Graft Copolymers of Wood Pulp and 1-Phenylethene. I. Generality of Synthesis and Proof of Copolymerization

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SYNOPSIS

A method of grafting lignin-containing materials is now known that allows 1-phenylethylene (styrene, [100-42-5]) graft copolymers of a lignin source to be quantitatively made. The grafting reaction is a solution polymerization often run in aprotic, polar, organic solvents. Grafting changes solubility and surface properties of the lignin-containing material. The lignin-containing materials grafted are unbleached wood pulps produced by chemical, thermal, and mechanical pulping. Grafting wood pulp produces a wood-reinforced, thermoplastic composite. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Lignocellulosic materials are the largest form of biomass on this planet. Lignin is a biomass processing residue of paper production or ethanol fermentation that is often burned as fuel. Lignocellulose is the substance of every woody plant. Altering this material to produce products currently made from our slowly diminishing supply of petroleum requires a chemistry to alter the physical and thermodynamic properties of the solid. One such chemistry for the alteration of lignin involves the formation of complex, thermoplastic, graft copolymers of lignin. This is the reaction that will be discussed here.

Graft copolymer is formed by conducting a free-radical polymerization with 1-phenylethene in nitrogen-saturated, organic or aqueous/organic solvent containing a lignin source, calcium chloride, and a hydroperoxide. We have used solution polymerization to prepare numerous, laboratory-scale samples of poly[lignin-g-(1-phenylethylene)] copolymers from lignin contained within wood. The 1-phenylethylene copolymers illustrate the generality of this method for grafting wood, whereas solution polymerization gives us easy heat control and rapid production of products for testing.

Previously, we have shown that free lignin can be grafted with ethene monomers by free-radical copolymerization.[1-10] Alternatively, we have now shown that this method may be applied by use of wood pulp or wood fiber in place of lignin. Wood is defined as the hard fibrous substance, basically xylem, that makes up the greater part of the stems and branches of trees or shrubs. It is found beneath the bark and is also found to a limited extent in herbaceous plants. The Technical Association of the Pulp and Paper Industry recognizes several forms of wood pulp. These are groundwood pulp, refiner mechanical pulp, thermomechanical pulp, chemi-thermomechanical pulp, and chemical pulps. Groundwood pulp (GroundWoodPulp) is made by grinding between mechanically strong, synthetic composite stones produced from fine grits of silicon carbide or alumina embedded in a softer ceramic matrix. Groundwood pulp contains a considerable proportion (70–80 wt %) of fiber bundles, broken fibers, and fines in addition to the individual fibers. The fibers are essentially wood with the original cell-wall lignin intact. They are, therefore, very stiff and bulky and do not collapse like chemical-pulp fibers.

A machine called a refiner produces refiner mechanical pulp (RefineMechPulp). The refiners are rotating-disk attrition mills. The disk plates have a number of radial ever-diminishing channels leading from center to edge. The plates are paired face-to-face with a small interval between them. One disk rotates against a stationary disk or they both move

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in a counterrotating manner. The chips are fed into the channels near the shaft in one of the disks and they move toward the periphery while undergoing attrition. The chips are first broken down into matchsticklike fragments by the action of the breaker bars, then into progressively smaller bundles as they move through the intermediate and fine-bar sections. They emerge from the periphery as single fibers or fiber fragments, including ribbons and fibrils that were formed by the unraveling of the spiral fiber walls of individual fibers. This process is termed fibrillation. These thin, flexible materials considerably improve the bonding properties of the mechanical pulps.

A further form of wood useful in this reaction is thermomechanical pulp (ThermoMechPulp). If chips are presteamed to 110–150°C, they become malleable and do not fracture readily under the impact of the refiner bars. This modification is called thermomechanical pulping. A thermoplasticization of the wood occurs when it is heated above the glass transition point of wet lignin. Then, these chips are fiberized in a refiner at high consistency, and whole individual fibers are released; separation occurs at the middle lamella, and the same ribbonlike material described for RefineMechPulp is produced from the S_1 layer of the cell wall. The amount of fibrillization depends on the refining conditions and is critical to the properties of the pulp. There is much less fiber fragmentation than in groundwood pulps or in those produced by unheated refiners.

It is also possible to use chemithermomechanical pulp (ChemThermoMePulp). The strength properties of thermomechanical pulps can be increased further by mild pretreatment with sodium sulfite at pH 9–10. The chips are impregnated with chemicals, steamed to 120–170°C, then refined. The yield is 90–92%, which is 2–3% lower than in ThermoMechPulp. A range of properties can be obtained by adjusting processing variables but, in general, chemithermomechanical pulps have a greater long-fiber fraction and lower-fines fraction than a comparable thermomechanical pulp. The intact fibers are more flexible than ThermoMechPulp fibers. Further information on pulps is available.[11]

Polymers have been reinforced with many fibers, including glass,[12] asbestos, and kevlar. Wood, however, has many advantages of a reinforcing fiber. The advantages of using wood as a composite material reinforcing fiber are the following:

1. Compared to inorganic fillers, wood fibers possess lower density, high specific strength and modulus, renewable nature, and lower cost and suffer little damage during processing.[13]

2. Wood pulp fibers possess strength and modulus properties that compare favorably with glass fibers on an equal density basis.

3. Comparisons of the stiffness/weight efficiencies revealed that pulp composites equal or exceed the stiffness of most traditional materials of construction including steel, aluminum, glass-fiber composites, and talc-filled polyolefins, while retaining a major material cost advantage.

4. Wood fibers are nonabrasive so that relatively large concentrations may be incorporated into polyolefins without causing serious machine wear during mixing and fabrication.

5. Compared to glass fibers and aramid fibers (Kevlar), cellulosic fibers showed the least damage during processing.[12]

6. The wood–thermoplastics composite materials can be processed by traditional processing methods such as injection, press-molding, extruding, and casting. Mass production of their products can be easily realized.[14]

These advantages have allowed wood to be used in thermoset materials where reactions on the hydroxyl groups of the cellulose allow firm binding of the fiber to the continuous phase. In thermoplastics, reactions across the fiber–thermoplastic boundary will not occur. This produced several problems in trying to reinforce a hydrophobic plastic with hydrophilic wood. The disadvantages of making wood-reinforced, thermoplastic composite materials are the following:

1. The poor interfacial adhesion between the hydrophobic polymer and hydrophilic fiber. The problem of compatability of wood fibers can be overcome by (a) grafting short polymer segments onto the fiber surface, (b) use of coupling agents, and (c) use of adhesion promoting agents.[15]

2. The poor dispersion of wood materials in the polymer matrix. The wood fibers tend to clump into plastic-free, fiber vugs within the solid. Attempts to overcome this problem include adding dispersing agents, elevating the mixing temperature, and extending the mixing period in the mixer.[16]

3. The breakage of fiber during the mixing stage.

Two classes of chemicals mentioned as means of removing the disadvantages of thermoplastic com-

posites, coupling agents and dispersing agents, are added solely to alter the wood–plastic interface. A number of materials have been used as wood coupling agents in research on thermoplastic solids. The most common are maleic anhydride-modified polyprolylene (Hercoprime),[17] maleic anhydride, polyethylene–poly(phenyl isocyanate),[18] and Silane A172 [vinyltris(2-methoxyethoxy)silane].[17] The most common dispersing agents are stearic acid, paraffin wax, polyethylene wax, and mineral oil.[17]

Grafting removes the need for coupling or dispersing agents.[19] When a particular plastic is to be blended with wood, we react the wood with the monomer used to make that plastic.[20] This creates a hydrophobic surface of the plastic on the wood.[21] This plastic coating can readily bond to the continuous plastic phase. The products of this grafting reaction are thermoplastic composites with dispersed, bound fibers distributed throughout the continuous phase. In the following sections, the synthesis procedure, proof of grafting, purification procedures, and homopolymer/graft copolymer quantification results will be presented.

EXPERIMENTAL

Synthesis

The polymerization can be run in any one of several solvents. Dimethylsulfoxide has been used as the solvent for the reactions reported here. This reaction can be successfully run with concentrations or mole ratios of the reactants in the following ranges: (1) polymerizable solids content of the reaction: 50 wt % or less; (2) hydroperoxide to calcium chloride: 0.25 to 32; (3) hydroperoxide to lignin (number-average molecular weight): 21 to 113; and (4) weight fraction of monomer in polymerizable solids: 0.01 to 0.99.

Prepare solution A by placing pure 1-phenylethene in a conical flask and bubble it with nitrogen (N_2) for 10 min. Prepare solution B by placing the lignin source, calcium chloride, and dimethylsulfoxide solvent in a conical flask, stir until uniformly dispersed, and bubble the solution with N_2 for 20 min. Solutions A and B are stirred while being purged with nitrogen. Add H_2O_2 to solution B, and bubble it with N_2 for 20 min. Add solution A to solution B. After 5 min of stirring and bubbling N_2 through the reaction mixture, the flask is stoppered and placed in a $30 \pm 0.1°C$ bath for 48 h.

The reaction should be stirred throughout the synthesis. The stirring rate and force will depend on (1) the amount of 1-phenylethene monomer in the monomer mixture with higher mole fractions of 1-phenylethene requiring higher rates of stirring, and (2) the shape and structure of the reaction vessel. High shear rates in the reaction should be avoided because they will cause the formed polymer to mechanically degrade. The preferred stirring rate in the conical flask used in laboratory synthesis is 2–5 Hz. This produced a shear rate of approximately 10–200 per s in the reaction mixture and this is the preferred shear rate for high yield synthesis. All reactions are terminated by opening the reaction vessel. This terminated slurry can then be added to 10 times its volume of distilled water and the polymer recovered by filtration.
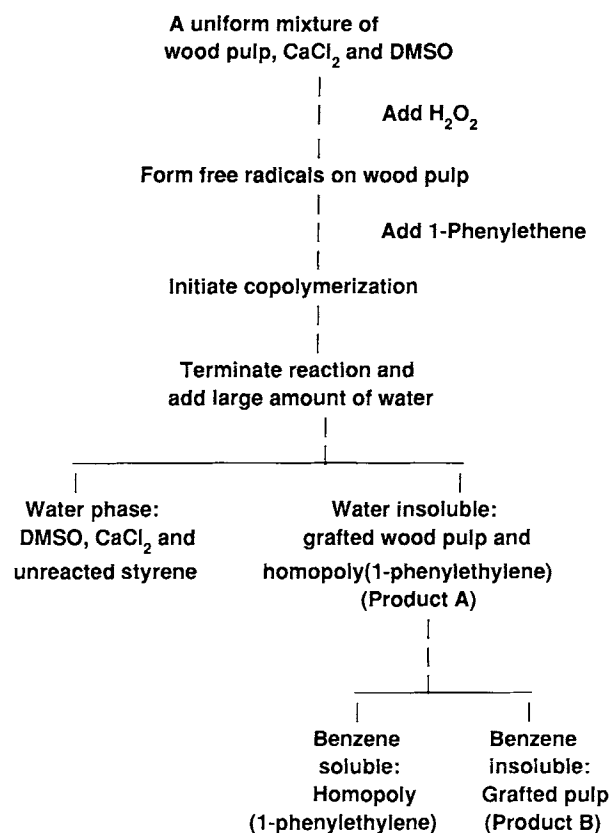
Assays

Analysis procedures for oxidizing equivalents by iodine/thiosulfate titration and elemental composition are given in Ref. 19. Analysis for grafted fraction of converted poly(1-phenylethylene) and homopolymer were done by benzene extraction. Benzene extraction was run for 48–100 h at 79°C on a weighed portion of the reaction product, product A, contained in type N, Sargent Welch filter paper. After extraction, the benzene solution and residue in the filter were allowed to dry. The weight of the benzene solution residue was measured and the solid was labeled poly(1-phenylethylene) homopolymer. The weight of unextractable material was measured and the solid was labeled Product B. A diagram of the synthesis and purification procedure is given in Figure 1.

Mixtures of poly(1-phenylethylene) homopolymer and wood pulp precipitated from suspension were used as blanks in the extraction tests. Two blanks were made by dispersing 2.03 g Mechanical Pulp and 2.02 g ChemTherMePulp, respectively, in 50 g N,N-dimethylformamide (DMFA) by continuous agitation until a uniform dispersion was formed. A total of 9.34 or 4.44 g Amoco poly(1-phenylethylene), respectively, were added to the slurries, and the slurries were stirred until a uniform mixture formed. The mixture was poured into 1 L of distilled water to precipitate a uniform mechanical mixture of wood pulp and poly(1-phenylethylene). The mixture was filtered and dried.

Materials

A total of six samples of lignin-containing-material and one blank were prepared for use in the grafting reaction. The first sample was made by passing as-

A uniform mixture of
wood pulp, CaCl$_2$ and DMSO

|

| Add H$_2$O$_2$

|

Form free radicals on wood pulp

|

| Add 1-Phenylethene

|

Initiate copolymerization

|

|

Terminate reaction and
add large amount of water

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| |
Water phase: Water insoluble:
DMSO, CaCl$_2$ and   grafted wood pulp and
unreacted styrene   homopoly(1-phenylethylene)
                          (Product A)

|

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| |
Benzene   Benzene
soluble: insoluble:
Homopoly   Grafted pulp
(1-phenylethylene) (Product B)

Figure 1 A diagram of synthesis and fractionation of reaction product.

pen chips through a refiner to produce a refiner mechanical pulp, labeled RefineMechPulp. A second sample was made by passing chips made from a mixture of 70% spruce and 30 other wood through a mechanical grinder. It was labeled Mechanical Pulp. Four samples of wood pulp were prepared from a mixture of white spruce and balsam fir chips contaminated with 0–8 wt % poplar. The initial sample was made by impregnating the chips with 2.2 wt %, aqueous sodium sulfite at pH 8.0 for 2 min at 120°C. The chips were then ground in a pressurized refiner to produce 93% yield pulp, which was labeled ChemTherMePulp. The next sample was ground under a stone wheel and the 96 wt % of the input wood that was recovered was dried and labeled GroundWoodPulp. Another sample was produced by pressing the chips through a pressurized, two-stage refiner. Yield was 95 wt % and the pulp was labeled ThermoMechPulp. The final sample was made by digesting the chips with 10 wt % SO$_2$, aqueous sodium bisulfite at pH 6.0 for 120 min at 160°C. The pulp constituted 87% of the wood used and was labeled VeryHighYldSulf. All pulps were

dried at room temperature before storage. The blank, medical-grade cotton was obtained from the campus infirmary and was used as received. Properties of these pulps are given in Table I.

Measurements of the length, diameter, and aspect ratio of the wood fibers were made in triplicate on a Varimex microscope for at least five randomly chosen fibers. The compound 1-phenylethene was obtained from the Laboratory and Research Products Division of Kodak, Rochester, NY 14650. The 1-phenylethene was purified to remove the stabilizer by washing the monomer three times with aqueous base at a ratio of 1 g 1-phenylethene to 1 mL of 2N NaOH. The stabilizer-free monomer was washed with distilled water to pH 7 and dried with anhydrous calcium chloride for 2 days. It was then distilled under vacuum at 40°C and 20 mmHg pressure. The central cut was collected in dark bottles and stored in a freezer at −15°C. Hydrogen peroxide was also from Kodak and was nominally defined as 30% hydrogen peroxide in water. Assays of the two bottles used[22] showed them to be (1) 28.99% H$_2$O$_2$ in water, 1.704 × 10^{-2} equivalents per gram, 1.907 × 10^{-2} equivalents per milliliter, and (2) 29.86% H$_2$O$_2$ in water, 1.756 × 10^{-2} equivalents per gram, 1.947 × 10^{-2} equivalents per milliliter. Reagent-grade anhydrous, 8-mesh calcium chloride, and dimethylsulfoxide were used in these experiments. Other salts were reagent-grade materials and were used as supplied. Nitrogen used in the syntheses was commercial grade bulk gas.

Equipment

Reactions were run in a water bath heated and circulated by a Brinkmann IC-2 heater stirrer. The reactions were mixed with a 40 W, Telemodul 40 S submersible magnetic stirrer. Weighings were done on a Mettler H6, 4-decimal-place balance. All extractions were done in a Soxhlet apparatus. Fibers were measured on a Varimex MWM, microscope with a goniometric head.

RESULTS AND DISCUSSION

A large number of monomers have been added to lignin using this free-radical grafting process,[23-26] but most of these materials are polar compounds prone to the formation of hydrogen bonds. This previous work has shown that lignin is a critical reagent for the initiation of copolymerization and, in general, the lower the lignin content of the material to be

Table I Wood Material Data

Sample No.	Pulp Name	Lignin (wt %)	Source	Manufacturer
1.	Refiner mechanical (RefineMechPulp) (pH 7)	—	Aspen	Mead Paper Co., Publishing Paper Division, P.O. Box 757, Escanaba, MI 49829
2.	Mechanical pulp (Mechanical Pulp)	29	Spruce (70%) Bulk (30%)	Stora Forest Industry Ltd., P.O. Box 59, Port Hawkesburg Nova Scotia, B0E 2V0, Canada
3.	Chemithermomechanical (ChemTherMePulp) (pH 8.0)	25–29	White Spruce, Balsam Fir, and Poplar (0–8%).	Research and Technical Dept., Research and Technical Development Center, Stone-Consolidated Inc., 255 1st Street, Grand'Mere, Quebec, Canada G9T 5L2
4.	Stone ground wood (GroundWoodPulp)	29	*Ibid.*	*Ibid.*
5.	Thermomechanical (ThermoMechPulp) (pH 7.0)	25–29	*Ibid.*	*Ibid.*
6.	Very high yield sulfite (VeryHighYldSulf) (pH 6.0)	25	*Ibid.*	*Ibid.*
7.	Degreased cotton (Cotton)	0.00	CB340 Cotton Balls	Parke Davis, Inc. 201 Tabor Rd. Morris Plains, NJ 07950

grafted into a plastic, the less effective the process for adding side chains or surface coats is. In the reaction on wood, the "lignin" referred to in a discussion of the process is the lignin in—and on the surface of—the wood fiber or pulp. Pulps such as thermomechanical pulp or mechanical pulp have surfaces with a high lignin content and are readily altered by grafting chemistry to make a plastic. Use of wood in place of extracted lignin allows easier recovery of the reaction product since the treated wood can be recovered from the reaction mixture by filtration and all byproducts of the reaction, such as dissolved graft copolymer, can be recovered by simple separations such as dialysis, precipitation in nonsolvent, and freeze-drying. The product of a reaction on pulp is a surface-modified pulp that has a polymeric side chain grown off of the surface of the pulp fiber or particle.

The process gives a product with the structure shown in Structure 1, where R_i, with $i = 1, 2, 3,$ or 4, is any group that does not interfere with free-radical polymerization. Plastic side chains described above for grafting to lignin can be attached to pulp, wood, or wood fiber by the method described in the Experimental section.

$$-\left(-\overset{\overset{\displaystyle R_1}{|}}{C}-\overset{\overset{\displaystyle R_2}{|}}{\underset{\underset{\displaystyle R_4}{|}}{C}}-\right)_n$$

PULP FIBER OR PARTICLE
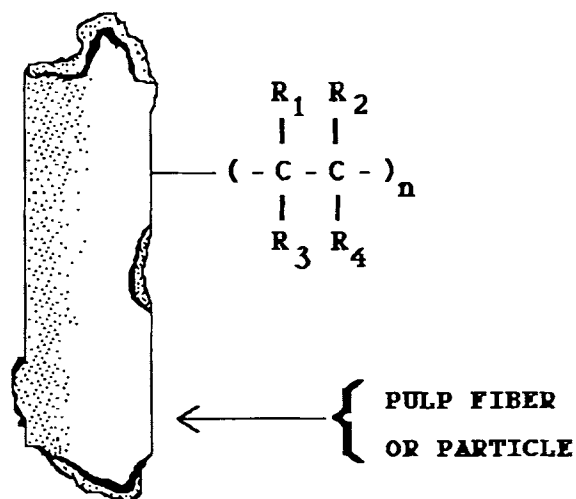
Structure 1

Table II   Copolymerization Reactions of Lignin-containing Materials and 1-Phenylethylene

| Sample No. | Reactants (g) | | | | | Yield[a] (g)/(wt %) | Type of Lignin-containing Material |
	1-Phenyl-ethene	Lignin Material	CaCl₂	H₂O₂ (mL)	Solvent		
2-1	4.67	2.02	2.04	3.0	60.06	3.09/46.19	RefineMechPulp
2-2	6.02	2.04	2.03	3.0	60.05	4.55/56.45	RefineMechPulp
2-3	8.00	2.03	2.01	3.0	60.16	7.75/77.27	RefineMechPulp
2-4	11.38	2.04	2.00	3.0	60.11	10.17/75.78	RefineMechPulp
2-5	18.00	2.03	2.02	3.0	60.15	12.97/64.75	RefineMechPulp
2-6[b]	8.03	2.00	2.01	3.0	60.02	8.07/73.16	RefineMechPulp
2-7[b]	11.34	2.01	2.02	3.0	60.09	8.56/59.65	RefineMechPulp
2-8[b]	18.00	2.01	2.01	3.0	60.03	4.67/22.22	RefineMechPulp
2-9	4.67	2.00	2.01	3.0	40.12	5.45/81.71	RefineMechPulp
2-10	6.00	2.03	2.02	3.0	40.07	5.14/64.01	RefineMechPulp
2-11	8.01	2.04	2.01	3.0	40.03	8.57/85.27	RefineMechPulp
2-12	11.37	2.00	2.04	3.0	40.05	10.81/80.85	RefineMechPulp
2-13	18.06	2.01	2.04	3.0	40.00	6.98/34.78	RefineMechPulp
2-14	3.53	2.04	2.01	3.0	40.02	4.15/74.51	RefineMechPulp
2-15	3.53	2.00	2.03	3.0	51.32	4.51/81.56	Mechanical Pulp
2-16	4.67	2.00	2.04	3.0	53.73	4.91/73.61	Mechanical Pulp
2-17	6.00	2.01	2.04	3.0	50.03	6.40/79.90	Mechanical Pulp
2-18	8.00	2.01	2.05	3.0	50.02	8.37/83.62	Mechanical Pulp
2-19	11.37	2.02	2.03	3.0	50.04	11.33/84.62	Mechanical Pulp
2-20	18.06	2.04	2.05	3.0	50.52	16.29/81.04	Mechanical Pulp
2-21	10.52[c]	2.03	2.05	3.0	50.03	11.34/90.36	Mechanical Pulp
2-22	18.00[d]	2.04	2.03	3.0	50.02	17.80/88.82	Mechanical Pulp
2-23	3.53	2.01	2.00	3.0	50.02	2.87/51.81	ChemTherMePulp-1[f]
2-24	7.67	2.00	2.02	3.0	50.03	3.56/53.37	ChemTherMePulp-1
2-25	6.00	2.05	2.02	3.0	50.00	4.96/61.61	ChemTherMePulp-1
2-26	8.00	2.00	2.03	3.0	50.01	6.09/60.90	ChemTherMePulp-1
2-27	11.37	2.01	2.05	3.0	50.00	8.48/63.38	ChemTherMePulp-1
2-28	18.06	2.03	2.00	3.0	50.00	6.40/31.86	ChemTherMePulp-1
2-29	3.57	2.02	2.01	3.0	50.02	4.00/71.56	ChemTherMePulp-2[f]
2-30	4.64	2.04	2.06	3.0	50.06	5.14/77.41	ChemTherMePulp-2
2-31	6.03	2.00	2.02	3.0	50.00	6.40/79.70	ChemTherMePulp-2
2-32	8.04	2.03	2.04	3.0	50.12	8.13/80.73	ChemTherMePulp-2
2-33	11.34	2.03	2.02	3.0	50.08	11.94/89.30	ChemTherMePulp-2
2-34	18.16	2.02	2.06	3.0	50.04	16.38/81.17	ChemTherMePulp-2
2-35	3.55	2.02	2.03	3.0	50.01	3.62/64.99	GroundWoodPulp-1
2-36	4.64	2.01	2.04	3.0	50.02	3.94/59.25	GroundWoodPulp-1
2-37	6.05	2.00	2.01	3.0	50.02	4.95/61.49	GroundWoodPulp-1
2-38	8.00	2.01	2.02	3.0	50.08	7.28/72.73	GroundWoodPulp-1
2-39	11.37	2.01	2.00	3.0	50.01	9.12/68.16	GroundWoodPulp-1
2-40	18.10	2.04	2.03	3.0	50.03	12.53/62.21	GroundWoodPulp-1
2-41	3.59	2.00	2.05	3.0	50.08	3.84/68.69	GroundWoodPulp-2
2-42	4.65	2.02	2.01	3.0	50.06	4.56/68.37	GroundWoodPulp-2
2-43	6.07	2.02	2.00	3.0	50.07	6.05/74.78	GroundWoodPulp-2
2-44	8.05	2.00	2.01	3.0	50.00	7.02/69.85	GroundWoodPulp-2
2-45	11.34	2.03	2.04	3.0	50.04	10.06/75.24	GroundWoodPulp-2
2-46	18.14	2.03	2.06	3.0	50.10	15.28/75.76	GroundWoodPulp-2
2-47	8.05	2.05	2.00[c]	3.0	50.05	7.74/76.63	GroundWoodPulp-2
2-48	11.78[d]	2.02	2.05	3.0	50.02	12.73/92.25	GroundWoodPulp-1
2-49	18.05[e]	2.00	2.02	3.0	50.10	18.09/90.22	GroundWoodPulp-1

Table II   (*Continued*)

Sample No.	Reactants (g)					Yield[a] (g)/(wt %)	Type of Lignin-containing Material
	1-Phenyl-ethene	Lignin Material	CaCl$_2$	H$_2$O$_2$ (mL)	Solvent		
2-50	3.58	2.00	2.01	3.0	50.05	3.39/60.75	ThermoMechPulp
2-51	4.64	2.02	2.01	3.0	50.04	4.03/60.51	ThermoMechPulp
2-52	6.05	2.00	2.02	3.0	50.03	5.25/65.22	ThermoMechPulp
2-53	8.08	2.00	2.00	3.0	50.03	7.54/74.80	ThermoMechPulp
2-54	11.35	2.02	2.01	3.0	50.00	10.26/76.74	ThermoMechPulp
2-55	18.12	2.00	2.01	3.0	50.16	11.72/58.25	ThermoMechPulp
2-56	3.58	2.02	2.02	3.0	50.05	3.97/70.89	VeryHighYldSulf
2-57	4.67	2.01	2.01	3.0	50.12	4.67/69.91	VeryHighYldSulf
2-58	6.04	2.03	2.01	3.0	50.07	6.15/76.21	VeryHighYldSulf
2-59	8.06	2.02	2.07	3.0	50.00	8.04/79.76	VeryHighYldSulf
2-60	11.34	2.01	2.02	3.0	50.03	10.58/79.21	VeryHighYldSulf
2-61	18.13	2.01	2.02	3.0	50.05	15.81/78.50	VeryHighYldSulf
2-62	8.06	2.01	2.00[c]	3.0	50.06	8.08/80.24	VeryHighYldSulf
2-63	3.53	1.01	3.04	3.0	50.08	1.12/3.12	Cotton
2-64	4.67	1.00	3.06	3.0	50.12	0.93/0.00	Cotton
2-65	6.07	1.00	3.02	3.0	50.06	0.94/0.00	Cotton
2-66	8.05	1.00	3.02	3.0	50.05	0.91/0.00	Cotton
2-67	11.36	1.00	3.01	3.0	50.01	0.96/0.00	Cotton
2-68	18.10	1.01	3.04	3.0	50.04	0.97/0.00	Cotton

[a] Yield of product = (wt. of product recovered)/(wt. of monomer added + wt. of pulp added).

[b] This sample was prepared with lignin as well as wood pulp in the reaction mixture. The lignin is kraft pine lignin and the sample received 1.00 g of lignin.

[c] The calcium chloride added to 2-47 and 2-62 was ground, 40 mesh material.

[d] This sample was prepared using 1-(4-bromophenyl)ethene as the monomer.

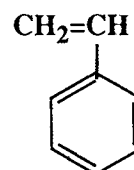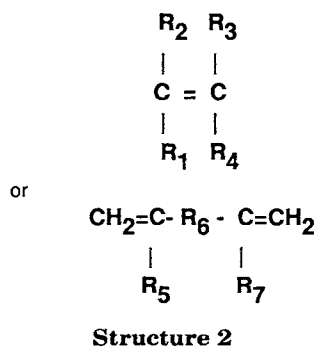[e] This sample was prepared using 1-(4-chlorophenyl)ethene as the monomer.

[f] -1 and -2 are different batches of the same pulp.

This grafting process can create both thermoplastic and thermoset materials in that both di- and higher functionality monomers can be grafted onto lignin-containing materials. This change that can be achieved by choice of the alkene monomer is illustrated by Structure **2**, where R_i, with $i = 1, 2, 3, 4, 5, 6,$ or 7, is an organic or inorganic functional group that does not interfere with free-radical polymerization. The difunctional monomers with side

groups R_1-R_4 would produce thermoplastic wood-reinforced materials, whereas the tetrafunctional monomers with $R_i = R_5-R_7$ would produce cross-linked composites.

Synthesis

In the samples described here, the monomer used is 1-phenylethene, [100-42-5]:

$$R_2 \quad R_3$$
$$| \quad |$$
$$C = C$$
$$| \quad |$$
$$R_1 \quad R_4$$

or

$$CH_2 = C\text{-} R_6 \text{-} C = CH_2$$
$$| \qquad |$$
$$R_5 \qquad R_7$$

Structure 2

CH$_2$=CH

1-Phenylethene

Data for a spectrum of reactions run to optimize yield and create grafted samples of six different wood pulps are given in Table II. All these reactions were

stirred at a rate of about 4 Hz throughout the synthesis. The data of Table II show clearly that all of these lignin-containing materials can be used as a reaction site for the production of a polymeric product. In all of the reactions of Table II, the pulp was stirred for at least 24 h before the reaction was initiated. If the pulp is not mixed in the reaction until uniformly dispersed, low conversion of monomer to polymer and reduced levels of grafting may occur. Further, the reaction temperature should be between 20 and 50°C and the weight percent halide ion in the reaction mixture should be at least 0.1 wt % to insure high yield from the reaction. **WARNING: Reactions initiated with reagents that are above 35°C when mixed might cause foaming or an explosion.**

The structures of the monomers mentioned in the footnotes of Table II are shown below:

CH = CH₂

Cl

1-(4-Chlorophenyl)
ethene

CH = CH₂

Br

1-(4-Bromophenyl)
ethene
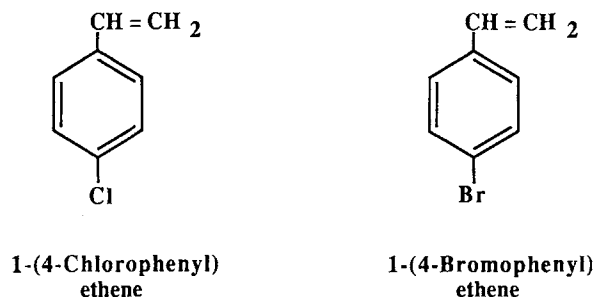
The data of Table II show that 1-phenylethene and related monomers can be reacted in the presence of a number of types of pulp, differing in the source of the wood and the means of forming the pulp. Note that additional lignin can be added to a reaction on wood to increase the fraction of lignin contained in the product. This is shown by the results from reactions 2-6-8, where 1 g of kraft lignin was added to the reaction mixture. The reaction proceeded and produced both grafted lignin and pulp. However, the yields of these reactions are less than the yield of identical reactions run without free lignin, 2-3-5. Free lignin thus inhibits grafting on pulp.

The table contains results from two pairs of reactions run under identical conditions but with the first having 8 mesh calcium chloride added to it and the second having 40 mesh calcium chloride added to it. A comparison of the yields of the paired reactions, 2-59 vs. 2-62 and 2-44 vs. 2-47, shows that fine grinding of the halide salt added to the reaction increases yield of polymerized monomer and wood. A comparison of the yields of reactions 2-56 to 62 and the yields from groundwood (2-35, 49), thermomechanical (2-50, 55), and refiner pulp (2-1, 14) show that pretreatment of the pulp with sulfite increases yield. Weight percent wood in the product goes down for all pulps, however, as the amount of monomer in the reaction mixture goes up. This is shown in Figure 2.
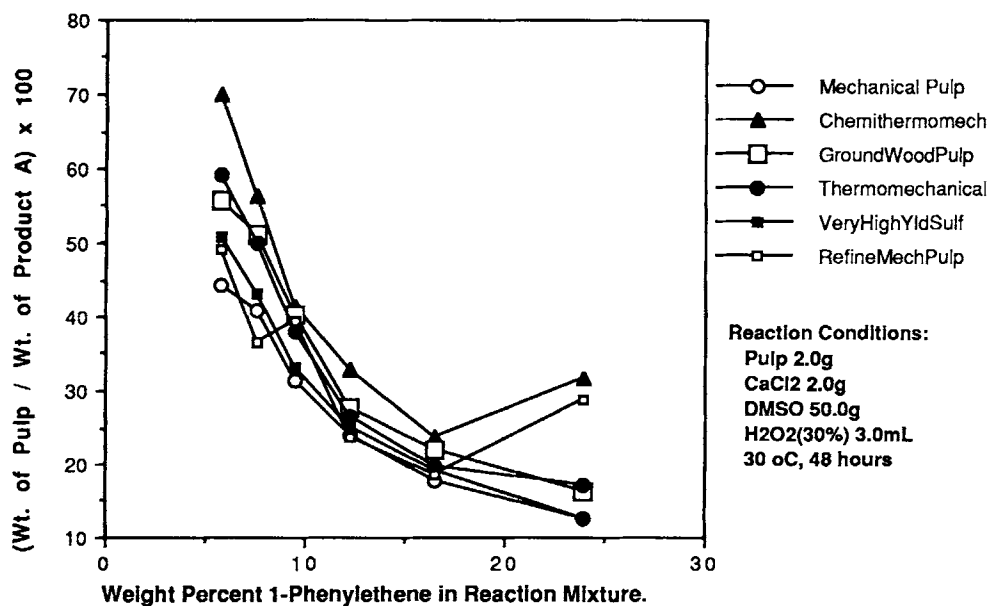

Figure 2   Weight percent wood pulp in the reaction product plotted vs weight percent 1-phenylethene in the reaction mixture.

Comparison of the data of Table II to that of Table III, where one of pulp, hydrogen peroxide, or halide salt have been left out of each reaction, shows that all three of these reagents must be present to produce reaction and grafting. The series of reactions presented in Table III are blank reactions. These blank reactions give the following results:

1. When no halide was added to the reaction, the conversion of monomer was 0.00%. That means that no polymerization or copolymerization occurred.

2. When no pulp was added to the reaction, the conversion of monomer was zero. If the starting temperature of the reactants was decreased from 30°C to between 0 and 5°C, the conversion of monomer was low, 16.3 weight percent or less. That means that only a little homopolymerization occurred.

3. When no hydrogen peroxide was added to the reaction, the conversion of monomer was zero. That means that no polymerization or copolymerization occurred.

4. When no 1-phenylethene was added to the

Table III   Results of Blank Reactions

1. No Wood Pulp Added						
	Expt No. 2					
	69	70	71	72	73	74
1-Phenylethene (g)	3.55	4.67	6.05	8.09	11.34	18.14
$CaCl_2$ (g)			2.0			
DMSO (g)			50.0			
H_2O_2 (30%) (mL)			3.0			
Reaction temp (°C)			30			
Reaction time (h)			67			
Conversion of 1-Phenylethene (%)			0			

2. No $CaCl_2$ Added						
	Expt No. 2					
	75	76	77	78	79	80
1-Phenylethene (g)	3.57	4.66	6.05	8.07	11.37	18.08
Mechanical pulp (g)			2.0			
DMSO (g)			50.0			
H_2O_2 (30%) (mL)			3.0			
Reaction temp (°C)			30			
Reaction time (h)			48			
Conversion of 1-Phenylethene (%)			0			

3. No H_2O_2 Added						
	Expt No. 2					
	81	82	83	84	85	86
1-Phenylethene (g)	3.55	4.63	6.05	8.03	11.36	18.04
Mechanical pulp (g)			2.0			
$CaCl_2$ (g)			2.0			
DMSO (g)			50.0			
Reaction temp (°C)			30			
Reaction time (h)			69			
Conversion of 1-Phenylethene (%)			0			

Table IV Grafted Copolymer That Cannot Be Extracted with Benzene

A. Pulp = Refiner Mechanical

	Sample No. 2-					
	87	88	89	90	91	92
Amount of product extracted with benzene (g)	2.505	4.03	3.44	4.00	1.51[a]	1.53[a]
Amount of product insoluble in benzene (g)	1.28	1.30	1.43	1.43	1.47	1.44
Weight increase of pulp (%)	+20.60	+24.70	+44.00	+40.50	−2.60	−5.90
Weight percent of monomer in insolubles (%)	17.10	19.80	30.50	28.80	0.00	0.00

B. Pulp = Refiner Mechanical

	Sample No. 2-					
	9	10	11	12	13	14
Amount of product extracted with benzene (g)	2.52	2.42	3.31	3.49	3.16	1.84
Amount of product insoluble in benzene (g)	0.99	1.03	0.87	0.88	1.26	0.92
Weight increase of pulp (%)	+7.06	+7.77	+10.42	+36.29	+38.47	+1.72
Weight percent of monomer in insolubles (%)	6.59	7.21	9.43	26.62	27.78	1.69

C. Pulp = Mechanical

	Sample No. 2-					
	15	16	17	18	19	20
Amount of product extracted with benzene (g)	2.82	3.12	3.32	3.21	3.96	3.85
Amount of product insoluble in benzene (g)	1.40	1.44	1.22	0.95	1.06	0.94
Weight increase of pulp (%)	+12.00	+13.30	+17.00	+23.24	+50.14	+94.97
Weight fraction of monomer in insolubles (%)	10.67	11.75	14.53	18.86	33.39	48.71

D. Pulp = ChemThermoMech

	Sample No. 2-					
	23	24	25	26	27	28
Amount of product extracted with benzene (g)	1.99	2.01	2.66	2.65	2.84	2.72
Amount of product insoluble in benzene (g)	1.53	1.32	1.35	1.20	0.99	1.55
Weight increase of pulp (%)	+9.78	+16.90	+22.80	+37.89	+47.07	+79.66
Weight fraction of monomer in insolubles (%)	8.91	14.45	18.56	27.48	32.01	44.34

Table IV   (*Continued*)

E. Pulp = ChemThermoMech

	Sample No. 2-					
	29	30	31	32	33	34
Amount of product extracted with benzene (g)	2.06	2.18	2.39	2.19	2.19	2.59
Amount of product insoluble in benzene (g)	1.17	1.03	0.98	0.83	0.74	0.87
Weight increase of pulp (%)	+12.47	+19.4	+31.22	+51.78	+98.74	+172.34
Weight fraction of monomer in insolubles (%)	11.08	16.00	23.79	34.12	49.68	63.29

F. Pulp = Groundwood

	Sample No. 2-					
	35	36	37	38	39	40
Amount of product extracted with benzene (g)	1.86	2.02	1.98	2.96	3.04	3.85
Amount of product insoluble in benzene (g)	1.10	1.15	0.93	1.10	0.94	1.18
Weight increase of pulp (%)	+5.99	+11.6	+16.25	+34.60	+40.30	+88.25
Weight fraction of monomer in insolubles (%)	5.65	10.39	13.98	25.70	28.72	46.88

G. Pulp = Groundwood

	Sample No. 2-					
	41	42	43	44	45	46
Amount of product extracted with benzene (g)	2.05	2.15	2.33	2.32	2.40	2.36
Amount of product insoluble in benzene (g)	1.09	1.15	0.90	0.77	0.66	0.61
Weight increase of pulp (%)	+2.09	+20.75	+15.69	+16.50	+36.28	+94.56
Weight fraction of monomer in insolubles (%)	2.05	17.18	13.56	14.16	26.62	48.60

H. Pulp = ThermoMech

	Sample No. 2-					
	50	51	52	53	54	55
Amount of product extracted with benzene (g)	1.62	1.73	2.02	3.03	3.00	3.63
Amount of product insoluble in benzene (g)	0.96	0.95	0.86	1.07	0.92	1.41
Weight increase of pulp (%)	+0.45	+9.55	+11.76	+33.13	+55.76	+134.07
Weight fraction of monomer in insolubles (%)	0.45	8.72	10.52	24.89	35.8	57.28

Table IV   *(Continued)*

	I. Pulp = VeryHighYldSulf					
	Sample No. 2-					
	56	57	58	59	60	61
Amount of product extracted with benzene (g)	1.96	2.17	2.40	2.38	2.76	3.34
Amount of product insoluble in benzene (g)	1.28	1.27	1.24	1.10	1.36	1.84
Weight increase of pulp (%)	+28.35	+35.98	+56.63	+83.96	+159.25	+333.32
Weight fraction of monomer in insolubles (%)	22.09	26.46	36.11	45.64	61.43	76.92

	J. Pulp = Cotton					
	Sample No. 2-					
	63	64	65	66	67	68
Amount of product extracted with benzene (g)	1.12	0.93	0.94	0.91	0.96	0.97
Amount of product insoluble in benzene (g)	1.00	0.93	0.94	0.91	0.96	0.97
Weight increase of pulp (%)	+3.12	0.00	0.00	0.00	0.00	0.00
Weight fraction of monomer in insolubles (%)	1.20	0.00	0.00	0.00	0.00	0.00

Calculations:

(1) Weight increase of pulp $= \dfrac{\text{wt. of benzene insoluble side chain} \times 100}{\text{wt. of pulp in extraction solids}}$

(2) Monomer content in pulp (monomer in insolubles, %) $= \dfrac{\text{wt. of benzene insoluble side chain} \times 100}{\text{wt. of product B recovered after benzene extraction}}$.

ª Blank reaction products without 1-phenylethene added to the reaction.

reaction, the degradation of pulp from the oxidation process of the reaction was small, and more than 95% of the pulp could be recovered.

5. The copolymerization must be coinitiated by H_2O_2, a halide, and lignin-containing materials.

Proof of Grafting

Figure 1 shows a diagram of synthesis and fractionation of the reaction product. The starting reaction mixture contained wood pulp, $CaCl_2$, DMSO, H_2O_2, and 1-phenylethene, whereas the final reaction mixture contained grafted wood pulp, homopoly(1-phenylethylene), unreacted 1-phenylethene, $CaCl_2$, DMSO, and H_2O. By fully mixing the final reaction mixture with a large amount of distilled water, the grafted wood pulp and homopoly(1-phenylethylene)

were separated as insoluble solids from the liquid phase that contained $CaCl_2$, DMSO, and unreacted 1-phenylethene.

Further separation was done by benzene extraction of the insoluble solids. It is well known that homopoly(1-phenylethylene) is very soluble in benzene, especially at 80°C (the boiling point of benzene). To show that the reaction permanently attached the polymerized monomer to the pulp, the product solids were extracted for 48 or more hours. The extraction data are shown in Table IV. These data show that Soxhlet extraction of the grafting reaction product with benzene does not remove much of the polymerized monomer. However, a benzene, Soxhlet extraction of uniform mechanical mixtures of pulp and poly(1-phenylethylene) under the same experimental conditions removed all of the poly(1-phenylethylene) and left behind the original amount or less of pulp. Thus, for example, the two "blank" mechanical mixtures of homopolymer and

pulp described in the Experimental section were also extracted. The dried mixture was extracted with benzene in a Soxhlet apparatus for 48 h. The weight of recovered, unextractable Mechanical Pulp and ChemTherMePulp was 2.008 and 1.991 g, respectively. This was 98.9 and 98.6% of the pulp in the original sample, respectively. In contrast, if reaction products 2-55 and 2-61 are extracted with benzene, the benzene-unextractable fractions constitute 234 and 433 wt % of the original pulp placed in the reaction vessel. The reaction has increased the weight of the pulp by 134 and 333 wt %, respectively. Further extraction of 0.47 and 0.44 g, respectively, of these benzene-unextractable solids with 50 g benzene at room temperature for 15.5 h produced no weight loss after recovery and drying of the solid. The results of these two experiments show that after extraction all the external homopoly(1-phenylethylene) in the reaction product is removed. These data further show that the product is polymerized monomer bound into the pulp.

The weight gain and permanent inclusion of poly(1-phenylethylene) is general for all the copolymerization reactions conducted in this research. After benzene extraction of the reaction products (Product A) in a Soxhlet apparatus for 48–100 h, the weight of the unextractable fractions (Product B) is always larger than the weight of the wood pulp added to the reactions. For example, the weight increase ranges from 11.95 to 94.97 wt % for Mechanical Pulp and from 28.4 to 333.3 wt % for VeryHighYldSulf pulp. These weight gains correlate with the changes in physical properties that would be expected from the inclusion of poly(1-phenylethylene) into the wood. The cellulose, hemicellulose, and lignin of wood contains a high weight fraction of hydroxyl groups. When

1. pure wood pulp,
2. blank reaction wood pulp (no 1-phenylethene was added to the reaction), or
3. the wood pulp recovered after benzene extraction of a uniform mechanical mixture of wood pulp and poly(1-phenylethylene)

is put into water, it will wet, absorb water, and sink. But Product B, the "pulp" that experienced copolymerization with 1-phenylethene and extraction with benzene, is a very hydrophobic material. When any Product B is put into water, it will not wet, will not absorb water, and will not sink. This hydrophobic behavior even includes product 2-50B, with only 0.45 wt % benzene-unextractable poly(1-phenylethylene) on it. It is evident that after the copolymerization the surface properties of the original

wood pulp were greatly changed because poly(1-phenylethylene) had been grafted (chemically bound) on the surface of the wood.

Also, a comparison of the yield of benzene-insoluble material from samples 2-56 to 2-62 and the yield of insolubles from GroundWood-, ThermoMech-, and RefineMech-Pulp listed in Table IV show that pretreatment of the pulp with sulfite sharply increases the amount of side chain permanently bound to the wood. This is clearly shown by the graphs of permanent weight increase vs. amount of monomer placed in the reaction vessel given in Figure 3. The VeryHighYldSulf pulp gains almost twice as much mass in the reaction as does any of the other pulps. The cause for this reactivity differential is unknown. It is, however, reproducible and definitely correlated with the pretreatment of the pulp with a sulfite solution.

There is also a general trend in amount of monomer retained as permanent weight increase in the pulp as a function of weight fraction of monomer in the reaction mixture. As the amount of 1-phenylethene added to the reaction increases, the weight increase of the wood pulp after the reaction and benzene extraction also increases. This is shown in Figure 4. This is to be expected if the reason for the weight gain is graft copolymerization of the monomer. Both the rate of initiation and the rate of propagation depend on the concentration of monomer in the reaction mixture. As this concentration increases, the two rates will increase in proportion to the square root and first power of the monomer concentration, respectively. This will result in higher conversion of monomer to polymer in a given reaction time, as shown by the plots of Figure 5.

The data of Tables II and III also show that lignin is critical to the conduct of this grafting reaction. This observation was further tested by conducting the reaction on cotton. The pure medical-grade cotton used in reactions 2-63–68 of Table II contains no lignin. This backbone produced no polymerization and no weight gain in five of the six reactions run. In one reaction, 2-63, there was a 3.12 wt % conversion of 1-phenylethene to polymer, but this product was washed out of the cotton when it was extracted with benzene. Extraction data on the six cotton reactions is given in Table IV. Further, the cotton product of the reaction was hydrophilic despite exposure to the grafting reaction. All the cotton products of the grafting treatment absorbed water quickly and sank in water when placed on the surface of it. Since only 0.45% permanent weight increase causes wood pulp to become hydrophobic, these data show that the lignin-free cotton could not be used as a site for grafting.
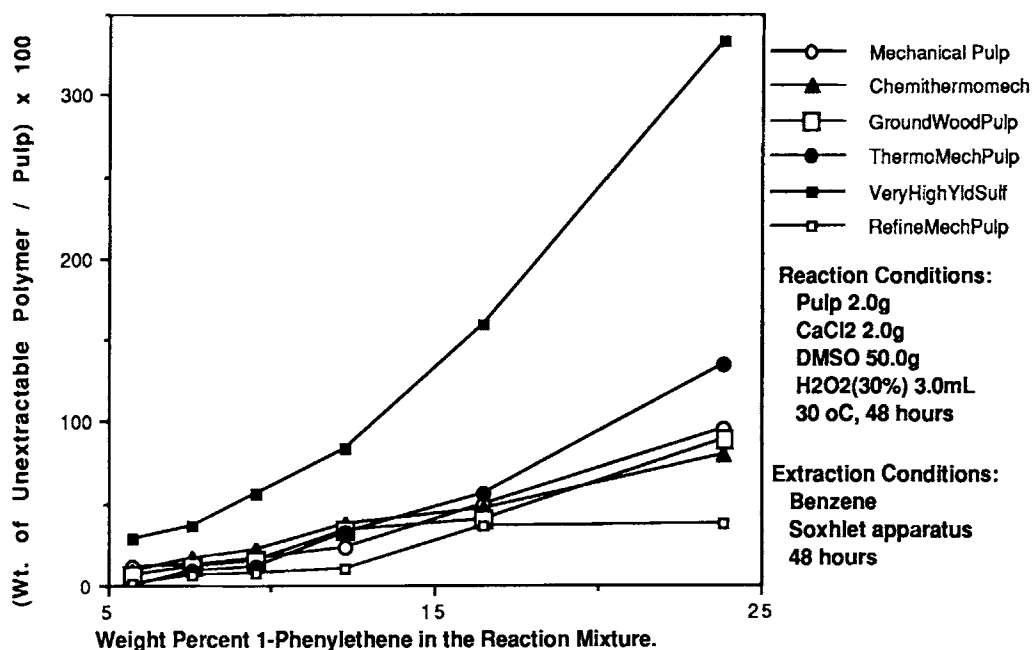
Figure 3 Weight increase of wood pulps after copolymerization with 1-phenylethene and extraction with benzene.

Thermoplastic Properties of the Products

Any of the products of Table II that contained 52 wt % or less wood pulp could be successfully thermally compressed into light yellow, translucent, uniform composite thermoplastic films. This was not true for the two uniform mechanical mixtures made from Mechanical Pulp and ChemTherMePulp, which contained 17.9 and 31.3 wt % wood pulp, respectively. After thermal compression of the mixtures, no uniform composite plastic films could be formed. The pulp gathered together into small
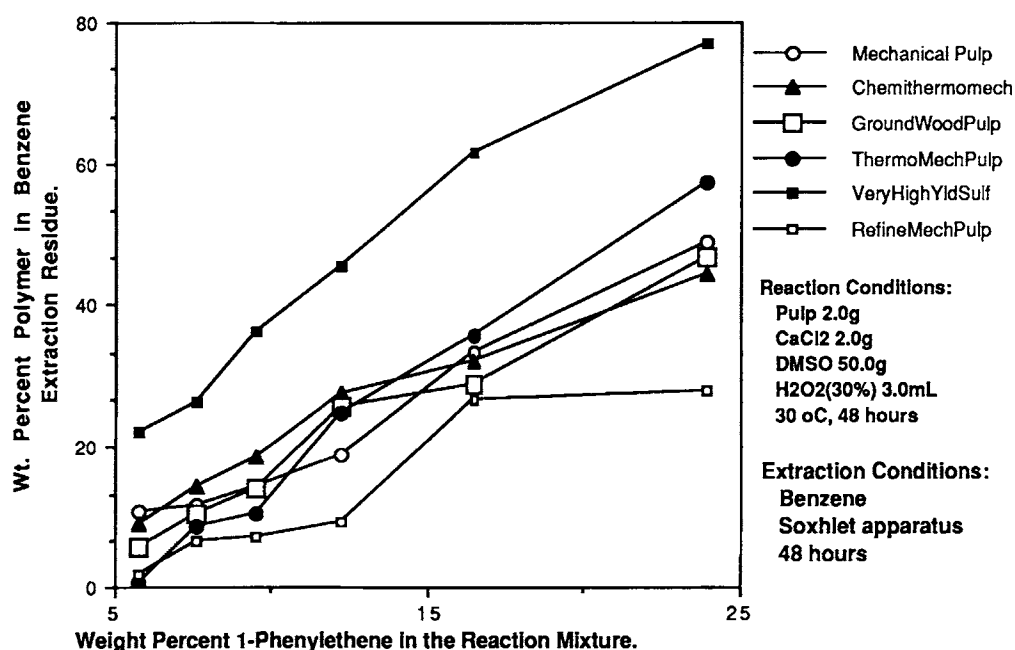
Figure 4 Weight percent poly(1-phenylethylene) in the unextractable solids from benzene extraction plotted vs. weight percent monomer in the reaction.
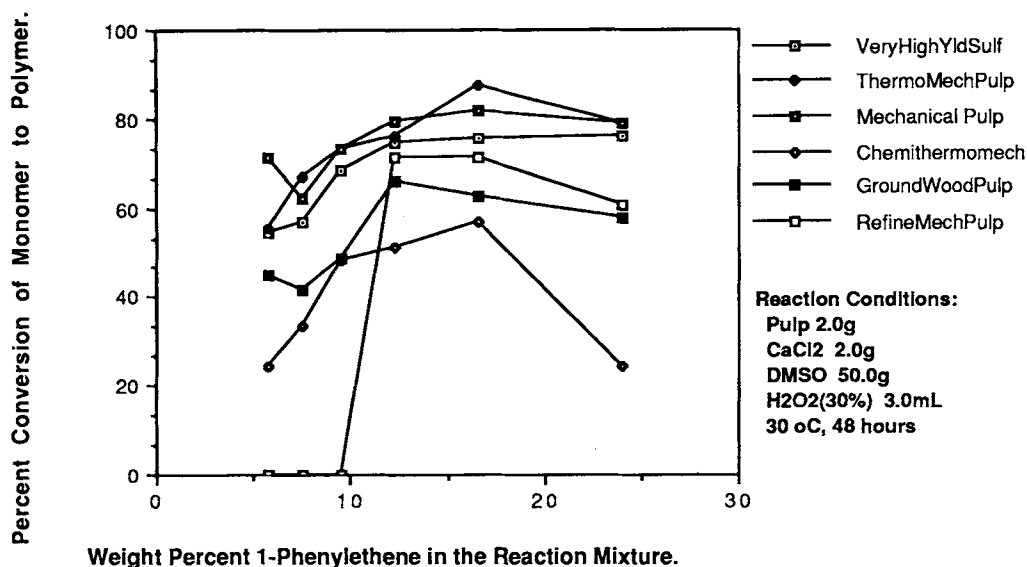
Figure 5 Conversion of monomer to polymer plotted vs. weight percent of 1-phenylethene in the liquid phase of the reaction mixture.

lumps. The different results were caused by different surface properties of the grafted and mixed wood pulp. For grafted wood pulp fibers, the surface was coated with chemically bound poly(1-phenylethylene), which is compatible with a poly(1-phenylethylene) matrix. For the ungrafted pulp fibers of the mixture, there was no chemically bound poly(1-phenylethylene) on their surface. The hydrophilic–hydrophobic boundary between the ungrafted pulp and the plastic is a very high energy surface when compared to the hydrophilic–hydrophilic and hydrophobic–hydrophobic interactions that occur when the two phases separate. Thus, the poly(1-phenylethylene) and pulp segregate into pure thermoplastic and pulp clumps. Thus, this grafting process is necessary to produce useful, uniform thermoplastic solids.

Further, any product B from extraction of a product of Table II that contained more than 45 wt % of benzene–unextractable poly(1-phenylethylene) could be successfully thermally compressed into yellow to light brown, translucent, uniform, thermoplastic films. When the thermoplastic films were extracted with benzene at room temperature for 15.5 h, the plastic films disintegrated very quickly. However, upon filtering the benzene slurry and recovering the extracted pulp, there was still 87.0 to 95.5 wt % of the original benzene–unextractable poly(1-phenylethylene) in the recovered powder. The process of heating to 150°C and compressing for 1–2 min removed only 4.5–13.0 wt % of the original benzene–unextractable poly(1-phenylethylene). When the recovered powder was again ther-

mal-compressed, it formed thermoplastic films again. These experiments show that the benzene–unextractable poly(1-phenylethylene) must be grafted poly(1-phenylethylene).

The small loss of the original benzene–unextractable poly(1-phenylethylene) might be caused by

(a) Physical forces in thermal compression. During compression, heat energy and very strong squashing–shearing mechanical force might cause melted grafted poly(1-phenylethylene) side chains to move much faster than wood pulp fiber backbones, thus leading to the breakage of the grafted poly(1-phenylethylene) side chains to form homopoly(1-phenylethylene). This homopolymer was removed by benzene extraction.

(b) Homopoly(1-phenylethylene) left inside the wood pulp fibers. After thermal compression, fractured or sheared fibers might allow the internally grown homopolymer to come out.

CONCLUSIONS

A grafting reaction can be initiated on groundwood pulp, refiner mechanical pulp, thermomechanical pulp, chemithermomechanical pulp, chemical pulps, wood chips, wood, wood fiber, wood strips, or any

other plant product. Particularly effective as a wood is chemithermomechanical pulp treated with sodium sulfite to improve amount of monomer bound to the wood and conversion of monomer to polymer. Sulfite pretreatment increases both yield and amount of synthetic side chain permanently bound to the pulp. By initiation with calcium chloride and hydrogen peroxide in a stirred reaction, a thermoplastic side chain of poly(1-phenylethylene) can be grafted onto the lignin of wood via free-radical polymerization.

The reaction produced yields of 32–92 wt % of polymerizable material placed in the reaction mixture. This product is a mixture of homopolymer and grafted copolymer that can be separated by benzene extraction. The extraction data show that an amount of poly(1-phenylethylene) equal to between 0.45 and 333 wt % of the original weight of pulp can be permanently attached to the pulp fibers. The conversion, yield, and retention of polymer by the pulp is partially controlled by the source of the wood used to make the pulp but significantly affected by the pulping method used to form the pulp. Of the six pulps tested, mechanical pulp from spruce produced the highest yield followed by spruce high-yield sulfite pulp, aspen refiner pulp, spruce ground wood pulp, spruce thermomechanical pulp, and, last, spruce-fir chemithermomechanical pulp. When ranked according to the largest fraction of polymer retained in the pulp after extraction, the order of the pulps is almost the same but spruce, very high yield sulfite pulp retains the most polymer, followed by mechanical pulp, and then the other pulps in the same order as for yield. Lignin must be present in the wood to initiate the grafting reaction. Thus, cotton generally did not initiate the grafting process and both yield and amount of polymer permanently retained by the backbone generally increase as the lignin content of the backbone material increases. Yield is also affected by the physical state of the halide salt used in the reaction. High surface area, numerically high-mesh-size calcium chloride gives a larger yield and conversion of monomer to polymer than does a courser form of the salt. Both yield and amount of polymer permanently retained by the backbone increase as the monomer content of the synthesis reaction increases.

The copolymerization must be coinitiated by H_2O_2, a halide, and lignin-containing materials. When no halide is added to the reaction, neither polymerization nor copolymerization occur. When no lignin-containing material is added to the reaction, the conversion of monomer is 17 mol % or less. That means that polymerization is normally initiated from the lignin in the reaction mixture. More

than 95 wt % of the pulp placed in a reaction that received no 1-phenylethene could be recovered by simple filtration. This implies that the degradation of pulp from the oxidation process of the reaction is minor and does not degrade the structure of strength of the pulp fibers.

Extraction of the grafted pulps for 48–100 h with boiling benzene removed unbound homopolymer from the pulp but left the reacted pulp with weight gains of 0.45–333 wt %. Since solution-precipitated mixtures were readily separated by the extraction process, these data support the idea that the weight gain of the pulp after reaction is due to permanently grafted copolymer. The weight gain and permanent inclusion of poly(1-phenylethylene) is general for all the copolymerization reactions conducted in this research. These weight gains correlate with the changes in physical properties that would be expected from the inclusion of poly(1-phenylethylene) into the wood.

One such physical property change is the alteration of the surface of the wood to make it chemically equivalent to a bulk sample of the plastic formed by the synthetic side chain. The cellulose, hemicellulose, and lignin of wood contains a high weight fraction of hydroxyl groups. When

1. pure wood pulp,
2. blank reaction wood pulp (no 1-phenylethene was added to the reaction), or
3. the wood pulp recovered after benzene extraction of a uniform mechanical mixture of wood pulp and poly(1-phenylethylene)

is put into water, it will wet, absorb water, and sink. But the "pulp" that experienced copolymerization with 1-phenylethene and extraction with benzene is a very hydrophobic material. When any a grafted pulp is put into water, it will not wet, will not absorb water, and will not sink. This hydrophobic behavior can be induced with only 0.45 wt % benzene–unextractable poly(1-phenylethylene) in the wood. It is evident that after the copolymerization the surface properties of the original wood pulp were greatly changed because poly(1-phenylethylene) had been grafted (chemically bound) on the surface of the wood.

Grafted wood that contained 52 wt % or less wood pulp could be successfully thermally compressed into light yellow, translucent, uniform composite thermoplastic films, but uniform, solvent-precipitated mixtures could not be compressed into uniform composite plastic films. The mixtures always formed clumped, macroscopically heterogeneous films. Fur-

ther, extracted, grafted wood that contained more than 45 wt % of benzene–unextractable poly(1-phenylethylene) could be successfully thermally compressed into yellow to light brown, translucent, uniform, thermoplastic films. These films would dissemble in benzene but could be reformed from the powder recoverable from the benzene slurry.

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