM-260 hardener) resins were modified for use in the honeymoon system (11). The RF/RF system was made by applying RF-900 with the pH adjusted to 14 on one side (component A) and the RF-900 with paraformaldehyde (component B) on the other side. The PRF/PRF system was modified by adjusting the resin pH to 14 (100 grams of LT-75 plus 20 grams of sodium hydroxide pellets) for component A and doubling the formaldehyde source (100 grams of LT-75 plus 20 grams of paraformaldehyde) for component B.

When the components A and B were applied separately to the mating surfaces of the end-joint profiles, the tensile strength of the joints increased at very similar rates, advancing to a level of about 3,000 psi in 20 to 30 minutes at ambient temperature in both resin systems (Figure 2). Because of the negligible difference in tensile strength development and the comparatively low cost of the PRF resin, the Borden LT-75 resin was used in the component B in all further testing.

**Tensile Strength Development in Tannin/PRF Honeymoon Adhesives.** Plots of the tensile strength against the natural log of press time show two distinct reaction rates (Figure 3) that can be interpreted as a first stage of paraformaldehyde dissociation and mixing followed by a second stage where polymerization had advanced sufficiently for rapid development of bond strength. In comparison with a PRF/PRF adhesive (Borden's LT-75), the tannin sulfonate/PRF honeymoon adhesive (D-Series) had a slightly slower first-stage reaction rate. The rates of reaction in the second stage for the PRF/PRF and tannin sulfonate/PRF adhesives were very similar. Between 10 and 14 minutes at ambient temperature is required for the first stage of the reaction. A further 10 to 15 minutes is required for the polymerization stage to advance to the development of a tensile strength equal to 50% of the ultimate bond strength. The rate of mixing and paraformaldehyde dissociation would be expected to be increased by increasing the amount of sodium hydroxide in the adhesive. However, strength values in the early stages of cure were too variable to establish this relationship. Addition of small amounts of Methocel did not alter the rate of strength development.

In adhesives formulated in the F- and M-Series (Table I), approximately 5 to 10 minutes at ambient temperature was required to reach an end-joint tensile strength of 500 psi, a value deemed adequate to permit gentle handling of the end-jointed members. Between 15 and 20 minutes at ambient temperature was required to reach a tensile strength of 1,500 psi (11).

**Ultimate Tensile Strength.** The tensile strengths of fully cured end-joints in lodgepole pine or Douglas-fir when tested dry after vacuum-pressure water

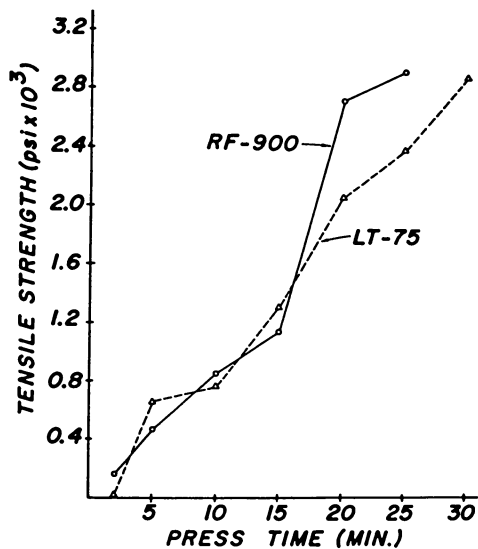


Figure 2. Comparison of the rate of tensile strength development in RF/RF and PRF/PRF honeymoon adhesive systems.

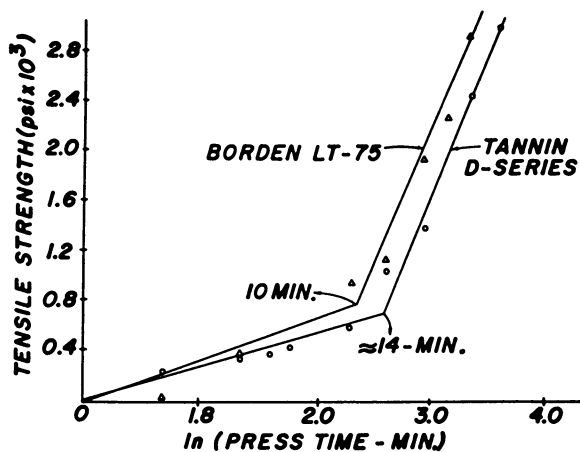


Figure 3. Comparison of the rate of tensile strength development in PRF/PRF and tannin/PRF honeymoon adhesive systems.

soak and after 2 hours in boiling water were very high, equal to or exceeding those commonly accepted by industry. Many of the adhesives examined gave bonds that had tensile strength values in excess of 5,000 psi even after vacuum-pressure water soak or submersion in boiling water for 2 hours (Tables II and III).

Table II. Gluebond Quality of Lodgepole Pine End-joint and Douglas-fir Parallel Laminates Obtained with the F-Series Adhesive Formulations

Resin	Strength or Wood Fail (WF)	End-joint			Parallel Laminate		
		Dry	VPS	Boil	Dry	VPS	Boil
F-A	psi	4830	3390	3371	1830	1068	914
	kPa x 10 <sup>3</sup>	33.3	26.8	23.3	12.4	7.4	6.3
	% WF	97	74	84	65	27	73
F-B	psi	6051	5107	4730	2029	933	1945
	kPa x 10 <sup>3</sup>	41.8	35.2	32.6	14.0	6.4	13.4
	% WF	93	79	86	75	6	26
F-C	psi	5841	4569	4301			
	kPa x 10 <sup>3</sup>	40.3	31.5	29.7			
	% WF	100	87	76			
F-D	psi	6878	5750	5353	1825	1008	957
	kPa x 10 <sup>3</sup>	47.5	39.7	36.9	12.6	7.0	6.6
	% WF	90	81	55	91	20	86
F-E	psi	4942	4663	4032	1976	1253	1090
	kPa x 10 <sup>3</sup>	34.1	32.2	28.3	13.6	8.6	7.5
	% WF	100	89	78	90	78	86
F-F	psi	5265	4384	4152	1699	1169	1014
	kPa x 10 <sup>3</sup>	36.3	30.3	28.6	11.7	8.1	7.0
	% WF	98	81	87	74	78	78
F-G	psi	5609	5054	5469	1662	1096	992
	kPa x 10 <sup>3</sup>	38.7	34.9	37.7	11.5	7.6	6.8
	% WF	93	77	93	79	67	71

Although not normally measured and not a requirement of an industry standard, the high wood failure values of the end-joints obtained with these adhesives are further evidence of water-resistant bonds. It was difficult to discern differ-

ences in quality of the adhesive formulations because most of the variation observed in ultimate tensile strength was due to differences in substrate strength rather than bond quality as evidenced by the high degree of wood failure in these end-joints. Adhesive formulations providing good bonds in finger-joint application did not necessarily give satisfactory bonds when used to bond parallel laminates. Part of this is attributable to differences in requirements for bonding end-joints and face-laminations. Another reason may rest on the importance of mixing. When end-joints are mated, there is always some physical mixing as one face slips past the other. When pressing parallel laminates, there is less control over movement between the plies unless this is done as part of the panel layup process.

Table III. Gluebond Quality of Douglas-fir End-joints and Douglas-fir Parallel Laminates Obtained with the M-Series Adhesive Formulations

Resin	Strength or Wood Fail (WF)	End-joint			Parallel Laminate		
		Dry	VPS	Boil	Dry	VPS	Boil
M-A-1	psi	6342	5174	4768	1689	814	679
	kPa x 10 <sup>3</sup>	43.7	35.7	32.9	11.6	5.6	4.7
	% WF	96	57	84	96	47	86
M-A-2	psi	7127	5268	5466			
	kPa x 10 <sup>3</sup>	49.2	36.4	37.7			
	% WF	92	37	74			
M-B-1	psi	5425	4145	4336	1837	956	824
	kPa x 10 <sup>3</sup>	37.4	28.6	29.9	12.7	6.6	5.7
	% WF	90	79	82	73	71	85
M-B-2	psi	5704	4698	4616			
	kPa x 10 <sup>3</sup>	39.4	32.4	31.9			
	% WF	90	84	81			

Ultimate bond strength of the end-joints was not influenced by press time providing that 1) full joint consolidation is achieved and 2) the joint is not disturbed by transport of the assembly during the gel and cure period (Figure 4). For plant applications of this system, press times of less than 1 minute should be explored, including the use of several levels of end pressure. At this time, it appears that the press time can be limited to the minimum time necessary for full joint mating. In bonding Douglas-fir end-joints with the M-Series adhesives,

an increase in mating pressure from 440 to 660 psi did not change the ultimate tensile strength values.

During the spreading of the tannin solution onto end-joint profiles as well as on the parallel laminates, it was soon noticed that the tannin solution behaved more like a solution of a low molecular weight material rather than a typical adhesive polymer. Even when applied as 45% solids content solutions, the tannin component A had a tendency to penetrate rapidly, especially into the end grain. In formulations containing 7.6 to 10.6 parts of sodium hydroxide added to component A, this problem was particularly noticeable, so a thickener was added. Both dry and wet tensile strengths were improved by addition of Methocel in amounts of about 0.1 to 0.2 parts per 100 parts of the component A (Figure 5). In this experiment, Dow's Methocel F4M was used. For commercial application, other viscosity builders more suitable for use at high pH should be explored.

Considering all the data obtained in the F-Series formulations, there was not a consistent change in ultimate tensile strength or resistance to degradation by exposure to water when the sodium hydroxide content of the component A was varied over wide ranges (Figure 6). The adhesive formulated with 7.5 parts of sodium hydroxide in the component A gave higher tensile strength values than that with 1.25 parts of sodium hydroxide in bonding of Douglas-fir end-joints (Table III). Some caution must be exercised in interpreting this result, since a high proportion of these end-joints had wood failure values in the 70 to 90 percent range. As with the results of the studies of lodgepole pine, bond strength values were primarily related to differences in substrate strength rather than the adhesive bonding capability.

## Conclusions

Extracts from southern pine bark obtained by extracting finely ground bark with 4.0% sodium sulfite and 0.4% sodium carbonate at 100 °C can be used to replace 50% of the PRF resin in a honeymoon system for bonding exterior quality structural end-joints in lodgepole pine or Douglas-fir.

A number of tannin sulfonate/PRF honeymoon adhesive systems gave bonds in lodgepole pine and Douglas-fir finger-joints with ultimate tensile strength values above 5,000 psi even after being subjected to a vacuum-pressure water soak (AITC 110) or 2 hours of boiling. The excellent water resistance of these gluelines was further demonstrated by the high wood failure values in the range of 70% to 90% after vacuum-pressure water soak.

Use of southern pine bark extracts as 50% of the reactive phenolics in end-jointing adhesives applied in a honeymoon system has good commercial potential. With proper plant layout and design, the installation, operation, and maintenance of radio-frequency units and their resulting high costs can be avoided.

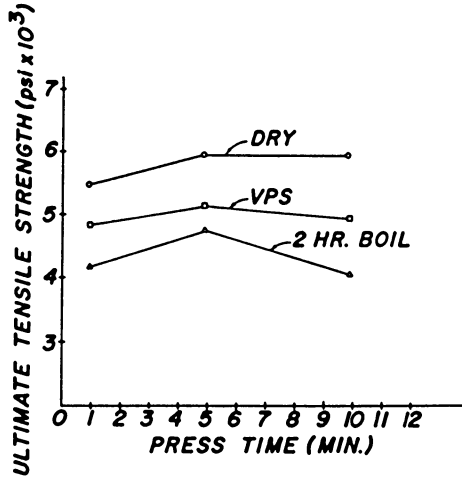


Figure 4. Effect of press time on ultimate bond strength.

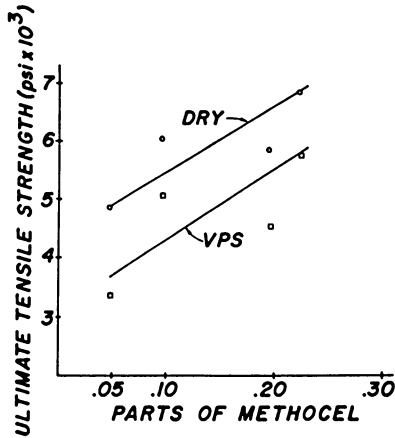


Figure 5. Effect of Methocel content on ultimate bond strength.

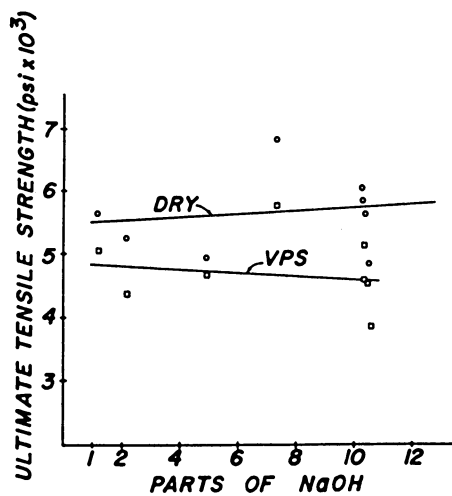


Figure 6. Effect of sodium hydroxide content on ultimate bond strength.

## Acknowledgments

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# Chapter 16

## Activation of Some Condensed Tannins via Facile Ring Isomerizations Potential Adhesive Applications

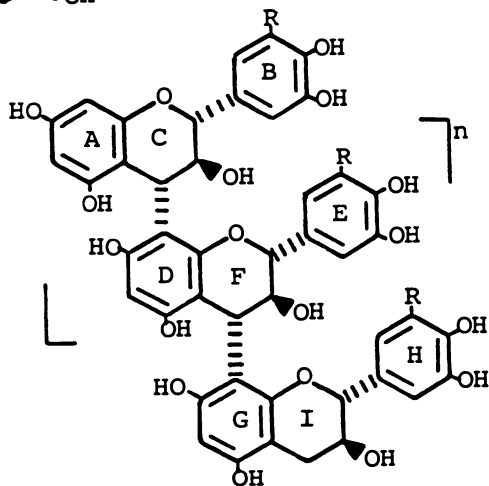
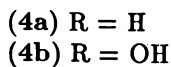
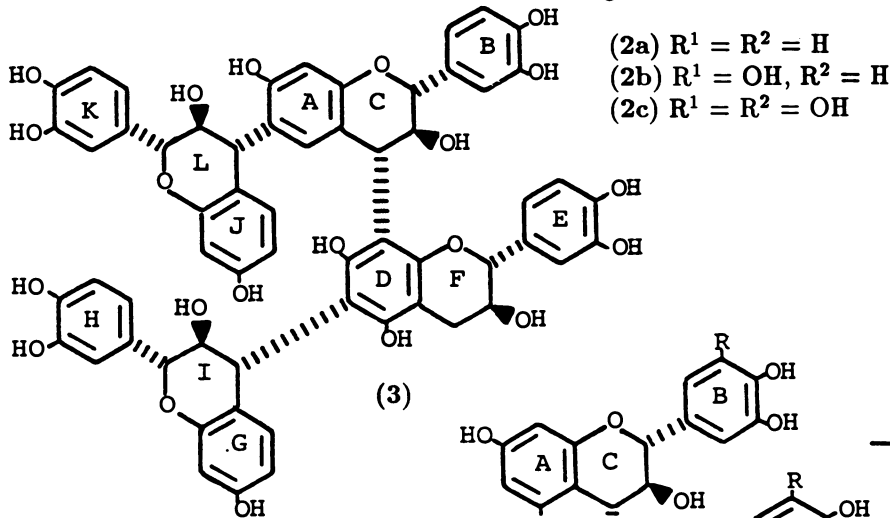
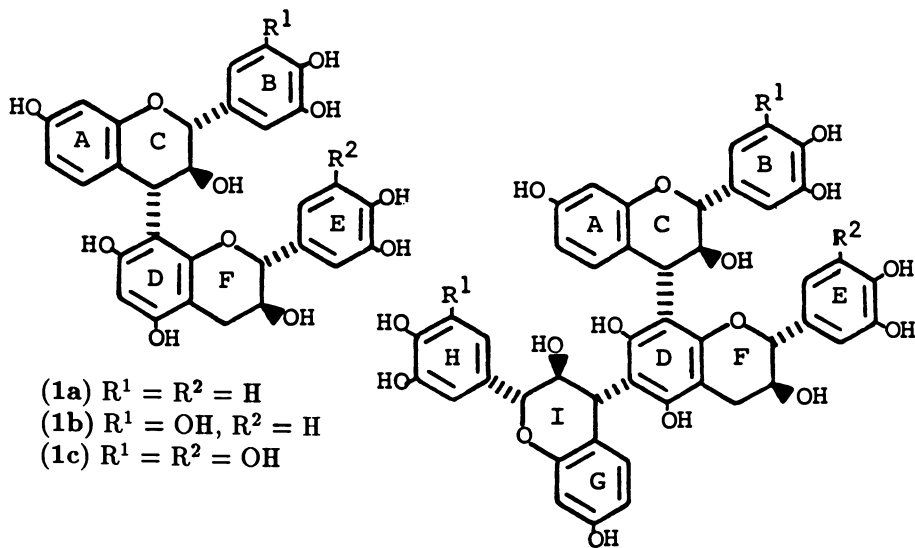
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[4,8]-2,3-*trans*-3,4-*trans*(-)-Robinetinidol-2,3-*trans*(+)-catechin (**1b**) and its (-)-fisetinidol homologue (**1a**) as prototypes of mimosa and quebracho tannins, respectively, are to a varying degree subject to positional isomerization) in NaHCO<sub>3</sub> - Na<sub>2</sub>CO<sub>3</sub> buffer under nitrogen, with "liberation" of reactive nucleophilic resorcinol units to form a range of bifunctional phlobatannins. The potential of this efficient method of inducing strong bifunctionality is discussed in relation to the cold-set adhesive application of these commercially available extracts.

The use of commercial mimosa extract in adhesive applications is firmly established in South Africa, and it is in fact completely dominant in particleboard and plywood manufacture (1). Similar formulations are currently also in use in Australia and elsewhere, while fortification with resorcinol permits application of mimosa extract in fingerjointing and beam lamination (2).

Chemical differences are apparent between the condensed tannins that constitute upward of 70% of mimosa and quebracho extracts on the one hand and those commonly encountered elsewhere outside the respective Leguminosae and Anacardiaceae. These devolve mainly on subtle differences in functionality affecting both the degree of condensation of the tannins and their reactivity, and hence their physical behavior during condensation with formaldehyde. This is obvious when comparing prototype dimeric, trimeric, and tetrameric oligoflavanoid units (1) to (3) from mimosa (3,4,5) and quebracho (6,7) extracts with their procyanidin homologues (4) present, for example, in the barks of western



hemlock, Douglas-fir, southern pine, and redwood from North America. Salient differences between these two groups may be summarized as follows:

1) Prototypes (1) to (3) possess resorcinol-type flavanyl units attached to (+)-catechin or (+)-gallocatechin, whereas, procyanidin prototypes (4a) are uniformly based on phloroglucinol-type flavanyl units.

2) Due to the greater predisposition of their electrophilic flavanyl precursors (leucocyanidins) to condensation (8, 9), the procyanidin tannin mixtures [(4a)  $n = 0$  to 10] exhibit general emphasis on the more highly condensed units, whereas, dimeric and trimeric prototypes (1) and (2), respectively, are prominent if not dominant among profisetinidins ( $R^1 = R^2 = H$ ) and prorobinetinidins ( $R^1 = H$ ,  $R^2 = H$  or  $OH$ ). Procyanidins may, therefore, be generally considered to occur naturally in more highly condensed mixtures.

3) Procyanidin oligomers [(4a)  $n = 0$  to 10] apparently possess mainly "linear" conformations, compared with the proven "angularity" of profisetinidin and prorobinetinidin analogues (2) and (3).

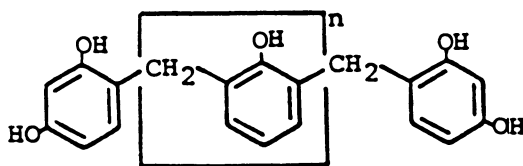
4) Probably mainly as the result of a more uniform mass distribution and with considerable emphasis on lower mass units, prorobinetinidins and profisetinidins (1) to (3) occur in mixtures that are more readily water-soluble than those of procyanidins (4a) and prodelphinidins (4b). However, oxidative effects as the result of weathering of barks may also play a role in reducing the solubility of the latter group.

Despite the aforementioned differences, both tannin types exhibit levels of reactivity with formaldehyde under neutral or mildly alkaline conditions which are intermediate between those of resorcinol and phenol or phenol-resorcinol-formaldehyde (PRF) or phenol-formaldehyde (PF) adhesives. This follows logically from the more reactive phenolic units present in each type of tannin i.e., predominant resorcinol monoether A, G, and J units, for example, in the oligoflavanoids (1) to (3), [the phloroglucinol monoether D-ring of (1) being an exception], and also the exclusively phloroglucinol monoether A, D and G-rings of procyanidins/prodelphinidins of type (4), when both types are compared with the highly reactive resorcinol or resorcinol "terminal" units in PRF adhesives on the one hand and the relatively unreactive phenol or phenol units in PF resin on the other. The last mentioned require ionization (high pH) to promote reactivity.

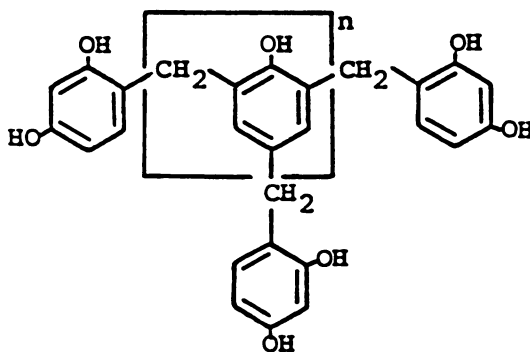
The intermediate order of reactivity of unmodified mimosa and quebracho tannins makes them unsuitable for cold-set applications at neutral pH. However, procyanidins offer the prospect of higher reactivity compatible with that of resorcinol or PRF adhesives with formaldehyde. Unfortunately, low solubility at neutral pH coupled with (and as a function of) their high number average mass leads to premature gelling phenomena. Structural rigidity of these oligomers would undoubtedly also limit the desirable degree of crosslinking that can occur, resulting in brittleness.

In cold-set applications, the cost of resorcinol as a commercial commodity has led to its well-known "grafting" onto phenol-formaldehyde resols to provide

reactive terminal units as represented in the idealized PRF formulae (5) and (6). Highly reactive bifunctionality (5) and polyfunctionality (6) are, accordingly, provided under neutral cold-set conditions during final crosslinking with formaldehyde. With this type of application in mind, attempts were made to liberate resorcinol units in mimosa and quebracho prototypes (1) and (2) by fission of the heterocyclic ether rings C and I, while accommodating recyclization elsewhere.



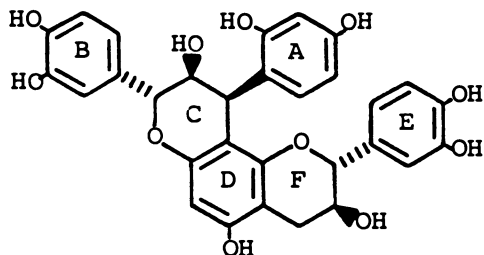
(5)



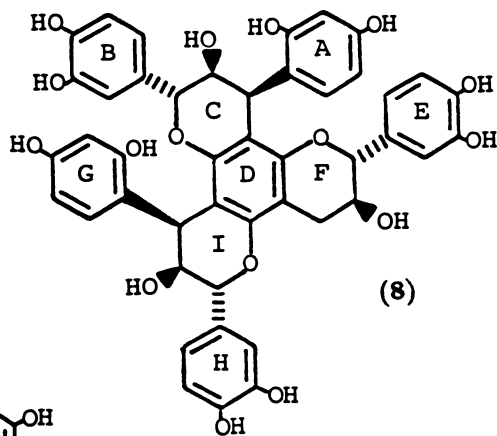
(6)

Inspiration for our successful attempts at effecting the release of resorcinol came from our initial recognition (10) of a new class of ring isomerized condensed tannins, termed phlobatannins, (11) in the heartwoods of *Colophospermum mopane* (the African mopane tree) and *Guibourtia coleosperma* (false mopane). Both African species belong to the Anacardiaceae as do *Schinopsis* spp. (quebracho) from South America. In these African species, the ring isomerized compounds (7) and (8) and also the partially ring isomerized products (9) and (10) occur in association with their presumed precursors (1a) and (2a). The isomeric nature of the phlobatannins with their putative precursors made structural recognition of the former by nuclear magnetic resonance spectroscopy difficult, although their spectra are significantly devoid of rotational isomerism. In order to establish the "liberation" of the resorcinol rings in phlobatannins, it

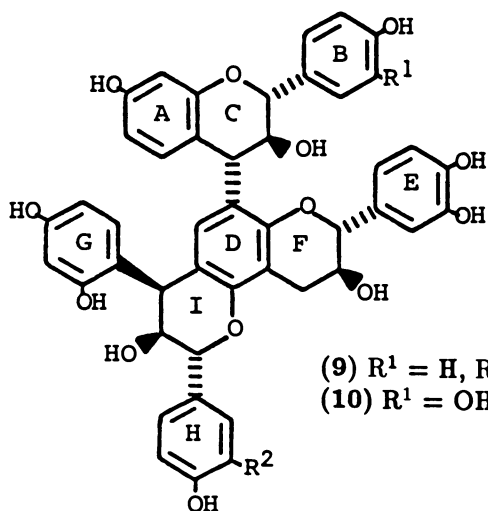
was, therefore, necessary to resort to nuclear Overhauser effect (n.O.e) difference spectroscopy of their methyl ether acetates (10) as shown in Figure 1.



(7)



(8)

(9)  $R^1 = H, R^2 = OH$ (10)  $R^1 = OH, R^2 = H$ 

[Nuclear Overhauser effect difference spectroscopy is of great significance in the elucidation of structures. If, for example, the Boltzmann distribution (ratio of nuclear spins) of one type of proton is disrupted by the application of a second field,  $H_2$ , that is strong enough to saturate the system partially, but not strong enough to cause tickling or decoupling effects. Should the saturated proton interact via a dipole-dipole mechanism with another proton, the second

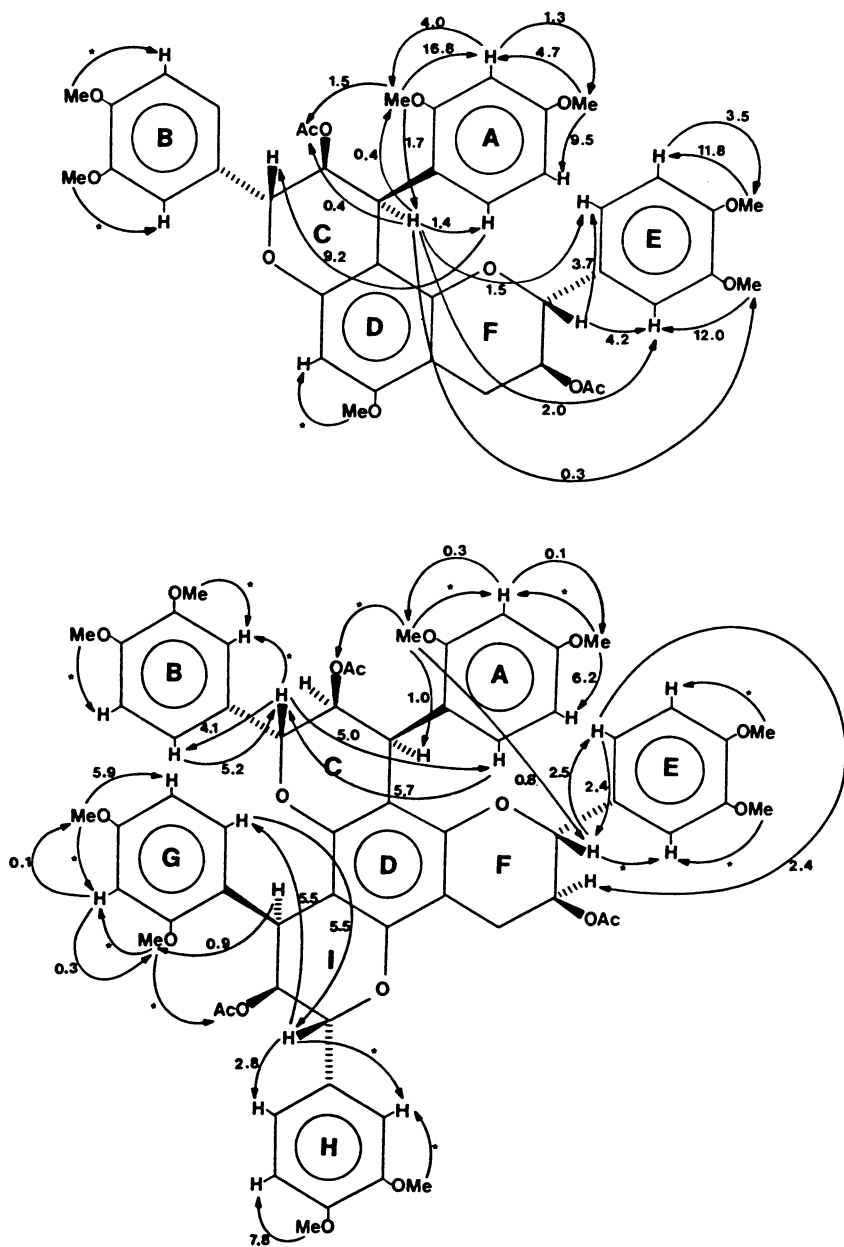
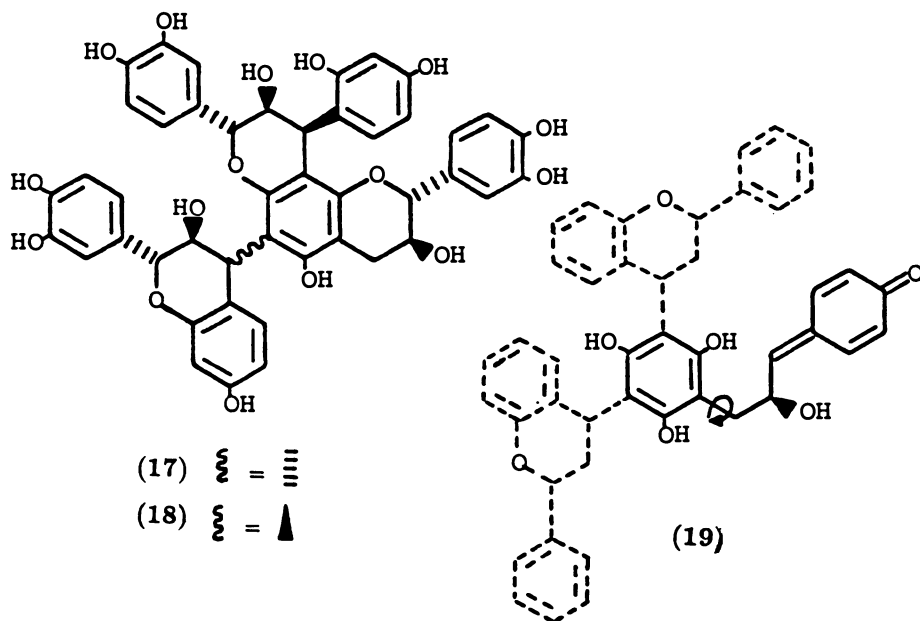


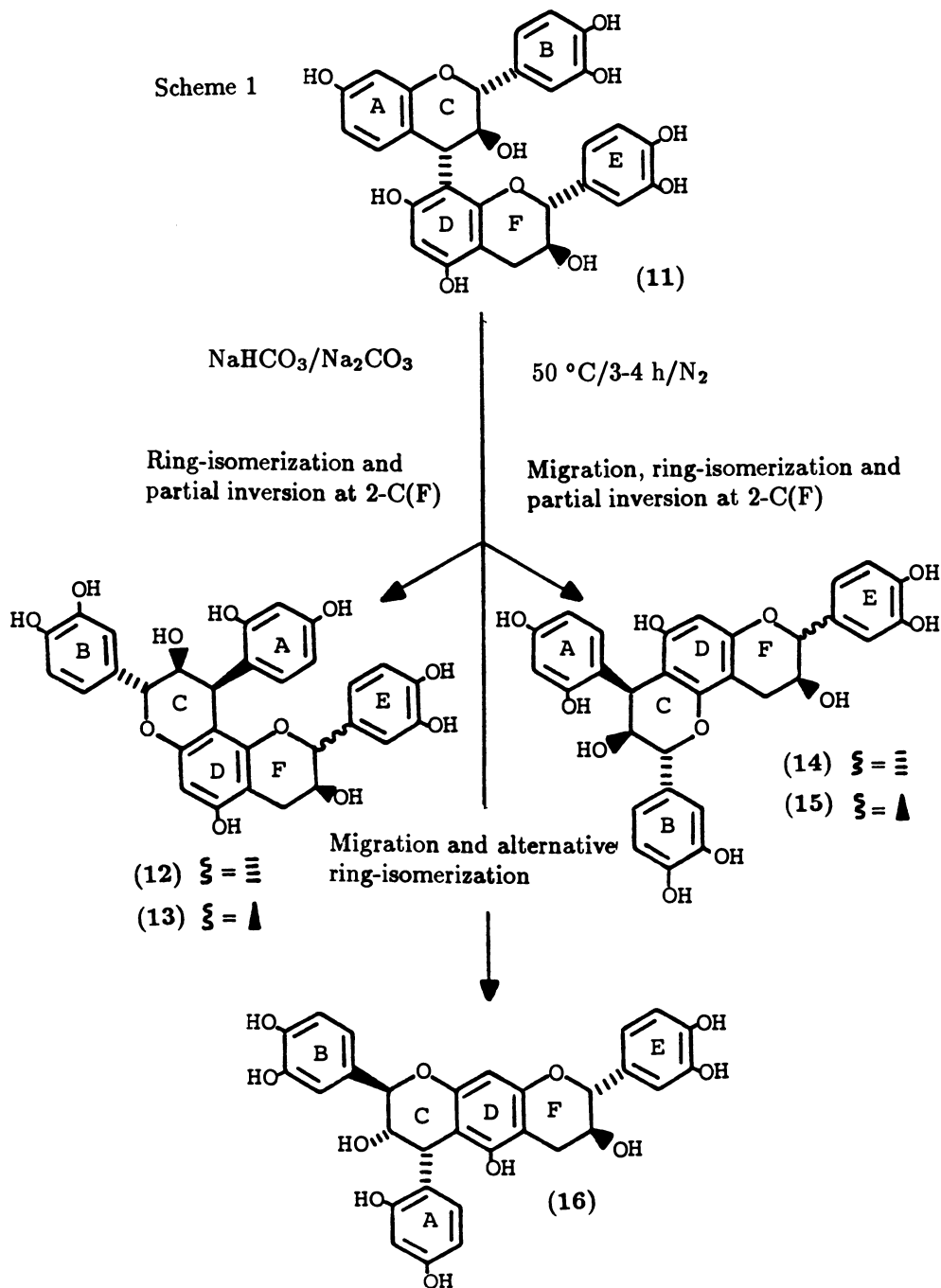
Figure 1. Percentage n.O.e. enhancements as determined for the methyl ether acetates of (7) and (8). Those marked \* are evident but cannot be calculated owing to signal overlap [cf. (12)].

proton will experience a disruption of its Boltzmann distribution and hence a change in the intensity of its resonance line. The utility in structure and conformational determination lies in the fact that dipole-dipole interactions vary inversely with the cube of the distance between the dipoles, so that information on spatial orientation of nuclei may be extracted in favorable cases. Modern NMR equipment permits direct measurement of changes in the spectrum with application of  $H_2$ , rather than the spectrum itself]. The association of protons as shown by the percentage enhancements proved the various structures and, therefore, the "liberation" of the resorcinol units in the phlobatannins and, hence, the desired bifunctionality in each instance.



Once recognized, the synthetic achievement of the isomerization process (12) proved a relatively simple matter using Freudenberg and Purrman's (19) epimerization procedure developed for the conversion of (+)-catechin into (+)-epicatechin. Applying a  $NaHCO_3 - Na_2CO_3$  buffer system at 50 °C under nitrogen for 5 hours to [4,8]-(-)-fisetinidol-(+)-catechin (11) gave (Scheme 1) the desired ring isomerization of the C-ring (12) but also epimerization of the (+)-2,3-*trans*-catechin moiety at C-2 (F-ring) to give the (+)-epicatechin isomer (13). These products were accompanied by the positional isomers (14), (15), and (16). The isomerization compounds are all bifunctional in the sense that a single highly reactive center at C-6 (D-ring) in the case of (12) and (13), or at C-8 (D-ring) for (14) to (16) of the original (+)-catechin unit survives, together with the enhanced nucleophilicity of the now "free" resorcinol A-ring in each. However, the continued dominance of the nucleophilicity of the phloroglucinol

Scheme 1





D-ring to bulky flavanyl electrophiles is demonstrated (12) by substitution of the phlobatannin (12) by the flavan-3,4-diol (+)-mollisacacidin under mildly acid conditions to give the [4,6]-(-)-fisetinidol derivatives (17) and (18). Differentiation between the entire range of biflavanoid and triflavanoid homologues was possible only via n.O.e. difference spectroscopy of their respective methyl ether acetates.

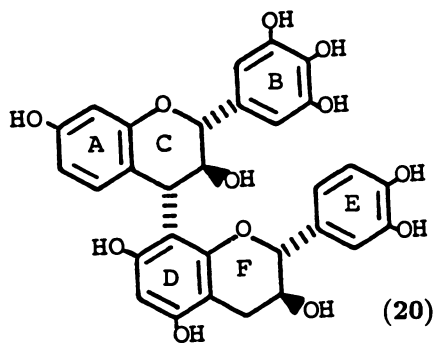
The mechanism by which ring isomerization proceeds is obvious, the driving force being the enhanced nucleophilicity of the phloroglucinol D-ring relative to the resorcinol A-ring or, better, the enhanced stability of the transition state associated with cyclization of the former. The phlobatannins (14), (15), and (16) result either via migration of the flavanyl unit or (more likely) via the quinone methide intermediate (19) (based on the E-ring), which is capable of rotation and recyclization, thereby simultaneously achieving positional and configurational isomerizations (12).

Recovery of ca. 10% of the starting material (11) under the conditions employed indicates most likely that equilibria exist between it and the various products (12) to (16). Also, maintenance of the elevated temperature (50 °C) over the relatively prolonged period (3-4 h), albeit under mildly alkaline conditions, introduces the possibility of significant side reactions such as the conversion of the (+)-catechin moiety to catechinic acid (14).

Whereas, the above describes those conditions applicable to bi- and triflavanoid profisetinidin prototypes of quebracho tannins for the formation of phlobatannins with the desired "liberation" of resorcinol units, much milder conditions were found to suffice for analogous conversions of prorobinetinidin units that predominate (4) in mimosa extract (Scheme 2). The reaction (20) → (21), (22), and (23) runs to completion at ambient temperatures (ca. 20 °C), and consequently, the composition of the phlobaphene mixture is much simpler. This is the result of enhanced electron release from the pyrogallol B-ring, thus permitting facile ring isomerization of the C-ring, and also subsequent inversion at C-2 (C-ring) of the product [(21) → (23)] under the mild conditions applied. No significant epimerization of the (+)-catechin apparently occurs. Obviously, where (+)-gallocatechin replaces (+)-catechin as in a number of mimosa oligoflavanoids (4), relative complexity similar to that illustrated in Scheme 1 may be anticipated for phlobaphenes derived from [4,8]-(-)-robinetinidol-(+)-gallocatechin and [4,6:4,8]-bis-[-(-)-robinetinidol]-(+)-gallocatechins under such mild conditions. The relative ease of these reactions is further emphasized by the observation that, under commercial conditions of hot extraction and subsequent spray-drying, a degree of complexity is introduced in mimosa extract as evident from chromatographic comparison with fresh bark extract obtained under ambient conditions. Closer examination of the commercial extract has revealed (Cronje, A.; personal communication) that a low degree of ring isomerization of the type outlined in Scheme 2 is presumably partially responsible for the increase in complexity.

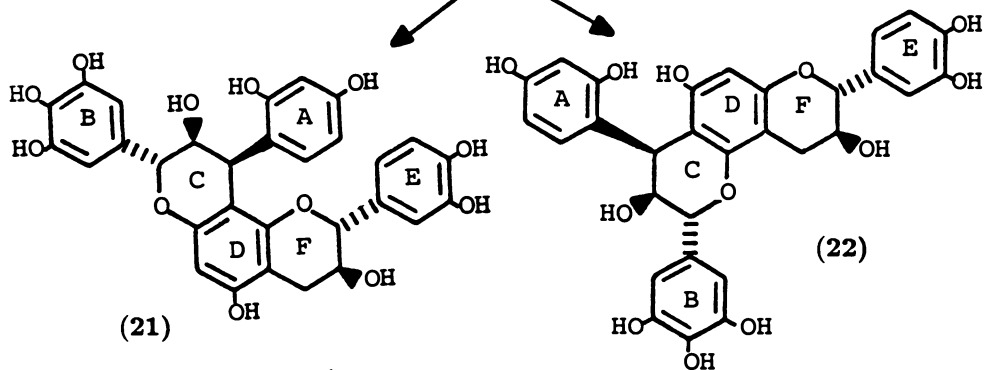
In order to assess the potential of resorcinol "release" via ring isomerization,

Scheme 2

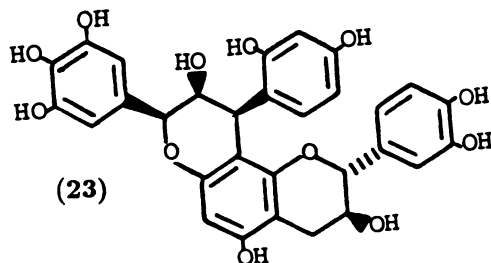

 $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$ 
 $20^\circ\text{C}/4\text{-}5\text{ h}/\text{N}_2$ 

Ring-isomerization

Migration and ring-isomerization



Inversion at 2-C(C)



the relative origins and hence extract compositions of quebracho and mimosa extracts must be considered, apart from the relative ease of ring isomerization of their phenolic components. Quebracho extract is derived from the heartwoods of *Schinopsis* spp., trees that usually reach 80-100 years of age before sufficient heartwood formation permits economic commercial exploitation. During this lengthy period of aging of the heartwood, progressive condensation occurs (15), so that in the process of extraction, a hot-water-soluble fraction is first obtained ("quebracho ordinary"), while the remaining highly condensed tannins are subjected to sulfitation in order to promote solubility and achieve complete extraction ("sulfited quebracho"). The proportion of the more highly condensed profisetinidin units in the ordinary extract and their potential for conversion via ring isomerization reactions are unknown. However, the structure of four tetrameric profisetinidin tannins from the chemically related heartwood extract of *Rhus lancea* (7), which has the composition of monomers, dimers, and trimers identical to that of quebracho extract (6) is known and also the conformation of a derivative of one of these (16). In these tetramers, the JKL profisetinidin unit at least is capable of ring isomerization. In the case of mimosa bark extract, the source of the tannins is unique in that a steady-state composition of oligoflavanoids is maintained at least up to the point of harvesting (and also beyond) in an 8-year rotation cycle. Prorobinetinidin-catechin and prorobinetinidin-galocatechin "dimers" and "trimers" (also to a limited extent profisetinidin-catechin "dimers") (3,4) constitute  $\approx 50\%$  of the extract, but the composition of higher oligomers that include procyanidins and prodelfphinidins is unknown.

## Conclusions

Prorobinetinidins and profisetinidins representative of mimosa and quebracho extracts are subject to facile ring isomerizations under mildly alkaline conditions. This provides the first proof of "liberation" of resorcinol units from polyflavanoids present in these tannins to give reactive bifunctional phlotatanins, analogous to the PRF resins [cf. (5,6)] commonly used in cold-set applications. An earlier claim by Pizzi and Daling (17) of resorcinol "liberation" during sulfitation is without direct structural proof. Moreover, their claimed indirect evidence of enhanced reactivity of mimosa extract in support of this notion is based exclusively on the adhesive properties of sulfited mimosa in the presence of large admixtures (27 to 50%) of resorcinol. This effect could also be ascribed to the increased accessibility of reactive sites and (hence enhanced crosslinking) following reduced viscosity after degradative sulfitation, compared with the relative rigidity of higher oligomers when unsulfited.

However, the immediate prospect of tannin activation via facile ring isomerization and without introduction of solubilizing sulfonic groups, is the reduction of resorcinol requirements in those cold-set mimosa-resorcinol-formaldehyde

resins that have previously been found effective in beam lamination and finger-jointing (2). Ambient conditions applicable to prorobinetinidins strongly favor the use of mimosa extract, since phenolic "degradation" of the catechic type (14) almost certainly accompanies the sustained high temperature (50 °C) requirements for profisetinidins representing quebracho extract.

### Acknowledgments

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# Chapter 17

## Modification of Diisocyanate-Based Particleboard and Plywood Glues with Natural Polymers

### Polyphenols, Carbohydrates, and Proteins

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Investigations aimed at finding some fast-setting glues for exterior plywood and particleboard based on diisocyanates in combination with compounds from renewable resources like tannins, proteins, and starches revealed the following: The mechanical properties of particleboard bonded with unmodified tannin extracts from spruce (*Picea abies*) and pine (*Pinus sylvestris*) were inferior. The fortification of the tannin extracts with diisocyanate increased the bonding strength and reduced the thickness swelling. With one exception, particleboards bonded with nonemulsifiable diisocyanate modified with glutin or maize starch (extender content up to 20%) had exterior-grade quality (German standard V100 for flat-pressed boards). Veneer plywood, which is conditionally weatherproof (German standard AW), can be produced by applying diisocyanate together with tannins or starches. The veneer wood species, the glue mixtures, the pressing conditions, and the fillers have to be adjusted to the diisocyanate type and to the extender. Modified, emulsifiable diisocyanate gave plywood with better strength and wood failure than glue formulations with nonemulsifiable diisocyanate.

Wood-based panel products are usually bonded with synthetic adhesives based on condensates of phenol, resorcinol, urea, or melamine with formaldehyde. Particleboards and fiberboards can also be bonded with mineral binders like cement or gypsum. Wood adhesives derived from natural products have more

historical importance. Nowadays, only tannin-based adhesives are used in industrial production of panel products limited to certain areas (e.g., Australia, South Africa, and some countries in South America). Technical disadvantages of tannin adhesives are so dominant that the glue formulations generally have to be fortified by synthetic resins.

A relatively new synthetic adhesive for panel products is the diisocyanate. Diisocyanates have been used industrially with success in West Germany in particleboard production for more than 10 years. Advantages of the diisocyanates are: high reactivity, binding qualities for exterior-grade panel products, and no formaldehyde emission potential after curing. Furthermore, diisocyanates do not contain hygroscopic salts like phenolic resins. Disadvantages of diisocyanates are the higher price and higher toxicity of the uncured glue in comparison with other wood adhesives. The properties of natural glues are opposite to those of diisocyanates; high viscosity, mostly low reactivity, and inferior binding qualities.

Attempts to combine the natural glues with diisocyanates have led to success. Several tannin adhesive formulations fortified with diisocyanates for particleboards and beechwood have been described in the literature (1-4).

Diisocyanates have also generated interest as adhesives for plywood, but they have mainly failed in use because of economics and adhesive application problems (adhesive distribution, penetration into veneer, etc.). Further experiments have shown that mixtures of diisocyanates with the usual fillers and extenders have a very short potlife or give nonhomogeneous glues (5,6).

## Research Goals

Plywood bonding is usually restricted to adhesives based on phenolics and aminoplasts. Phenolics often have low reactivity and unfavorable hygroscopic properties. Aminoplasts, though they have higher reactivity, emit formaldehyde even years after production and lack durability in adverse environments [i.e., high temperatures  $>150$  °F (65 °C)] and cyclic wetting and drying. To expand the range of plywood adhesives, the Fraunhofer-Institute for Wood Research has started to develop formulations based on diisocyanates in combination with compounds from renewable resources like tannins, lignins, proteins, and starches.

The aim of the research was the development of the combination of fast-setting glues for exterior plywood (Type AW, DIN 68 705, part 2) with sufficiently high viscosity but without formaldehyde emission. Some of these adhesive formulations were tested in particleboard production. All tests were done on a laboratory scale, taking into consideration the limits given by the technology and economics in the industry. The results presented in this chapter are part of a comprehensive research program affirming the benefits of natural products in adhesive formulations for wood-based panel products.

## Experimental Procedures

Nonemulsifiable and emulsifiable polymeric methylene diisocyanates (Desmodur VP PU 1520 A 31 and 1520 E, Messrs. Bayer, West Germany) were combined with maize starch and solutions of tannin extract or protein.

The gluing experiments were done with commercially available starch, proteins (casein, gluten) and tannins of mimosa (*Acacia* spp.), *Pinus radiata*, and quebracho (*Schinopsis* spp.) and with tannins extracted from the bark of spruce (*Picea abies*) and common pine (*Pinus sylvestris*). The extractions were carried out with water or organic solvents under alkali and/or sulphite conditions on a laboratory scale aiming at optimization of yield and polyphenolic extract content. After extraction, the solutions were concentrated under reduced pressure and freeze dried. One pine bark extract was modified with phenol. A summary of the tannin extracts and their properties is given in Table I.

For the plywood glues, the ratio PMDI/extender was 7:3 or 6:4 (w/w). The glue did not contain further additives if not otherwise mentioned. Three-ply panels were pressed from spruce (100 mm x 85 mm x 1.8 mm), beech (100 mm x 85 mm x 1.5 mm), and gabun veneers (100 mm x 85 mm x 1.6 mm); the moisture content of the veneers was 8 to 9.5%. Plywood manufacturing conditions are given in Table II. With each glue formulation, seven panels were made. From the panels, 20 test specimens were cut. The shear strength according to building-veneer plywood (DIN 68 705, part 3) and the wood failure (delamination test, DIN 53 255) of test specimens were assessed. Pretreatments were a cold water storage for 24 hours and a boiling-dry-boiling test (boiling in water for 4 hours, storage at 60 °C in an oven for 16 to 20 hours, boiling in water for another 4 hours). According to the German standard for weatherproof building veneer plywood (type BFU 100, DIN 68 705, part 3), the minimum shear strength is 1 MPa. According to the German standard for exterior-grade plywood for general use (type AW, DIN 68 705, part 2), the quality of the bonding must be at least grade 3 (see remark in Table III).

Particleboard manufacturing conditions are given in Table IV. With each glue formulation, two particleboards were made. The German standard for flat-pressed boards for buildings without wood preservatives (DIN 68 763) distinguishes type V20 (bonding not stable at high moisture) and type V100 (bonding stable at high moisture). The limits for strength and thickness swelling are given in Tables IV and V.

## Results and Discussion

**Adhesives from Diisocyanates and Tannins.** The tannin extracts were mixed as powders or solutions with nonemulsifiable or emulsifiable diisocyanate. The potlife of the formulations of extract powders with nonemulsifiable diisocyanate was sufficient; the viscosities of the mixtures remained nearly constant for more than 5 hours. With extract solutions, the viscosity of the glue increased

Table I. Extraction Conditions and Properties of Tannin Extracts

Extract Code	Bark/Wood	Extraction		Polyphenol (% Dry Wt.) <sup>1</sup>	Hydroxyl Content % NE <sup>3</sup>
		Solvent	Chemicals		
SI	Spruce	Water	1% NaOH/1% Na <sub>2</sub> SO <sub>3</sub>	55.0	
PI	Pine	Water	7% NaOH <sup>2</sup>	61.2	NE
SII	Spruce	Ethanol/ Water (3:2)	2% NaOH	68.0	NE
PII	Pine	Ethanol/ Water (3:2)	5% NaOH	73.9	NE
M	Mimosa	Commercial Product		84.2	5.7
Q	Quebracho	Commercial Product		90.6	4.9

<sup>1</sup>Formaldehyde reactive polyphenolic compounds (Stiasny number).

<sup>2</sup>Extract modified with 2% phenol (ovendry weight).

<sup>3</sup>NE: Not estimated.



Table II. Strength of Plywood<sup>1</sup> Bonded with Formulations of Nonemulsifiable Diisocyanate and Spruce or Pine Bark Extracts (40% Solution)

Extract <sup>2</sup>	Paraform (% on Glue)	Shear Strength (MPa)	
		Dry	Cold Water Soak (24 h)
SI	–	3.1	2.0
	0.5	3.3	2.3
PI	–	3.0	No strength
	0.5	3.4	2.2
PII	–	2.3	1.1 <sup>3</sup>
	0.5	2.9	2.0
SII	–	2.6	0.9 <sup>3</sup>
	0.5	3.2	2.8

<sup>1</sup>Manufacture of plywood:

vener species : beech

panel construction: 3 ply, each 1.5 mm thick

panel size : 80 mm x 100 mm

press temperature : 140 °C

pressure : 1.5 MPa

press time : 6 min

prepressing : none

assembly time : 5 to 5 min

glue spread : 210 g/m<sup>2</sup> (double glueline)

glue : ratio diisocyanate/extract solution: 7:3

<sup>2</sup>Extract code, see remark in Table I.

<sup>3</sup>Partly no strength.

Table III. Strength and Wood Failure of Plywood<sup>1</sup>  
Bonded with Formulations of Diisocyanate (PMDI) and  
Tannin Extracts (50% Solutions)

PMDI	Tannin	Veneer	Shear Strn. (MPA)		Wood Fail <sup>2</sup>	
			A <sup>3</sup>	B <sup>4</sup>	A <sup>3</sup>	B <sup>4</sup>
Nonemul- sifiable	Mimosa	Beech	0.0	0.0		
		Spruce	1.5	1.0		
		Quebracho	Beech	1.7	0.0	
		Spruce	2.3	1.6		
		Gabun	2.9	2.1		
Emul- sifiable	Mimosa	Beech	4.3	2.7	2	3
		Spruce	2.4	1.6	2	4
	Quebracho	Beech	4.5	2.6	1	2
		Spruce	2.7	2.2	2	3
		Gabun	3.3	2.8		

<sup>1</sup>Manufacture of plywood: see remark in Table II.

<sup>2</sup>Judgment of DIN 53 255:

- 1: excellent bonding;
- 2: good bonding;
- 3: satisfactory bonding;
- 4: insufficient bonding.

<sup>3</sup>A: Cold water soak.

<sup>4</sup>B: Boiling test.

Table IV. Mechanical Properties of 13-mm Particleboard<sup>1</sup> Bonded with Unmodified Tannin Extracts and with Tannin Extracts Diisocyanate (PMDI) Formulations<sup>2</sup>

Extract Code <sup>3</sup>	Extract Content % on Dry Weight	PMDI Content Weight	Modulus of Rupture (MPa)	Internal Bond (V20) (MPa)	Thickness Swelling (%/24 h)
SI	10.0	–	9.5	0.3	43.3
PI	10.0	–	10.1	0.2	23.4
SII	10.0	–	5.8	0.1	54.0
PII	10.0	–	No bonding	because of	precurving
SI	6.0	3.0	21.2	0.6	15.9
PI	6.0	3.0	13.9	0.5	20.0
SII	6.0	3.0	13.8	0.5	22.1
PII	6.0	3.0	14.5	0.6	24.1
SI	4.5	4.5	16.6	1.0	15.5
PI	4.5	4.5	15.6	0.9	15.5
SII	4.5	4.5	15.6	0.9	15.8
PII	4.5	4.5	15.3	1.0	17.1
–	–	4.5	17.2	1.2	14.1
–	–	6.0	21.2	1.4	11.5

<sup>1</sup>Requirements of DIN 68 763 (board thickness 13...20 mm)  
MOR V20  $\geq$ 16; V100  $\geq$ 18; IB V20  $\geq$ 0.35;  
TS V20  $\leq$ 16; V100  $\leq$ 12

<sup>2</sup>Manufacture of boards:  
construction : one-layer  
size : 500 mm x 500 mm  
density : 700 kg/m<sup>3</sup>  
press temperature: 180 °C  
press time : PMDI-boards - 5 min  
press time : tannin extract-boards - 10 min  
hardener : 10% paraformaldehyde (ovendry extract)  
sizing : 0.6% paraffin (ovendry weight).

<sup>3</sup>Extract code, see Table I.

Table V. Mechanical Properties of 19-mm Particleboard<sup>1</sup> Bonded with Mixtures of Nonemulsifiable Diisocyanate (PMDI) and Starch or Glutin

Extender Type	Extender Content (%) <sup>2</sup>	PMDI Content (%) <sup>2</sup>	Modulus of Rupture <sup>3</sup> (MPA) <sup>3</sup>	Internal Bond		Thickness Swelling (%/24h)
				V20 (MPA) <sup>3</sup>	V100 (MPA) <sup>3</sup>	
None	-	6.0	25.0	1.34	0.49	8.5
Starch	0.9	5.1	24.5	1.22	0.44	8.6
	1.8	4.2	24.8	1.25	0.38	9.4
Glutin	0.9	5.1	23.9	0.88	0.23	9.5
	1.8	4.2	20.3	0.79	0.10	11.1

<sup>1</sup>Manufacture of boards:  
 construction : one-layer  
 size : 500 mm x 800 mm  
 density : 700 kg/m<sup>3</sup>  
 press temperature: 180 °C  
 press time : 5 min  
 sizing : 1% paraffin<sup>2</sup>

<sup>2</sup>% of oven-dry board weight

<sup>3</sup>See Table IV for requirements of  
 DIN 68 763 (board thickness 13 to 20mm)

significantly within 2 or 3 hours. Comparable formulations with an emulsifiable diisocyanate had higher viscosities and much lower potlives (10 to 15 min).

For acceptable performance of modified or extended diisocyanate, the reaction of the diisocyanate group with reactive groups of the extender is important. The relative content of isocyanate groups in an adhesive can be determined by IR spectroscopy comparing two absorbance bands at  $2270\text{ cm}^{-1}$  and  $1720\text{ cm}^{-1}$  (carbonyl band). From spectroscopic analyses of (isocyanate band) polyurethane foams and of diisocyanate-bonded particleboards, it is well known that an astonishingly high proportion of the isocyanate groups remains unchanged in the glue matrix over long periods (6,7).

For our experiments, mixtures of emulsifiable or nonemulsifiable diisocyanate and tannin extract were heated for 1 hour at different temperatures. Even at room temperature ( $20\text{ }^{\circ}\text{C}$ ), the relative content of isocyanate groups in the glue formulation decreased rapidly during the first minutes after mixing before a stable level was reached. At high temperatures, the content of isocyanate groups decreased faster, leading to much lower levels. Results of the potlife and viscosity tests disclosed that the formulations with the nonemulsifiable diisocyanate were more stable than those with the emulsifiable diisocyanate. After optimization of some formulation properties (viscosity, potlife, etc.), combinations of diisocyanates and tannins, proteins, or starch, respectively, were used as adhesives for particleboard and plywood.

The mechanical properties of particleboard bonded with unmodified tannin extracts from spruce and pine bark were inferior (Table IV). In agreement with the results of Pizzi (1), it was found that the fortification of the tannins with diisocyanate increased the bonding strength. The thickness swelling was reduced, but the V100 standard for exterior-grade particleboard was not attained using these extracts. The low bonding qualities of spruce and pine bark extracts may be due to the type of polyphenolic, as well as to the lower content of polyphenolics in comparison with mimosa or quebracho tannins or with extracts from other softwood barks (*Pinus brutia*, *Pinus radiata*).

Plywood veneers bonded with diisocyanate and tannin extract powder gave no strength after hot pressing. The diisocyanate had penetrated into the veneers during pressing. In comparison, strength was attained with formulations of diisocyanate and extract solutions. Therefore, gluing experiments were done with mixtures of diisocyanate and tannin extract solutions. Mixtures with a nonemulsifiable diisocyanate were liquid. In comparison, mixtures with the emulsified resin had a pastelike consistency and could not be spread on the veneers without problems. For plywood binding, the spruce and pine bark extracts were mixed with nonemulsifiable diisocyanates (Table II). Only one formulation with a modified spruce bark extract gave wet bonding strength. The addition of paraformaldehyde improved the strength significantly. All samples showed wet bonding strength but at a low level. The test results for plywood bonded with formulations of mimosa or quebracho tannins and diisocyanates are shown in Table III. The strength of the plywood was influenced by the wood species. Beechwood veneers bonded with tannin and nonemulsifiable diisocyanate had

no or only low strength properties, whereas, spruce or gabun wood veneers had better strength. Furthermore, the glue formulations with an emulsifiable diisocyanate gave plywood with better strength. Contrary to the results with the formulations with a nonemulsifiable diisocyanate, the best bonding strengths were obtained with beechwood.

Lowering the spread (double glueline) from 210 g/m<sup>2</sup> to 140 g/m<sup>2</sup> per veneer did not influence the strength properties of the plywood. Furthermore, the strength was not influenced when the press temperature was varied between 100 and 140 °C or when press time was varied between 3 and 9 minutes.

In some experiments with nonemulsifiable diisocyanates, adhesive squeezeout was observed during pressing. It could be reduced by using fillers like gypsum, chalk, or wood flour. All in all, the use of fillers increased the binding qualities of the glue formulations (Table VI).

Table VI. Influence of Fillers on Strength of Beech Plywood<sup>1</sup> Bonded with Formulations in Nonemulsifiable Diisocyanate (PMDI) and Tannin Extracts (50% Solutions)

Tannin Extract	Filler <sup>2</sup>	Shear Strength (MPA)	
		A <sup>3</sup>	B <sup>4</sup>
Mimosa	—	No	Strength
	Gypsum	2.7	1.4 <sup>5</sup>
	Chalk	2.4 <sup>5</sup>	No strength
	Wood flour	3.7	1.9
Quebracho	—	1.6	No strength
	Gypsum	3.7	2.7
	Chalk	3.7	1.7 <sup>5</sup>
	Wood flour	3.5	2.3 <sup>5</sup>

<sup>1</sup>Manufacture of plywood: see remark in Table II.

<sup>2</sup>5% on extended PMDI.

<sup>3</sup>A: Cold water soak.

<sup>4</sup>B: Boiling test.

<sup>5</sup>Partly no strength.

**Adhesives from Diisocyanates and Starch.** Reactions between diisocyanates and carbohydrates are possible, resulting in polyurethane-like polymers. Starch as a most abundant natural polymeric carbohydrate is, without additives, an inefficient wood adhesive, giving weak and nonwater-resistant bonds. Another disadvantage of starch is that, even at low concentrations, the viscosity of the starch solution is too high for application. In our tests, maize starch was used as an extender for diisocyanates. The potlife of formulations of three parts starch powder and seven parts diisocyanate was more than 24 hours.

Beech plywood bonded with formulations of both diisocyanate types and maize starch had low strength after the boiling water test (Table VII). The shear strength of spruce plywood was significantly higher. With respect to wood failure, the requirements of DIN 53 255 for plywood type AW were fulfilled. Variations of glue spread and press temperature had no significant influence on bond strength. The addition of wood flour as filler for formulations with nonemulsifiable diisocyanate considerably increased strength.

Table VII. Strength and Wood Failure in Plywood<sup>1</sup> Bonded with Formulations in Diisocyanate (PMDI) and Maize Starch

PMDI	Ratio PMDI:Starch	Veneer Species	Shear Str. (MPA)		Wood Fail <sup>2</sup>	
			A <sup>3</sup>	B <sup>4</sup>	A <sup>3</sup>	B <sup>4</sup>
Nonemul- sifiable	7:3	Beech	1.7	0.7 <sup>5</sup>	—	—
	—	Spruce	2.7	1.5	1	1
	6:4	Beech	2.1	0.9	—	—
	—	Spruce	2.4	1.4	1	3
Emul- sifiable	7:3	Beech	2.7	0.8	1	1
	—	Spruce	2.5	1.7	1	1
	6:4	Spruce	2.5	1.6	1	1

<sup>1</sup>Manufacture of plywood: see remark in Table II.

<sup>2</sup>Judgment of DIN 53 255: see remark in Table III.

<sup>3</sup>A: Cold water soak.

<sup>4</sup>B: Boiling test.

<sup>5</sup>Partly no strength.

In Table V, the mechanical properties of particleboard bonded with nonemulsifiable diisocyanate modified with maize starch are given. The extender content for the diisocyanate was up to 20%. However, with increasing extender content, the internal bond of the boards decreased, and the thickness swelling increased; the boards had V100 quality. First tests with adhesives of diisocyanates and starch were encouraging, and more attempts in developing new glue formulations

are necessary. Naturally occurring in common plant species, these biopolymers are available in a homogeneous and pure quality at low cost, an outstanding feature for natural resource-derived compounds.

**Adhesives from Diisocyanates and Proteins.** Protein-based adhesives have been used as traditional binders for wood since the beginning of wood products manufacture. Glutin and casein binders can provide interior-grade wood products; but with modified casein binders, even panels for exterior use are possible. For economic and technical reasons, protein-based wood adhesives have been replaced more and more by synthetic adhesives since the beginning of the century.

In our experiments, only alkali casein solutions gave uniform mixtures with diisocyanate. The potlife of the formulations was sufficient for gluing experiments. The mechanical properties of particleboard bonded with nonemulsifiable diisocyanate modified with glutin (extender content up to 20%) are given in Table V. With increasing glutin content, the strength of the boards decreased considerably. The board bonded with an adhesive of 90% diisocyanate and 10% glutin had V100 quality, whereas, board bonded with diisocyanate modified with 20% glutin only had V20 quality. Formulations with a nonemulsifiable diisocyanate gave plywood with low and insufficient strength (Table VIII). With the use of emulsifiable diisocyanates, strength was improved, but the wood failure property was inferior. Apparently, the alkali content of the casein solutions accelerated the reactions of diisocyanate groups so much that the adhesive cured before pressing.

Table VIII. Strength and Wood Failure of Plywood<sup>1</sup> Bonded with Formulations of Diisocyanate (PMDI) and Casein (20% Solution in 0.1 MOL/L NaOH)<sup>2</sup>

PMDI	Veneer Species	Strength (MPA)		Wood Failure <sup>3</sup>	
		A <sup>4</sup>	B <sup>5</sup>	A <sup>4</sup>	B <sup>5</sup>
Nonemulsifiable	Beech	2.7	No strength		
	Spruce	2.6	1.4	3	4
Emulsifiable	Beech	4.4	3.9	3	4
	Spruce	2.0	1.5	2	3

<sup>1</sup>Manufacture of plywood: see remark in Table IV.

<sup>2</sup>Ratio PMDI: Casein solution: 7:3.

<sup>3</sup>Judgment of DIN 53 255: see remark in Table III.

<sup>4</sup>A: Cold water soak.

<sup>5</sup>B: Boiling test.



## Conclusions

Formulations for particleboard and plywood adhesives based on combinations of diisocyanates and compounds from renewable resources like tannins, starch, and proteins have been developed and tested at the Fraunhofer-Institute. All in all, the results of gluing tests indicated the potential for using diisocyanates combined with natural polymers for adhesive purposes where each natural product used alone will fail. More attempts will be necessary to find precise mixtures to produce successful adhesives for panel products. The development of adequate particleboard and plywood glue formulations based on diisocyanates and natural polymers has to be accompanied by more sophisticated technologies than those used in conventional production processes. The results presented here may give some hints on how these technologies can evolve.

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# Chapter 18

## Condensed Tannins as Substitutes for Resorcinol in Bonding Polyester and Nylon Cord to Rubber

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Nylon and polyester cords used to reinforce tires are coated with a reactive resorcinol-formaldehyde-latex (RFL) adhesive dip to strongly couple the rubber and cord. Condensed tannins from pecan nut pith, bark of southern pine trees, or peanut skins can be used to replace some or all of the resorcinol in a standard RFL dip. When the tire cord adhesion test (TCAT) geometry is used, pullout forces for dipped nylon cords embedded in a typical styrene-butadiene rubber (SBR) vulcanizate nearly equaled those obtained with the standard dip when resorcinol was replaced with tannins from peanut skins or pine bark sulfite extracts. When bonding polyester cord, resins formulated with pecan pith sulfite extracts and purified pine bark tannins gave pullout forces substantially higher than the standard RFL dip. Resins made with peanut skin tannins or pine bark sulfite extracts as substitutes for resorcinol were marginally inferior to the standard RFL dip. When bonding to nylon cord, tannin preparations of low molecular weight appear to provide the stronger bonds. Bond strength was not influenced by the presence of sulfite ion or carbohydrates in nylon adhesion. Tannin preparations containing low proportions of carbohydrates gave the higher bond strengths in adhesion to polyester cord.

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Nylon and polyester cords are commonly used in tire body plies to impart strength and durability. To function properly, the cords must be firmly bonded to the surrounding rubber. Some coupling of cord to rubber occurs because of simple mechanical interlocking of rubber that has penetrated into the cord. However, this type of bonding is insufficient, and an adhesive interlayer is required. Typically, the cord fabric is dipped into a water-based adhesive, then dried before calendaring into a rubber ply. The origin for the adhesives currently used dates to a patent by Charch and Maney (1). This class of adhesives is based on reactive mixtures of resorcinol, formaldehyde, and a rubbery latex (RFL) dips. A representative RFL composition (2) suitable for bonding nylon to a diene elastomer is detailed in Table I. In the adhesive, the resorcinol and formaldehyde react to form a product that reinforces the rubbery major portion (3). It is also the RF part of the adhesive that is thought to be principally responsible for the adhesive's strong interaction with the cord (4). During the vulcanization of a cord-RFL-rubber composite, co-curing across the rubber-adhesive interface is expected (5). One function of the pyridine moiety of the styrene-butadiene-vinylpyridine polymer is to increase the interaction between the latex rubber and the RF, thereby enhancing the cohesive strength of the dip (6).

Table I. Standard RFL-Type Adhesive Dip Composition

Component	Amount
Resorcinol	11 g
Formalin sol'n (37%)	16.4 mL
NaOH sol'n (10%)	3.0 g
Distilled water	236 g
Styrene-butadiene-vinylpyridine latex (41% solids)	244 g

The reactivity of resorcinol with formaldehyde is essential for developing the cohesive strength of the interlayer and its bonding characteristics. Condensed tannins are known to be very reactive with formaldehyde (7-9), so these renewable phenolic polymers are good candidates as resorcinol replacements. Indeed, condensed tannins from wattle and pine bark extracts have been successfully used in cold-setting, wood-laminating adhesives, and the former are used extensively in the commercial production of laminated timbers in South Africa (Pizzi, A., National Timber Research Institute, Pretoria, South Africa, personal communication, 1982) (10-13).

The purpose of the research described here was to explore the feasibility of using condensed tannins as replacements for resorcinol in RFL-type adhesive

dips for bonding of cord to rubber products. Success in this effort would greatly increase the markets for condensed tannins, since far more resorcinol is used in the rubber industry than in bonding of wood products.

### Experimental Methodology

**Materials.** Two types of standard tire cord obtained from Gen Corporation were used in this investigation: polyester, 1300/3, and nylon 66, 1260/3. The rubber composition to which the adhesively dipped cords were bonded had the following composition in parts by weight: styrene-butadiene rubber (SBR) 1502, 100; N330 carbon black, 50; zinc oxide, 5; stearic acid, 0.5; sulfur, 1.7; 2-morpholiniothio-benzothiazole, 2. Master batches were mixed 7 min in a 350-mL Brabender Plasticorder, and curatives were added on a cool two-roll mill. Cure characteristics at 155 °C were determined with an oscillating disc rheometer (ASTM D 2084). The time to reach 90% of the final cure state was 23 min, and the Shore A hardness of the final vulcanizate was approximately 60.

Four types of condensed tannins were studied in the adhesive dips: 1) extracts from pecan nut pith obtained by digestion with aqueous sodium sulfite-sodium carbonate solutions, 2) purified tannins from southern pine bark, 3) extracts from southern pine bark obtained by digestion with aqueous sodium sulfite-sodium carbonate solutions, and 4) tannins extracted with acetone-water solutions from peanut skins.

The sulfite extract of the pecan nut pith was obtained by extracting the finely ground red powder (509 gm) with sodium sulfite (20.4 gm) and sodium carbonate (2.0 gm) in 2549 mL of water. Approximately 1 hr was required to reach reflux temperature, and the suspension was heated at reflux for 2 hr. The suspension was cooled, the volume adjusted to a constant by addition of water, and it was filtered twice through glass wool. Aliquots (100 mL) of the recovered liquor were freeze-dried to determine the extract yield. The remainder was also freeze-dried to recover a dark brown solid.

The purified pine bark tannin was obtained in the following manner. The phloem of freshly felled loblolly pine trees was removed by carefully peeling the outer bark away at the cork cambium and then peeling the white phloem from the xylem cambium. Strips of phloem were cut into sections of about 2 to 5 in<sup>2</sup> and immediately immersed in acetone-water (70:30, v/v). The extraction flasks were kept at ambient temperature, protected from exposure to light, for 48 hr, after which the solvent was recovered by filtration. The acetone was removed under vacuum on a rotary evaporator, and the aqueous solution was extracted four times with an approximately equal volume of ethyl acetate to remove low molecular weight phenolics. The remaining water-soluble extract was freeze-dried. Aliquots (about 50 gm) were redissolved in methanol-water (1:1, v/v), and the solutions were applied to 2.4 X 90 cm Sephadex LH-20 columns packed in this same solvent. The columns were eluted with methanol-water until no more colored material was eluted. The condensed tannin polymers absorbed

on the column packing were then eluted with acetone-water (50:50, v/v). The acetone was removed by evaporation under vacuum on a rotary evaporator, and the aqueous solution was freeze-dried.

The sodium sulfite-sodium carbonate extracts of pine bark were prepared from southern pine tree barks obtained from logs at a plywood plant in central Louisiana. The bark was collected from transfer chains immediately following the debarkers. After air-drying, the bark was first processed in a garden mulcher and then refined in a Sprout-Waldrin disk refiner fitted with breaker plates. The finely ground bark was divided into lots of approximately 30 lb (100 parts by weight), which were then extracted with 4.0 parts of sodium sulfite and 0.4 parts of sodium carbonate in 700 parts of water in a 40-gal capacity stainless steel tank. The solution was heated to 95 to 100 °C over 1 hr and maintained at temperature for 2 hr. The suspension was cooled, adjusted to a constant volume, and the extract liquor was filtered twice through fiberglass mats. Typically, 60% of the added liquor was recovered from the pulp. Approximately 100 gal of extract were dried in a hot pan evaporator.

For the preparation of the peanut skin tannin, the red skins were separated from residual nut and hull material by hand sorting, and then about 30 lb of skins were extracted with acetone-water (60:40 v/v) at a liquor-to-skins ratio of 5 to 1 at 50 °C for 4 hr in a stainless steel tank. The extract was filtered through a fiberglass mat, the acetone was removed under vacuum on a rotary evaporator, and the aqueous solution was freeze-dried.

**Adhesive Preparation.** The standard RFL dip that was used is given in Table I. In the dips containing the tannins, all ingredient amounts were held constant except the ratio of resorcinol to tannin. Starting with the control dip (Table I), tannin was simply substituted for resorcinol, such that dips containing resorcinol/tannin of 100/0, 75/25, 50/50, 25/75, and 0/100 were prepared as follows. Resorcinol, tannin, formalin, NaOH solution, and distilled water were mixed together and allowed to react for 2 hr. Then, the styrene-butadiene-vinyl pyridine latex (Gentac 118 from Gen Corporation) was added, and the dip was allowed to age 24 hr before use. In some cases, the adhesive became a soft gel. This, however, could be "broken" by mixing, and it was still possible to coat the dip onto the test cord. The dip was applied to a cord by immersing the cord in the dip for 30 s. The cord was then removed and dried 5 hr at room temperature before preparing pullout test specimens. In industry, a short heat treatment after dip application is often employed, however, this was not done in the present investigation.

**Pullout Tests.** The method to determine the adhesion between the dipped cords and the SBR vulcanizate was the tire cord adhesion test (14,15), Figure 1. Here, two cords are embedded (to a depth of 10 mm) into opposite ends of a rubber block (76 mm x 13 mm x 6.4 mm). Samples are then cured 23 min at 155 °C and allowed to rest 1 day. Bond strengths are determined by clamping the two free cord ends in an Instron and pulling at the rate of 50 mm/min.

Failure occurs when one of the cords is pulled-out; the strength is denoted by the maximum force during cord pullout.

## Results and Discussion

In the presentation of data and discussion that follows, the four types of condensed tannin extracts are designated: pecan pith sulfite extract (1), purified pine bark tannin (2), pine bark sulfite extract (3), and peanut skin tannin (4). Pullout strengths for the polyester and nylon cords coated with dips containing the four tannins are given in Figures 2 to 7. All data points are the average of six pullout forces. Pullout forces as a function of percent resorcinol (based on the total of resorcinol and tannin) in the dip are given in Figures 2 and 3 for the polyester and nylon cord, respectively. The rightmost data points are values for the control dip containing no tannin. It is worthwhile to note first that many of the dips containing the condensed tannins had pullout strengths nearly equal to or exceeding those of the control containing only resorcinol. This is especially true with the polyester cord.

The type of tannin markedly influences the pullout force. With the polyester cord, the highest pullout force was obtained with a dip containing 25/75, resorcinol/pecan pith sulfite extract. However, this same dip gave among the lowest strengths when applied to the nylon cord. On the other hand, quite good bonding to nylon was obtained with a 50/50, resorcinol/peanut skin tannin dip, while this composition led to a quite low pullout force with the polyester cord. A comparison between the behavior of nylon and polyester with the various dips is better shown in Figures 4 to 7, where pullout forces for each of the four types of tannin-containing dips are presented. Generally, the pecan pith sulfite extract and purified pine bark tannin give superior results with polyester cord, whereas, just the opposite is true for the pine bark sulfite extract and the peanut skin tannin.

The tannin extracts examined in this preliminary study represent a wide range of properties. For example, both the peanut skin and purified pine bark tannin extracts are predominantly polymeric procyanidins (3,5,7,3',4'-penta-hydroxyflavans), but the peanut skin tannin is much lower in molecular weight (16-19). In bonding to nylon, the resins formulated with peanut skins performed much better than those made with purified pine bark tannins. The condensed tannins from pine bark undergo interflavanoid bond cleavage with the formation of flavan- or procyanidin-4-sulfonates when reacted with sulfite ion (20); so, even though experimental evidence is lacking for the molecular weight of sulfite extracts of bark, it seems probable that the sulfite extracts from pine bark are of a lower molecular weight than the purified tannins.

The sulfite extract performed nearly as well as the peanut skin tannin in bonding to nylon. Use of a tannin sulfonate derivative does not seem to hinder the development of strong bonds (compare peanut skin and sulfite extracts from pine bark). Likewise, the presence of carbohydrates in the tannin extracts does

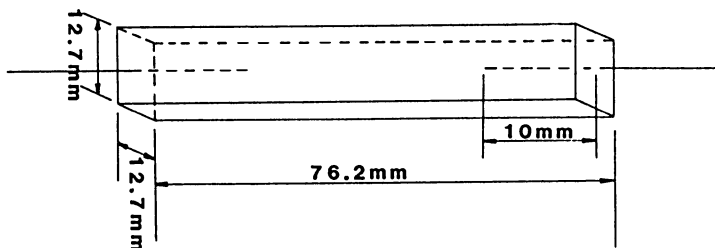


Figure 1. TCAT pullout test geometry.

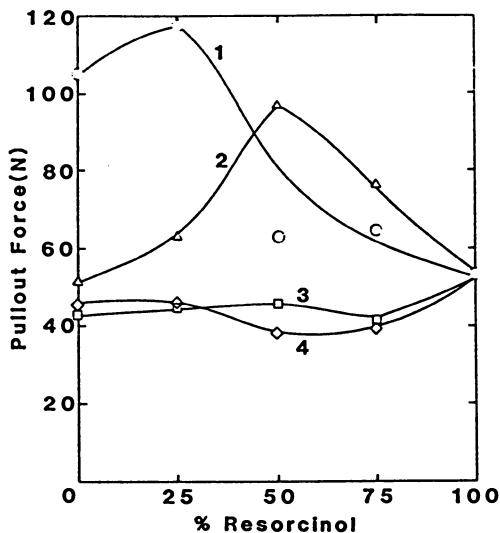


Figure 2. Pullout forces of polyester cords for various tannin-containing adhesive dips as a function of percent resorcinol. 1, pecan pith sulfite extract; 2, purified pine bark tannin; 3, pine bark sulfite extract; 4, peanut skin tannin.

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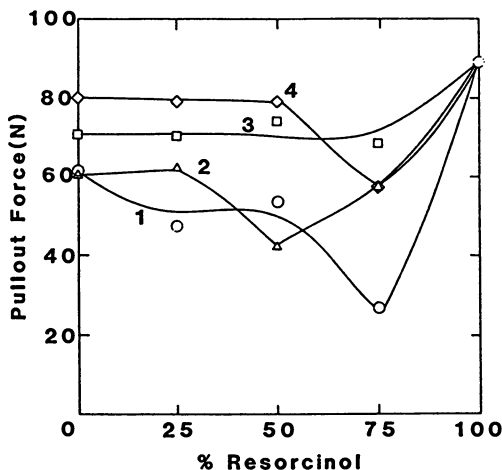


Figure 3. Pullout forces of nylon cords for various tannin-containing adhesive dips as a function of percent resorcinol. Designation same as Figure 2.

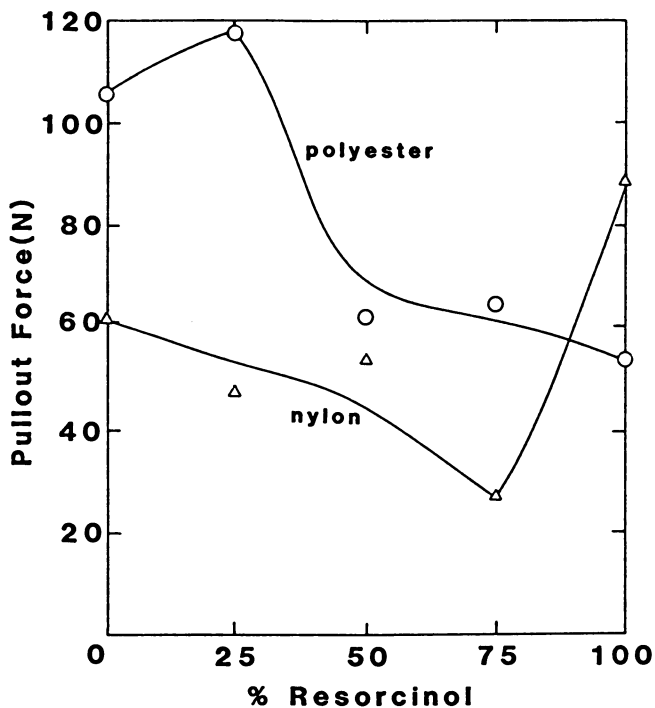


Figure 4. Comparison of the pullout forces of polyester and nylon cords for dips containing pecan sulfite extract.



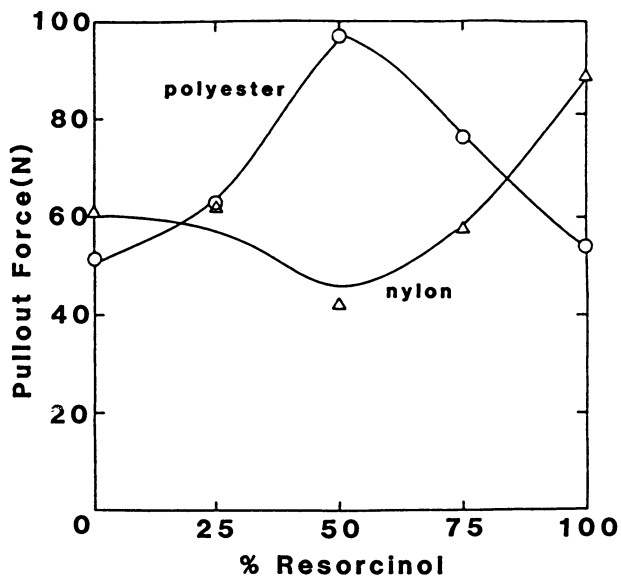


Figure 5. Comparison of the pullout forces of polyester and nylon cords for dips containing purified pine bark tannin.

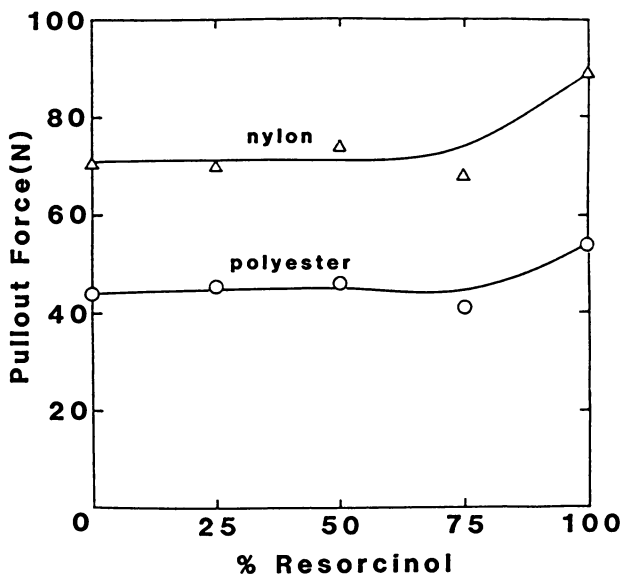


Figure 6. Comparison of the pullout forces of polyester and nylon cords for dips containing pine bark sulfite extract.

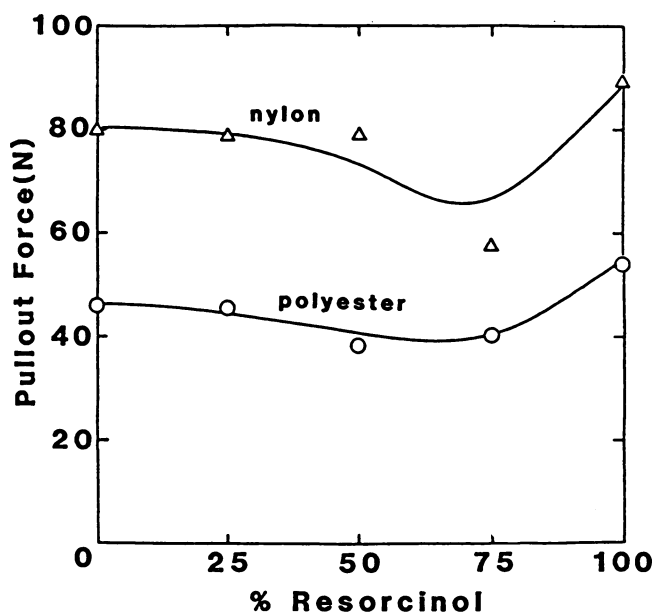


Figure 7. Comparison of the pullout forces of polyester and nylon cords for dips containing peanut skin tannin.

not seem to reduce bond strength. The purified pine bark extract contains no measurable amounts of carbohydrates, whereas, the extracts from peanut skins and sulfite extracts from pine bark contain between 15 and 20% of co-extracted carbohydrates.

At this time, it is not possible to pinpoint the reason for the poor performance of the pecan pith extract in bonding to nylon. The tannin is predominantly a prodelphinidin (3,5,7,3',4',5'-hexahydroxyflavan) instead of procyanidin (Hemingway, R. W., Southern Forest Experiment Station, unpublished results), but that would not seem to be a reasonable cause for such a large difference in behavior. A comparison of elemental composition and carbohydrates obtained after hydrolysis shows much lower amounts of carbohydrates in the pecan pith extract (Table II). The low proportion of carbohydrate obtained after hydrolysis is consistent with comparatively high Stiasny polyphenol content of 87% for the pecan pith extract.

Table II. Elemental Composition and Carbohydrate Content of Sulfite Extracts from Pecan Nut Pith and Southern Pine Bark

Property	Pecan	Pine
Yield		
Percent of dry weight	52	18
Elemental Composition		
Carbon	46.2	45.4
Hydrogen	4.4	4.7
Sodium	7.2	5.8
Sulfur	4.4	3.8
Carbohydrates		
Glucose	—	4.9
Xylose	4.5	2.4
Galactose	0.7	4.5
Arabinose	—	3.0
Mannose	1.4	4.4
Total sugars after hydrolysis	6.6	18.2
Stiasny polyphenols	87	52

The pecan pith extract was the best of the tannin extracts examined in bonding to polyester cord. Pullout forces using this extract to totally replace resorcinol were nearly twice as high as in the standard dip. The purified pine bark extract also gave very good results. One commonality in these two extracts

was the low proportion of carbohydrates. Bond strengths to polyester cord using resins based on peanut skin tannins and pine bark extracts obtained by extraction with sodium sulfite were about the same and only marginally lower than those obtained using the standard RFL dip. As was noted in bonding to the nylon cord, sulfonation seems to have little influence on bond strength. These types of extracts have also proven to be good resorcinol substitutes for cold-setting, wood-laminating adhesives. Even though the extracts carry sulfonic acid functions, durable water-resistant bonds are produced (13,21). The results with the polyester cord are particularly encouraging, since the simple RFL control dip is not that well suited for greige polyester cord. It should be noted that this research effort has made no attempt to optimize the formulation of dips containing condensed tannins. Rather, the procedure for the dip modification was a simple substitution by weight of tannin for resorcinol. The ratio of ingredients is expected to greatly influence viscosity, cure rate, and pH, as well as the bonding characteristics. In a patent search following this preliminary work, a 1967 Japanese patent (22) was discovered that had not been previously noted. The influence of type of tannin extract or modifications in resin formulation were not disclosed in this patent either. Therefore, additional studies to examine these effects are planned. This additional work will hopefully allow a better understanding of the bonding properties that will lead to improved strength and durability of adhesion of cord to rubber matrices.

## Conclusions

Condensed tannins have considerable promise as substitutes for resorcinol used in resin formulations for bonding of nylon or, particularly, polyester cord to rubber. Although much more work needs to be done, preliminary results suggest that refinement of extract properties and adhesive formulations could lead to a large, high-value market for condensed tannin extracts.

## Acknowledgments

Authors Hamed and Chung are grateful to the Southern Forest Experiment Station, USDA Forest Service, for a cooperative grant (19-86-037) supporting this work. We thank Boise Cascade Corporation for supplies of southern pine bark, the Robertson Corporation for supplies of pecan nut pith, Associates Research Management Corporation for peanut skins, and Gen Corporation for resins and cord materials.

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# Chapter 19

## Research vs. Industrial Practice with Tannin-Based Adhesives

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Problems and facts that “in the author’s personal experience” arise in the industrial application of tannin-based adhesives for timber sometimes indicate lack of correspondence with laboratory practice and results. These are often problems related to unusual characteristics of the adhesive itself, or of its application technique, which could not be noticed during research under laboratory conditions, but the existence of which could easily jeopardize successful implementation of laboratory technology into industrial practice. Correcting the “credibility gap” between research focus and industrial usage is seen as a critical step toward market expansion for these new products. Important considerations are: consistency of tannins, extracts and adhesives properties due to the natural raw material variability; formulation in cold-setting adhesives; and application conditions (such as wood moisture and adhesive-content or pressing time) in particleboard adhesives. These problems have been overcome in use of wattle tannin-based adhesives as shown by a visual comparison of tannin-, phenolic-, and melamine-bonded particleboards exposed to the weather for 15 years and the growing use of tannin-based adhesives in other countries.

Comparing research results obtained in a clean, almost clinical, laboratory situation with industrial application realities is always an interesting exercise. It is interesting because good correspondence between the two situations does and must exist but often it is far from satisfactory or even outright poor.

Wattle (mimosa extract) tannin adhesives have been industrially produced and used in South Africa for many years. From the first, mostly unsuccessful, attempts in 1968 has evolved the consistent manufacture, industrial application,

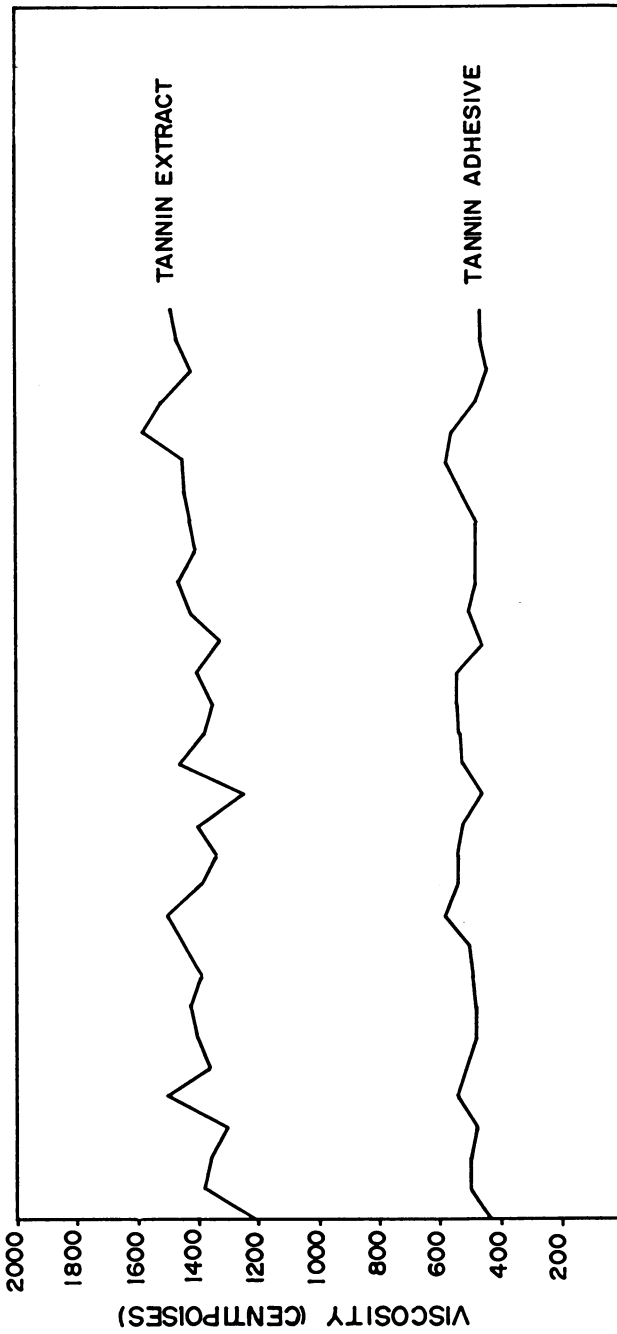
and export of exterior-grade particleboard adhesives at the end of 1971, 1972, and 1973, respectively; of cold-setting laminating and finger-jointing adhesives in 1973; of phenolic-fortified plywood adhesives in 1973-1974; of zinc acetate-catalyzed plywood formulations in 1975; of UF-fortified plywood resins in 1976-1977, and of "honeymoon" fast-setting adhesives for finger-joints in 1982-83.(1).

Wattle tannin resins are also used to manufacture other resins, such as foams comparable to phenolics, as waterproofing additives, and binders for corrugated cardboard or charcoal briquettes. This discussion, however, deals only with particleboard, plywood, glulam, and finger-jointing exterior-grade wood adhesives. Formulations of the adhesives will be mentioned "ad hoc," if at all necessary, as they have already been extensively discussed in articles and reviews in the relevant literature.(1)

### **Tannin Extract Adhesive Consistency**

One of the first objections to tannin adhesives advanced by industrial manufacturers regards the consistency of the raw material, hence of the resins and adhesives produced from it. The consistency and composition of tannin extracts do vary considerably with tree location, season, tree age, climatic conditions, tree species, and extraction process. The combination of all these factors can indeed cause a considerable variation in the composition of the raw material if one takes as a comparative standard other industrial synthetic raw materials. (After all, the tree does not produce tannin specifically to allow us to produce adhesives!) This objection is generally difficult to counteract by researchers. If you have not done fairly extensive industrial runs, no industrialist is likely to believe your desperate pleas that, after all, the raw material or the finished product is consistent enough not to cause problems in the factory or prompt claims against the manufacturer. There is then a credibility gap between research and industrial application in this context that is always difficult to fill in this first step toward industrial application of tannin adhesives. It is, in my experience, the first of the two greatest obstacles anyone will find when moving toward industrialization of research results, the second one being: "Tannin adhesives? What's tannin?" "Hence: What we're describing is market resistance by unaware people." Both these problems are emotional, not technical, and thus difficult to deal with. As a consolation, an industrial study carried out in 1979 on the viscosity of a series of industrial batches of tannin extract and of particleboard adhesive prepared from it appeared as related in the discussions that follow.

The experience of tannin extract manufacturers, and of companies dealing with tannin adhesives is even more extensive, but results are similar to those illustrated in Figure 1. Thus, the first feedback from any industrial application is that the formulations must smooth and reduce the greater variability of the natural raw material. It is amazing, but in all the articles presented by all the research groups, this point is only hinted at, or not mentioned at all! Many



INDUSTRIAL BATCHES

Figure 1. Consistency in the viscosity of tannin extract solutions and adhesives made with them.



innovative adhesive formulations have been presented, but if this point is not taken into account, one can forget even arriving on the floor of a factory! I must point out that no laboratory study of this kind, naturally, will be sufficient to convince manufacturers, but also that many difficulties must be overcome to carry such a study out properly. Where large-scale afforestation and industrial extraction of tannin is practiced, at least a certain amount of control is exercised on the consistency of the product. If the source of tannin is not an established industrial one, one may indeed have an unsurmountable problem at hand.

### Where Lies the Secret to Applied Success?

Where does the secret of technical industrial success with tannin adhesives lie? It varies: for certain adhesives, it is in the formulation of the adhesives only; for others, it lies in the application conditions and techniques only; for most, success requires a good balance of both. While excellent correspondence between laboratory and plant results can often be obtained in adhesives that depend for success on resin formulation, this is usually not the case when success is more dependent on application techniques and conditions (Table I).

Table I. Approximate Industrial Success Dependent on Formulation and Application by Adhesive Type

Adhesive Application	Critical Aspect
Cold-set adhesives:	80% of success dependent upon adhesive formulation
Particleboard adhesives:	70% success dependent upon application conditions and techniques
Plywood adhesives:	50/50 dependent upon formulation and application

An adhesive can be considered successful if, when used consistently in industrial practice, it provides products whose performance is comparable or superior to existing products at a lower effective cost and with fewer or comparable handling problems. Let's now analyze (with examples) two cases related to Table I.

### Cold-Setting Glulam Finger-Jointing Adhesives

In cold-setting adhesives, the combination of resorcinol with the tannin in some form, be it added or partly generated from the tannin itself, hides a multitude

of sins. It is easy, furthermore, to replicate industrial application conditions for such adhesives in the laboratory. As regards correlation between industrial and research results, the important points to watch are discussed below.

**In Resin Manufacture.** Proper control of the exothermic reaction of formaldehyde with the tannin/resorcinol mixtures is essential. Full water cooling should be applied already at temperatures as low as 25 to 30 °C, otherwise, without it, a 1-ton industrial batch can sometimes pass from ambient to 80 °C in less than 2 minutes! I have seen the stainless steel door of a reaction vessel fly 20 meters into the air as a consequence of this mistake, and the operator was lucky! The vessel may easily explode or the reaction mixture boil over through the condenser, if the reaction is not properly controlled at its beginnings.

A peculiar phenomenon is the slow but continuous increase in viscosity of a batch once drummed. It is something you will not notice easily in laboratory batches. It is counteracted by mixing some water with the batch after some period of time. The phenomenon is marked, the viscosity can go up more than 50%, at constant solids over a period of time, by some process of aggregation. Generally, vigorous mechanical mixing with addition of 0.5 to 1 kg water on 4 to 5 tons liquid resin is enough to restabilize the batch. The only hypothesis I can advance is that this peculiar behavior is due to the thixotropic nature of the resin.

**In Adhesive Application.** Tannin cold-setting adhesives have a tendency to dry out more rapidly than synthetic cold-setting adhesives after application to the wood surface. This may become a serious problem as it limits the assembly time of glulam to shorter times than PRF's. Although several tricks, such as addition of glycols, have improved the situation so considerably that under many application conditions there is practically no difference between tannin and phenolic cold-sets, under particularly harsh conditions, high temperature and high speed of air circulation, the problem may still become evident in glulam plants that are slow in assembly; this may cause a drop in the performance of the bonded joint. The problem of dry-out has well-defined theoretical causes. We have recently found (by conformational analysis means) that while the average energy of interaction of PF dimers with cellulose is higher than the average energy of sorption of the water monolayer, the average energy of interaction of flavonoid tannin dimers with cellulose is lower due to steric factors. This means that while PF resins are likely to retain water longer when applied in liquid form to a lignocellulosic surface, TRF resins are not, hence their dry-out characteristics.

CCA preservatives interfere with the curing of any phenolic adhesive, but particularly so with tannin cold-sets. This is due to the higher capability of complexation Cu and Cr with ortho-diphenols (such as the catecholic and pyrogallolic B rings of flavonoids). The problem is not grave under normal ambient gluing conditions, but it becomes more evident at ambient temperatures of 30 °C or higher. The problem, of course, lies with CCA as a wood preservative rather

than with the tannin adhesive. Appropriate application conditions are certain to be developed in the future to further minimize or eliminate this problem.

As regards correspondence of laboratory results with industrial manufacture and gluing, the industrially produced batches are generally and consistently better performers than laboratory ones, due to better reaction controls. Strength of glued joints is comparable. If you have a good formulation in the laboratory, you can be sure the industrial batches will also be good.

### Particleboard Adhesives

In tannin-based particleboard adhesives, the application techniques and conditions outweigh the importance of the formulation: this does not mean that the formulation of the adhesive is not important. It means only that many more usable adhesive formulations can be found. For certain, some are good and some may be not so good, but several certainly produce acceptable boards. The variety of formulations is great, for instance: 1) unmodified tannin extracts with adjusted pH only, 2) unfortified tannin extracts in which simple chemical treatments have reduced the viscosity and improved bond strength and water resistance, 3) formulations in which the tannin extract is fortified with a variety of synthetic polymers such as small percentages of PF, PRF, UF resins or even with diisocyanates, 4) metal-catalyzed tannin extract formulations, or even 5) an old Australian formulation (now somewhat expensive) that was used commercially for many years and consisted of just adding 5% resorcinol chemical to the tannin extract and to adjust the pH. However good the formulation, and there are some really good ones around, none of them will work if the application conditions are not correct, and good application conditions for tannin adhesives are often very different from those for PF resins.

The most important factors determining the application conditions (there are others too, of course) are the percentage moisture content of the glued particles, the rate of pressing, the method of application of the glue mix to the wood particles, and the percentage of adhesive solids on wood.

**Percentage Moisture Content (MC) and Pressing Rate.** These two factors are related in many ways, but their relationship acquires an astonishing new dimension with tannin adhesives. Many particleboard adhesives appear to require a narrow range of MC to function properly. If the pressing time is slow 7 to 7-1/2 minutes for a 12-mm board), the properties of the tannin-bonded board (exterior grade) improve with increasing MC. I mean that a board in which the glued wood chips had a MC of 30% is better than that prepared at MC of 25%, which is better than the one prepared at MC of 20%! We are talking here of moisture ranges that could be considered as a hallucination for any other adhesive! This is particularly true in the laboratory, but even in industrial conditions, I have seen boards pressed at 28% MC that did not blister at all at press-opening. This is a characteristic of wattle tannin-based particleboard: they never really blister. For all practical purposes, the MC and

pressing times used for both three-layer, multidaylight processes and continuous belt continuously chip-size-graded single daylight processes differ considerably. An approximate comparison of industrial conditions is shown in Table II.

It is noticeable from Table II that pressing times of tannin-based boards can be very fast, faster than for UF-bonded particleboard! (You can achieve this fairly easily in an industrial plant, but I have never seen it achieved in a laboratory press!) This is a considerable advantage that, coupled with the fact that a higher amount of lower cost tannin adhesive than PF resin (higher cost) must be used, renders tannin adhesives an economically exciting alternative to PF resins. The reason for the need of higher resin content when using tannin adhesives (10-12% on wood instead of 8% for PF resins) is mostly due to the presence of sugar and hydrocolloid gums in tannin extracts (Figures 2 and 3).

Table II. Comparison of Approximate Industrial Conditions of Application for Particleboard Bonded with Wattle Tannin Adhesives

	Pressing Time (sec/mm)	Glued Surface Chips Moisture Content (%)	Glued Core Chips Moisture Content (%)	Pressing Temperature (°C)
Three layers multidaylight	35	23-25	18	160
Three layers multidaylight	17.5	18-22	10	160
Graded single daylight	6	14-17	10-14	190

It is quite likely that high spread rates would not be needed with pure tannins from which the high amounts of sugars and gums have been eliminated. Purification may, however, be an expensive exercise if carried out on industrial scale.

**Glue Mix Application to the Wood Particles.** The techniques used to obtain fast pressing times when using tannin adhesives vary considerably according to the type of adhesive blender available. Adhesive blenders, in which the wood particles are resinated, can be divided as regards the application of tannin-based adhesives into two broad classes: 1) spraying blenders, i.e., blenders in which the liquid adhesive is sprayed onto the wood particles by means of compressed air-operated spraying nozzles; and 2) spreading and spraying blenders in which the liquid adhesive is spread and/or sprayed by pumping the liquid at high pressure

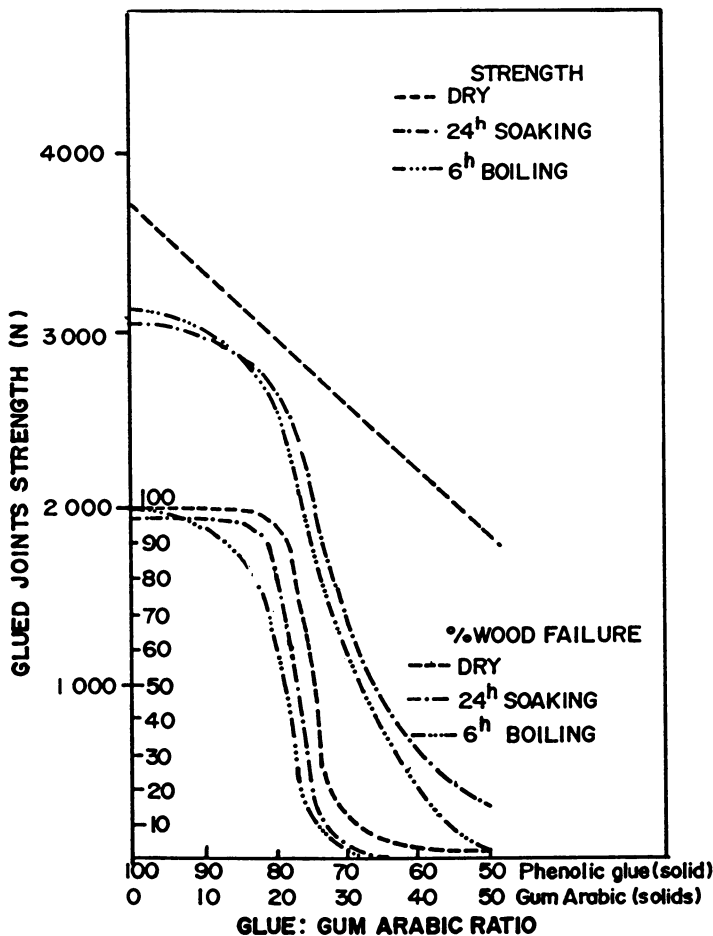


Figure 2. Effect of gum arabic on bond strength and wood failure of phenol-formaldehyde bonded wood.

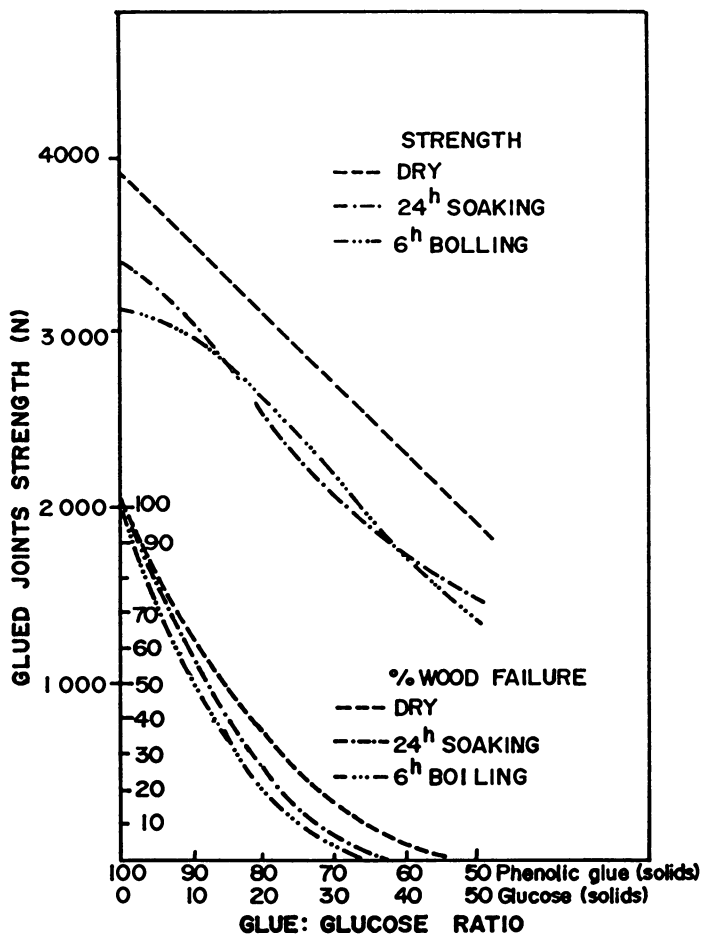


Figure 3. Effect of glucose on bond strength and wood failure of phenol-formaldehyde bonded wood.

through nozzles, i.e., Drais Turboplan blenders. Both types of blenders are able to produce good tannin-bonded particleboard using fast pressing times when the appropriate technique is used.

In the use of spraying blenders, the following technique can be successfully applied. All the paraformaldehyde powder hardener and 30% of the tannin adhesive spray-dried powder is removed from the liquid glue mix. The paraformaldehyde and wattle adhesive powder are then added to the wood chips just before the adhesive blender where the liquid glue mix is sprayed onto the wood particles. Core material MCs of 10 to 12% and face material MCs of 20 to 22% can then easily be achieved in spite of the high viscosity of tannin solutions. The percentage of paraformaldehyde used should be 14% based on wattle extract solids. The adhesive pH should be, in optimal cases, 6.5 to 6.7 for face material and 6.9 to 7.3 for core material. The percentage of resin solids on dry wood should be 11% for core material and 14 to 18% for face material.

In the use of spreading and spraying blenders, as in the case of Drais Turboplan blenders, the following technique can instead be successfully applied. The wattle-based adhesive is diluted with water to approximately 30% solids content and blended to the chips in the glue blender. All the adhesive is applied as a liquid glue mix. After resination, the wood particles have a very high MC, as high or higher than 30%. Before reaching the board-forming station, the wood particles are passed through a forced air countercurrent predrier (that in many industrial systems, is nothing other than the air flow chips conveyor from the gluing station to the spreading station on the line, to which a heat exchanger has been fitted) at a temperature variable between 70 and 90 °C. The maximum period for the resinated wood particles to remain in the predrier is approximately 4 seconds. During the time of their heating in the predrier, their MC decreases to the low values required for fast pressing times, namely 10 to 14% for core particles and 16 to 22% for face particles. The air temperature in the predrier as well as the flow rate of the resinated wood particles through it must be regulated so as to obtain the required MC. The short heating time of the resinated particles in the predrier does not impair the performance of the adhesive. Also in this system, the paraformaldehyde powder hardener must be added in powder form by means of a screw conveyor to the particles before they are resinated.

While the second system described can be applied to all types of blenders, the first cannot be applied to the second type of blender described. In the case of a Drais Turboplan machine, the first system can produce good exterior particleboard in runs no longer than 1 hour as the machine is slowly choked by a solid ring composed of resin and the finer wood particles, hardened by the paraformaldehyde present and the heat of particle friction. This choking ring of bakelite-type consistency forms in the first half of the gluing blender and on the inner wall of its casing. Its direction of growth is from the casing wall toward

the central axis of the blender. These problems are not likely to be encountered if taken care of at the time research at the laboratory level is taking place.

### **Longterm Performance of Exterior-Grade Tannin-Bonded Particleboard**

Innumerable data exist in the relevant literature from many accelerated laboratory tests on particleboard bonded with wattle tannin adhesives. However, since a picture is worth a thousand words, and a field test is worth a thousand accelerated ones, in the following photographs (Figure 4), commercial wattle-tannin-bonded, MUF-bonded and PF-bonded 12-mm-thick particleboard, exposed to the elements for a period of 15 years in our testing ground in Pretoria, are shown. It is easy to see why MUF- and PF-bonded particleboards have become extinct species in South Africa for many years! For almost 18 years tannin-bonded particleboards have been used extensively as the exterior cladding of houses, and for road signs in aggressive climatic condition. These pictures can easily be used as examples that if adhesives are sold mainly on price, quality is instead what sells exterior boards.

### **Commercial Use of Tannin Adhesives**

Countries where tannin adhesives have found commercial application and are commercially used now or have been commercially used at some time in the past are shown in the accompanying map (Figure 5). It is important to recognize that wattle tannin-based adhesives are now items of world commerce and not restricted to use in South Africa. The growing use of wattle tannin-based adhesives has been built on a sound background of understanding of their fundamental chemistry and a relentless effort to use this understanding in rational approaches to adhesive formulation. Wattle tannin-based adhesives are examples of successful transfer of technology from the laboratory to industrial practice.

### **Conclusions**

In conclusion, it is worthwhile to note that in 1970-71, when I started to be involved with tannin adhesives, there were no more than three laboratories, academic or industrial, conducting research on tannin adhesives. By 1986, I have had direct or indirect contact with 42 different laboratories in many countries that have carried out at some time, or are now carrying out, research on these bonding materials. The increase in industrial usage has also been fast but for various reasons has lagged behind the technical and scientific interest. However, after practically zero consumption in 1970, indications are that about 12,000 tons of exterior-grade tannin resin solids per year are now produced and consumed in the timber industry based on reliable information from several



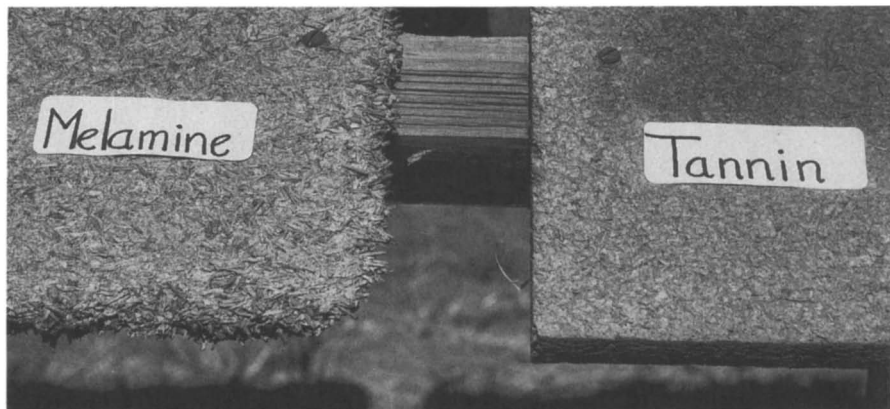


Figure 4. Photographic comparison of 12 mm thick exterior grade commercial particleboards manufactured in the same industrial plant and bonded with MUF, wattle tannin-formaldehyde, and PF resins. The panels were exposed at the CSIR testing site (4,500 feet above sea level) at Pretoria, South Africa for 15 years. Note the extensive degeneration of MUF board (commercially imported MUF resins from West Germany). Also note the more marked edge and surface degeneration of the PF in comparison to the TF-bonded boards.

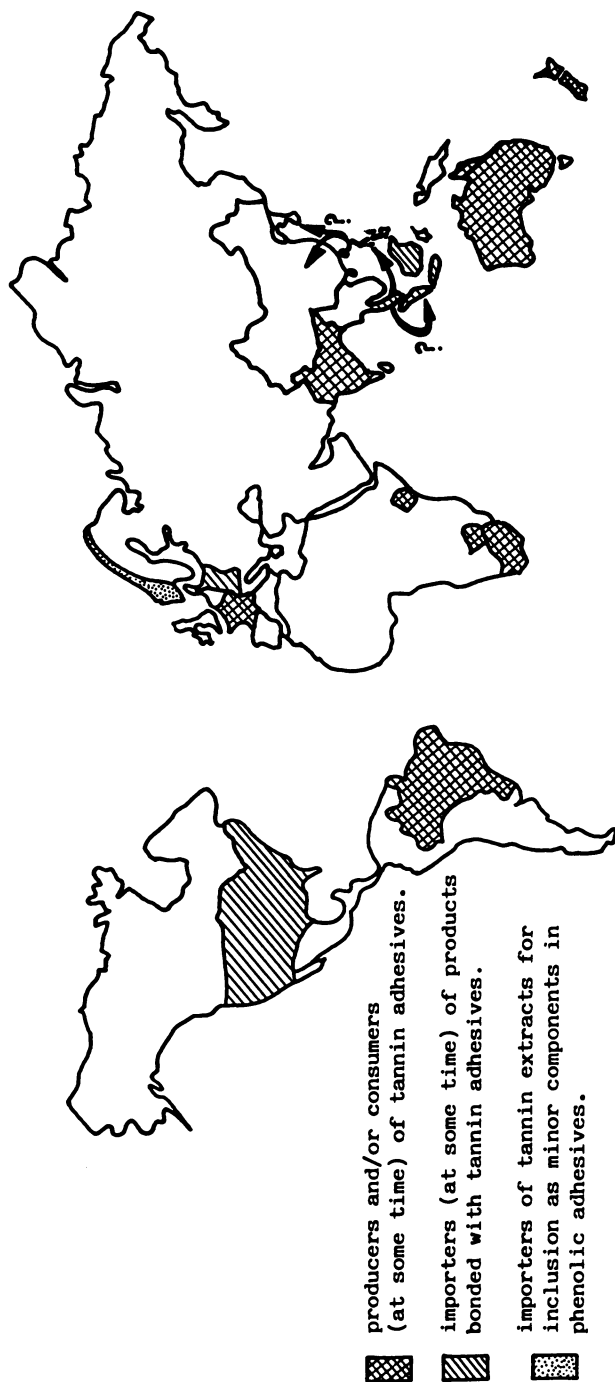


Figure 5. World production and use of wattle tannin-based adhesives.

countries. These values do not include countries known to use these materials but whose consumption data are unknown. It is easy to see then, that while the increase in production and consumption of these materials has been rapid, considerable scope for expansion still exists. Bridging the gap between new results obtained in the laboratory and industrial application of them is never an easy matter; it is essential, however, if the much-publicized search for non-oil-derived adhesives is to be a really serious undertaking and not just lip service. This chapter has related a few of the more important problems observed by the author in translating laboratory results to industrial practice. It is hoped that it will help others in translating their laboratory findings to usable industrial products for a class of wood adhesives based on non-oil-derived raw materials.

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# Chapter 20

## Carbohydrates in Adhesives

### Introduction and Historical Perspective

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Carbohydrates, in the form of gums, polysaccharides, oligomers, and monomeric sugars, are readily available in large quantities from renewable biomass resources. Each of these substances, either directly or in a chemically modified form, is a source of intermediates (derivatives) that have potential use in adhesive formulation. Carbohydrates have been utilized historically for and in adhesives and are likely to be used more and more in the future as petroleum-derived chemicals become scarce and prices increase. Appropriate research emphasis can effectively further their use as adhesive raw material.

This section of the book deals with the utilization of carbohydrates in adhesives. It includes a number of excellent chapters that give a good flavor for present research into the use of carbohydrates in adhesives.

As an introduction to this section, I would like to give a brief overview of the use of carbohydrates in adhesives. This overview is presented from a personal perspective. It will probably skim over some very important areas and may miss others entirely. I hope, however, to give you some indication of the breadth of possibilities for using carbohydrates in adhesives and some indications of possible areas where future research would be appropriate.

Carbohydrates, in the form of gums, polysaccharides, oligomers, and monomeric sugars, are readily obtainable from renewable biomass sources. Each of these has potential use in the formulation of adhesives. This has been true historically and will be increasingly true in the future as petroleum-derived chemicals become scarce and their prices rise.

Carbohydrate polymers are available in large quantities from both plant and animal sources. These include cellulose and hemicellulose from woody plants,

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starch and gums from a number of different plants and microorganisms, and chitin from animal sources. Oligomers and monomers can be obtained directly from biomass, but generally are obtained by selective hydrolysis of polymers. The types of monomeric sugars that can be obtained by hydrolysis of the polymers include both pentoses (e.g., xylose and arabinose) and hexoses (e.g., glucose, glucosamine, and mannose). The polymers, oligomers, and monomers can be converted to a variety of chemical intermediates (derivatives or degradation products) by either chemical or biological means. These also have potential as sources of adhesive materials.

This chapter deals with each of these types of carbohydrates, how they have been used in adhesives, and how they might be used in the future. In many cases, I will only allude to possible uses because detailed discussion of specific uses of certain carbohydrate materials is covered by others in chapters that follow.

### Carbohydrate Polymers in Adhesives

Carbohydrate polymers are a major constituent of all plants, the exoskeletons of various marine animals, and some microorganisms. Because up to three-quarters of the dry weight of plants consists of polysaccharides, it is not surprising that many polysaccharides are readily available at low cost. Polysaccharides, especially from plant sources, have served a variety of uses in mankind's history, ranging from basic necessities, such as food, clothing, and fuel, to paper and adhesives.

Carbohydrate polymers historically have been used for or in adhesives. Indeed, my first encounter with adhesives, and possibly your first encounter, involved the use of a carbohydrate polymer to glue paper. As a child, I used a paste made from flour and water to glue paper-mache into some very interesting forms. And as a parent, I used this same technique to build many a tunnel and hill for my son's miniature train layout, thus passing along (in disguised form) a bit of knowledge about the use of carbohydrate polymers as an adhesive that was surely first discovered before recorded history.

As I have already indicated, the polymeric carbohydrate materials available from natural sources include gums, starch and dextrans, cellulose, hemicellulose, chitin, and bacterial polysaccharides.

**Gums.** Gums are hydrophobic or hydrophilic polysaccharides derived from plants or microorganisms that upon dispersing in either hot or cold water produce viscous mixtures or solutions (i.e., gels (1)). As used in the modern sense, the term gum includes any water-soluble or water-swelling polysaccharide or its derivative. This includes starch and dextrans and various derivatives of cellulose. The latter, however, are considered separately.

Natural gums include plant exudates, seed gums, plant extracts, seaweed extracts, and the extracellular microbial polysaccharides. Plant exudates include gum arabic, gum ghatti, gum karaya, and gum tragacanth. Seed gums include

guar gum, locust bean gum, and tamarind. The arabinogalactan obtained from larch is an example of a polysaccharide that can be extracted from plants. Examples of seaweed extracts are agar, algin, and funoran. Xanthan gum and dextran are microbial polysaccharides. Table I indicates the distribution of gums for a number of industrial purposes (2,3). Their utilization in adhesives is a major end use. In recent years, synthetic polymers and microbially produced gums increasingly have replaced plant-derived gums.

Historically, several adhesives have been derived from natural carbohydrate polymers (1,4-6). In a few cases, they have been utilized because of their own particular adhesive quality. However, natural carbohydrate polymers are usually utilized as modifiers for more costly synthetic resins, especially as thickeners, colloidal stabilizers, and flow controllers. Table II lists examples of the use of natural gums in adhesives (7-40).

Table I. Distribution of Polysaccharide Gums by Commercial Usage

Product Type	Percent
Detergents and laundry products	16
Textiles	14
Adhesives	12
Paper	10
Paint	9
Food	8
Pharmaceuticals and cosmetics	7
Other	24

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**Starch and Dextrins.** Starch is a readily available mixture of polysaccharides. Starchy foods have been an important component of the human diet from prehistoric times to the present day. It is not surprising, therefore, that very practical uses for starch products developed very early and have continued throughout human history. Today, starch has a number of applications not only in the food industry but in other industries as well. In addition to its use in food, starch is also a source of chemicals (41) and sweeteners (42) and is used extensively in the paper industry (43-45) as a sizing agent and an adhesive.

The utilization of starch as an adhesive can be traced at least to 3,500-4,000 B.C., when it was used by the Egyptians to bond papyrus strips. Today, starch and dextrins derived from starch find a variety of applications in adhesives (46). Dr. H. M. Kennedy of Grain Processing Corporation presents a detailed overview of the use of starch and dextrins in Chapter 23.

**Cellulosics.** Cellulose is the major chemical constituent of plants. It is a homogeneous polysaccharide formed from  $\beta$ -D-glucopyranose units linked together

Table II. Examples of the Use of Natural Gums in Adhesives

Gum	Applications	References
Agar	Pressure sensitive tape	7
	Adhesive in gloss finishing paper products	8
	Denture adhesives	9
	Clear adhesive applicator crayon	10
	Binder for silica gel TLC plates	11
Algin	Viscosity stabilizer for starch-dextrin and latex-type adhesives used for corrugated boards	12-14
Gum Arabic	Pharmaceutical tablet binder	15
	Adhesive for miscellaneous paper products	4, 16
	Adhesive in combination with animal glues	17
	Water remoistenable adhesive (especially for postage stamps)	18
	Adhesive for glassine paper	19
	Wallpaper paste	20
Funoran	Adhesive for regenerated cellulose	18
	Household adhesive	21-23
Guar Gum	Adhesive for wood and paper	24, 25
	Medicinal adhesives	26-28
Gum Karaya	Medicinal adhesives	26-28
	Denture adhesive	28, 31-35
Tamarind	Paper adhesives	36
	Label pastes	36
	Label pastes	37
	Extender for urea-formaldehyde adhesives	38
	Pharmaceutical tablet binder	1
Gum Tragacanth	Denture adhesive	39
	Labeling adhesive	40

by (1→4)-glycosidic bonds. In addition to cellulose use in paper and textiles, a large number of cellulose derivatives are produced commercially. These derivatives are formed by either esterification or etherification of the available hydroxyl groups. A range of products with a variety of physical properties having a number of important commercial uses is obtained (47-51).

Cellulose forms the backbone of many important industrial adhesives (52). Professor David Hon of Clemson University reviews the use of cellulosic adhesives in Chapter 21.

**Hemicellulose.** Hemicelluloses are a noncrystalline group of heterogeneous polysaccharides that, next to cellulose, constitute the most abundant source of carbohydrates in plants. Like cellulose, the hemicelluloses are located in the cell wall of plants and in the bast fibers of bark. On hydrolysis, cellulose gives only glucose. Hydrolysis of hemicelluloses yield a mixture of D-glucose, D-mannose, D-xylose, D-galactose, L-arabinose, and small amounts of D-glucuronic acid, 4-*O*-methyl-D-glucuronic acid, and D-galacturonic acid. G. H. van der Klashorst of the National Timber Research Institute, Pretoria, South Africa, discusses the use of a soda bagasse hemicellulose in a corrugated board adhesive in Chapter 22.

**Chitin.** Chitin refers to the fibrillar polymer formed from  $\beta$ (1→4) linked 2-acetamido-2-deoxy-D-glucopyranose units (53,54). The N-acetylation of chitin is usually incomplete. The term *chitosan* is generally used when the nitrogen content is greater than 7% by weight; also, this term is generally used for artificially deacetylated chitins. Chitin and chitosan are the only naturally occurring polysaccharides that are basic in character. Chitin can be isolated from a large number of organisms, including insects, fungi, and crustaceans.

Chitin is the major source of glucosamine, which is used in significant quantities by the pharmaceutical industry. In addition, chitin and chitosan find a number of other medical uses including artificial kidney membranes, biodegradable pharmaceutical carriers, and blood anticoagulants. Industrially, chitin is used also as a chelating agent for toxic metals, as paper and textile additives, in textile finishes, in photographic products and processes, and for dewatering municipal sludges.

Chitin and its derivatives are known to occur in natural adhesive systems and have been suggested by several researchers as adhesives for bonding various materials together.

Barnacles secrete an adhesive to attach themselves to rocks, ships, and other objects. This adhesive hardens rapidly, even in seawater. This adhesive, which is predominately calcium carbonate in a proteinaceous matrix, contains chitin (55). Eggs of lice are attached to the bristles of hogs by a very hydrolysis-resistant adhesive that contains chitin and *p*-benzoquinone (56).

Solutions of chitosan salts are well known for their adhesive properties (53). Chitosan itself adheres well to nonconducting surfaces, such as paper, rayon, cellophane, wood, leather, rubber, and glass, but not to metal surfaces (57,58). For smooth surfaces, a stronger bond is formed by first applying a thin primer



coat. The use of chitosan for the manufacture of safety glass, plywood, laminated paper, and furniture was patented (59). The adhesive develops considerable water resistance when thoroughly dried, heated at 100-150 °C for a short time, or chemically treated. Chemical treatment consists of either reaction with ammonia or alkali to form an insoluble chitosan, washing with an acid solution to form the insoluble chitosan salt, or incorporation of formaldehyde into the adhesive.

Chitosan has been reported to be an excellent binder for pelletized fertilizers and feeds (60). Xanthation of chitin with carbon disulfide gives a viscous golden brown solution that some claim to be useful as an adhesive in the production of plywood and hardboard (61).

**Bacterial Polysaccharides.** Many bacterial species release exopolysaccharides into their environment. The synthesis of capsular and slime polysaccharides or similar sticky surface materials serves as an adhesive to attach the bacteria to solid substrates, even in a marine environment. These polysaccharides range from compositionally simple homopolymers to very complex heteropolymers composed of several individual sugars linked in a variety of ways.

**Modified Polymers.** Future applications of carbohydrate polymers or oligomers derived from these polymers as adhesives will depend on modifying the polymer provided by nature to give a component that can undergo further crosslinking to form adhesive materials.

Carbohydrate polymers typically have one primary and two secondary hydroxyl groups. Polymers like chitin contain an amine group in addition to the hydroxyl groups. These groups offer positions at which reactive moieties can be attached. If these moieties are sufficiently reactive, and the substitution of the hydroxyls is adequate, then one could form a three-dimensional polymeric network during a curing stage that would function as an adhesive. The carbohydrate polymer is already formed and therefore the degree of substitution for the reactive group does not have to be large. In fact, the physical properties of such reactive polymers might be tailored for use in a variety of adhesive applications.

The trick, of course, is to find a chemical compound that can be reacted readily with the carbohydrate polymer to give the desired reactive moieties along the backbone of the carbohydrate polymer. Here, the adhesives chemist will have to borrow from and extend the work that has been and is now being done on the formation of modified starches (62), cellulose (48-51, 63, 64), and textiles. Professor Narayan of Purdue University illustrates the potential adhesive applications of grafted cellulosic polymers in Chapter 24.

In the case of adherends such as wood, the possibility exists that the carbohydrate polymers or lignin, or both, can be modified *in situ* to give activated surfaces (65, 66) or surfaces containing reactive groups. Then, the surfaces are bonded by direct reaction or by reaction with a reactive, gap-filling compound.

Another interesting approach used to bond wood involves the swelling (66) or dissolution (with cellulose solvents) of the carbohydrate matrix (67) at the surface. Bonding then takes place when two surfaces are brought into contact and the volatile components evaporated by heating. Crosslinks form through reformation of H-bonds or possible complex formation with metal ions, in the case of cellulosic solvents.

### Monosaccharides, Disaccharides, and Oligosaccharides in Adhesives

Monosaccharides (e.g., glucose), disaccharides (e.g., sucrose), and oligosaccharides can be obtained readily from natural sources, either directly or by hydrolysis of natural carbohydrate polymers. These can be used to either modify synthetic adhesive resins or to replace them altogether. In addition, reactive derivatives could be synthesized from these compounds and used to formulate adhesive polymers.

**Modified Synthetic Adhesives.** Phenol-formaldehyde (68) and urea-formaldehyde (69) are important synthetic adhesives. Phenol-formaldehyde adhesives (PF) find a variety of applications including bonded abrasives, foundry applications, fiber bonding, and wood bonding. Urea-formaldehyde adhesive resins (UF) are used generally to bond wood products. I will illustrate the modification of synthetic adhesives with carbohydrates using both these general types of adhesives.

Figure 1 illustrates the fact that resins and adhesives formed by the possible combinations of a phenolic compound, a nitrogenous compound, an aldehyde compound, and a carbohydrate have been reported in the literature. The exact conditions used to formulate the resins and adhesives represented in Figure 1 vary considerably. For example, additional circles representing acidic, basic, and neutral reaction conditions could be added. In most instances, the exact chemistry that occurs during the formulation of resins at each intersection is not known. Indeed, in many cases, the component actually reacting into the resin or adhesive system may not be the original carbohydrate added at the start. In this and other respects, these formulations will overlap with those discussed in the next section.

Table III lists a number of selected references that describe the formulation of resins or adhesives at each intersection in Figure 1. PF, UF, UF modified with phenolics, and PF modified with nitrogenous compounds (e.g., urea) have not been included, because they do not contain carbohydrates and because they are in common use. The resin and adhesive systems that have been investigated most recently are those formed by the combination of carbohydrates with PF, both with and without the addition of a nitrogenous compound. Our attempts at the Forest Products Laboratory to use carbohydrate modified PF to bond wood are discussed in Chapter 25.

The incorporation of a nitrogenous compound (typically urea or ammonia) modifies the overall chemistry during adhesive formulation, apparently in a

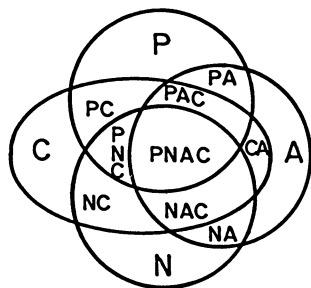


Figure 1. Resins can be classified as being formed from combinations of a phenolic compound (P; typically phenol), an aldehyde (A; typically formaldehyde), a nitrogenous compound (N; typically urea), and a carbohydrate (C).

beneficial manner. This is especially true when the resins are formulated under basic conditions with reducing carbohydrates that are readily degraded at basic pHs. Dr. Christiansen of the Forest Products Laboratory and Professor Karchesy of Oregon State University discuss their experiences with carbohydrate-phenol-urea based adhesive resins in Chapters 26 and 27.

Table III. Selected References that Describe the Formulation of Resins and Adhesives Named in Figure 1

System <sup>1</sup>	References
Phenol-Carbohydrate (PC)	70-79
Phenol-Aldehyde-Carbohydrate (PAC)	80-94
Phenol-Nitrogenous compound-Carbohydrate (PNC)	70,95-98
Nitrogenous compound-Carbohydrate (NC)	78,99-103
Nitrogenous compound-Aldehyde-Carbohydrate (NAC)	99,104-113
Phenol-Nitrogenous compound-Aldehyde-Carbohydrate (PNAC)	114-123
Carbohydrate-Aldehyde (CA)	108,124-126

<sup>1</sup>Acronyms correspond to those used in Figure 1.

Professor Viswanathan of the University of Arkansas discusses his research into the formulation of formaldehyde-free, thermosetting adhesives from whey permeate with urea and phenol or both in Chapter 28.

Polymeric carbohydrates of an undetermined degree of polymerization have also been used to modify synthetic adhesive resins. In particular, cellulosic papermill sludges have been used to modify PF and UF resins (127). A carbohydrate polymer was reported to be an excellent extender and modifier for polyvinyl alcohol adhesives (128).

A thermosetting/thermoplastic adhesive has been reported that is composed of a protein (i.e., animal glue) containing liginosulfonate and a carbohydrate or polyhydric alcohol (129). Although this is not an example of the modification of a synthetic adhesive, it does further indicate the wide range of adhesive types that have been modified with carbohydrates. Also, it is interesting to note the further connection between a nitrogenous component (protein) and a carbohydrate.

**Replacement of Synthetic Adhesives.** Total replacement of synthetic adhesives with an adhesive system based entirely on carbohydrates, except as indicated above (i.e., NC and CA), has not been reported. And, as discussed above, it is not clear that the carbohydrate in fact is reacting as the carbohydrate component that was originally added.

Carbohydrate-based adhesives, in which the formulation begins with the carbohydrate, have been reported (130), but the acid system used during formulation readily degrades the original carbohydrate to furan intermediates that

polymerize. The formulated resins are subsequently mixed with crosslinking agents (formaldehyde or triethylenetetramine) prior to curing.

Stofko (131-133) has reported an interesting adhesive system for wood products in which carbohydrate is presumably converted to furfural and hydroxymethylfurfural *in situ*, reacting with both the lignin in wood and homopolymerizing in the bond line to form the adhesive joint.

**Reactive Derivatives.** As with the polymeric carbohydrates, one method that might lead to future utilization of carbohydrates as adhesives involves the formation of reactive derivatives attached at the hydroxyls. This would give a component capable of crosslinking to form adhesive polymers. Here again, the adhesives chemist will have to borrow from and extend the work that has been and is now being done on the formation of modified starches, cellulose, and textiles.

Two interesting reactive groups that might be considered, at least for purposes of illustration, are the allyl (134) and vinyl groups (135). The preparation of allyl ethers of carbohydrates and their polymerization have been described (136-138). Their polymerization is slow even with added catalysts such as peroxides. Allyl starch was studied at the Forest Products Laboratory in the mid-forties as an adhesive for wood, but without success. The preparation of vinyl cellulose (139) and vinyl carbohydrates (140) has been described. The polymerization of 6-*O*-vinyl-1,2:3,4-di-*O*-isopropylidene-D-galactopyranose has been investigated (140). Very high molecular weight polymers were obtained in relatively short reaction times. Compounds such as these or their further reaction products (e.g., epoxides) might be useful in adhesives, especially if methods could be found for increasing the rapidity with which they polymerize.

### Carbohydrate Degradation Products in Adhesives

The reaction of carbohydrates in acid or alkaline solution results in a number of products, many of which have been identified over the past century (141). With the exception of anhydrosugars (e.g., 1,6-anhydro- $\beta$ -D-glucopyranose) and oligosaccharides, which are concentration-dependent and equilibrium components (reversion products) formed in acid solution, all of these products result from reactions associated with the Lobry de Bryn-Alberda Van Ekenstein transformation or intermediates formed from this transformation.

In acid solution, pentoses and hexoses form furan compounds. Pentoses give high yields of 2-furaldehyde (furfural). Hexoses give 5-(hydroxymethyl)-2-furaldehyde (hydroxymethylfurfural), which can further react to give levulinic acid and polymeric materials.

It is interesting to speculate that these compounds, both because of their reactivity and their ability to form polymeric materials, might be useful in adhesives formulations.

**Furans.** The last statement is certainly true of furans derived from sugars (142,143), particularly furfural and furfuryl alcohol, which is readily derived from furfural (144). Dr. McKillip of QO Chemicals discusses furan resin chemistry and furan polymers in Chapter 29. Dr. Stanford and his colleagues at the University of Manchester Institute of Science and Technology discuss the use of a diisocyanate derived from furfural for polyurethane production in Chapter 30.

**Levulinic Acid.** Levulinic acid is formed by the acid catalyzed degradation of hexose sugars via the intermediacy of hydroxymethylfurfural (145). Although its formation was reported as early as 1836 (146), the mechanism of its formation has been studied at least as recently as 1985 (147).

Levulinic acid is a highly reactive keto acid that is readily available from renewable materials. It has been proposed as a renewable basic chemical raw material (148-150) that can be used for a variety of purposes. These uses include plasticizers, pharmaceuticals, solvents, food additives, flavoring compounds, chemical intermediates, and resins and polymers. Recently,  $\alpha$ -angelicalactone, which is formed on distillation of levulinic acid by the loss of a molecule of water, has been proposed as a liquid fuel extender (151).

Diphenolic acid, the condensation product of levulinic acid and phenol, is useful in the preparation of modified phenol-formaldehyde resins, polyether resins, or as monocarboxylic acid chain stoppers in alkyd resins (152). It can be substituted for bisphenol-A, the primary raw material in the production of epoxy resins (153).

Several interesting resins and polymers have been obtained from levulinic acid. These and similar polymers might have potential application in adhesives. A heat-setting resin was produced from a fusion of levulinic acid and amines (154). The resins were described as hard and tough with good adhesion to glass. Levulinic acid reacts rapidly with formaldehyde; a hard, flexible, infusible resin is formed (155). The preparation of polyamides from furfural and levulinic acid has been described (156). Adhesive compositions having good water resistance were prepared from atactic polypropylene and levulinic acid (157). This adhesive was used for bonding polypropylene to itself or to plastics, wood, and paper. Copolymerization of butadiene with dichloroallyl levulinate (158) or with methyl or ethyl levulinate (159) gives copolymers with rubberlike properties.

**Levogluosan.** Levogluosan, 1,6-anhydro- $\beta$ -D-glucopyranose, is a thermal degradation product of materials containing cellulose or other polysaccharides formed from D-glucose. Usually, it is produced by pyrolysis *in vacuo* of cellulose, starch, or wood. A method for isolating levogluosan from lignocellulose pyrolysis has been patented (160). The synthesis of levogluosan has been reviewed (161).

Various reports in the literature indicate that levogluosan might be of interest in relation to adhesives. The indications are that levogluosan and its derivatives can undergo ring-opening polymerization, that reactive derivatives

of levoglucosan can be produced and used to form polymers, and that phenol, a major adhesive component now produced from petroleum, can be synthesized from levoglucosan.

Levoglucosan has been polymerized either thermally or in the presence of acid catalysts, such as zinc chloride and monochloroacetic acid, to give oligo- and polysaccharides (161,162). The molecular weight and yields of the final polymers are strongly dependent on the experimental conditions. Copolymerization with alcohols and ethers has been reported. Although the exact structures of the resulting polymeric systems are not known, they appear to offer promise for the preparation of adhesives and lacquers (162), although no specific references to the use of these polymers as adhesives were found.

Ring-opening polymerization of the 2,3,4-tri-*O*-substituted levoglucosan, especially the benzyl ether, has generally proven more successful than polymerization of the unsubstituted levoglucosan and yields polysaccharides of high molecular weight (161,162). In either case, the polymerization conditions reported in the literature, especially in terms of time, temperature, and catalysts, probably would preclude polymerization within the bondline. However, the possibility of ring-opening polymerization afforded by this compound and similar anhydrosugars would suggest that further research might be warranted.

Two interesting polymeric systems have been formed from reactive levoglucosan derivatives and will serve to indicate the possibilities of this approach. These two systems are 1,6-anhydro-2,3,4-tri-*O*-methacryl- $\beta$ -D-glucopyranose and the corresponding tri-*O*-acryl derivative (163). They were polymerized with benzoyl peroxide as radical initiator to give a three-dimensional structure with a thermal degradation temperature of 300 °C. The second polymeric system can be formed from 1,6-anhydro-2,3,4-tri-*O*-glycidyl- $\beta$ -D-glucopyranose using an amine catalyst (164). This compound is formed by epoxidation of the tri-*O*-allyl derivative of levoglucosan.

Phenol and substituted phenols can be obtained from lignin by pyrolysis, alkali fusion, and hydrogenolysis (165-167). This methodology could be used to prepare an adhesive starting material, presently obtained from petroleum sources, from a renewable source, although technical difficulties require solution through further research.

The conversion of levoglucosan derivatives to phenol in reasonable yields has been reported (168-175). This affords the possibility of also obtaining phenol from the cellulose portion of renewable resources. The reaction is carried out in liquid ammonia with sodium metal and thus probably is impractical on a commercial scale. But further research might lead to simpler, less costly, and more efficient methods for this conversion.

## Conclusions

Carbohydrates are readily available from renewable biomass sources. In this introduction, I have given a broad overview of how carbohydrate polymers,

oligomers, monomers, and degradation products historically have been utilized in and for adhesives. In addition, I have pointed out some examples of where research might further the use of carbohydrates as adhesive raw materials.

The replacement of petroleum-derived (nonrenewable) sources of adhesive raw materials with renewable sources will follow three basic strategies: 1) renewable materials will be used to replace part of the required petroleum-derived adhesive systems, 2) new polymeric adhesives will be synthesized from renewable materials and totally replace petroleum-derived adhesive systems, or 3) the adhesives systems now based on petroleum-derived materials will continue to be used, but the adhesive raw materials will be derived from renewable sources instead of from nonrenewable ones. Carbohydrates are very versatile chemicals that can be utilized in all three strategies as demonstrated by the preceding discussion.

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# Chapter 21

## Cellulosic Adhesives

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Cellulose is an old polymer with new industrial applications. The derivatization of cellulose has opened up tremendous production and marketing possibilities for the adhesives industry. Various important adhesives have been derived from cellulose ethers. The structure and molecular size of cellulose and their influence on swelling and solubility are important considerations in the preparation of cellulose derivatives for adhesive applications. Modern cellulosic adhesives derived from grafted copolymers and polyblends are also proving very useful.

Since the energy and chemical raw material crunch of 1973, many alternatives to petroleum and other imported chemical stocks have been explored. What are the needs of the adhesive industry? What other sources can be tapped? Cellulose, a polysaccharide produced in great abundance in nature, is a prime candidate as a raw material for use in adhesives because of its availability and relatively low cost and because of its readiness to be converted into a variety of useful adhesive products. In essence, cellulose is a wonder material with a promising future (1).

### Structure and Molecular Weight

Cellulose is a polydisperse, linear syndiotactic polymer. Its basic monomeric unit is D-glucose, which links successively through a glucosidic bond in the  $\beta$ -configuration between carbon 1 and carbon 4 of adjacent units to form long chain 1,4- $\beta$ -glucans. Figure 1 shows a structural diagram of a portion of a cellulose chain. Because of the  $\beta$ -configuration of the intermonomer links, the glucose units effectively alternate up and down in the chain. Hence, scientists consider cellobiose as the repeating unit of cellulose, on which a syndiotactic configuration of the macromolecule is formed. The size of the cellulose molecule

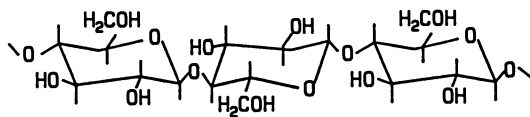


Figure 1. The partial molecular structure of cellulose.

occurring in nature, indicated by its degree of polymerization (DP) or chain length, is dependent heavily on its source (Table I). In some cases, the DP may exceed 10,000.

Table I. Degree of Polymerization of Cellulose from Various Sources

Source	Degree of Polymerization
<i>A. xylinum</i>	2,000 - 3,700
Bagasse	700 - 900
Bast fibers	1,000 - 5,000
Cotton fibers	8,000 - 14,000
Cotton linter	1,000 - 5,000
Flax fibers	7,000 - 8,000
Pulp cellulose (bleached)	500 - 2,100
Ramie fibers	9,000 - 11,000
Rice straw	700 - 800
Valonia	25,000 - 27,000
Wood fibers	8,000 - 9,000

Cellulose never occurs in pure form; in softwood and hardwood, it constitutes about 40 to 50% of the weight, in flax 70 to 85%, whereas, cottonseed hairs, which are the purest source, contain more than 90% (Table II). In these materials, cellulose macromolecules serve as a structural material within the complex architecture of the plant cell walls. Commercial production of cellulose is concentrated on the highly pure sources like cotton or easily harvested sources like wood.

### Adhesives and Adhesion

Adhesives hold two surfaces together by developing internal or cohesive strength. In order to hold surfaces together, adhesives must be applied to the substrate in a fluid form to wet, spread, and penetrate the surface completely and leave no voids. Hence, adhesives must be low in viscosity at the time of application. In order to provide strong cohesive strength, the adhesive must be set or solidified by either cooling, crosslinking reaction, or evaporation of solvents, depending on whether the adhesive is hotmelt (thermoplastic), thermoset, or solvent-based. This also implies that in order to provide enough bonding strength, an adhesive must be a polymer with high molecular weight. As a rule of thumb, the higher the molecular weight, the higher the bonding power. However, for thermoplastics, as for cellulosic adhesives, the higher the molecular weight, the more difficult it becomes to process the adhesives. Hence, the molecular weight range of this type of polymer is carefully chosen to represent the best compromise



between processability and final properties. For adhesive application, many adhesives and hotmelts have a lower molecular weight. The adhesives with lower molecular weight have better solubility in solvents, a wider range of compatibilities with other resins and plasticizers, and lower melting or softening points.

Table II. Natural Sources of Cellulose

Source	Cellulose Content (%)
Bagasse	35 - 45
Bamboo	40 - 55
Cotton	90 - 99
Flax	70 - 75
Hemp	75 - 80
Jute	60 - 65
Kapok	70 - 75
Ramie	70 - 75
Straw	40 - 50
Wood	40 - 50

Cellulose is a polymer that meets these requirements as an adhesive. However, due to its semicrystalline structure, highly hydrogen-bonded cellulose cannot be dissolved easily in conventional solvents, and it cannot be melted before it burns. This is because the attractive forces and stability of crystal structures are greater than those that result from interaction between polymer and solvent. Hence, cellulose itself is not suitable for use as an adhesive. The same can be said of regenerated cellulose. In order to make cellulose soluble or meltable, the hydrogen bonds must be broken (i.e., cellulose molecules must be more flexible and possess high entropy, so that they can be separated easily).

Cellulose is a semicrystalline polymer. In the crystalline region, the linear polymeric chains are held together by relatively strong intermolecular hydrogen bonds. Derivatives, grafting, and polyblending of cellulose can reduce the strength of intermolecular bonds, making cellulose soluble in water and in organic solvents. Some cellulose derivatives are also meltable under heat. As a matter of fact, cellulose derivatives are a very good class of thermoplastic adhesives. They can be used in the form of solutions, dispersions in water, or solids. Their properties are in many cases influenced by factors such as molecular weight and degree of chemical substitution and, in copolymers, the monomer ratio; in graft copolymers, the degree of grafting.

## Swelling and Dissolution of Cellulose

A polymer dissolves in two stages. First, solvent molecules diffuse into the polymer, swelling it to a gel state. Then, the gel gradually disintegrates, and the molecules diffuse into the solvent-rich regions. In essence, solubility and swelling of a polymer in a solvent depend upon competitive intermolecular attraction between solvent and polymer molecules versus adjacent polymer molecules. If the interactive force between the polymer molecule and solvent molecule is stronger than the polymer-polymer secondary force, the polymer will initially swell and dissolve. Although cellulose molecules hold together strongly via intermolecular and intramolecular hydrogen bondings, some liquids can penetrate cellulose completely and thus will cause intracrystalline as well as intercrystalline swelling. Water is a good swelling agent for cellulose; however, swelling only occurs either in intercrystalline regions or on the surfaces of the crystallites and the gross structure. Water does not penetrate the crystalline region. There are many reagents, such as alkali metal hydroxides, salts in strongly alkaline solution, some inorganic acids and salts, and certain amines and related compounds that can cause intracrystalline swelling of cellulose.

In order to make cellulose soluble or meltable, chemical reagents must be introduced into the cellulose to destroy the intermolecular hydrogen bonding. Once the original hydrogen bonds have been broken and intramicellar swelling is achieved, the cellulose hydroxyls are capable of reacting like ordinary aliphatic hydroxyl groups. Hence, sodium hydroxide is a popularly used agent to swell cellulose prior to substitution reactions. Generally, the substitution of hydroxyl groups in cellulose by a bulky reagent allows separation of cellulose chains so that a solvent may penetrate and solvate the molecules. This action has been found useful in bringing cellulose into solution or lowering its melting point. Consequently, based on this principle, many adhesive and coating materials have been prepared from cellulose by different substitution reactions. Two major groups are cellulose esters (2-4) and cellulose ethers (2-4).

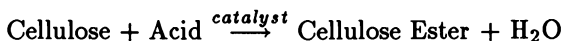
The substitution of hydrogen and hydroxyl groups with a polymer by a graft copolymerization reaction has also been found useful in bringing cellulose into solution and lowering its melting point. The grafting of acrylonitrile with subsequent hydrolysis produces a water-soluble cellulose-acrylic acid graft-copolymer. Occasionally, the blending of cellulose with a compatible polymer has also been found useful in lowering the softening point of cellulose or increasing its applicability in use as an adhesive. For instance, the blending of cellulose with natural rubber to make surgical adhesives has been commercially successful. Hence, the adhesives industry has a wide variety of cellulosic products from which to select and create an end product with varying adhesive properties.

### Cellulose Derivatives: Esters and Ethers

Since cellulose is a polyhydroxyl alcohol, it can undergo esterification and etherification modifications. The properties of the derivatives depend heavily on the

type, distribution, and uniformity of the substituent groups. For each  $\beta$ -D-glucopyranosyl ring, there are three hydroxyl groups available for the nucleophilic substitution reaction. Reactions at these sites can occur either on a one-to-one basis or with formation of side chains depending on choice of reagent employed to modify the cellulose. The term "degree of substitution" (DS) is used to identify the average number of sites reacted per ring. The maximum value is 3, corresponding to the number of hydroxyls available for reaction. When side-chain formation is possible, the term "molar substitution" (MS) is used to denote the length of side chain, and the value can exceed 3.

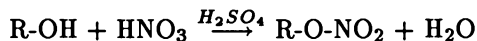
**Cellulose Esters.** Cellulose contains primary and secondary hydroxyl groups. Hence, cellulose esters can be made with all inorganic and organic acids. Traditionally, cellulose esters are made by a controlled acid-catalyzed reaction between an acid or acid anhydride and the hydroxyl groups of cellulose. The reaction requires the absence of water for completion because it is a reversible reaction. The general reaction scheme can be illustrated as shown in Scheme 1.



Scheme 1

Historically, the first thermoplastic synthetic adhesive was the cellulose inorganic ester, cellulose nitrate. Schonbein (5) is generally regarded as having discovered cellulose nitrate in 1845 by nitrating cellulose with a mixture of nitric and sulfuric acids. Most early work was aimed at utilizing cellulose nitrate in explosives, but later, it found use in plastic, adhesives, and coating applications. Today, it is still one of the most important adhesives.

Cellulose nitrate can be prepared by treating highly purified cellulose with a mixture of nitric and sulfuric acid (6). The reaction scheme may be represented as shown in Scheme 2.



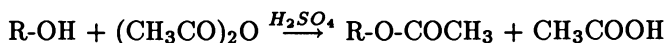
Scheme 2

For adhesive application, the acid mixture is made up of nitric acid (25%), sulfuric acid (55%), and water (20%). The function of sulfuric acid is to remove the water of reaction so that nitration may be carried to the desired degree more readily. The various products may be characterized by nitrogen content, which corresponds to the degree of substitution. The nitrogen content also determines the solubility of cellulose nitrate. With 11.8 to 12.2% nitrogen content,

cellulose nitrate will be soluble in esters, ketones, ether-alcohol mixtures, and glycol ethers. It will also have excellent aromatic hydrocarbon tolerance but less tolerance for aliphatic hydrocarbons. With 11.3 to 11.7% nitrogen content, it will have approximately the same solvency; however, it will also tolerate high percentages of low-molecular weight anhydrous alcohols. With 10.9 to 11.2% nitrogen content, it can dissolve in alcohol. In practice, the nitration of cellulose is allowed to proceed only far enough to give an average dinitrate (nitrogen content ranging from 10.7 to 12.2%), since the trinitrate is explosive.

Because of its wide range of solubility, cellulose nitrate has become a popular "household" cement. It is a waterproof, clear, flexible adhesive for use with plastics, cloth, wood, paper, china, glass, metal, and leather. A medium or high-viscosity type cellulose nitrate is generally used with solvents that are fairly rapid in evaporation rate. A plasticizer is used to give flexibility. Several commercial grades of cellulose nitrate with characteristic properties are listed in Table III.

Cellulose acetate is universally recognized as the most important organic ester of cellulose. It is widely used in plastics and textiles but finds only limited application in adhesives and coatings. It can be prepared by reacting high-purity cellulose with acetic anhydride, utilizing acetic acid as the solvent and sulfuric acid as a catalyst (3) as shown in Scheme 3.



Scheme 3

The degree of nitration of cellulose nitrate can be regulated by choice of reaction conditions; however, the degree of acetylation is not regulated until triacetate is obtained. This is because, if acetylation is interrupted before complete esterification, a heterogeneous mixture of the triacetate and unreacted cellulose will result. The diacetate is normally obtained by partial hydrolysis of the triacetate so that products with various degrees of esterification are obtainable. As an adhesive, it is used in solution without additives or fillers. It finds use in building models and joining plastics, leather, wood, and china. Plasticized cellulose acetate films have found use for protecting archival documents. A laminate of the document and a sheet of cellulose acetate film are made under heat and pressure. The cellulose acids act not only as an adhesive but also in giving protection against soiling, aging, and mechanical abuse. Cellulose acetate films can all be activated by brushing them with acetone and then laminated with documents without using heat and pressure.

Cellulose esters of butyric and propionic acids have limited adhesive use. However, cellulose caprate, having a refractive index near that of glass and good resistance to photochemical change, is a useful hotmelt optical cement for the manufacture of compound lenses.

Table III. Characteristics of Commercial Cellulose Nitrate Adhesives

Manufacturer/Supplier	Bond Adhesives Co.	Bond Adhesives Co.	G. C. Electronics
Commercial name	Bond 9164	Bond 5275	Electronic Cement 34-2S
Features	Special tube for controlled dispensing	Versatile, tough films, resists water	Waterproof, vibration resistant bond
Substrates	1. Mineral 2. Glass 3. Mineral 4. Plastic 5.	Wood Leather Plastic Glass Metal	Metal Paper Textile
Characteristics			
1. Color	Clear	Clear	Clear-light straw
2. Weight per gallon (lb/gal)	7.30	7.20	7.90
3. Solids content, %	17.0	25.0	23.0
4. Solvent	TIn	Ac	BAC, EAc, TIn
5. Flash point (°C)	Flammable	Flammable	-9
6. Storage conditions	>6 mo/RT	>2 yr/RT	>2 yr/RT
7. Form	Thin syrup	Medium syrup	Liquid
8. Cure conditions	24 hr/RT	30 min - 24 hr/RT	10-15 min/RT
9. Application procedure	Brush, dip, tube	Brush, knife, tube	Brush

Table III. Characteristics of Commercial Cellulose Nitrate Adhesives  
(continued)

Manufacturer/Supplier	G. C. Electronics	G. C. Electronics	G. C. Electronics
Commercial name	General Purpose 45-2	Plastic Cement 10-324	Service Cement 10-302
Features	Universal type, waterproof, quick drying	Waterproof, quick drying will not become brittle	Waterproof, quick drying, strong, hard, resists vibration
Substrates	1. Paper 2. Leather 3. Metal 4. Glass 5. Ceramic	Plastic Textile Wood	Metal Plastic Wood Paper Ceramic
Characteristics			
1. Color	Clear-light straw	Clear-light straw	Clear-light straw
2. Weight per gallon (lb/gal)	7.90	7.90	7.90
3. Solids content, %	23.0	23.0	30.0
4. Solvent	BAc, EAc, TIn	BAc, EAc, TIn	BAc, EAc, TIn
5. Flash point (°C)	-9	-9	-9
6. Storage conditions	>2 yr/RT	>2 yr/RT	>2 yr/RT
7. Form	Liquid	Liquid	Liquid
8. Cure conditions	10-15 min/RT	10-15 min/RT	10-15 min/RT
9. Application procedure	Brush	Brush	Brush

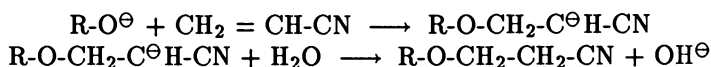
Interestingly, mixtures of esters of cellulose such as the acetate/butyrate and acetate/propionate are in many ways superior to the straight acetate in having, for instance, lower water absorption and greater flexibility. They have found use in adhesive application. Cellulose acetate-butyrate is prepared by using a mixture of acetic anhydride and butyric anhydride with sulfuric acid as catalyst, and then the product is slightly hydrolyzed. Depending on the reaction conditions, various products may be obtained. Cellulose acetate-butyrate can be used in hotmelt adhesives or dissolved in ketone-ester solvent mixtures. It has been used in the manufacture of safety glass. The composition of a typical commercial grade of cellulose acetate-butyrate for adhesive application is shown in Table IV.

Table IV. Properties of Typical Commercial Grades of Cellulose Acetate-Butyrate for Adhesive Application

Acetyl Content (%)	Butyryl Content (%)	Hydroxy Content (%)	Degree of Esterification (DS)		
			Acetyl	Butyrate	Hydroxy
29.5	17	1.0	2.1	0.7	0.2
20.5	26	2.5	1.4	1.1	0.5
13.0	37	2.0	0.95	1.65	0.4

Additional information on physical and chemical properties of cellulose esters is summarized in Table V.

**Cellulose Ethers.** Cellulose ethers are formed when cellulose, in the presence of alkali or as alkali cellulose, is treated with alkyl or arylalkyl halides. Two types of reaction are employed in the preparation of cellulose ethers. The most common is nucleophilic substitution. Methylation of alkali cellulose with a methyl halide is an example of this type. The other type of etherification reaction is Michael addition. This reaction proceeds by way of an alkali-catalyzed addition of an activated vinyl group to the cellulose. The reaction of acrylonitrile with alkali cellulose is a typical example. The general reaction is outlined in Scheme 4.



Scheme 4

Cellulose ethers have found popular applications due to their solubility characteristics. The introduction of a small number of alkyl (e.g., methyl or ethyl)

Table V. Physical and Chemical Properties of Cellulose Esters

	Nitrocellulose	Cellulose Acetate	Cellulose Acetate Butyrate	
			High Acetyl	High Butyl
Bulking value, (gal/lb)	0.0704	0.0925	0.104	0.0965
Specific gravity	1.70	1.30	1.25	1.17
Tensile strength, [psi (1-mil film)]	9,000-16,000	8,500-11,000	2,500-6,500	
Elongation, [psi (1-mil film)]	10-50	4-55	40-60	
Softening point, °F	155-220	235-255	240	165
Solubility	Esters, ketones, ether alcohols, glycol ethers	Ketones	Ketones, esters	Alcohols, aromatic hydrocarbons
Resin compatibility	Good	Limited	Limited	Wide
Plasticizer compatibility	Excellent	Limited	Limited	Wide
Resistance to:				
Weak acids	Fair	Good	Good	Poor
Strong acids	Poor	Poor	Poor	Poor
Weak alkalis	Poor	Good	Poor	Poor
Strong alkalis	Poor	Poor	Poor	Poor
Water	Good	Good	Good	Good
Sunlight	Fair	Good	Excellent	Excellent
Heat	Fair	Very good	Very good	Fair
Viscosity range	Wide	Limited	Fair	Fair
Flammability	High	Very low	Low	Low
Color of film	Water white	Water white	Water white	Water white
Use of adhesives	Wide	Limited	Fair	Wide

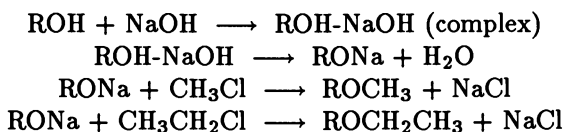


groups into the cellulose molecule sufficiently opens up the structure to permit solubility in aqueous sodium hydroxide. As substitution increases, the products become soluble in decreasing concentrations of alkali, and at length, they are soluble in water. As the number of alkoxy groups increases, the products become less soluble in water and more soluble in polar organic solvents. At higher degrees of substitution, solubility in polar organic solvents declines, whereas, solubility in nonpolar solvents increases. During the past 20 years, cellulose ethers have progressed from materials of largely experimental and developmental importance to products of considerable industrial importance. The most important products that have been used in adhesive application are listed in Table VI.

Table VI. Important Cellulose Ethers Used in Adhesive Applications

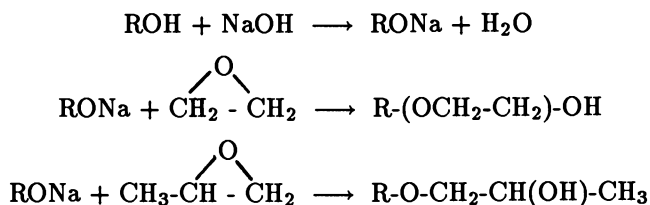
Substance	Symbol
Carboxymethylcellulose	CMC
Ethylcellulose	EC
Methylcellulose	MC
Hydroxyethylcellulose	HEC
Hydroxypropylcellulose	HPC
Ethylhydroxyethylcellulose	EHEC
Hydroxybutylmethylmethylcellulose	HBMC
Hydroxyethylmethylmethylcellulose	HEMC

Methyl- and ethylcelluloses are prepared by reacting purified woodpulp or cotton linters having a high  $\alpha$ -cellulose content with aqueous sodium hydroxide and then with methyl chloride or ethyl chloride according to the following scheme:



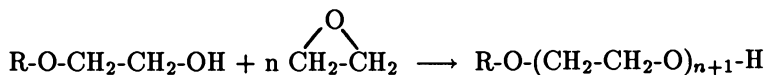
Scheme 5

Hydroxyethylcellulose (HEC) and hydroxypropylcellulose (HPC) are prepared by reacting cotton linter or woodpulp with aqueous sodium hydroxide, and the resulting alkali cellulose is reacted with ethylene oxide and propylene oxide, respectively.



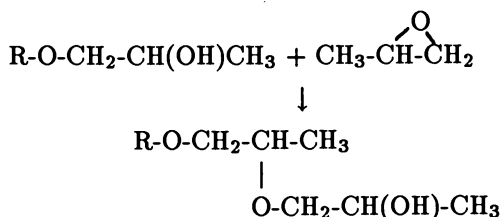
Scheme 6

The hydroxyl groups can also undergo reaction with ethylene oxide; hence, two or more poly(oxyethylene) units can form polymers as shown in Scheme 7.



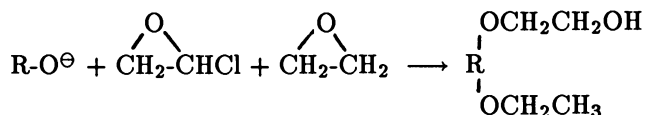
Scheme 7

Likewise, the secondary hydroxyl group in the hydroxypropyl group can undergo hydroxypropylation to give a side chain:



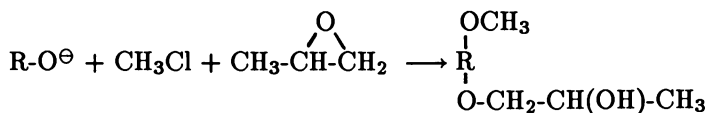
Scheme 8

The reaction of alkali cellulose with a mixture of ethyl chloride and ethylene oxide can produce ethylhydroxyethylcellulose (EHEC), as illustrated in Scheme 9.



Scheme 9

The reaction of alkali cellulose with a mixture of methyl chloride and propylene oxide can produce hydroxypropylmethylcellulose (HPMC).



Scheme 10

In general, these groups of cellulose ethers have been used for their innate adhesive properties and to provide thickening to adhesive formulations. They are used for plywood adhesives, industrial adhesives, wallpaper paste, library paste, and latex adhesives. For example, methylcellulose is used in some adhesives as an additive to control viscosity, especially in the heat-cure phenol-formaldehyde glues and other hot-pressing adhesives. Hydroxyethylcellulose is used as an ingredient in polyvinyl acetate emulsions, where it acts as a thickener and protective colloid.

Cellulose ethers have also been used in the ceramic industry (7). Since their appearance in 1959, water-based cellulose ethers have replaced solvent-based adhesives. The adhesives used for ceramic tile are ready-mixed products based on natural or synthetic rubber, polyvinyl acetate, and other resins, and they all contain cellulose ethers of one kind or another (e.g. MC, EC, HPMC, HEMC, HEC). These cellulose ethers reduce water loss, modify the viscosity of the mix, and can provide excellent adhesion for dry, very porous tiles.

Sodium carboxymethylcellulose (Na-CMC) is also a water-soluble anionic linear cellulose ether. It is prepared by treating cellulose with aqueous sodium hydroxide followed by reaction with sodium chloracetate as shown in Scheme 11.



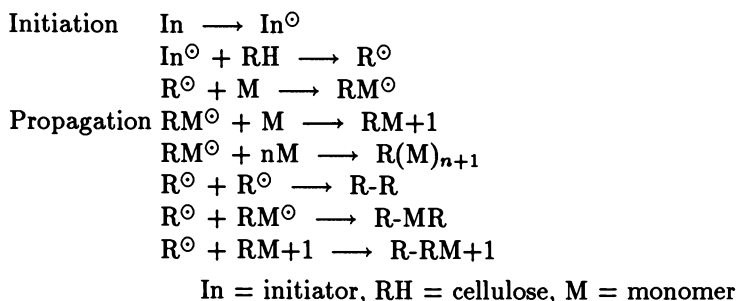
Scheme 11

CMC has been widely used as a nonstaining wallpaper adhesive. It has also been used as an adhesive in the paper and textile industries. Characteristics of CMC that are important for this application are its ease of "slip," nonspilling property, high adhesive efficiency, and ease of makeup. CMC has found use in the ceramics industry where its ability to bind and suspend materials during various stages of manufacture is important. It is used in glazes for sanitaryware, structural tile, and dinnerware.

### Graft Copolymers of Cellulose

Cellulose esters and cellulose ethers are prepared based on the substitution of cellulose hydroxyl groups with short chain reagents. Cellulose can also be modified by introduction of long chain polymer(s) onto its main chain. The products are mostly grafted copolymers, and in some cases, block copolymers can also be made.

Many different methods of grafting have been developed. By far the greatest effort has been via free-radical vinyl-polymerization routes. The general reaction scheme is shown below:



Scheme 12

Vinyl monomers that can be grafted to cellulose to achieve adhesive properties are acrylic acid, acrylonitrile, methyl methacrylate, and many others. Graft copolymers of cellulose derivatives have also found use as adhesives. For example, vinylacetate-grafted hydroxyethylcellulose can be used as an adhesive for packaging and tile (8). Grafting of vinyl monomers onto lignocellulosic materials can convert them into suitable adhesive materials (9).

### Cellulose Polyblends

Cellulose can also blend with natural or synthetic polymers to produce adhesives. The recent development of new cellulose solvents(10), such as lithium chloride/dimethylacetamide solvent, dinitrogen tetroxide/dimethylformamide solvent, dimethyl sulfoxide/paraformaldehyde solvent, have provided the potential to produce uniform cellulose polyblends.

The Pharmaceutical Research Institute has developed an adhesive bandage that sticks to mucous membrane for 5 hours or more and has been found to reduce bleeding and the risk of infection after tooth extraction. Bandages are actually made up of a mixture of carboxymethyl-cellulose, polyisobutylene, gelatin, and pectin that becomes increasingly more adhesive as it absorbs moisture from

the mouth. Another surgical adhesive, Stomadhesive made by Squibb, also uses carboxymethylcellulose blended with polyisobutylene to produce adhesives.

## Conclusions

Cellulose constitutes a ubiquitous and renewable natural material that has great potential for chemical conversion into high-quality adhesive products. The resurrection of research and development of cellulose derivatives, such as cellulose esters and ethers, cellulose graft-copolymers, and cellulose polyblends, has instituted new avenues for adhesive applications. There is little doubt that new solvent systems for cellulose have created the potential of developing uniform cellulose products with superior properties for adhesive applications.

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# Chapter 22

## Utilization of Soda Bagasse Hemicellulose As Corrugated Board Adhesive

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Large quantities of hemicellulose are produced as a waste byproduct during chemical pulping of sugarcane bagasse. The hemicellulose present in soda bagasse spent liquors has a high molecular weight that enables its easy reclamation and gives it good potential for use in polymeric products. A corrugated board adhesive was developed from industrial soda bagasse hemicellulose and evaluated on laboratory scale. The gel properties of the adhesive were similar to those of commercial starch binders. The adhesive gave a ply adhesion comparable to that obtained with conventional starch-based adhesive.

Large quantities of hemicellulose and lignin are produced as waste products during the soda pulping of wood or other plant material. The lignin produced by the industrial pulping of sugarcane bagasse was shown to have an exceptionally high reactivity (*I*), making it useful as a raw material for the preparation of cold set and thermosetting adhesives (Figure 1). This property of the lignin results partially from the mild conditions used for the industrial pulping of bagasse. The mild pulping conditions also cause only superficial degradation of the hemicellulose. The resulting hemicellulose in the spent pulping liquor consequently has a relatively high molecular weight, which enables its easy reclamation.

Soda bagasse spent liquor thus contains two useful renewable polymeric chemical feedstocks: hemicellulose and lignin. The uses developed so far for these materials are depicted graphically in Figure 1. The use of the hemicellulose as a corrugated board adhesive is discussed in this chapter.

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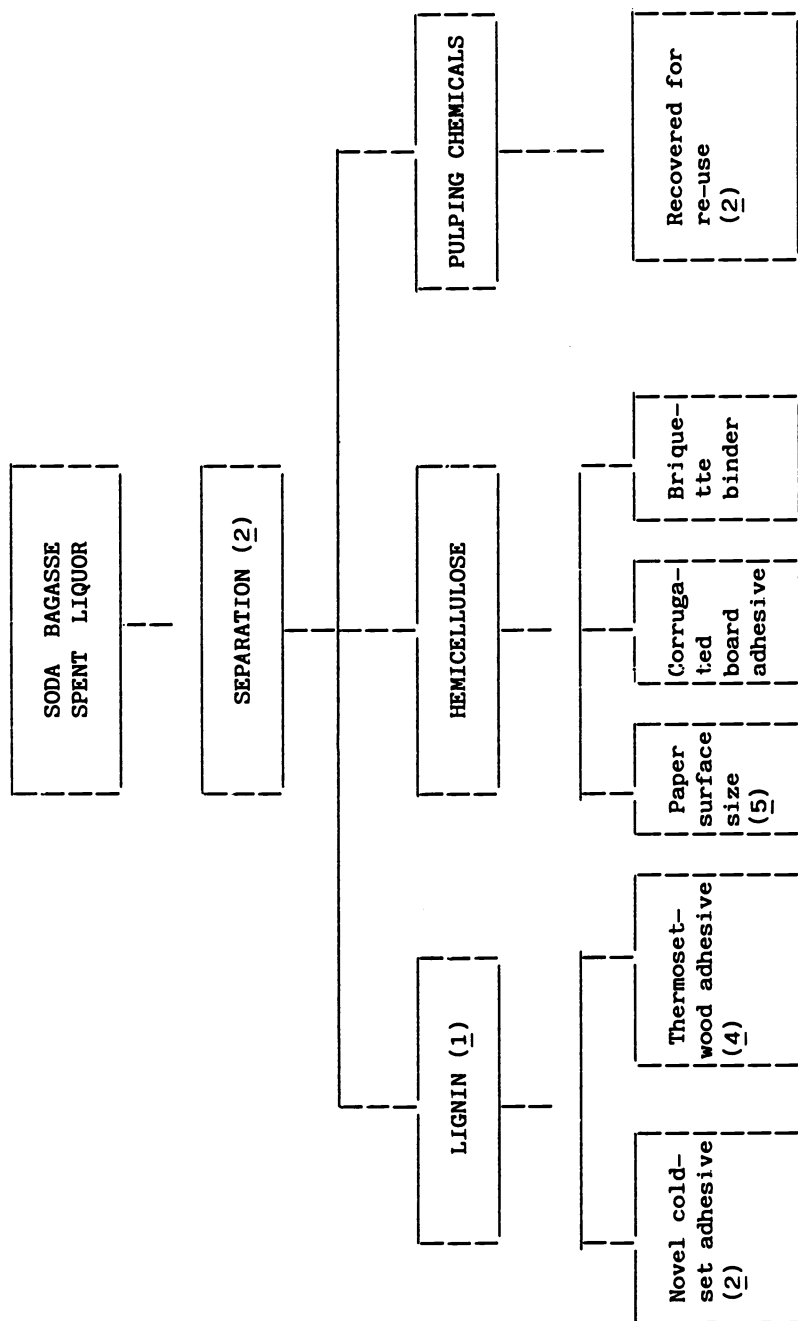


Figure 1. Products from industrial soda sugarcane bagasse spent pulping liquors.

## Experimental Methodology

Hemicellulose was reclaimed from industrial soda bagasse spent pulping liquor by precipitation with methanol as was done in earlier studies (2-5). The hemicellulose precipitate obtained was submitted to different degrees of washing with 50% aqueous methanol, resulting in hemicellulose preparations containing different quantities of ash and lignin. The pH of the hemicellulose was adjusted and borax or  $\text{CaCl}_2$  added, after which it was dried and ball-milled to the indicated particle sizes.

The Klason lignin content was determined by the TAPPI procedure (6), and the ash content was determined at 750 °C. Viscosity determinations on a number of hemicellulose preparations indicated an average degree of polymerization of between 60 and 70 (7).

Gel filtration of the hemicellulose was done on a G-50 Sephadex column with water as eluent by the National Food Research Institute of the CSIR. Neutralized samples were applied to the column and fractions (6 mL) collected, of which 1-mL aliquots were assayed by the phenol-sulfuric acid test (8). Approximate calibration (D.P. versus elution volume on the G-50 column) was done by total carbohydrate and reducing sugar end group analysis (9) using enzymatically debranched starch as reference material.

The hemicellulose adhesives were evaluated on 50- by 100-mm<sup>2</sup> A-flute corrugated board samples. Commercial single-faced board (125 to 160 g/m<sup>2</sup>) bonded with a maize starch adhesive and liner (160 g/m<sup>2</sup>) was obtained. The liner and fluting material were prepared from virgin kraft pulp and were not surface-sized with starch. The single-faced material was cut into samples (50 x 100 mm<sup>2</sup>) with the flutes in the 50-mm direction. Liner samples were cut in 60- by 110-mm<sup>2</sup> samples.

The liner and single faced material, the latter with a 30-g metal weight stuck to it with two-sided tape, was heated on a hot-plate at 120 ± 2 °C for 30 seconds. The adhesive was applied with a doctor blade on a glass plate in a thin measured layer. The single-faced material was removed from the hotplate, with a magnet, placed firmly on the adhesive on the glass plate, and immediately put back on top of the liner on the hotplate. After heating further for 30 seconds on the hotplate, the samples were conditioned at 50% relative humidity and 23 °C for 12 hours and tested for ply adhesion. Ply adhesion tests were done on an Instron universal testing machine (Model 1122).

The gel times of the different adhesives were compared as follows. The liner and single-faced material were heated as before to 120 ± 2 °C. The single-faced material was placed on the adhesive on the glass plate and back on the liner in a single swift movement. Seconds were counted from the moment the two pieces met. After different time intervals, the glued samples were removed from the hotplate and separated by hand. Proper fiber failure and bond strength were taken as indicating that the adhesive had set. The minimum required for an adhesive to set is given as the set time.



Viscosities were determined with a Brookfield viscometer (model RVF) at 20 rpm and are shown in Figure 2. Temperature control was done in a waterbath. Three different types of adhesive preparations were used:

*Dissolved hemicellulose adhesive.* Finely ground hemicellulose was heated with borax (3.8% on solids) and sodium hydroxide (1.3% on solids) to 70 °C for 15 minutes. The solution was cooled and used as the cooked hemicellulose adhesive.

*Suspended hemicellulose adhesive.* Finely ground hemicellulose (below 0.2 mm) was mixed with borax (3.8% on solids) and sodium hydroxide (1.3% on solids) and water at ambient temperature. The proportion of water was varied to obtain the different solids contents required for the adhesive.

*Partially dissolved/suspended hemicellulose adhesive.* One-sixth of the hemicellulose used for this preparation was heated at 70 °C for 15 min with sodium hydroxide (1.3% on total solids) and half the water required for the whole mixture. After being cooled to ambient temperature, the remainder of the water, hemicellulose, and borax (3.8% on solids) was added. In some cases (Table I), the borax and sodium hydroxide contents were varied.

*Starch control.* The starch control was prepared by the same procedure used to prepare the partially dissolved hemicellulose adhesive.

The gel curves (Figures 5-11) were obtained by measuring the viscosity of hemicellulose suspensions while the temperature was increased at a rate of 1 °C/minute to approximately 90 °C. The hemicellulose mixture was then cooled at the same rate.

## Results and Discussion

The hemicellulose reclaimed from industrial soda bagasse spent liquors consists mainly of xylose units (10). Gel filtration experiments on a Sephadex column indicated a molecular mass higher than 10,000 units (Figure 2). Viscosity determinations (CED) (7,10), though not strictly applicable to hemicellulose, indicated an average degree of polymerization of between 60 and 70 for the purified hemicellulose. Clearly, soda bagasse hemicellulose has a high molecular mass. This enables its easy reclamation and also explains its suitability for uses such as paper surface sizing and briquette binding (Figure 1).

Current corrugated board adhesives are prepared from starch that has a much higher molecular weight (> 100,000 mass units). The largest portion of starch in the commercial adhesive preparation is in an undissolved (i.e., kernel)

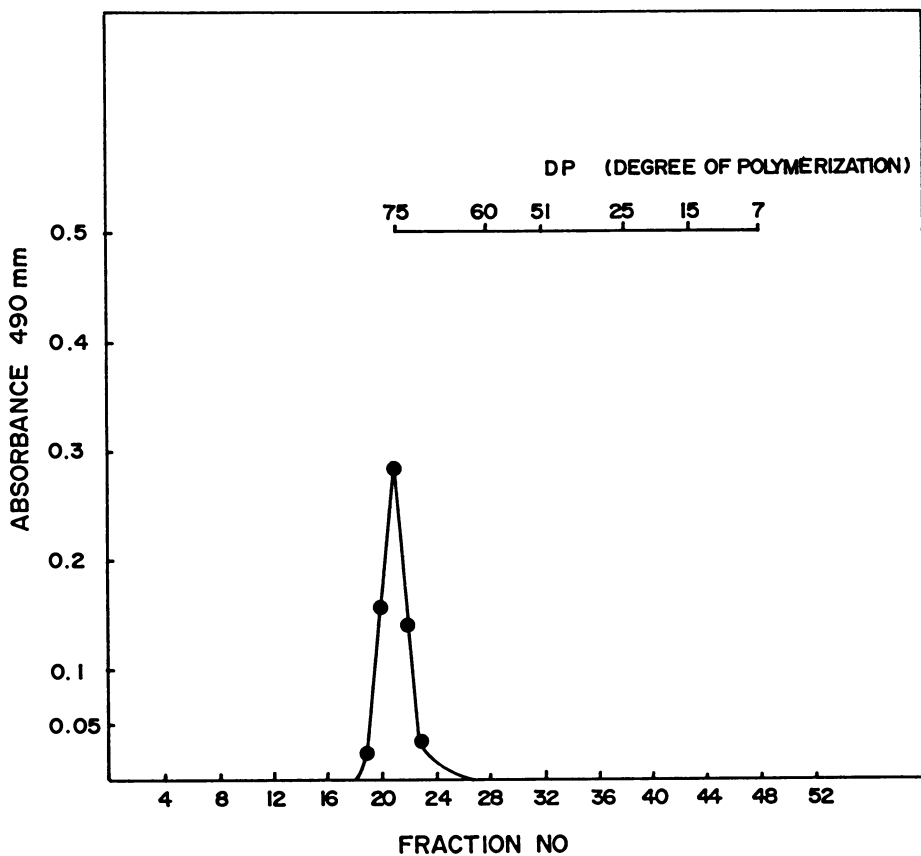


Figure 2. Molecular mass distribution of soda sugarcane bagasse hemicellulose as determined on a G-50 sephadex column.

form. Upon application, the temperature is increased above the gel temperature, resulting in the gelling of the starch, which enables it to glue the paper together. Clearly, the soda bagasse hemicellulose was obtained in a totally different form when compared with starch. The use of the hemicellulose as corrugated board adhesive was therefore evaluated.

Table I. Ply Adhesion for Test Samples Glued with Hemicellulose Corrugated Board Adhesive (15% Solids)

Entry	NaOH <sup>1</sup>	Borax <sup>1</sup>	Ply Adhesion N/m		Coeff. Var. (%)	Double Backer Fail (%)
			Ave.	Minimum		
1	0.0	0.0	478	426	5.8	78
2	0.0	1.3	529	417	10.7	33
3	0.0	2.5	603	528	9.5	47
4	0.0	3.8	558	534	11.6	43
5	0.0	5.0	588	475	11.8	22
6	0.7	0.0	510	481	3.4	45
7	0.7	1.3	537	502	5.9	36
8	0.7	2.5	534	433	16.9	30
9	0.7	3.8	622	532	13.4	32
10	0.7	5.0	560	453	8.2	30
11	1.3	0.0	540	487	10.4	28
12	1.3	1.3	577	484	8.6	70
13	1.3	2.5	605	508	15.4	25
14	1.3	3.8	606	496	12.3	27
15	1.3	5.0	574	483	13.7	37
16	2.5	0.0	533	481	6.1	62
17	2.5	1.3	562	478	12.4	36
18	2.5	2.5	557	480	10.5	52
19	2.5	3.8	590	537	10.2	53
20	2.5	5.0	579	510	10.0	50
21	3.7	0.0	486	443	7.2	97
22	3.7	1.3	540	492	9.3	67
23	3.7	2.5	629	552	11.0	75
24	3.7	3.8	603	563	8.3	47
25	3.7	5.0	575	493	13.7	13

<sup>1</sup>Prepared by dissolving one-sixth of finely ground hemicellulose and suspending the other five-sixths.

**Ply Adhesion of Soda Bagasse Hemicellulose.** First, various hemicellulose mixtures were evaluated solely on a ply adhesion basis. A suspension (15% solids) of hemicellulose, of a particle size below 0.2 mm, was prepared at ambient

temperature. After 24 hours, the hemicellulose particles were not dissolved but remained in suspension. Each particle seemed to be contained in a gel-like outer layer that probably prevents the settling of the hemicellulose particles.

For preparing the hemicellulose adhesive, it was decided to use a portion of dissolved hemicellulose. One-sixth of the hemicellulose powder used to prepare the adhesive was thus dissolved (cooked) by heating in water to 70 °C for 15 minutes. After cooling, the remainder of the hemicellulose powder was added. The final mixture had a solids content of 15%. Six corrugated board samples were glued and tested and gave an average ply adhesion strength of 478 N/m with 100% fiber pickup (Table I, entry 1). The average dry strength of the hemicellulose adhesive was higher than the 445 N/m required for the minimum dry ply adhesion of export apple boxes (11). Some individual values were lower than the specified minimum strength, however.

Under alkaline conditions, boric acid (or at this pH, boron tetrahydrate) forms complexes with diols (11). The formation of such a complex between two polysaccharide molecules can lead to crosslinking. The use of borax can, therefore, be expected to increase the stability of the bonds between the hemicellulose and between the hemicellulose and cellulose fibers in the paper.

The effect of borax on the strength of the hemicellulose adhesive was subsequently investigated. A factorial experiment was done employing five concentrations of borax and five concentrations of sodium hydroxide. The sodium hydroxide variable was included, since formation of the diol-boron complex is pH sensitive (12).

The results listed in Table I indicate that the ply adhesion of the hemicellulose adhesive increased with increasing amounts of borax and sodium hydroxide. The increase in strength, however, leveled off after an optimum was reached. Optimum strength results were obtained with 3.8% borax and 1.3% NaOH on hemicellulose solids. These quantities of additives were subsequently used in all further experiments.

The hemicellulose adhesive used consisted of one-sixth of the hemicellulose in the dissolved (cooked) state and the remainder in a suspended (raw) state. This preparation was subsequently compared with a hemicellulose adhesive with all the powder dissolved (70 °C treatment) and with a preparation with all the hemicellulose powder suspended (raw). The same amounts of borax and NaOH were used in each case. A starch adhesive prepared according to the Steinhall procedure (13) was used as control.

Samples were glued and tested for ply adhesion at different solids contents of the adhesives. These results are illustrated in Figure 3. All the adhesives tested gave 100% fiber failure for all the consistencies tested.

The set time of each adhesive was also determined. According to the method employed, these values can only be used for comparative purposes. The set times of all the adhesives were between 4 and 5 seconds under the conditions used. This indicates that little difference exists in the set time of the hemicellulose adhesives and the starch control. The only exception is the longer set times

of the dissolved hemicellulose adhesive at solids contents below 17% (i.e., 15 seconds set time at 12% solids and 12 seconds at 14% solids).

The ply adhesion values of test samples glued with the suspended hemicellulose adhesive leveled off at consistencies above 16% solids. The strength of this adhesive above 16% solids was similar to the strength values of industrial corrugated board samples. The industrial board was collected from the mill that supplied the single-faced and liner material.

The ply adhesion of the dissolved hemicellulose adhesive was high at low solids content but decreased somewhat at higher solids contents (Figure 3). The set time of this adhesive was, however, long at low consistencies.

The strength of the suspended/dissolved hemicellulose adhesive increased when the solids content was increased and leveled off at 13% solids (Figure 3). The raw-cooked hemicellulose adhesive thus reached the plateau of maximum strength at a lower solids content than the raw hemicellulose adhesive.

The viscosities of the three hemicellulose adhesives and the starch control are given in Figure 4. The viscosity of the suspended hemicellulose adhesive was lower when compared at different solids contents than that of the starch control. It was, on the other hand, much higher than the viscosity of a raw starch suspension (30 cP at 35% solids). The higher viscosity of the raw hemicellulose adhesive is probably caused by the gel-like outer layer of the raw hemicellulose-suspended particles. The suspended starch particles showed no such surface gel effect, but remained totally undissolved. The viscosities of the cooked and raw-cooked hemicellulose adhesive were similar to those of the starch adhesive (Figure 4).

The adhesives evaluated thus far were applied to the test samples using an adhesive film thickness of approximately 0.4 mm. This film resulted in the uptake of 2 to 3 g/m<sup>2</sup> of adhesive solids from adhesive suspensions containing 15% solids. The effect of adhesive uptake was subsequently evaluated. The raw-cooked hemicellulose adhesive was applied to the glass plate in different thicknesses, resulting in different adhesive uptakes. The ply adhesion values (Table II) increased with increasing quantities of adhesive. The above ply adhesion tests were done on liner and corrugating medium that is used for the production of citrus boxes and is much stronger than previous test samples, which explains why higher strength results could be obtained.

The stability of the hemicellulose adhesives and the effect of particle size were subsequently assessed. Hemicellulose adhesives were prepared with a portion (one-sixth) cooked and the remainder raw with borax and sodium hydroxide as before. Different particle sizes of hemicellulose were used for the suspended portion. The mixtures were used to glue corrugated board test samples after 4 hours' or 4 days' standing. The results (also on citrus box material) shown in Table III clearly indicate that the ply adhesion strength of the adhesives was not affected by standing or by particle size.

**Gel Properties.** The ply adhesion results so far indicate a good potential for bagasse hemicellulose as an adhesive for corrugated board. The industrial

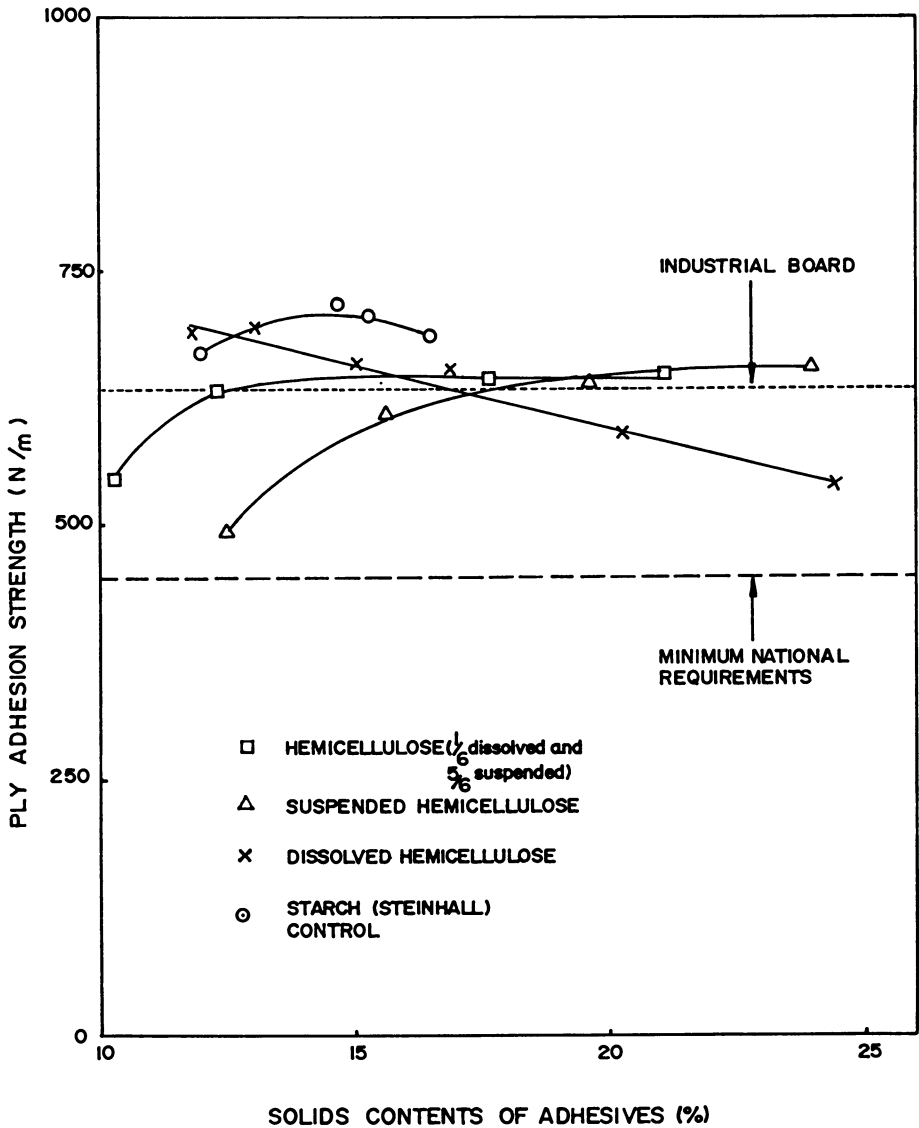


Figure 3. Ply adhesion of corrugated board adhesives.

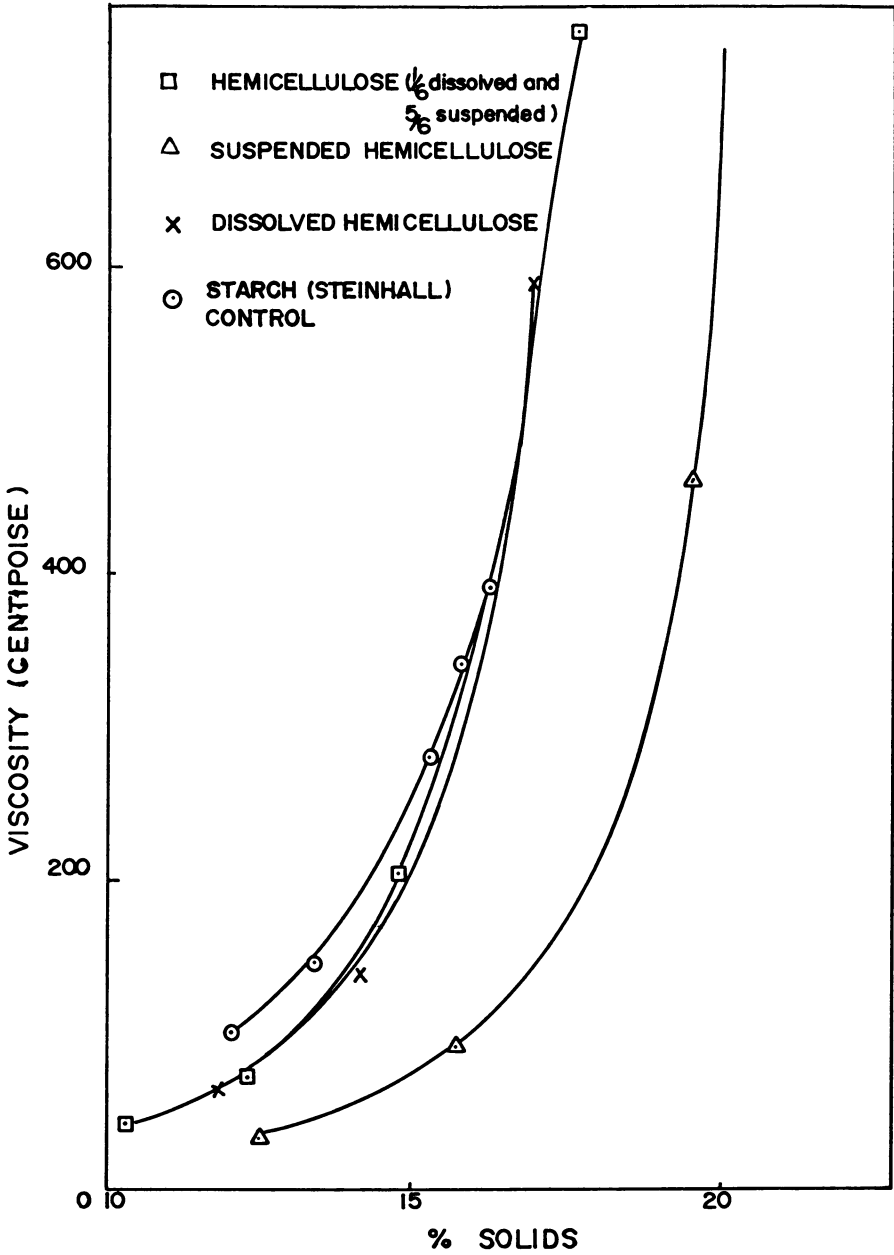


Figure 4. Viscosity of corrugated board adhesives.

application of the adhesive, however, requires the adhesive to gel in very short times, since the application is done at high speeds. The gel properties of the bagasse hemicellulose were subsequently investigated.

Bagasse hemicellulose samples (32% ash and 12% lignin) were dissolved in water and the pH adjusted with dilute sulfuric acid to 4.6, 7.5, 10, and 12 (no pH change). The neutralized samples were dried and ground to particles below 0.2 mm. A suspension of each at 15% solids was heated at a constant rate of approximately 1 °C/minute to approximately 90 °C, after which the solutions were cooled at the same rate to ambient temperature. The viscosities of the mixtures were determined after short intervals and are illustrated in Figure 5.

Table II. Ply Adhesion of Hemicellulose-Bonded Corrugated Test Samples (Citrus Box) Employing Different Quantities of Hemicellulose

Entry	Adhesive Thickness (mm)	Approximate Adhesive Uptake (g/m <sup>2</sup> )	Ply Adhesion Average (N/m)	Coeff. Var. (%)	Set Time (s)
1	0.2	0.9	495	26.2	5
2	0.3	2.4	522	10.4	5
3	0.5	3.0	823	3.2	5
4	0.7	4.0	764	2.9	5
5	1.0	7.0	904		15

The gel curves of the different hemicellulose solutions presented in Figure 5 differ dramatically. At pH 4.6, the hemicellulose particles remained unsolubilized during the entire heat treatment. The gel temperature of the hemicellulose at this pH is clearly above the maximum temperature of 87 °C reached during the experiment. At pH 7.5, some solubilization of the hemicellulose particles occurred at the higher temperatures as is indicated by the increased viscosity of the suspension. The hemicellulose solution at pH 9.8 seemed to have gelled at the maximum temperature during treatment as the viscosity of the solution just started to decrease at temperatures above 80 °C. During lowering of the hemicellulose solution's temperature at pH 9.8, its viscosity increased dramatically, indicating that extensive solubilization of the hemicellulose had occurred. The viscosity of the hemicellulose solution at pH 11.6 and at ambient temperature has a much higher value than that of the other suspensions. This indicates that partial solubilization of the hemicellulose occurred at ambient temperature in highly alkaline solution. At about 65 °C, complete solubilization of the hemicellulose particles occurred as indicated by the lowering of viscosity at higher temperatures.

An increase in pH of the hemicellulose solution thus clearly decreases the gelling temperature of the hemicellulose suspension. The gel curves of the



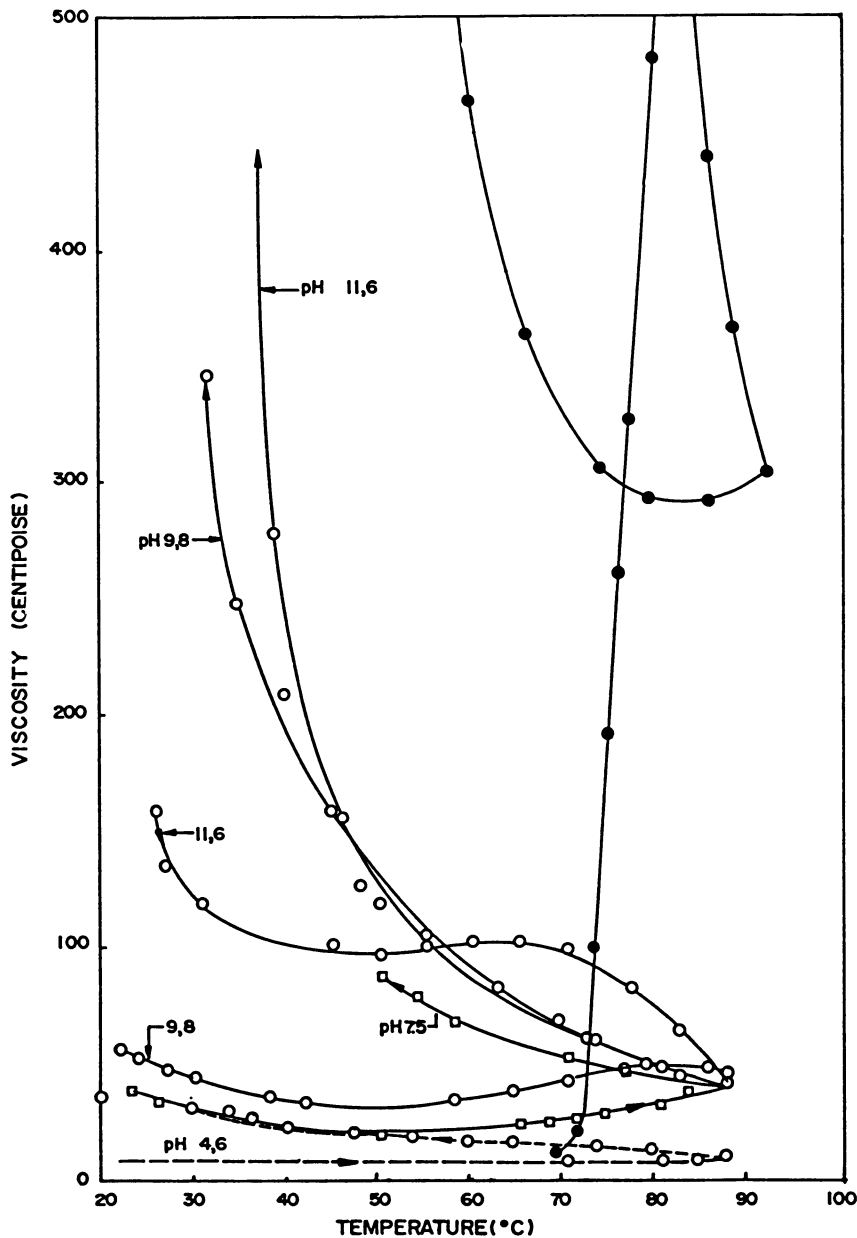


Figure 5. Gel curves of hemicellulose (32% ash) suspensions (15% solids) (1). The pH of the hemicellulose was adjusted to the indicated values before drying and grinding.

hemicellulose solutions, however, do not show an increase in viscosity at the gel point or gel region. This behavior is a prerequisite for the adhesive to give proper gelling during application as corrugated board adhesives. The gel curve of a commercial starch adhesive prepared by the Steinhall procedure is also presented in Figure 5 and clearly indicates the deficiencies of the hemicellulose gel curves.

A new batch of hemicellulose containing only 20% ash instead of 32% (as with the previous batch) was subsequently prepared. The new hemicellulose was neutralized to pH 8.3 (dilute sulfuric acid) and the gel curves obtained as before (Figure 6). The gel curve of the hemicellulose shows a more pronounced gel effect when the temperature of the suspension increased above 70 °C. A decrease in the ash content thus results in some improvement of the gelling of the hemicellulose. The pH of two more hemicellulose suspensions (20% ash) was adjusted to 10.5 and 13, respectively, and their gel curves obtained (Figure 6) (i.e., hemicellulose particles prepared at pH 8.3 are suspended in water and the pH of the suspension changed to 10.5 or 13). The results presented in Figure 6 show a decrease in gel temperature for the hemicellulose suspension at pH 10.5 when compared with that at pH 8.3. The viscosity of the hemicellulose suspension at pH 13, however, differs substantially from suspensions at pH values of 8.3 and 10.5. The gel temperature is much lower and the viscosity on cooling lower when compared with those of hemicellulose at pH 8.3 or 10.5. An explanation could be that the solubility of the hemicellulose macromolecules is increased by the very high pH.

Table III. Properties of Corrugated Board Glued with Bagasse Hemicellulose Adhesive<sup>1</sup>

Entry	Particle Size (Mesh)	Glued After 4 Hours		Glued After 4 Days	
		Ply Adhesion (N/m)	Coeff. Var. (%)	Ply Adhesion (N/m)	Coeff. Var. (%)
1	60-100	838	10.8	808	9.9
2	100-150	868	8.5	800	8.2
3	below 150	774	11.5	764	4.4

<sup>1</sup>A one-sixth portion of the hemicellulose adhesive was dissolved (cooked) while the remainder was used as a suspended powder (raw) of different particle sizes.

The studies on the ply adhesion of the hemicellulose adhesive showed that the addition of 2 to 3% of borax on hemicellulose led to substantial improvements in the strength of the adhesive. A hemicellulose solution was subsequently prepared containing 2% borax (on hemicellulose) at pH 8.5. The solution was

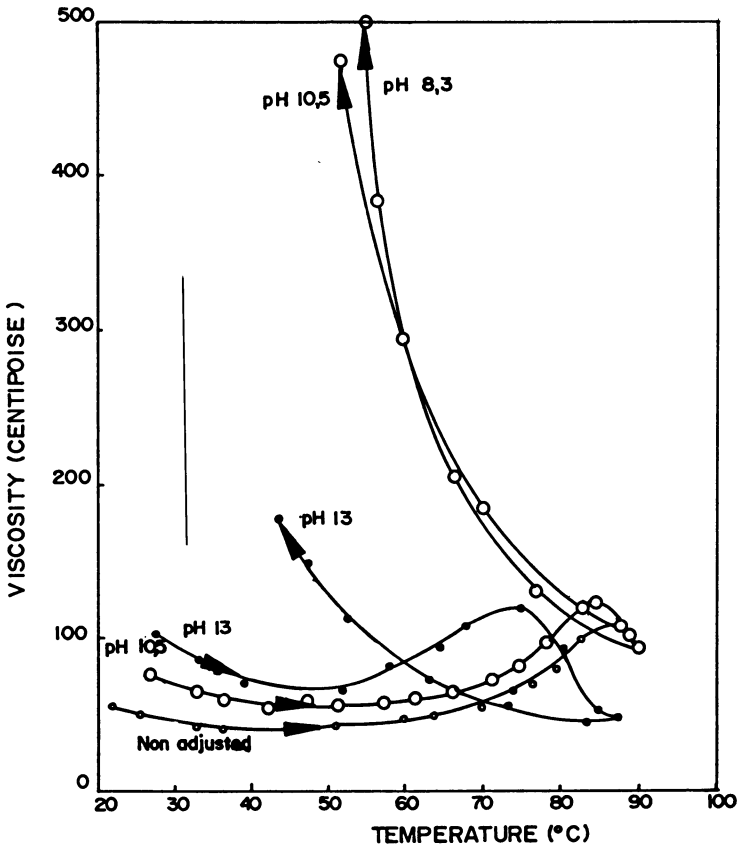


Figure 6. Gel curves of hemicellulose suspensions (15% solids) (2). The pH of the hemicellulose suspension solution was adjusted to pH 8.3 prior to drying and milling. The pH of the suspensions was adjusted as indicated.

dried and ground as before. The gel curves of suspensions of this mixture were determined as is, or after the pH was adjusted to pH 10.5 or 13. The results are illustrated in Figure 7. The addition of the borax, however, resulted in almost doubling of the viscosity of the hemicellulose solutions prior to heating. The viscosity of the borax-modified hemicellulose solutions was higher at the gel temperature when compared with that of hemicellulose without borax. The required increase in viscosity during gelling was, however, not achieved by borax addition.

The improvements obtained earlier by changing from hemicellulose with a high ash content to hemicellulose with a low ash content were taken one step further. New hemicellulose powder was prepared by including more washing steps in the purification sequence (proper washing can be achieved easily on industrial scale by the use of centrifuges), resulting in the production of two more hemicellulose samples. These had ash contents of 14.8 and 11.8%, respectively. The gel curves of the high-purity hemicellulose (Figure 8) are more comparable with those of starch than the previous hemicellulose curves (Figures 5 to 7). Clearly, a low ash content is required for a proper increase in viscosity during gelling. The gel curves of the hemicellulose with ash contents of 11.8 and 14.8% are virtually identical. No purer hemicellulose suspensions were subsequently evaluated.

In Figure 9, the gel curves of purified hemicellulose treated with borax and acid to obtain different pH's before drying are illustrated. These curves are almost identical over a wide pH range. The main difference is the temperature where the viscosity of the suspension starts to increase. This temperature increases with a decrease in pH. The temperature of complete gelling, as indicated by the maximum temperature during the heating stage, increases from 72 °C at pH 9 to 78 °C at pH 5.

The amount of borax added has only a limited influence on the viscosity behavior of the low ash hemicellulose solutions (Figure 10). An increase in the amount of borax seems to increase the gel temperature somewhat.

If the borax is added to the hemicellulose suspension, the viscosity behavior differs substantially when compared with a hemicellulose suspension with the borax inside the hemicellulose particles. In Figure 11, the viscosity behaviors of two such suspensions are presented. The hemicellulose with the borax added to the suspension of hemicellulose powder clearly gels at a lower temperature. The viscosity upon cooling of this mixture is also much lower when compared with the hemicellulose with borax inside the powder particles. The sodium hydroxide added with the borax to the hemicellulose suspension again may have caused this phenomenon.

## Conclusions

Soda bagasse hemicellulose gave acceptable ply adhesion of corrugated board when evaluated by a laboratory application procedure. The gel properties of the

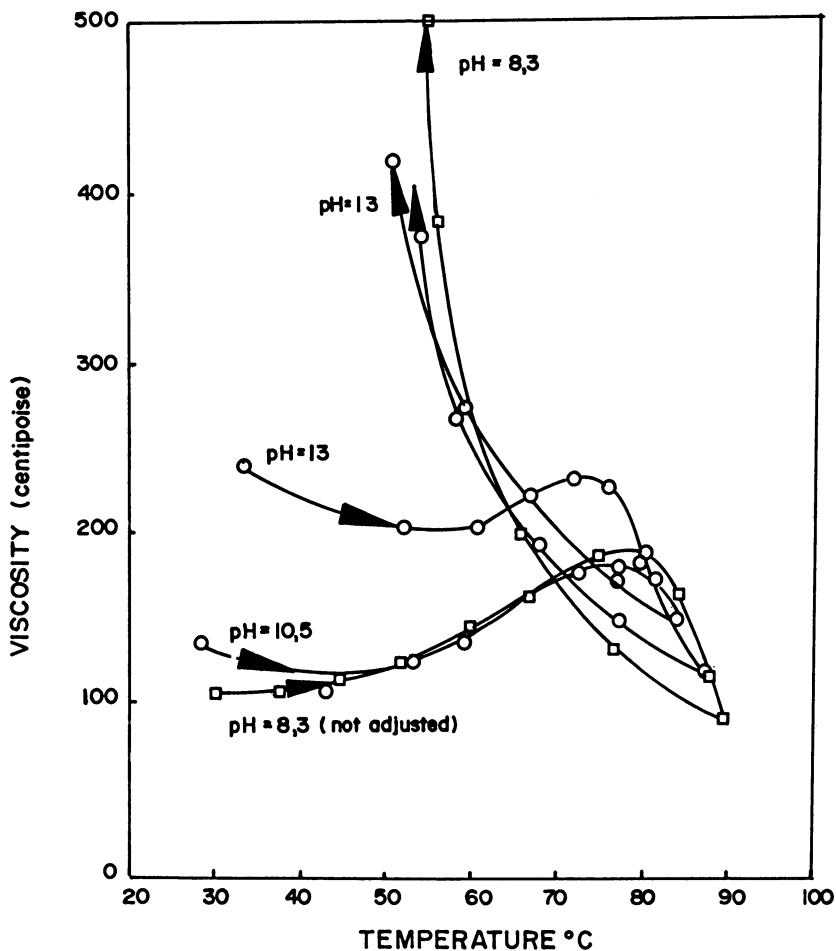


Figure 7. Gel properties of hemicellulose suspensions (15% solids) at different pH's (9). The hemicellulose was treated with borax (2.0%) and the pH adjusted to 8.5 before drying and ball-milling. The pH of each suspension was adjusted as indicated.

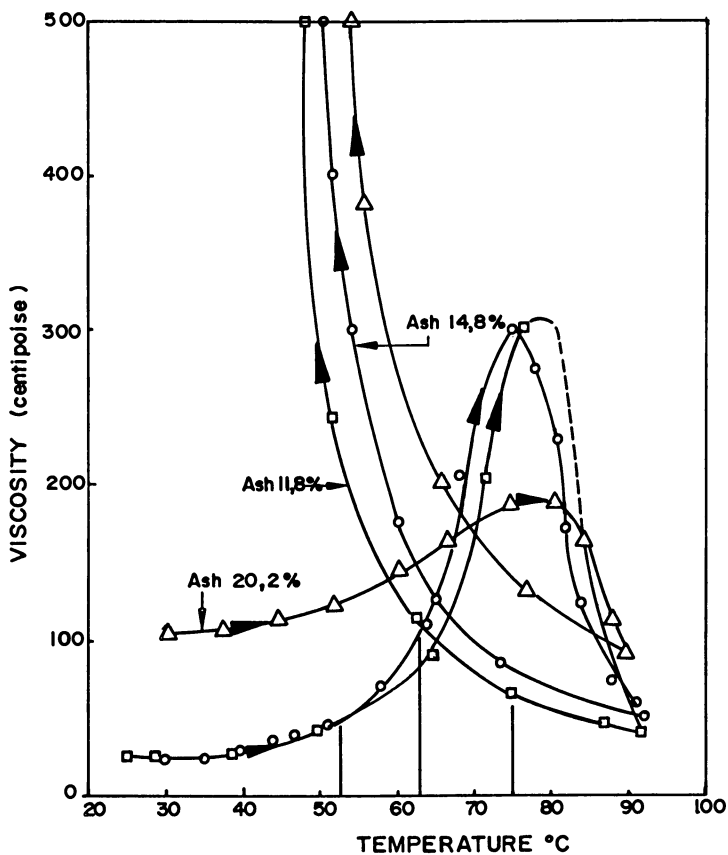


Figure 8. Gel curves of hemicellulose suspensions (12.5% solids) containing different quantities of ash ( $\Delta$ ). Each hemicellulose was treated with 2% borax and diluted with sulfuric acid to pH 7.5 to 8.0 before drying and ball-milling.

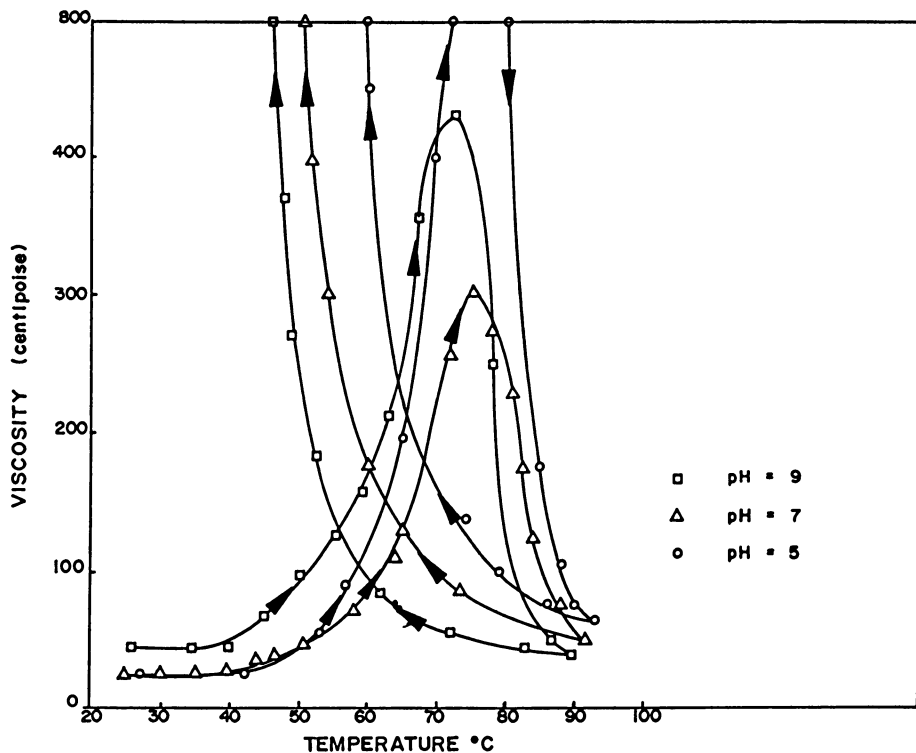


Figure 9. Gel curves of hemicellulose (14.8% ash) suspensions (12.5% solids) (5). The pH of the hemicellulose suspensions was adjusted to 9.7, or 5, and each treated with 2.0% borax on hemicellulose solids before drying and ball-milling.

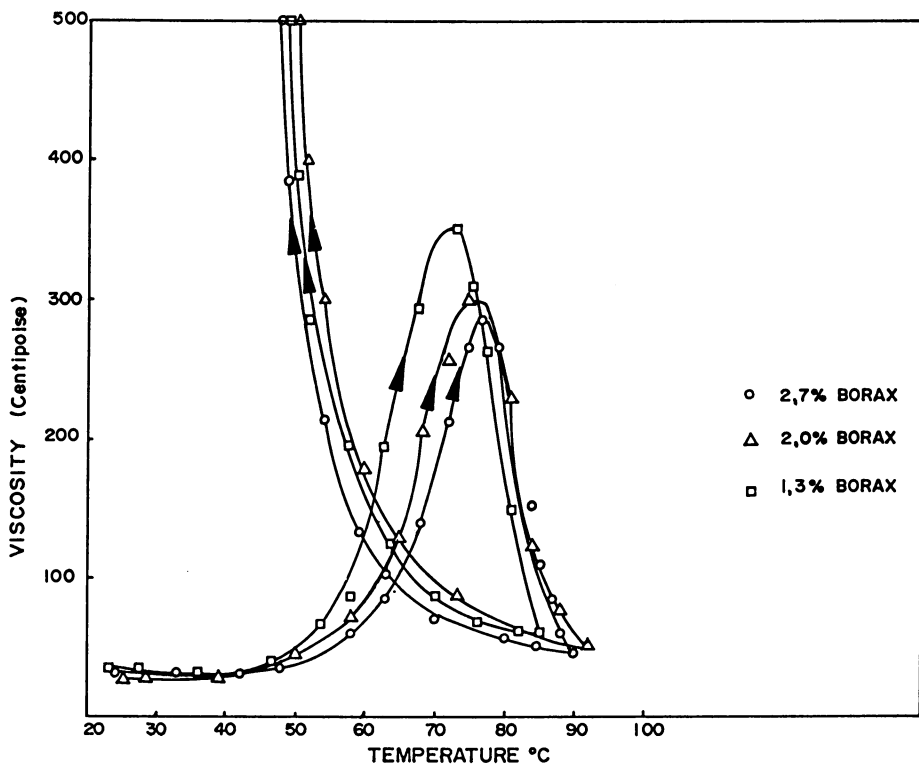


Figure 10. Gel curves of hemicellulose suspensions (12.5% solids) (6). Each hemicellulose suspension has been prepared from hemicellulose powder containing 1.3, 2.0, or 2.7% borax on hemicellulose solids.



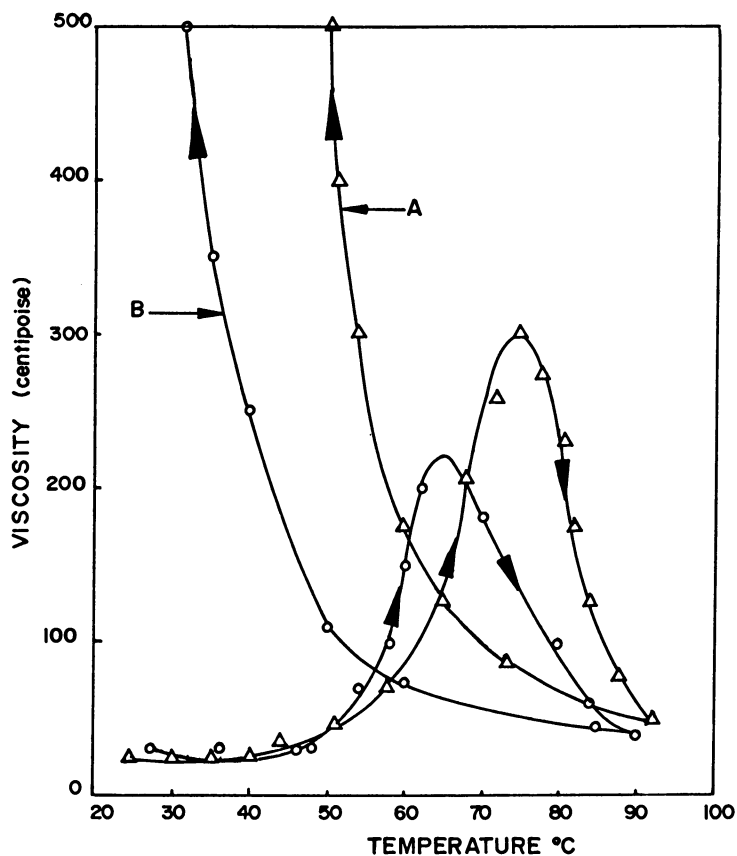


Figure 11. Viscosity of hemicellulose suspensions (12.5% solids) (7): A, suspension of hemicellulose powder obtained from a solution of hemicellulose (14.8% ash) neutralized (pH 7), and mixed with borax (2.0%) before drying and grinding; B, suspension of hemicellulose powder (4.8% ash) mixed with borax (2.0%) and sodium hydroxide (2.0%).

hemicellulose can be improved by varying the purity of the hemicellulose during reclamation. Soda bagasse hemicellulose clearly is an exciting alternative for corrugated board adhesives.

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# Chapter 23

## Starch- and Dextrin-Based Adhesives

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Despite present trends toward use of synthetic polymers developed over the last 10 or 20 years, starches are still being widely used as an adhesive in such applications as the production of paper and paperboard products, warp sizing, and bonding charcoal briquettes. Because of a unique combination of properties and low cost, these adhesives are almost impossible to exclude from many applications, especially those involving the use of hot paste (size) for anchoring fibers. For starch molecules to act as an adhesive, they must be chemically or thermally hydrated. Then, their adhesive character is developed and modified in different ways by chemicals or other additives for different end uses. As renewable resources that are both economical and reliable, starch and dextrin are likely to continue to be significant factors in the adhesive market for many years.

In these modern, "high tech" times, starch-based adhesives are often relegated to the category of "other adhesives," while synthetic polymers are gaining high visibility with their amazing capacity to bond a vast array of substrates that enable us to land men on the moon and even repair living tissue and bones in the operating room. One of the faster growing product areas is that of pressure-sensitive adhesives. There were almost a half-billion pounds of pressure sensitive adhesives sold in 1985 (1), but with all the publicity on these newer more versatile products, most people are left believing that not much starch is used in adhesives anymore. Even the library paste that was used by children for decades is being replaced by poly(vinyl acetate). But the fact is that over 3.5 billion pounds of starch were utilized last year to bond products that are used practically every day. Major markets include the paper and corrugating industries, solid fiber laminates, wound paper tubes, grocery bags, textiles, and briquettes.

This chapter's purpose is to define these "low profile" markets where starches and dextrans are being used and to describe how the adhesive character of starch is developed in different ways for different end uses.

### Developing Starch's Adhesive Character

Most of the cornstarch sold to industry comes from wet milling plants that process the farmer's shelled corn in such a way that pure starch is recovered. The dried starch is shipped in bulk rail cars, trucks, or in bags to customers. After receiving the starch, the customer must slurry it in water at the appropriate solids content and then heat the slurry or add caustic to it to gelatinize the granules.

Ungelatinized starch is incapable of gluing anything together because the molecules within the unpasted granules are already tightly bonded to one another. As the molecules are formed within the growing corn kernel, they are packed so close to one another that the ordered arrangements become nearly crystalline. More precisely, there are crystalline regions and amorphous regions within the granules.

In order for starch molecules to become detached from one another, they must be hydrated, a process accomplished in water slurry by using either thermal or chemical energy. Only then will the molecules be separated and uncoiled enough to be able to latch onto other separate particles and act as an adhesive. The most common form of chemical hydration of starch is through the use of aqueous alkali. Sodium hydroxide is capable of hydrating starch molecules without heat, but a specific minimum concentration must be reached for that to occur (2).

As a starch slurry is heated to higher and higher temperatures, a dramatic increase in viscosity becomes obvious as the swelling granules soak up more and more water until they begin to rupture, so molecules can leach out of the granule fragments. Only then can the starch begin to do the job of adhesion. In order for the maximum amount of adhesion to take place, the molecules should be maximally dispersed in the pasting process and maintained in that state until just seconds before application.

### Adhering Cellulose Fibers Within Paper

The largest market for starch is its use as a surface sizing agent for a wide variety of paper and board products. The purpose of sizing paper is to anchor the loose or dangling fibers to the body of the sheet in order to avoid their being torn out during the printing process, which would have poor visual results. Other objectives of sizing with starch are to decrease porosity, increase oil resistance, and increase total sheet strength.

Paper is made by slurrying cellulose fibers at a very low concentration and filtering off most of the water on the moving wire screen of a Fourdrinier machine.

The fibers form a wet mat, which is then carried over hot dryer rolls where the continuous sheet of paper is dried. Often, the paper then goes through a size press where a hot starch paste is applied. Most likely the starch is unmodified by the starch supplier and converted to the appropriate viscosity with ammonium persulfate in a thermal-chemical converter. This converted starch increases the strength of the paper. Applying starch with a size press can be expensive, since the sheet has to be dried twice. Nonetheless, about 1.2 billion pounds of starch were used at the size press last year.

If the need for a strong sheet of paper is the main reason for adding starch, there is another place it may be added without having to dry the paper twice. It also may be added at the wet end of the machine prior to the cellulose fibers being pumped to the continuous wire. In this case, however, the starch must be modified with a cationic reagent to give it a positive charge. The cationic group on the starch is required so each starch molecule will be attracted to the negatively charged fibers and thus be retained on the wire (with the fibers) rather than being washed through the wire along with the fines and solubles. It is estimated that perhaps 400 million pounds of cationic starch were consumed last year in this use.

### **Making Corrugated Board**

Approximately 900 million pounds of starch were used in the production of corrugated boxboard last year. Most of this was unmodified starch. The paste used on a corrugating machine is most commonly produced by the "two-tank" method, a process involving cooking out a starch paste using caustic, which is then used to "carry" unpasted starch to the bonding zone. The paste is prepared by adding starch and caustic to water in the upper mixer. The water is heated to 71.1 °C, which is sufficient to swell and paste the starch due to the caustic present. Some cooling water is then added to the hot paste. To the lower mixer is added water, borax, and more starch, and the starch paste from the upper mixer is slowly dropped into the lower one with agitation. This adhesive is then applied to the flute tips of the corrugated medium where the pasted starch will hold the ungelled starch granules in place. When the liner sheet is brought into contact with the flute tips and the resultant "sandwich" is heated by a roll or steam table, the granules are swollen. This produces an extremely high solids paste with an extremely high tack that bonds the sheets together, allowing the corrugator to run at very high speeds.

### **Bonding Pigments to Paper**

About 600 million pounds of starch were used in 1986 as paper-coating binders, and again, most were unmodified by the starch supplier (9). The paper mills convert the starch to the necessary viscosity by either enzyme or the thermal-chemical converting process. Hydroxyethyl starch is also used quite successfully as is some oxidized starch.

The major function of the starch is to bond the pigment (clay, calcium carbonate, titanium dioxide, etc.) to the paper surface, making the sheet whiter, brighter, and smoother for printing. In addition to bonding strength, starch also provides the proper rheological characteristics to the coating color. This enables the color to thin down under the shear of the coating blade so the coating can be applied smoothly to the fast-moving web of paper.

Another major function of the starch is to increase the waterholding capacity of the coating. This reduces the tendency for the binder system (there is usually a cobinder present) to migrate excessively during the high-temperature drying process. Any alteration in the binder distribution within the coating can drastically affect the appearance and performance of the coated sheet.

### Sizing Textile Yarn

In the past several years, between 100 and 150 million pounds of starches and dextrans have been used by the textile industry for weaving and finishing cloth, almost 85% of which is acid-modified and derivatized starches. Very little dextrin or unmodified starch is used in warp sizing.

Sizing yarn involves the application of a hot starch paste (or "size") to the yarn prior to its being woven into fabric. Other modifying agents may be present, but starch has been found to be the most cost-effective binder to use for cotton yarn. Besides its low cost, the value of starch lies in its ability to provide a pliable film on the yarn surface without excessive penetration. The need for this filming action is that it effectively ties down the loose cotton fibers or ("hairs") on the yarn surface. If this is not done, the hairiness of the warp yarns will cause a clinging of adjacent fibers during the separation of the individual yarns rather than allowing them to be cleanly separated to form an open "shed" through which the weft yarn can pass unobstructed. In the normal loom operation, the mechanism carrying the weft yarn through the shed will encounter clinging warp yarns and sever them, causing an immediate shutdown of the loom. Too many loom stops may cause a textile mill to suffer economic losses (4).

### Bonding Charcoal Briquettes

Almost 100 million pounds of starch are now being used to bond charcoal dust into easy-to-handle, pillow-shaped briquettes. In order to get the proper strength characteristics, from 5% to 8% of the charcoal weight must be starch; and to be an effective binder, the starch must be cooked-out before addition to the charcoal. Thus, it may be either a pregelled starch that has been cooked and dried by the starch manufacturer, or it may be a granular starch that the briquetter must paste. Unmodified cornstarch processed through a jet cooker has proven to be the most effective binder for this market.

## Other Adhesive Applications

The amount of starch and dextrin sold to the "other" adhesive markets can be roughly estimated at from 200 to 300 million pounds. It may even be in excess of 300 million pounds due to the inexact reporting procedures for the many specific end uses that comprise this market area.

Although, as previously pointed out, the many synthetic adhesives developed during the past two decades are replacing the natural adhesives to a large extent in a number of areas, starch-based adhesives are almost impossible to remove from some markets because of specific properties and cost savings. Some of those markets are discussed below.

**Adhesives for Paper Bags.** Paper bags glued with starch or dextrin pastes range from small sacks for a few pieces of candy or hardware items through grocery bags to multiwall paper sacks used for shipping 50 to 100 pound quantities of chemicals, building products, starch, etc. Two adhesives are used to produce a sack like a grocery bag: a side seam adhesive allowing the paper to be formed into a tube, and a bag bottom adhesive sealing the bottom. The large multiwall bags require a third type of paste in addition. This is a cross-paste used to glue the several plies of paper together to form a laminated sheet of two- to six-sheet thicknesses before the tube is formed.

The seam and cross-pastes are both normally based on the rather tacky and fast-setting borated dextrans, are of moderate viscosity (2,000 to 4,000 cP) at room temperature, and 20% to 30% solids (5). The cross-paste usually has some mineral filler or even some latex to prevent bleeding through to the bags above or below. Adhesive bleeding will cause the stacked bags to stick together during drying. High-fluidity starches may also be used to make seam and cross-pastes, and about 1% sodium chloride may be added (based on the total adhesive) to give greater adhesive stability and improve the dewatering of the bond during drying. A urea-formaldehyde resin may be added for water resistance as well as poly(vinyl alcohol) or poly(vinyl acetate). (6).

Bag bottom paste must be viscous enough to inhibit flow until shear is applied by the applicator rolls. It must have a "short" character so it will not be thrown during high-speed application and must have a high degree of tack so the green bond will not allow the folded bottom to open up before stacking (7). Naturally, the final dry bond must be very strong to support bag contents. Pregelled starches, dextrans, and acid-modified starches have all been used to prepare good bottom pastes, but unmodified cornstarch has proven to be very effective as well. The formulation of such an adhesive with water resistance is given in Table I.

This slurry is heated to 90 °C and held for 15 minutes before cooling. At room temperature, the paste should be 60,000 to 70,000 cP.

**Adhesives for Laminating.** Solid fiberboard for boxes and shipping containers is tough and durable due to a combination of two or more plies of paperboard bonded with a solid fiber laminating adhesive (8). Warping can be a problem,

Table I. Bag Bottom Paste Formula

Ingredients	Parts by Weight
Unmodified starch	12.6
Poly(vinyl alcohol)	4.5
Poly(vinyl acetate)	0.9
Soap	0.1
Water	81.9

since the multiple plies can cause significant strain while the adhesive is drying. Therefore, this adhesive is usually high solids (50-55%) and contains a rather high level (30-50%) of plasticizer (sugar, sodium nitrate, urea) to reduce strains. Naturally, a good dry bond is required, and water resistance is so important that up to 25% of a urea-formaldehyde resin may be used. The high solids are achieved by using high-soluble white dextrans or high-fluidity starches (6). More recently, blends of poly(vinyl alcohol), starch and clay are used to provide both good water resistance and improved tack for faster laminating speeds (6). A more marketable shipping carton made of lightweight coated paper or aluminum foil laminated to the top side and printed before construction of the box requires a more general purpose adhesive formulated at high enough solids to have good tack and no warp. The adhesive should also be incapable of bleeding through the top sheet. These adhesives are made according to the formula in Table II.

Table II. General Purpose Laminating Adhesive

Ingredients	Parts by Weight
White dextrin (high soluble)	20.2
Clay	13.5
Urea	6.7
Borax (10 mol)	5.0
Water	54.6

This formula must also be cooked and cooled prior to application (8).

**Adhesives for Case and Carton Sealing.** Once the corrugated board or the solid fiberboard boxes are constructed, they must be glued, filled with product, and the top flaps folded down and glued closed before shipment. The adhesive



for this application must be of moderate but stable viscosity (1,000 to 3,000 cP) with high tack and good bond (5). Although synthetics have practically taken over this market, borated dextrin adhesives are still being used. A typical finished, pasted out formulation is shown in Table III.

Table III. Case and Carton Adhesive

Ingredients	Parts by Weight
White dextrin (high soluble)	37.5
Sodium metaborate	5.0
Borax (10 mol)	1.3
Water	56.2

Poly(vinyl alcohol) may also be added if water resistance is required. Another formulation that does not require cooking to develop its adhesive characteristic is based on the cold, caustic conversion of an acid-modified starch (75 fluidity) (6). Clay filler may be added to any case or carton sealing adhesive if the board being glued is too porous.

**Adhesives for Tube Winding.** Many products, such as cores, cans, cones, and containers, are produced from paper tubes. Convolute wound tubes or the continuously produced spiral wound tubes require different glues. Convolute tube winding is accomplished by feeding paperboard through a two-sided adhesive application system to a rotating mandrel whose shape determines whether the tube is hexagonal, octagonal, or round. The width of the paperboard will determine tube length, or different finish lengths may be cut. Winding the board around the mandrel the proper number of times gives the tube the desired wall thickness to provide appropriate strength. Pregelled starches may be mixed on site, but prepared pastes based on regular or borated dextrans are often purchased from the adhesive suppliers (5). Spiral wound tubes are produced by means of multiple plies fed through adhesive stations and wound around the mandrel at an angle so the newly formed tube continuously slides down the mandrel until cut to the desired length. Faster bonding pastes are required for acceptable production. The typical adhesive is based on a high solids, borated dextrin, but oxidized and hydroxyethyl starches are also used (9).

**Adhesives for Bottle Labels.** The adhesive used to glue a label to a glass, polyethylene, or treated polypropylene bottle has long been called a "jelly gum," which describes the adhesive's consistency when it is ready to be applied—a heavy, gummy, rubbery, tacky character. The high tack is necessary to keep up with the high-speed bottling machines and to stop the labels from sliding once they are placed on the bottle (10). The solids of these pastes are about 40% to 50% and the viscosity 80,000 to 150,000 cP at room temperature (6). Labels must also be able to be washed off if bottles are returnable and reused (11). Both dextrans and acid-modified starches have been used for this application,

but starches are necessary for any degree of water resistance ( $\delta$ ). Acid-modified, waxy starches are very effective bottle label adhesives. One formulation is listed in Table IV.

Table IV. Bottle Label Adhesive

Ingredients	Parts by Weight
Waxy starch (40 fluidity)	38.0
Urea	3.0
Sodium nitrate	3.0
Water	56.0

Some beer bottle manufacturers have added poly(vinyl alcohol) to the adhesive to ensure resistance to iced water yet retain washability in the bottling operation. Others have used the starch paste to extend the more water-resistant casein adhesives (9). Newer adhesives are being developed based on double treatments of starches such as hydroxyalkyl ethers of oxidized starch, blending these products with other specified polymers (12,13) or adding synthetic resins (14).

**Adhesives for Envelopes.** Adhesives on envelope flaps must obviously be remoistenable and thus are often based on high-soluble white dextrans or canary dextrans from regular or waxy cornstarch. Normally around 55% to 65% solids, about 2,000 to 10,000 cP, these adhesives machine well during application and dry fairly quickly. The dried film on the flap must be glossy, low in color, noncurling, and nonblocking in humid weather (5). A general formula is given in Table V. The sodium bisulfite acts as a color reducer, and the poly(ethylene glycol) is a nonhumectant plasticizer (6).

Table V. Envelope Flap Seal Adhesive

Ingredients	Parts by Weight
Waxy dextrin (high soluble)	63.0
Sodium bisulfite	1.0
Poly(ethylene glycol)	0.5
Water	35.5

The adhesive for the seams on envelope backs must also be at a high solids to prevent strike through, allow fast production speeds, and provide lay-flat. Dextrans or pregelled starches may be used, but are usually heavily plasticized with the lower cost humectant-type plasticizers since blocking is not a factor on

the back side. Poly(vinyl acetate) may be added to increase the solids (10). A flexible formula is listed in Table VI (6).

Table VI. Envelope Back Seam Adhesive

Ingredients	Parts by Weight
Pregelged starch (low viscosity)	30-35
Dextrose	10-35
Sodium nitrate	8-15
Urea	0-6
Poly(vinyl acetate)	5-15
Water	27-30

**Adhesives for Gummed Paper and Tape.** Remoistenable adhesives for paper and tape are not unlike those used for envelope front seals. Producing gummed labels or trading stamps has conventionally been a matter of applying a high-solids (50%) cooked dextrin paste to the paper. The problem of paper shrinkage causing curling is usually dealt with by running the sheet over a breaker bar that fractures the brittle film, making it discontinuous and non-curling. More frequently, producers are applying a binder dissolved in a solvent "carrying" the cold water-soluble starch or dextrin that produces a discontinuous film not susceptible to curling.

Sealing tape has 35 to 90 pounds per ream of kraft paper as a substrate, whereas, reinforced sealing tape is based on a bonded laminate of kraft paper, reinforcing fibers, and kraft paper. The adhesives applied to these substrates may be thin-boiling, waxy starches alone, or blended with a soluble dextrin (5). More recently, blends of a soluble dextrin with oxidized potato or a hydroxypropyl ether of an oxidized potato starch are being used (9). Also, the acetate or succinate of an oxidized waxy starch may be used (15) as well as specially produced waxy starch acrylamide graft copolymer products (16).

**Adhesives for Wallpaper.** Homeowners can still buy the small packages of wheat starch to mix paste for hanging wallpaper. Paste prepared by adhesive manufacturers is more easily applied directly from the container and is widely used by professionals. Prepared wallpaper pastes must obviously have good viscosity stability, have good wet tack, and good slip properties to allow careful seam alignment while hanging. Pregellatinized starches and acid-modified starches are being used to prepare these pastes, and borax adds good tack while plasticizers provide the slip required. Clay may be added for ease in stripping paper later. A typical paste formula is shown in Table VII (6).

**Adhesives for Miscellaneous Uses.** Starch is also used to prepare children's library paste. A blend of low-soluble white dextrin and unmodified cornstarch is cooked up with glycerine and water to about 55% solids and set back to obtain a firm but smooth texture (6). Cornstarch is also used in the production

of cigarette seam paste at the cigarette-manufacturing plant. This adhesive is a proprietary blend of ingredients, but its base is a very high-solids paste of unmodified starch that is allowed to set back overnight so it is capable of being extruded onto an applicator wheel.

Table VII. Prepared Wallpaper Paste

Ingredients	Parts by Weight
Pregelged starch (acid modified)	25.0
Clay	20.0
Urea	3.75
Sodium metaborate	1.25
Water	50.0

## Conclusions

Starch is still quite widely used as an adhesive in our modern, "high tech" world. Its adhesive properties are developed differently for different products, and starch-based adhesive is used in a large variety of applications. From the standpoint of its being a renewable resource, a reliable performer, and a low-cost raw material, starch would seem to be an adhesive ingredient on the market for a long time into the future.

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# Chapter 24

## Cellulose Graft Copolymers for Potential Adhesive Applications

### Bonding of Plastics to Wood

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Bonding of hydrophobic plastic materials to wood to create new wood-plastic (polystyrene) materials with improved mechanical and physical properties that incorporate the desirable features of each constituent is difficult to achieve. This is due to poor interfacial adhesion between the wood and polystyrene components because of their inherent incompatibility. New, well-defined, tailored cellulose-polystyrene graft copolymers have recently been prepared using anionic polymerization techniques. Preliminary bonding studies showed that these graft copolymers can function effectively as compatibilizers or interfacial agents to bond hydrophobic plastic (polystyrene) material to wood, evolving into a new class of composites.

The concept of combining two or more unique polymers to prepare new material systems with the desirable features of their constituents is widely practiced in the polymer industry (1-5). The primary issue confronting the design of such polymer systems involves guaranteeing good stress transfer between all components of the multicomponent system. This is the only way to ensure that the components' individual physical properties are efficiently utilized to produce mixtures with the desired performance characteristics.

Obtaining good stress transfer is possible in systems where the mixture forms a miscible amorphous phase (where interphase stress transfer is not an issue);

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however, obtaining a miscible phase of two chemically incompatible components is difficult to achieve. Preparing new materials by mixing two incompatible polymers results in products with reduced physical properties (6-9). Strength and toughness values are minimal and are lower for the mixture than for any of the pure components (10). This condition is due to poor interfacial adhesion between the individual components because of the inherent incompatibility.

One potential solution to this incompatibility problem that is currently practiced in the polymer industry uses block or graft polymers of the form A-B as compatibilizers or interfacial agents to improve adhesion between immiscible A-rich and B-rich phases. The physical affinity of the A portion of the graft polymer for the A phase and the B portion for the B phase serves to locate the graft polymer at the interface and physically connect the two phases through covalent bonds to the graft polymer backbone. The net result of this improved adhesion is a finer dispersion of the minor component that provides significant improvements in the mechanical properties of elongation and tensile strength (11-15).

This chapter reports successful initial efforts to bond wood in the presence of hydrophobic plastic material [polystyrene (PS)] using well-defined and tailored cellulose-polystyrene graft polymers as compatibilizers or interfacial agents. The synthesis of these tailored cellulose graft polymers is also presented.

As previously stated, the major problem confronting the development of new composite systems from wood and plastic polymers is the inherent incompatibility of the components: hydrophobic polystyrene and the polar wood-adhesive matrix. In order to create new materials with improved mechanical and physical properties, it is imperative to employ an interfacial agent like well-defined cellulose-polystyrene graft polymers. The cellulose backbone of the graft polymer is available for bonding to the wood with existing commercial resins, while the heat employed to cure the resin causes the polystyrene side chains to melt and flow into the polystyrene component of the mixture. Upon cooling, the polystyrene solidifies, creating a strong bond between the incompatible wood and polystyrene components, which are joined via the direct polystyrene to cellulose linkage within the graft polymer (Figure 1).

It may also be possible to eventually extend this bonding concept to the preparation of flakeboards and other wood-base composite materials. If plastics like polystyrene are incorporated into the composite matrix, and successful bonding between the wood and plastic is developed through the graft polymers, the three-dimensional network of plastic material throughout the composite matrix may lead to enhanced physical and mechanical properties as well as improvements in dimensional stability (Figure 2).

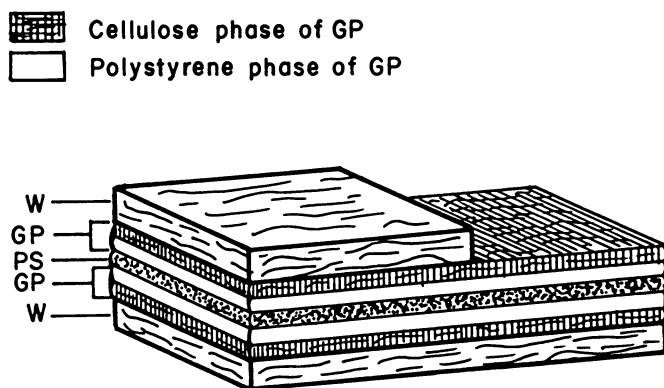


Figure 1. Exploded view of the use of graft polymers (GP) to compatibilize the linking of wood (W) and polystyrene (PS) materials.

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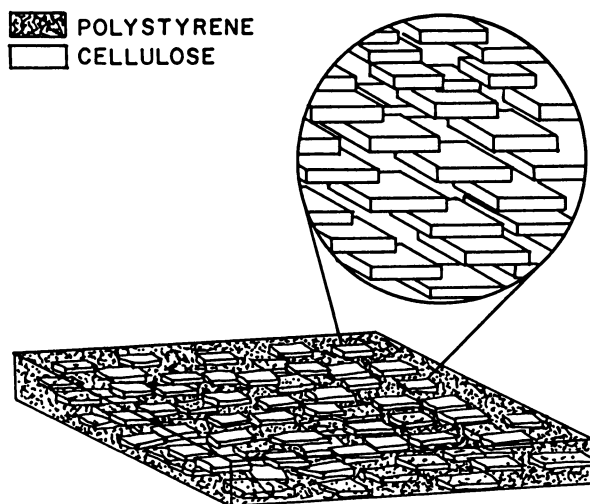


Figure 2. Continuous three-dimensional network of plastic (polystyrene) linked to wood via a cellulose-polystyrene graft copolymer.

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## Experimental Methodology

**Preparation of Cellulose-Polystyrene Graft Copolymers.** The polystyryl mono- and di-carbanions were prepared in THF at  $-78\text{ }^{\circ}\text{C}$  by using *n*-butyl lithium and sodium naphthalene as the initiators, respectively. The carbanions were reacted with dry carbon dioxide. The products were precipitated in methanol, filtered, washed with water and methanol, and dried. Size exclusion chromatography (SEC) established that the molecular weight of the polystyryl monocarboxylate was 6,200 and that of the polystyryl di-carboxylate 10,2000. The mono- and di-carboxylates were reacted with mesylated cellulose acetate in dimethylformamide at  $75\text{ }^{\circ}\text{C}$  for 20 h to give the cellulose-polystyrene graft copolymer (GP 1) and crosslinked cellulose-polystyrene graft copolymer (GP 2), respectively.

**Bonding Studies.** Test specimens were constructed of two plies of 1/8" thick yellow poplar veneer. They were conditioned in an Aminco conditioning chamber at  $46\text{ }^{\circ}\text{C}$  and 12% relative humidity, which resulted in wood specimens with an average moisture content of 2.7%. All plies used in this experiment were conditioned in the chamber for at least 14 days prior to sample fabrication. Cascophen-16 (Borden Chemical, Inc.) was selected as the commercial oriented strand board adhesive to be used in the study. The resin was poured directly into a commercial paint spray gun and applied to the 1/8" wood plies using a homemade system developed by the authors. The system consisted of a small motorized cart capable of holding a cartridge of wood plies as they passed through the resin stream emitted by the stationary spray gun. The amount of resin delivered to each ply was controlled by regulating the air pressure of the spray gun and the speed of the motorized cart. Test specimens (composed of two plies) with 0.18 g resin evenly distributed across 4 sq. inches of glueline were prepared with the system. Polystyrene, graft copolymer, and polystyrene-graft copolymer mixtures were added in powdered form to one ply from each test specimen using a homemade column-loading system. This system allowed the delivery of measured amounts of evenly distributed powders onto the test areas. Table I lists the various compositions of the test specimens and the number of the test specimens used in the study.

The test specimens (composed of two plies) were loaded onto aluminum cauls and placed in the press. Each specimen was pressed at 50 psi and  $149\text{ }^{\circ}\text{C}$  for 3 min. Upon cooling, a band saw was employed to remove 1/2 in. from each end of the specimen (to enable them to fit into the 4 in. grips on the testing machine). A high-speed drill press (12,000 rpm) fitted with a 1/8 in. router bit was then used to cut the cross grooves into each specimen to isolate the glueline for testing. The specimens were conditioned at  $21\text{ }^{\circ}\text{C}$  and 50% relative humidity for 7 days. Prior to actual testing, a caliper (precision of  $\pm 0.001\text{ in.}$ ) was used to measure the glueline area isolated for testing. The specimens were then inserted into the grips on a Reihle strip shear testing machine and loaded

at a constant rate of 10 lb per sec until failure. The ultimate load at failure and visual estimate of the amount of wood failure were recorded for each sample.

Table I. Composition of the Test Specimens

Population	Number of Test Specimens	Composition
A	45	Controls, PF resin only
B	10 <sup>1</sup>	0.02 g of PS only (no resin)
C	10 <sup>1</sup>	0.02 g of GP1 only (no resin)
D	10 <sup>1</sup>	0.02 g of GP2 only (no resin)
E	48	PF resin and 0.02 g of PS
F	45	PF resin and 0.02 g of GP 1
G	18 <sup>2</sup>	PF resin and 0.02 g of GP 2
H	46	PF resin and 0.02 g of PS-GP 1 mix <sup>3</sup>
I	50	PF resin and 0.04 g of PS-GP 1 mix <sup>3</sup>
J	25 <sup>2</sup>	PF resin and 0.02 g of PS-GP 2 mix <sup>3</sup>

<sup>1</sup>In populations B, C, and D, no bonding occurred, and sample fabrication was halted after 10 specimens.

<sup>2</sup>The number of test specimens was limited due to insufficient supplies of GP 2.

<sup>3</sup>The PS-Graft Polymer (GP) mixture was made up of 50% by weight of each component.

### Synthesis of Tailor Made Cellulose-Polystyrene Graft Copolymers

**Problems Encountered.** Most of the work done to date in preparation of cellulosic graft polymers has involved free-radical polymerization methods. With these procedures, very few high-molecular-weight molecules were actually grafted as illustrated by low levels of graft substitution [only a small portion of the cellulose substrate was grafted (16,17)]. The molecular weight distribution of the grafted side chains was difficult to control or change, and no knowledge of the nature of the backbone-graft linkage existed. Substantial homopolymer formation occurred; there was poor reproducibility and little control over the grafting process, graft yields, resulting properties, and other features of the graft polymer (18). Clearly, these types of ill-defined and poorly characterized graft polymers with only a few very high molecular weight grafts and low levels of graft substitutions (0.03 to 0.8 polystyryl chains per cellulosic chain and molecular weights ranging from 354,000 to 960,000) would be poor interfacial compatibilizers. In fact, the high molecular weights of the grafts and the low levels of graft substitution would make these materials behave more like blends than graft polymers.

It has been reported that homopolymer blends or random copolymers do not show interfacial activity (19). Therefore, the cellulose graft polymers from free-radical polymerization processes would not be effective compatibilizers. Preferred materials would be precise, well-defined cellulose graft polymers with known backbone-graft linkages developed through procedures that permit variation and control of molecular weight and degree of graft substitution. Higher degrees of substitution than obtained in the free-radical processes would be required.

**New Technology.** As the previous section illustrates, if cellulosic graft polymers are to be employed in adhesive applications, new synthetic approaches must be developed. The new synthetic procedures must allow control of the molecular weight and number of resulting side chain grafts (degree of graft substitution), elimination or drastic reduction of concurrent homopolymer formation, and exercise of direct knowledge and control over the linkage between the cellulosic backbone and the attached side chains.

New synthetic approaches to cellulosic graft polymers have been developed through use of anionic polymerization techniques that allow this to come about (20-24). Thus, the properties of the graft polymers can be tailored by control of parameters such as the molecular weight of the side chain grafts, elimination of concurrent homopolymer formation, the number and type of grafted side chains, knowledge of the linkage between the cellulose backbone and the side chain graft. The method involves: 1) introduction of electrophilic or leaving groups onto the cellulose backbone by chemical modification (i.e., introduction of reactive sites onto the cellulose backbone); 2) preparation of the "living" synthetic polymer of desired molecular weight by anionic polymerization techniques; and 3) reaction of the "living" synthetic polymer with the modified cellulose under homogenous reaction conditions.

Anionic polymerization methods provide an extensive and unprecedented control mechanism over polymerization processes. This includes polymer composition, microstructure, molecular weight and molecular weight distribution, and monomer sequence distribution. This is the key to our approach because we now have the ability to control the essential parameters of the side chain synthetic graft that dictates the properties of the graft polymer. Through regulation of the ratio between the reactive sites on the cellulose backbone and the synthetic polymer anion (the "living" synthetic polymer), the degree of substitution (DS) of the graft can be controlled. The synthetic polymer anion we have used is generally a carbanion (21-23) or a carboxylate anion (24), and the reactive sites on the cellulose backbone are good leaving groups like tosylate (23) and mesylate (24). Thus, the reaction chemistry essentially involves an  $S_N2$  type nucleophilic displacement reaction of the tosylate or mesylate group by the synthetic polymer anion. Therefore, there is no uncertainty in the nature of the backbone-graft linkage in our synthetic approach. Concurrent homopolymer formation is eliminated, and any homopolymer formed during the coupling stage is easily extractable.

Thus polystyryl carbanions and polyacrylonitrile carbanions prepared by anionic polymerization were reacted with cellulose acetate or tosylated cellulose acetate in tetrahydrofuran under homogenous reaction conditions. The carbanions displaced the acetate groups or the tosylate groups in a  $S_N2$ -type nucleophilic displacement reaction to give CA-g-PS and CA-g-PAN. Mild hydrolysis to remove the acetate/tosylate groups furnishes the pure cellulose-g-polystyrene (Figure 3).

Cellulose graft polymers having ester linkages with control over the molecular weight of the side chain graft (24) have also been prepared. In this synthesis, the polystyryl carbanion prepared by anionic polymerization techniques has been modified by capping with carbon dioxide to generate the polystyryl carboxylate anion (1) (Figure 4). While this anion is not sufficiently reactive to displace acetate groups from cellulose acetate, it is, however, sufficiently nucleophilic to displace better leaving groups like the mesylate group from a mesylated cellulose acetate backbone with the concomitant formation of an ester linkage.

A further advantage of the direct use of polystyrene carboxylate anions over polystyryl carbanion is that water does not interfere with the grafting reaction. The reaction is essentially complete at 75 °C after 20 hours. Grafting yields appear to be limited by the efficiency of carboxylation of the polystyrene. We have, for example, prepared a graft polymer product having one polystyryl ester chain of molecular weight 6,200 for every 17 anhydroglucose units of the cellulose backbone. With this approach, monodisperse polystyryl ester chains of any predetermined molecular weight can be grafted onto the cellulose backbone in a consistent manner.

Anionic polymerization of styrene with sodium naphthalene as the initiator gave the difunctional polystyryl carbanion of desired molecular weight that, on reaction with  $CO_2$ , furnished the polystyryl polystyryldicarboxylate anion (2) (Figure 5). Reaction of this anion with mesylated cellulose acetate resulted in the formation of a solid gel, indicative of crosslinking. Crosslinking is to be expected, since both ends of the polystyrene chain could potentially react with the mesylate groups on the cellulose backbone as shown in Figure 5 (24). We have prepared crosslinked graft polymers with polystyrene of molecular weight 10,000 and one polystyryl crosslink for every 23 anhydroglucose units. These well-defined, tailor-made cellulosic graft polymers prepared by the newly developed anionic polymerization procedures show promise in serving as compatibilizers of interfacial agents for developing new polymer blends of wood, phenolic resins, and polystyrene. A series of relatively simple bonding experiments was designed to support or reject the ability of the new graft polymers to facilitate bonding between wood and plastic materials.

## Bonding Studies

The potential use of cellulose graft polymers to compatibilize the linking of a natural polymer (wood) with a synthetic polymer (polystyrene) is based on

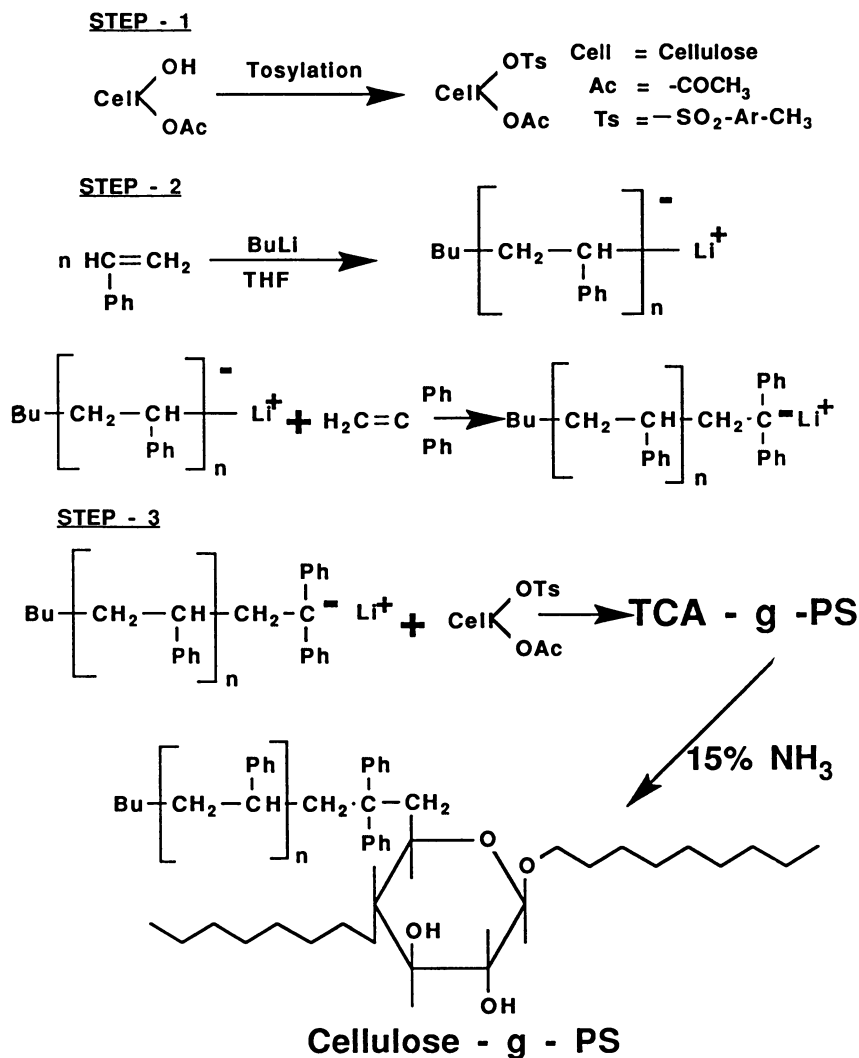


Figure 3. Grafting of polystyrylcarbanion onto tosylated cellulose acetate. Reprinted with permission from ref. 27. Copyright 1988 Humana Press.

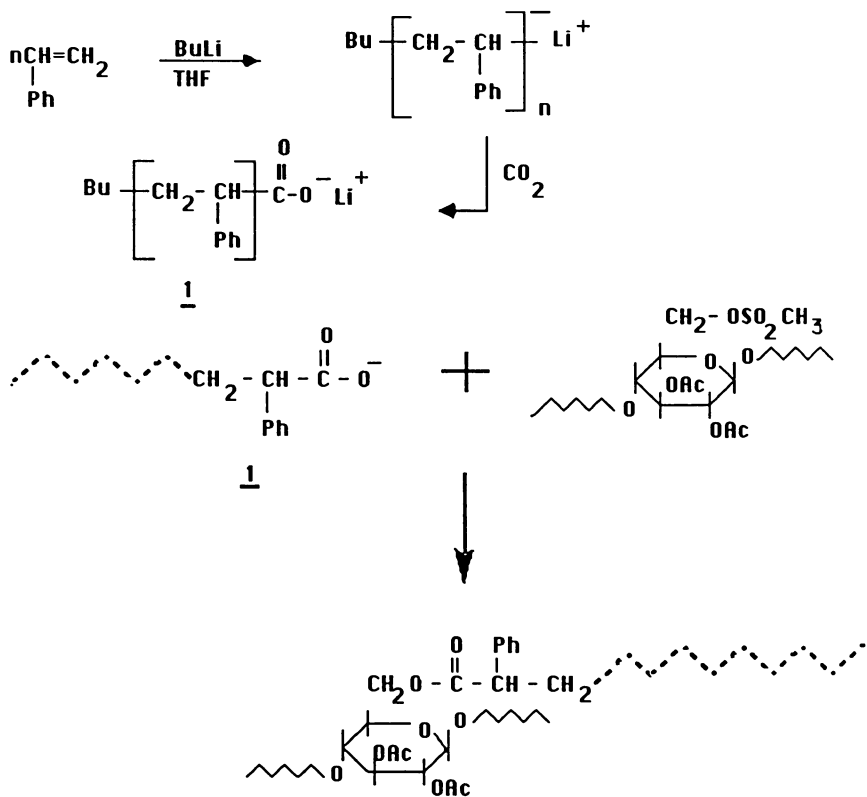


Figure 4. Grafting of polystyrylcarboxylate anion onto mesylated cellulose acetate.

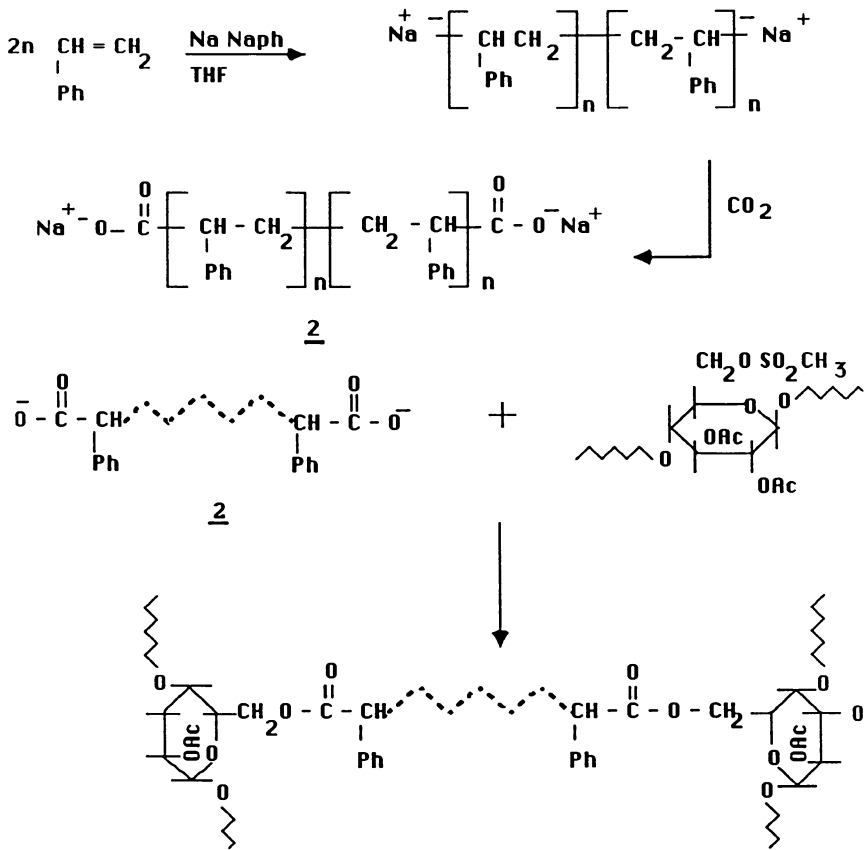


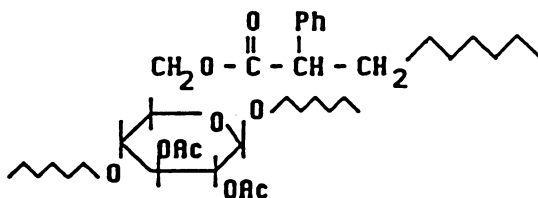
Figure 5. Formation of crosslinked graft copolymer by using polystyryldicarboxylate anion.

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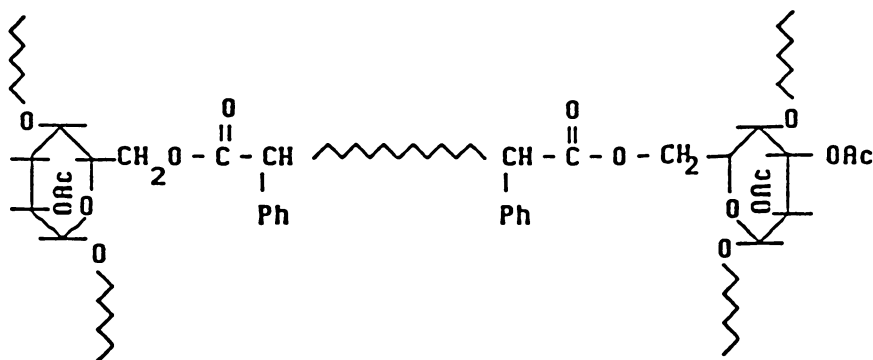
the premise that the graft polymer will link the wood and polystyrene through the cellulose and polystyrene phases of the graft polymer, respectively, and not adversely affect the bonding of wood. As previously discussed, the polymer literature documents the use of graft polymers to successfully compatibilize dissimilar synthetic polymers to produce materials with enhanced bond strengths and properties, but this procedure has never been applied to combining wood with plastics.

A set of limited, exploratory investigations was initiated to test the proposed bonding concept with the newly developed graft polymers. Two different graft polymers were selected and prepared for initial observation. They were:



**GP 1, Cellulose-g-PS**

(MW of PS = 6,250, PS content = 58%)



**GP 2, Crosslinked Cellulose - g - PS**

(MW of PS = 10,900. PS content = 64%)

The initial research objectives included developing a simple experimental procedure to study how the graft polymers, polystyrene, and a commercial phenol formaldehyde resin interact when combined with wood under heat and pressure. Two-ply lap shear test specimens were used for a comparative test.

All specimens were prepared and tested according to ASTM D 2339-82 (25), with modifications as described in experimental sections. The results are shown in Figure 6. Under the conditions selected for this study, good bonding was achieved with most of the control specimens - population A. The median percent wood failure for the population was 70%. An analysis of the test populations shows support for the premise that the graft polymers have a favorable influence on bond formation when compared to polystyrene alone. Samples containing PF resin and 0.02 grams of polystyrene resulted in an average bond strength of 334 psi (population E), demonstrating the inherent incompatibility of the wood and polystyrene phases. It is also possible that this incompatibility may be between the polar phenol formaldehyde resin and the hydrophobic polystyrene. When the polystyrene was replaced with the same amount (by weight) of one of the two graft polymers, bond strengths increased to 658 and 819 psi, respectively (populations F and G). Thus, when the polystyrene plastic phase is covalently linked to a cellulose backbone, it can be bonded to the wood. Bond strengths for these specimens fell just below those for the control population. However, it must be noted that the cellulose in the graft polymer had very few free hydroxyl groups available for bonding. Hydrolysis of the acetate groups to hydroxyl groups may produce graft polymers capable of even greater bond strengths.

Replacing the 0.02 grams of polystyrene with 0.02 grams of 50:50 mixture (by weight) of polystyrene and one of the graft polymers also led to increases in bond strengths. Samples produced with a PS/GP mixture containing the linear graft polymer yielded an average bond strength of 415 psi (population H), and samples containing a mixture with the crosslinked graft polymer showed an average bond strength of 519 psi (population J).

Additional specimens were prepared with 0.04 grams of the PS/GP 1 mixture (population I). In these specimens, an attempt was made to overload the PF resin with an excess of the powdered materials. This amount of powder completely covered the area under investigation and caused difficulty in assembling the samples. Even under these extreme loading conditions, a bond strength of 446 psi was obtained, which represents a statistically significant increase when compared to the 334 psi bond strength developed in population E.

The results from this study are very encouraging and provide support for continued investigations into the proposed bonding theory. We believe that the bond strengths can be significantly raised from present levels as a number of different parameters that can impact bonding efficiency are adjusted. Simply modifying the manner in which the graft polymer and polystyrene are added to the wood resin matrix may lead to significant increases in bond strengths.

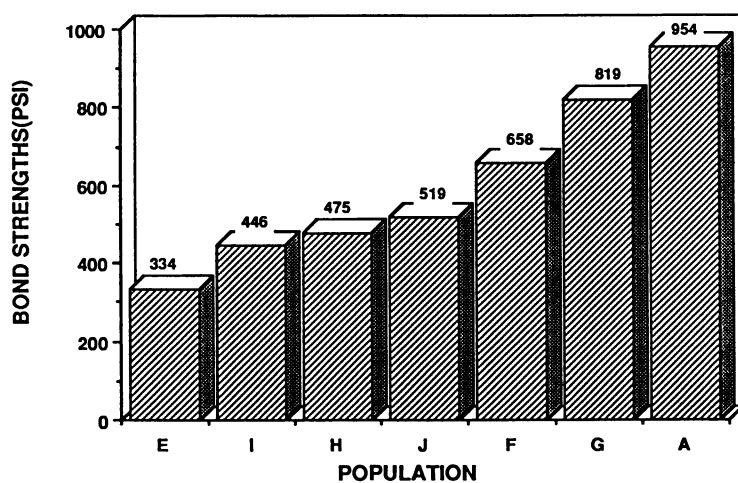


Figure 6. Preliminary bonding test results.

In the completed study, exact amounts of the powdered materials were sprinkled onto the wood-resin surface. Analysis of the test specimens revealed that under the press times and temperatures used the phase transition of the polystyrene side chains on the graft polymer was not efficient. Further, in order for the graft polymer to be effective as an interfacial agent, it must locate preferentially at the blend interface (21). The research team hopes to develop procedures in the future to allow the polystyrene and graft polymers to be dissolved in an organic solvent for application to the wood resin surface. This should allow the graft polymer to locate at the blend interface and improve bonding efficiency.

Results from the initial resin studied are also being employed in the development of additional experimental procedures. Plans are currently being drafted to prepare three-ply test specimens that are similar to the specimens used in the initial study, with the middle ply consisting of solid polystyrene. Comparing specimens with and without the graft polymers introduced to the ply interfaces should provide additional information on the ability of the cellulosic graft polymers to facilitate bonding between wood and plastic materials. If this approach proves successful, additional procedures will then be developed for the production of simple composite specimens.

**Statistical Analysis.** Each population was compared to all other populations at the 95 and 99% significance levels to determine if a statistical difference was presented between the populations. The test used followed the outline presented in Neter et al. (26). The results of this analysis can be illustrated on a number line. The average bond strength for each population is included, and the bracketed lines group populations that are not statistically different (Figure 7).

## Conclusions

This research project represents initial studies into a new approach to blending thermoplastic materials like polystyrene with wood materials, leading to a new class of wood-plastic composites. Traditional wood-plastic composites have involved the impregnation and subsequent *in situ* polymerization of vinyl monomers. This procedure has been adopted for selected products for which improved physical properties justify increased production costs. While producing mixtures or blends of wood and plastics, these types of composites do not demonstrate significant chemical bonding between the wood and plastic components.

Encouraging results on the bonding of plastics to wood using tailor-made cellulose-polystyrene graft polymers as compatibilizers or interfacial agents may offer a new approach to the engineering of wood-plastic products with improved mechanical and physical properties for a variety of applications. It also holds the potential of opening up new markets for renewable resources in the form of woody materials. For example, polystyrene production is currently 3.9 billion

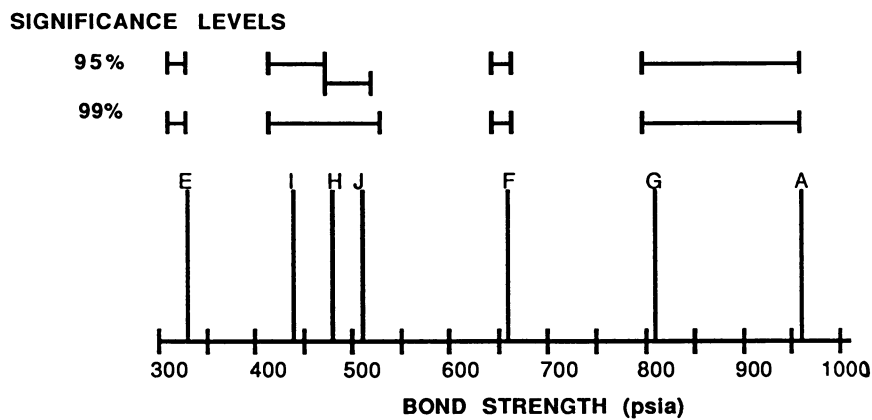


Figure 7. Statistical analysis of the bond strengths for the test populations.

lbs per year with a dollar value over 1.6 billion. This material is extensively used in packaging, appliances, housewares, and serviceware. It is conceivable that if the renewable resource materials (especially various byproducts like sawdust, generated by the wood industry) could be blended with polystyrene for processing and fabrication similar to existing styrenic plastics, a completely new market in disposable cups, trays, molded containers, and packaging materials, would be created. Environmental concerns caused by discarding nonbiodegradable plastics should make the "biodegradable," renewable resource-based materials very attractive. The study described here on the blending and bonding of two incompatible polymers (wood and polystyrene) using a novel cellulose graft polymer as the interfacial agent (compatibilizer) presents all of these exciting renewable resource utilization possibilities.

### Acknowledgments

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# Chapter 25

## Carbohydrate-Modified Phenol-Formaldehyde Resins Formulated at Neutral Conditions

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New adhesive systems are needed in which part or all of the petroleum-derived phenolic component is replaced by a readily available, renewable material without sacrificing durability or bonding ease. In this study, up to about 50% of the phenol-formaldehyde was replaced with carbohydrates and the modified resins used to bond wood veneer panels. The carbohydrate modified resins were formulated and cured under neutral conditions. The resins bond wood with acceptable dry- and wet-shear strengths, and wood failures. Reducing as well as nonreducing carbohydrates can be used as modifiers. The carbohydrate modifiers are being incorporated into the resin via ether linkages between the hydroxyls of the carbohydrate and methylol groups in the phenol-formaldehyde resin. The resins formulated under neutral conditions are very light in color.

Phenolic adhesives continue to be the most significant adhesives for the production of weather-resistant wood products. The energy crisis of the seventies, the cost of phenol, and the inevitable decline in petroleum reserves have caused the wood industry to focus attention on obtaining adhesive self-sufficiency (1). This concern arises primarily from the questionable longterm availability of resins and secondarily from the economics of adhesive resin use. Ready availability of adhesive resins is critical to the manufacture of bonded wood products. In practical terms, this means that new adhesive systems are needed in which part, or perhaps all, of the petroleum-derived phenolic component is replaced

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by a readily available, renewable material without sacrificing high durability or bonding ease.

In an earlier paper (2), we determined that carbohydrates could replace a significant portion of the phenol-formaldehyde resin used for bonding plywood veneer. Carbohydrates from renewable resources such as wood can replace up to 50% of the phenol and formaldehyde in resins formulated under basic conditions without significant loss of bond quality. Two-ply, Douglas-fir-veneer panels bonded with these carbohydrate-modified resins have shear strengths approximately equivalent to those for panels bonded with unmodified phenol-formaldehyde resin.

Reducing sugars or wood fractions containing reducing sugars (e.g., prehydrolysates) cannot be used directly as modifiers because they are degraded to saccharinic acids in the alkaline conditions used to formulate the resins. The acids interfere with the bonding or cure of the resin, or both. Reducing sugars can be used to successfully modify phenol-formaldehyde resins if they are reduced to the corresponding alditols or converted to glycosides.

Water extraction studies of the carbohydrate modified resins in the earlier study indicate that a portion of the carbohydrate is apparently incorporated into the final cured resin. The absolute amount of modifier incorporated into the cured resin increases with the amount initially added during resin formulation. IR studies indicated that the carbohydrate derivative is probably incorporated into the resin via ether linkages.

During cure of phenol-formaldehyde resins both ether and methylene linkages are formed. Unfortunately, there are insufficient experimental data on the effect of pH on the yields of ether and methylene linkages (3) formed during the cure of phenolic resins. Lilley (4), using urea-formaldehyde resins as an example, postulated that for phenolic resins methylene derivatives predominate at both high ( $\approx 10$ ) and low ( $\approx 3$ ) pH. At pH near neutral (6 to 8), ethers form although the effect of pH on ether formation over this range is rather complex. At pH 7, methylene linkages are apparently favored. Rossouw et al. (5) found that ether linkages form at pH 4.3 to 5.0, and that no ether linkages form at pH 9 with either phenol, resorcinol, or phloroglucinol. The ether linkages are unstable with time and temperature. Woodbrey et al. (6) found from NMR studies on resol resins that ethers are formed in the pH range 4 to 8 and that the number of ether linkages increases as the resin advances.

If ether linkages are involved in the incorporation of carbohydrates into phenol-formaldehyde resins as suggested by our previous work, and if ether linkages are favored at or near neutral pH, then curing carbohydrate-modified phenol-formaldehyde resins near neutral pH might enhance the incorporation of carbohydrates into the cured resin. Reducing sugars are relatively stable at neutral pH; therefore, it might be possible to use reducing sugars to modify phenol-formaldehyde resins directly. Our studies on bonding wood veneer with carbohydrate modified phenol-formaldehyde resins near neutral pH show that this is indeed the case.

## Experimental Methodology

**Adhesive Formulation.** Analytical grade reagents are combined in the following order:

- phenol (solid), 1.0 mole
- sodium hydroxide, 0.1 mole plus water to make a 50% solution
- paraformaldehyde, 2.3 moles
- water, 45 ml

The mixture was heated for 30 minutes at 85 to 90 °C, then cooled to about 50 °C, and neutralized with 85% phosphoric acid. The modifier was added and the reaction continued at 85 to 90 °C for 30 additional minutes. The resulting solids content of the resins was in the range of 70 to 85%.

**Veneer.** Rotary cut Douglas-fir veneer (3 mm thick) was conditioned to equilibrium moisture content at 27 °C and 30% relative humidity. Pieces 150 x 150 mm<sup>2</sup> were cut and bonded into panels.

**Bonding.** About 2 to 3 grams of the phenol-formaldehyde adhesive was spread as evenly as possible with a spatula on one piece of veneer, which was then dried at room temperature for 10 minutes. The coated piece of veneer was assembled into a two-ply panel with an uncoated piece of veneer with the grain in both plies parallel and held at room temperature for 15 minutes. The panel was placed into a heated press and pressed at 1 MPa (145 psi) for five minutes at 170 °C.

**Determination of Shear Strength.** Each panel was conditioned at 27 °C and 30% relative humidity for about 1 to 2 weeks before cutting into 14 two-ply lap shear specimens. Five specimens from each panel were tested for dry shear strength using a universal testing machine at a loading rate of 1 cm/min. Another five specimens from each panel were subjected to a standard vacuum-pressure soak (7). A vacuum of 85 kPa (25 inches of mercury) was drawn on the specimens while they were in water and held for 30 minutes. The vacuum was broken and a pressure of 450 to 480 kPa (65 to 70 psi) was applied to the specimens still in water and held for 30 minutes. The shear strength was determined on the wet specimens. The remaining specimens were held in reserve.

**Prehydrolysis of Southern Red Oak.** Green southern red oak (*Quercus falcata* Michx.) whole wood chips (650 grams, 150% moisture content) were prehydrolyzed with steam at 170 °C for 30 minutes in the apparatus previously described (8). The prehydrolyzed chips were extracted successively with three 2-liter portions of hot water. The water extract was concentrated to dryness *in vacuo* to give a yellow-brown semisolid (120 grams). The semisolid contained 22% total reducing sugars as measured by Nelson's colorimetric modification of the Somogyi method (9); after hydrolysis to monomeric sugars as described in ASTM D 1915 (10), the reducing sugars content was 60%. Analysis of the monomeric sugars by high-pressure liquid chromatography (HPLC) (11) showed

they were composed of 80% xylose, 10% galactose, 4% glucose, and 6% other sugars.

**Extraction of Cured, Modified Phenol-Formaldehyde Resins.** A sample of the modified resin was spread as a thin coating on a sheet of aluminum foil and cured in an oven at 170 °C for 5 minutes. The cured resin was removed from the aluminum foil, weighed, and broken into small pieces that were placed in water (10 to 15 mL) for extraction at room temperature. After 1 to 2 hours, the water was decanted from the solid resin. The resin was extracted in this manner an additional three to four times. The residue from the water extraction at room temperature was dried and ground using a mortar and pestle. The ground resin was extracted with hot water in a Soxhlet apparatus for 24 hours. The room temperature extract and hot water extract were combined, concentrated, and diluted to a known volume for analysis. The quantity of modifier in the extract was determined by HPLC (11).

**Isolation of Compounds VI-VIII.** Methyl  $\beta$ -D-xylopyranoside (0.4 g) and saligenin (2-hydroxybenzyl alcohol, 0.3 g) were reacted in water (0.25 ml) at 140 °C for 80 minutes. A portion of the mixture (150 mg) was dissolved in 50% methanol in water and separated into fractions by preparative HPLC on a reversed-phase Waters Prep/PAK 500 C<sub>18</sub> column with 50% methanol in water as solvent at 0.25 L/min with RI detection. The first (1L) fraction contained three peaks that were further separated on a reversed-phase Bondapak C<sub>18</sub> column (4.6 mm x 30 cm). The solvent was a gradient of 30 to 90% methanol in water at 1 ml/min and the compounds were detected by UV at 280 nm.

Thin-layer chromatography (TLC) of the reaction mixture and saligenin was on Whatman K5F silica gel plates (250 thick) developed in 8% methanol in chloroform and visualized by spraying with 50% concentrated sulfuric acid in ethanol and heating at 140 °C for 5 minutes.

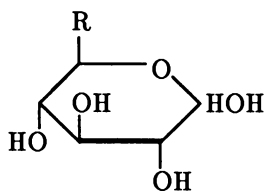
## Results and Discussion

**Bonding Veneer Panels.** The "neutral" resins were formulated in two stages. The first stage consists of forming a resol resin from phenol and formaldehyde in basic conditions. The second stage consists of neutralizing the resol (pH 6 to 7) with phosphoric acid, adding the carbohydrate modifier, and formulating the modified resin for bonding. Details are given in the Experimental Methodology section.

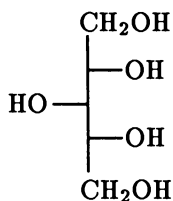
Figure 1 compares the dry- and wet-shear strengths of two-ply, Douglas-fir veneer panels bonded with a commercial phenol-formaldehyde resin (basic), a phenol-formaldehyde resin prepared in the laboratory under basic conditions, and an unmodified neutral resin prepared in the laboratory. The shear strengths obtained with these three resins served as control data for further experiments. The dry-shear strengths of panels bonded with the unmodified neutral resin are lower than those for panels bonded with the resins cured under basic conditions; however, the wet-shear strengths of panels bonded with the three resins are all

essentially the same. The differences in dry-shear strength are reproducible and thus apparently real.

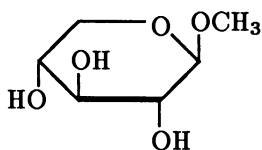
*Xylose Modified Phenol-Formaldehyde Resins.* Xylose (I) and byproducts streams containing xylose (e.g., wood prehydrolysates from the production of chemical pulps and waste liquors from the wet process for hardboard production) are readily available. Our previous experiments (2) showed that free reducing sugars are not acceptable modifiers for phenol-formaldehyde resins cured under basic conditions.



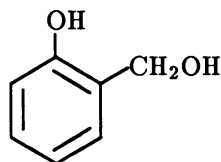
I. Xylose (R = H)  
IV. Glucose (R = CH<sub>2</sub>OH)



II. Xylitol



III. Methyl Xyloside



V. Saligenin

Neutral resins formulated with various xylose contents were used to bond Douglas-fir veneers into two-ply panels at 170 °C as opposed to 140 °C used for the basic resins. This temperature was chosen for bonding since differential scanning calorimetry (DSC) showed that the unmodified and modified neutral resins produce a major exotherm at about this temperature, whereas, resol resins cured under basic conditions produce an exotherm at about 140 °C.

Phenol-formaldehyde resins modified directly with reducing sugars successfully bond wood veneers at neutral conditions. The dry- and wet-shear strengths of two-ply panels bonded with xylose-modified resins are not adversely affected until the amount of xylose is increased to between 0.6 and 1.0 moles xylose per mole of phenol (Figure 2). However, even resin with 2 moles xylose per mole of

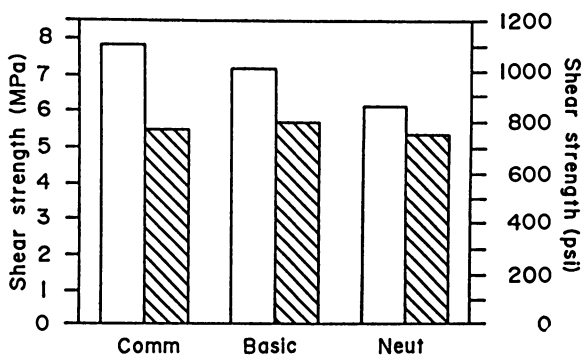


Figure 1. Comparison of dry- and wet- (hatched) shear strengths of resins: Comm = commercial resin (basic); Basic = resin formulated under basic conditions in laboratory; Neut = resin formulated under neutral conditions.

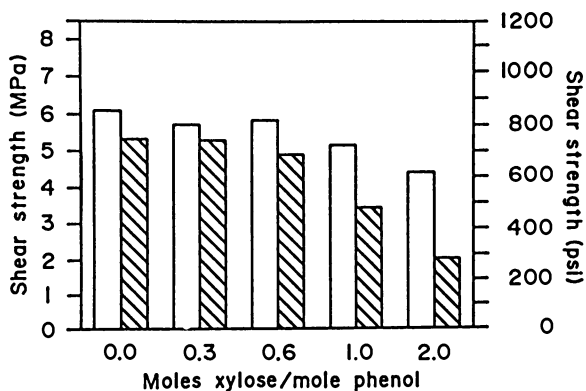


Figure 2. Variation of the dry- and wet- (hatched) shear strengths of two-ply Douglas-fir panels bonded with xylose-modified neutral resins. Moles of xylose per mole of phenol were varied as indicated. The mole ratio of phenol to formaldehyde was 1:2.3.

phenol produces panels with significantly better wet-shear strength than xylose-modified basic resins (2).

*Prehydrolysate Modified Phenol-Formaldehyde Resins.* Neutral resins were also formulated with the addition of varying amounts of a prehydrolysate obtained from southern red oak wood. This material consists of xylose, xylose oligosaccharides, and soluble lignin. The dry- and wet-shear strengths of two-ply, Douglas-fir-veneer panels bonded with these resins were very similar to those of the xylose modified resins (compare Figures 2 and 3). Prehydrolysate does not adversely affect the physical properties of the modified resins until between 0.6 and 1.0 moles of prehydrolysate per mole of phenol is added. The dry-shear strength of the neutral resin containing 0.6 moles of prehydrolysate is essentially the same as that for the basic resin (2) modified with 0.6 moles of prehydrolysate. The wet-shear strength of the neutral resins containing prehydrolysate is about three times greater than that of the corresponding basic resin.

The amount of wood failure in the two-ply specimens decreases as the amount of modifier in the resin is increased. The wood failure data also indicate that the performance of the modified resin is not severely affected until greater than about 0.6 moles of modifier per mole of phenol has been added to the neutral resin (Figure 4).

*Phenol-Formaldehyde Resins Modified with Carbohydrate Derivatives.* Because the nonreducing carbohydrate derivatives, xylitol (II) and methyl xyloside (III), are excellent modifiers for basic resins, we wanted to determine if they are also good modifiers for neutral resins, and if they are better modifiers than free reducing sugars. We found no additional advantage gained by using nonreducing carbohydrates instead of reducing carbohydrates in neutral resins.

*Color of Bond Line.* Two-ply veneer panels bonded with carbohydrate-modified resins formulated under neutral conditions had bond lines that are extremely light colored in contrast to the dark red-black color characteristic of resins cured under basic conditions. The color ranges from a light yellow-tan with unmodified and xylose-modified resins to a medium tan with the prehydrolysate modified resins. These resins would therefore be suited for bonding wood used for decorative purposes.

To determine the stability of the resin color, samples were exposed to UV in an Atlas Xenon Arc Weather-ometer. Samples previously tested for dry shear strength and samples of the cured, neat resin were exposed for 100 and 200 hours in the weather-ometer. One hundred hours of exposure is approximately equivalent to 1 year of exposure to sunlight at the latitude of Chicago. The resin was the same color as the wood or lighter after both lengths of exposure.

*Viscosity of Neutral Resins.* The neutral resins, both unmodified and carbohydrate-modified, were very viscous. The resins have a consistency of taffy candy. This might present problems in their utilization with present commercial equipment, although equipment for applying foamed resins might be suitable.

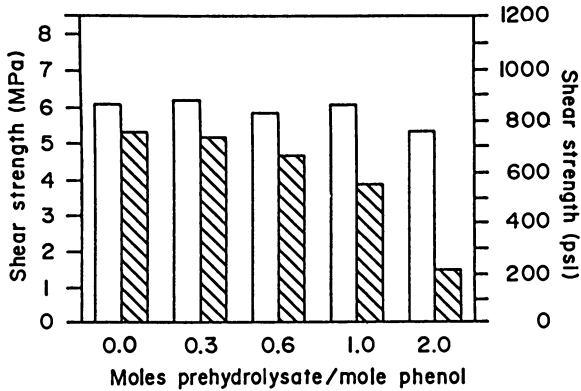


Figure 3. Variation of the dry- and wet- (hatched) shear strengths of two-ply Douglas-fir panels bonded with phenol-formaldehyde resins modified with a prehydrolysate obtained from southern red oak wood. Moles prehydrolysate per mole of phenol were varied as indicated. The mole ratio of phenol to formaldehyde was 1:2.3.

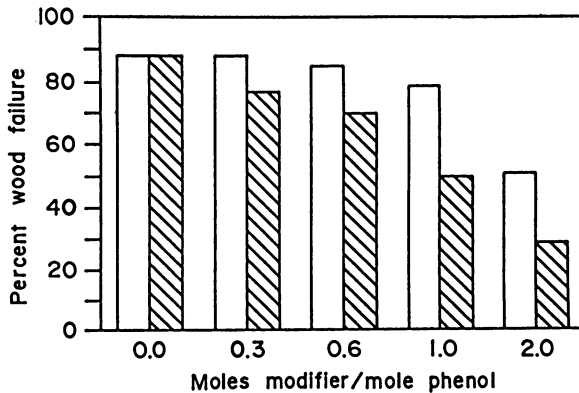


Figure 4. Variation of the dry- and wet- (hatched) wood failures of modified phenol-formaldehyde resins. The moles of modifier were varied as indicated. The mole ratio of phenol to formaldehyde was 1:2.3. The wood failures of xylose- and prehydrolysate-modified resins were similar and were averaged.



Some neutral resins can be solubilized in, for example, methanol by vigorous shaking.

*Optimization of the Resins.* Except as indicated above, no attempt was made to optimize these resins. Further studies to determine the optimum proportions of reactants and pressing conditions are planned.

**Incorporation of Carbohydrate into Cured Resin.** Several methods were used to determine whether the carbohydrate component is chemically incorporated into the final cured resin. These methods were water extraction of the modifier from the cured resin, IR spectroscopy, and isolation of reaction products formed between a carbohydrate and a model compound that contained a phenolic methylol group.

*IR Spectroscopy.* We presumed that the carbohydrate modifier is incorporated into the final cured phenol-formaldehyde resin via ether-type linkages, based on previous IR experiments (2). We found that IR spectra of xylose-modified resins cured under neutral conditions contain a major absorption peak at  $1060\text{ cm}^{-1}$ , indicating ether linkages. However, an unmodified neutral resin also contains absorption peaks in this region indicative of ether linkages having been formed. Therefore, it was not possible to assign the peak in the IR spectrum of the xylose-modified resin to ether linkages exclusively between xylose and phenolic methylol groups.

*Extractability.* About 60 to 70% of the total modifier added is extractable from resins cured under basic conditions and modified with alditols and methyl glycosides (2). In contrast, only about 0 to 20% of the xylose and prehydrolysate is extractable from samples of cured resin modified with 0.6 moles of either modifier per mole of phenol. Approximately 20 to 30% of xylitol (II), methyl xyloside (III), or glucose (IV) is extractable from neutral resins modified with these carbohydrates, indicating that neutral resins incorporate the carbohydrate more effectively than resins formulated and cured under basic conditions. In addition, free reducing sugars can be used directly.

*Reactions with Model Compounds.* To test whether carbohydrates were actually reacting with the phenolic resin, the reaction of methyl xyloside (III) and saligenin (V) under neutral conditions was studied. This reaction system was used as a model for the curing reaction.

The mixture obtained on reacting methyl xyloside with saligenin was compared by thin layer chromatography (TLC) (Figure 5) and high-pressure liquid chromatography (HPLC) (Figure 6) with the mixture obtained on reacting saligenin with itself. Both the TLC and HPLC of the reaction products formed on reacting methyl xyloside and saligenin indicate that compounds other than those formed by reaction of saligenin with itself form during the reaction. These are probably reaction products of methyl xyloside and saligenin.

The products from reaction of methyl xyloside and saligenin were separated into fractions by preparative HPLC on a reverse-phase  $C_{18}$  column. One fraction contained a mixture of compounds VI-VIII as indicated in Figure 6. The

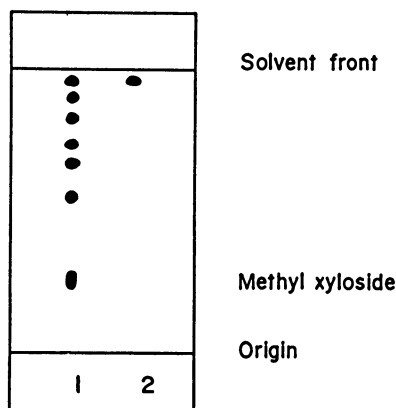


Figure 5. TLC on Whatman K5F silica gel of (1) the reaction mixture of saligenin and methyl xyloside heated at 140 °C for 80 minutes and (2) the reaction of saligenin with itself when heated at 140 °C for 60 minutes. The TLC plate was developed in 8% methanol in chloroform and visualized by spraying with 50% concentrated sulfuric acid in ethanol and heating at 140 °C.

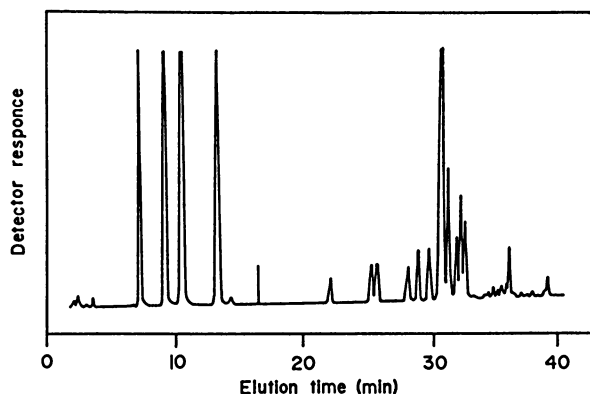


Figure 6. HPLC of the mixture obtained by reaction of saligenin and methyl xyloside on a reversed-phase Sepsalyte-CH column. The solvent was a gradient of methanol/water (0:100 to 90:10) and the peaks were detected by UV at 280 nm. Saligenin has a retention time of 7 min. The peak at 30.86 min represents the reaction of two molecules of saligenin. The peaks at 8.98 (Peak I), 10.30 (Peak II), and 13.10 (Peak III) are the reaction products of saligenin and methyl xyloside.

mixture was separated into individual compounds by preparative HPLC chromatography on a Bondapak C<sub>18</sub> column.

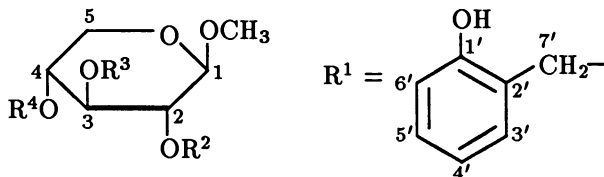
The <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were obtained for each of the three components. The spectra of the components are compared with those of methyl xyloside and saligenin in Tables I and II. The spectra are consistent with the three components having been formed by the reaction of one hydroxyl substituent on methyl xyloside with the methylol group of saligenin to form an ether linkage. Formation of similar compounds has been reported on reacting carbohydrates with vanillyl alcohol (12).

The assignments of Peak I as isomer VI in which the saligenin is linked via the hydroxyl at C-3 of methyl xyloside and of Peak III as isomer VII in which saligenin is linked via the hydroxyl at C-2 are made primarily on the basis of the <sup>13</sup>C-NMR spectra. In the <sup>13</sup>C-NMR of Peak I, the chemical shifts of all the carbons in the methyl xyloside portion of the molecule are unchanged, as compared to those for the corresponding carbons in methyl xyloside, except that C-3 is shifted upfield by about 4 ppm. This shift is apparently due to shielding by the aromatic moiety and establishes that saligenin is attached via the hydroxyl at C-3. In the case of isomer VII (Peak III), all the chemical shifts of the carbons in the methyl xyloside portion of the molecule are unchanged except that of C-2.

Peak II is then the isomer in which the saligenin moiety is attached at the C-4 hydroxyl of the methyl xyloside moiety. The chemical shifts of both C-4 and C-5 in the <sup>13</sup>C-NMR of isomer VIII (Peak II) are shifted as compared to the corresponding carbons in methyl xyloside. This is presumably due to the conformation that isomer VIII (Peak II) adopts in solution to reduce steric crowding of the C-4 saligenin moiety with the hydroxyl at C-3.

The chemical shifts of the carbons in the saligenin-derived portion of these compounds are not much different from those in saligenin itself, except for the methylene carbon of the methylol group (C-7'). The chemical shift of this carbon is shifted down field as expected on formation of an ether linkage.

These data indicate that as carbohydrate-modified neutral phenol-formaldehyde resins cure, the carbohydrate is incorporated into the resin. An ether forms between the hydroxyl groups of the carbohydrate and the methylol groups of the resin. Crosslinking could take place via, for example, the three hydroxyl groups of methyl xyloside, assuming that steric hindrance does not limit this possibility. If crosslinking occurs, the hydroxyl groups of the sugar modifier would be covered, which would explain why the incorporation of carbohydrates does not affect the resins' physical properties in the wet state, at least up to the 0.6 to 1.0 moles modifier per mole of phenol level. We do not know whether these linkages remain at the temperatures used to fully cure the resin, or whether water or formaldehyde are split out, as is the case with the cure of phenolic resin under basic conditions and presumably under neutral conditions. The reactions of sugars with model compounds are being studied further.

Table I.  $^{13}\text{C}$ -NMR Spectra of Reaction Products Formed Between Methyl  $\beta$ -D-xylopyranoside and SaligeninVI  $\text{R}^3=\text{R}^1$ ,  $\text{R}^2=\text{R}^4=\text{H}$ VII  $\text{R}^2=\text{R}^1$ ,  $\text{R}^3=\text{R}^4=\text{H}$ VIII  $\text{R}^4=\text{R}^1$ ,  $\text{R}^2=\text{R}^3=\text{H}$ 

Carbon	Chemical Shift (ppm)		
	Peak I (VI) <sup>1</sup>	Peak II (VIII) <sup>2</sup>	Peak III (VII) <sup>2</sup>
Methyl Xyloside <sup>1</sup>			
1	106.1 (104.6) <sup>3</sup>	106.1	106.0 (103.6)
2	74.8 (73.1) <sup>3</sup>	74.5	74.9 (73.5)
3	77.8 (76.4) <sup>3</sup>	73.4	76.9 (72.6)
4	71.3 (69.5) <sup>3</sup>	71.0	70.1 (71.6)
5	66.9 (65.5) <sup>3</sup>	66.9	64.7 (62.0)
OCH <sub>3</sub>	57.2 (55.9) <sup>3</sup>	57.2	57.1 (56.8)
Saligenin <sup>1</sup>			
1'	156.2 (151.7) <sup>4</sup>	157.1	<sup>5</sup> (5) <sup>5</sup> (156.4)
2'	116.1 (113.1) <sup>4</sup>	116.9	116.5 (117.0)
3'	129.3 (126.2) <sup>4,6</sup>	130.4	130.2 (129.2)
4'	120.5 (118.5) <sup>4</sup>	120.7	120.5 (120.2)
5'	129.4 (126.2) <sup>4,6</sup>	131.0	131.0 (130.1)
6'	128.4 (125.1) <sup>4</sup>	126.0	<sup>5</sup> (5)      126.0 (5)
7'	61.4	86.4	79.2 (7)      83.3 (80.5)

<sup>1</sup>In CD<sub>3</sub>OD.<sup>2</sup>In CD<sub>3</sub>OD (CDCl<sub>3</sub>).<sup>3</sup>Reported: McEwan *et al. Carbohydr. Res.* 1982, 104, 161. In DMSO-d<sub>6</sub>.<sup>4</sup>Calculated.<sup>5</sup>Buried in noise.<sup>6</sup>Assignments may be reversed.<sup>7</sup>Buried under solvent peaks.

Table II.  $^1\text{H-NMR}$  Spectra of Reaction Products Formed Between Methyl  $\beta$ -D-xylopyranoside and Saligenin

Hydrogen	Chemical Shift (ppm) <sup>1</sup>			
	Methyl xyloside	Peak I (VI)	Peak II (VIII)	Peak III (VII)
H-1	4.31 (d) J=5.9 Hz	4.30 (d) J=6.2 Hz	4.26 (d) J=6.2 Hz	4.29 (d) J=6.8 Hz
H-2	3.46 (q) J=5.9,7.2 Hz	3.59 (q) J=6.2,7.7 Hz	3.43 (q) J=6.2,7.8 Hz	3.28 (q) J=6.8,8.2 Hz
H-3	3.60 (t) J=7.2 Hz	3.50 (t) J=7.7 Hz	3.73 (t) J=7.8 Hz	3.58 (t) J=8.2 Hz
H-4	3.75 (m) J=4.3,7.2, 7.8 Hz	3.78 (m) J=4.5,7.7, 8.5 Hz	3.58 (m) J=4.2,7.7, 8.3 Hz	3.68 (m) J=4.6,8.2, 8.9 Hz
H-5 <sub>ax</sub>	3.38 (q) J=7.8,11.9 Hz	3.34 (q) J=8.5,11.7 Hz	3.38 (q) J=8.3,11.8 Hz	3.26 (q) J=8.9,11.6 Hz
H-5 <sub>eq</sub>	4.05 (q) J=4.3,11.9 Hz	4.05 (q) J=4.5,11.7 Hz	4.08 (q) J=4.2,11.8 Hz	4.00 (q) J=4.6,11.6 Hz
OCH <sub>3</sub>	3.52 (s)	3.54 (s)	3.51 (s)	3.55 (s)
H-7' (2H)		4.89 (AB dd) $\delta_A=4.78$ $\delta_B=4.99$ J=10.8 Hz	4.80 (AB dd) $\delta_A=4.76$ $\delta_B=4.83$ J=11.4 Hz	4.84 (AB dd) $\delta_A=4.79$ $\delta_B=4.88$ J=11.0 Hz
Aromatic (4H)		approx. 6.8-7.3	approx. 6.8-7.3	approx. 6.8-7.3

<sup>1</sup>In CDCl<sub>3</sub>.

## Conclusions

Based on these results, it can be concluded that phenol-formaldehyde resins modified with 0.6 to about 1.0-mole of carbohydrate per mole of phenol and cured at neutral conditions can bond wood with acceptable dry- and wet-shear strengths, and wood failures. Also, reducing as well as non-reducing carbohydrates can be used as modifiers for neutral phenol-formaldehyde resins. It was found that the resins formulated under neutral conditions are very light in color and would thus be useful in the preparation of decorative products. Carbohydrate modifiers are incorporated into the resin via ether linkages between the hydroxyls of the carbohydrate and the methylol groups in the resin. Apparently carbohydrates, at least in theory, can participate in a crosslinked network.

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# Chapter 26

## A Glucose, Urea, and Phenol-Based Adhesive for Bonding Wood

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Earlier studies have reported on adhesive development with a carbohydrate/urea/phenol/formaldehyde resin system. Building on those results, this study shows how the adhesive shear strength of bonded wood panels is decreased by using much lower levels of urea in the synthesis. Weight loss studies reveal that urea itself plays a role in dehydrating sugars during heating. Products of resin syntheses and model compound reactions were analyzed by chromatography and  $^{13}\text{C}$ -NMR to clarify the sequence of reactions leading to polymeric resins.

Since the oil shortages of the 1970s, there has been a sustained search for materials to replace the petroleum-based resins used as durable adhesives for exterior wood products. Such alternatives are considered important, because supplies of petrochemicals for use in the wood industry could again become undependable. Ideally, the source of material for an adhesive would be readily available, possibly from materials already found near or used by wood processing plants, for example, agricultural or wood-based renewable resources. The purpose of this investigation was to explore the use of carbohydrates as constituents in water-resistant adhesives.

Phenol-formaldehyde type polymers had been the only exterior-durable adhesives for wood bonding, until the recent limited use of isocyanates. Both systems are petrochemical-based. Several researchers substituted carbohydrates for part of phenolic adhesives (1-4), producing solid, fusible novolak resins. Recently, reaction of carbohydrate acid-degradation products with phenol and formaldehyde has produced liquid resols (5). Gibbons and Wondolowski (6,7) replaced a considerable amount of phenol with carbohydrate and urea to pro-

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duce solid, fusible resins crosslinkable with hexamethylenetetramine. In a subsequent patent (8), a few examples show how to synthesize liquid resol resins and cite initial results showing wood bonds of promising durability. The procedure consists of reacting the carbohydrate with urea or diamines in acidic solution (with or without phenol present), neutralizing, and reacting with formalin. The adhesive is formulated by adding caustic, water, and fillers.

Exploring that system, this investigator (9,10) showed that the carbohydrate, essentially in the reducing monosaccharide form, reacted under acid catalysis only with urea. Any phenol in the mixture does not react until mixed with formaldehyde and heated further. Both hexose and pentose sugars worked in the system, providing bond strengths that were the equal of neat phenolic resins. Durability after 2 hours boiling was essentially equivalent to that of phenolic resins, but wood failure readings were generally much lower for the trial resins. The bonding temperatures for the carbohydrate-containing resins were higher than for the phenolic resins by 10 to 20 °C, depending on the saccharide. Contrary to an earlier hypothesis (6,8), this study found that the reaction between the saccharide and urea showed no signs of proceeding through a furfuryl type structure, but first produced a glycosyl ureide intermediate, which further reacted to form a multitude of products having aliphatic character.

This chapter reports work on two aspects of this adhesive system: 1) tests on the strength of panels bonded with phenol/carbohydrate/urea/formaldehyde (P/C/U/F) adhesive compositions outside the ranges previously reported (9,10) and 2) analysis of chemical reactions in this resin system.

## Experimental Methodology

**Materials.** The following chemicals were used in the syntheses:  $\alpha$ -D-glucose (2%  $\beta$ -anomer); D-xylose (approximately 98%); phenol (reagent grade); urea (mp 132.1-132.8 °C); formaldehyde (37% with 5% methanol); xylitol; cyclohexanol (m.p. 22-23 °C); tetrahydro-2H-pyran-2-ol (tech. grade, bp 115-122 °C/15 mm); 2,4-dimethylphenol (97%); 1,1-dimethylurea; and furfural (99%, analytical reagent). Dehydrated sulfolane (tetramethylene sulfone), a high-boiling (bp 285 °C) polar compound inert to most hot acids and bases, was often added to syntheses as a reference compound for <sup>13</sup>C-NMR and high-performance liquid chromatography (HPLC).

The phenol-formaldehyde resin used as a control adhesive was a commercial resin (control P) characterized previously (9). A second phenolic resin (control C), used once, is reported to have 40.1% nonvolatiles, a viscosity of 0.42 Pa·s, and a specific gravity of 1.180 at 25 °C. Its measured pH was 11. For use, it was mixed with 15% walnut shell flour.

The wood adherends were clear, flat-grained, rotary-peeled yellow birch veneer with moisture content equilibrated at 27 °C and 30% relative humidity (RH). The pieces were 3.2 mm thick and 150 mm by 150 mm in area.



**Experimental Approach.** The first two experiments examined the effects on strength of reducing the adhesive's urea or caustic contents. The rest of the experiments were run to clarify the reactions involved in producing the resin. Among these, two experiments determined weight losses on heating carbohydrates, with or without urea and acid catalyst present. In the final experiments, samples taken from resin and model compound syntheses were examined by HPLC and  $^{13}\text{C}$ -NMR to find what products were formed and in what sequence.

**Shear Strength Tests of Resin-Bonded Panels.** The standard procedures for synthesizing the P/C/U/F types of resins, formulating the resins into final adhesives, and preparing and testing specimens were described previously (9,10). Two experiments that differed from the standard follow.

In the first experiment, resin was made with a P/C/U/F molar ratio of 1:1:0.125:2 to evaluate reducing the amount of urea by half of the previous minimum ( $\text{C/U} = 1:0.25$ )(9). Panels were pressed at 150 and 160 °C for the trial adhesive, and 140 and 150 °C for the control P adhesive.

The other experiment tested the effect on bond strength of reducing the levels of sodium hydroxide and sodium carbonate added during adhesive formulation. This experiment used a resin with P/C/U/F molar ratios of 1:1:0.25:2, which gave good strengths in the past. The resin was divided into four portions to be formulated with different amounts of the alkaline components: the normal level (6.6 wt % sodium hydroxide and 2.2 wt % sodium carbonate, based on liquid resin weight), two-thirds of normal, one-third of normal, and none. In each case, 8 to 10 mL of water was added to bring the viscosity down to desirable levels. For each of the four formulated adhesives, two parallel-laminated veneer panels were bonded at 160 °C. Two phenolic resins, control P and control C, were used as control resins; control panels were bonded at 150 °C.

**Weight-Loss Rate Experiments.** A large amount of condensate is generated during the acid-catalyzed reaction between urea and carbohydrate. The relative molar ratio of urea to carbohydrate had previously been varied between 0.50:1 and 0.25:1 (9,10). The effect of various urea-carbohydrate ratios on the weight loss of carbohydrate at elevated temperature was determined. Two grams of either glucose, xylose, three ratios of glucose and urea mixtures (1:0.5, at two slightly different initial weights; 1:0.25; and 1:0.125), or a xylose and urea mixture (1:0.5) were put into separate weighing bottles, each with 3 mL of water. Each bottle was partially immersed in an ultrasonic bath for 1 minute to hasten dissolution.

For the drying stage of this experiment, the weighing bottles, gathered in light aluminum trays, were put into an oven at 108 °C. At intervals, the samples were retrieved from the oven, cooled in a desiccator, closed, and weighed for residual weight. They were then reopened and put back into the oven for additional drying. The objective was to have them all come to a constant dry weight before the acid-catalyzed reaction process was started. After 18 hours, when the glucose sample finally came to its original dry weight, sulfuric acid (40 meq

per mole carbohydrate) was added to each bottle to begin the acid-catalyzed stage of the process. The bottles were reweighed and put into the oven, now at 120 °C. At intervals, the bottles were reweighed as before. After 30 hours, the weights were constant within 0.01 gram (5 percent), and the experiment was ended. As a reference point for urea weight losses, three 0.5-gram samples of urea were heated at 108 °C for 6 hours after being mixed with one of three levels of sulfuric acid: no acid, 0.66 meq, and 2.13 meq. The two higher acid levels represent about what would be seen above in carbohydrate/urea molar ratios of 1:0.125 and 1:0.5 respectively. Each weighing bottle contained 3 mL of water, including that in the acid.

To determine the importance of the glycosidic hemiacetal group to the dehydration, a polyol analog of a glucose was used. Xylitol contains the same number of hydroxyl groups as glucose but no aldehyde/hemiacetal group. The effects of urea on the weight loss rate of xylitol versus glucose was determined. Bottles of carbohydrate plus acid, carbohydrate plus urea, and carbohydrate plus urea and acid were used, formulated as described in the previous experiment. Molar ratios of carbohydrate to urea were all 1:0.5. Three mL of distilled water was added to dissolve the ingredients where no acid catalyst was used, and appropriately less where the acid would make up the difference in fluid volume. Elapsed heating periods in the 108 °C ovens were 2, 3, 4, 6, 8, 21, and 28 hours.

**Analysis of Reaction Products.** The major reactions in the acid-catalyzed state were found (9) to be those between urea and the carbohydrate. Phenol did not participate as a reactant. To follow the sequence of reaction steps, samples were taken from a glucose/urea/sulfolane mixture (molar ratios of 2:1:1) at various times for analysis by <sup>13</sup>C-NMR spectroscopy and HPLC. Sulfolane acted as the dispersing medium and a reference for concentration changes. Acidic samples were neutralized to prevent further reaction, here and in later experiments (except the last).

To determine whether xylose parallels the behavior of glucose in reacting to form ureides and other products, analyses were done on samples taken from a previous synthesis. That synthesis, using xylose and P/C/U/F molar ratios of 1:1:0.5:2.5, had yielded a strong resin (experiment 16 in references 9,10).

The reaction of formaldehyde with a mixture was investigated by <sup>13</sup>C-NMR analyses of samples taken from a synthesis with P/C/U/F molar ratios of 0.75:1:0.5:2.5. The carbohydrate was glucose.

The stability of the furan ring in the environment of acid-catalyzed mixtures was investigated by an experiment where 1 mole of furfural was added to a mixture containing 0.67 mole 1,1-dimethylurea (DMU), 1.33 moles 2,4-dimethylphenol, and acid catalyst. The hindered urea and phenol were chosen to limit products to simple, small compounds. To limit losses of the somewhat volatile furfural (bp 162 °C) over the 3-hour reaction time, the reaction flask was heated by a steam bath, using vapor temperatures (36 to 69 °C) much lower than in previous experiments.

To test whether urea could condense with a simple secondary alcohol group under acid-catalysis conditions, cyclohexanol, a simple high-boiling (bp 161 °C) alcohol, was substituted for carbohydrate in a reaction flask with urea (1:0.5 mole ratio) and acid. The mixture was heated at 65 to 122 °C for 2.5 hours.

Alternately, the importance of the hemiacetal group can be studied by using a compound that is an analog for a monosaccharide without the rest of the hydroxyl groups. Tetrahydro-2H-pyran-2-ol (THP) is such an analog for xylose. THP was reacted with an equimolar amount of DMU, in the absence of phenol, to follow the course of the hemiacetal-urea reactions. The acid-catalyzed mixture was heated between 81 and 116 °C over a 2-hour period. Samples were frozen to prevent further reaction prior to analysis.

**Analytical Methods.** Samples were analyzed by HPLC using one of two types of column: a Bio-Rad HPX87H<sup>+</sup> (acid) column or a Bio-Rad Micro-Guard cation-H cartridge, with 0.015N phosphoric acid eluant and an UV absorbance detector. The cation-H cartridges were used to get elution of simple urea compounds in less than 15 minutes, compared to over 2 hours on the acids column. Samples were filtered (0.45 micron pores) before injection.

<sup>13</sup>C-NMR spectra were collected on a Bruker WM-250 FT-NMR spectrometer (62.89 MHz) at 30 or 37 °C. Normal spectra were obtained with broad band decoupling. A quantitative <sup>13</sup>C-NMR spectrum was taken using an inverse-gated pulse sequence with a 45° angle, 0.27-s acquisition time, 30-s delay time, 91 scans, and a spectral width of 30 x 10<sup>3</sup> Hz. <sup>1</sup>H-NMR spectra were collected at 250.13 MHz, using a 45° pulse and a 2-second delay. For most samples for which <sup>1</sup>H-NMR spectra were taken, an additional spectrum was run after D<sub>2</sub>O was added to identify exchangeable hydrogen atoms. The chemical shifts for all NMR spectra were measured relative to internal tetramethylsilane. DMSO-d<sub>6</sub> was the solvent.

## Results and Discussion

**Shear Strength Tests of Adhesive Bonded Panels.** Results from previous work (9,10) showed that the most water-resistant bonds were formed when the phenol-to-carbohydrate mole ratio was at least 1:1 and the formaldehyde-to-phenol mole ratio was at least 1:0.5, whereas, the carbohydrate-to-urea mole ratio ranged from 1:0.5 to 1:0.25. From those acid-catalyzed reaction mixtures, it was necessary to drive off at least 2 moles of product water per mole of carbohydrate during resin formation. Six carbohydrates—glucose, fructose, sucrose, xylose, corn syrup, and methyl glucoside—had all performed satisfactorily, indicating that a wide variety of carbohydrate sources would be useable for such adhesives. For comparison with work being presented here, bond strength results on glucose-based adhesives from among those previous experiments are given in Table I.

In the experiment testing a lower urea/carbohydrate molar ratio (0.125:1), the reaction was stopped when distillate stopped being produced, and only half

as much condensate was collected as had been obtained with U/C mole ratios of 0.25:1. The dry bond strengths of trial panels pressed at 150 to 160 °C were equivalent to strengths for the control panels pressed at 140 to 150 °C (Table II). But as post-bonding conditioning became more severe—going to vacuum-pressure soak (VPS) and to 2-hour boil treatments—the strength of the trial panels generally weakened more than that of the controls.

Table I. Shear Strength Properties of Yellow Birch Panels Bonded with Glucose-Based Adhesives

Molar Ratio Reactants P/C/U/F <sup>1</sup>	Condensate		Shear Strength		
	H <sub>2</sub> O/C <sup>2</sup>	Phenol <sup>3</sup>	Dry (MPa)	VPS (MPa)	Wet 2-Hour Boil (MPa)
1.0:1.0:0.5:2.0	3.1	0.12	11.0	6.9	5.3
1.0:1.0:0.5:2.0 <sup>4</sup>	(3.6)	—	8.9	6.9	6.0
1.0:1.0:0.25:3.6	(3.6)	—	12.6	8.3	7.8
0.75:1.0:0.5:2.5	3.0	0.12	11.3	4.0	4.3
0.75:1.0:0.25:1.88	2.5	0.12	7.6	4.5	3.7
0.5:1.0:0.5:2.35	(0.9)	—	3.8	0	0
0.5:1.0:0.25:1.0	(2.8)	—	7.2	2.7	1.9
0.5:1.0:1.0:2.5	(1.4)	—	4.4	0.4	0
0.25:1.0:0.25:0.75	(2.0)	—	0.8	0	—
Phenolic adhesive			12.5	7.1	6.6

<sup>1</sup> Phenol/carbohydrate/urea/formaldehyde.

<sup>2</sup> Moles water/mole carbohydrate; numbers in parenthesis when total condensate collected is considered as only water.

<sup>3</sup> Weight fraction of original phenol recovered.

<sup>4</sup> Phenol added 140 minutes after reaction started.

<sup>5</sup> The standard errors of the mean for the strengths of the 23 control panels were ±0.3 MPa for dry, ±0.2 MPa for VPS/wet, and ±0.2 for 2-hour boil/wet specimens.

SOURCE: Reprinted from ref. 9.

The adhesive resins resulting from formulations with four levels of the caustic catalysts performed well compared to the controls, both in dry tests and the two kinds of wet tests. The dry strength of the trial panels (overall average 11.1 MPa) was 10 percent lower than that of the control panels (Table III). In the wet tests, the trial panels were slightly (insignificant statistically) stronger than the control panels, averaging 6 and 2 percent higher, respectively, for the VPS and 2-hour boil tests. The strengths of the trial panels were, however, more variable in the wet tests.

Table II. Effect of Urea/Carbohydrate Mole Ratio (0.125:1) on Adhesive Shear Strength of Yellow Birch Panels

Resin <sup>1</sup>	Press Temperature (°C)	Average Shear Strength		
		Dry (MPa)	Wet <sup>2</sup> (MPa)	Boil <sup>3</sup> (MPa)
Control P	140	12.4	7.9	6.9
	150	12.7	8.0	7.0
	150	10.4	7.4	6.3
Trial	150	12.7	4.8	3.0
	160	11.1	5.4	4.6
	160	14.1	7.6	7.9

<sup>1</sup> Phenol/carbohydrate/urea/formaldehyde resin with molar ratios of 1:1:0.125:2, 2.09 Pa·s viscosity, bonded between two parallel-laminated yellow birch veneers for 5 minutes.

<sup>2</sup> VPS-conditioned and tested wet.

<sup>3</sup> Boiled 2 hours and tested wet.

**Effect of Urea on Carbohydrate Weight Loss.** Drying uncatalyzed glucose or xylose samples caused essentially no solids weight loss, as expected. But the mixtures of glucose or xylose with various amounts of urea experienced weight losses of from 10 to 23% (Table IV). Apparently, a reaction occurs in the uncatalyzed state once the saccharide and urea are intimately mixed and heated. As the glucose/urea mole ratio changed from 1:0.125 to 1:0.25 to 1:0.5, the weight loss at the end of the drying stage increased from 10 to 17 to 23 percent, suggesting a nonlinear relationship between composition and weight loss. These weight losses are roughly twice the weight of urea in the initial samples. Micro-Kjeldahl analysis of the glucose mixtures with the highest and lowest levels of urea indicated no loss of nitrogen (even through the acid-catalyzed stage).

The actual weight lost goes beyond what would be predicted by loss of the water during formation of diglucosyl urea. For two glucose molecules reacting

with each urea molecule, one would expect a loss of one molecule of water per molecule of glucose. For drying of the higher urea-content mixtures, the actual weight losses correspond to over 2.64 moles of water per mole glucose. It seems the presence of urea hastens the dehydration or other degradation of glucose (and xylose). The mixtures containing urea were reddish-brown at this stage, compared to white for glucose and a yellowish-white for xylose.

Table III. Effect of Catalyst Reductions on Adhesive Shear Strength of Yellow Birch Panels

Resin	Catalyst level		DSS <sup>2</sup>		WSS <sup>3</sup>		BSS <sup>4</sup>	
	% of Normal <sup>1</sup>	pH	Ave (MPa)	Min (MPa)	Ave (MPa)	Min (MPa)	Ave (MPa)	Min (MPa)
Trial <sup>5</sup>	100	11.0	12.0	9.2	7.8	6.7	7.5	6.5
	67	10.3	11.0	9.2	7.7	5.9	7.2	4.2
	33	9.7	11.7	9.4	7.6	4.2	6.8	3.6
	0	8.2	9.7	8.7	8.4	5.8	6.3	4.7
Control C			12.7	11.0	7.6	6.9	7.3	5.9
Control P			11.9	10.5	7.2	4.9	6.3	5.4

<sup>1</sup>Normal levels are 6.6% sodium hydroxide and 2.2% sodium carbonate.

<sup>2</sup>Average (Ave) and minimum (Min) dry shear strength (DSS).

<sup>3</sup>Average (Ave) and minimum (Min) wet shear strength (WSS). VPS-conditioned and tested wet.

<sup>4</sup>Average (Ave) and minimum (Min) boil shear strength (BSS). 2-hour boil conditioned and tested wet.

<sup>5</sup>Phenol/carbohydrate/urea/formaldehyde molar ratios = 1:1:0.25:2.

Then, during the acid-catalyzed reaction, the weight equivalent of another 0.75 moles of water per mole of glucose was lost. After this stage, all samples were dark brown. Feather and Harris (11) describe a number of intra- and intermolecular dehydration mechanisms for carbohydrates in acidic solution. In that study, some of those mechanisms were aided by the presence of amines.

Because of large weight losses, samples containing glucose/urea mole ratios of 1:0.5 and 1:0.125 were analyzed for residual nitrogen content to see if nitrogen compounds were lost disproportionately fast. The solids were found to contain 8.84% and 2.35% nitrogen, respectively, versus 6.67% and 1.84% calculated for the initial uncatalyzed samples. Based on knowledge of 1) the weights of nonaqueous ingredients in the original mixtures, 2) the molecular weights of these, 3) the final weights of the products in the bottles, and 4) final nitrogen content of these products, and the assumptions that 1) the nonaqueous acid

was all retained and 2) the ureide NCON units remain as a unit, the amount of the original hydroxyl content of the initial glucose that could have been lost (assuming no carbon-containing glucose products were lost) could be calculated. For the G/U = 1:0.125 mixture, 40% of the hydroxyl weight could have been lost, and for the G/U = 1:0.5 mixture, 82% of the hydroxyl weight could have been lost. Of all the weight lost from the G/U = 1:0.5 mixture, 78% was lost during the nonacidic drying step. Theoretically, for the G/U = 1:0.5 mixture, if only diglucosyl urea were formed, 20% of the glucose hydroxyl weight would be lost. From these considerations and the observation of significant coloring in the carbohydrate-urea products, it seems that reactions other than simple condensation must have occurred.

Table IV. Effect of Urea on Carbohydrate Weight Loss

Carbohydrate →	Glucose					Xylose	
C/U <sup>1</sup> →	1:0.5	1:0.5	1:0.25	1:0.125	1:0	1:0.5	1:0
Urea (Weight %) →	14.3	14.3	7.7	4.0	0	16.7	0

Percentage Solids Weight Change<sup>2</sup>

EDS <sup>3</sup>	-22.7	-22.3	-16.7	-10.0	0.4	-23.1	-1.0
EACS <sup>4</sup>	-28.2	-27.9	-27.5	-24.7	-17.0	-28.0	-20.9

Moles Water/Mole Carbohydrate

EDS <sup>3</sup>	2.7	2.6	1.8	1.0	1.0	2.3	0.1
EACS <sup>4</sup>	3.3	3.3	3.0	2.6	1.7	2.8	1.7

<sup>1</sup>Mole ratio of carbohydrate/urea.

<sup>2</sup> Starting with solutions containing approximately 2.00 g carbohydrate, proportionate urea, and 3 mL distilled water.

<sup>3</sup>At the end of the drying stage (18 hours at 100 to 106 °C).

<sup>4</sup>At the end of the acid-catalyst stage. 0.09 mL of 5N sulfuric acid added at beginning; this stage took 30 hours at 120 °C.

Urea affects weight loss of glucose differently than it affects xylitol, a polyhydroxy compound without a hemiacetal functional group. For glucose-based samples, acid-catalyzed glucose with urea lost more weight than did acid-catalyzed glucose without urea until 22 hours of heating had passed (Figure 1). Surprisingly, uncatalyzed glucose with urea lost more weight than either of those two samples, between 4 hours and at least 28 hours. By micro-Kjeldahl analysis of the uncatalyzed glucose-urea products, 13% of the original nitrogen was determined to have been lost during the 28 hours. If this was lost only as gaseous

urea decomposition products, then 25% of the original glucose was also lost, presumably as water (2.5 moles of water per mole of glucose). For the catalyzed glucose without urea, 23% was lost during dehydration (2.3 moles of water per mole of glucose).

For reference, a sample of uncatalyzed urea solution heated at 108 °C lost 1.2% of its weight in 3 hours and 3.2% in 6 hours. The less acidified urea solution (simulating conditions for G/U = 8:1) lost 6.2% in 2 hours and 13.8% in 6 hours. The highly acidified urea solution (as in G/U = 2:1) lost 6.7% in 2 hours and, surprisingly, only 10.3% in 6 hours. All retained their original white color. A separate 2-gram sample of dry urea solids heated in a 110 °C oven showed 1% weight loss in the first 1.5 hours and 7.1% weight loss after 17 hours. Thus, without acid catalysis, urea weight loss was slow at these temperatures, and the rate increased by a factor of about 4 to 5 with addition of acid.

The xylitol-based samples exhibited a much different behavior (Figure 2). The acid-catalyzed xylitol lost weight much faster initially than did glucose, though it seemed to level out with less total weight loss (18%, or 1.5 of moles of water per mole of xylose). The mixture of uncatalyzed xylitol and urea showed a much slower rate of weight loss and had a different type of behavior, namely, linear with time. Here, the 72% nitrogen weight loss calculated from a nitrogen analysis, if considered as urea weight loss by decomposition, accounts for the total sample weight loss. Adding acid catalyst to the xylitol-urea mixture produced behavior similar to that of the uncatalyzed mixture, but slowed the loss of weight.

Thus, for glucose, the acid seems to slow down the more severe urea-linked degradation in the long early stage, whereas, for xylitol, urea stops the severe acid-catalyzed degradation in this period.

**NMR Analyses of Reaction Products.** Interpretation of mixtures of materials by  $^{13}\text{C}$ -NMR is complicated, and such interpretation was attempted only when the spectra were fairly simple or when known species could be picked out readily.

The progression of carbohydrate and urea products from a reaction conducted in sulfolane was followed by HPLC and  $^{13}\text{C}$ -NMR (10). Some of the glucose converted to fructose, as expected, but both declined as other reaction products formed. The early predominant products were glucosyl ureides, confirmed earlier (10) by comparison with synthesized glucosyl ureides analyzed by HPLC and  $^{13}\text{C}$ -NMR. The glucosyl ureides subsequently decreased as a few other simple species (unidentified at present) and polymeric species increased. This same sequence of products was noted in other resin syntheses, whether or not the unreacting phenol was present. For example, the progression of the xylose-urea reaction mixture also showed this behavior, and a species believed to be a xylosyl ureide was observed. The  $^{13}\text{C}$ -NMR signals for the glucosyl and assumed xylosyl ureide species are given in Table V, along with the values obtained for urea, glucose, and xylose monomers. The values for these last two compounds agree well with literature values (12). The shifts for the xylosyl



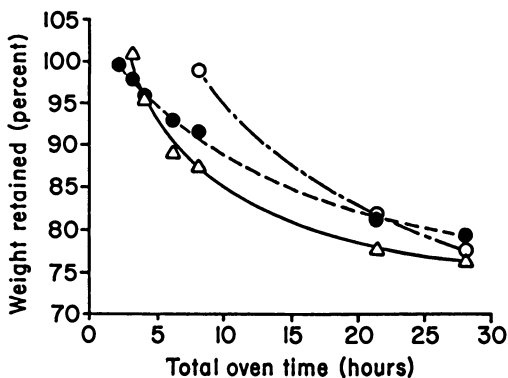


Figure 1. Weight loss from glucose and glucose-urea (2:1) mixtures at 110 °C: acid-catalyzed glucose — - ; uncatalyzed glucose-urea — ; and acid-catalyzed glucose-urea - - - -.

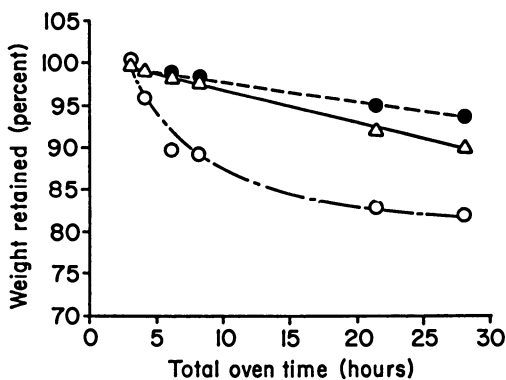


Figure 2. Weight loss from xylitol and xylitol-urea (2:1) mixtures at 110 °C: acid-catalyzed xylitol — - ; uncatalyzed xylitol-urea — ; and acid-catalyzed xylitol-urea - - - -.

ureide C-1 and C-2 carbons are in line with substitution of hydroxyl groups with an amide linkage, and the other three signals are close to the original  $\beta$ -xylopyranose values. The HPX87H<sup>+</sup> column chromatograms for the first sample from this synthesis (taken just after acid was added to the reaction mixture) showed retention times for xylose at 11.1 min, phenol at 53 min, and urea at 180 min. At this point, a compound eluting at 14.7 min, assumed to be monoxylureide based on its early appearance and its elution time relative to xylose, gave the third largest peak, and a compound eluting at 8.9 min, similarly assumed to be dixylureide, was fifth largest. After 30 min of reaction, the supposed monoxylureide peak was not visible, whereas, the supposed dixylureide peak persisted to become the strongest peak after reaction of formaldehyde with the system. Thus, the compound identified as a 30-minute reaction product by <sup>13</sup>C-NMR is probably the dixylureide.

Table V. <sup>13</sup>C-NMR of Three Carbohydrate-Urea Products and Their Precursors (ppm<sup>1</sup>)

Carbon Position	Urea <sup>2</sup>	Glucose <sup>2</sup>		Glucosyl Ureide <sup>3</sup>		Xylose <sup>2</sup>		Xylosyl Ureide <sup>4</sup>
		$\alpha$ -pyr	$\beta$ -pyr	mono-	di-	$\alpha$ -pyr	$\beta$ -pyr	
C=0	160.1			158.2	156.3			156.7
C-1		92.2	96.8	81.3	80.8	92.5	97.7	81.8
C-2		72.4	74.8	72.9	72.9	72.4	74.8	72.7
C-3		73.1	76.7	77.7	77.7	73.3	76.7	77.4
C-4		70.6	70.4	70.3	70.3	70.2	69.9	69.8
C-5		71.9	76.6	77.6	77.6	61.7	65.7	62.6
C-6		61.3	61.2	61.2	61.2			

<sup>1</sup>Relative to internal TMS, in DMSO-d<sub>6</sub> solvent.

<sup>2</sup>Commercially obtained material.  $\alpha$ -pyr =  $\alpha$ -pyranose,  $\beta$ -pyr =  $\beta$ -pyranose.

<sup>3</sup>Compounds synthesized previously (10).

<sup>4</sup>Assumed identity of material in a resin mixture; possibly the dixylureide.

The phenol/glucose/urea resin, to which formaldehyde was later to be added, showed the usual sequence of products formation, but by the end of the acidic reaction stage, there were no distinct glucose or glucosyl ureide species identifiable by <sup>13</sup>C-NMR or HPLC. After neutralization and addition of formalin, signals for formalin immediately showed in the 49 to 55 ppm (methoxy) and 82 to 90 ppm (hemiformal and hemiacetal) regions of the spectrum. After the end of an hour of reaction with formaldehyde, the <sup>13</sup>C-NMR spectrum of the reaction mixture showed that the signals due to phenolic species had reduced in size relative to the sulfolane internal reference, but their number had multiplied

greatly, indicating that many phenol-formaldehyde species had been created. Some distinct peaks appeared in the 58 to 70 ppm region, where one expects to find signals for hydroxymethyl groups attached to phenol, 58 to 65 ppm (13,14), and to urea, 64 to 72 ppm (13,15). The xylose-based resin showed the same effect on its spectrum because of formaldehyde addition.

**Stability of the Furan Ring.** In the experiment to determine the stability of furan rings in the presence of acid, urea, and phenolic species, incremental additions of furfural to an initial DMU and DMP mixture resulted in progressively more intense signals at 106.8 and 110.3 ppm in the  $^{13}\text{C}$ -NMR spectrum. These are not the 122.3 and 112.8 ppm signals for the C-3 and C-4 positions in furfural, whose signals were present at very low levels for much of the time. However, those former signals are in a region consistent with C-3 and C-4 carbons of a furyl species attached to an alkyl carbon (16,17). Acting as an aldehyde, furfural could lose its aldehydic oxygen and combine with two aromatic rings, creating a tertiary alkyl carbon in the process. Perhaps a tertiary alkyl carbon is the source of an increasingly intense signal at 48.6 ppm, an appropriate value by our calculations. Several other signals increased with each addition of furfural and may be related to other furyl carbon species. Signals that appeared to change during the addition of both furfural and formaldehyde were predominantly near those for the original phenolic ring and its methyl substituent carbons.

**Reactions of Urea with Model Compounds.** Urea did not noticeably react with the simple secondary alcohol of cyclohexanol during 2.5 hours of heating. The major components remaining in the flask were found to be cyclohexanol, urea, and a compound whose  $^{13}\text{C}$ -NMR spectral lines seem to correspond to dicyclohexyl ether. Ethers are often dehydration products of alcohols. The condensate contained cyclohexanol and cyclohexanone, the latter apparently an impurity in the cyclohexanol. The signal for urea decreased with time, and two small, slightly lower frequency signals (154 to 156.5 ppm) that appeared may be due to urea degradation products, such as biuret. If any cyclohexylurea was formed, it was present at very low levels. This leaves the mechanism of substantial weight loss for non-acid-catalyzed urea-saccharide mixtures a mystery.

THP, a simple cyclic hemiacetal, was reacted with DMU in the final synthesis. Even though a liquid chromatogram of THP showed one peak, the signals in a quantitative  $^{13}\text{C}$ -NMR spectrum appeared to group into three species, based on the relative intensities (Table VI). The three assumed THP species appear to be close variations of the tetrahydropyran ring form. The assignments of signals follow the trends of values given by Ji et al. (18) for one species of this same compound and by rough, calculated values based on the spectral simulation approach of Cheng (19). THP and sulfolane eluted together from the cation-H cartridge 0.75 minutes after injection, while the DMU retention time varied from 12.5 to 13.0 minutes.

A sample was taken from the acid-catalyzed reaction of THP with DMU after 30 minutes. The  $^{13}\text{C}$ -NMR spectrum of this sample showed depletion

of the most abundant THP species, relative to the second, and formation of a major product. From the major product's  $^{13}\text{C}$ -NMR signals (Table VI), it appears to be 1,1-dimethyl-3-(2-tetrahydropyranosyl)urea, (DMTHPU). In a liquid chromatogram of this sample, only one new peak was evident, at 1.91 minutes elution time.

For a sample taken after 80 minutes, a  $^{13}\text{C}$ -NMR spectrum showed little DMTHPU left, but the second THP species was still evident. Many new signals appeared in the 18 to 35 ppm and 59 to 70 ppm regions. New signals also appeared at 136.4 and 146.1 ppm, which could be produced by aromatic C=C and C=N bonds or alkene carbons, for the 136.4 ppm value. A liquid chromatogram for the (filtered) sample also showed little DMTHPU, but no other new distinct peaks.

Table VI.  $^{13}\text{C}$ -NMR Chemical Shift Values for THP<sup>1</sup> and Proposed Derivatives

Designation:	Species of THP				Proposed Derivatives	
	Present Work		Reported (18)		DMTHPU <sup>2</sup>	DMTHPA <sup>3</sup>
Rel. Area <sup>4</sup> :	1	2	3			
	4.0	1.9	0.7			
Ring						
Carbon No. <sup>5</sup>						
2	93.5	93.3	97.3	92.99	79.7	93.4
3	32.4	30.3	30.6	29.62	30.6	29.7
4	20.4	19.2	19.2	18.42	23.0	23.6
5	25.3	25.1	25.1	24.52	25.0	26.0
6	62.6	61.7	62.1	61.19	66.1	66.6
					CH <sub>3</sub>	35.8
					C=O	157.1

<sup>1</sup>Tetrahydro-2H-pyran-2-ol; commercial material with only one HPLC peak.

<sup>2</sup>1,1-Dimethyl-3-(2-tetrahydropyranyl)urea, in a product mixture.

<sup>3</sup>Dimethyl-(2-tetrahydropyranyl)amine, in the lighter phase of the distillate.

<sup>4</sup>Relative area by quantitative  $^{13}\text{C}$ -NMR integration.

<sup>5</sup>Relative to ring oxygen numbered 1.

A  $^{13}\text{C}$ -NMR spectrum of the final product showed the addition of a number of distinct peaks in the 129 to 152 ppm unsaturated carbon region. An  $^1\text{H}$ -NMR spectrum of the sample showed nonexchangeable hydrogen signals in the 7.3 to 8.7 ppm region (about 4% of the total integrated hydrogen signal), which are most likely associated with heteroaromatic ring hydrogens. There were also some nonexchangeable hydrogen signals in the 4.5 to 4.8 region, which could be associated with a nonconjugated alkene CH<sub>2</sub> group.

A sample of the upper phase of condensate distilled from the reaction mixture gave a comparatively simple  $^{13}\text{C}$ -NMR spectrum. This spectrum's signals indicated the presence of three species: the second species of THP, a small amount of the third THP species, and a new compound. Calculations [according to the approach used by Cheng (19)] indicate that the new compound, whose signals are given in Table VI, could be dimethyl-(2-tetrahydropyranosyl)amine. This would indicate a dimethylamine group split off from the dimethylurea, as ammonia can split off from amides reacting with alcohols at elevated temperatures under acid conditions (20). The lower phase of the liquid condensate had a  $^{13}\text{C}$ -NMR spectrum, which indicated that it might contain at least two unidentified compounds, including urea-type carbonyl groups, dimethylamino groups, and pyran ring groups.

The work presented thus far represents the reactions occurring mainly in the acid-catalyzed stage of the synthesis. The urea and saccharide first form glycosyl ureides, which decompose. Subsequent products are not identified, but seem to be numerous. Although these later products are mostly aliphatic, there are indications of possible minor amounts of heteroaromatic structures. In this respect, this system is somewhat similar to products from Maillard reactions of reducing saccharides and amino acids (21,22) and in melanoidins and organic soil (23). Most work on Maillard products has been done at near neutral or alkaline pH values. However, Samuely (24) heated glucose with acids in the presence of varying amounts of urea and other nitrogenous compounds and found melanoidins. A review of model reactions for amine compounds and reducing sugars (25) notes that a wide variety of reactions may occur, depending on the temperature, pH, specific reactants, and the presence of water. The review article further notes that in the nearly dry state, the sugar-amine condensation and Amadori rearrangement are the key reactions leading to brown nitrogenous polymers by a variety of pathways. A difficulty common to these studies has been the wide variety of products formed.

One unanswered question is whether the saccharide-urea products actually react with phenol through the intermediary of hydroxymethyl groups that are added to both phenol and urea during the neutral reaction stage. Tomita and Matsuzaki (26) have shown that hydroxymethylphenols can condense with urea at a pH range of 4.8 to 10.0, a key sign being a  $^{13}\text{C}$ -NMR signal at 44.2 ppm. They note that phenol self-condensation can be suppressed by excess urea at the acidic end, but not at the neutral and basic conditions that occur in the formaldehyde reaction stages in the present study's syntheses. Alternately, there are indications that polyols can react to a limited extent with phenols under alkaline conditions to form ether links (27). If such reactions do not frequently occur, the durable adhesive may be the result of an interpenetrating network of the urea-saccharide and phenol-formaldehyde polymers. The need for as many moles of phenol as monosaccharide and the need for at least 2 moles of formaldehyde per mole of phenol to achieve the best properties (10) point to

this as a distinct possibility. Lower molecular weight phenolic resin molecules may be needed for penetration of the wood to give good longterm durability.

## Conclusions

In experiments with bonded wood panels, a urea/carbohydrate mole ratio of 0.125:1 in a carbohydrate/urea/phenol/formaldehyde resin gave slightly lower strengths than previous resins that had urea levels at least twice as high. Drastically reducing the amounts of sodium hydroxide and sodium carbonate added during adhesive formulation produced wider strength variability than for control resins, but did not reduce average wet shear strengths of bonded panels.

Experiments on reaction mechanisms showed that urea enhanced the dehydration (weight loss) reactions of monosaccharides in nonacidic environments. Addition of acid to a glucose-urea mixture slowed its dehydration at 108 °C. The addition of sufficient urea to an acid-catalyzed polyol solution appears to prevent, or at least delay considerably, the normal acid dehydration reaction of the polyol.

The first step in the acid-catalyzed resin formation is production of glycosidic mono- and diureides, but subsequent products are numerous and still unidentified.

Furan rings, if formed in the syntheses, can survive under the acidic conditions of the initial reaction stage with urea and phenol compounds.

Tetrahydro-2H-pyran-2-ol, a model for the xylose ring hemiacetal without other hydroxyl groups, reacted with a monofunctional urea to produce the expected ureide. Continued reaction resulted, as for normal saccharides, in a multitude of products, predominantly aliphatic, in much lower concentration.

Urea did not react with cyclohexanol (a simple secondary alcohol) under acid catalysis to produce a product containing urea fragments.

In summary, the strength of wood panels tested here did not hold up when the urea/carbohydrate molar ratio was lowered to 0.125:1, but did not suffer drastically when the caustic components of the adhesive were reduced by a third. Glycosyl ureides were the only intermediates identified in the sequence of reactions leading from monosaccharide to polymer, because of the quickly-escalating multiplicity of products.

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# Chapter 27

## Fast-Curing Carbohydrate-Based Adhesives

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A new carbohydrate-phenolic-based resin was synthesized by grafting resorcinol on a known glucose-urea-phenol-based resol. The new resin was formulated into fast-curing adhesives that were used to glue high-moisture-content veneers under hot-pressing conditions and glulam under cold-setting conditions. While generally favorable gluing results were achieved, microscopic analyses of gluelines made with veneers having 18% and higher moisture content indicate problems with tracheid compression. Structural elucidation of the new resin and its precursors is in progress. N-glucosylurea and N,N'-diglucosylurea have been identified among the first formed reaction products in the synthesis of these resins.

Carbohydrate-phenolic-based resins have shown promise for partial replacement of phenol and formaldehyde in exterior plywood adhesives (1,2). Such resins are produced in a two-stage reaction sequence. First, the carbohydrate is reacted with phenol, and sometimes urea, under acid catalysis at elevated temperatures (up to 150 °C), to produce an acid-stage resin. The acid-stage resin is then made basic, formaldehyde added, and the reaction continued at lower temperatures to produce a resol-type resin. Adhesives formulated from these resins have curing speeds consistent with present-day plywood production needs; in the western United States, veneers are typically dried to 0 to 7% moisture content and the adhesive cured by hot pressing the panels at approximately 140 to 150 °C and 1.2 MPa.

Future wood composites will likely require the gluing of low-quality wood with higher moisture content. Faster curing rates (compared to phenol-formaldehyde resins) will also likely be desirable in new adhesives. Employment of faster curing adhesives to shorten press time, lower press temperature, and glue



high-moisture-content wood translates into savings in time, energy, and cost. Even today, the desire to glue high moisture content veneers in the American plywood industry has come about from efforts to reduce time and energy spent in drying veneer. If veneers of 15 to 20% moisture content could be used instead of the usual 0 to 7%, then substantial savings could be realized. However, at such moisture contents, present traditional hot-pressing, phenol-formaldehyde adhesives fail because of panel blows, overpenetration, and other problems.

The potential for modification of carbohydrate-phenolic-based resins into a fast-curing adhesive resin has recently been demonstrated by Clark et al. (3). Resorcinol was grafted onto a known glucose-urea-phenol-based resol (1) to produce a new resin (CPR) with the properties shown in Table I. Originally, this resin was synthesized using resorcinol as a model to establish reaction conditions for later research, which is aiming at grafting condensed tannin derivatives onto the carbohydrate-based resin system. However, the CPR resin is effective as an adhesive itself. Furthermore, its phenol and resorcinol contents are somewhat less than the current commercial phenol-resorcinol-formaldehyde (PRF) laminating resins that contain around 35% phenol and about 16 to 20% resorcinol.

Table I. CPR Resin Properties

Percent phenol <sup>1</sup>	14.3
Percent resorcinol <sup>1</sup>	12.6
Molar ratio of reactants G/P/U/F/R <sup>2</sup>	1:1:0.5:2:0.8
Percent solids <sup>1</sup>	60
Viscosity (cP) <sup>3</sup>	1,950
pH <sup>3</sup>	8.1

<sup>1</sup> Percent of total resin weight.

<sup>2</sup> Glucose/phenol/urea/formaldehyde/resorcinol.

<sup>3</sup> Room temperature.

## Experimental Methodology

Resin synthesis, adhesive formulation, and evaluation techniques are described by Clark et al. (3,4). Plywood shear specimens were prepared according to U.S. Product Standard PS 1-83 for exterior plywood (5). Glulam shear specimens were tested according to the American Institute of Timber Construction (AITC) standards AITC-T107 and AITC-T110 for dry shear and vacuum-pressure soak (6). Glulam test specimens were also subjected to a 2-hour boil treatment (not an AITC test) prior to shear (7,8). <sup>13</sup>C-NMR spectra were recorded at 100.6 MHz on a Bruker AM-400 NMR spectrometer. Gel permeation chromatography

was carried out on a Waters model 6000A liquid chromatograph equipped with a model R401 differential refractometer and a model 440 ultraviolet detector operating at 254 nm. A series of Microstyrigel columns (100 Å, 500 Å, 10<sup>3</sup> Å, and 10<sup>4</sup> Å) were eluted with tetrahydrofuran at 2 mL/min. The system was calibrated with polystyrene standards, and molecular weight calculations were carried out on a Spectra Physics model SP 4200 computing integrator equipped with a GPC + PROM program. Vapor phase osmometry (VPO) of the CPR resin peracetate was done at Galbraith Laboratories, Knoxville, TN. Authentic N-glucosylurea (I) was synthesized by Hynd's procedure (9).

## Results and Discussion

Adhesives made from the CPR resin were tested for their ability to bond high-moisture-content veneers under hot-pressing conditions as well as to bond glulam under cold-setting conditions (3,4). Adhesive formulation typically involved adjustment of the resin to pH 9.5 to 10 with 50% sodium hydroxide and addition of a hardener consisting of walnut shell flour, paraformaldehyde, and a small amount of 50% aqueous formaldehyde (3). Preliminary studies with these adhesives indicated veneers up to 22% moisture content could be bonded to make two-ply laminates, provided that the adhesive viscosity was at least 12,000 cP and adhesive gel times were under 1 hour at room temperature. More detailed studies using 18%-moisture-content veneers (1/10-in rotary-peeled Douglas-fir) were carried out to make three-ply gluebond specimens. The three-ply specimens were prepared using an average glue spread of 61 pounds per 1,000 square feet of double guelinel and pressed at 127 °C and 175 psi for 8 minutes.

Average wood failure values of 85% or better were obtained for gluebond specimens that were either sheared dry or obtained following a vacuum-pressure soak treatment. Specimens sheared after 8 hours of boiling (two 4-hour cycles) gave only 75% average wood failure. The reason for the low wood failure values for boiled specimens is not entirely clear at present. An average of 85% wood failure is required of these shear tests for commercial exterior plywood (5). For a control test and comparison of the effectiveness of the CPR adhesives for bonding high-moisture-content veneers, a commercial phenol-formaldehyde plywood adhesive was tested on 18% MC veneers under the same conditions. The commercial plywood adhesive completely failed to bond the high MC veneers (i.e., there was 0% wood failure in all test specimens) (3).

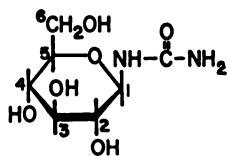
Microscopic examination of guelinelines in plywood specimens made using the CPR adhesive and 18% MC veneers showed severe tracheid compression in the earlywood zones of growth rings (4). This observation indicates that 175 psi is an excessive pressure for such high-moisture-content veneers. Loss in panel thickness due to wood compression during hot pressing is of concern in present commercial plywood production and is addressed by the use of step-pressing

techniques (10,11). In the case of panels made from high-moisture-content veneers, much lower pressing pressures will also have to be investigated.

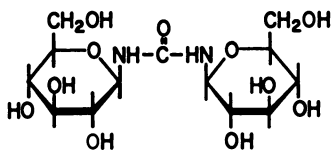
To test the cold-setting ability of the CPR adhesives, glulam specimens were prepared using vertically planed Douglas-fir boards with an initial moisture content of 11% (9). Adhesive was applied at an average rate of 70.5 pounds per 1,000 square feet of single glueline, and the specimens pressed at room temperature and 150 psi for 24 hours. Wood failure values above 90% were obtained for dry, vacuum-pressure soak, and 2-hour boil-treated shear specimens. The American Institute of Timber Construction Standards requires a minimum of 70% wood failure for dry shear (AITC T107); and in addition, the adhesive has to pass a six-ply end delamination test (AITC T110) (6). The 2-hour boiling test is increasingly done to test new laminating adhesives (7,8).

Little is known about the molecular structure of the carbohydrate-urea-phenolic-based resins, and their formation appears complex. Molecular weight distributions obtained for the peracetylated CPR resin by gel permeation chromatography (GPC) differ depending on the detection method. Figure 1 compares detection by refractive index (RI) to detection by UV (254 nm). Three distinct components seem to be formed in the CPR resin as indicated by the RI curve. However, only one component of the resin is detected by UV absorption, indicating incorporation of phenol and resorcinol into that resin component. Vapor phase osmometry (VPO) of the peracetylated CPR resin gave  $M_n$  of 1,121, which is in close agreement with the GPC results using RI detection.

Although one might have expected furans to be involved in polymer formation because of the well-known degradation of glucose under acid conditions to produce 5-hydroxymethylfurfural (12), Christensen and Gillespie (2) and Clark et al. (3) have noted the absence of furan resonances in the  $^{13}\text{C}$ -NMR spectra of these resins. Moreover, the  $^{13}\text{C}$ -NMR spectra of the peracetylated CPR resin, its precursor acid stage resin, and resol stage resin all show strong resonances in the 60 to 80 ppm region, suggesting the formation of glucosylurea derivatives (4). In particular, the C-1 or anomeric carbon resonance, which occurs at 97 ppm in  $\beta$ -D-glucose (13), is shifted upfield to about 80 ppm in the resins (Figure 2) and 82 ppm in an authentic sample of N-glucosylurea (I). The resonances occurring between 60 and 75 ppm are very close to the chemical shifts for the C-2 to C-6 carbons of  $\beta$ -D-glucose and N-glucosylurea (I).



I



II

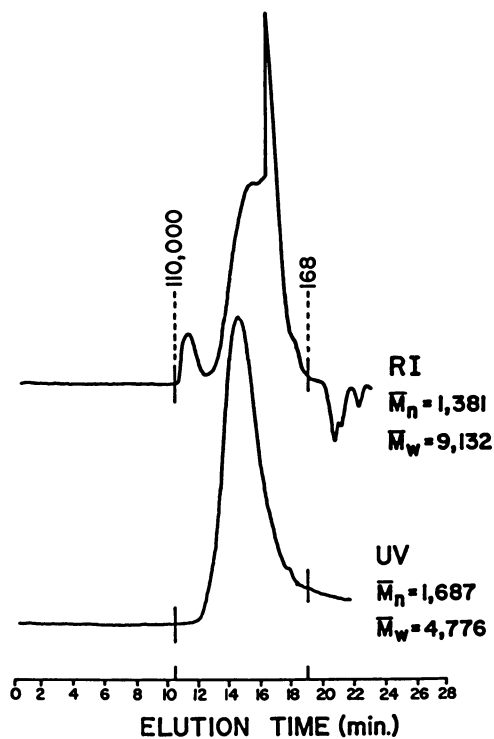


Figure 1. Molecular weight distributions of paracetylated CPR resin by GPC.

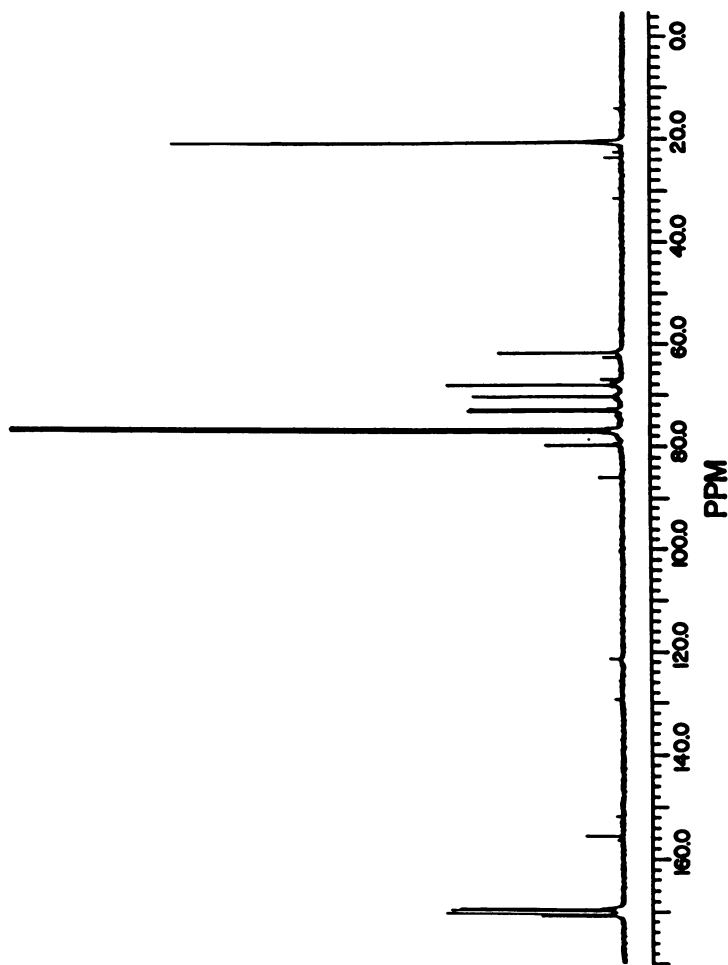


Figure 2.  $^{13}\text{C}$ -NMR spectrum (in  $\text{CDCl}_3$ ) of peracetylated glucose-urea-phenol-based acid stage resin.

More recently, Karchesy et al. (Oregon State University, unpublished data) have identified both N-glucosylurea (I) and N,N'-diglucosylurea (II) in the glucose-urea-phenol-based acid stage resin. Other highly colored, water-soluble reaction products are also formed. The identification of these colored reaction products as well as the determination of the role of the glucosylureas in CPR resin formation are currently under investigation.

Benn and Jones have shown glucosylureas to be very stable in aqueous solutions up to pH 11 where degradation becomes significant (14). Their observation correlates well with our observation that CPR-based adhesives are completely waterproof when cured with formulation pH's between 7.8 and 10.8 (9), but were not waterproof when formulated above pH 11. However, the stability of glucosylureas below pH 11 (and into the acidic range) is unusual when compared to other glucosylamine compounds. This may be due to the low basicity of the nitrogen group at C-1, which is  $\alpha$  to the urea carbonyl. For instance, both glucosylurea and N-acetyl-D-glucosylamine do not undergo many of the usual degradation reactions of hexoses substituted with amines at C-1 (14,15). When glucose is reacted with methylamine under only slightly acidic conditions, a vast array of reaction products including furans and pyrroles is produced (16). The low basicity of glucosylurea nitrogens should not be confused with their nucleophilicity, which depends more on polarizability (17). The glucosylurea nitrogens are quite capable of entering into polymerization and crosslinking reactions with methylol or similar functional groups. On a more speculative note, the hydroxyl groups of the glucosyl moiety may also be entering into condensation reactions with phenolic methylol groups in the second base-catalyzed reaction stage of resin synthesis. Conner et al. (18) have recently shown evidence that hydroxyl groups of sugars and other polyols are bonding via an ether linkage (to at least a limited extent) in carbohydrate extended or modified phenol-formaldehyde-based resols.

## Conclusions

Carbohydrate-phenolic-based resins can be modified to change their physical and chemical properties, and faster curing adhesives can be made from these modified resins. However, the nature of the research presented here is exploratory, and much remains to be done. In particular, the molecular structure of these resins needs to be defined.

## Acknowledgments

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# Chapter 28

## Thermosetting Adhesive Resins from Whey and Whey Byproducts

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The disposal of whey and whey byproducts derived from the cheese industry represents a serious economic and environmental problem due to the high biological oxygen demand of lactose—the major constituent of whey solids. Maillard and caramelization reactions associated with the thermal degradation and polymerization of the milk sugar can be exploited to convert lactose in whey to a thermosetting resin that can serve as an adhesive for binding solid lignocellulosic materials. The resin synthesis may be accomplished in one step using a batch reaction (Phase I) or prepared more readily using a continuous plugflow reaction with a two-step synthesis (Phase II). Resins have been shown to perform well as adhesives for sawdust and/or rice hull reinforced boards. Preliminary thermal studies indicate an exothermic polymerization occurring at around 200 °C for the Phase I resin preparation.

A waste disposal problem of significant proportions exists because of the 23 billion pounds of excess whey produced in the United States each year as a byproduct of the cheese industry (1). The nutritious proteins present in whey may be separated by ultrafiltration, resulting in large volumes of ultrafiltrate or “permeate,” consisting of 5% lactose and traces of inorganic salts. This permeate stream is essentially useless and exacerbates the disposal problem due to its high biological oxygen demand (25,000 mg/L) mainly owing to lactose. In addition, salt whey (resulting from pressing cheese curd after salting) represents a particularly difficult disposal problem due to the added presence of sodium chloride. The generation of excess whey permeate in the United States is depicted in Figure 1. Typical composition of wheys and permeates is shown in Table I. Table II shows the amount of total whey solids available for use throughout the world.



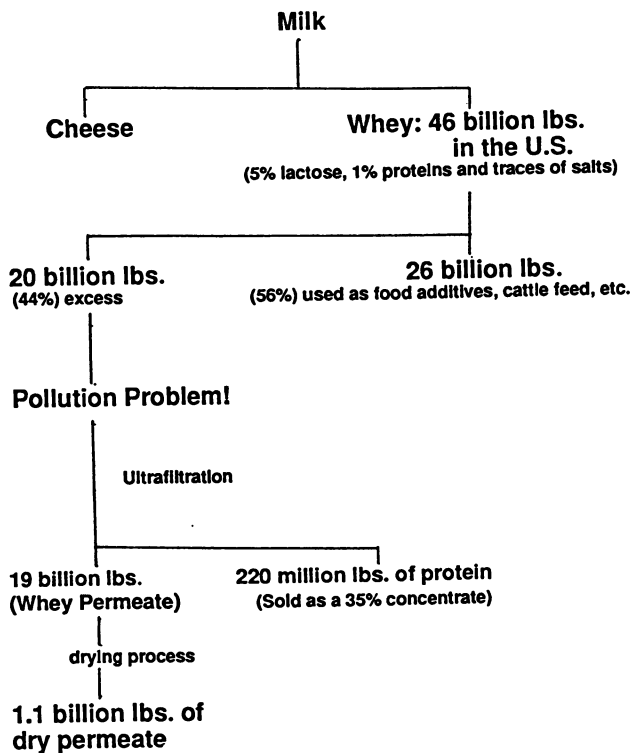


Figure 1. Generation of whey and whey permeate from the cheese industry in the United States.

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To a large extent, the utilization of whey and whey byproducts (including salt whey and whey permeate) is a problem of utilizing the milk sugar, lactose. Since the excess lactose produced in the United States each year amounts to more than a billion pounds, one must consider its use in large volume products. One such product is lactose-based polyether-polyol used in the manufacture of low-density rigid polyurethane foams (2).

Table I. Typical Composition (%) of Wheys and Permeate

Component	Fluid Sweet Whey	Fluid Acid Whey	Salt Whey	Whey Permeate
pH	5.9-6.3	4.4-4.6	5.2	4.5-5.8
Total solids	6.35	6.5	10.7	6.1
Moisture	93.7	93.5	89.26	94.2
Fat	0.5	0.04	0.04	-
Total protein	0.8	0.75	0.7	0.1
Lactose	4.85	4.90	4.35	4.9
Ash	0.5	0.8	5.25	0.7
Lactic acid	0.05	0.4	-	0.4
Sodium choride	-	-	4.7	-

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Table II. Amount of Total Whey Solids Available for Use Worldwide in 1981 [Thousand Tons (18)]

Country	Whey Solids <sup>1</sup> Production
EEC	2141
Other Western Europe	322
Canada	104
USA	1144
Australia	80
Japan	40
New Zealand	53
Czechoslovakia	66
Hungary	25
Poland	176
USSR	411
Other countries	1499
Total world	6065

<sup>1</sup>Whey solids calculated using 10 lb whey/lb of cheese made times 6% total solids.

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Another problem of a seemingly unrelated nature is the formaldehyde emission from building boards that are currently manufactured using urea-formaldehyde adhesive resins. Formaldehyde has been implicated as a carcinogen and can also cause severe upper respiratory problems and contact dermatitis in some individuals (3-5).

The use of formaldehyde-free adhesive resins from whey and whey byproducts for manufacturing construction-quality boards could resolve these problems simultaneously. The demand for formaldehyde-based thermosetting adhesive resins in the United States was estimated to be 1.9 billion pounds in 1983 (6). The anticipated requirement for resins and the potential availability of raw materials from whey are a fortuitous combination.

Research by others has established the feasibility of using sugars and starches for binding wood. Such uses have been investigated by Stofko (7-9), Usmani and Salyer (10), Gibbons and Chiang (11), and Gibbons and Wondolowski (12), among others. The work of Gibbons in collaboration with Chiang (11) and Wondolowski (12) has dealt with the partial replacement of formaldehyde in resins by sugars or starches. Because of the fluid nature of the available raw material and the desire to prepare resin solutions with high solids content, a slightly different approach is required from that employed in the use of starches or cellulose as resin ingredients.

In the author's research, ammonium nitrate was used to catalyze transformation of lactose to polymeric compounds. The amount of ammonium nitrate was kept at 8% (w/w of final solution) because this amount was sufficient to produce a final pH of 2 to 3 while yielding an insoluble polymer (13). (Lower pH values would be detrimental to strength retention over a period of time). Tailoring of the resin was possible by adding condensing agents such as urea and/or phenol to produce concentrated solutions of variable viscosity and pH. (The addition of these crosslinkers, however, resulted in increased cure time for resin preparation). Minor amounts of copper salts (e.g.,  $\text{CuCl}_2$  or  $\text{CuSO}_4$ ) were added to the reaction mixture during resin synthesis to catalyze Maillard browning reactions, which are known to result in high molecular weight heterocyclic polymers. Figure 2 shows the proposed reaction pathways for synthesis of whey-based resins.

Even though the structural aspects of the polymers have not been worked out due to the many possible reaction products, it is safe to propose a general linear structure with a large number of carbonyls due to the oxidation of -C-OH groups in an oxidizing  $\text{HNO}_3$  environment. Size exclusion chromatography of the methanol-insoluble but water-soluble whey-resin fraction indicates a molecular weight in the range of 10,000 to 80,000 [in comparison to proteins of known molecular weight used as standards (14)]. This molecular weight is consistent with the constituents in cane sugar refiner's final molasses (15) that are known to result from advanced Maillard browning reactions, among others.

In a recent study, a two-step method was used to make whey permeate resin (16,17). The process consisted of injection of gaseous ammonia into a reaction

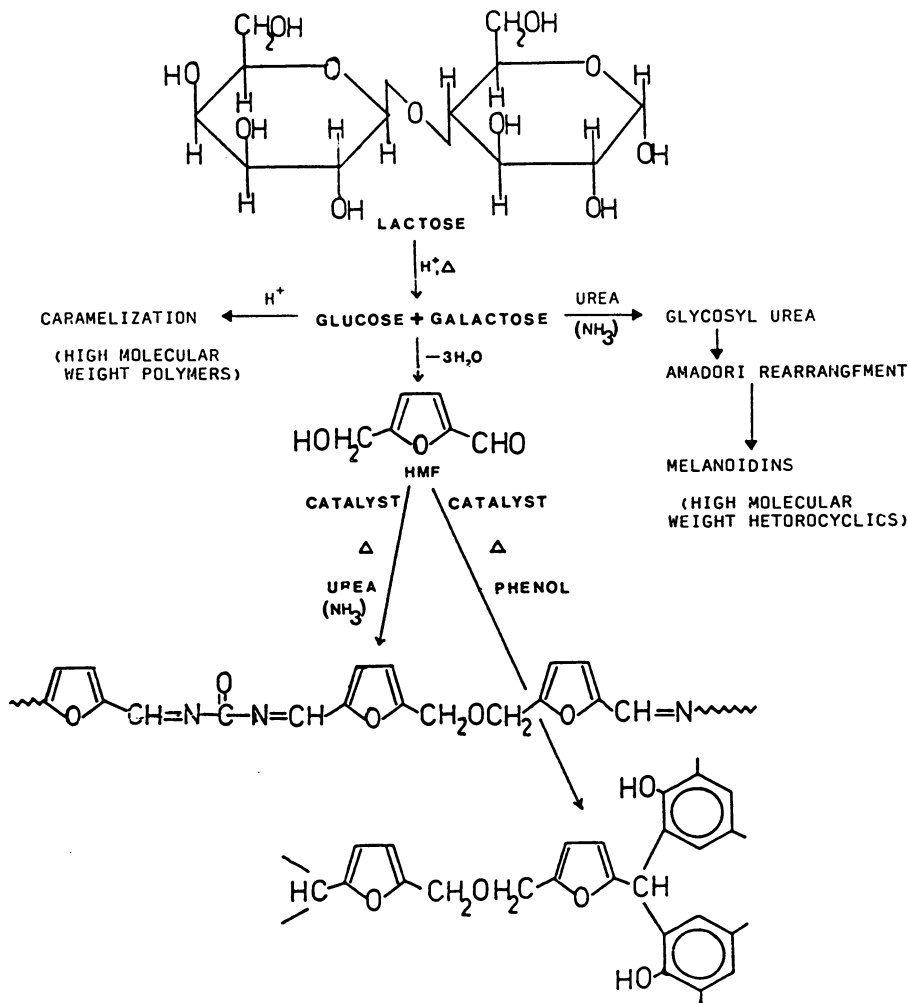


Figure 2. Proposed reaction pathways for the synthesis of whey-based resins. Ammonia gas may be used in a two-step reaction scheme. Structures of polymers shown here are hypothetical.

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mixture containing degradation products of whey solids produced by sulfuric acid at high temperature and pressure in an enclosed Parr reactor. The first step consists of acid-catalyzed hydrolysis and dehydration of sugars at pH 0.5 and high temperatures. Figure 3 shows the formation of the methanol-insoluble product (MIP) as the reaction progresses. The MIP portion of the reaction was determined by withdrawing aliquots of the reaction mixture (1.25 g), mixing with 100 mL of methanol, filtering, and drying. The value of approximately 50% MIP obtained for time zero is probably due to immediate hydrolysis of lactose to galactose and glucose on addition of acid. Over time, dehydration of the monosaccharides should take place, producing methanol-soluble products such as hydroxymethylfurfuraldehyde. This in turn would lead to a decrease in methanol-insoluble fraction. If the reaction is continued, the MIP falls to a minimum value and is then followed by an increase in the value, indicating formation of higher molecular weight products that tend to be generally insoluble in methanol.

At the point where the MIP is at a minimum, injection of ammonia gas results in a steep increase in the amount of high-molecular-weight materials with a concurrent rise in pH value. Both these processes are highly desirable. Ammonia is added until the desired pH value is obtained ( $\approx 3.5$  to 4.0). At this point, the resin preparation is a viscous emulsion of dark brown color. The advantage of this method of resin preparation is its adaptability to continuous plug-flow reaction, unlike the Phase I resin, which is more suited to batch reaction.

Table III shows the properties of particleboards prepared with Phase I whey permeate-based resin. Table IV shows the properties of rice-hull-reinforced building boards using Phase II resin. Low-quality boards are prepared with rice hulls, but their qualities may be improved by using ground hulls or adding sawdust to the formulation. Although whey-based resins have been found to be excellent adhesives for binding solid lignocellulosic materials, these resins tend to require higher cure temperatures and longer cure times as compared to formaldehyde-based resins.

This chapter describes preliminary investigation into the thermosetting process of one whey-based resin preparation using differential scanning calorimetry (DSC).

## Experimental Methodology

A Mettler TA 3000 system consisting of a TC 10A TA processor and a DSC 20 measuring cell was used to investigate the curing reaction of the whey-based resin prepared as follows. A mixture of 171-g whey permeate, 73.2-g  $\text{NH}_4\text{NO}_3$ , 2.85-g  $\text{CuCl}_2$ , and 200-mL  $\text{H}_2\text{O}$  was placed into a Parr pressure reactor and heated with stirring at 125 °C for 90 min. The pH of the final preparation was 3.6.

Approximately 7- to 10-mg samples of this resin were weighed in sealed-glass, high-pressure crucibles. Pressure cells were used to contain any volatile, reactive

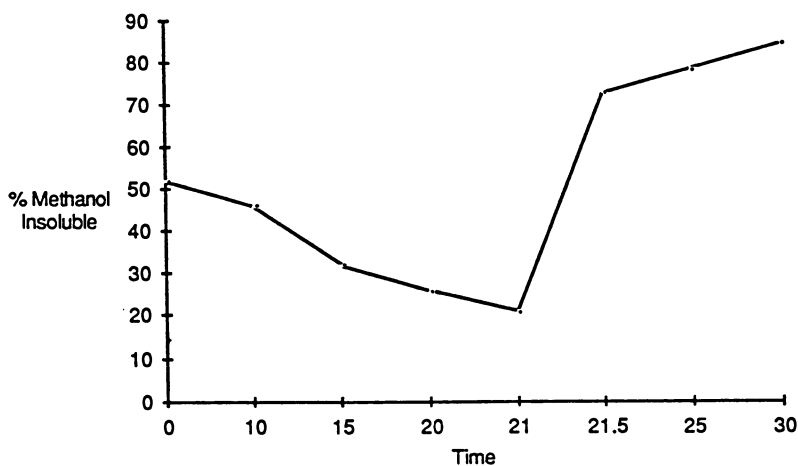


Figure 3. Percentage of methanol-insoluble product obtained during the reaction of 233.4 g of dry whey permeate and 90.3 mL of sulfuric acid in an enclosed reactor at 145 °C. Ammonia was injected after a reaction time of 21 minutes to increase the pH to 4.0.

species and to simulate the pressure conditions at which the resin might be cured in practice. An empty sealed-glass crucible was used as an inert reference. The DSC sensor used was a five-part Au/Ni thermocouple having a sensitivity of approximately 20 microvolts per K. Temperature scan rates of 5 to 10 K/min were generally used to scan the temperature range from 30 to 250 °C.

Table III. Properties of Particleboards<sup>1</sup> Prepared with the Whey Permeate Resin

Resin (Dry Basis) (%)	Temperature- pressed <sup>2</sup> (°C)	Density (lb/ft <sup>3</sup> )	IB (psi)	Thickness Swell		Dried <sup>4</sup> Strength (psi)
				2 hr (%)	24 hr (%)	
7	165	55.7	81	50	—	—
	185	53.7	125	11	20	21
10	165	53.9	92	19	25	—
	185	61.6	132	7.4	18	30

<sup>1</sup>Single-layer boards of local pine sawdust, 3/8 in thick.

Values represent the average of duplicate tests.

<sup>2</sup>The particleboard mat (moisture content 6%) was pressed at 500 psi for 7 min.

<sup>3</sup>Pounds per square inch.

<sup>4</sup>The internal bond strength recovery was determined after the specimens (24 hr water immersed) were dried in an oven at  $103 \pm 2$  °C until approximately constant weight was obtained.

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## Results and Discussion

The DSC thermogram of the whey-based resin prepared above indicated an exothermic peak occurring at approximately 185 to 190 °C. The solid mass obtained prior to the exotherm is rubbery, but becomes brittle after this transition. The change in enthalpy during the course of polymerization, which corresponds to the amount of heat liberated during the exothermic process, may be determined by the area under the DSC curve. A computer program written as part of the TA processor's kinetic method indicated  $E_a = 633.44$  kJ/mol. Assuming that the heat change is proportional to the extent of reaction, the area under the curve may serve as an analytical parameter, and the reaction kinetics may be derived in a straightforward manner. In the case of whey-based resins, however, the sequence of reactions occurring during the polymerization process is sufficiently complex that only qualitative aspects of the DSC thermogram may be considered.

The complexity of the whey-based resin thermosetting process can be illustrated by considering several isothermal investigations. Samples of the resin

were heated isothermally at various temperatures ranging from 140 to 185 °C, and the reaction was monitored with respect to time. When the resin sample was heated isothermally at 140 °C for 15 min, no exotherm was observed. The sample was allowed to cool slowly to room temperature and then heated isothermally at 185 °C for 15 min. Again, no exotherm was observed.

Table IV. Properties of Particleboards Prepared with Phase II Resin  
[Whey Permeate/H<sub>2</sub>SO<sub>4</sub>/NH<sub>3</sub> (17) ]

Composition	Resin	Press	Density (lb/ft <sup>3</sup> )	IB (psi)	MOR (psi)	Thickness
	(Dry Basis) (%)	Cycle (min)				Swell (%)
Rice	10	8	57.0	12.9	864	125.9
75% Ground rice & 25% dust	7	7	53.2	49.8	984	37.8
Dust	7	7	55.9	144.4	2047	27.0
50% Ground rice & 50% dust	7	7	56.9	79.8	838	49.4
Ground rice	7	7	54.3	29.4	—	38.8

<sup>1</sup>Final pH = 3.

<sup>2</sup>The boards are a single layer of pine dust and/or rice hulls (ground and unground). Values given represent average of duplicate runs. Final thickness of the boards was 1/4 inch.

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However, when a fresh sample of the resin was heated isothermally at 185 °C, there was an exothermic process evident that peaked within the first minute and reached completion within approximately 4 to 5 min. Thus, it is evident that the cure mechanism may change with change in reaction conditions, revealing the complexity of the whey-based resin thermosetting process.

Since a dynamic run described earlier revealed an exothermic polymerization at around 185 to 190 °C, crosslinkers were added in an attempt to lower the temperature for polymerization. The crosslinking agents (10% w/v of resin preparation) used were phthalic anhydride, maleic anhydride, tallow diamine, and *p*-toluenesulfonic acid. We were unable to lower the temperature of initiation of polymerization by the addition of the first three reagents, but did observe a shift to a lower temperature (≈ 165 °C) in the presence of *p*-toluenesulfonic acid. The pH of the mixture prior to heating was around 2.0, whereas, the



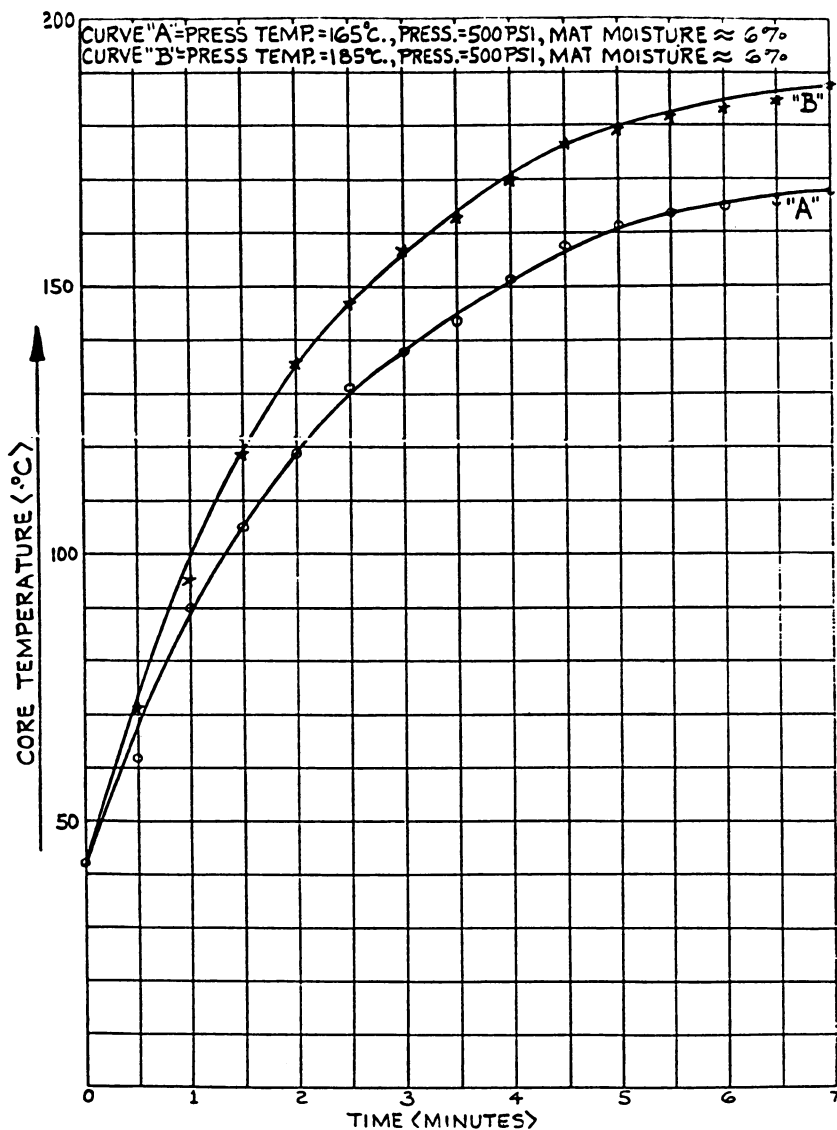


Figure 4. The influence of press temperature, pressure, and time on core temperature rise during hot pressing. Amount of resin used was 7% (by dry weight) in the board. The resin applied had 65% solids content. Mat moisture content was 6% prior to pressing.

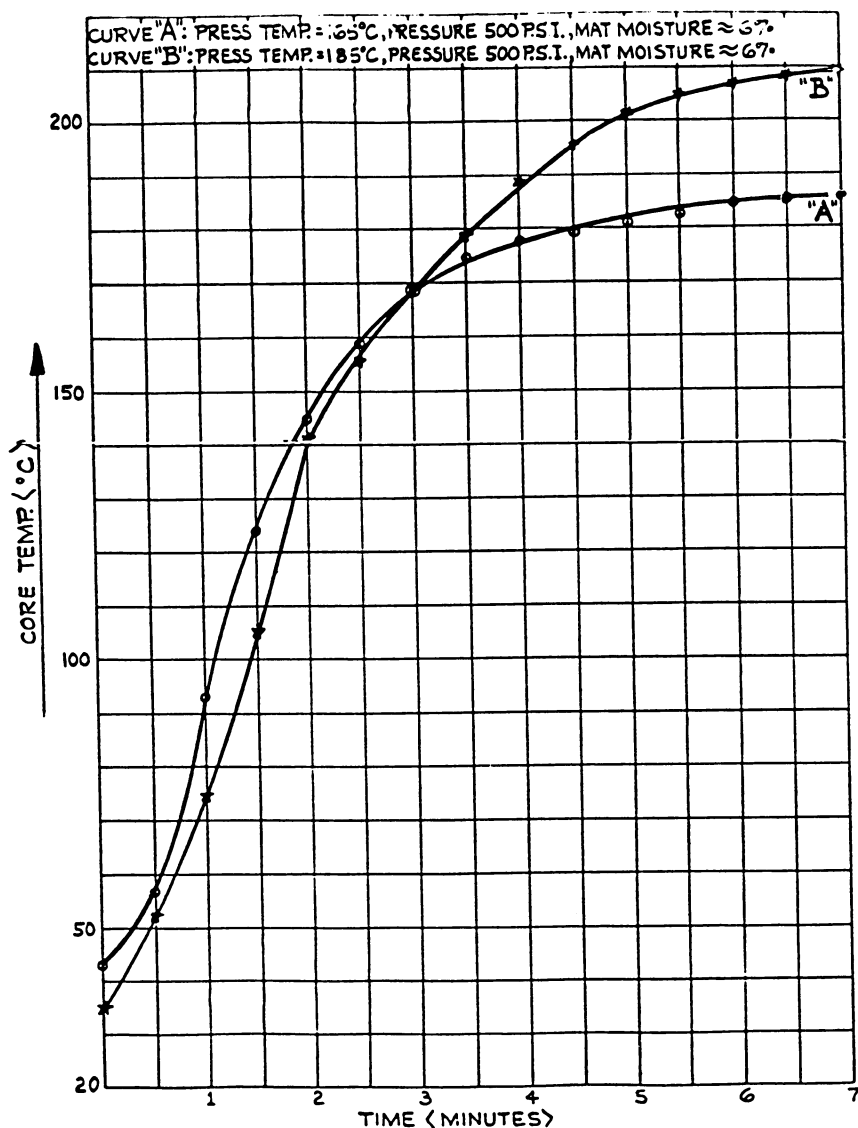


Figure 5. The influence of press temperature, pressure, and time on core temperature rise during hot pressing. The amount of resin used was 7% (by dry weight) in the board. The resin applied had a 65% solid content with 10% w/w of phthalic anhydride. Mat moisture content was 6% prior to pressing.

others had a pH around 3.0 to 3.5. When the pH of the mixture containing *p*-toluenesulfonic acid was raised to 3.5, the advantage in terms of lower temperature for the initiation of polymerization was lost.

Since we (19) have reported that there is an improvement in internal bond strength of high-density particleboards on addition of phthalic anhydride, we decided to investigate the influence of press temperature, pressure, and time on core temperature rise during hot pressing. Figures 4 and 5 indicate the results obtained under the conditions stated. The amount of phthalic anhydride in Figure 5 was 10% w/v of a 65% resin solution. The mat thickness was three-eighths of an inch, and the board was prepared by pressing under continuous pressure without stops.

It is clear from the results obtained that the core temperature rises above the platen temperature in the presence of phthalic anhydride. Since no unusual differences in the DSC thermogram of whey-based resin in the presence and in the absence of phthalic anhydride were seen, the exothermic phenomenon being observed under conditions of board preparation deserves further investigation.

## Conclusion

Work done with whey-based resins so far has demonstrated the feasibility of using the thermal degradation/polymerization products of lactose as an adhesive for binding lignocellulosic materials. This offers an exciting solution to the whey disposal problem, which takes on not only national but international significance. The major drawback in board manufacture using whey-based resins is the prolonged cure time and darker color. The major advantages are the lower cost and the lower formaldehyde emissions. Both should encourage the forest products industry to consider this viable alternative. Governmental decisions regarding formaldehyde toxicity will have an enormous bearing on the future of research on adhesives from renewable resources.

## Acknowledgments

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# Chapter 29

## Chemistry of Furan Polymers

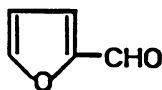
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Furfural, derived from renewable agricultural resources, has been a significant industrial chemical for many years, used mainly as a selective solvent. Furfuryl alcohol is manufactured worldwide in substantial volumes and principally used in the foundry industry. Other derivatives of furfural, namely furan, methylfuran, and tetrahydrofuran, are important as solvents, building blocks for chemical synthesis, and as monomers for polymerization. While furfural is competitive with today's petrochemicals, the prospect of lower cost in the future based on byproduct furfural from solvent pulping technology in the wood industry provides an opportunity for researchers to rediscover the versatility of these oxygen-containing heterocyclic chemicals. Adapting their specific pseudo-aromatic/dienic properties to applications requiring performance-effective chemicals offers many opportunities for furfural's potential to be fully realized.

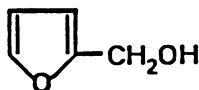
Furfural (1), derived from annually renewable agricultural byproducts, is an important industrial chemical manufactured and used throughout the world. It is the feedstock for a number of derivative chemicals generically known as "furans" –the structural characteristic of which is the five-membered oxygen-containing heterocyclic ring. Furfuryl alcohol (2) is the most important derivative of commerce, where it is used primarily in synthesis of adhesive polymers.

In addition, furan, available by decarbonylating furfural, has been employed commercially to produce other industrial chemicals including thiophene, pyrrole, and N-substituted pyrroles. These sulfur and nitrogen-containing heterocyclic chemicals are used as solvents and chemical building blocks. Hydrogenation of furan is done commercially to produce tetrahydrofuran, which is used as an industrial solvent and a monomer for the production of polytetramethylene ether glycol. Furfural, as a feedstock, plays a role in the manufacture of these industrially important heterocyclic chemicals. Considering that the materials consumed to make furfural are accessible in large quantities and naturally

renewed, the production of furan derivatives becomes an attractive alternative to petroleum-based chemicals.



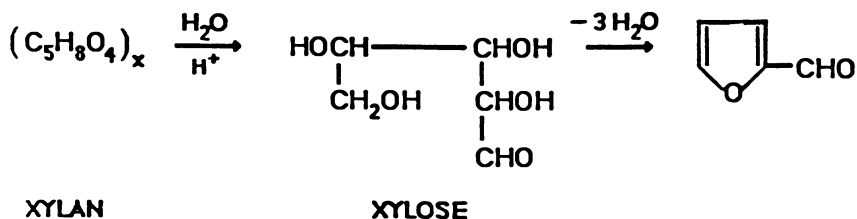
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Five-membered heteroaromatic ring compounds have been available for some time, and their relative reactivities and properties have been studied. The aromaticity of the furan ring is the lowest in the series: thiophene > pyrrole > furan (1). The dienic character of furan follows the reverse order as shown by studies on the Diels-Alder and other addition reactions (2). As a consequence, furan shares both aromatic and dienic properties. The predominance of one of these two addition characteristics among the many derivatives depends on the nature and position of the ring substituents. Chemical reactions, particularly involving polymer types and reactivity, are influenced by this duality. Polymerization systems where the furan ring is present in the monomer, either as the reactive entity or as a pendent group to the function responsible for the polymerization, are the subject of this discussion. Consideration will be given to both condensation and addition polymerizations.

While there are many chemicals possessing the furan nucleus, furfural and furfuryl alcohol are of major industrial significance. The chief source of furfural in plant materials is the pentosan fraction, predominantly xylan (Scheme 1).



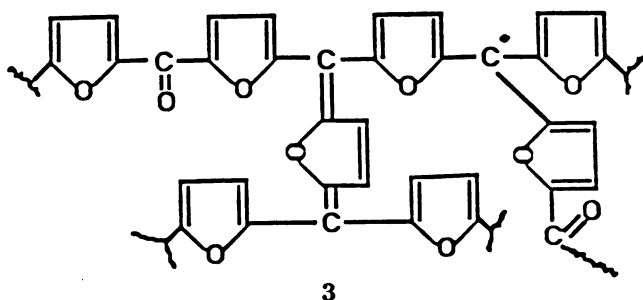
Scheme 1

Furfuryl alcohol is manufactured on an industrial scale by employing both liquid-phase and vapor-phase hydrogenation of furfural (3,4). Copper catalysts are preferred because they are selective and do not promote hydrogenation of the ring.

Many industrial applications utilize the solvent properties of furfural and furfuryl alcohol; however, both chemicals also display unique features as monomers for condensation polymerization. Most of the furfuryl alcohol sold is used as monomer in the manufacture of resins for industrial application.

### Furfural Polymers

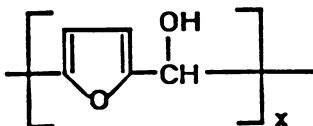
Homopolymers of furfural, as reported by Gandini, polymerize to black cross-linked products when heated to high temperature in an inert atmosphere (5,6). This investigator showed the resulting thermoset polymer to be paramagnetic, indicating the presence of highly stabilized free radicals that inhibit radical reactions. The color is suggested as arising from the unpaired electrons and extensive conjugation. The following composition (3) has been proposed (6):



Furfural reacts with Lewis and Brönsted acids under anhydrous conditions to yield black insoluble resins. The rate of polymer formation is dependent upon the hydrogen ion concentration and temperature when furfural is polymerized by dilute acid (7). Polymerization under aqueous conditions occurs with some furan ring opening. Conditions of polymerization, whether aqueous or anhydrous, inert or oxygen atmosphere, all affect the composition of the polymer. Investigators have recently reported (8,9) that condensation reactions involving the C-5 hydrogen and the protonated or complexed carbonyl group occur, leading to three-dimensional crosslinking.

The photopolymerization of furfural by UV radiation has not received much attention. Although the products of heat polymerization of furfural are branched polycondensates with highly conjugated structures, the photopolymer of furfural is a linear polyaddition product (8,9). The gas-phase photolysis of furfural in the  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  transitions (10) proceeds with fragmentation to carbon monoxide, furan, and  $C_3$  hydrocarbons, but a certain amount of resinification has also been noted (about 5% quantum yield with excitation of the  $n \rightarrow \pi^*$  transition). Vacuum liquid-phase photolysis by UV radiation at room temperature has produced linear polymers (4) with a degree of polymerization of about

5 (8,11). The presence of one carbonyl group per oligomer molecule has also been observed. The fact that furin was isolated is supportive of the proposed mechanism. No evaluation has been done to date on the usefulness of these liquid linear polymers.



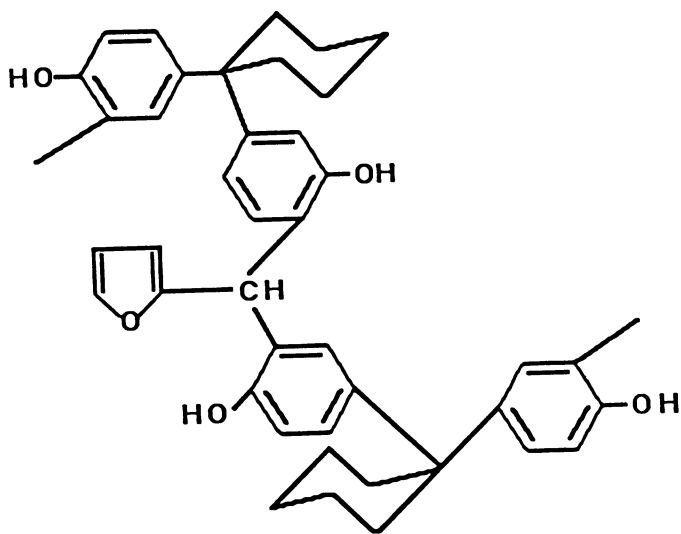
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Copolymers of furfural with phenol or phenol-formaldehyde polymers have been available commercially for many years. Since the acid-catalyzed reaction of furfural and phenol has been difficult to control, most industrial applications involve the use of alkaline catalysts. Furfural-phenol resins are used for their alkali resistance, enhanced thermal stability, and good electrical properties compared to phenol-formaldehyde resins.

Recently, investigators have studied the reaction of furfural with other hydroxyl-bearing aromatics. In the case of bisphenol A (12,13), furfural has been shown to react in the *ortho* positions, yielding the alcohol adduct and ultimately resulting in reaction products bearing fufuryl-diphenol methane groups. The products formed, used in molding powders, show superior thermal, mechanical, and chemical properties compared to phenol-formaldehyde polymers. For a given degree of polymerization, the molecular weight of bisphenol A-furfural resin is more than twice that of phenol-formaldehyde. As a result, bisphenol A-furfural polymers have a molecular weight in the range of 1,600 to 1,800 compared to phenol-formaldehyde resins with molecular weight of 700 to 800. Moreover, due to the higher functionality of bisphenol A, a three-dimensional rigid crosslinked structure with a unique spacial configuration contributes to a quick curing system. Improved adhesion properties are seen due to the unique cyclic ether functionality of the furan ring. The condensation reaction of bisphenol A and furfural mainly depends on the nature and concentration of the catalysts, the reaction temperature, the reaction time, and the molar ratio of reactants.

Polycondensation of bisphenol C (phenol + cyclohexanone) and furfural, catalyzed by base, leads to resins such as 5 that are more easily cured than phenol-furfural condensates, and such resins have higher softening ranges (14). Under acidic catalysis, some ring opening occurs as evidenced by the infrared spectrum. Crosslinking in the acid-catalyzed resin is also suggested by its higher softening range. The acid-cured resin is more temperature stable than the base-catalyzed resin; however, thermal gravimetric analysis data show that phenol-furfural resins on the whole are more stable than the bisphenol C-furfural resins.



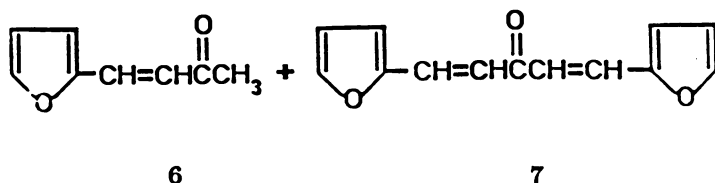


5

Furfural-resorcinol oligomers have been known for many years (15,16). The reaction velocity of furfural with resorcinol is the fastest compared to other hydroxy substituted aromatics. Furfural-resorcinol polymers, when heat cured, give excellent bonding strengths, especially under conditions of high humidity. Their oligomers, even in the presence of acids, show good shelf life until reacted with a suitable methylene donor.

Furfural-ketone copolymers have found commercial use, particularly in the Soviet Union, in applications ranging from floor coverings, anti-corrosion coatings, wood adhesives, and binders for carbon/graphite. When an alkaline catalyst is used, furfural is known to react with acetone to form the so-called "furfurylidene acetone monomer," a mixture of 2-furfurylidene methylketone (6), bis(2-furfurylidene) ketone (7), mesityl oxide, and other oligomers.

Treatment of the "monomer" with an acidic catalyst leads initially to polymers of low molecular weight and ultimately to crosslinked, black, insoluble, heat-resistant resin (17). Despite their reportedly excellent properties, virtually no commercial use of such resins exists outside the Soviet Union. The structure and polymerization mechanism of these furfural-ketone polymers are described in a recent study (18). An excellent combustion-resistant resin has been reported (19) from the addition of dialkylphosphites to bis(2-furfurylidene) ketone (6). Furfural condensates with other aliphatic and aromatic ketones have been reported (20,21) to provide photo-crosslinkable resins and hypergol components.



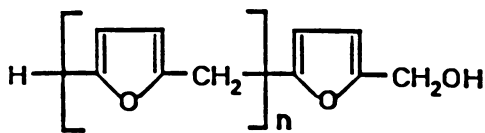
Copolymers of furfural with pyrrole have been reported to yield carbon fibers of remarkable quality (22). More recent reports include the use of poly(*N*-vinylcarbazole) with furfural and furfural-amine copolymers (23) to make both cation/anion exchange resins. A considerable amount of additional work needs to be done in this area to determine the commercial usefulness of such systems.

### Furfuryl Alcohol Polymers

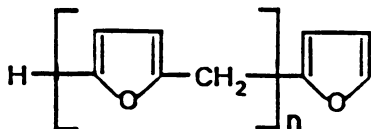
Since the late 1950's, acid-catalyzed resinification has been the most important industrial reaction of furfuryl alcohol. The polymerization mechanism proposed up to the early 1950's for furfuryl alcohol was reported by Dunlop and Peters in their excellent treatise on the furans (24). Their mechanism has not been altered to any great degree since that time. However, with furfuryl alcohol polymers (resins) growing in importance, the chemistry of furfuryl alcohol polymerization initiated by heat, acids, and alumina has been studied at a number of laboratories and has proven to be complex, particularly after the first stage of oligomer production. Studies dealing with the identification of components by spectroscopic and chromatographic techniques (25-28), the reaction kinetics involved in polymerization (29-31), the structure of polymers (32), and the nature of the oxygen or acid-catalyzed crosslinking of the initial resin (33) have all led to a better understanding of this complex chemistry. Gandini, in his comprehensive review (5), examined the literature up to 1977 and has provided an excellent summary and interpretation of the resinification mechanisms proposed. This work, coupled with his recent review of furan polymers (34), significantly contributes to the understanding of this complex polymerization.

Based on the accumulated data, furfuryl alcohol has to be considered a bifunctional monomer in the initial stage, and its "normal" reactions give linear chains or oligomers containing essentially two repeating units, a methylene bridge and a methylene ether bridge, with the former predominating. The polymerization or resinification of furfuryl alcohol is exothermic and, depending upon the activity and concentration of the catalyst used, requires careful control of the reaction temperature. Control is generally accomplished by cooling the reaction mixture with refluxing solvent and/or an external cooling fluid. In extreme instances, emergency neutralization of the catalyst is essential to avoid loss of control.

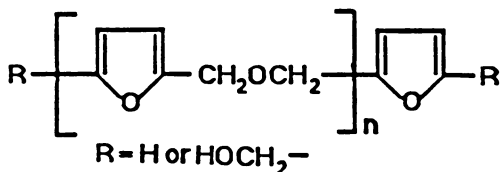
The degree of first-stage polymerization is carried out to the desired point as measured by viscosity. When the proper viscosity has been reached, the reaction is terminated by adjusting the pH of the system to between 5 and 8. Such liquid resins can be stored for 6 months or longer without any appreciable buildup in viscosity. The liquid resins have linear structures formed by intermolecular dehydrations of the hydroxyl group of one molecule and the active  $\alpha$ -hydrogen atom of another. Furfuryl alcohol dimer and higher homologues (8) are major constituents in the product mixture. However, other components are present, including homologues of difurfuryl methane (9), and both furan-terminated and hydroxymethyl-terminated homologues of difurfurylmethylene ether (10), in addition to 2,5-bis(hydroxymethyl) furan and its homologues (11) as determined by thin layer chromatographic (TLC) densitometry analysis.



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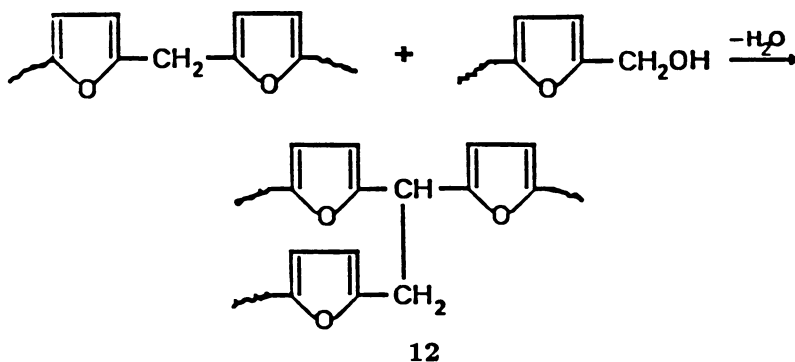
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As shown, the polymer end groups of these oligomers are hydroxymethyl and/or unsubstituted furan rings. Identification of 2,2'-difuryl methane and higher homologues indicates that formaldehyde, detected as a gaseous byproduct of the reaction, is released by terminal hydroxymethyl groups and/or from internal ether bridges.

An adjunct to the understanding of this mechanism is the evidence obtained that polymerization of 2,5-bis(hydroxymethyl) furan produces no 2,2'-difuryl methane or higher homologues (35). Analysis by thin-layer chromatography shows such resin having greater than 95% difunctional components (terminal hydroxymethyl groups) as compared to less than 50% for the resin from a conventional furfuryl alcohol polymerization (35).

A competing reaction to polymer growth through functional group condensation occurs in acid-catalyzed polymerization of furfuryl alcohol. In the later stages of such polymerizations, ring hydrolysis occurs, resulting in the development of aliphatic carboxylic and ketonic groups. Researchers have frequently suggested the formation of levulinic acid, although no levulinic acid has ever been isolated, no doubt due to its reactive nature.

While earlier investigators postulated crosslinking through the C-3 and C-4 positions, more recent studies (36), on the basis of analytical data, suggested that the main cause of branching and crosslinking involves a condensation reaction between methylene groups within a chain and a hydroxymethyl group at the end of another (Scheme 2) to yield structures such as 12.



Scheme 2

The only feature not explained by this mechanism is the dark color of the final resins. Gandini, in his review (34), suggests as with furfural resins, small amounts of very intense chromophores must be present along the repeating chains; their concentrations are too low to be detected by NMR or IR spectroscopy. Homopolymers of furfuryl alcohol or copolymers with formaldehyde as final crosslinked thermoset polymers display outstanding chemical, thermal, and mechanical properties (37). Heat treatment of furfuryl alcohol resins leads to the formation of glasslike porous carbon, possessing properties of molecular sieves as well as performance phenomena similar to those observed in superconducting materials (38-42). Though the exact mechanism of the carbonization process as well as the structural changes are not fully explained, a scheme of pyrolysis chemistry has been proposed (39). The main changes in structure occur in the temperature region 150 °C to 450 °C, where a rupture of methylene bridges, opening of furan rings, and formation of aromatic systems takes place. Above 450 °C, the remaining methylene C-H residue capable of forming

a crosslinked aromatic system arises. NMR studies of furfuryl alcohol resin carbonized over the temperature range 60 °C to 860 °C show the following results in terms of structural and chemical changes taking place during heat treatment: heating up to 240 °C results in increases in molecular weight and crosslinking; up to 320 °C, crosslinking increases sufficiently to form rigid structures; temperatures of 380 °C and higher lead to hydrogen release and appearance of paramagnetic centers.

Furfuryl alcohol polymers are used in a variety of applications including sand cores and molds for metal casting, corrosion-resistant fiberglass-reinforced plastics, low flammability and low-smoke-generating composites and foams, carbonaceous products, polymer concretes, wood adhesives, and others. Their thermoset characteristics give these polymers advantages over resin systems in applications demanding thermal stability, corrosion control, and low smoke generation and flame spread in fire situations.

### Difunctional Furan Monomers

Within the past 10 years, a number of investigators have explored the use of 2,5-disubstituted furan monomers in polymer condensation reactions. In spite of this attention, no significant commercial application has developed thus far. The general unavailability and high price of these monomers are drawbacks as are the lower temperature and oxidative stability and enhanced color development characteristics of some of the polymers developed from them.

Furfuryl alcohol, reacted with formaldehyde in the presence of acetic acid, is selective in yielding 2,5-bis(hydroxymethyl) furan. This crystalline solid monomer has been used in preparing polyesters and polyurethanes. Color stability has been a limitation in certain instances. Hydrogenation of 2,5-bis(hydroxymethyl) furan to 2,5-bis(hydroxymethyl) tetrahydrofuran provides a water-white, stable, liquid diol that shows promise as a polyurethane/polyester component. In this instance, exceptionally color-stable products are produced (49).

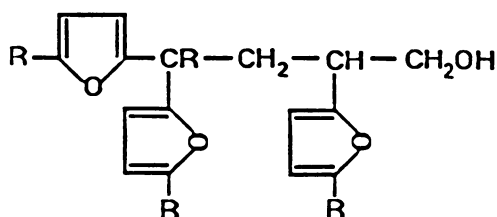
Resinification of 2,5-bis(hydroxymethyl) furan occurs in the presence of acid-catalyst similar to furfuryl alcohol, although the end groups of the resulting resins are hydroxymethyl. These resins are characterized by enhanced reactivity compared to acid-catalyzed furfuryl alcohol resins (49). They convert to highly crosslinked thermosetting polymers that demonstrate unique characteristics in composites including high char yield on carbonization, low smoke evolution and low flame spread, corrosion resistance, and superior high-temperature stability compared to other thermosetting resin systems.

2,5-Bis(hydroxymethyl) furan and 5-hydroxymethyl furfural (available from C<sub>6</sub> sugars) have been oxidized to furan-2,5-dicarboxylic acid (44). Linear polyesters, polyurethanes, and polyamides containing these monomers have been described in the literature (45-48) and have been made via condensation polymerization techniques including bulk, solution, and interfacial mixing procedures. Gandini (5,34) reviewed the polycondensation reactions up to 1986 and

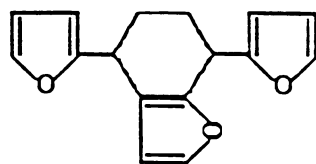
postulated on the possible reasons for lack of performance of these furan ring containing polymers.

### Furan Polymers

Furan, available through the decarbonylation of furfural employing a noble metal catalyst, and 2-methylfuran, available from the catalytic hydrogenation of furfural using nickel catalysts, are monomers widely investigated recently. Acid-catalyzed polymerization of furan and methylfuran has been reviewed (49), and a later publication (50) has identified tetramers and related structures such as 13 and 14. Strong chromophores must be present in minor concentrations, in addition to structures like 13 and 14, since these reactions result in polymers that are highly colored. Hydrogenation of these furan oligomers would provide unique polysaturated cyclic ethers.



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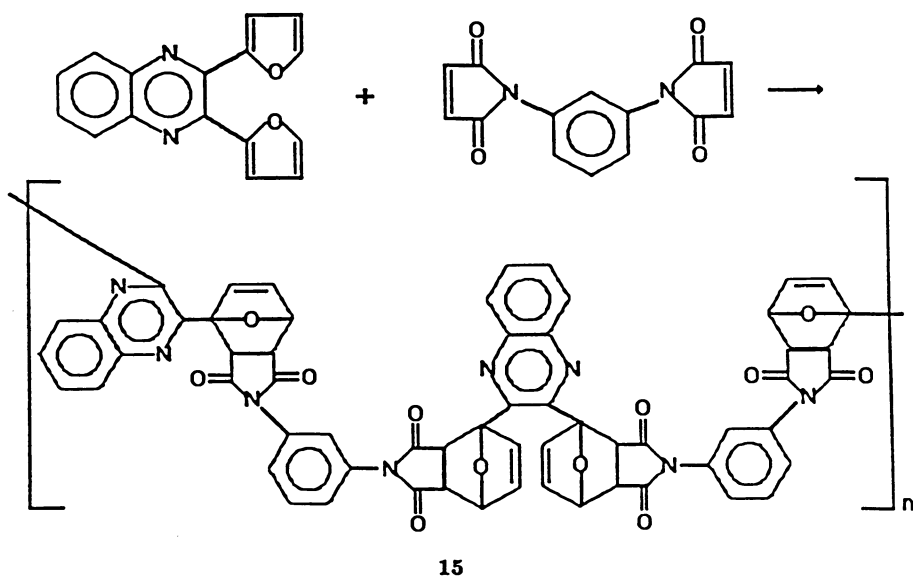


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The copolymerization of furan and 2-methylfuran with dienophiles such as maleic anhydride leads to polymer structures with furan pendent functionality. Furan, 2-methylfuran, and 2,5-dimethylfuran have been copolymerized with acrylic monomers (51,52) and acrylonitrile (52,53). The furan ring of furan, 2-methylfuran, and 2,5-dimethylfuran participates as a diene in a free radical copolymerization with acrylonitrile. The initial step for furan and for 2,5-dimethylfuran is the attachment of an acrylonitrile radical at the 2-position, but for 2-methylfuran, the attack is at the 5-position. Propagation proceeds by the attack of the furan radical on an acrylonitrile molecule, to leave one olefinic bond in the structure derived from the furan ring. If this bond is in the 4,5- or 2,3-position, it may be involved in a second additional reaction by the return of the propagating chain.

Furan and 2-methylfuran can undergo other Diels-Alder reactions with strong dienophiles. Crosslinked polymers have been obtained from reaction of a linear polyimidazole or polyquinoxaline, containing pendent furan groups, with an olefinic and end-capped aromatic compound (Scheme 3) (54,55). These polyquinoxaline polymers (15) have alicyclic oxy-crosslinks repeated throughout the polymer where the furan constituent has undergone a Diels-Alder reaction with

the aromatic olefin group. The alicyclic oxy-linkage is subsequently aromatized by application of heat to produce high-performance polymers suitable for use at temperatures up to 400 °C.

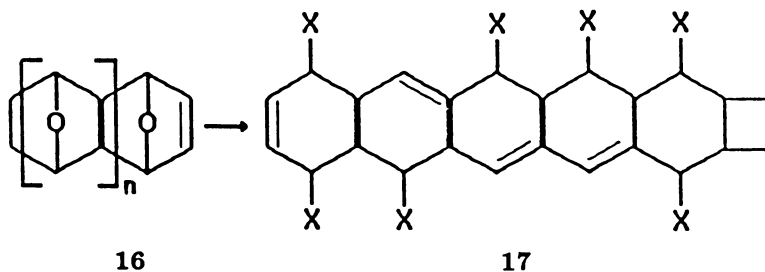


Scheme 3

Other linear polymers suitable for high-temperature structural laminates are obtained by the reaction of bis(furfuryl) imide via Diels-Adler reactions (56,57). Stability in air up to 500 °C has been reported for these polymers. The prepolymers have pendent phenyl substituents and are soluble in organic solvents, an important processing improvement for hetero-aromatic polymers.

Polymeric addition compounds (16) of furan and ethylene, where  $n$  is a whole number from 1 to 50, have been prepared (58) by addition of  $>2$  mole furan to 1 mole ethylene at 120 °C to 250 °C and high pressures followed by fractional extraction of the solid product formed. These polymers have interesting physical and chemical properties. They appear to be highly crystalline on analysis by X-ray. As a consequence, the polymers show good thermal stability, which increases directly with molecular weight. The presence of ether bridges makes possible conversion (Scheme 4) to other compounds that retain the double hydrocarbon chain (ladder) structure and may bear various func-

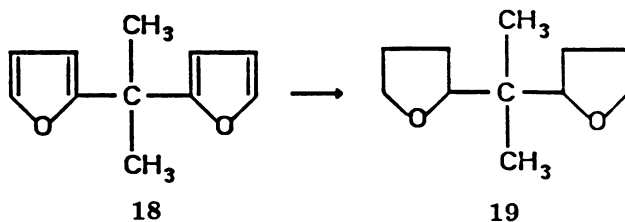
tional groups, such as hydroxyl or halogen, and isolated or conjugated double bonds (17).



Scheme 4

### Furan/Alkylfuran Condensation Polymers

Formation of the difurylalkane skeleton has been accomplished by condensation of a 2-substituted furan derivative with a carbonyl compound under acidic conditions; in other words, difurfuryl propane (18) has been produced by the condensation of furan with acetone (60).



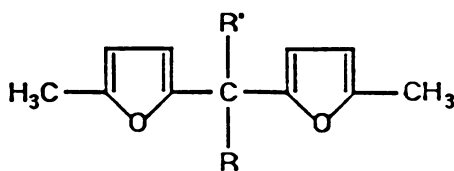
Scheme 5

Subsequent hydrogenation (Scheme 5) using a nickel catalyst affords the saturated ditetrahydrofurfuryl propane (19) (59). Ditetrahydrofurfuryl propane (60) is a solvent and co-catalyst for the selective polymerization of dienes to 1,2-polydienes.

Other 2-substituted furan derivatives, including 2-furfurylamine and 2-methylfuroate, have been condensed with aldehydes or ketones to form difunctional difuryl alkane derivatives (61). Previously, the condensation of 2-methylfuran with aldehydes and ketones, including formaldehyde, furfural, acetone, and the



like, have afforded di(methylfuryl) alkanes (20) (62). These chemicals can be functionalized to provide interesting monomers for further polymerization.

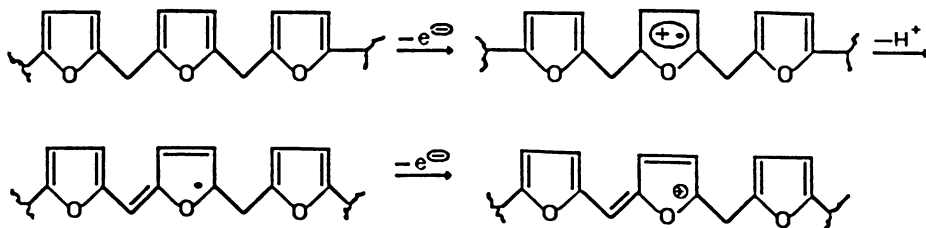


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Copolymers of acrylonitrile with furfuryl alcohol, furfuryl acetate, 2,5-bis-(hydroxymethyl) furan, and 2,5-bis(acetoxymethyl)furan by free radical catalysis have recently been reported (63). Proton and  $^{13}\text{C}$ -NMR spectroscopy characterizes the products as addition reactions to the 4,5-positions of furfuryl alcohol or the 2,3 addition to the 2,5-bis(hydroxymethyl) furan ring. These products are susceptible to acid and undergo a rearrangement that removes the clefinic structure. The copolymers are decomposed to a hard, glassy, carbonaceous material by heating in nitrogen. The conversion was studied by thermogravimetric and elemental analysis. The copolymers prepared from furan monomers containing a methyl group decompose more readily at a lower temperature than those lacking the group or those in which the alcohol has been acetylated.

### Furfuryl Acetate Polymers

Furfuryl acetate undergoes an interesting acid-catalyzed polymerization in acetonitrile to give poly(2,5-furandiyl methylene)(polyfurfuryl) (64). The polymerization is accompanied by chromophoric side reaction as evidenced by the polymer solution turning a deep green color. Because the investigators recognized that the color was very likely caused by polyconjugated species, they studied the chromophoric side reaction further as a possible route to a soluble conductive polymer (Scheme 6) (65).



Scheme 6

Cyclic voltammetry was used to determine the extent of electroactivity. Oxidation peaks were observed associated with the furan ring at positive voltage, while reduction peaks were observed at negative potential. Transient oxidation products are now present that can be reduced at less negative potentials. Electrochemical oxidation experiments exactly parallel those of chemical oxidation. In the electrochemical oxidation sequence, the loss of an electron from a furan ring generates a cation radical which, upon loss of a proton from the adjacent methylene group and a further one-electron oxidation, generates a delocalized cation. Successive sites on the same chain can be similarly oxidized by alternate steps of deprotonation and one-electron oxidation.

The resultant charged species can then take part in hydride, proton, and electron transfer equilibria in the solution. Intermediate oxidation products, which have not had time to engage in the bimolecular equilibria, thus have shorter lengths of conjugation. The behavior of oxidized polyfurfuryl in solution may prove to be a useful model for the conductivity of insoluble conductive polymers.

## Conclusions

While acid- or heat-cured polymers based on furfural and furfuryl alcohol have been of industrial significance for many years, new polymeric types based on difunctional derivatives and polymers derived from exploiting the dienic characteristic of furans are surfacing and present possibilities for unique performance properties. The potential availability of furfural as a byproduct from solvent pulping technology could provide the next generation of chemists with a feedstock competitive with oil and gas. These renewable agricultural resources offer significant new opportunity as chemical feedstock.

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# Chapter 30

## Polyurethanes from Renewable Resources

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Liquid polyols and diisocyanates specially synthesized from renewable resource materials have been used in separate studies to form various polyurethanes. The polyols studied were hydroxy-functionalized polytetrahydrofuran monoglucoside and bisglucoside, and poly-myrcene prepolymers. The polyols, characterized by end-group analysis, GPC, VPO and NMR, were reacted with 4,4'-methylene diphenylene diisocyanate (MDI) to form materials ranging from segmented copolyurethane elastomers to rubber-toughened, glassy polyurethane resins. In addition, different furan-based diisocyanates (FDI) with structures analogous to MDI were synthesized and characterized by elemental analysis, IR and NMR. Comparative kinetics studies indicated that FDI reactivities were intermediate between those of MDI and alkyl diisocyanates. FDI-based segmented copolyurethanes were formed using mixtures of polytetrahydrofuran and 1,4-butanediols. Polyurethane materials were evaluated by DSC, dynamic mechanical, tensile stress-strain, and fracture measurements. The feasibility of deriving liquid polyols and diisocyanates for polyurethane formation from agricultural and wood wastes is discussed.

Polyurethanes are a versatile class of polymers due mainly to their rapid and easy processing and to some excellent chemical and physical properties, which can be tailored to suit a very wide range of applications (1) including bulk

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plastics, elastomers, fibers, foams, surface coatings, and specialized adhesive products. Typically, the reactants used to form homopolyurethanes are polyisocyanates and polyols or, in the case of segmented copolyurethanes, polyols blended with chain extenders such as ethylene glycol or 1,4-butanediol. These reactants are generally obtained from oil-based sources.

The chemical and morphological structure and final properties of polyurethanes depend mainly on polyol structure, molar mass, and functionality, and, to a lesser extent, on the nature of the polyisocyanate. The stoichiometric ratio of isocyanate to hydroxyl groups, the amount of chain extender used, and the processing method also have significant effects on polyurethane properties (2). The polyols used are usually hydroxy-terminated polyether- or polyester-based liquids with mean molar masses in the range 500 to 7,000 g·mol<sup>-1</sup> and functionalities of 2 (diols), 3 (triols), and 4 (tetrols). Other low functionality hydroxy prepolymers are used, notably the liquid rubbers (2) based on polybutadiene and butadiene-acrylonitrile copolymers. Higher functionality polyols, although derived from nonoil-based polyhydric compounds such as sorbitol and sucrose, tend to result in the formation of stiff, brittle polyurethanes and are used mainly for rigid foam production.

The major polyisocyanates used (2) are toluene diisocyanate (TDI) and the less volatile 4,4'-methylene diphenylene diisocyanate (MDI), which, because it is a crystalline solid in the pure form, has to be used in a relatively "crude" form. The crude polyisocyanate is a mixture of MDI variants that is conveniently a liquid product with a mean functionality greater than 2. The use of a pure, liquid diisocyanate, however, would enable polyurethanes to be formed having relatively enhanced physical properties (2) and would also greatly simplify processing by removing the need to use elevated temperatures, solvents, or isocyanate prepolymers as with MDI.

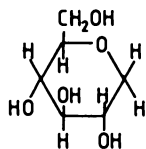
This chapter presents the results of studies on the syntheses and characterization of novel liquid polyols (3-6) and diisocyanates (7,8), and their use in the formation of various polyurethane materials. The polyols are of two different structural types, namely 1) liquid polytetrahydrofuran (PTHF) glycosides derived from glucose and PTHF diols and 2) liquid rubbers that are hydroxy-functional, substituted butadiene prepolymers derived from myrcene. Glucose and the furan-based PTHF diols, the precursors to the liquid glycosides, are both readily available from naturally occurring carbohydrate sources. The precursor to the liquid rubber, myrcene, is a terpene obtainable from the turpentine fraction of black liquor produced essentially as a waste product in the sulphite wood-pulping process used in papermaking. The liquid diisocyanates are pure difunctional compounds, analogous in structure to pure MDI, and are based on furan and its derivatives, commercially available in large quantities from agricultural waste products such as corn cobs and oat husks.

Comparative studies are presented that demonstrate that homopolyurethane and segmented copolyurethane elastomers and plastics and rubber-modified polyurethane glasses with properties similar to counterparts formed from oil-

based reactants can be derived from the renewable resource polyols and diisocyanates.

### Polyurethanes Based on Polytetrahydrofuran Glycosides

**Liquid Polyols from Glucose: Synthesis and Characterization.** Liquid polyols were prepared from  $\alpha$ -D-glucose (**1**) and the aglycon, a PTHF diol (**2**), by acid-catalyzed reactions under nitrogen at 130 °C in N-methyl pyrrolidone, NMP, solutions (*6-9*).

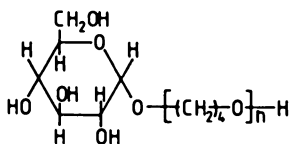


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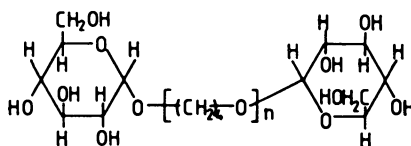


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Reaction of one mole of glucose with one mole of the aglycon yields PTHF-monoglucoside (**3**), whereas reaction of two moles of glucose with one of the aglycon yields PTHF-bisglucoside (**4**). The products are mixtures of anomers



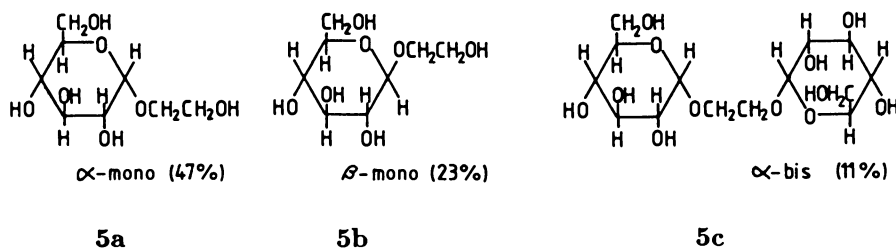
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(ca. 80% w/w) together with more complex products (ca. 20% w/w) as shown by Otey (*10*) for ethylene glycol glucoside (EGG (**5a-c**)) derived from starch via a transglycosidation reaction, *in bulk*, using excess ethylene glycol. Thus, structures **3** and **4** are idealized representations of the chemical structures of

the PTHF-glucosides and actually depict the  $\alpha$ -anomers, PTHF-mono or bis- $\alpha$ -glucosides that are present in the mixed product.



A range of monoglycosides and bisglycosides was synthesized (9) by varying the molar mass of the PTHF aglycon from 90 to 2,000  $\text{g}\cdot\text{mol}^{-1}$ , that is, increasing  $n$  from 1 to 28 in structures 2 to 4. (PTHF90 thus corresponds to 1,4-butanediol and yields a solid polyol glucoside similar to EGG, as discussed later.) The products were fully characterized, and typical data are presented in Table I for a monoglycoside, PTHF629m, and a bisglucoside, PTHF629b, prepared from PTHF629 ( $M_n = 629 \text{ g}\cdot\text{mol}^{-1}$ ) and glucose. Calculated values of molar mass ( $M_n$ ) and equivalent weight ( $E_n$ , the molar mass per OH group) were based on idealized structures 3 and 4 for PTHF629m and PTHF629b, respectively. The effective functionalities of both polyols toward MDI were determined as  $2.05 \pm 0.05$ . Glass transition, premelt crystallization, and crystalline melting temperatures,  $T_g$ ,  $T_c$ , and  $T_m$ , were determined by DSC; the aglycon, PTHF629, had values of -93, -67, and 16  $^\circ\text{C}$ , respectively.

Table I. Characterization Data of PTHF629m and PTHF629b Liquid Polyols

Polyol	$E_n^1$ ( $\text{g}\cdot\text{mol}^{-1}$ )	$E_n^2$ (calc)	$M_n^3$ ( $\text{g}\cdot\text{mol}^{-1}$ )	$M_n^2$ (calc)	$M_w/M_n^3$	$T_g$ ( $^\circ\text{C}$ )	$T_c$ ( $^\circ\text{C}$ )	$T_m$ ( $^\circ\text{C}$ )
PTHF629m	183.0	158.2	651	791	1.42	-87	-56	13
PTHF629b	154.0	119.1	663	953	1.43	-85	-45	14

<sup>1</sup>Acetylation, acetic anhydride.

<sup>2</sup> $E_n$  and  $M_n$  calculated from idealized structures 3 and 4.

<sup>3</sup>GPC, PPO calibration.

The percentage glucose conversions for PTHF629m and PTHF629b were 83.5 and 79.0%, respectively, and both polyols had less than 0.1% w/w residual



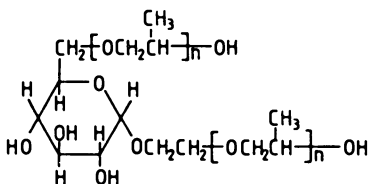
NMP solvent and low acid contents. The liquid polyols thus prepared and characterized were then amenable for direct use in bulk polymerizations with MDI to form polyurethane materials.

**Polyurethane Formation from Glycosides.** Relatively simple glycosides formed from carbohydrates by reactions with low molar mass aglycons are generally amorphous solids with high softening points or crystalline solids with high melting points. Additionally, these glycosides are highly polar and do not mix readily with diisocyanates as required for polyurethane formation in bulk. These features apply to EGG and to the monoglucoside from PTHF90 (1,4-butanediol) prepared in the present work. The PTHF90m was a solid, immiscible with MDI, and had a similar product distribution to EGG (5).

In order for such glycosides to be utilized for polyurethane formation, further chemical modification is required to reduce hydrogen-bonding interactions. Chain extension, often by alkoxylation at elevated temperature and under pressure, is used to obtain suitable liquid polyols. Otey (11), for example, has modified EGG in this manner in a *bulk* alkoxylation to yield polyols that could then be used to form polyurethane foams.

In the present work, however, a more controlled oxypropylation process (12) carried out in solution and at atmospheric pressure was developed and used to convert EGG into a liquid polyol. This polyol, with the idealized structure (6) in which  $n = 3$ , had an equivalent weight toward MDI of  $293 \text{ g}\cdot\text{mol}^{-1}$ .

On reaction of oxypropylated EGG with molten MDI (stoichiometric ratio,  $r = 1.01$ ) at  $50 \text{ }^\circ\text{C}$  for 5 minutes followed by curing at  $90 \text{ }^\circ\text{C}$  for 14 hours, a transparent, amber, glassy polyurethane resin was obtained. The  $T_g$  of the resin by DSC was  $57 \text{ }^\circ\text{C}$ , and its mechanical properties ( $23 \text{ }^\circ\text{C}$ ) were similar to poly(methyl methacrylate) with a Young's modulus of 2.78 GPa, tensile strength of 46.3 MPa, ultimate elongation of 2.6%, and Charpy impact energy of  $1.5 \text{ kJ}\cdot\text{m}^{-2}$ .



However, the disadvantage of using this route to liquid polyols and then to polyurethanes is that several separate stages are involved, and the chain extension stage, despite the success of the solution alkoxylation method, utilizes an oil-based chemical. The direct conversion of glucose by reaction with an aglycon from renewable resource, as described in the previous section, thus demonstrates the advantages and viability of a one-stage synthesis of liquid polyols. In addition, the acid hydrolysis of cellulose derivatives with *in situ* reaction involving low molar mass aglycons has also been shown to yield liquid polyols suitable for direct, bulk polyurethane formation (6).

The range of PTHF polyols synthesized by the one-stage glycosidation process was used to form various polyurethanes ranging in properties from soft elastomers to stiff plastics (9). The polyurethanes were formed by reaction of MDI with 1) PTHF diols, 2) PTHF-monoglucosides, and 3) PTHF-bisglucosides, both alone to yield homopolymers and blended with ethylene glycol (EG) to yield segmented copolymers with 48% w/w hard segment content. As examples, the formation and properties of polyurethanes are described for systems based on the PTHF629 polyols detailed in Table I. Each polyol, with and without EG, was reacted at 50 °C with molten MDI ( $r = 1.05$ ) for 5 minutes, cast into molds at ambient temperature, and then cured at 100 °C for 16 hours. The materials were characterized by DSC, dynamic mechanical analysis (DMA, torsion pendulum), and tensile stress-strain measurements. Comparative data for the homopolyurethane series, PU1 to PU3, and the copolyurethane series, c-PU1 to c-PU3, together with that for oxypropylated EGG, are shown in Table II.

Table II. Thermal and Mechanical Properties of Polyurethanes Based on PTHF629 Diols, Monoglucosides, and Bisglucosides

Material	Polyol	$E_n^1$	$T_g$ (°C)		$E^2$	$\sigma_u^2$	$\epsilon_u^2$
			DSC	DMA			
PU1	PTHF629	315	-32	-32	1.47	8.91	1,400
PU2	PTHF629m	183	-45	-44	0.387	0.02	1,100
PU3	PTHF629b	154	-46	-44	0.513	0.29	430
c-PU1	PTHF629/EG	315	-15	-5	609	12.70	2.2
c-PU2	PTHF629m/EG	183	29	30	1,900	24.10	1.2
c-PU3	PTHF629b/EG	154	36	50	2,940	13.30	0.4
Resin	Oxyprop. EGG	47	57	53	2,780	46.30	2.6

<sup>1</sup>Polyol equivalent weight (acetylation) in  $g \cdot mol^{-1}$ .

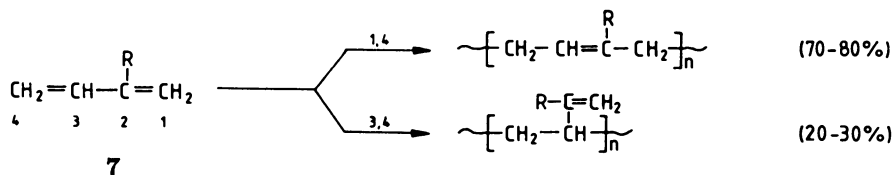
<sup>2</sup> $E$ ,  $\sigma_u$ , and  $\epsilon_u$  are tensile modulus, strength, and elongation.

Homopolyurethanes PU1 to PU3 were transparent, pale yellow/amber materials with properties typical of soft, highly extensible rubbers. Increasing

the proportion of glucose units tends to decrease  $T_g$  and to soften the rubbers. However, the opposite trends were observed in the copolyurethanes, which were opaque, phase-separated materials ranging from a white, semirigid plastic (c-PU1) to a dark brown, very stiff and brittle plastic (c-PU3). Although the copolyurethanes are clearly phase separated, the increase in  $T_g$  along the series as the glucose content increases indicates increasing degrees of phase mixing between PTHF629-based soft segments and EG/MDI-based semicrystalline hard segments. Overall, the incorporation of glucose units into copolyurethanes significantly improves the stiffness and strength of the materials.

### Polyurethanes Based on Hydroxy-Functionalized Polymyrccenes

**Liquid Polyols from Myrcene: Synthesis and Characterization.** A range of hydroxyfunctional prepolymers was prepared from myrcene (**7**) using hydrogen peroxide initiator in n-butanol solution at 100 °C (*9*). In the reaction (Scheme 1), R is  $-\text{CH}_2\text{CH}_2\text{CH}=\text{C}(\text{CH}_3)_2$  and the principal microstructural units shown were obtained by NMR (the 1,2 units being less than 4%). As the concentration of hydrogen peroxide used in polymerizations was increased from 0.5 to 5.4% w/w, the equivalent weight (acetylation) of the polymyrccene (PM) polyols decreased from 3,185 to 1,345, molar mass ( $M_n$ , GPC) decreased from 4,030 to 3,100, and the functionality increased from 1.30 to 2.32. The polydispersity,  $M_w/M_n$  (GPC), of the PM-polyols was unaffected. Some of the PM-polyols were then used either to form homopolyurethane and segmented copolyurethane elastomers or as reactive liquid rubbers to toughen highly crosslinked polyurethane resins.



Scheme 1

**Elastomers from Myrcene-Based Polyols.** A series of polyurethanes was formed using a PM polyol in admixture with various amounts of 1,4-butanediol (BD) and reacted with MDI (*4*). For comparison, a corresponding series of elastomers based on a commercially available polybutadiene (PB) polyol (Arco R45-HT, Cornelius Chemical Company) was also prepared. Characterization data of the PB and PM polyols are given in Table III.

Both series of polyurethanes were prepared using a prepolymer technique in which reactants were mixed at 70 °C/1 hour, cast into molds at 105 °C/2 hours, and cured at 80 °C/14 hours. The BD/MDI hard segment contents ranged from 0% (transparent, colorless homopolyurethanes) to 30% w/w (opaque, white copolyurethanes). All elastomers were characterized using DSC, dynamic mechanical, and tensile stress-strain measurements.

Table III. Characterization Data of PB and PM Polyols

Polyol	$E_n^1$ (g·mol <sup>-1</sup> )	$M_n^2$ (g·mol <sup>-1</sup> )	$M_w/M_n^2$	$f_n$	1,4-content (%)	$T_g$ (°C)
PB	1,088	2,919	1.70	2.7	65	-80
PM	1,322	2,950	1.39	2.2	68	-60

<sup>1</sup>Acetylation (acetic anhydride).

<sup>2</sup>GPC (PPO calibration).

The copolyurethanes comprise a two-phase morphological structure in which the continuous soft segment phase formed from the PM or PB polyols contains a dispersed, semicrystalline, glassy hard segment (HS) phase formed from MDI/BD oligomers. This two-phase morphology was confirmed by DSC and DMA analyses. Figure 1, for example, shows typical dynamic relaxation spectra for myrcene- and butadiene-based homopolyurethanes (0% w/w HS) and copolyurethanes (30% w/w HS). Overall, three molecular relaxations are observed occurring at increasing temperatures designated  $T_\beta$ ,  $T_g^S$ , and  $T_g^H$ .  $T_\beta$  at about -140 °C corresponds to small  $\beta$ -relaxations associated with secondary segmental motions within the PM and PB chains, whose intensity appears to decrease as HS content increases.  $T_g^S$  and  $T_g^H$  are, respectively, the glass transition temperatures of the soft segment phase and the amorphous regions of the hard segment phase. The location (and intensity) of the largest peaks at  $T_g^S$  (-35 and -60 °C for myrcene- and butadiene-based polyurethanes) are almost independent of HS content and indicate that these are well phase-separated materials. The relaxation at  $T_g^H$  (absent in the homopolyurethanes, HS=0% w/w) is much less intense than that at  $T_g^S$  as expected and is only evident in the myrcene-based copolyurethane as a broad shoulder between 0 and 100 °C.

These observations were confirmed by DSC data (4) obtained from samples quench-cooled from temperatures above 200 °C that gave  $T_g^H$ -values of about 80 and 60 °C, respectively, for myrcene- and butadiene-copolyurethanes. Corresponding  $T_g^S$ -values, -57 and -81 °C, from DSC were almost identical to the  $T_g$ -values reported in Table III for the parent polyols and confirm that phase

separation between hard and soft segments is almost complete in these materials. The melting behavior of the semicrystalline hard segment phase is complex with a clearly defined premelted crystallization exotherm occurring at 130 °C and a sharp crystalline melting endotherm ( $T_m$ ) at 210 °C for the 30% w/w HS myrcene-based material. The melting behavior of the butadiene-based copolyurethane was similar but less clearly defined.

The tensile stress-strain data showed the myrcene-based materials to be much softer and weaker, but more extensible than those based on the butadiene polyol, as shown in Figure 2 by the plots of tensile properties versus HS content. Differences between the two series were shown to be the result of higher sol-fraction contents and lower crosslink densities of the soft segment phase in the myrcene-based materials. The sol fraction of the myrcene-based homopolyurethane was 21.5% w/w, which decreased to 5.3% w/w at 30% HS content; the corresponding sol-fractions for the butadiene-based materials were 3.8 and 0.7% w/w. Analysis (4) of the sol-fraction extracted from the former showed the presence of low molar mass material formed from oligomers with hydroxy functionalities of less than two contained in the original myrcene polyol. Crosslink densities in terms of  $M_c$ , the mean molar mass of PM or PB network chains between crosslinks, were determined from Mooney-Rivlin (13,14) analysis of the tensile stress-strain data using the statistical theory of rubber elasticity. Even allowing for the presence of sol-fraction, the value of  $M_c$  (25,605 g·mol<sup>-1</sup>) for the PM network was much higher than that (3,934 g·mol<sup>-1</sup>) for the PB and, when compared with the  $M_n$ -value (2,950 g·mol<sup>-1</sup>) of the parent polyol, further confirmed the presence of low functionality species in the original myrcene prepolymer. The results overall, however, do show that substantial improvements in elastomer properties are achieved by incorporating a hard segment phase, and that polyols derived from myrcene can be used to form copolyurethane materials comparable to those formed from similar oil-based polyols.

**Glassy Polyurethane Resins, Rubber-Modified by Myrcene-Based Polyols.** In a previous study (15), highly crosslinked glassy polyurethanes, formed from fast-reacting systems (ca. 5 minutes), were shown to have properties equivalent to epoxy resins often used as adhesives. The epoxy resins, however, are intrinsically brittle but may be significantly toughened by incorporating a reactive liquid rubber during polymerization (16). During the competitive polymerizations, the developing high molar mass rubber and crosslinking resin become incompatible and phase separate to give a heterogeneous material comprising discrete and finely dispersed rubber particles in a highly crosslinked resin matrix. The liquid rubbers used to toughen epoxy resins are usually carboxyfunctional, butadiene-acrylonitrile copolymers.

In this study, the use of a PM polyol as a rubber modifier for a highly crosslinked, polyurethane resin ( $T_g = 150$  °C) was assessed again in comparison with an oil-based PB polyol. The polyurethane resin matrix was formed from pure MDI and a polyol blend comprising a polyoxypropylene triol, LHT240 (Union Carbide) of equivalent weight 227.6 g·mol<sup>-1</sup>, and trimethylol propane,

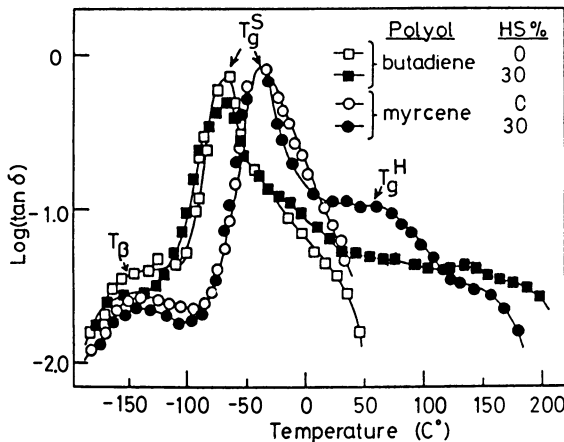


Figure 1. Dynamic relaxation spectra (torsion pendulum, 1 Hz) of polyurethanes based on polymyrcene and polybutadiene polyols. Typical relaxation peaks are shown at the temperatures designated  $T_{\beta}$ ,  $T_g^S$  and  $T_g^H$ .

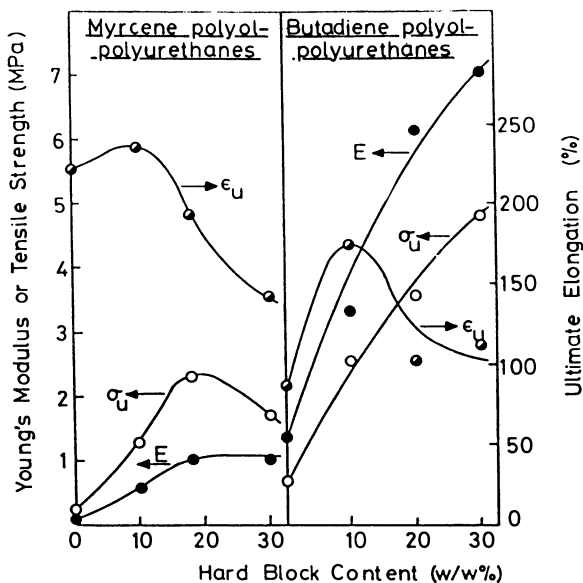


Figure 2. Variation of tensile modulus  $E$  (●), tensile strength  $\sigma_u$  (○), and ultimate elongation  $\epsilon_u$  (◐), with hard block content, for polyurethanes based on polymyrcene and polybutadiene polyols.

TMP, with a ratio of TMP:LHT240 equal to 9:1 by equivalents. A series of rubber-modified materials was prepared by a one-shot process (5,15) using increasing amounts of added hydroxy-functional PM (synthesized as described previously), with an equivalent weight of 1410, molar mass (GPC) of  $2,810 \text{ g}\cdot\text{mol}^{-1}$  and mean functionality of 1.99. The PB polyol used was that reported in Table III. All materials formed showed physical characteristics typical of amorphous, glassy polymers and were evaluated using DSC, tensile stress-strain, and Charpy impact measurements (5,15). The formation of a finely dispersed, particulate rubber phase was confirmed by scanning electron microscopy of fracture surfaces of various materials (Figure 3), and a high degree of phase separation between rubber and resin matrix was achieved. This implied minimal dissolution of rubber in the matrix and was confirmed by DSC data that showed the  $T_g$ -values (153 to  $156 \text{ }^\circ\text{C}$ ) of all materials to be almost independent of rubber content.

The tensile properties of the PM-modified series are summarized in Table IV together with one set of comparative data for a 4% w/w PB-modified material. Increasing the rubber content significantly improves material toughness in terms of  $U_y$  (the energy to rupture obtained from the area under a stress-strain curve) due to the increases in ultimate strain ( $\epsilon_u$ ) and tensile strength ( $\sigma_u$ ), despite the gradual and expected decrease in Young's modulus ( $E$ ). The improvement in toughness is observed to reach a maximum at rubber contents between 4 and 6% w/w; above 8% w/w, the properties begin to deteriorate rapidly with respect to the unmodified polyurethane resin. The Charpy impact data were obtained from razor-sharp notched beams in which the notch depth was systematically varied (5,15). The data were analyzed using the linear elastic fracture mechanics method of Williams (17) to give values of  $G_c$ , the critical strain-energy release rate, or absolute fracture energy, for each material. Values of  $G_c$  for rubber-modified materials relative to the unmodified matrix ( $G_c = 1.5 \text{ kJ}\cdot\text{m}^{-2}$ ) are plotted against rubber content in Figure 4 for both PM- and PB-modified series. The results show differences in toughening behavior between the PM and PB rubbers, with the former giving improved impact resistance with a maximum  $G_c$ -value at about 2% w/w rubber content, whereas, the polybutadiene-modified materials show a gradual and almost linear decrease over the composition range. The disparate fracture behavior may be attributed to differences in mean particle diameter,  $d$  (Table IV), and in the elasticity behavior of the dispersed homopolyurethane rubbers discussed in the previous section. Figure 4 also shows the variation of tensile toughness ( $U_y$ ) with rubber content from the data in Table IV illustrating the maximum in toughening enhancement at rubber contents between 4 and 6% w/w. This apparent anomaly between  $G_c$  and  $U_y$  data is attributed to the different nature and deformation rates of the impact and tensile tests.

Overall, the relatively brittle polyurethane resin matrix was transformed by the incorporation of a discrete rubber particle phase into a semiductile material

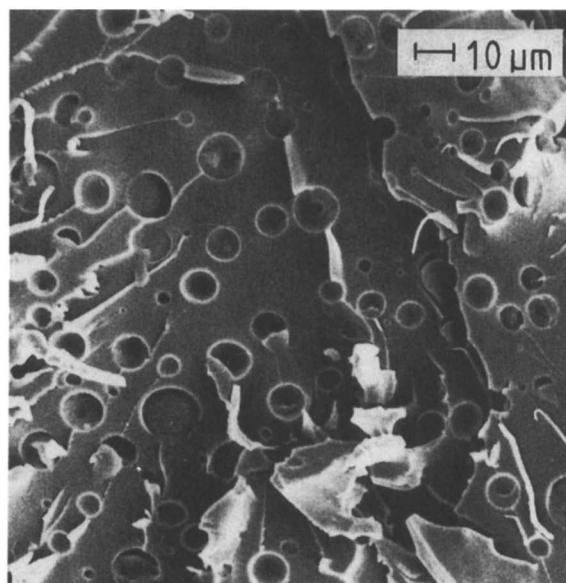


Figure 3. Scanning electron micrograph of a typical fracture surface of a highly crosslinked polyurethane resin containing 8% w/w of dispersed polymyrcene-based rubber particles.



with improved fracture properties, and these studies show that PM polyols are effective as rubber-modifiers for brittle resins.

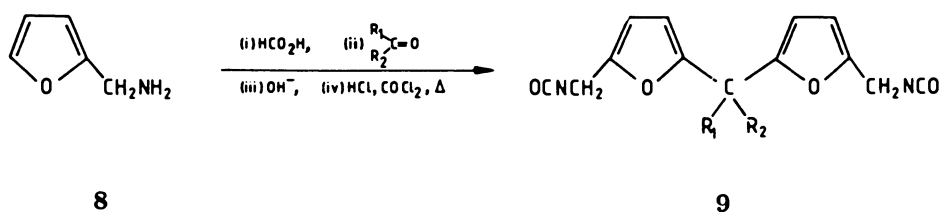
Table IV. Tensile Properties of Polymyrcene-Modified, Polyurethane Resins

Rubber	w/w (%)	d <sup>1</sup> (μm)	E (GPa)	σ <sub>u</sub> (MPa)	ε <sub>u</sub> (%)	U <sub>y</sub> (MJ·m <sup>3</sup> )
Matrix	0	—	3.00	79.4	4.8	1.92
PM	2	2.9	2.71	79.1	5.6	2.22
PM	4	3.2	2.76	81.4	7.1	3.08
PM	6	5.2	2.53	77.5	7.8	3.39
PM	8	5.8	2.34	67.0	5.6	1.90
PM	10	8.1	1.90	57.1	5.7	1.80
PB	4	11.8	2.73	82.2	8.3	4.90

<sup>1</sup>d = mean diameter of rubber particles.

### Polyurethanes from Furan-Based Diisocyanates

**Synthesis and Characterization of Furfuryl Diisocyanates (FDI).** Furan and its derivatives are obtainable from maize and oat husks and, as such, are attractive renewable resource materials for the synthesis of monomers and derived polymers. Furfurylamine (**8**) in particular is readily available and was chosen for the synthesis of a series of diisocyanates having structures analogous to the oil-based MDI used extensively for polyurethane production. Novel furfuryl diisocyanates of general structure **9**, in which R<sub>1</sub>, R<sub>2</sub> are either H, H or CH<sub>3</sub>, CH<sub>3</sub> or H, CH<sub>3</sub>, (Scheme 2) were prepared using a four-stage synthesis route reported in detail elsewhere (7).



Scheme 2

Essentially, the amine group on **8** had to be protected by conversion (i) to the formamide before the coupling reaction (ii), involving either formaldehyde, acetaldehyde, or acetone to generate the difuryl-alkane nucleus, could be effected.

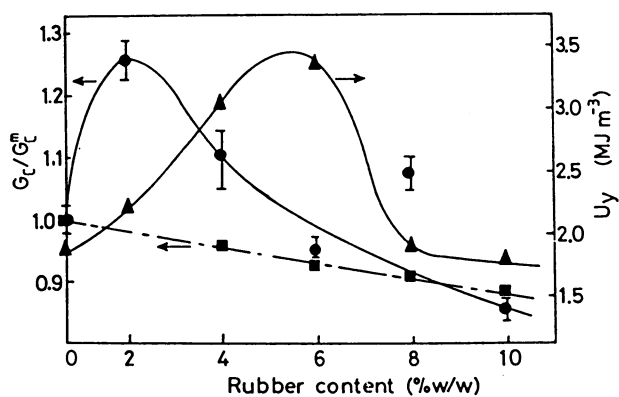
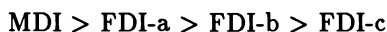


Figure 4. Variation of relative fracture energy,  $G_c/G_c^m$ , and tensile toughness,  $U_y$ , with rubber content for rubber-modified, highly crosslinked polyurethane resins.  $G_c/G_c^m$  (-●- polymyrcene, -■- polybutadiene);  $U_y$  (-▲- polymyrcene).

After coupling, the diformamide was hydrolyzed (iii) under alkaline conditions to give the diamine. Finally, the diamine was converted (iv) via the hydrochloride to the diisocyanate by phosgenation. The three diisocyanates, designated FDI-a ( $R_1, R_2 = H$ ); FDI-b ( $R_1 = H, R_2 = CH_3$ ); and FDI-c ( $R_1, R_2 = CH_3$ ), were purified by vacuum distillation with yields between 60 and 70% and were fully characterized by IR, NMR, and combustion analysis together with the preparation of suitable derivatives (7). The FDI compounds in the pure state were stable liquids down to at least 0 °C and showed little tendency to form crystalline dimer or other impurities on storage. The diisocyanates have molar masses comparable to pure MDI and possess low viscosities and volatilities (b.p.  $\approx 125$  °C at 0.02 mm Hg), making them highly attractive for bulk polyurethane formation.

Further characterization of the FDI compounds, in comparison with pure MDI, was obtained from urethane-forming kinetics data (7), following the method of Burkus and Eckert (18). Diisocyanates were reacted with n-butanol in toluene solutions at  $40 \pm 0.05$  °C using either triethylamine (TEA) or triethylene diamine (TED) as catalyst. The data were analyzed using second-order kinetics expressions in order to evaluate the apparent rate constants,  $k_{app}$ . Values of  $k_{app}$  for TED-catalyzed reactions for the FDI compounds ranged from 0.112 to 0.087  $\text{mol}^{-1} \text{min}^{-1}$ , compared with 1.5  $\text{mol}^{-1} \text{min}^{-1}$  for MDI, with the reactivity order decreasing along the series



Although less reactive than MDI, the furan-based diisocyanates were shown to behave as benzylic-type compounds with reactivities intermediate between those of aryl and alkyl diisocyanates.

**Formation of Polyurethanes from Furfuryl Diisocyanate, FDI-a.** Comparative studies were carried out on homopolyurethanes and copolyurethanes formed from FDI-a (F) and MDI (M) reacted with, respectively, PTHF diol (PTHF,  $M_n = 1,010 \text{ g}\cdot\text{mol}^{-1}$ ) and blends of PTHF and 1,4-butanediol (BD). FDI-a was chosen as it was the most reactive of the furan-based diisocyanates, and because of the methylene nuclear bridging group, it bore the closest structural resemblance to MDI. An end-capping process (7) was used to prepare copolyurethanes with increasing hard segment contents between 0 and 50% w/w. The overall stoichiometric ratio of NCO to OH groups was 1.05. For MDI-based polymers, an end-capping time of 15 minutes was used, but with FDI-a, longer times of 40 and 120 minutes were required to produce satisfactory materials. The polyurethane materials produced were characterized by DSC and DMA measurements.

The transition behavior from DSC studies, summarized in Table V, is consistent with the two-phase structure expected. The low-temperature glass-transition,  $T_g^S$ , is associated with the continuous (PTHF) soft segment phase, whereas, the transitions at  $T_g^H$  and  $T_m$  are associated with the amorphous and

crystalline regions, respectively, of the dispersed hard segment phase, formed from either FDI-a/BD or MDI/BD oligomers. Table V also shows transition data for homopolyurethanes M-PTHF and F-PTHF (isolated soft segment phases, transparent rubbers), and oligomeric homopolyurethanes M-BD and F-BD (isolated hard segment phases, whitish glassy powders). The lower  $T_g^S$ -values for F-PTHF and F50-B and the presence of  $T_g^H$  for F50-B (absent in M50) suggest the FDI-based materials to be more phase separated than those based on MDI. Also, the lower  $T_m$ -values of the crystalline F-BD hard segments reflect the more flexible nature of FDI-a in which the NCO groups are attached to the furan rings via methylene groups (9), whereas, in MDI, the NCO groups are attached directly to the benzene rings.

Table V. Transition Behavior (DSC) of Polyurethanes Derived from MDI (M) and FDI (F)

Polymer	Hard Segment (% w/w)	$T_g^S$ (°C)	$T_g^H$ (°C)	$T_m$ (°C)
M-PTHF	0	-55	-	-
F-PTHF	0	-67	-	-
M50	50	-61	( <sup>1</sup> )	181
F50-A <sup>2</sup>	50	( <sup>1</sup> )	( <sup>1</sup> )	112-121
F50-B <sup>2</sup>	50	-64	31	118-145
M-BD	100	-	84-89 <sup>3</sup>	193-209
F-BD	100	-	28 <sup>3</sup>	156

<sup>1</sup>Not observed.

<sup>2</sup>A and B refer to 40- and 120-minute, end-capping times.

<sup>3</sup>Quench-cooled, amorphous samples.

The dynamic mechanical results confirm the two-phase morphology present in both sets of copolyurethanes. Figure 5 shows typical shear modulus ( $G^1$ ) versus temperature behavior for FDI-a (F) and MDI (M) based materials containing 50% w/w HS. M50, an opaque, semirigid elastomer at room temperature ( $G^1 = 128$  MPa), showed an initial drop in modulus at  $T_g^S$  around -40 °C followed by a plateau region where the modulus decreases gradually until the onset of hard segment melting at about 180 °C. The furan-based materials, however, showed broad soft-segment transitions ranging from -60 to 40 °C, and their higher temperature behavior was strongly dependent on the end-capping time used during copolyurethane preparation. Thus, F50-A, a transparent rubber at room temperature ( $G^1 = 48$  MPa), was much less phase separated than F50-B, which is a translucent, semirigid elastomer ( $G^1 = 78$  MPa). Hence, the longer end-capping time enabled a higher molar mass soft-segment phase to develop in F50-B, resulting in a better phase-separated material with properties

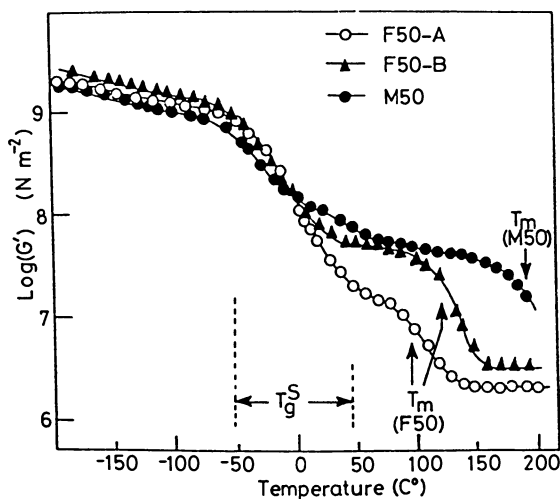


Figure 5. Dynamic shear modulus-temperature behavior (torsion pendulum, 1 Hz) of 50% w/w HS copolyurethanes based on diisocyanates FDI-a (F) and MDI (M). Soft segment glass transition and hard-segment melting are in the temperature regions indicated, respectively, by  $T_g^S$  and  $T_m$ .

closer to those of M50. Finally, despite the lower crystalline melting behavior of F50-A ( $T_m \approx 100$  °C) and F50-B ( $T_m \approx 120$  °C) shown in Figure 5, the modulus plateau above 150 °C is indicative of stable crosslinks that render the furan-based copolyurethanes more dimensionally stable compared to MDI-based materials at temperatures around 200 °C.

## Conclusions

These studies have shown that:

(1) Glucose can be reacted with an aglycon from a renewable resource in a one-stage synthesis to yield liquid polyols suitable for direct bulk polyurethane formation;

(2) Hydroxy-functionalized liquid rubbers can be prepared from myrcene that are suitable for polyurethane elastomer formation, and as rubber toughening agents;

(3) Pure liquid diisocyanates can be synthesized from the renewable resource furfural, and used with low and high molar mass diols also derived from furfural to form block copolyurethanes.

The overall physical and mechanical properties of the various materials prepared utilizing renewable resource diisocyanates and polyols have been shown to be comparable to those of materials derived from oil-based chemicals.

## Acknowledgments

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# Chapter 31

## Blood and Casein Adhesives for Bonding Wood

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Adhesives made from blood and casein were some of the first used in the wood products industry. They have been replaced in many applications by petroleum-based adhesives, which show improved performance or better economics. Despite this competition, they remain important in certain specialty areas due to their unique curing and bonding characteristics.

In the context of a book on adhesives from renewable resources, blood- and casein-based adhesives are worthy of mention because of their great historical importance to the adhesives industry. Caseins are particularly important because they were the first adhesives recognized for forming structurally capable bonds in wood products. They have been used since 1880; and they are still the preferred materials for many types of bonding due to their excellent adhesive properties and ease of cure. Despite their animal origins, these materials are far from plentiful. This makes them quite expensive in terms of wood adhesives, which is the viewpoint of this discussion. The review of the history, nature, manufacturing, and uses of these materials that follows may help to develop a perspective on their future usefulness to the adhesives industry.

### History

There is archeological evidence to indicate that early Egyptians used casein adhesives 5,000 years ago (1). Caseins have been used in Germany since about 1880 and in the United States since around 1900 (2). Impetus for the use of blood and caseins in wood gluing was generated by their extensive use in airplane construction during World War I (1-3). This led to broader commercial



use in furniture, plywood, and flush door manufacturing in the years that followed. Also during this period, casein glues were heavily promoted by adhesives manufacturers for all sorts of consumer uses. The list is too long to cover here, but it is interesting to note that it included such diverse applications as cementing linoleum, repairing plaster, bookbinding, making sandpaper, gluing rubber to metal, making tire paint, and repairing canoes. The list of industrial uses was nearly as amazing and included such applications as airplane propellers, masts for racing yachts, boats, roof trusses, and wooden automobile parts (5-8).

Despite the many consumer and wood gluing uses mentioned here, an estimated 75% of casein production went into paper coatings until World War II (4). Casein use for adhesives reached its peak in 1973, at about 121 million dry pounds (9). Today, very little casein glue is used by household consumers, paper coaters, and plywood manufacturers. In 1986, nearly all U.S.-casein adhesive production was used by the door manufacturing industry, where the total volume was less than 10 million pounds.

The use of blood glues by the plywood industry continued to grow until about 1960, mainly in response to overall industry growth. Almost 50 million pounds of blood were used for glue in 1960 (9). This declined to about 3.3 million pounds in 1980 (9) and to about 1 million pounds in 1986. Most blood glue usage was lost to competition from phenol-formaldehyde (PF) and urea-formaldehyde (UF) resins; use of these synthetic glues was aided by the invention of hot-pressing in 1932. The changes in casein volume usage are far more complex due to its larger range of uses. The historical trends for the usage of these materials may be summarized by saying that they have seen their zenith, and they are now gradually being replaced by synthetic materials.

### Raw Materials Production

The preparation of blood for adhesives involves the collection of fresh blood followed by immediate spray-drying to prevent putrefaction. This sounds very simple, but it is far from it. The spray-drying, storage, and handling all have significant effects on blood quality. The source of the blood (i.e., beef, hog, or chicken) and the presence of contaminants and microbes can also have dramatic effects. As a result of losses due to these factors, only a small percentage of the blood that is spray-dried is useful for wood adhesives. Scarcity makes the price of adhesive-grade blood quite high compared to synthetic alternatives.

Casein is the material that curdles when acid is added to skim milk. Most of us think of it as cottage cheese. It normally comprises about 3% of the weight of whole milk. Since the type of acid used for curdling has a noticeable effect on the quality and purity of casein, it is normally classified as lactic, hydrochloric, or sulfuric acid material. Lactic acid casein is the product of natural self-souring, although this is normally promoted by inoculating skim milk with lactobacillus. A small portion of casein is produced by the rennet process. This material is

primarily used by the plastics and cheese industries and is not important to adhesives.

After the skim milk is curdled at pH 4.6, the whey is drained off, and the curd is washed with water to remove the acid. The temperature of the wash water has a significant effect on the quality of the finished product. New Zealand casein is washed with boiling water that removes most of the acid, bacteria, and enzymes to give a high-grade casein. The water is squeezed out to a moisture content of about 50%, then the press-cake is broken up and oven-dried, normally by some continuous process. The drying method, uniformity of drying, drying temperature, drying time, etc., are all very important to the quality and storage stability of the finished casein. Drying processes range from sun-drying to cooking. The dried casein is ground, and then screened to various mesh sizes for packaging and shipping. The process described here is general, but there are as many variations as there are casein producers.

Due to the economic incentives for conversion of skim milk to powdered lowfat milk in the United States and Canada, nearly all of the casein used by U.S.-adhesives manufacturers comes from overseas. Casein has, at various times, been imported from 20 different countries. Australia, New Zealand, Uruguay, France, Norway, Holland, Ireland, and Argentina are probably the most important producers in the Western World today. The worldwide nature of casein production leads to a wide range in product quality.

### Raw Material Characterization

The active ingredient in blood glues is albumen. It is a protein with a molecular weight of about 69,000 (9). In the adhesives industry, the physical characteristics of the blood, such as solubility and viscosity in solution, are more generally used to characterize it than are more fundamental chemical traits. The suitability of blood for adhesives is generally determined on a supplier-by-supplier and lot-by-lot basis.

Casein has been well studied and is well characterized in the literature. Salzberg *et al.* (4) characterize it as a globular polypeptide of molecular weight 33,600 to 375,000, osmotic pressure measurements leading to lower values and sedimentation giving higher ones. Macy *et al.* (10), in their compilation of 1,500 reports, break casein down into the amino acids and elements shown in Table I. Since casein is variable, these are representative compositions. Commercial caseins for adhesives use are generally characterized as shown in Table II.

In general, high protein content and solubility are desirable casein properties. Fat, lactose, moisture, ash, bacteria, and odor are expected to be low. Light-colored material is also preferred. The viscosity and particle size sought depend on the compounding practices and intended use of the adhesive.

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## Making the Adhesive

The compounding of blood adhesives generally involves little more than the dry-blending of certain grades of blood with various fillers, extenders, and antifoams to obtain a product that will have the desired viscosity, mixing, and adhesive properties. Typical components of a modern blood adhesive might be 1 to 3 types of blood, 1 to 3 grades of wood or bark flour, soy flour, and antifoam agents. The blood content of the compounded adhesive will normally be 50 to 80% by weight. More than one grade of blood or flour is normally used to compensate for variability. Adhesive formulations are developed on the basis of gluing studies that simulate field use conditions and meet industry specifications. The main quality control tools are mixed viscosity development and stability over time.

Table I. Chemical Characterization of Casein

Elemental Analysis		Protein Components	
	%		%
Ash	0.06	1. Alanine	2.30
C	53.20	2. Arginine	3.77
H	7.02	3. Aspartic acid	5.80
N	15.55	4. Cystine	0.34
O	22.56	5. Glutamic acid	21.70
P	0.82	6. Glycine	0.40
S	0.76	7. Histidine	2.25
	99.97	8. Isoleucine	6.10
		9. Leucine	10.80
		10. Lysine	6.80
		11. Methionine	2.88
		12. Phenylalanine	5.50
		13. Proline	9.80
		14. Serine	5.40
		15. Threonine	4.35
		16. Tryptophan	1.22
		17. Tyrosine	5.96
		18. Valine	6.60

SOURCE: Reprinted with permission from ref. 10.

When the compounded adhesives are used in the mills, they are normally mixed with various alkaline materials and water to form the glue. The alkaline materials may be combinations of caustic soda, lime, soda ash, sodium silicate, and trisodium phosphate to obtain the right viscosity, working life, bond

strength, and durability. The blood content of the mixed glue will normally be less than 10%. The glued products are generally evaluated for dry strength and a one-cycle soak delamination and shear strength. About the only current use for blood glues in the wood products industry is in hot pressed plywood for carpet strips. Although blood glues will cold set, they are no longer used that way because of production costs. The advantage of blood glues for carpet strips lies in the high flexibility of the plywood product. This is obtained by virtue of the ability of the blood glue to tolerate high veneer moisture and to simultaneously achieve a rapid cure. Essentially all other plywood is made with UF or PF resin.

Like blood adhesives, caseins are usually compounded in dry form by the adhesive manufacturer. Unlike blood products, all of the alkali and other ingredients are added directly to the dry mix by the adhesive manufacturer. The mill mix is made by simply adding water. A great deal of technology goes into the compounding of a casein adhesive to ensure long storage life, easy mixing characteristics, adequate working life, reasonable cure speed, bond strength, and durability. The grade of casein specified is critical. Particle size must be large enough to prevent lumping and premature reaction with the alkali in dry form, but small enough to permit rapid dissolution. The casein must be coated with oil or some other protective film to further protect it from premature exposure to the alkali.

Table II. Typical Properties of Commercial Caseins

Property	Normal Values (dry basis)
Precipitation	lactic, hydrochloric, sulfuric
Protein	83 to 93%
Fat 0.9 to 2.0%	
Acidity (0.1N NaOH)	0.2 to 1.3 mL/g
Lactose	trace-1.0%
Moisture	8 to 12%
Ash	0.4 to 2.5%
pH (10% slurry)	4.2 to 4.8
Bacteria	ca. 2900 count/g
Viscosity (14% solution)	100 to 250 rmp (21 °C Stormer)
Solubility (15% borax)	3 to 12 minutes (60-65 °C)
Color	white - cream
Mesh analysis	as reported

The casein content of the dry adhesive varies from 30% to 70% depending on its use. Extenders and fillers such as soy and wood flours are added to obtain an economical adhesive. One or more alkalis such as sodium hydroxide, lime,

trisodium phosphate, soda ash, or borax are used. The balance of these materials is adjusted to obtain the right dispersion, solubility, viscosity, working life, and bond strength of the adhesive. A preservative such as pentachlorophenol, borax, or sodium fluoride is added to protect the adhesive from attack by mold, fungi, and insects. Carbon disulfide, zinc oxide, zinc sulfate, and other materials are added to improve water resistance. Recent legislative restrictions on certain preservative materials have reduced the attractiveness of many casein adhesives to manufacturers and users alike. Antifoam agents are used to facilitate mixing and spreading of the adhesive. A good analysis of the effects of adhesive formulation variables on adhesive characteristics is offered by Salzberg *et al.* (4). The manufacturing of casein is well covered by Spellacy (1).

### Performance Factors

Much of the loss in popularity of blood and casein glues results from their high cost and low durability relative to competing adhesives. In the area of bond strength, most synthetic resins do not surpass these materials. These are the only wood adhesives that are gap-filling and can be used without clamping. They are cold-setting. They are rigid and strong. Despite these virtues, the use of blood glues was rapidly curtailed when the price of PF solids dropped from about 27 cents a pound in 1960 to around 11 cents a pound in 1967. The added durability of PF adhesive brought changes in plywood specifications that eliminated blood from exterior uses except as additives to phenolic glue lines.

Casein adhesives experienced similar problems. Once the industry recognized that they were not waterproof, as was originally believed, they were rapidly replaced by resorcinols in most structural, cold-set applications where pressure was easily applied. Crosslinking polyvinyl acetates became preferable in some nonstructural, cold-set applications. Cheaper PF resins took over those exterior applications that allowed the use of heat and pressure. UF resins took over many interior applications on the basis of superior costs and mold resistance. Although the basic raw material cost is not a complete picture of the costs of its adhesive derivatives, it is a fairly good index. Table III shows how casein and blood compare with their competition at the present time. Although the exact prices of these materials fluctuate considerably, the approximate order of their costs has not changed much in the last 15 years. The materials are listed in order of cost.

### Conclusions and Outlook

The future of blood adhesives is definitely limited. They are expensive and nondurable. Raw material availability is limited and likely to be shrinking. It is probably only a matter of time until they are completely replaced by synthetic adhesives.

Caseins are relatively expensive. Their gap-filling and cold-setting characteristics give them an advantage in situations where heat and pressure may be

Table III. Approximate Costs and Durability of Common Wood Adhesives Systems

Basic Raw Material	Cost (1987 \$)	Durability <sup>1</sup>
1. Resorcinol	1.70	Waterproof
2. Casein	1.10	Water resistant
3. Isocyanate	0.90	Waterproof
4. Crosslinking polyvinyl	0.80	Water resistant
5. Melamine	0.70	Waterproof
6. Blood	0.45	Interior
7. Phenolic	0.30	Waterproof
8. Soy	0.15	Interior
9. Urea	0.08	Interior

<sup>1</sup>The approximate ranking of durabilities of wood adhesives in terms of water resistance is resorcinol = phenolic > melamine  $\approx$  isocyanate > crosslinking polyvinyl  $\approx$  casein > urea > blood  $\approx$  soy. The durability of caseins and polyvinyls can be considerably improved by the presence of catalysts and additives. Blood and soy are subject to attack by bacteria and mold, whereas, the synthetic adhesives are not. The apparent durability of an adhesive is dependent upon the substrate glued and the test method used for the evaluation.

objectionable, as in door manufacturing. They are durable enough to pass the door manufacturer's criteria for exterior use. Crosslinking polyvinyl acetate emulsions and other vinyl-based resins are now competing successfully in some door manufacturing applications. Caseins require inclusion of toxic materials to impart mold resistance. Many of these materials are now regulated, and this will have an unfavorable impact on both manufacturers and users. Caseins are no longer acceptable in waterproof applications such as marine use, structural beams, and plywood. They are far more costly than interior resins such as urea. They will be around, on an industrial scale, until door manufacturers modernize their plants, or they are regulated out of existence due to preservative requirements. Their thermal stability and excellent adhesive properties may preserve some small-volume, specialty applications for many years. As with bloods, however, the market for caseins is declining quite rapidly.

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# Chapter 32

## Development of a Microbial System for Production of Mussel Adhesive Protein

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The polyphenolic adhesive protein of the mussel *Mytilus edulis* is an unusual protein composed mainly of repetitive decapeptide and hexapeptide sequences. In the mussel, the protein is first produced in a precursor form and is converted to an adhesive by post-translational modification. To develop an efficient renewable resource for production of the polyphenolic protein, we have used genetic engineering technology. cDNA sequences encoding portions of the polyphenolic protein were identified and expressed in the yeast *Saccharomyces cerevisiae*.

Marine molluscs reside in turbulent aquatic environments in which survival depends upon adherence to a wide variety of surfaces (1). In response to such challenging conditions, mussels and other molluscs produce a byssus for strong, water-resistant adhesion (1-6). To the biotechnologist, the adhesion mechanism developed by these bivalves is of great interest because of the need to formulate adhesives that can be applied and cured in aqueous environments and that might be biocompatible. Although the commercial potential of this and similar adhesive materials has been well known for many years, its production is quite limited in the natural host, thereby restricting use for many potential applications (2). For example, the mussel adhesive can be extracted from the phenol gland, but only at quantities of about 10 mg per mussel (7).

Our research has focused on the efficient production of derivatives and analogs of the molluscan adhesives through recombinant DNA technology. This chapter discusses the development of yeast strains for production of mussel ad-



hesive and describes the important impact genetic engineering will have on the development of a potential new class of adhesives.

Waite and his colleagues have examined the process of adhesion in the mussel *Mytilus edulis* (1,2,7-10). Through a combination of biochemical and ultrastructural studies, Waite has determined that byssal adhesion is primarily controlled by a polyphenolic protein (2). Characterization of this protein has been greatly facilitated by the observation that the mussel retains small quantities in a preadhesive, noncrosslinked form in the phenol gland (8). A series of biochemical studies has revealed that the polyphenolic protein has an apparent molecular weight of 130,000 daltons and contains repeated decapeptides and hexapeptides with the sequence ala-lys-pro-ser-tyr-hyp-hyp-thr-dopa-lys and ala-lys-pro-thr-tyr-lys and hydroxylated derivatives (7-9). Both post-translationally hydroxylated residues (i.e., hydroxyproline and dopa) and unhydroxylated residues (i.e., proline and tyrosine) occur in the two peptides at the underlined positions. The post-translational hydroxylation of the tyrosine residues is unusual and likely plays an important role in determining adhesivity. It has been suggested that oxidized derivatives of tyrosine residues (dopa and quinone) play a crucial role in adherence and crosslinking and that lysine residues are involved in the crosslinks (2).

We have several objectives in mind in applying recombinant DNA technology to the study and application of the molluscan adhesives. By cloning DNA sequences encoding the polyphenolic protein, we will further elucidate the primary amino acid structure of this repetitive protein. For example, sequence analysis of the DNA molecule encoding the polyphenolic protein will reveal whether the protein is composed of tandem peptide repeats, and whether there are other unique regions that also play a role in adhesivity. Such knowledge will provide important insight into the character of adhesives developed by nature for aqueous environments. Expression of these cloned DNA sequences in a microorganism and subsequent purification will provide an important renewable resource for efficient production of adhesive proteins. In addition, the advanced state of DNA chemistry permits the rapid creation of synthetic genes that encode analogs of natural adhesive proteins (Anderson, D. M.; Strausberg, S. L.; Filpula, D.; Strausberg, R. L.; unpublished data). Through the use of synthetic DNA technology, microorganisms producing a family of adhesive proteins in which members differ in amino acid composition and molecular weight can be generated. We anticipate that in this protein family some members will be ideally suited to a particular commercial application, whereas, other members of the family be more appropriate for other applications.

This paper describes preliminary experiments that suggest that efforts in this area will be successful and result in the development of a new class of medically and industrially important adhesives.

## Experimental Methodology

**mRNA Isolation and Clone Bank Preparation.** Phenol glands were extracted from live mussels and homogenized in liquid nitrogen. The frozen tissue was dissolved in 4M guanidine thiocyanate as the first step in the RNA isolation procedure (11). mRNA was purified from total RNA using oligo-d(T) cellulose chromatography (12), and cDNA was prepared as described by McCandliss et al. (13). The cDNA was fractionated on a sucrose gradient because very little high molecular weight cDNA was obtained. cDNA molecules greater than 500 base pairs were pooled and cloned into  $\lambda$ gt10 (14) using *EcoRI* linkers. The recombinant DNA was packaged into bacteriophage  $\lambda$  heads for introduction into *E. coli* (15). As a host for titration and propagation of the phage, *E. coli* strain BNN102 (14) was used.

**Hybridization Screening of the Clone Bank.** A clone bank of approximately 500,000 plaques was developed for screening. The clone bank was plated at a density of  $\approx$  25,000 plaques per 14-cm dish and replicated in duplicate onto nitrocellulose filters (16) for hybridization screening. Clones carrying cDNA encoding the polyphenolic protein were identified by hybridization with an oligonucleotide probe (5' GCG AAA CCA AGT TAC CCA CCG ACC TAC AAA). The oligonucleotide was radioactively labeled to a specific activity of approximately  $10^8$  cpm/mg with  $\lambda$ -[ $^{32}$ P]-ATP and T4 polynucleotidekinase. The radioactive oligonucleotides (approximately 3.0 mg) were added to 250-mL hybridization solution containing 20% formamide, 6X SSC (17), 5X Denhardt's solution, 50-mM phosphate buffer (pH 6.8), 100 mg/mL sonicated denatured salmon sperm DNA, and 10% dextran sulfate. The filters were hybridized for 14 hours at 30 °C, then washed five times briefly with 300-mL 6X SSC at 22 °C, one time with 300-mL 1X SSC at 22 °C, and once at 42 °C for 30 minutes with 500-mL 1X SSC. The filters were air-dried and autoradiographed at -80 °C with Kodak XAR X-ray film for 12 hours.

Plaques giving signals by autoradiography on the duplicate filters were purified by picking, diluting, plating, and repeating the hybridization screen described above. Isolated individual plaques giving radioactive signals were picked and grown as plate lysates for DNA preparation (17).

**DNA Sequence Analysis.** DNA from  $\lambda$ gt10 clone 14-1 was digested with restriction endonuclease *EcoRI* and cloned into M13 mp11 (18). The bacteriophage M13 derivatives were constructed using methods described by Messing (19). Both orientations of the inserts were represented in independent clones that were sequenced by the dideoxy method (20).

**Yeast Genetics.** The yeast strain used in these studies was YGXD8 (MAT  $\alpha$  *leu2-3 leu2-112*). Yeast cells were transformed by the spheroplast method of Hinnen et al. (21). The transformed cells were maintained in YNB medium (0.7% yeast nitrogen base) supplemented with 5% glucose. For induction of polyphenolic protein synthesis, the cells were cultured in YP medium (1% yeast extract, 1% bacto-peptone) supplemented with 4% glucose and 2% galactose.

## Results and Discussion

**Isolation and Characterization of cDNA Clones Encoding the Polyphenolic Protein.** Characterization of the primary amino acid sequence of the mussel adhesive protein has been hindered by the large size of the protein and the repetitiveness of the amino acids. In such cases, the practical (and perhaps only) approach for determining the complete amino acid sequence is to clone DNA sequences encoding the protein and to deduce the amino acid sequence from the genetic code carried by that DNA. To accomplish this, we obtained mRNA from mussels and synthesized cDNA *in vitro*.

To screen for clones carrying cDNA encoding the polyphenolic protein, hybridization with an oligonucleotide probe (5' GCG AAA CCA AGT TAC CCA CCG ACC TAC AAA) was performed. The probe was designed based on the amino acid sequence of the decapeptide identified by Waite (9). Because of the degeneracy of the genetic code, it was not known how similar this oligonucleotide would be to sequences encoding the decapeptide in the mussel. Therefore, non-stringent hybridization conditions and duplicate filters were utilized to identify potential positive clones. Approximately 20 clones potentially carrying coding sequence for the polyphenolic protein were identified.

The first clone to be fully characterized by DNA sequencing was clone 14-1 (Figure 1). This clone appears to carry coding information for the carboxyl terminus of the polyphenolic protein. It contains the typical eucaryotic polyadenylation signal (AAT AAA), a poly A tail, and a 216 base 3' nontranslated region.

The coding sequence of clone 14-1 provides interesting insight into the organization of repeat units in the polyphenolic protein. The entire polypeptide sequence encoded by this clone consists of related peptides organized as tandem repeats (Figure 2). Coding sequences for the decapeptide ala-lys-pro-ser-tyr-pro-pro-thr-tyr-lys, identified by Waite as an important component of the polyphenolic protein, are present four times in the clone 14-1. However, the sequence complexity of the repeat units is much greater than expected, since out of 19 decapeptides encoded by clone 14-1, 14 different amino acid sequences are observed. An examination of these sequences provides useful insight into key amino acid organization in the mussel adhesive. Amino acids at positions 2 (lys), 5 (tyr), 6 (pro), and 9 (tyr) are identical in all decapeptides, and only a single decapeptide without lysine at position 10 is identified.

The high level of conservation of tyrosine and lysine residues suggests an important role for these amino acids and their post-translational derivatives in both adhesive and cohesive processes. As mentioned earlier, Waite has proposed that lysine and quinone residues are involved in protein crosslinking. Substitutions at other positions generally result in the presence of serine, threonine, proline (perhaps hydroxyproline), alanine, and isoleucine residues, with an emphasis on polar residues that can interact with most biological surfaces. The resulting protein is rich in the six amino acids: tyrosine, lysine, alanine, serine, threonine and proline. Preliminary characterization of cDNA clones encoding

```

                    5           10           15
GAA TTC CAT Lys Pro Lys Pro Ser Tyr Pro Pro Ser Tyr Lys Pro Lys Thr Thr Tyr Pro
EcoRI AAA CCA AAA CCA AGT TAT CCA CCA TCT TAT AAA CCT AAA ACA ACT TAT CCT

                    20           25           30           35
Pro Thr Tyr Lys Pro Lys Ile Ser Tyr Pro Pro Thr Tyr Lys Ala Lys Pro Ser Tyr Pro
CCA ACT TAT AAA CCT AAG ATA AGT TAT CCT CCA ACT TAT AAA GCA AAA CCA AGT TAT CCA

                    40           45           50           55
Ala Thr Tyr Lys Ala Lys Pro Ser Tyr Pro Pro Thr Tyr Lys Ala Lys Pro Ser Tyr Pro
GCA ACT TAT AAA GCA AAA CCA AGT TAT CCT CCA ACT TAT AAA GCA AAA CCA AGT TAT CCT

                    60           65           70           75
Pro Thr Tyr Lys Ala Lys Pro Ser Tyr Pro Pro Thr Tyr Lys Ala Lys Pro Thr Tyr Lys
CCA ACT TAT AAA GCA AAA CCA AGT TAT CCT CCA ACT TAT AAA GCA AAG CCA ACT TAT AAA

                    80           85           90           95
Ala Lys Pro Thr Tyr Pro Pro Thr Tyr Lys Ala Lys Pro Ser Tyr Pro Pro Thr Tyr Lys
GCA AAG CCA ACT TAT CCT CCA ACT TAT AAA GCA AAA CCA AGT TAT CCT CCA ACA TAT AAA

                    100          105          110          115
Pro Lys Pro Ser Tyr Pro Pro Thr Tyr Lys Ser Lys Ser Ile Tyr Pro Ser Ser Tyr Lys
CCA AAG CCA AGT TAT CCT CCA ACT TAT AAA TCC AAG TCA ATA TAT CCC TCT TCA TAC AAA

                    120          125          130          135
Pro Lys Lys Thr Tyr Pro Pro Thr Tyr Lys Pro Lys Leu Thr Tyr Pro Pro Thr Tyr Lys
CCT AAG AAA ACT TAT CCC CCC ACA TAT AAA CCT AAA CTA ACC TAT CCT CCA ACA TAT AAA

                    140          145          150          155
Pro Lys Pro Ser Tyr Pro Pro Ser Tyr Lys Pro Lys Ile Thr Tyr Pro Ser Thr Tyr Lys
CCA AAG CCA AGT TAT CCA CCA TCT TAT AAA CCT AAG ATT ACT TAT CCC TCA ACT TAT AAA

                    160          165          170          175
Leu Lys Pro Ser Tyr Pro Pro Thr Tyr Lys Ser Lys Thr Ser Tyr Pro Pro Thr Tyr Asn
TTG AAG CCA AGT TAT CCT CCA ACA TAC AAA TCT AAA ACA AGT TAC CCT CCT ACA TAT AAC

                    180          185          190          195
Lys Lys Ile Ser Tyr Pro Ser Ser Tyr Lys Ala Lys Thr Ser Tyr Pro Pro Ala Tyr Lys
AAA AAG ATC AGC TAT CCA TCA TCA TAT AAA GCT AAG ACA AGT TAT CCC CCA GCA TAT AAA

                    200
Pro Thr Asn Arg Tyr ***
CCA ACA AAC AGA TAT TAA TCT CAA TAT TAA AAG TAT TAA CTA AAA TAT TCA CAT TAC TGT

ACT ACA CAT TTT AAC GTT TGT ATT GAT GAG GAA CAG ATG AAC ATT TGA AAG TAA TAC ATA

ATC GGG GTT AAT GAT TTG TTA TAT TCA ATC TTA ATA TGT TTG TGA TTT GTT ATG TTC TTG

AAG TAT TGT TTC AAA TAA AGT TTA TTC TTT TCT GGT AAA AAA AAA AAA AAA GGA ATT CC
EcoRI

```

Figure 1. DNA sequence and translation product of 14-1 cDNA clone. The *EcoRI* sites at the 5' and 3' ends were generated by oligonucleotide linkers.

larger segments of the polyphenolic protein demonstrates that repetitive amino acid sequences account for most of the protein molecular weight.

**Insertion of the 14-1 cDNA Sequence Into a Yeast Expression Vector.** Based on the expectation that lower molecular weight derivatives of the polyphenolic protein might show adhesive properties (although tensile strength might be lower than for a full-length protein), a microbial production system was developed for this protein. Efficient expression of the polyphenolic protein in microorganisms presents an unusual challenge because of two characteristics of the polyphenolic protein. First, because the protein is composed of an unusual spectrum of amino acids, the microbial cell might have difficulty in translating the mRNA for this protein. For example, it has been suggested that codon choice in a heterologous mRNA may reduce microbial expression of foreign proteins because of limiting tRNA molecules in the cell (22). That effect could be more pronounced for a repetitive protein encoded by relatively few codons. Second, because the DNA sequence encoding the protein is also highly repetitive, DNA recombination might generate unequal crossover events (23), thereby resulting in production of an array of polyphenolic derivatives and reducing the reproducibility and quality of the product.

In spite of these potential difficulties, we have been successful in developing an efficient yeast production system for the polyphenolic protein. The yeast *Saccharomyces cerevisiae* was chosen for these studies because it is a safe organism with GRAS status; it naturally carries stable repetitive DNA sequences encoding protein products (24,25), and we have recently developed expression vectors capable of producing foreign proteins at levels of up to 20% of the total cell protein (Strausberg, R. L.; Strausberg, S. L.; unpublished data). This yeast has previously been used for production of a variety of pharmaceutical products (26-30).

To introduce the polyphenolic protein coding sequence into yeast, the DNA sequence was transferred from an M13 vector used for DNA sequence analysis into a yeast-*E. coli* shuttle vector, YpGX285 (Figure 3). This vector carries replication origins and selectable markers both for *E. coli* and *S. cerevisiae*, thereby permitting genetic constructions to be completed using *E. coli* cells, which simplifies the manipulations. For plasmid replication and maintenance in yeast, the plasmid carries a replication origin from the natural yeast 2-micron plasmid and the LEU2-D gene as a selectable marker (31). By growth in media lacking exogenous leucine, this plasmid can be easily maintained in yeast cells carrying mutations in the chromosomal LEU2 gene. Following transformation, the LEU2 gene product provided by the plasmid-borne gene allows the cells to grow in media lacking leucine.

For expression of the polyphenolic protein, the coding sequence is inserted into an expression cassette composed of a promoter, translation initiation sequence, signal sequence, and transcription terminator. The promoter sequence in YpGX285 is derived from two yeast genes, GAL1 (32) and alpha factor (MF- $\alpha$ 1) (25). This hybrid promoter provides for efficient, regulated, transcription of

```

Pro Lys Pro Ser Tyr Pro Pro Ser Tyr Lys
Pro Lys Thr Thr Tyr Pro Pro Thr Tyr Lys
Pro Lys Ile Ser Tyr Pro Pro Thr Tyr Lys
Ala Lys Pro Ser Tyr Pro Ala Thr Tyr Lys
Ala Lys Pro Ser Tyr Pro Pro Thr Tyr Lys
Ala Lys Pro Ser Tyr Pro Pro Thr Tyr Lys
Ala Lys Pro Ser Tyr Pro Pro Thr Tyr Lys
Ala Lys Pro Thr Tyr Pro Pro Thr Tyr Lys
Ala Lys Pro Ser Tyr Pro Pro Thr Tyr Lys
Pro Lys Pro Ser Tyr Pro Pro Thr Tyr Lys
Ser Lys Ser Ile Tyr Pro Ser Ser Tyr Lys
Pro Lys Lys Thr Tyr Pro Pro Thr Tyr Lys
Pro Lys Leu Thr Tyr Pro Pro Thr Tyr Lys
Pro Lys Pro Ser Tyr Pro Pro Ser Tyr Lys
Pro Lys Ile Thr Tyr Pro Ser Thr Tyr Lys
Leu Lys Pro Ser Tyr Pro Pro Thr Tyr Lys
Ser Lys Thr Ser Tyr Pro Pro Thr Tyr Asn
Lys Lys Ile Ser Tyr Pro Ser Ser Tyr Lys
Ala Lys Thr Ser Tyr Pro Pro Ala Tyr Lys

```

Figure 2. Repeat sequences encoded by the 14-1 cDNA clone.

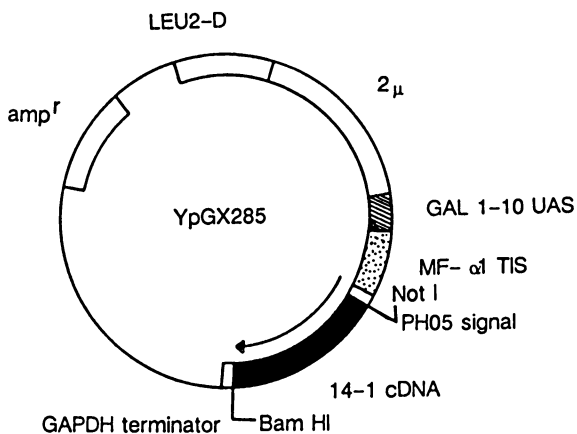


Figure 3. Yeast expression vector for production of polyphenolic proteins.

DNA sequences placed under its control. Expression of foreign genes is tightly controlled simply by adding galactose to the culture media, which induces expression from this promoter. Such regulated expression of foreign gene products is often desirable or essential because constitutive expression of the foreign gene product can limit cellular growth, resulting in selective pressure for nonproducing cells in the population.

The plasmid carries a PH05 (39) signal-coding sequence immediately 3' to the promoter sequence. Normally, a signal-coding sequence is present in an expression vector to direct secretion of the foreign protein from the cell. However, for expression of the polyphenolic protein, the PH05 signal sequence is present mainly to provide for efficient translation initiation of the foreign gene product. A methionine residue is positioned between the PH05 signal and polyphenolic protein to provide a cyanogen bromide recognition site for *in vitro* excision of the signal sequence. The YpGX285 vector also carries a transcription termination sequence derived from a yeast glyceraldehyde-3-phosphate dehydrogenase (GAPDH) (34) gene.

**Microbial Expression of the 14-1 cDNA Encoded Polyphenolic Protein.** Following transformation of a haploid yeast strain with the YpGX285 expression vector, initial studies were performed at the shake-flask level to determine whether polyphenolic protein was produced by the yeast cells upon galactose induction. Those studies demonstrated that the cells were producing the polyphenolic protein derivative and that the product was homogeneous and of the expected molecular weight.

Therefore, fermentation studies were conducted, first at the 2-liter scale and subsequently in 10-liter and 250-liter fermentors to determine efficiency of production and stability of the recombinant strain. An example of the results of these studies is shown in Figure 4. In this experiment, a batch fermentation was performed at the 2-liter scale. The cells were fermented in YP medium containing 4% glucose and 2% galactose as the carbon sources, and the insoluble cellular protein was examined by SDS polyacrylamide gel electrophoresis (35). Early in the fermentation, as glucose was being utilized, expression of the polyphenolic protein was not observed (Figure 4, lane A). As the glucose was depleted and galactose metabolism commenced (Figure 4, lanes B and C), production of the polyphenolic protein began and reached a steady-state level of about 5% of the total cell protein (Figure 4, lanes D-F).

Physiological studies of the recombinant yeast have shown that maintenance of the cells in media containing only glucose as the carbon source results in good genetic stability and cellular growth rates comparable to those of the nonrecombinant host strain. In addition, the plasmid-borne polyphenolic coding sequences undergo very little genetic recombination. The latter finding was unexpected because a priori we anticipated that a very repetitive DNA sequence carried by a plasmid replicating at high copy number in the cell would be a good substrate for genetic recombination. However, that has not been the case

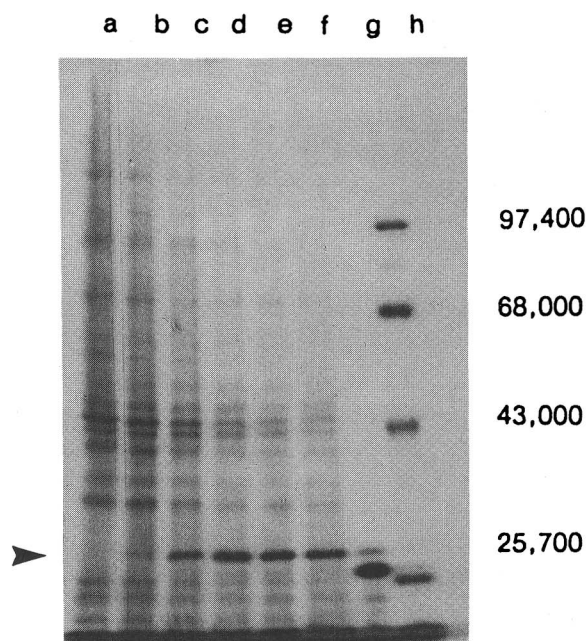


Figure 4. Regulated production of polyphenolic protein in yeast. The arrow indicates the polyphenolic protein. Purified yeast-derived polyphenolic protein, treated *in vitro* with cyanogen bromide, is present in lane G.



and suggests that yeast may be a very good production organism for proteins encoded by repetitive DNA sequences.

After fermentation, the yeast cells were harvested and broken mechanically in a bead mill, and differential centrifugation was used to partition the cellular components into water-soluble and insoluble fractions. SDS-polyacrylamide gel electrophoresis in conjunction with Western blot analysis (36) revealed that the polyphenolic protein aggregated with the insoluble cellular protein.

For the production of many recombinant proteins, cellular insolubility is a major problem because it is often difficult to achieve biological activity starting with such products (37). However, because the polyphenolic protein produced *in vivo* is a preadhesive, *in vitro* activation to the adhesive form is required. Therefore, *in vivo* insolubility may actually be desirable in the case of the polyphenolic protein because this could result in increased resistance to yeast proteases and better product uniformity and quantity.

**Purification of the Polyphenolic Protein from Yeast.** Unlike most insoluble yeast proteins, the polyphenolic protein is highly basic. This suggested that an efficient purification of the polyphenolic protein could be achieved by acid extraction of the total insoluble protein. After the cells were broken mechanically, cellular materials were segregated by centrifugation into water-soluble and insoluble fractions. The insoluble material was extracted into 70% formic acid, resulting in solubilization of the polyphenolic protein. After removal of the acid by rotary evaporation and several washes with water, the polyphenolic protein was precipitated with 10% sodium chloride in a dilute acidic solution. The polyphenolic protein is about 60% pure on a weight basis at this stage (T. Wei, unpublished data). Following resolubilization in 6M guanidine hydrochloride and 5% 2-mercaptoethanol, the partially purified proteins were chromatographed on a Sephacryl S-300 column. Fractions containing the highly purified polyphenolic protein were pooled, adjusted to pH 4.0 with acetic acid, dialyzed against 0.1% acetic acid, and then lyophilized. The recovered polyphenolic protein is at least 90% pure on a weight basis. If desired, the yeast PH05 signal sequence can be excised from the polyphenolic protein by cyanogen bromide cleavage.

**Conversion of the Microbially Produced Preadhesive to an Adhesive Protein.** The polyphenolic protein purified from yeast adheres to a wide variety of surfaces including glass and plastic. The adherence probably results from the presence of many polar residues capable of hydrogen bonding and lysine residues that can form ionic interactions. However, this protein does not generate water-resistant bonds to surfaces nor does it have cohesive strength. For those purposes, it is necessary to convert at least a portion of the tyrosine residues to dopa and permit crosslink formation to occur after surface adhesion is achieved. That is, it is necessary to mimic the natural mussel process in which the dopa form of the polyphenolic protein is applied and then rapidly

crosslinked. Therefore, it is important to demonstrate that these proteins can be hydroxylated *in vitro*.

Mushroom tyrosinase has previously been used to convert tyrosine residues in chemically synthesized polyphenolic decapeptides to dopa residues (38). This enzyme also can convert dopa residues to quinones, but the enzymatic product can be maintained in the dopa form if reducing conditions are utilized. Using mushroom tyrosinase, we have converted at least 50% of the tyrosine residues to dopa and have evidence for quinone-lysine crosslinks in an oxidizing environment (T. Wei and R. Link, unpublished data). When these conditions are carefully controlled, we have observed adhesive properties for the recombinant polyphenolic protein. We are currently studying the parameters that can increase adhesivity and moisture resistance through better surface interactions and more extensive crosslinking.

## Conclusions

**Future Research to Develop Genetically Engineered Molluscan Adhesives.** The preliminary tests of the recombinant polyphenolic protein suggest that, when hydroxylated, this type of protein will have the expected properties of strong, moisture-resistant adhesion. Studies currently underway will reveal whether this protein will be nontoxic and nonimmunogenic for *in vivo* medical and dental uses. Although characterization of the microbially produced mussel polyphenolic protein is in its early stages, it is likely that these studies will provide important insight into nature's mechanisms for solving the problem of long-lasting moisture-resistant adhesion. It will be interesting to compare the mechanism devised by the mussel with that of other invertebrates such as the barnacle. Our goal is to produce these generally unavailable adhesives in recombinant microbial systems, thereby providing an economical, renewable, commercial production source.

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# Chapter 33

## Adhesives from Marine Mussels

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The common blue mussel, *Mytilus edulis* L., has evolved an adhesive mechanism that performs optimally in the marine environment. The functional unit of this system is a polyphenolic protein (MAP) rich in 3,4-dihydroxyphenylalanine (L-dopa) and lysine. Several systems that demonstrate the utility of this adhesive protein have been developed. This extracted protein alone is a highly efficient mediator of the attachment of mammalian, yeast, and bacterial cells to inert substrates. Two-part adhesive formulations were examined *in situ* for tissue repair efficacy on ocular tissues. *In vitro*, corneal permeability studies showed that the ocular formulation of MAP freely allows the diffusion of even high molecular weight (42K) moieties, and that proteolytic enzymes will attack the adhesive matrix. The biocompatibility of MAP alone and MAP adhesive formulations was evaluated using mammalian cell growth rate and cell growth inhibition assays *in vitro*. The environment of the sea is similar in many ways to the internal environment of mammalian organisms. Tissues are bathed in fluids with a pH and ionic and enzymatic composition similar to saltwater. Theoretically, the attachment mechanisms that some marine invertebrates have evolved for survival should be useful as surgical or wound repair adhesives *in vivo*.

Best understood of the invertebrate adhesive-mediated attachment mechanisms is that of the common blue mussel, *Mytilus edulis*, and its close relative, *Mytilus californianus* L. The "mechanism" includes the byssus, an acellular proteinaceous organ produced by glands inside the mussel, combined with a delivery system that secretes the byssus efficiently underwater. The protein that is the functional unit of the adhesive mixture was first purified from the gland where it originates and characterized by Waite and Tanzer (1). Called mussel adhesive protein (MAP), it is a high molecular weight ( $120,000 \pm 10,000$  MW) basic protein,

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rich in lysine, hydroxylated amino acids, and 3,4-dihydroxyphenylalanine (L-dopa).

While the composition and sequence of the amino acids have been known since 1983 (2,3), methods for increased-scale extraction were not developed until 1985. This scaled production has allowed for the development of single-part adhesive systems (Cell-Tak adhesive) for the immobilization of biologically active moieties to inert substrates. It has also permitted research on two-part adhesive formulations for the bonding of tissues. This paper specifically addresses the biocompatibility issue with descriptions of the immobilization of cells to Cell-Tak protein-coated plasticware, methods for wound closure, and preliminary toxicology data.

### Experimental Methodology

**Cell Attachment Mussel Adhesive Protein (MAP).** MAP has been specially formulated for delivery to an inert substrate in single-component form for the immobilization of biologically active materials (Cell-Tak). Three mammalian cell types were used to compare attachment to Cell-Tak adhesive with attachment to uncoated tissue culture plasticware and plasticware coated with other commercially available attachment factors. Baby hamster kidney cells (BHK-21; ATCC CCL 10) were grown in modified Eagle's medium (MEM) containing 10% calf serum and 10% tryptose phosphate broth. Human histiocytic lymphoma cells (U-937; ATCC CRL 1593) were grown in RPM1 1640 medium containing 10% calf serum. Bovine corneal endothelial cells (BCE) derived from primary isolates were maintained in MEM plus 15% calf serum. The attachment of two bacteria, *Staphylococcus aureus* and *Escherichia coli*, and one yeast, *Saccharomyces cerevisiae*, to MAP-coated plasticware and uncoated plasticware was also evaluated. All three organisms were grown in trypticase soy broth.

Cell-Tak protein was coated on tissue culture plasticware by a solution casting method. For all experiments, 5  $\mu\text{L}$  of the 10 mg/mL solution was spread and dried onto 35-mm, 10-cm<sup>2</sup> plastic dishes for a final density of 5  $\mu\text{g}/\text{cm}^2$ . After being air dried, the plates received one ethanol (95% v/v) and two distilled water rinses. All other attachment factors were used according to manufacturers' recommendations. Collagen (Ethicon, Inc., Somerville, NJ)-coated plates were prepared by diluting one part cold (4 °C) collagen dispersion (6 mg/mL) into six parts of cold 50% methanol. This mixture was vortexed vigorously for several minutes and pipetted onto a tissue culture dish so that only the bottom of the dish was covered. Within 20 seconds, the collagen was removed by aspiration, and the dish was inverted such that it rested against a lid at a 30° angle. Following 1 hr of undisturbed drying in a laminar flow hood, the dishes were ready for use. Laminin (Collaborative Research, Lexington, MA) was supplied in 1-mg quantities in 1 mL of 50 mM Tris solution in physiological saline. Following a slow thaw of laminin solution at 0 to 4 °C from -20 °C storage, 10 to 15  $\mu\text{g}$  of laminin solution was pipetted onto tissue culture petri

dishes in 0.5 mL of 0.01M phosphate buffer, pH 7.4, the dishes were dried at 37 °C. Immediately upon drying, the dishes were prepared for use. Fibronectin (Collaborative Research, Lexington, MA) was supplied in 1-mg quantities as a lyophilized powder. Prior to use, fibronectin was allowed to equilibrate to room temperature after 4 °C storage. The powder was reconstituted with 1-mL sterile distilled water and allowed to stand for 30 min for solubilization. Twenty  $\mu\text{g}$  of fibronectin were added to each tissue culture dish in 0.5 mL and allowed to air dry. At this time, the dish was ready for cell seeding. High-molecular-weight poly-D-lysine (Collaborative Research, Lexington, MA) was supplied in quantities of 5-mg lyophilized powder. Prior to use, this powder was allowed to equilibrate to room temperature after 4 °C storage before solubilization. Dishes were coated with 50  $\mu\text{g}$  in 1 mL of sterile distilled water and allowed to stand at room temperature for 5 min. At that time, the solution was aspirated and the dishes rinsed two times with 1.5 mL of sterile distilled water. Following each rinse, liquid was aspirated for complete removal of unattached polymer. The dishes were dried and used immediately.

The attachment assays were designed to quantify attached cells after various incubation periods at 37 °C. BHK and BCE cells were trypsinized from stock plates, washed in fresh medium by centrifugation, and suspended in fresh RPM1 1640 with 10% calf serum at a density of  $2 \times 10^5$  cells/mL. U-937 cells, which are grown in suspension, were washed by centrifugation and resuspended to similar densities. Suspensions were seeded onto untreated tissue culture dishes (control) and dishes treated with attachment factors. At 5, 12.5, and 20 min, triplicate experimental and control plates were chosen at random for quantification of unattached cells. These were removed from the dishes after gentle agitation and counted on a hemacytometer. Data were calculated as percent of cells attached by subtracting the number of unattached cells obtained from dishes (average of three) from the total number of cells plated, dividing the result by the total number of cells plated, and multiplying the quotient by 100%.

A similar type of assay was done with bacterial and yeast cultures treated similarly. Cultures were washed by centrifugation in 0.1 M phosphate buffer (pH = 7.0) and resuspended to an  $\text{OD}_{580} = 0.3$ . Attachment after 30 min at room temperature to plastic and Cell-Tak-coated plastic was evaluated qualitatively by microscopic visualization.

The growth rate of mammalian cells in the presence of Cell-Tak adhesive was assayed to evaluate any potential adverse effects caused by this protein. Bovine corneal endothelial cell (BCE) stocks were grown to confluency in MEM plus 15% calf serum, trypsinized, and washed several times by centrifugation on MEM. Suspensions ( $5 \times 10^4$  cells/mL) were seeded onto untreated 35-mm dishes (control) and dishes with Cell-Tak protein ( $5 \mu\text{g}/\text{cm}^2$ ) in MEM with 15% calf serum. At various time points during the incubation at 37 °C with 5%  $\text{CO}_2$ , triplicate plates were removed. The attached cells were then trypsinized from the surface, washed, and counted in a hemacytometer.

**Ocular Tissue Bonding *In Vitro*.** Two model systems were designed for the evaluation of MAP adhesives *in vitro*. Bovine eyes obtained the same day from abattoirs were always used.

The first system was developed to demonstrate the ability of MAP to strongly adhere to corneal stroma as a prelude to repairing wounds *in situ*. This system also assisted in the development of MAP formulations and protocols for use. Endothelial and epithelial cells were removed from freshly isolated bovine cornea by scraping, and a 1-cm<sup>2</sup> area from each of two sections of cornea was treated with 50  $\mu\text{g}$  of MAP. The sections were bonded by overlapping the two strips and allowing them to set (or cure) at room temperature. The tissue was kept moist and flat by overlaying with a distilled water-filled dialysis bag. After 20 min, the corneal bond was subjected to a shear test to determine adhesive strength. One end of the overlap joint was suspended vertically from a clamp, and a second clamp was attached to the lower end together with an empty plastic bag. Weight was increased to the joint at a constant rate of 14 g/min by the addition of water to the bag using a peristaltic pump. At joint failure, the water flow was turned off, and the bag was weighed to yield bond strength. Adhesive strength was considered to be the maximum weight of water suspended divided by the bond area and is represented in g/cm<sup>2</sup>.

The second model system was designed to demonstrate the feasibility of using MAP adhesives in sealing small and large tissue perforations. Epithelial cells from whole bovine eyes were removed with a scalpel from a 15- to 20-mm region of the cornea. A perforation was prepared by lacerating the center of the scraped cornea with a scalpel. An 18-gauge needle attached to a 10-mL syringe containing saline was inserted into the anterior chamber at the corneal/scleral junction. A full thickness perforation was assured by inserting saline into the anterior chamber and looking for fluid leakage through the corneal puncture. The scraped area was then rinsed with deionized water and excess water is removed by swabbing. MAP adhesive (50  $\mu\text{g}/\text{cm}$ ) was then applied immediately peripheral to the perforation site. A hydrogel therapeutic contact lens (Hypan, Kingston Technologies, Inc.) that had been presoaked for 30 min in phosphate-buffered saline (PBS) was overlaid onto the wound site and gentle pressure added to the lens-corneal interface to ensure direct apposition of the patch to the tissue. A dialysis bag was applied over the joint for 20 min during curing. Strength of bond was measured using a manometer attached to the needle inserted into the anterior chamber.

The dialysis bag was removed and the eye pressurized at about 120 in/min with a syringe connected to the manometer, while leakage and pressure were monitored. The water pressure recorded was the reading attained at the first sign of leakage. The pressure was converted to mm Hg by dividing by 0.535. Data represent the average of at least two assays.

**Biocompatibility at the Cell Culture Level.** The evaluation of cytotoxicity on a cell culture agar overlay following the application of liquid MAP, liquid enzymatic crosslink catalyst, and extracts of crosslinked solids was done to de-

tect the response of a mammalian cell culture monolayer (mouse L-929, ATCC CCL 81) to readily diffusible components of the preparations. Liquid MAP (4.0 mg/mL) in water and catechol oxidase (4.5 mg/mL, Sigma Chemical Company) in 0.1M phosphate buffer were used as is. Two formulations, one high crosslinked (15 U enzyme:1  $\mu$ g MAP) and one low crosslinked (5 U enzyme:1  $\mu$ g MAP), were prepared by allowing the reaction to occur for 1 hr at room temperature followed by quick freezing and lyophilization. The resultant flakes were extracted with irrigation saline (USP), cottonseed oil, and ethanol (95% v/v) at 20-mL solvent per 6.0-mg flakes at 60 °C for 4.5 hr. The supernatants were used in the assay within 24 hr.

The mouse L-929 fibroblast line was cultivated in Eagle's Minimal Essential Medium (MEM) plus 10% calf serum. Cells were seeded in 100-mm-diameter cell culture plates at  $4 \times 10^6$  cells per plate and allowed to become established for 24 hr prior to use. After the monolayer was washed, 10 mL of an agar overlay consisting of 2% Bacto-Agar and 2 x MEM was added to each plate and allowed to solidify.

The extracts and liquid components were delivered in duplicate to the agar as 20- $\mu$ L liquid on 1-cm-diameter Whatman No. 2 filter paper. The solids (100  $\mu$ g) were implanted directly onto the agar. Negative controls included filter paper with 20  $\mu$ L of each solvent and filter paper with no solvent. The positive control was polyvinylchloride (PVC) sheeting containing 1% tin stabilizer (Travenol Laboratories, Inc.), cut into 1-cm-diameter disks and implanted directly onto the agar. Plates were incubated at 37 °C in a humidified incubator with 5% CO<sub>2</sub> for 24 hr. At this time, all plates were fixed with 10% buffered formalin and rinsed with water, the agar was peeled off, and the cells were stained with 0.1% neutral red solution for 15 min. The areas of lysis zones were measured, and lysis indices were calculated as described later in this paper (see Table III in the results section). Appearance of the monolayer surrounding the test or control sample was described as nontoxic (same as untreated monolayer), slightly toxic (pink but not as darkly stained as untreated monolayer), or toxic (very faint pink or no color).

A quantitative approach was taken to evaluate the effect of various concentrations of water extracts of the two crosslinked solids and individual liquid components on cell growth of L-929 cells *in vitro*. Both cells and adhesive materials were prepared as described above. For this assay, dilutions of an aqueous extract of the solids were prepared for a dose-response evaluation. The following weight per volume ratios were used: 4,000, 500, 100, 50, 4, 3, 2, 1  $\mu$ g per 20-mL water. Extraction was performed for 4 hr at 60 °C followed by 20 hr at room temperature. Supernatants were transferred to clean containers. The negative control consisted of sterile, triple distilled water, and the positive control was 40 mg/mL dextran sulfate.

Mouse fibroblast cells (L-929), trypsinized from stock plates, were suspended in complete Eagle's Medium at a density of  $10^6$  cells per mL. For the assay, liquid extracts (1-mL final volume) were mixed with 1-mL double strength MEM, to



which 0.2 mL of the cell suspension ( $2 \times 10^5$  cells) was added at time zero. Ten replicates were made for each extract. Immediately after mixing, five tubes were centrifuged and the cells washed and resuspended in phosphate buffered saline (PBS) and stored at 4 °C for zero time reference points. After 72-hr incubation at 37 °C in a humidified incubator, during which time the cells had grown in monolayers, the remaining tubes were decanted, the monolayers were washed gently and trypsinized. The cells were recovered and washed twice by centrifugation with PBS.

The extent of cell growth as indicated by total protein concentration was done using the Folin-Phenol method of Lowry (4) with a bovine serum albumin standard on cell samples solubilized with 0.05% sodium lauryl sulfate. Data are presented as percent inhibition of cell growth relative to untreated controls.

## Results

**Cell Attachment to MAP.** The attachment of two cell types, one anchorage-dependent and the other anchorage-independent, was compared over time on Cell-Tak adhesive-coated dishes with the attachment on other commercially available factors. BHK-21 cells normally attach and grow in monolayers. Figure 1A graphically shows the attachment of BHK-21 cells, which attained 70 to 90% efficiency in 20 min to laminin, fibronectin, and Cell-Tak adhesive and 60% to poly-D-lysine. Maximum attachment occurred at a faster rate on Cell-Tak protein, where 90% efficiency was achieved in 12.5 min. The anchorage-independent, or suspension cell line, U-937, achieved 75-85% attachment efficiency on Cell-Tak adhesive (Figure 1B) but less than 30% attachment to any of the other factors.

The mechanism by which Cell-Tak protein accomplishes this efficiency at the molecular level is addressed with the observation that different cell types attach with the same kinetics (Figure 2A). The lymphoma line (U-937), BHK cells, and bovine corneal endothelial cells attach with varying efficiencies to plastic (Figure 2B) but exhibit the same rate and overall efficiency on Cell-Tak protein. The attachment lacks the specificity that would indicate receptor-mediated attachment and supports the roll of nonspecific interactions. Moreover, other data (not shown) suggest that the attachment of cells is due to Cell-Tak and not to any component such as fibronectin that is found in serum. This is seen in experiments involving the preincubation of Cell-Tak-coated dishes with either fibronectin or serum. Cell-Tak-coated plates were preincubated with cell culture medium containing 20% calf serum for 30 min, and fibronectin was dried onto other plates coated with Cell-Tak before U-937 cells were plated. Cell attachment on fibronectin-coated Cell-Tak plates was identical to attachment to Cell-Tak alone, and attachment efficiency was inhibited by 40% on plates preincubated with serum.

The immobilization of microorganisms to Cell-Tak protein was monitored microscopically. Figures 3, 4, and 5 show the sparse attachment to plastic

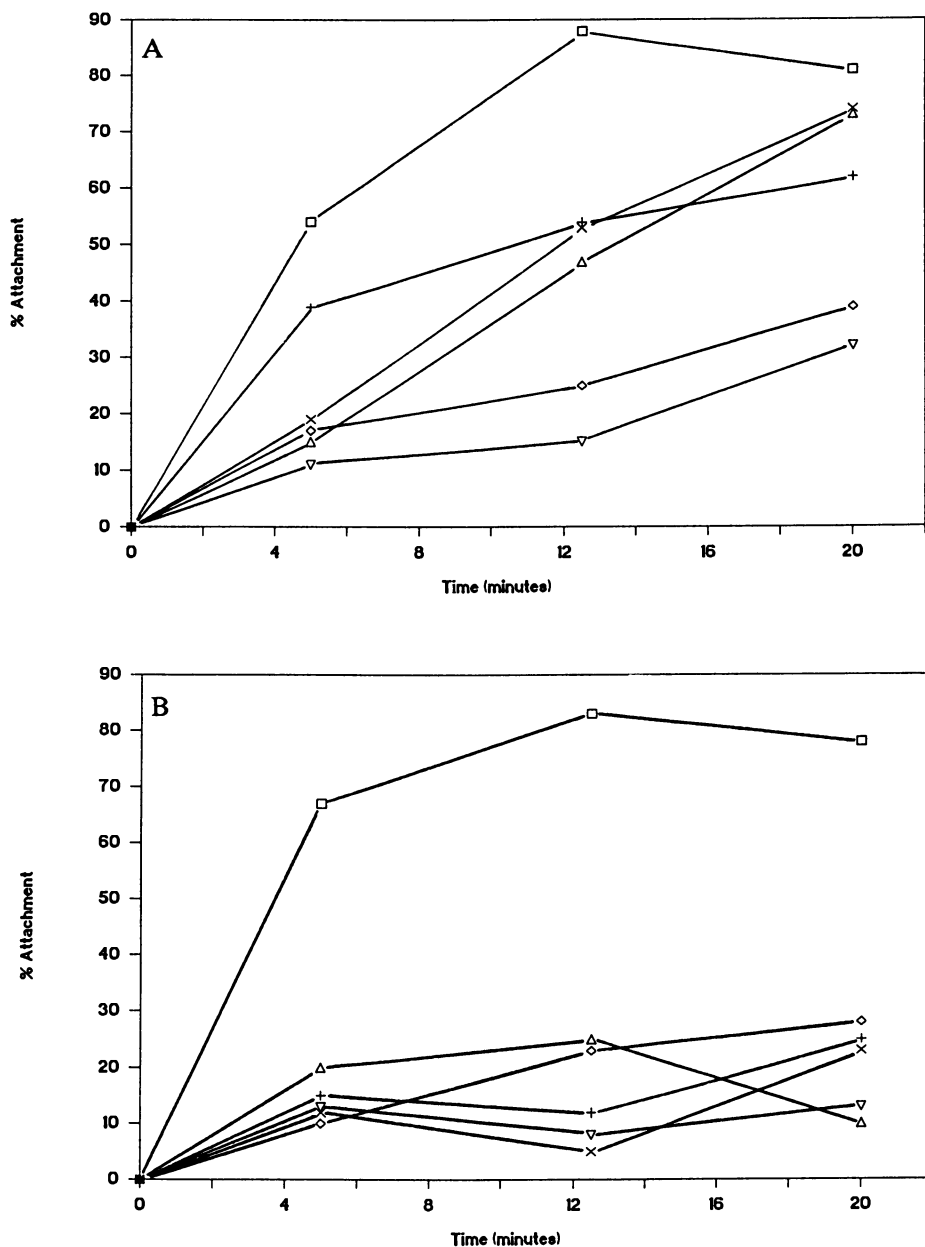


Figure 1. The attachment of adherent BHK-21 cells (Figure 1A) and nonadherent U-937 cells (Figure 1B) to Cell-Tak adhesive, □; collagen, ◇; poly-D-lysine, +; laminin, X; fibronectin, △; and plastic, ▽, was monitored by counting unattached cells at 5, 12.5, and 20 min. Data were then converted mathematically to percent attached of those seeded.

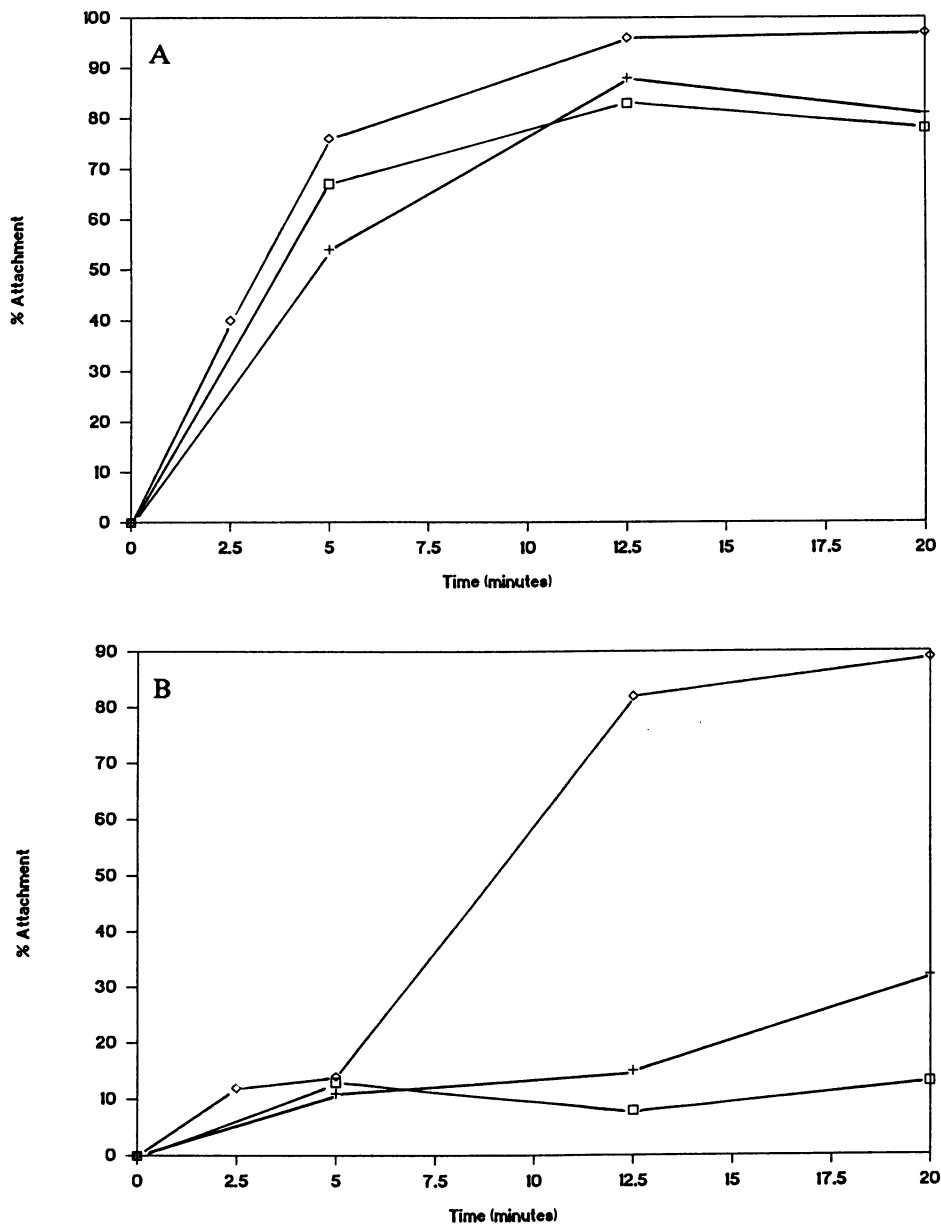


Figure 2. The attachment kinetics of adherent BCE cells,  $\diamond$ ; BHK-21 cells, +; and nonadherent U-937 cells,  $\square$ , were compared directly on Cell-Tak adhesive (Figure 2A) and uncoated tissue culture plasticware (Figure 2B).

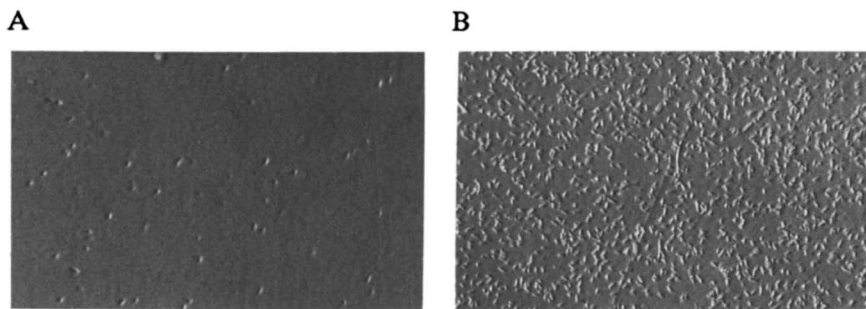


Figure 3. The attachment of *E. coli* to plastic (Figure 3A) and Cell-Tak adhesive (Figure 3B) was microscopically compared at 3300 x magnification.

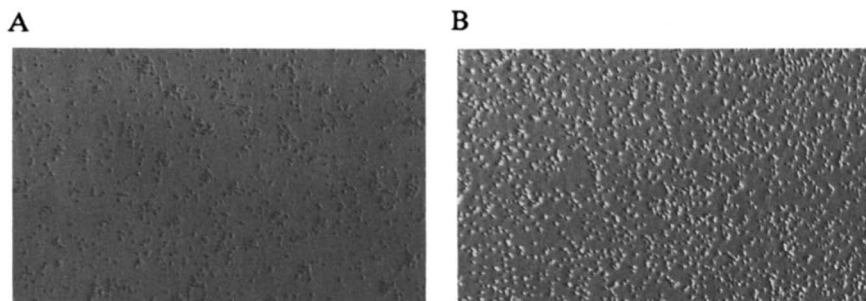


Figure 4. The attachment of *S. aureus* to plastic (Figure 4A) and Cell-Tak adhesive (Figure 4B) was microscopically compared at 3300 x magnification.

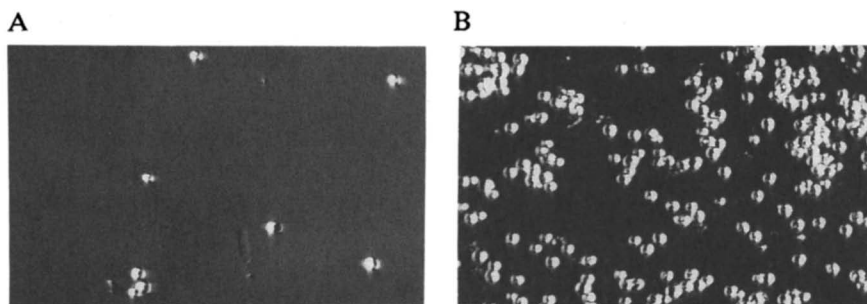


Figure 5. The attachment of *S. cerevisiae* to plastic (Figure 5A) and Cell-Tak adhesive (Figure 5B) was microscopically compared at 3300 x magnification.

(A series) compared to the enhanced attachment with Cell-Tak protein-coated plastic (B series).

The growth rate of BCE cells is not altered in the presence of Cell-Tak protein (Figure 6). The same data have been obtained with other adherent types (BHK-21, data not shown). After attachment, nonadherent cells do not grow as discrete colonies, precluding the same type of evaluation with U-937 cells.

**Ocular Tissue Bonding *In Vitro*.** Three factors were found to be critical to the development of the model system for wound repair. These were the age of the eyes following enucleation, the degree of curvature of the cornea at the time of testing, and the amount of adhesive protein or ratio of crosslinker to protein used to close the wound. Eyes used more than 20-hr postslaughter never yielded bond strengths in excess of 30 g/cm<sup>2</sup>. In untrimmed corneas from which both the epithelial and endothelial cell layers had been removed, a general trend with increasing protein concentration was seen (Table I). With higher amounts of

Table I. Cornea to Cornea Bond Strengths with MAP

Model Variable	MAP ( $\mu\text{g}$ )	Catechol Oxidase (U/ $\mu\text{g}$ )	Breaking Load (g/cm <sup>2</sup> )
Cornea scraped, not trimmed	50	13	60
	50	16	63
	50	18	46
	50	16	106
	50	18	72
	56	16	86
	58	10.5	82,100
	75	13	46
	75	18	83, 79
	100	18	105
Cornea trimmed, and scraped	52	9	72
	52	12	183, 122, 261, 89, 95
Cornea trimmed, not scraped	52	12	40

protein, higher enzyme:substrate ratios were required to achieve similar bond strengths. The cornea has a natural curvature; with the bond formation and incubation on a flat surface, it was found that more reproducible data were obtained on flatter, scraped, and trimmed corneas. With better definition of

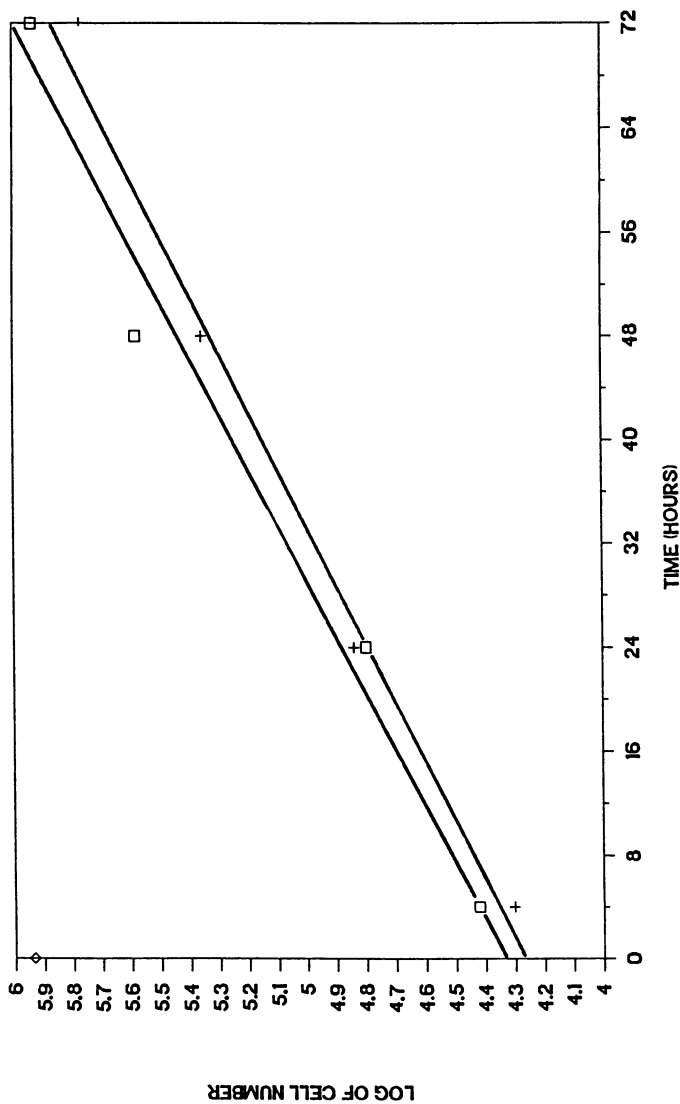


Figure 6. The growth rate of adherent BCE cells on plastic, +, was compared directly with the growth rate on Cell-Tak adhesive, □.

the model system, less protein with less crosslink catalyst achieved high bond strengths. The amount of adhesive used was insufficient to form an opaque film between the two tissue pieces; the bond was clear, and clarity of the corneas appeared unchanged.

The second model system for MAP adhesion was designed to evaluate efficacy in sealing small or large tissue perforations in a clinically relevant manner. Full thickness corneal holes were created in bovine eyes *in situ* with a scalpel. Internal fluid pressure caused aqueous humor to immediately flow out of the eye with consequent flattening of the cornea. A transparent hydrogel disc (Hypan) designed for use as a contact lens in conjunction with MAP was used to seal the perforations. With the corneas flat, small volumes (10-12  $\mu\text{L}$ ) of MAP (5-6 mg/mL in water) plus catechol oxidase (8-9 U/ $\mu\text{g}$  MAP protein) were applied around the perimeter of the perforation from which the epithelial cell layer had been removed. The Hypan disc (13-mm diameter, 0.2-mm thickness) was then centered over the perforation and gently smoothed out to permit good contact with the cornea. A water-filled dialysis bag was then placed over the cornea to prevent desiccation during the room temperature incubation. Various cure times were tested, after which pressure was induced by water via a syringe connected to a manometer, and burst strength was recorded in mm Hg.

The measurement system had an upper limit of approximately 110-120 mm Hg; in the cases where the bond did not fail, the data were recorded as mm Hg (Table II). Bond cure was rapid with maximum measurable bond strengths achieved in 10 min with only slightly lower bond strengths seen at 5 min. As with the cornea overlap bonds, MAP at this concentration plus the transparent Hypan produced a seal that was also clear.

Table II. Corneal Perforation Seal with  
MAP Plus Hypan

Incubation Time (minutes)	Burst Strength (mm Hg)
5	84, > 82
10	> 101, > 110, > 99
20	> 110, 64, > 112, > 116 116, 110

**Biocompatibility at the Cell Culture Level.** The liquid components, MAP and catechol oxidase, and extracts of two solid crosslinked materials were tested for cell culture toxicity and growth inhibition. The evaluation of cell culture cytotoxicity in an agar overlay method detects the impact on cells of any freely

diffusible components or extractable materials. Mouse fibroblasts (L929) were grown in monolayers, overlaid with agar, and incubated for 24 hr with filter paper discs impregnated with liquids on the surface of the agar. Solid crosslinked materials were placed directly on the agar.

Table III shows the cytotoxicity results obtained in this study. Plates receiving no treatment stained an even pink color, indicating the presence of a healthy confluent cell monolayer. The positive control (PVC) placed in each of the plates along with test samples caused the expected toxic response with greater than 80% lysis of the cells within the zone surrounding the samples. Negative controls, which consisted of Whatman No. 2 qualitative filter paper (for solid and liquid samples) and the same filter paper impregnated with the appropriate extracting solvent (for extracts), variably yielded slightly positive results. Slight toxicity in the form of a lighter stained monolayer was observed under three dry filter papers (out of eight) and on four filter papers impregnated with saline. Toxicity was also evident surrounding one of four filter papers impregnated with ethanol. No toxicity was observed under the four filter papers impregnated with cottonseed oil.

Table III. Agar Overlay Cytotoxicity Results

Test Substance	Positive Control	Test <sup>1</sup>	Negative Control
Liquid MAP	T,T	ST,ST,ST,ST	ST,NT
Liquid enzyme	T,T	T,T,T,T	ST,NT
High crosslinked:			
Solid	T,T	NT,NT,NT,NT	ST,NT
Saline extract	T,T	T,ST,ST,NT	ST,NT
Cottonseed oil extract	T,T	ST,ST,ST,NT	NT,NT
Ethanol extract	T,T	ST,ST,ST,NT	T,NT
Low crosslinked:			
Solid	T,T	NT,NT,NT	NT,NT
Saline extract	T,T	ST,ST,ST,NT	NT,NT
Cottonseed oil extract	T,T	ST,NT,NT,NT	NT,NT
Ethanol extract	T,T	T,NT,NT,NT	NT,NT

<sup>1</sup>T = toxic; NT = nontoxic; ST = slightly toxic. One entry for each sample.

Four samples were tested without extraction or any other treatment: liquid MAP, liquid enzyme, high crosslinked MAP solid, and low crosslinked MAP solid. The cell monolayer under the liquid MAP was slightly lighter in color than the surrounding monolayer (see "slight toxicity" in Table III). Since a similar observation was noted for one of the negative controls, the liquid MAP can be



considered to be nontoxic in this system. When stained zones were examined under an inverted microscope, the few remaining adherent cells within the zone appeared to be swollen though not fragmented. The toxicity zone is comparable to that obtained with the PVC positive control. Neither solid materials, high and low crosslinked MAP, induced any effect on the cell monolayers. Saline, cottonseed oil, and ethanol extracts of the high and low crosslinked solid MAP showed low reactivity.

A second index of biocompatibility was the quantitative analysis of cell growth inhibition, again on mouse fibroblast L929 cells, induced by the liquid components of the adhesive system and water extracts of two solid crosslinked materials. Table IV is a summary of the percent inhibition of cell growth (percent ICG). The mean protein values at 4 °C have been subtracted from the mean protein values (five test samples) at 37 °C for each treatment condition. The percent inhibition of cell growth (percent ICG) is shown for each treatment condition. The precision of the assay is approximately  $\pm 10\%$ .

Results for the negative and positive controls are shown at the bottom of the table. Tubes receiving no treatment, but held at 4 °C, had a mean protein content of 89.7  $\mu\text{g}$ ; after 72 hr of incubation, the protein content in untreated tubes had increased to 313.5  $\mu\text{g}$ . The difference in these two values (223.8  $\mu\text{g}$ ) is taken to represent 100% growth for this experiment. A positive control, Dextran Sulfate, was tested at 40 mg/mL. A percent ICG greater than 100 can result from the calculation of this value if the protein content of tubes held at 4 °C exceeds that of the incubated tubes. This is possibly due to lysis of the cells such that the released protein was removed during subsequent washings.

The percent ICG for each test sample at each concentration (based on calculations utilizing the mean protein values for each treatment condition) appears to indicate that the liquid MAP and extracts of the high crosslinked solid sample had essentially no effect on the growth of L929 cells in this assay. The liquid enzyme at 4,000  $\mu\text{g}/20\text{ mL}$  caused a 125.9% ICG. When the liquid enzyme was tested at lower concentrations (from 1  $\mu\text{g}/20\text{ mL}$ ), the percent ICG ranged from 40.3 to 73.8%. Although the concentrations of liquid enzyme that were tested in this experiment did not provide sufficient data to generate an apparent dose response curve (absence of test concentrations between 4,000 and 500 in the experimental design), this enzyme inhibits the growth of L929 cells.

Extracts of the low crosslinked solid also caused inhibition of cell growth in this assay. The percent ICG of the extracts ranged from 15.4 to 59.3%. Again, no dose response was apparent with the extracts of the low crosslinked solid.

The high crosslinked solid increased the protein content of L929 cells after a 72-hr exposure in a concentration-dependent manner. This increase might be explained either by a growth-enhancing effect of the test material or by the contribution of the test protein material itself. The low crosslinked solid decreased the protein content of L929 cells after a 72-hr exposure period in an inverse concentration-dependent manner. This finding is statistically significant at the 0.001 level but influenced heavily by only one single set of data points at the

highest extract concentration (4,000  $\mu\text{g}/20\text{ mL}$ ). The liquid enzyme decreased the protein content of L929 cells after a 72-hr exposure in a concentration-dependent manner and was comparable in toxicity at the highest concentration to the positive control.

Table IV. Percent Inhibition of Cell Growth (% ICG)

Sample	Extract ( $\mu\text{g}/20\text{ mL}$ )	ICG (%)
Liquid MAP	4,000	-6.4
	500	-5.2
	100	10.1
	50	-3.2
	4	-13.7
	3	-0.7
	2	4.4
	1	0.2
Liquid enzyme	4,000	125.9
	500	57.6
	100	48.1
	50	70.7
	4	40.3
	3	73.8
	2	61.1
	1	58.1
High Crosslinked	4,000	14.4
	500	18.8
	100	-15.4
	50	17.4
	4	-8.1
	3	-11.0
	2	-30.1
	1	-20.7
Low Crosslinked	4,000	15.4
	500	31.5
	100	53.1
	50	44.9
	4	59.3
	3	49.7
	2	36.4
	1	40.2
Negative control		0
Positive control		119.9

## Discussion

The potential utility and biocompatibility of MAP-based adhesives have been addressed in the series of experiments presented here. MAP formulated as Cell-Tak adhesive is an efficient mediator of mammalian, bacterial, and yeast cell attachment. It has also been demonstrated to support normal cell growth *in vitro*.

MAP formulated with a crosslink catalyst is capable of bonding tissue to tissue as demonstrated with corneal stroma and bonding alloplastic materials to tissues, as shown in the bonding of a hydrogel to corneal stroma. Moreover, two adhesive formulations of MAP with catechol oxidase at different ratios were shown to be biocompatible in a cell culture agar overlay system.

Numerous cell types attach efficiently and rapidly to MAP. Anchorage-dependent mammalian cells, BCE, and BHK-21 cells normally attach to plastic and tissue culture plasticware coated with cell culture attachment factors. Once attached, cells flatten and spread as a prerequisite for normal metabolism and growth. In reality, with the manipulations required to subculture or seed cells, only a certain percentage of the population successfully completes the process. Those that do not attach and flatten quickly frequently do not survive. This is especially true for newly isolated cells from a variety of tissues, although it also applies to established cultures. Cell-Tak adhesive promoted rapid attachment of cells (greater than 90%) seeded and, therefore, suggests the successful recovery of a high percentage of the population. Numerous other cell types and primary isolates (5) have been studied with successful isolation and subculture on Cell-Tak protein with maintenance of normal cell function and morphology.

Anchorage-independent cells grow as spheres in suspension in tissue culture broth and are not dependent on the flattening and spreading mechanism for normal cell growth to occur. Efficiency of recovery of these cells is determined by the density of Cell-Tak adhesive. The amount used here,  $5 \mu\text{g}/\text{cm}^2$ , is sufficient for 85% cell recovery. For cells that flatten, lower densities are sufficient (data not shown). Cells that remain as spheres present a much smaller surface area to the adhesive.

The purpose for immobilizing anchorage-independent cells, such as the U-937 human histiocytic lymphoma line studied here, is not for enhanced recovery or for growth. Rather, experimental manipulations that are most readily done on immobilized cells can now be performed on these and other suspension cells. Examples include the various immune assays. A specific example is an assay where the efficient recovery of all cells (such as T-cells) is critical. T-cells normally do not attach to glass slides or tissue culture plasticware. The ability to quantify the relative proportions of T-cell subpopulations would enable the rapid diagnosis of the immunological competence of patients undergoing cancer therapy or with specific immune-system diseases. Another example of utility is in the studies of cell-cell interactions between populations of nonadhering cells. With the ability to immobilize one of the two populations (or two of three, etc.),

the populations can be easily separated after an incubation period together, and dynamic interactive effects can be analyzed. Since U-937 cells quickly attach with high efficiency to Cell-Tak, this approach to immobilizing cells appears very promising.

The kinetics of attachment for the diverse cell types studied here were identical. The composition of MAP in Cell-Tak adhesive is well understood. As much as 60% of the high molecular weight protein is hydroxylated, and 20% is lysine, which contributes to a large net positive charge. The protein is a repeating polymer of peptides, the sequences of which are known (6) and are dissimilar from the specific recognition site on fibronectin (7,8). We suggest that the efficient attachment of mammalian cell types, with the same kinetics, plus the immobilization of bacteria, both gram positive and negative, and a yeast could only be mediated by a nonspecific mechanism comprised of entanglement, hydrogen bonding, and ionic interactions. The role of L-dopa in this system (10-15% of the amino acid composition) cannot be ignored. While these groups are capable of hydrogen bonding through the double hydroxyl groups, their position and orientation enables chelation through trivalent and tetravalent ions. It is well known that L-dopa is a highly efficient scavenger of ions (9).

Unlike cell culture, wound repair requires at least a two-part adhesive system: MAP plus a crosslinking agent. The issue of biocompatibility is inherent in the use of MAP in Cell-Tak adhesive. Throughout these experiments, living cells were maintained in the presence of MAP. The introduction of the crosslinking component into the system required a reevaluation of compatibility at the cell culture level. This was done using standardized assays developed for the evaluation of the biocompatibility of medical devices. It is apparent that MAP alone did not interfere with cell growth or cause damage to cells in either assay. The components of high or low crosslinked MAP that diffused through agar were not found to be cytotoxic. The catechol oxidase enzyme alone did affect cells in culture in both assays. The water extract of low-ratio crosslinked MAP also inhibited cell growth but to a lesser degree. The catechol oxidase catalyzes the hydroxylation of tyrosine to L-dopa and the conversion of L-dopa to a quinone. The possibility exists that enzyme, incompletely immobilized or inactivated within the adhesive matrix, could catalyze the reactions on cell surface proteins, thereby damaging the cells. With careful use of formulations blended at higher crosslink ratios, this situation can be avoided.

The development of methods for the use of MAP in wound repair required two parallel sets of definitions. The first involved MAP itself with the investigation of concentrations of protein and ratios of crosslinking catalyst that yielded sufficient bond strengths. The second was the choice of model systems and the analysis of tissue-related parameters that impinged on adhesion testing. The complexity of tissues necessitated that special attention be given to many details so that reliable test data could be obtained.

Two test systems were used here. With the development of the overlapping corneal bond system, it was learned that the epithelial and endothelial cell lay-

ers were a weakly adhering surface layer on the corneal stroma and had to be removed prior to testing in order to maximize joint strengths. The stroma of enucleated eyes begins to decompose and weaken with time, even with storage at 4 °C and, therefore, had to be used on the day of slaughter. The curvature of the cornea had to be reduced as much as possible to permit close apposition of the tissues. This was accomplished by trimming the curved cornea into strips, which were then used for testing. Even with these measures, the data were not always consistent. Trends were seen with a requirement for increased crosslink catalyst ratios with increased protein amounts, suggesting that higher cohesive strength is required with increased protein. However, in this system, increased MAP protein did not necessarily yield higher bond strengths. Lower total protein amounts (50  $\mu\text{g}/\text{cm}^2$ ) consistently yielded the highest bond strengths. Increased protein could be retarding close tissue apposition by creating an undesirable bond depth that in turn would require increased crosslinking for increased cohesive strength.

The sealing of corneal perforations using whole enucleated bovine eyes required the same attention to tissue preparation. The epithelial layer in the bond area was removed. After the puncture of the cornea, the stroma was rinsed and blotted to remove potentially interfering aqueous humor components. The Hypan hydrogel material, which is 80-90% water, was routinely presoaked in PBS. Maximum bond strengths using 53  $\mu\text{g}$  of MAP per  $\text{cm}^2$  patch were obtained in 10 min after application.

Several other investigators have conducted experiments to address dynamic aspects of MAP formulations used in our studies. The adhesive has been found to be freely permeable to inulin, which has a molecular weight of 42,000 (10), at the enzyme to MAP ratio of 12:1 (12 U/ $\mu\text{g}$  MAP protein) with up to 200 mg of total protein per  $\text{cm}^2$ . This suggests that, at this concentration, MAP does not form a solid film and that corneal cells and tissues would not be damaged due to retarded gas or nutrient permeability. The potential exists for wound healing to occur not only around but also through the adhesive matrix. Additionally, at the crosslink catalyst ratio used here and a higher ratio of 15:1, the adhesive matrix remains susceptible to proteolytic digestion (Twining, personal communication). The rate of digestion has not yet been established. It is anticipated that the rate is dependent on degree of crosslinking and, therefore, that formulations could be tailored to meet healing rate requirements of diverse tissues. Studies have begun that address this issue *in vivo* in rabbits. Preliminary results show that both the corneal overlap and perforation sealant models developed here *in vitro* are feasible *in vivo*. Donor and recipient corneas were bonded with MAP adhesive in conjunction with a minimum number of temporary sutures. Both corneas remained clear and functioned normally. With large (4 mm) perforations of rabbit corneas, the Hypan hydrogel plus MAP adhesive system facilitated the formation of a solid plug within 24-hr postsurgery. With the exception of minimal inflammation due to the injury induced experimentally, the eyes appeared normal, and there was no leakage at the plug site. Histopathology

on subsequent days following repair of the eyes showed that the plug appeared fibrous, but the nature of the material is yet to be established. None of the animals showed any tissue damage as a result of the adhesive.

### Conclusions

Numerous studies are planned or in progress to further establish the efficacy of MAP for use in medical and surgical applications. Tissues other than those described here may have special requirements necessitating tailoring of the formulations. Alternate mechanisms for crosslinking and the addition of fillers are being investigated. We have not yet fully achieved all the characteristics of the mussel-produced adhesive, but the formulations and delivery systems used here show great potential in soft tissue wound repair.

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# Chapter 34

## Opportunities for Future Development of Adhesives from Renewable Resources

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Adhesives derived from natural resources and the possibilities for their industrial utilization, particularly in the forest products industry, have been a focus of considerable attention in recent times. While such adhesives have been used for most of mankind's history, substantial progress has been made in the last 15 years in producing durable adhesives from renewable resources that come close to meeting today's exacting industry standards. A number of important opportunities exist for further refinement of promising adhesive systems and for the development of new ones. Recent advances demonstrate the breadth of available possibilities for using nature's own storehouse for adhesive production and offer an excellent starting point for future research effort needed for its optimum exploitation.

A primary source material for natural resource-based adhesives is byproduct streams of the forest products industry. For this reason, and the fact that the industry is both a producer of huge tonnages of residues and a major consumer

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of adhesives, this book's major focus is on industry utilization of adhesives from renewable resources derived from trees.

The amounts of lignins, tannins, and carbohydrates available as residues from processing of forest trees dwarf the commodity adhesive market. At the same time, the forest products industry is especially reliant on adhesives, since over 70% of all wood products are bonded, and their production consumes about 45% of all phenolic and 85% of all urea-formaldehyde resins produced in the United States.

A selection of chapters drawn from other industries has been included because they offer particularly interesting applications of natural products as adhesive polymers. These chapters emphasize the extraordinary sophistication that can be involved in manipulating the structure of adhesive polymers through genetic engineering as described in Robert Strausberg's chapter (Chapter 32) and the application of natural polymers to particularly difficult bonding situations as discussed by Christine Benedict (Chapter 33). The breadth of natural polymer classes that can be applied in such a wide variety of adhesives testifies to the great potential for renewable resources to regain their prominence as a source of adhesive polymers as petrochemicals become scarce and their price increases.

The chapters presented in this volume show that considerable progress has been made in the laboratory over the past 15 years. With only a few exceptions, such as the longstanding use of starch in the paper industry and more recent use of wattle tannins as a basis for adhesives in the South African wood industry, little of this technology has been transferred to the industrial sector. The frustrations being felt by scientists pursuing the development of adhesives based on natural polymers surfaced in the discussions on the first morning of the symposium and lasted in both formal and informal fashion throughout the week. The comparatively large research effort with so few examples demonstrating the implementation of new adhesive technology by industry suggests a careful consideration of prospects for the future.

## Industry Needs

The forest products industry is faced with two very significant problems: 1) what to do with processing residues other than using them to recover low-value heat, and 2) how to meet the demand for materials should the petroleum crunch of the early 1970's recur. Alan Lambuth, who opened the symposium, speaks not only from the needs felt by his company but also as the Chairman of the National Forest Products Association's Wood Adhesive Committee on Evaluation of Research. His committee's longterm support for research on the development of new adhesives based on renewable resources confirms that the forest products industry in the United States ranks this as high-priority research. The excellent participation by industry in the symposium that laid the foundation for this book is further evidence that many companies have deemed that investments in



research and development of adhesives based on renewable resources have good potential economic returns.

Most of the chapters in this volume directly address the research needs expressed in Alan Lambuth's overview (Chapter 1). Although this book can only be representative of the much wider attack on the problem of obtaining adhesives from renewable resources, it does demonstrate that research is currently underway in industry, universities, and government laboratories that is focused on a critical future need of industry.

### Obstacles to Use of New Adhesive Technology

Given the high priority for new adhesive technology based on renewable resources, why then is there not a higher degree of technology transfer from the laboratory bench to industrial practice? In North America at least, a significant answer to that question must be touted in economics (i.e., the comparatively low price for phenol-formaldehyde and urea-formaldehyde resins). Graham Allan (Chapter 5) focuses on the economic considerations that need to be addressed in the development of any new adhesives based on renewable resources. Clearly, the price differential between currently-used adhesives based on petrochemicals and new renewable resource-based formulations must be substantial to entice industry to attempt a substitution. As pointed out in Alan Lambuth's introduction, industry would prefer to make this substitution with essentially no modification to current manufacturing processes. This is often a difficult requirement to meet.

Tony Pizzi's discussion (Chapter 19) of the problems faced in getting industry approval for use of tannin-based adhesives in South Africa focuses on a number of other problems, whether real or only perceived, that impeded the adoption of this technology by manufacturers of bonded wood products. Much of the problem must be ascribed simply to man's resistance to change no matter how small the real or perceived change might be. Research scientists dedicate their lives to change, but a plywood manufacturer, for example, wants no surprises in meeting production quotas. Pizzi's experience is important for all of us to consider. We must expect questions such as: "What is a carbohydrate or lignin?", "Why is the color of the glue different from that of a phenol-formaldehyde resin?", "Why isn't the resin at pH 10.5, since all the previous resins have been used at this pH?" And these types of questions must be answered in a way that satisfies those in the mills who will actually use the resin.

Another, and perhaps the most important, obstacle to increased use of adhesive polymers based on natural products relates to our inadequate knowledge of the fundamental chemistry of these systems. A large body of empirical formulation work is generally required in the development of new adhesives, and success often rests on how well that work is done. However, knowledge of the structures and reactions of these polymers is just as important and usually re-

quired to guide the adhesive formulator to rational approaches. The response to the petroleum shortage of the early 1970s was to invest very heavily in applied research because of the urgent need to keep plants operating. Investments in more fundamental research lagged far behind, and they continue to be rare in today's more normal environment of adequate petrochemical supplies.

### Opportunities for the Future

One of the highlights of the symposium was the dialogue that occurred among adhesive chemists from diverse backgrounds. Unfortunately, the discussions that followed the formal presentations of the individual papers could not be included in this book. The majority of the participants expressed considerable optimism about the future for adhesives based on renewable resources. Many of the carbohydrate-based adhesives, like starch, described in detail by Harry Kennedy (Chapter 23), and cellulose, summarized by David Hon (Chapter 21), already have substantial technical as well as economic advantages over petrochemical-based products, and these polymers hold significant markets. Bill Detlefsen (Chapter 31) showed that other adhesives such as those derived from blood and casein have a particularly fascinating history and still find use in special bonding applications. Industry's need for further development of adhesives based on renewable resources is being addressed with some interesting new formulations based on lignins, tannins, carbohydrates, and proteins as shown in the preceding chapters.

**Lignins.** Norman Lewis's introduction (Chapter 2) to the use of lignins in adhesives reminds us that major research and development efforts have been undertaken with no significant application of lignins in adhesives to date. Even more must be learned about the chemistry of lignins, particularly as related to their modification to provide suitable properties as adhesive polymers and their reaction with crosslinking agents. New NMR experiments like those described by Larry Landucci (Chapter 3) can be of considerable help in studying these polymers. Wolfgang Glasser's review (Chapter 4) of various approaches to crosslinking of lignins after different modification reactions shows the many varied approaches to this problem that certainly need additional research. Subsequent to Shen and Calve's work on lignosulfonates for bonding of particleboard, there has been little research on the use of these lignins in North America, possibly because of the comparatively few sulfite mills and the water-solubility conferred by the sulfonate function. Graham Allan's discussion (Chapter 5) of the comparative prices between lignosulfonates and kraft lignins and the large tonnages that are being produced makes one question whether the focus on kraft lignins is advisable. His phenolysis modification reaction certainly seems to impart suitable properties and at acceptable costs.

Pizzi and colleagues (Chapter 7) have cleverly taken advantage of the special circumstances offered in the kraft lignins from bagasse to develop both cold-setting wood laminating and particleboard adhesives. Lignin oxidations

are considered from two quite different viewpoints. Tor Schultz and his coworkers (Chapter 6) are taking a new look at an old reaction used to produce vanillin from lignin in an attempt to formulate low-molecular-weight phenolics for adhesive synthesis. Annegret Haars and her colleagues (Chapter 10) take the opposite approach in using phenoloxidase enzymes to polymerize lignins in the bond line as a particleboard adhesive. Both Hse (Chapter 8) and Gillespie (Chapter 9) have developed adhesive formulations that incorporate substantial proportions of kraft lignins after hydroxymethylation. The rapidly expanding oriented strandboard industry in the United States can be expected to substantially increase demands for phenolic resins, and the studies just referred to suggest that kraft lignins can be used to substitute for significant proportions of the phenol usage in these resins.

All of the studies mentioned are directed to lignins derived from pulp and paper manufacture. This requires that a traditionally conservative pulp and paper industry embark on further development as a chemical producer. However, Helena Chum and her colleagues (Chapter 11) derive their phenolics from lignin by fast pyrolysis of wood rather than as byproducts from the pulp and paper industry. Opportunities might be better for development of adhesives from a chemical manufacturer drawing on waste wood as a raw material much the same as has developed in the production of furan resins derived from agricultural residues described by Bill McKillip (Chapter 29).

An area not treated in detail and covered only in Norman Lewis's review (and one that deserves attention in the future) is the use of hydrolysis and organosolve lignins in wood adhesives. Should wood pulp production by steam explosion or organosolve pulping become more significant commercial processes, more attention will certainly be directed to these lignins.

In summary, progress on the use of lignins in wood adhesives has been made, but the level of effort directed to lignin utilization in general has been small in comparison with the enormity of the problem, possibly because of the limited advances that have been made in this field in the past. Unless high petroleum prices return, we can expect to see slow continual improvement in opportunities to use lignins as a basis for adhesives.

**Tannins.** Herb Hergert's introduction (Chapter 12) to the use of condensed tannins in adhesives is especially interesting because he provides some reasons why commercial success is lacking in the use of condensed tannins from conifer barks despite substantial effort worldwide to parallel the South African success in the use of wattle tannins. Much of the problem in the use of conifer bark tannins remains centered on our inadequate understanding of the fundamental chemistry of these polymers. For example, Lawrence Porter (Chapter 13) provided the first measurements of the viscosities of solutions of purified condensed tannin isolates of known molecular weight and the reactions of these polymers with formaldehyde. It is incredible that this has not been done previously considering the hundreds of papers that have been published on tannin use in wood adhesives. Further evidence for the comparatively limited knowledge

of the fundamental chemistry of reactions of these polymers is provided by the need for research on the reactions of methylolphenols with tannins. Crosslinking of condensed tannins with polymethylol phenols has been advocated since McLean and Gardner's paper in 1952, and this approach has been used in many tannin-based resin formulations. However, little is known about these reactions. Wayne McGraw (Chapter 14) describes competitive reactions of *ortho*- and *para*-hydroxybenzyl alcohols with model compounds for condensed tannins. In comparison with their extremely rapid reaction with formaldehyde, the condensed tannins react only sluggishly with *ortho*-methylols.

Roland Kreibich (Chapter 15) has taken advantage of the rapid condensation of conifer bark tannins with formaldehyde in further development of end-jointing adhesives using his honeymoon principle. Analogous wattle tannin-based end-joint adhesives are used commercially in South Africa, but Kreibich has shown that inexpensive sulfonate extracts from southern pine bark can provide end-joint bonds meeting the essential requirements of the American Institute of Timber Construction. The development of these adhesives was based on fundamental studies of the sulfonation and desulfonation of polymeric procyanidins and the rearrangement of these polymers in alkaline solution done by Hemingway and his collaborators. David Roux (Chapter 16) describes his group's studies of the base-catalyzed rearrangement of the profisetinidins and prorobinetinidins in quebracho and wattle tannins. His chapter emphasizes the importance of and difficulty involved in understanding the behavior of condensed tannins even in such simple situations as their solution in mild alkaline conditions.

The commercialization of conifer bark extracts in adhesive systems requires larger markets than are afforded by the timber laminating industry. In one approach, Bridgette Dix and Rainer Marutzky (Chapter 17) have explored the use of bark extracts as well as carbohydrates and proteins in combination with diisocyanates for the plywood and particleboard industries. In another approach, Gary Hamed and colleagues (Chapter 18) have examined the potential for use of condensed tannins as substitutes for resorcinol-based adhesives in the comparatively large rubber industry. Both appear to have promise. Pizzi's discussion (Chapter 19) of the trials faced in obtaining commercial acceptance of wattle-based adhesives in South Africa is particularly apropos to Hamed's efforts to gain acceptance of condensed tannins in the high-value, large-volume rubber market.

Progress in the use of condensed tannins in adhesive formulations might be expected to be more rapid than is the case for lignins because of the impetus provided by the commercialization of wattle tannin-based adhesives and because of the extraordinarily high reactivity of tannins in reactions with formaldehyde. This reactivity offers an opportunity to substitute tannin for resorcinol (currently priced at about \$1.80/lb) instead of phenol (about \$0.40/lb). Now that wattle tannins have been successfully introduced, their application can be expected to continue to expand. The situation remains difficult, on the other hand, for use of conifer bark tannins in adhesives. Herb Hergert is certainly

correct in his assessment that one of the more important advances that needs to be made is the improvement of extract yields. This must be accomplished with the retention of high reactivity, a requirement that would seem to exclude the use of alkaline extraction at elevated temperature. We must also continue to improve on our understanding of the chemistry of these polymers, particularly in terms of their reactions.

**Carbohydrates.** Carbohydrates are available in huge quantities from plant and animal sources. They represent the single most important class of components obtainable from renewable resources. Tony Conner demonstrates in his overview (Chapter 20) that carbohydrate polymers, oligomers, and monomers, as well as products formed from their reactions, have been historically utilized in adhesives. In addition, he shows that each of these classes of carbohydrate materials offers excellent opportunities for further utilization in adhesives.

The use of carbohydrate polymers in adhesive systems is addressed from five very interesting, and in some respects very divergent, viewpoints. David Hon (Chapter 21) and Harry Kennedy (Chapter 23) thoroughly explore the use of two very important carbohydrate polymers in adhesives—cellulose and starch. Both polymers have long histories associated with their use as industrial raw materials in general and as adhesives in particular. Both continue to be important in present adhesive applications. Gerrit van der Klashorst (Chapter 22) investigates the use of hemicellulose (an important class of heterogeneous carbohydrate polymers) from soda bagasse pulping liquors as an adhesive in corrugated board adhesives. Studies of adhesives systems such as this offer much insight into the chemistry of durable adhesives based on carbohydrate polymers. Ramani Narayan and colleagues (Chapter 24) explore an area that will become increasingly important in the very near future, the bonding of hydrophobic plastic materials to natural polymers, for example, during the formation of plastic/wood composites. The techniques used in their study will be of interest to researchers investigating other areas of adhesion and adhesives.

Several chapters also demonstrate the use of smaller molecular-weight carbohydrates (i.e., monomers) in adhesives. Tony Conner and his colleagues (Chapter 25) explore the partial replacement of phenol-formaldehyde adhesives used to bond wood with various wood-derived carbohydrates. Al Christiansen (Chapter 26) and Joe Karchesy and his coworkers (Chapter 27) investigate the very complicated chemistry and the practical application of adhesives based on the reaction of a carbohydrate with urea and phenol. Tito Viswanathan (Chapter 28) describes his attempts to utilize a very large carbohydrate waste stream, whey permeates from the processing of cheese, for the production of wood adhesives.

A number of very reactive compounds can be obtained from carbohydrates. Furfural, a furan, is one such compound that is produced by reacting a pentose carbohydrate under acidic conditions. Bill McKillip (Chapter 29) gives an excellent overview of furan resin chemistry and the use of furans for the production of polymeric materials such as adhesives. Furans, in particular furfural,

can be readily made from a number of renewable resources (e.g., corncobs and wood) and are already used as a source of a number of important polymeric and adhesives systems. However, the chemistry of these types of compounds is very rich and offers a number of exciting and innovative possibilities. An example is presented in John Stanford's excellent research (Chapter 30) into producing polyurethanes from renewable resources.

**Proteins.** The chapters presented in the section on proteins best dramatize the interesting history of and future for adhesives from renewable resources. Bill Detlefsen's account (Chapter 31) of the use of blood and casein adhesives through history is an important reminder that the age of adhesives from petrochemicals has been a brief period in time. His chapter also reminds us that the peak production of these protein glues occurred in comparatively recent times (1960 for blood and 1973 for casein). The pessimistic outlook for their future stands in stark contrast to the excitement surrounding the development of mussel adhesive protein for bonding under extremely difficult conditions. Robert Strausberg's summary (Chapter 32) of efforts to produce analogues of MAP polymers by genetic engineering processes was an excellent example of the future innovative applications for natural polymers designed with very specific properties. Likewise, Chris Benedict's discussion (Chapter 33) on the use of mussel adhesive protein in bonding of cells to inert substrates or bonding of animal tissues such as in eye surgery dramatizes the enormous, as yet untapped, potential for future development of adhesives from renewable resources.

### Concluding Remarks

A vast body of research lies ahead of us if we are to effectively utilize renewable resources as adhesives. The content of this book emphasizes that all classes of natural polymers hold promise if only we can learn enough about their chemistry to make use of their special properties. We must not wait for another petroleum shortage for research to be funded for the development of new adhesives from renewable resources. Many of the formulations described in the chapters included in this volume are economically and technically competitive with today's widely used adhesives, and there are enhanced opportunities to enlarge on their advantages. The increasing use of composites as materials in most aspects of our lives places great demands on adhesives, but this further expands the potential for new adhesive system technology. The research highlighted in this book amply demonstrates the breadth of possibilities that exists for the creative researcher to explore the formulation of adhesives from nature's own storehouse. In this sense, this book ends on a note of expectant optimism.

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