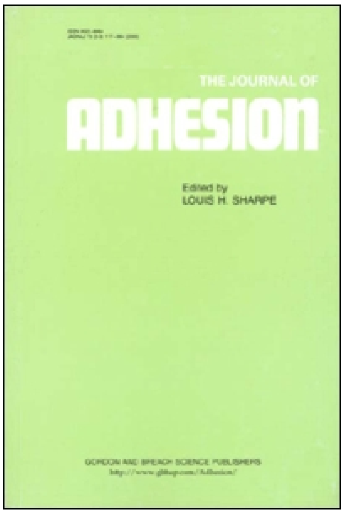

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Hydroxy Propylated Lignin-Isocyanate Combinations as Bonding Agents for Wood and Cellulosic Fibers

Wolfgang G. Glasser[a]; Vasudev P. Saraf[a]; William H. Newman[a]
[a] Department of Forest Products and Department of Chemical Engineering, Virginia Polytechnic Institute and State University, Blacksburg, Virginia, U.S.A.

To cite this Article Glasser, Wolfgang G. , Saraf, Vasudev P. and Newman, William H.(1982) 'Hydroxy Propylated Lignin-Isocyanate Combinations as Bonding Agents for Wood and Cellulosic Fibers', The Journal of Adhesion, 14: 3, 233 — 255
To link to this Article: DOI: 10.1080/00218468208073206
URL: http://dx.doi.org/10.1080/00218468208073206

J. Adhesion, 1982, Vol. 14, pp. 233–255
0021-8464/82/1404-0233 $06.50/0

Printed in Great Britain

Hydroxy Propylated Lignin–Isocyanate Combinations as Bonding Agents for Wood and Cellulosic Fibers

WOLFGANG G. GLASSER,† VASUDEV P. SARAF and WILLIAM H. NEWMAN

Department of Forest Products and Department of Chemical Engineering, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061, U.S.A.

(*Received January 27, 1982; in final form, May 6, 1982*)

Lignin and hydroxy propylated lignin derivatives were reacted with diisocyanates in the presence of cellulose fibers and wood particles. The attachment of lignin and lignin derivates to hydroxyl-rich surfaces of lignocellulosic materials proved to be a convenient way for increasing strength properties of reconstituted fiber and particle materials. Results indicate that hydroxypropylated lignin derivatives are capable of contributing equal or even greater strength increases to relignified fiber composites than do monomeric or polymeric diisocyanates alone. With reinforced fiber mats, it was found that strength properties were virtually unaffected up to a level of approximately 50% replacement of diisocyanates by lignin-based materials. This beneficial contribution by lignin to bonding properties could not be verified for reconstituted wood products, the strength and swelling properties of which suffered in relation to lignin content. These differences are explained with differences in method of adhesive preparation and application. Lignins were obtained from the spent pulping liquor of the Kraft process, and by alkaline extraction of steam exploded Aspen wood chips. These lignins were, for the most part, reacted with propylene oxide.

INTRODUCTION

When plants experience the need for mechanical support of their fibrous tissues, they produce lignin and deposit it as a reinforcing agent.[1,2] In addition,

---

Presented at the First Annual International Symposium on Adhesion and Adhesives for Structural Materials, Washington State University, Pullman, WA 99164, U.S.A., Sept. 29–Oct. 1, 1981.

† To whom inquiries should be addressed.

lignin performs as a sealant and decay retarder, to name only a few of its many service functions to the woody plant. Lignification proceeds by the enzymatically-triggered free radical polymerization of p-hydroxy cinnamyl alcohols to form randomly linked polyphenylpropane molecules with between 1 and 2 dozen different types of interunit linkages.[3] Although only 26–28% by volume, lignin comprises approximately 40% of the total enthalpy of wood (softwoods).[4] Separation of saccharidic from aromatic wood components usually employs aqueous alkaline or acidic solutions; more recent technological development studies have also considered the employment of organic solvents.[5] Lignin is potentially available at prices marginally greater than its fuel cost equivalent at factories producing pulp for papermaking in quantities in excess of 16 million tons/year in the United States.[4,6] Whereas the naturally occurring process of plant lignification as well as the industrial processes of delignification are reasonably well understood, attempts to employ lignin for "relignification" by converting it into an adhesive for wood and cellulose fiber products are only recently beginning to receive attention.[6,7]. These efforts are concentrating on using lignin as an extender for, or replacement of, phenolformaldehyde resins, and as a co-reagent of isocyanate binders. Both are being discussed in the following section.

The use of lignin in conjunction with phenol-formaldehyde (PF) type resins has recently been advanced in England, Canada, and in the United States. A PF resin product called KARATEX has been developed that contains 40–70% lignin isolated from a spent pulping liquor by ultra filtration.[8,9] The resin is claimed to be less expensive and yet as strong as conventional PF resin.[9] Many U.S. patents have dealt with lignin extended resins. The treatment of ligninsulfonates with ammonia followed by reaction with an aldehyde resulted in a thermosetting resin.[10] Mixtures of lignin and aldehyde were converted into a water soluble thermosetting adhesive which was suitable for extending phenol and urea formaldehyde adhesives.[11,12] Whereas many patents have demonstrated that ligninsulfonates can replace some of the phenol in preparations of phenolic resins,[13–17] another patent[18] describes the formulation of a lignin based adhesive with up to 70% lignin content by copolymerization with melamine and formaldehyde. Clarke and Dolenko[19] have reported on the preparation of a resin with lignin by precipitating the lignin from the "black liquor" of a Kraft pulping process, and mixing this with phenol formaldehyde. Precipitation by acidification was thereby preceded by methylolation. The investors estimated that 70% of the present petroleum-based phenolic resins could thus be replaced by lignin-phenol mixture.

Although most attempts to employ lignin as an adhesive in the forest products industry have concentrated on its use in phenol formaldehyde resin systems, some work has been concerned with cross-linking soluble and/or liquid derivatives with urea, melamine, or diisocyanates. Whereas most of these studies have concentrated on water soluble sulfonated lignin products (lignin sulfonates or spent sulfite liquor components), other work has focused on convenient methods of liquifying lignin by way of oxyalkylations. This reaction converts lignin into a liquid polyol, which is miscible with a variety of organic solvents, and which has been demonstrated to be a useful coreagent for the manufacture of a variety of polyurethane products. Lignin-derived polyols have been used in polyurethane network polymers by means of a reaction with diisocyanates.[21–24]. The conversion of lignin into a polyol was accomplished by treatment with a 1,2- alkylene oxide, a 1,2-alkylene sulfide, or a 1,2-alkylene carbonate.[25,26] Oxyalkylations of Kraft lignin have been performed with propylene oxide before and after carboxylation with maleic anhydride.[25] Using this reaction sequence, a lignin-based polyester—polyether polyol can be formed whose chemical composition can be controlled *via* degree of carboxylation, concentration of ester bonds, concentration of aliphatic ethers, and length of polyether chains. This flexibility in terms of chemistry and properties, however, is gained at the expense of a multi-step reaction sequence and lignin content of the final product.

Isocyanates have been found to be an effective group of adhesives for wood.[27–41] Their performance is attributed to the formation of a chemical bond, urethane bond, between the isocyanate and the hydroxyl groups on the wood surface[42–44] These bonds anchor the adhesive to the wood. A Polymeric network is formed when the moisture of the wood particles react with more isocyanates to form polyurea bonds and a small amount of biuret bonds.[30,32,34]

Deppe[28,29] was one of the first researchers to prove that there are covalent bonds between wood and isocyanates. Rowell and Ellis[42–44] reported that the increase in wood volume observed when wood was treated with isocyanates, is proportional to the calculated volume of chemical added. This shows that the reaction is taking place in the wood cell walls, and is not simply a result of filling the cell lumina with homopolymer. Wittman[37] provided experimental evidence for the formation of polyurea linkages by measuring the CO_2 release of particleboard mats during pressing with isocyanate adhesives. It was calculated that if each amino group that was formed by the reaction of water with isocyanate reacted with an NCO group, then more than 50% of the adhesive introduced by bonding leads to formation of polyureas. Further evidence of chemical bonding between isocyanates and wood was generated by infrared spectroscopy:[43] After treatment with an isocyanate, a prominent carbonyl appeared in the IR spectrum of composite material. The increase in this bond was attributed to the formation of urethane bonds.[43] Isocyanates were first used for the production of particleboard by Deppe and Ernst in 1971.[28] The most commonly used isocyanate is 4.4-diphenylmethane diisocyanate (MDI).[29,31,33,38] Particle boards manufactured with isocyanate are superior with regard to most performance standards to boards made with conventional adhesives, *i.e.*, phenol formaldehyde and urea formaldehyde.[27–38] McLaughlin[40] reports that isocyanate-bonded particleboards have equivalent or superior strength properties to conventionally bonded boards at reduced resin contents. At 3% resin content, isocyanate-bonded boards give the same internal bond strength as PF-bonded boards at 7–7½% resin content. Press time can be reduced by 30%. The use of isocyanate adhesives for the manufacture of particleboard offers the advantages of freedom from formaldehyde release and a much longer shelf life compared to conventional adhesives. The boards can have lower resin contents or be less dense at equivalent strength properties. The boards have better dimensional stability than PF or UF-bonded boards, and can be produced in existing facilities with little modifications.[30,32,33,35,37,40]

There are four major limitations that deter the use of isocyanates in particleboard. The first is cost: isocyanate adhesives are up to four times as expensive as conventional adhesives.[36] This may partially be offset by lower production costs due to lower resin contents, faster press times, higher allowable chip moisture contents and less dense boards.[21,31,40] The second limitation has in the past concerned problems associated with the use of water as a solvent with isocyanates. This has been solved by the development of an emulisifiable MDI, developed by ICI Ltd. and Rubicon Chemical Company.[38] The third limitation of isocyanates has previously been its strong adherence to metal surfaces in the form of caul plates. This problem has recently been overcome by a "self releasing" isocyanate adhesive, one that will not adhere to caul plates.[31,40] The final major limitation of isocyanate-bonded particleboards is its poor durability: Durability for a particleboard with 7–7½% resin content is the same for either phenol formaldehyde on isocyanate-bonded boards.[44] This could prohibit the use of low resin content isocyanate boards even though strength properties are acceptable.

The aim of this study concerned the formation and testing of composite materials made from cellulose fibers or wood particles and isocyanate adhesives extended with lignin or lignin adhesives.

MATERIALS AND METHODS

1. Materials

Commercially available Kraft lignin (INDULIN ATR-C1 from Westvaco, Charleston, South Carolina), isolated from the spent pulping liquor of a pine-based Kraft pulping process, and alkali extracted lignin from steam exploded Aspen chips (IOTECH lignin from IOTECH CORP., LTD, Ottawa, Ont., Canada) were used as lignin sources. The preparation and isolation of

IOTECH lignin is illustrated in Figure 1. Kraft lignin, a solid brown powder with a glass transition temperature (T_g) of approximately 180°C[4] and poor solubility in organic solvents, was liquefied by oxyalkylation with propylene oxide. IOTECH lignin was employed either as solution in an organic solvent (dimethylformamide) or following liquefaction by oxyalkylation. This reaction, which has been described elsewhere,[24,45] proceeds at approximately 180–250°C in *c.*90 minutes in the presence of KOH as catalyst and toluene as solvent. A commercial polymeric diphenylmethane diisocyanate, PMDI (ISOBIND 100 by Upjohn, Inc.) and hexamethylene diisocyanate, HDI, were used as diisocyanates in this study. The wood furnish used to form the boards was obtained from a commercial particleboard plant of the MASONITE Corporation in Salem, Virginia. This was produced from a mixture of southern pines by hammermilling up to $\frac{3}{8}$ in size, and screening to uniform particle size. The moisture content of the chips was 10%.

2. Methods

A. Analysis Molecular weight distributions were determined by gel permeation chromatography in open columns on Sephadex LH 20, using ethanol as

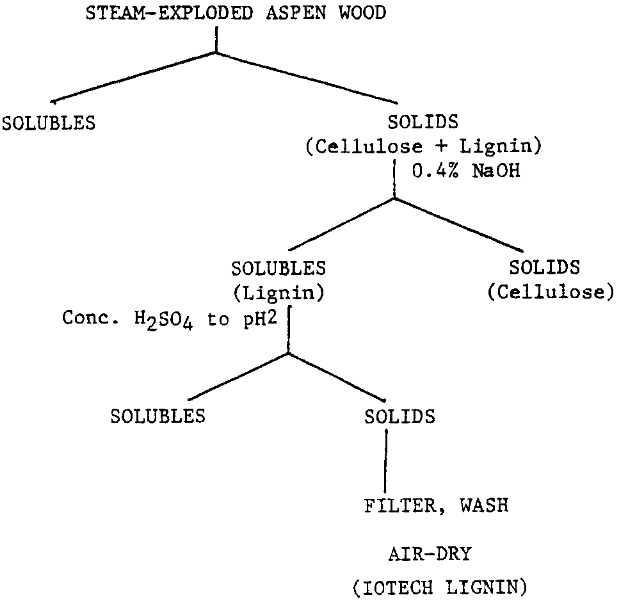

FIGURE 1 Isolation scheme for IOTECH lignin (IOTECH CORP. LTD, Ottawa, Ontario, Canada).

solvent. Effluent monitoring was by UV absorbance in sequence with refractive index detection. Hydroxyl contents were determined by acetylation with pyridine/acetic anhydride (60°C overnight in sealed ampules), and titration of the unreacted acetic anhydride. Determinations were performed in duplicate.

B. Polyol isolation and purification Hydroxypropylated lignins were separated from homo-oligomer fractions of propylene oxide by continuous liquid–liquid extraction of polyol solutions in acetonitrile with hexane.

C. Fiber mat impregnation and testing The liquid lignin derivatives were converted into polyisocyanates by reaction with HDI in stoichiometric or excess quantities. The experiments employed polyols with hydroxy contents ranging from 5.5 to 13.1%, and a ratio of polyol to isocyanate on weight basis from 1 : 1 to 1 : 4. The reactants used in the preparation of polyols and their hydroxy percentages are listed in Table I. Polyisocyantes based on lignin-derived polyols were prepared with mixtures of benzene and dimethyl formamide as solvent, and catalysts T-9 and A-1 (Union Carbide), under reflux for one hour. The formulations for the polyisocyanates are given in Table II. The polyisocyanates produced were reasonably stable and clear. After suitable dilution with solvent, the polyisocyanate preparations were used for impregnating blotting pulp strips once or several times. Curing involved blowing the impregnated blotting pulp dry with compressed air or drying in a laboratory oven at 105°C. Tensile strength was determined on an Instron/testing machine, table top model TM-M-L. Scanning electron micrographs were taken on an Advanced Metals Research (AMR) model 900 instrument.

D. Particle Board Preparation Particleboards were prepared with five different mixtures of lignin–propylene oxide copolymer and isocyanate

TABLE I

Polyol preparation data

Polyol #	Lignin [g]	Propylene oxide [g]	KOH [g]	Yield[1] [g]	Hydroxy content [%]
#35	20	34	0.1	33	5.5
#74	40	68	0.8	79	9.2
#69	60	68	1.22	90	13.1
#77	30	34	0.6	44.5	6.6

[1] Determined following liquid–liquid extraction with hexane, and solvent evaporation.

TABLE II

Polyisocyanate preparation data

Polyol #	Hydroxy content (%)	Isocyanate used	Approximate OH:NCO ratio	Actual weight ratio (g/g)	Polyol content (%)
#35	5.54	HDI	1:4	10:11.124	47
		ISOBIND	1:4	10:18.246	35
#74	9.22	HDI	1:2	10:9.120	52
		ISOBIND	1:2	10:14.940	40
#69	13.12	HDI	1:2	10:12.960	44
		ISOBIND	1:4	10:42.514	19
#77	6.6	HDI	1:2	10:6.490	61

(ISOBIND 100). Four groups were made as well as a set of conventional urea formaldehyde boards. Table III shows the composition of the six different sets. All 24 boards were prepared according to the specifications given in Table III.

The polyisocyanate, ISOBIND 100, was used as a "neat", non-diluted and non-emulsified, liquid that was mixed with a copolymer solution in DMF immediately prior to application by spraying with the spray gun. Additional single test specimens were made for reasons of comparison by successively spraying an emulsified (with SCRIPSET 100 by Monsanto) polyisocyanate and a lignin copolymer solution. The properties tested for these boards were similar to those obtained with a single spraying with component mixing before spraying, and this method was discontinued. The urea formaldehyde adhesive

TABLE III

Composition and preparation data for particle boards

Density	41 pcf
Resin content	6.5%
Resin composition	Polyiscocyanate: copolymer ratio (by wt.) 100:0, 75:25, 50:50, 25:75, 0:100; and commercial urea formaldehyde preparation
Moisture content	12% mat/6% final
Particle geometry	$\frac{3}{8}$ in hammermilled Southern Yellow Pine (Industrial product)
Particle density	38.5 lb/cf
Board thickness	$\frac{1}{2}$ in
Press temperature	350°F
Press pressure	400 psi
Press time	6 min
Press closing	45 sec

was a commercial blend, and was emulsified for sprayability. Resin contents of 6.5% dry weight on OD chip basis were used for all boards. No blotching occurred, indicating uniform adhesive distribution. The chips were used as received, at 10% moisture content for all boards except the urea formaldehyde boards. The chips for the UF-bonded boards were oven dried to 6% moisture content. The chips were then sprayed with adhesive in the rotary drum, placed in a wooden mold, and prepressed for five minutes in an INSTRON testing machine at 10,000 psi (cold). After prepressing the wooden mold was removed and aluminum caul plates were added. Except for the first run with each caul plate set, there was no adhering of polyisocyanate-coated chips to the plates. The boards were pressed in an HPP hot press according to the conditions listed in Table III. A final board thickness of $\frac{1}{2}$-inch was chosen to facilitate testing. Press temperature and press pressure were as recommended by the manufacturers of ISOBIND 100. A press time of 6 minutes is much longer than required for ISOBIND 100, but helped simplify the comparison of data to the urea formaldehyde boards. Sample boards made at lower press pressures were poorly formed. Target press closing time was 45 secs, or a maximum of 60 sec owing to limitations of the hydraulic system of the press used. Faster press closing times are reported to influence board strength beneficially.[31,40] No problems were encountered with pressing even the very high moisture content particle mats with ISOBIND 100, even if moisture contents reached 20% after addition of the adhesive emulsion. Once removed from the press, the boards were allowed to cure for 24 hours.

ASTM 1037-78 specifications were followed in the testing of these boards. Modulus of elasticity and modulus of rupture were measured with the bending test performed and an INSTRON machine. Boards were tested to failure, and moisture content and densities were measured. Linear expansion was measured by use of a 2-h boil test.

RESULTS AND DISCUSSION

1. Lignin sources

Lignin is a natural polyphenolic plant substance of amorphous character. Its cross-linked network structure prevents it from dissolving readily in organic solvents of any type. Following extensive mechanical action (ball milling) or hydrolytic depolymerization, lignin is isolated as a solid power with a distinct tendency to form association products.[46,47] The chemical composition of a multitude of lignin products has been evaluated,[48] and key features of several lignins are summarized in Table IV. A comparison between the structure of mildly isolated milled wood lignins with stream explosion lignins of softwood

TABLE IV

Comparison of several types of lignin in terms of structure and properties

	Milled wood Lignin		Steam explosion Lignin[1]		Kraft Lignin[2]
Property	Softwood (Pine)	Hardwood (Red Alder)	Poplar	Aspen I	
I. Elemental analysis					
C (%)	61.6	57.2	62.3	62.5	64.3
H (%)	5.9	5.8	5.7	5.4	5.8
S (%)	—	—	—	—	2.1
II. Functionality					
OCH_3 (%)	14.0	18.2	15.0	18.4	13.7
OCH_3 ($/C_9$)	0.9	1.4	1.0	1.2	0.8
Total OH (%)	10.5	10.1	9.8	12.6	11.9
Total OH ($/C_9$)	1.1	1.2	1.2	1.1	1.4
Phenolic OH ($/C_9$)	0.3	0.23	0.5	0.4	0.6
Aliphatic OH ($/C_9$)	0.8	0.9	0.6	0.7	0.8
SYR : GUA ratio	0.02	0.7	1.4	1.6	0.2
III. Impurities					
ASH (%)	0.1	0.4	—	—	0.7
Carbohydrates (%)	3.1	8.0	3.3	0.7	0.7
IV. Interunit linkages (Total per 100 C_9 units)					
Alkyl-aryl ethers	50	55	15	30	Hi 30; Lo 15
Non-hydrolyzable (C-C and C-phenylether)	45	40	50	45	50
V. Molecular properties					
$\bar{M}_N$ (VPO)	4000	1500	600	1150	1450
T_g					185

[1] Obtained from IOTECH Corp., Ottawa, Ontario.

[2] Obtained from WESTVACO Corp., North Charleston, South Carolina ("INDULIN-AT").

and hardwood, and softwood Kraft lignin illustrates differences in terms of elemental composition, functionality, typical contaminants, inter-unit linkages, and molecular properties. Differences between phenolic hydroxyl functionality, alkyl-aryl ether inter-unit linkage concentrations, and molecular weights, in particular, are likely to exert a significant influence on the properties and utilization potential of different types of lignins. The range of functional groups includes aliphatic and aromatic hydroxyl groups, carbonyls, and carboxyls. Molecular weights range from several hundred to several million with the likelihood for great polydispersity. Reports of glass transition temperatures range between just below 100 and 185°C, depending on the nature of the preparation used.[49]

Kraft lignin is isolated by acidification of the alkaline spent pulping liquor of the Kraft process, which results in an amorphous powderous precipitate which is separated and dried. Steam explosion lignin (IOTECH lignin) is prepared in accordance with the flow chart given in Figure 1. These lignins have been liquefied by a reaction with propylene oxide in the presence of an alkaline catalyst. This reaction may either be performed in excess propylene oxide or propyl ether or in the presence of an inert organic solvent as reaction medium. The reaction product is a liquid, with viscosity ranging between 500 and 50,000 cPs, depending on the reaction conditions and the amount of lignin incorporated. These lignin derivatives are soluble in various organic solvents, and they may be fractionated and isolated by liquid–liquid extraction of acetontrile solutions with hexane, as indicated in Figure 2. The copolymers may be converted into prepolymers of crosslinked network polymers *via* their hydroxyl functions, most notable with di- and poly-isocyanates. Attempts to convert lignin or carboxylated lignin directly into a polyisocyanate have largely failed;[24] however, derivatization of lignin-derived polyols by capping with diisocyantes has been reported to have been successful.[7] These lignin-based polyisocyanates have been found to contain sufficient solubility in nonpolar solvents to be used for impregnation of cellulosic fiber assemblages.

The liquid polyols produced by the reaction of lignins with propylene oxide are composed of mixtures of lignin propylene oxide copolymer, propylene oxide homo-ligomers and propylene glycol. The composition of the mixtures is conveniently analyzed by gel permeation chromatography using UV and refractive index detection in sequence. The application of this method to a lignin derived polyol is illustrated in Figure 3. Whereas the UV detector response is sensitive to the aromatic copolymer, the refractive index detector is sensitive to both homo- and copolymers. The results in Figure 3 show that the highest molecular weight fractions of the reaction products with lignin absorb UV light, whereas the low molecular weight-fractions are detected only by the refractive index monitor. Liquid–liquid extraction with hexane removes selectively the low molecular weight fraction from the mixture; and the lowest molecular weight peak in the chromatograms constitutes a water-soluble, non-UV absorbing substance, presumably propylene glycol.

II. Polyurethane products

Polyurethanes are versatile materials with a wide range of product applications.[50] Among them are foams, coatings, and thermoset adhesives.

Foams have previously been prepared from lignin derived polyols by mixing them with Freon (blowing agent) and tolylene diisocyanate (TDI), and allowing the mixture to rise.[21] These foams were found to be of low density, to possess good spring-back characteristics, and to resist water sorption. The

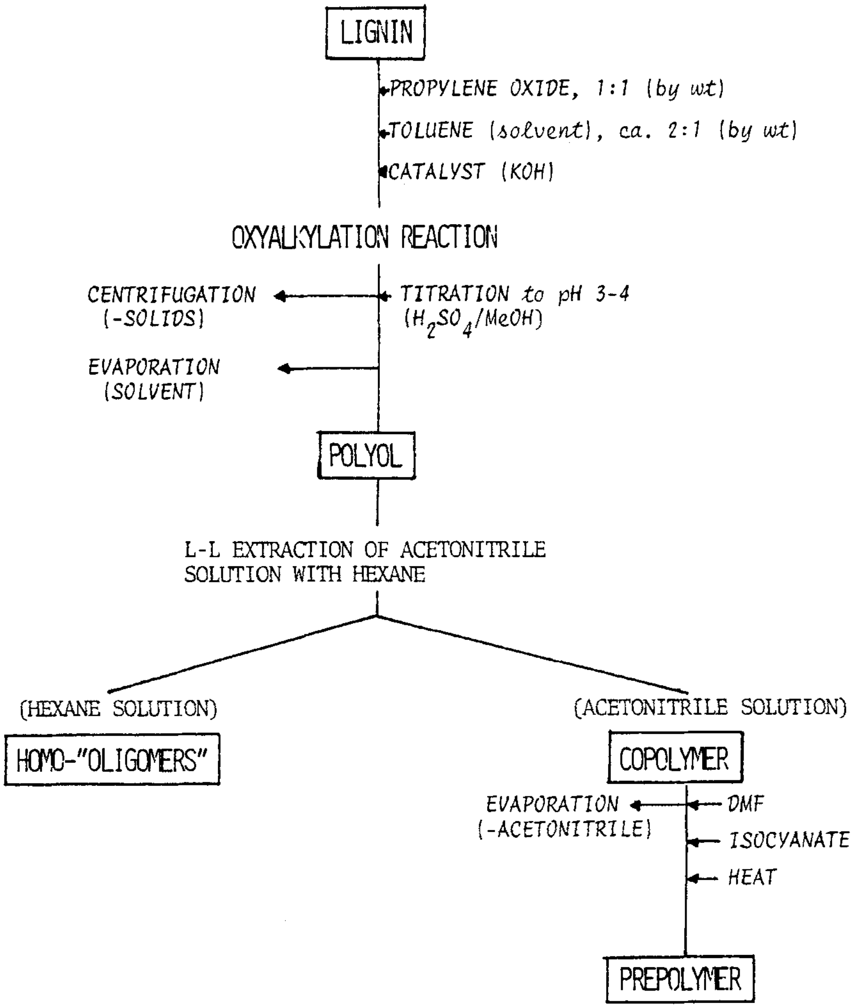

FIGURE 2 Preparation and purification scheme for lignin-derived polyol, copolymer, and (polyisocyanate) prepolymer fractions.

physical shape of a foam resembles the shape of lignin in woody tissues: that of a skin (middle lamella) surrounding a void (lumen), which, in the case of wood, is partially filled with cellwall substance. An illustration of this similiarity is given in the micrograph composition of Figure 4. Where Figure 4A represents a scanning electron micrograph of a cross-section of a hardwood, Figure 4B represents a "natural lignin foam" obtained from wood by bacterially

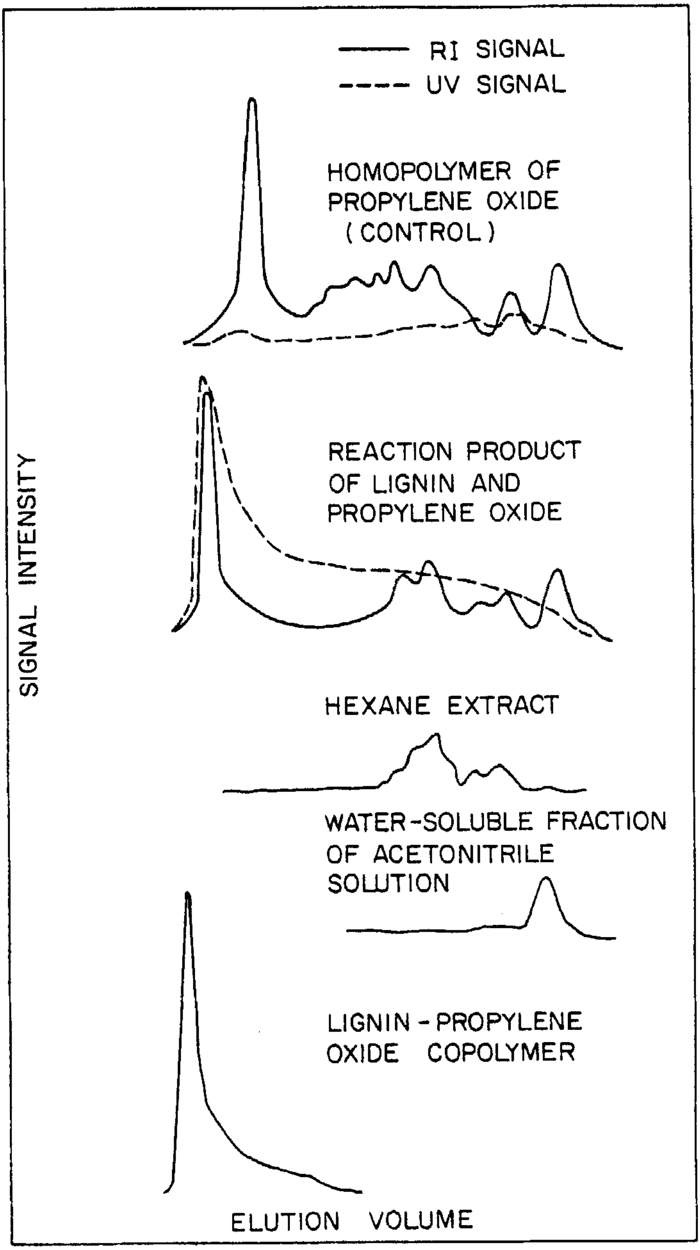

FIGURE 3 Gel permeation chromatograms of various reaction products of propylene oxide with lignin (Sephadex LH 20; ethanol).

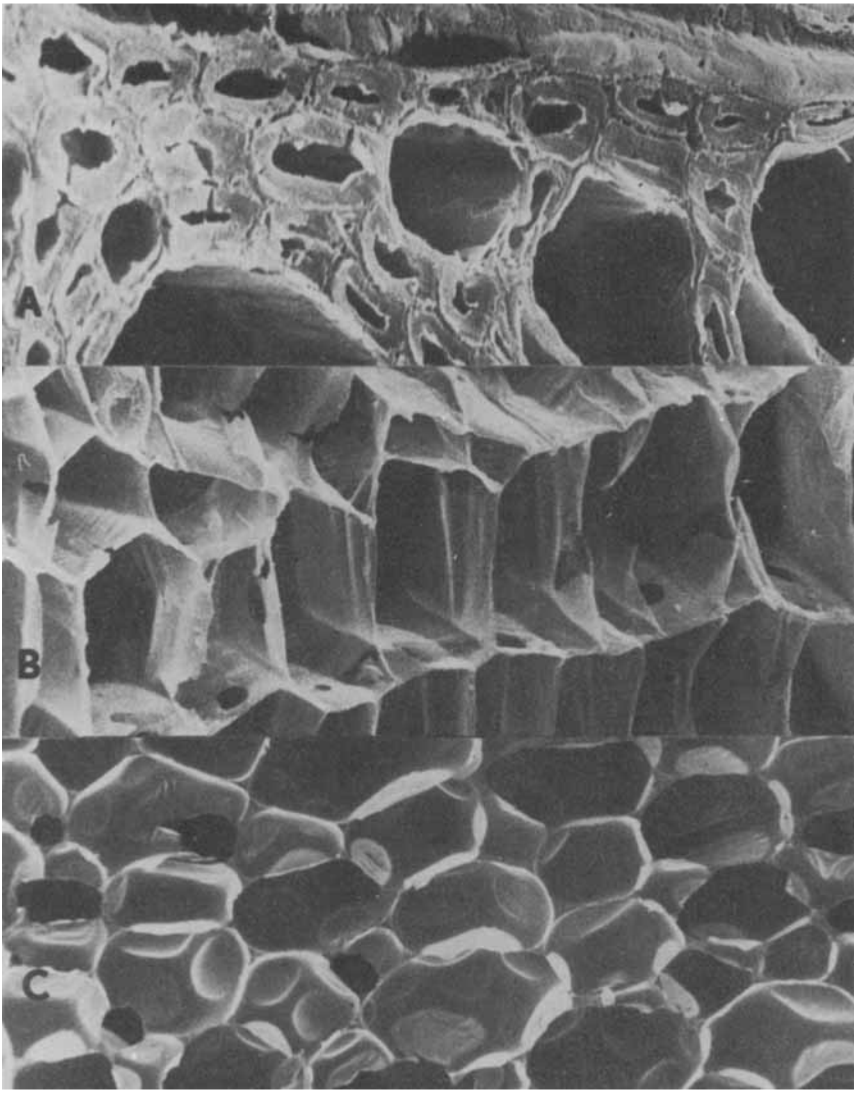

FIGURE 4 Scanning electron micrographs of (A) a cross-section of a hardwood tissue; (B) the cross-section of a woody tissue in which the cell wall substance was degraded bacterially, leaving only the middle lamella intact; and (C) cross-section of a synthetic lignin-containing polyurethane foam.

(Figure 4B reproduced with permission from work by W. Liese and O. Schmidt, Hamburg, Germany).

degrading and removing cell wall substances away from the lignin-rich middle lamella. This is compared with the picture of a synthetic lignin-derived polyurethane foam in Figure 4C. The resemblance of the natural and synthetic foams in physical appearance is striking, and raises the hope that lignin can be reconstituted in its original shape.

The bonding of lignin-containing isocyanates to the surfaces of cellulosic fibers from non-aqueous solutions proceeds with surprising ease and seemingly instantaneously. Similar fiber reinforcement experiments have been carried out previously, and are described in the patent literature.[51] The invention concerns a process for treating unsized paper by contacting the paper with an aqueous emulsion containing a polyurethane prepolymer so as to impregnate the paper sheet with 5 to 150% of its weight with the polymer, drying the impregnated paper, and curing the polyurethane prepolymer. The aqueous emulsion was prepared by emulsifying a liquid isocyanate-terminated polyurethane polymer in an aqueous medium at temperatures between 20 and 95°C with agitation in the presence of a water soluble organic emulsifying agent of the type which will give an oil-in-water emulsion. The emulsion is applied to the paper at temperatures between 20 and 95°C within 24 h of its preparation. The isocyanate terminated polyurethane polymer is the reaction product of an aromatic isocyanate (TDI) and an organic polyol (polytetramethylene ether glycol). Table V lists the properties reported[51] as

TABLE V

Tensile strengths (lb/in^2) of isocyanate treated pulp strips

	20% pick-up level		40% pick-up level	
Binder	Tensile strength	Tensile incr. (%)	Tensile strength	Tensile incr. (%)
HDI	4950	102	5500	124
ISOBIND	4400	79	6050	146
Polyol #35-HDI	4900	100	6100	148
Polyol #35-ISOBIND	4650	89	6050	146
Polyol #74-HDI	4300	75	5450	122
Polyol #74-ISOBIND	5050	106	6400	161
Polyol #69-HDI	4050	65	5700	132
Polyol #69-ISOBIND	5500	124	6900	181
Polyol #77-HDI	3800	55	4550	85
B-1[1]			1350	400
B-2[1]	850	215		
B-3[1]	766[2]	183[2]		

[1] Results reported by DuPont Inc., US Patent #3, 178, 310.
[2] For 19.5% binder pick-up level.

TABLE VI

Properties of lignin-isocyanate treated paper strips

Pick-up %	Breaking length m	Tensile strength kg/m	Modulus of elasticity kPa × 10^6	Stretch %	Density kg/m^3
		Air-drying method			
0.0	3768	867	2.58	1.30	540
6.2	6071	1480	3.47	1.67	546
8.7	6000	1500	3.20	1.85	555
15.5	6589	1750	3.50	1.95	590
21.5	7156	2000	3.98	1.91	599
27.4	7565	2215	4.02	1.98	617
30.5	8322	2500	4.26	2.15	629
		Oven curing method			
0.0	3768	867	2.58	1.30	540
5.8	6025	1567	3.73	1.50	532
7.8	6320	1867	3.79	1.45	535
14.3	7600	1950	4.11	1.65	559
14.9	7380	2200	4.15	1.77	578
21.6	7865	2283	4.23	1.80	593

compared to those found with the lignin based polyisocyanates. These were prepared by briefly immersing paper strips, and curing them at room temperature by evaporating the solvent with compressed air, or by heating briefly at 105°C. Depending on polyisocyanate concentration in solution and number of treatments, binder pick-up by the fiber mat ranged between 5 and 31% by weight. Mechanical properties of "re-lignified" fiber composite strips were measured and the results are summarized in Table VI. The data indicate that strength properties double with 10–20% pick-up of isocyanate binder. The comparison of oven-cured and air-dried samples at equivalent pick-up levels shows higher gains in properties for the former than for the latter. The reaction between the hydroxyl groups of cellulose fiber surfaces and the isocyanate groups of the lignin isocyanate is expected to be more extensive and more complete at elevated temperatures. In addition, partial consumption of the isocyanate groups by atmospheric moisture must be expected for the air drying technique. The results also indicate that the rate at which strength gains are recorded declines with the number of treatments, indicating thereby that either the hydroxyl groups were fully consumed or became inaccessible.

Tensile strength of polymeric MDI (ISOBIND 100) and lignin containing polyisocyanate prepolymer impregnated fiber mats is plotted against degree of polymer retention in Figure 5. Prepolymers capped with polymeric MDI were prepared from lignin-based polyols with 19, 35, and 40% lignin content; and a HDI-capped prepolymer was prepared with 61% lignin content. The results of

Figure 5 indicate a positive relationship between the tensile strength and the pick-up level of isocyanate terminated polymers by cellulosic fiber sheets; and it furthermore illustrates that lignin can contribute beneficially to the strength properties of polyisocyanate adhesives, and may even exceed the contribution to strength by MDI. Both the 19 and 45% lignin containing prepolymers exceeded the strength of straight PMDI in the range below 30% pick-up; the 40% lignin content polyisocyanate was equivalent in strength properties to ISOBIND 100 equivalent. Thus it can be concluded that lignin can indeed replace commercial PMDI as a bonding agent up to approximately 50% substitution level. The influence of lignin polyol content of polyisocyanate prepolymers on the modulus of elasticity (MOE) of isocyanate bonded cellulose fiber mats is illustrated in Figure 6. At between 10 and 40% polymer retention levels, MOE's showed only insignificant strength deterioration up to a level of almost 50% polyol content. Deteriorating strength properties were noticed at lower polyol contents with PMDI containing polyisocyanates than

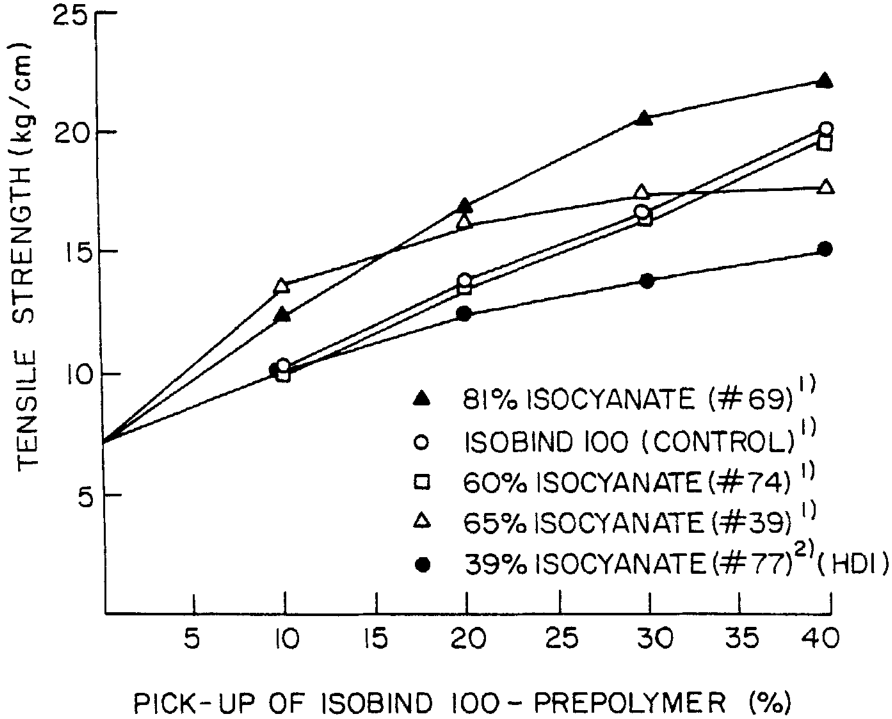

FIGURE 5 Relationship between tensile strength and lignin prepolymer pick-up level for several prepolymers.

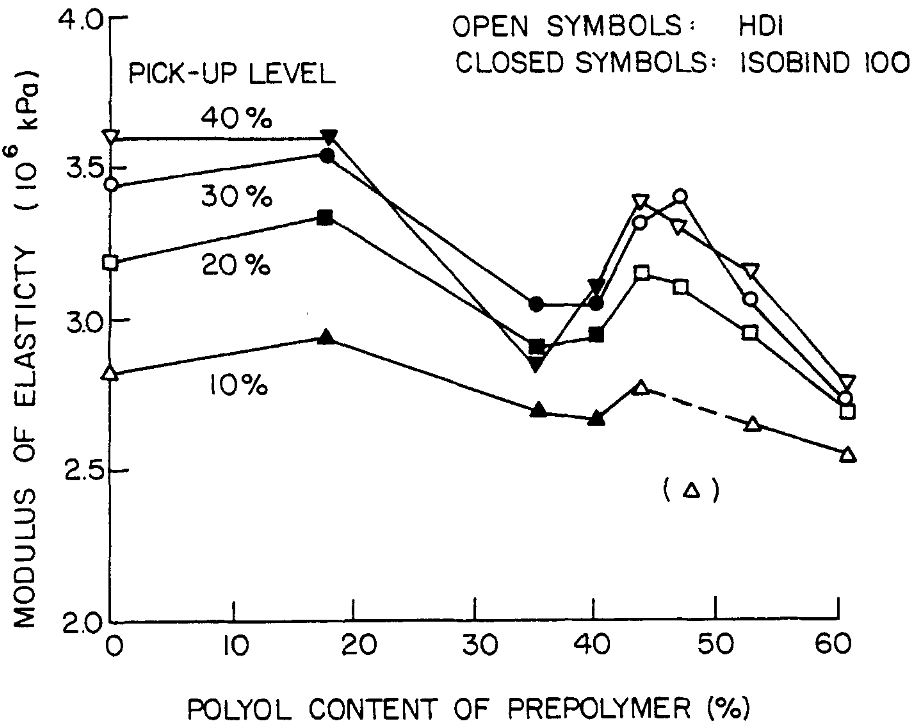

FIGURE 6 Relationship between MOE and polyol content of prepolymer at 10, 20, 30, and 40% pick-up level.

with those prepared with HDI. This result does not surprise in view of the fact that PMDI's isocyanate functionality is 39% less per weight than that of HDI.

Scanning electron micrographs taken of surfaces of untreated and treated fiber assemblages, Figures 7A and 7D, reveal a distinct coating and enveloping effect of individual fibers by the polyurethane polymer. Figure 7 illustrates significant increases in inter-fiber bonding with increasing pick-up levels, and this is obviously responsible for the increased strength properties observed. The micrographs of the fractured areas on testing indicate significantly reduced fiber slippage during breaking.

III. Particle Boards

The use of steam explosion lignin (IOTECH lignin), either before or after hydroxy propylation and purification, in conjunction with polymeric MDI applied either neatly or in emulsified form, has been attempted for the

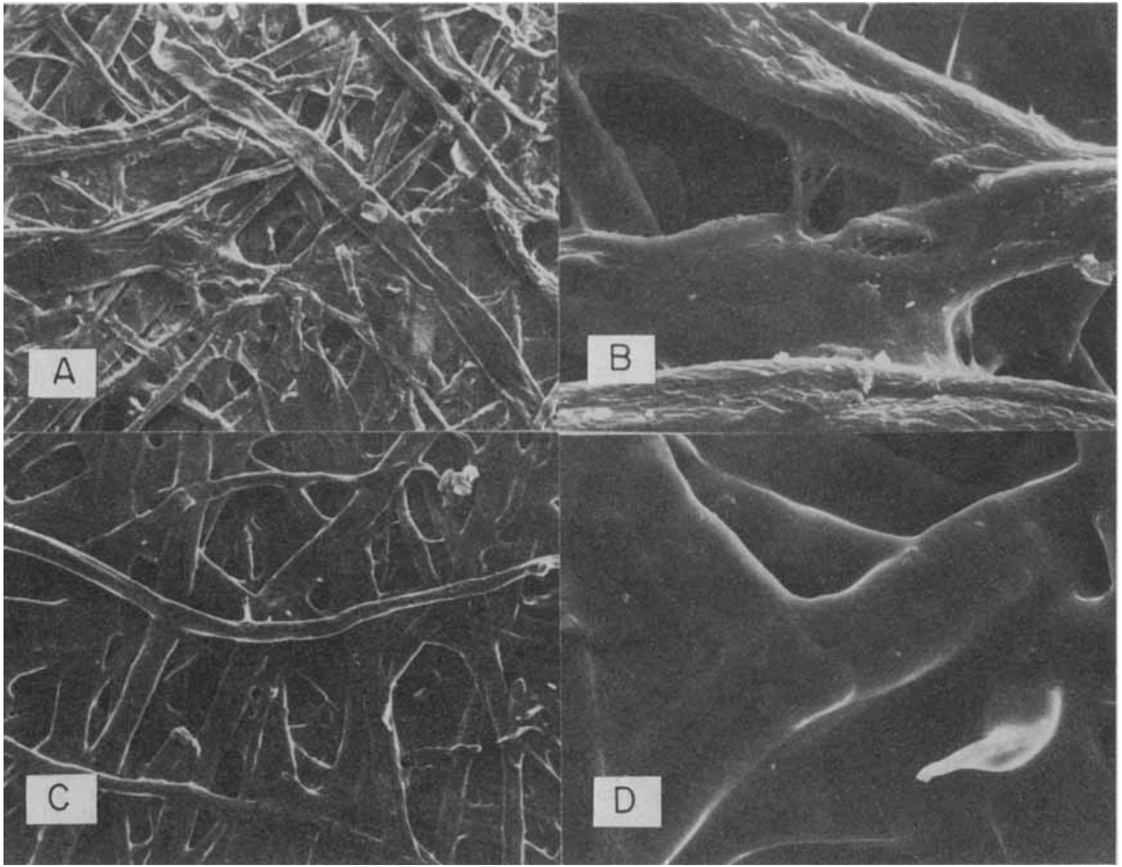

FIGURE 7 Scanning electron micrographs of paper surfaces containing 0 (A), 8.1% (B), 21.5% (C), and 27.4% polyisocyanate prepolymer (D).

production of isocyanate bonded particle boards on southern yellow pine basis. Table III summarizes several target board properties of this experimental series. Each individual experiment was performed in quadruplicate. The influence of isocyanate to copolymer ratio on strength properties in the form of MOR is illustrated in Figure 8. The results suggest that copolymer containing polyisocyanates do not perform as well as unblended PMDI. A rapid decrease in MOR values is experienced for increasing copolymer content. This result differs from the observations made with isocyanate-bonded cellulose fiber mats, but must be explained with differences in reaction conditions in terms of prepolymer preparation, emulsification, differences in isocyanate contents, etc. The influence of (a) hydroxypropylation; (b) copolymer contamination with homo oligomers; and (c) preparation of isocyanate prepolymers on strength properties (MOR) are explored in Figure 9. Particle boards were made 75:25 PMDI: copolymer ratio with the copolymer, the polyol, unaltered IOTECH lignin, and a PMDI-capped prepolymer. Each of these experiments was repeated 4 times. The results suggest that unmodified IOTECH lignin and purified copolymer are both superior in terms of contribution to strength properties as compared to polyol and isocyanate capped prepolymer. The fact that IOTECH lignin by itself appears as a suitable co-reactant with isocyanates for adhesive applications

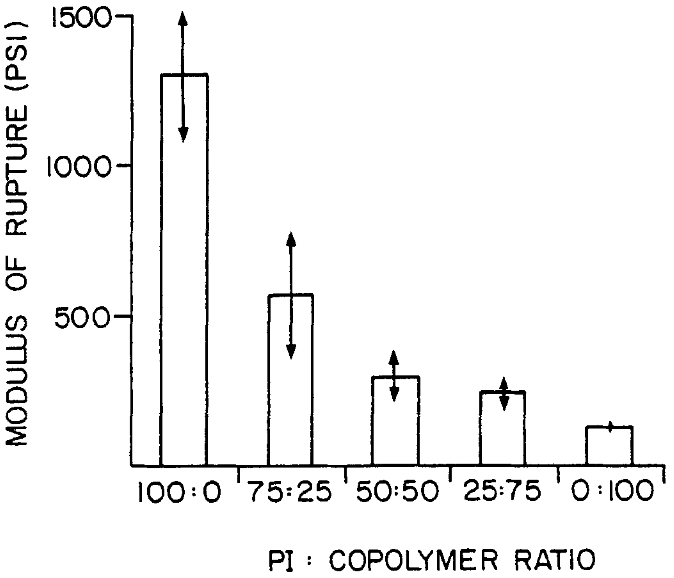

FIGURE 8 Relationship between polyisocyanate : copolymer ratio and MOR for experimental particle boards.

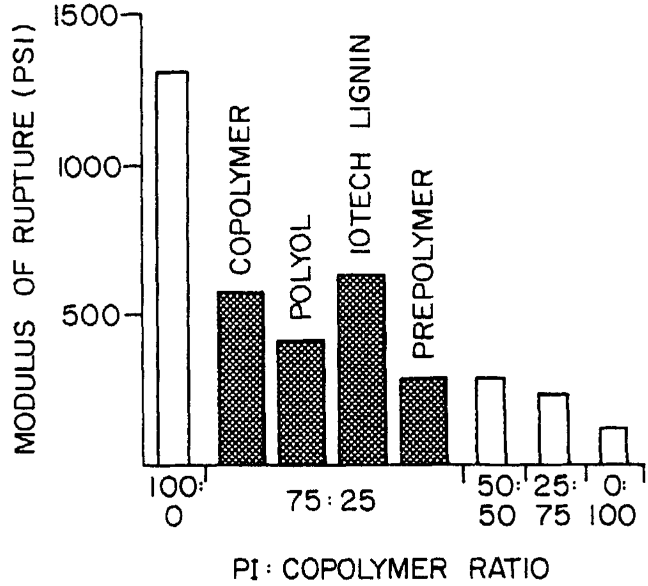

FIGURE 9 Influence of hydroxypropylation, homo-oligomer contamination, and prepolymer formulation on the MOR of particle boards at 75:25 polyisocyanate: copolymer ratio.

must be explained with its low molecular weight, its thermoplasticity, and its relatively flexible nature. Contamination of copolymers by propyl ether homo-oligomers appear to detract from the adhesive performance of the system; and prepolymer formation did not appear to constitute an improvement in properties either.

The interaction of copolymer/lignin-isocyanate bonded particle board with water was investigated by determining thickness swelling in relation to lignin content of the finished board product. The results obtained with hydroxy propylated lignin copolymers, and those reported recently in the patent literature for Kraft lignin and lignin sulfonates,[41] are given in Figure 10. A clear relationship seems to exist between lignin content and thickness swelling for all three types of lignin—copolymer, Kraft lignin, and calcium and amonium based lignin sulfonates. Thus, it must be concluded that lignin, as applied under the conditions explored, does not perform as well as it did in its native state. It must be suspected that insufficient cross-linking and changes in functionality (in particular, by sulfonate groups) contribute significantly to water sorption by lignin based adhesives. Further attempts will be made to find conditions under which physical properties with regard to strength and water swelling will be improved.

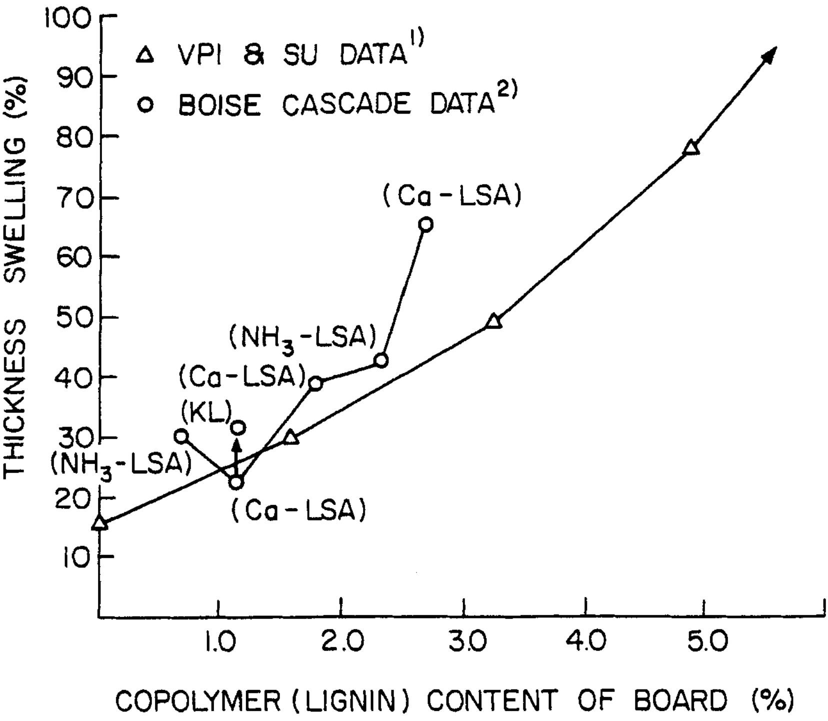

FIGURE 10 Relationship between thickness swelling and lignin or copolymer content of particle boards.

[1] VPI & SU Data obtained with boards with 6.5% resin content with lignin-propylene oxide copolymer, and 2-h boil test.

[2] BOISE CASCADE DATA obtained with boards with 3.5% resin content with lignin (lignin sulfonate—LSA or Kraft lignin—KL), and 24-h cold immersion test (Ref. 41).

CONCLUSIONS

1) Isolated Kraft and steam explosion (IOTECH) lignins can easily be liquefied by an oxyalkylation reaction with propylene oxide. Liquid lignin derivatives can be resolidified by cross-linking with bi-functional isocyanates. If this network polymer formation proceeds in the presence of cellulosic fiber assemblages, a “re-lignified”, wood-like composite material is produced.

2) Strength increases depend on the functionality of polyisocyanates and the degree of relignification. A doubling of the breaking strength of blotting paper is achieved with approximately 10% pick-up of lignin binder.

3) It appears that lignin can replace up to about one half of the isocyanate

content of an isocyanate adhesive without loss in strength properties. At below 30% replacement, lignin containing isocyanate binders have strength properties greater than that of the isocyanate control binder.

4) While lignin contributes beneficially to the performance of isocyanate-bonded cellulose fiber assemblages, isocyanate-bonded wood particle boards seem to suffer from the presence of lignin or hydroxy propylated lignin derivatives.

5) Unmodified IOTECH lignin performs as well as hydroxypropylated lignin in conjunction with isocyanates in terms of strength properties, or even slightly better. The presence of homo-oligomer fractions of propylene oxide negatively affects the performance of lignin based polyols.

6) Microscopic studies have revealed that cellulose fibers become intimately coated and enveloped by lignin binder, and it is likely that this cross-linking action is responsible for the strength increases observed.

Acknowledgements

This work has been made possible through the financial assistance of the National Science Foundation, Grant #79-13135, and revenue from the Robert J. Kennedy Endowment Fund at Virginia Tech. This support is gratefully acknowledged.

References

1. K. V. Sarkanen and C. A. Ludwig, Eds., *Lignins–Occurrence, Formation, Structure and Reactions* (Wiley Interscience, New York, 1971).
2. W. G. Glasser, chapter 2, "Lignin", in *Pulp and Paper*, 3rd. ed., Vol. I, J. P. Casey, Ed. (Wiley and Sons, Inc., New York, 1980), pp. 39–111.
3. K. Freudenberg and A. C. Neish, *Constitution and Biosynthesis of Lignin* (Springer Verlag, New York, 1968).
4. S. I. Falkehag, *Appl. Polym. Symp.* **28**, 247–257 (1975).
5. K. V. Sarkanen, in *Progress in Biomass Conversion*, Vol. 2, K. V. Sarkanen and D. A. Tillman, Eds. (Academic Press, Inc., New York, 1980), pp. 127–144.
6. W. G. Glasser, *Forest Products J.* **31** (3), 24–29 (1981).
7. W. G. Glasser, V. P. Saraf, and J. -F. Selin, *Organic Coatings and Plastics Preprints* (*ACS*), **45**, 551–555 (1981).
8. K. Forss and A. Fuhrmann, *Paperi ja Puu* **11**, 817–824 (1976).
9. K. Forss and A. Fuhrmann, *Forest Products J.* **29**, (7), 39–43 (1979).
10. W. G. Goss, US Patent 2, 849, 314 (1958).
11. C. Uschmann, US Patent 2, 786, 820 (1957).
12. F. J. Edler, US Patent 4, 194, 997 (1978).
13. F. J. Edler, US Patent 4, 244, 846 (1979).
14. C. H. Ludwig, A W. Stout US Patent 3, 658, 638 (1972).
15. C. H. Ludwig, A. W. Stout, US Patent 3, 597, 375 (1971).
16. L. Bornstein, US Patent 3, 677, 884 (1972).
17. V. F. Felicetta, D. E. Wenzel, US Patent 3, 880, 101 (1975).
18. L. Bornstein, US Patent 4, 130, 515 (1977).
19. A. J. Dolenko and M. R. Clarke, *For. Prod. J.* **28** (8), 41–46 (1978).
20. M. R. Clarke and A. J. Dolenko, US Patent 4, 113, 675 (1976).

21. O. H.-H. Hsu and W. G. Glasser, *Appl. Polym. Symp.* **28**, 297–307 (1975).
22. O. H.-H. Hsu and W. G. Glasser, *Wood Sci.* **9** (2), 97–103 (**9999**).
23. W. G. Glasser and O. H. -H. Hsu, US Patent 4, 017, 474 (1977).
24. W. G. Glasser, *et al.*, Chapter 21 in *Urethane Chemistry and Applications*, K. Edwards, Ed., *ACS Symposium Series No. 172*, 311–338 (1981).
25. G. G. Allen, US Patent 3, 476, 795 (1969).
26. O. T. Christian, *et al.*, US Patent 3, 546, 199 (1970).
27. W. G. Ball, R. P. Redmond, and A. D. Adams, *Wood World* **20** (2), 18–20, 35 (1979).
28. H. J. Deppe and K. Ernst, *Holz als Roh-und Werkstoff*, **29** (2), 45–50 (1971).
29. H. J. Deppe, *Proceedings Particleboard Symposium* **11**, 13–31, (1977).
30. W. E. Johns, *ibid.* **14**, 177–184 (1980).
31. A. McLaughlin, Adhesives Symposium, Madison, Wisconsin, Sept. 23–25 (1980).
32. J. W. Frink and H. I. Sachs, Chapter 20 in *Urethane Chemistry and Applications*, K. Edwards, Ed., *ACS Symposium Series No. 172*, 285–310 (1981).
33. O. G. Udvardy, *Proceedings Particleboard Symposium* **13**, 159–177 (1979).
34. J. White, *Forest Products J.* **29** (11), 14–19 (1979).
35. J. B. Wilson, *Adhesives Age*, May 1981, pp. 41–44.
36. J. B. Wilson, *Proceedings Particleboard Symposium* **14**, 185–194 (1980).
37. O. Whittman, *Holz als Roh und Werkstoff* **34**, 427–431 (1976).
38. A. D. Adams, *Proceedings Particleboard Symposium* **14**, 195–205 (1980).
39. J. T. Rice, 34 Annual FPRS Meeting, Boston, Mass., July 7 (1980).
40. A. McLaughlin and W. S. Farrissey, *ibid.*
41. A. L. Lambuth, US Patent 4, 279, 788 (1981).
42. R. M. Rowell and W. D. Ellis, *Wood Science* **12** (1), 52–57 (1979).
43. R. M. Rowell and W. D. Ellis, Chapter 19 in *Urethane Chemistry and Applications*, K. Edwards, Ed., *ACS Symposium Series No. 172*, 163–284 (1981).
44. R. M. Rowell and O. I. Gutzmer, *Wood Science* **7** (3), 240–246 (1975).
45. W. G. Glasser, *et al.*, Proceedings of the International Symposium on Wood and Pulping Chemistry (The Ekman Days 1981), Stockholm, Sweden, Vol 4, pp. IV: 39-IV: 43 (1981).
46. W. J. Connors, S. Sarkanen, and J. L. McCarthy, *Holzforschung* **34**, 80–84 (1980).
47. S. Sarkanen, *et al.*, *Macromolecules* **14** (2), 426–434 (1981).
48. W. G. Glasser, unpublished manuscript.
49. D. A. I. Goring, Chapter 17 in *Lignins–Occurrence, Formation, Structure and Reactions*, K. V. Sarkanen and C. H. Ludwig, Eds. (Wiley-Interscience, New York, 1971), pp. 695–768.
50. K. Edwards, Ed. *Urethane Chemistry and Applications*, ACS Symposium Series No. 172 (1981).
51. R. L. Berger and M. A. Youker, US Patent 3, 178, 310 (1965).

Editor's Note
Due to an error the manuscript here published is the unrevised version. For a copy of the revised manuscript, please contact the author, Dr Glasser.