Graft Copolymers of Lignin as Hydrophobic Agents for Plastic (Wood-Filled) Composites

Timothy Adcock,[1] Vipul Shah,[2] Meng-jiu Chen,[3] John J. Meister[2]

[1]*1 Warren Close, Markfield, Leicester, LE67 9SJ, United Kingdom*
[2]*Forest Products Research Center, 2008 Hendola Drive, NE, Albuquerque, New Mexico 87110-4808*
[3]*Research Division, Cardolite Corporation, 500 Doremus Avenue, Newark, New Jersey 07105-4805*

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ABSTRACT: Poly[lignin-*g*-(1-phenylethylene)] graft copolymers synthesized by free-radical, graft copolymerization on lignin and verified by fractionation, infrared spectroscopy, and solubility change possess macromolecular surface activity as indicated by their capacity to form stable emulsions between incompatible fluid phases, to adhesively bond to wood surfaces, and to change the contact angle of water on coated wood. The surface activity of the copolymer changes with its composition. As the weight percent lignin in the copolymerization reaction product increases beyond 20 wt %, the amount of the emulsion phase formed in a water–benzene mixture decreases. Maple wood flour could be solvent-coated with a copolymer and both coated and uncoated maple flour could be extruded through a stranding plate into a wood-filled composite with polystyrene. Physical property tests show that composite control samples are about 3% stiffer and less deformable than are the copolymer composites when dry and about 5 or more percent more deformable than are the copolymer composites when wet, showing that the copolymer coating increased the wet strength. The copolymer samples are always denser than are the controls. Copolymer coating on wood filler decreases the swelling in the composite, the partial molar volume of the imbibed water, and the dimensional change in the solid. These effects cause increase in the density of the copolymer composite upon imbibition of water. Coating the wood component of the composite with a copolymer creates a hydrophobic barrier that produces a decrease in water imbibition into the composite, which will not disappear in 20 or more years of water immersion. Expansion in water is highly dependent on the direction of extrusion. The length expands about 1%, the width expands about five times as much, and the thickness expands over 10 times as much as does the length. This differential expansion may be due to the 22% reduction in the width and a 71% reduction in the thickness of the melt as it passes through the die and the alignment of the long axis of the fiber with the direction of flow through the die. The reaction product is a thermoplastic solid stable below 200°C and thermoformable at between 150 and 180°C. Products which contain between 10 and 50 wt % lignin are heterogeneous solids. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 1266–1276, 2003

Key words: copolymerization; biomaterials; mechanical properties; surfactants; composites

INTRODUCTION

Lignin [8068-00-6] is a natural, renewable source of carbon that will play a much larger role in the synthesis of macromolecules in a future characterized by declining petroleum supplies. To allow such utilization, a chemical-modification method was developed to convert lignin into lignin-(1-ethenylbenzene) (styrene) graft copolymers. Since these are two-part molecules with a potential for surface-active behavior, the products were tested as wetting and compatibilizing agents and the results of these tests are presented here. Measurements showing thermal properties, thermoplasticity, surface activity, wetting alteration on a coated fiber, and phase-coupling behavior are detailed in this article. The properties of the copolymers can be used to minimize water uptake and to increase the wet strength of wood–thermoplastic composites.

EXPERIMENTAL

Synthesis of grafted lignin

Dimethyl sulfoxide (DMSO) is used as the solvent for the graft copolymerization reactions. This reaction is successfully run with concentrations or mol ratios of the reactants in the following ranges: (1) polymerizable solids content of the reaction: 53 wt % or less; (2) hydroperoxide-to-calcium chloride mol ratio: 0.25–32; (3) hydroperoxide to lignin (M_n) mol ratio: 21–113; and (4) weight fraction of the monomer in polymerizable solids: 0.01–0.95.

Prepare sample A by placing pure ethenylbenzene in a conical flask and bubble it with nitrogen (N_2) for

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Correspondence to: J. J. Meister (polysurlabs@cnsp.com).

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10 min. Prepare sample B by placing the DMSO solvent in a conical flask, dispersing lignin and calcium chloride in the solvent, and stirring until dissolved. Bubble solution B with N_2 for 10 min. Samples A and B are stirred while being purged with nitrogen. Add H_2O_2 to sample B, and bubble it with N_2 for 20 min. Add sample A to sample B. After 5 min of stirring and bubbling N_2 through the reaction mixture, the flask is stoppered and placed in a 30°C bath for 48 h. The reaction should be stirred throughout the synthesis. The preferred stirring rate in the conical flask used in the laboratory synthesis is 2–5 Hz. All reactions are terminated by opening the reaction vessel. This terminated slurry can then be added to 10 times its volume of acidified water (pH 2) and the polymer recovered by filtration. More detailed procedures for conducting the copolymerization and the proof of grafting are given in ref. 1.

Assays

Analysis procedures for oxidizing equivalents by iodine/thiosulfate titration and elemental composition are given in ref. 2. Solubility of the reaction products was determined in reagent-grade solvents at room temperature. The copolymer was tested for thermoplasticity by placing a fine powder of the reaction product of numerically more than 40 mesh in a Carver heated patent press and molding at 150°C and 192 kPa pressure for 1 min.

Emulsion tests

Emulsion tests were run by placing 20 mL of a 3.75 ± 0.15 wt % solution of a graft copolymer in benzene in a graduated cylinder with 60 mL of 0.5*M* aqueous sodium hydroxide. The cylinder was sealed and the 80 mL of fluid it contained was shaken for 30 seconds. It was then allowed to sit for 6 months at room temperature while the phase volumes were recorded as a function of time.

Process of spray coating

Prepare a 20% by wight copolymer solution in 1,4-dioxacyclohexane (*p*-dioxane). Weigh out 500 g of wood flour into a 3.7-L glass jar. A portion of the copolymer solution was transferred into a spray bottle and sprayed on 500 g of wood. The wood is tumbled until uniform and the process is repeated until all the coating is applied. The jar is then tumbled on a ball mill at 100 rpm for 1 h. The coated wood flour is put into an oven at 60°C for about 2 h to evaporate all the solvent.

A total of 30 kg wood flour was coated with the copolymer. This coated maple flour was used to make 52 kg of a wood–(Amoco R450 polystyrene) composite. The total concentration of the copolymer on the wood flour was 1 wt %.

The coated wood flour was shipped to Washington State University for extrusion into a polystyrene–wood composite and for composite property evaluation. The properties of all wood–poly(1-phenylethylene) panels were determined according to ASTM D-790, test method 1, for Modulus of Elasticity (MOE) and Modulus of Rupture (MOR) in static bending.

Composite formulation

All wood was dried to a moisture content of less than 1 wt % before use in a wood–plastic composite. The formulation used to prepare the composite was 58% wood flour, 31% polystyrene, 8% magnesium silicate (talc), 2% zinc octadecanoate (Zn stearate), and 1% wax by weight. The octadecanoate salt and wax were added as processing aids. The constituents were physically mixed in a Bespoke drum blender for 10 min at approximately 30 rpm to form the composite blend.

Composite formation

The composite was extruded on a Cincinnati Milicron, 30 kw, counterrotating, conical, twin-screw, 55-mm extruder at 16.5 rpm through a slit die 15.24 cm (6 in.) wide by 1.27 cm (0.5 inches) deep to form a plank of indeterminate length. The barrel temperature was 163°C and the die temperature was 171°C. The formulation residence time in the extruder was 4–6 min. A reduced pressure of 5 cm of mercury was maintained in the extruder barrel and its contents at all times during the extrusion. The extruder screw had a 25 to 1 length-to-diameter ratio and a compression ratio of 2.6 to 1. The torque of the extruder is 1.57 kJ. The composite flows through a "stranding plate" before being compacted into a plank.[3] This flat plate perpendicular to the direction of flow has a series of tubes welded to it which form the flow into a series of strands before entry into the die. This compacts the composite and fills the wood cell with plastic.

Composite testing

Testing was conducted in accordance with ASTM D790, test method 1, using a test span equivalent to a length-to-depth ratio of 16 to 1. Samples were cut from the extruded plank using a combination of band and table saws. Sample size was nominally 25.4 cm (10 in.) in length, 1.27 cm (0.5 in.) wide, and 1.27 cm (0.5 in.) in depth. The deflection rate for this size sample was 0.541 cm/min (0.213 in. min). The test span was 20.32 cm (8 in.). Static bending tests were conducted on a Instron Model 4466 tensile testing machine with the top pressure pylon at 0.0 cm on the specimen center and supporting lower pylons at ±10.16 cm (±4 in.) on the sample. The supports and pressure pylon had a loading nose radius of curvature of 5.5 mm. The supports were adjusted laterally to accept the specimen prior to testing. For testing, the supports were rigidly fixed to the test jig.

Failure was monitored during the tests, and when a distinct failure occurred, it was in tension, on the lower side of the sample. Deflection was not measured separately; it was deemed to be equivalent to the crosshead movement.

Moisture absorption

The tests for moisture absorption and thickness swelling were preformed according to ASTM D-1037, sections 100–107. All comparisons of the water uptake between samples are by weight percent change. The sample size was nominally 25.4 cm (10 in.) in length, 1.27 cm (0.5 in.) in width, and 1.27 cm (0.5 in.) in depth. There was a very limited number of 10.16 × 10.16 × 1.27-cm (4 × 4 × 0.5 in.) panel specimens soaked as well. All samples were immersed horizontally in distilled water for the time given in the data sets. Before measurement or testing, the samples were allowed to drip dry for 10 min, and after this time, any excess surface moisture was wiped off with a paper towel.

Mechanical testing on soaked samples was conducted in accordance with ASTM D-790, test method 1, as described above. The test span was 20.32 cm (8 in.).

Materials

Most of the lignin used in these studies is a kraft pine lignin prepared in "free acid" form with a number-average molecular weight of 9600, a weight-average molecular weight of 22,000, and a polydispersity index of 2.29. The ash content of the lignin is 1.0 wt % or less. The material was used as recovered from acidified black liquor. Elemental analysis is C, 61.66, N, 0.89, H, 5.73, S, 1.57, Ca, 0.08, and Fe, 0.014 wt %

The compound ethenylbenzene was obtained from the Laboratory and Research Products Division of Kodak (Rochester, NY). The ethenylbenzene was purified to remove the stabilizer by washing the monomer three times with an aqueous base at a ratio of 1 g ethenylbenzene to 1 mL of 2*N* 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 a 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 showed them to be (1) 28.99% H_2O_2 in water, 1.704×10^{-2} equivalents per g, 1.907×10^{-2} equivalents per mL and (2) 29.86% H_2O_2 in water, 1.756×10^{-2} equivalents per g, 1.947×10^{-2} equivalents per mL. Reagent-grade DMSO from Sigma–Aldrich (Milwakee, WI) and anhydrous calcium chloride were used in these experiments. Other salts were reagent-grade materials and were used as supplied. The nitrogen used in the syntheses was commercial-grade bulk gas. Nitrogen was purified by passing it through a copper filament at 500°C before use. The poly(1-phenylethylene) homopolymer reference material for thermal analyses, material RIPO, was used as received from the Amoco Chemical Co. (Naperville, IL). It is a pure poly(1-phenylethylene) with a weight-average molecular weight of 285,000, a melt-flow index of 1.8 (ASTM D-1238), a heat-deflection temperature of 93°C (ASTM D-648 at 1.82 MPa), and a Vicat softening point of 107°C (ASTM D-1525).

Wood flour was 40-mesh maple hardwood flour, code 4010, from American Wood Fibers (Columbia, MD). The poly(1-phenylethylene) used in the composites was resin R450 from the Amoco Chemical Co. (Chicago, IL). Under ASTM D-638, it has a tensile strength at break of 46 MPa and a tensile modulus of 3.28 GPa. Its Vicat softening point under ASTM D-1525 is 100°C. It was used as received.

Equipment

Synthesis weighings were done on a Mettler H6, four-decimal-place balance. All benzene extractions were done in a Soxhlet apparatus. Water-saturation test weighings were done on an A and D Corp. of Japan, Model HR-120, three-decimal-place balance.

RESULTS AND DISCUSSION

Synthesis

The products prepared to test the properties of the reaction products and to prepare coatings are summarized in Table I. The first 10 reaction products of this table were combined to make the "coating," which was the copolymer used to coat wood flour. Fractionation and spectroscopic analysis of several reaction products confirmed the presence of a graft copolymer.[4] Mixtures formed by both mechanical mixing and solution evaporation are separated by benzene and base extraction but the reaction products cannot be separated into lignin and poly(1-phenylethylene) fractions by the same procedure.[4] Fourier transform infrared spectroscopy (FTIR) of the fractions confirm the presence of lignin and poly(1-phenylethylene) in all fractions of the reaction product.[4] The distribution of the product in the fractions implies that little if any of the lignin is left ungrafted by the reaction. This distribution also implies that the product is a complex mixture of the poly(1-phenylethylene) homopolymer

TABLE I
Composition and Yield of Copolymer Reaction Mixtures

Synthesis identifier	Composition (g)					
	Lignin	1-Phenylethene	$CaCl_2$	H_2O_2 (mL)	DMSO	Yield (g/wt %)
1–1	32.2	38.54	24.0	27.8	161.8	59.38/83.94
1–2	32.2	37.72	24.0	27.8	160.4	53.49/76.5
1–3	32.3	37.78	24.0	28.0	161.6	55.2/78.76
1–4	32.2	37.50	24.0	28.0	161.1	61.4/88.09
1–5	32.3	38.80	24.0	28.0	161.6	59.79/84.1
1–6	32.2	37.35	24.0	28.0	162.2	63.87/91.84
1–7	32.2	37.75	24.0	28.0	161.0	60.86/87.00
1–8	32.3	37.90	24.0	28.0	161.8	58.30/83.05
1–9	64.5	74.75	48.1	56.0	321.2	112.9/81.05
1–10	64.5	74.90	48.6	56.0	320.7	110.1/79.00
1–16	2.00	18.76	2.02	1.0	20.04	17.80/85.74
1–17	2.00	18.76	2.01	2.0	20.00	20.28/97.69
1–18	2.00	18.76	2.07	3.0	19.99	20.37/98.12
1–19	2.01	18.77	2.02	4.0	20.02	19.10/91.92
1–20	2.01	18.78	2.02	5.0	20.02	18.53/89.13
1–21	3.03	18.78	2.00	2.0	20.00	19.14/87.76
1–22	2.00	18.76	1.01	2.0	20.10	18.84/90.75
1–23	2.01	18.79	1.52	2.0	20.01	18.77/90.24
1–24	2.00	18.79	2.01	2.0	20.05	18.81/90.48
1–25	2.01	18.76	2.52	2.0	20.07	18.98/91.38
1–26	2.01	4.69	2.04	2.0	20.01	5.68/84.78
1–27	2.01	9.39	2.02	2.0	20.00	10.42/91.40
1–28	2.01	14.07	2.03	2.0	20.10	14.95/92.79
1–29	2.01	18.76	2.03	2.0	20.01	19.52/93.98
1–30	2.02	23.45	2.04	2.0	20.07	23.76/93.29
1–32	2.00	18.79	2.00	2.07g	20.00	19.19/92.30
1–49	0.00	9.39	6.02	8.0	40.0	0.00/0.00

and a broad molecular weight distribution of the graft copolymer.

These products have been shown to be poly[lignin-*g*-(1-phenylethylene)]-containing materials by a series of solubility and extraction tests and are formed with 90% or more grafting efficiency for lignin. This shows that the reaction that we are running on lignin is that shown in Figure 1.

Solubility change

The solubility and solution properties of the reaction product and all its fractions are changed from the properties of the staring material. After the copolymerization of lignin and 1-ethenylbenzene,

1. A part of the original lignin was changed from a benzene-insoluble material to a benzene-soluble material. The original lignin is essentially benzene-insoluble and is completely benzene-insoluble after preextraction with benzene. However, after benzene extraction of the copolymerization product, the benzene extraction solution always had a dark brown color, showing solubilized lignin in the fluid. Thus, copolymerization with 1-ethenylbenzene has converted lignin to a benzene-soluble material. Previous studies by FTIR show that the benzene-soluble fraction contains lignin and poly(1-phenylethene) in an inseparable mixture.

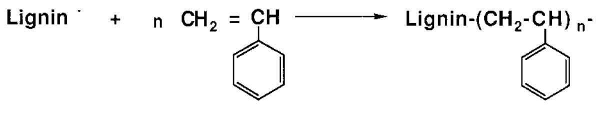

Figure 1 The grafting reaction.

2. A part of the original lignin was changed from a base-soluble material into a base-insoluble material. Pure lignin can be very easily dissolved in an aqueous base. After a benzene-extraction solution of the copolymerization product was fully mixed with 0.5*M* aqueous NaOH, the benzene layer had a dark brown color, which means that the lignin constituent still remained in the benzene and could not be extracted with a base. When a mechanical mixture of lignin, poly(1-phenylethene), and benzene was treated with 0.5*M* aqueous NaOH in the same way, all the lignin went into the base layer and the benzene layer was colorless. Infrared spectra of a series of reaction product fractions formed by extraction with benzene and the aqueous base showed peak identities and intensities that

TABLE II
Differential Scanning Calorimetry Data for Lignin, Poly(1-phenylethylene), and Graft Copolymer

Material identifier	Lignin (wt %) In reaction	Lignin (wt %) In product A	Peak (s °C)		Ramp (°C/min)
Amoco RIPO- Pure poly(1-phenylethylene) reference	0.0	0.0	98.9		10
2–2 Pure lignin	100.0	100.0	116.17		10
2–3 Blank reaction lignin	100.0	100.0	150.82		10
2–4	9.6	10.3	94.82	114.62[a]	10
2–5	22.0	27.3	98.43	133.97[a]	10
1–28	30.0	32.2	98.23	124.10[b]	10
2–7#	30.0	34.5	102.35	144.48[b]	20
2–8	30.0	32.3	95.73	133.25	10
1–32	46.0	50.5	94.11	125.12	10
2–10[c]	46.0	51.8	101.63	143.27	20
2–4B	9.6		143.40		10
1–28B	30.0		140.58		10
1–32B	46.0		146.73		10
2–4C	9.6		129.47		10
2–11C	9.6		109.14		10

[a] Very small peak.
[b] Small peak.
[c] Commercial kraft pine lignin used in synthesis of these samples.

> would only be produced by chemically bound lignin and poly(1-phenyethylene).

After a mixture of lignin from a blank reaction (no 1-ethenylbenzene added) and poly(1-phenylethene) was extracted with benzene, the blank reaction lignin was still a highly hydrophilic material. When it was put into water, it would wet and sink into the water. After a normal copolymerization, the surface properties of the original lignin added to the reaction were changed. The lignin-containing reaction residue that was left after benzene extraction was a very hydrophobic material. When it was put into water, it would not wet or sink. It floated on the surface of the water. It is evident by the reaction procedure and mass-balance calculations that these wetting changes were caused by poly(1-phenylethene) side chains grafted onto the lignin. The results of the wettability and infrared spectra tests show that almost all the lignin in the reaction mixture was grafted with poly(1-phenylethene).

Thermal properties

The reaction product was a powdery amorphous material. As the lignin content in the product increased, its color changed from light yellow to brown. When it was thermal-compressed at 150°C between Teflon-coated plates, it formed a ductile, plasticlike sheet in which grafted lignin was uniformly dispersed. These sheets underwent brittle failure when distorted too extensively. Warming the powder from the reaction above 150°C in a mold allowed the product to conform to the mold and produce a mold-shaped, solid object when cooled to room temperature. These data show that the reaction product is a thermoplastic.

Thermogravimetric analysis data of the reaction products of different lignin/poly(1-phenylethene) compositions show that, below 200°C, there is a 1–2% weight loss. This is probably caused by water absorbed by the product. These data show that the reaction product is relatively thermally stable and can stand thermal compression below 200°C without serious decomposition.

Differential scanning calorimetry data of the reaction product given in Table II show that the product has two thermal absorbance peaks. This means that in the reaction product there exists evident phase separation caused by homopoly(1-phenylethene) and grafted lignin. The higher the lignin content in the reaction product, the bigger the higher-temperature thermal-absorbance peak. The higher-temperature absorbance peak is produced by the lignin constituent in the copolymerization product.

When the reaction product is extracted with benzene for 48 h, the residue's material identifier is augmented with a "B." When this residue, B, is further extracted with an aqueous 0.5*M* base, the solid left after the extraction is labeled C. Product B, the benzene-insoluble fraction of the reaction product, and product C, the base-insoluble fraction, have only a single thermal absorbance peak because no phase separation exists in the solid. The temperature for the thermal absorbance peak of product C is well below

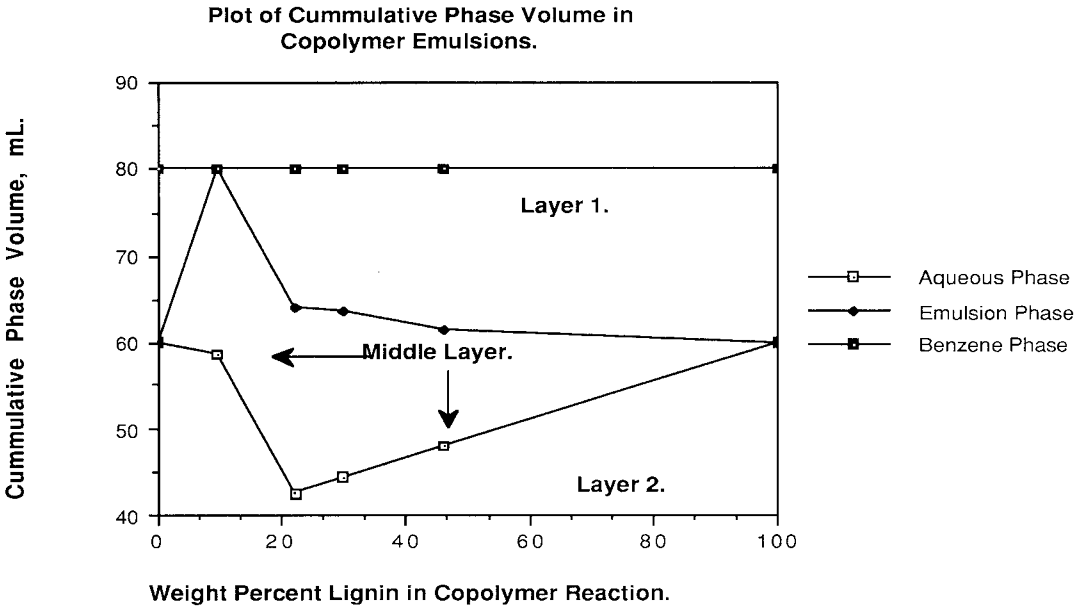

Figure 2 Diagram of phase volumes as a function of weight percent lignin in the reaction mixture used to make the copolymer that was placed in the fluid mixture.

that of product B because there is more grafted poly(1-phenylethene) in product C than in product B. In Table II, the RIPO is pure poly(1-phenylethene), sample 2–2 is pure lignin, sample 2–3 is lignin that has gone through a blank reaction with no monomer added so it has been exposed to reaction conditions but can contain no graft copolymer, samples 2–4 to 2–11 are reaction products, and samples 1–28 and 1–32 are portions of the reaction products synthesized as described in Table I.

Surface-active properties: emulsion formation

The reaction product and its fractions were interfacially active. When a benzene-extraction solution formed by extracting a reaction product with benzene (layer 1) was well mixed with an aqueous base or distilled water (layer 2), a "middle" or third layer forms. The middle layer was an emulsion layer which contained poly(1-phenylethene), graft copolymers, benzene, water, and/or base with an aqueous continuous phase. The appearance of the third layer is the result of small droplets of benzene being dispersed in the aqueous layer by a surfactant, a "soaplike" molecule that envelopes a microdroplet of the organic layer in an inner palisade of hydrophobic portions of the surfactant, poly(1-phenylethene) side chains, sheathed in an outer layer of the hydrophilic portion of the surfactant, lignin. This bilayer disperses the benzene in water. The formation of the third layer shows that the graft copolymer is populating an interface between an organic layer and an aqueous layer and is therefore surface active.[5,6] This opens the way to using the graft copolymer as a coupling agent between a ligninlike material such as wood and a hydrophobic material such as plastic. Under the same experimental conditions, a mixture of ungrafted lignin, poly(1-phenylethene), and benzene failed to form an emulsion with base or water.

The emulsion formed in the mixing tests was very stable. Phase volumes as a function of lignin content of the reaction product used to form the benzene-extraction phase are given in Figure 2. The cumulative phase volume is the reading on the graduated cylinder at the top of a phase. Layer 2 is the heavier, aqueous base phase, the middle layer is the emulsion or microemulsion that forms when the two fluids are thoroughly mixed, and layer 1 is the lighter, benzene phase. In a fluid with a pH numerically above 7, the hydroxyl groups on lignin exist in the form of oxygen anions which can disperse more organic-core micelles in water than hydroxyl groups because of anion–anion repulsion. If the system was acidic, the amount of the emulsion will be greatly decreased because acid will protonate the oxygen anions and allow the neutral micelles to coalesce.

These data suggesting interfacial activity and contact-angle data[7] showing that the reaction product could wet wood and change its surface contact angle from hydrophilic to hydrophobic against water support the idea that these new molecules can couple wood and poly(1-phenylethylene) together. This idea was verified by preparing bound birch wood-poly(1-phenylethylene) blocks with or without the reaction product at the interface between the joined blocks. A graft copolymer containing 51.7 wt % lignin increased the lap shear strength by 56%, from 1826 to 2840 kPa, and a graft copolymer extraction product from a 32.2

wt % lignin reaction increased the lap shear strength by 37%, from 1983 to 2716 kPa, when coated between the blocks.[8]

With this verification of the copolymers as coupling agents and related data showing similar effects in wood fiber-reinforced composites with poly(1-phenylethylene),[9] we conducted tests to determine if the copolymers would improve the properties of wood–poly(1-phenylethylene) composites made with wood flour rather than wood fiber. These wood-filled thermoplastics are being extensively used as "engineered wood."[3]

Composite tests

The composite planks were cut into sampling beams and tested for physical properties. A statistical sampling of 1 dozen pieces of each composite formulation were exposed to static bending using the procedures of ASTM Test D-790. The composites containing no copolymer and made with uncoated wood are termed control composites, while the composites made with a copolymer-coated wood are termed copolymer composites. The data for density, modulus of elasticity (MOE), modulus of rupture (MOR), and hyperbolic modulus (HE) before and after water saturation are given in Table 3(A) with standard deviations and coefficients of variation for each mean. The statistical comparisons at the 95% confidence level between these data are give in Table 3(B).

The structural properties of the control composite decrease sharply and significantly when wet with the modulus of elasticity, modulus of rupture, and hyperbolic modulus falling 64%. The density of the wet control composite is 0.8% lower that that of the dry form of this formulation, but this is not a statistically significant difference. An *F* test at 90% confidence for the standard deviations of the four pairs of control dry versus wet measurements shows that the standard deviations are equal for the structural properties, but the standard deviation for density is larger for the dry control composite versus the wet control composite.

The structural properties of the copolymer composite decrease sharply and significantly when wet with the modulus of elasticity, modulus of rupture, and hyperbolic modulus falling 61%. The density of the wet copolymer composite is 1.3% higher than that of the dry form of this formulation and this is a statistically significant difference. An *F* test at 90% confidence for the standard deviations of the four pairs of copolymer dry versus wet measurements shows that the standard deviations are equal for all properties.

Comparison of the dry control to the dry copolymer properties shows that there are statistically significant differences between the formulations. The dry copolymer has a 3.3% lower modulus of elasticity, a 2.0% lower modulus of rupture, and a 3.3% lower hyperbolic modulus than those of the dry control composite. These data show that the copolymer coating has made the dry composite slightly more ductile than is the control. A comparison of the densities also shows a statistically significant difference, with the copolymer-coated samples being denser.

Comparison of the properties of the wet control to those of the wet copolymer shows that there are, again, statistically significant differences between the formulations. The wet copolymer has a 4.5% higher modulus of elasticity, a 10% higher modulus of rupture, and a 7.5% higher hyperbolic modulus than those of the wet control composite. These data show that the copolymer coating has made the wet, coated composite slightly stiffer than the control. A comparison of the densities also shows a statistically significant difference, with the wet, copolymer-coated samples being 3.1% denser. A probable reason that the copolymer samples are denser is that the copolymer coating has a significantly higher density than that of the wood in the composite.

The physical property tests show that the control samples are about 3% stiffer and less deformable than are the copolymer composites when dry and about 5 or more percent more deformable than are the copolymer composites when wet. The copolymer samples are always denser than are the controls. The higher wet strength and modulus of the copolymer composites show that these materials would be preferred for high-water-exposure applications such as dock and pool decking.

Water saturation

The composites were tested for water uptake at 8, 17, 28, 35, 49, and 263 days after immersion. The mean percent water absorption for the control composites can be compared to the mean percent water absorption for the copolymer composites at six different times after the start of the saturation experiment. For all six pairs of means, mean(percent water uptake, control) versus mean(percent water uptake, copolymer), the control shows a higher water uptake at a 99.9% confidence level when compared to the water uptake of the copolymer samples measured at the same time. This statistically significant, higher water uptake by the untreated controls shows that the copolymer coating reduces the water uptake of the composites by over 13%. The difference in water uptake between the control and the copolymer composites decreases with time from 24.3% less water in the copolymer composites after 8 days of immersion to 13.8% less water in the copolymer composites after 263 days of immersion. With a declining difference in water uptake between the two groups of composites, it was important to determine if the differences be-

TABLE III
Results of the Static Bending and Water-saturation Tests on Coupled and Control Composites

TEST: Sample	Density kg/ (m**3)	Modulus of elasticity (MPa)	Modulus of rupture (MPa)	Hyperbolic modulus (MPa)
	A. Data			
Control composites, dry	1229	6634	35.73	6834
Standard deviation	6.26	227.0	0.85	184.9
Coefficient of variation (%)	0.5	3.4	2.4	2.7
Control composites, wet	1219	2371	12.54	2381
Standard deviation	29.5	248	0.77	264
Coefficient of variation (%)	2.4	10.4	6.1	11.1
Copolymer composites, dry	1242	6413	35	6608
Standard deviation	3.88	110	1.16	76.01
Coefficient of variation (%)	0.3	1.7	3.3	1.2
Copolymer composites, wet	1258	2484	13.96	2574
Standard deviation	4.4	207	0.78	133.5
Coefficient of variation (%)	0.4	8.3	5.6	5.2
B. Statistical Comparisons				
Control composites, comparison between wet and dry properties				
Pooled standard deviation, S(p)	21.32	237.7	0.8110	227.9
Maximum statistical difference between means[a]	14.90	166.1	0.5665	159.2
Actual difference between means	−10	−4263	−23.19	−4453
Mean difference significant?	No	Yes	Yes	Yes
Standard deviation ratio, wet to dry, Sw/Sd	4.712	1.093	1.104	1.428
Standard deviations equal?	No	Yes	Yes	Yes
Copolymer composites, comparison between wet and dry properties				
Pooled standard deviation, S(p)	4.148	165.8	0.9884	108.6
Maximum statistical difference between means[a]	2.898	115.8	0.6904	75.88
Actual difference between means	16	−3929	−21.04	−4034
Mean difference significant?	Yes	Yes	Yes	Yes
Standard deviation ratio, wet to dry, Sw/Sd	1.134	1.882	1.487	1.756
Standard deviations equal?	Yes	Yes	Yes	Yes
Control and copolymer composites, comparison between dry properties				
Pooled standard deviation, S(p)	5.208	178.4	1.017	141.4
Maximum statistical difference between means[a]	3.638	124.6	0.7103	98.74
Actual difference between means	13	−221	−0.73	−226
Mean difference significant?	Yes, copolymer denser	Yes, copolymer weaker	Yes, copolymer weaker	Yes, copolymer weaker
Standard deviation ratio, Scont/Scopoly	1.613	2.064	1.365	2.433
Standard deviations equal?	Yes	Yes	Yes	No
Control and copolymer composites, comparison between wet properties				
Pooled standard deviation, S(p)	21.09	228.4	0.7750	209.2
Maximum statistical difference between means[a]	14.73	159.6	0.5414	146.1
Actual difference between means	39	113	1.42	193
Mean difference significant?	Yes, copolymer denser	Yes, control weaker	Yes, control weaker	Yes, control weaker
Standard deviation ratio, Scont/Scopoly	6.705	1.198	0.9872	1.978
Standard deviations equal?	No	Yes	Yes	Yes

[a] These comparisons are made at the 95% confidence level.

tween the control and the copolymer composites would disappear with time.

The possibility of the composites becoming equivalent by prolonged soaking was tested by projecting the saturation out using the slope of the water saturation versus time curves given in Figure 3. Comparison of the control versus the copolymer curve in Figure 3 shows that the higher uptake of water by the control

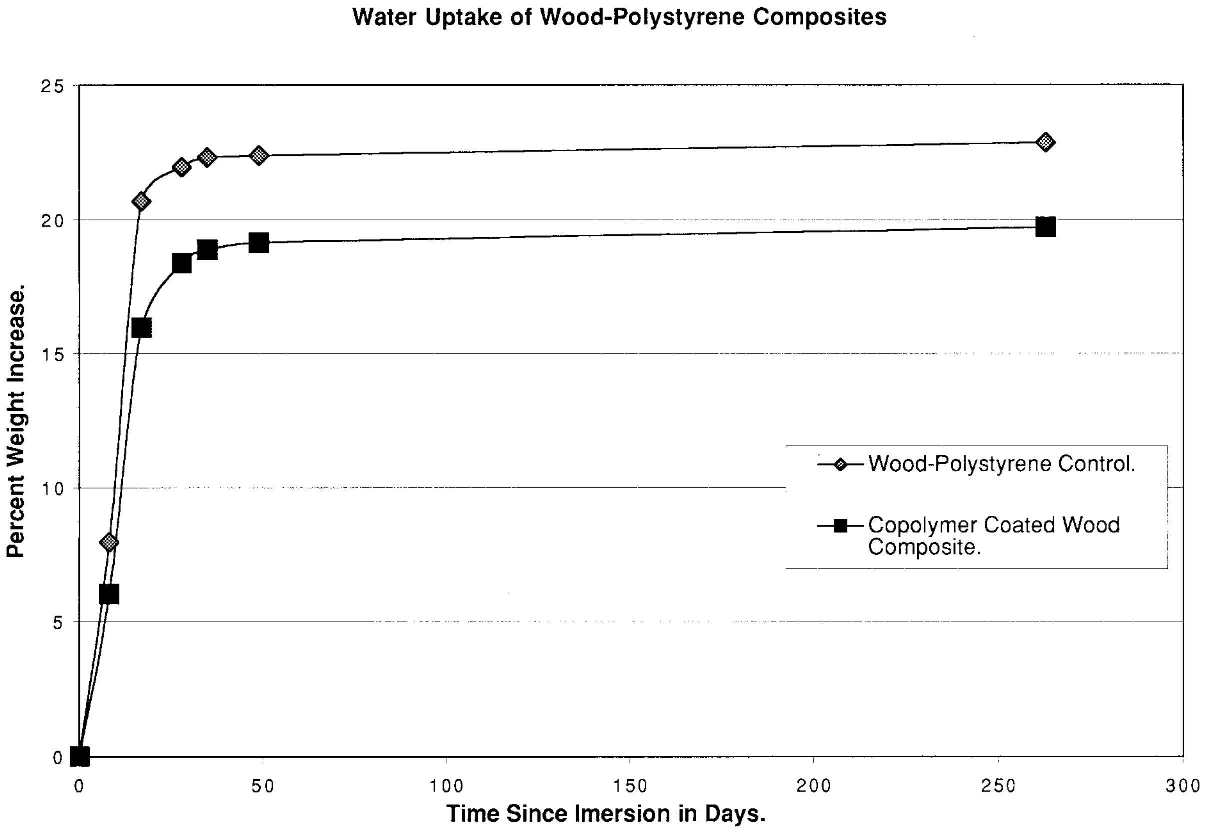

Figure 3 Percent increase in weight caused by water sorption into the wood–polystyrene–wood composite.

composite is due to a higher rate of water uptake during the first 30 days of water immersion. After those first 30 days of water exposure, the rate of water uptake by the copolymer composites is higher than that of the control composites. The time at which the copolymer composites will catch up to the control composites in water saturation is given as $t_{\text{sat.}}$, the time of saturation, in eq. (1):

$$\int_0^{t_{\text{sat}}} \frac{d(\%\ \text{water})}{dt} dt_{\text{copolymer}} = \text{percent weight increase}$$

$$= \int_0^{t_{\text{sat}}} \frac{d(\%\ \text{water})}{dt} dt_{\text{control}} \quad (1)$$

where the % water is the percent weight increase from water absorption. Using the slope between the weight measurements on days 35 and 49, the time to equal saturation for the two classes of composites would be 279 days or 9 months. Using the slope between the weight measurements on days 49 and 263, the time to equal saturation for the two classes of composites would be 26.3 years. From these rate of saturation data, we conclude that equal saturation will not be reached in the functional lifetime of the composites and that the copolymer coating provides a long-term barrier which reduces the maximum water saturation. Lower water saturation may increase the biodegradation resistance and long-term durability of copolymer coated, wood–plastic composites in high water-contact applications such as pool or ocean decking.

Water swelling

Submersion in water caused the extrudate to swell. The directions in the composite are defined by the extrusion. Length is the direction of extrusion, width is the 15.24-cm (6 in.) width of the die perpendicular to the direction of extrusion, and thickness is the 1.25-cm (0.5 in.) height of the die perpendicular to the direction of extrusion. The soaked, control polystyrene–wood composite expanded 1.05% in length, 4.5% in width, and 15.6% in thickness after 263 days in water. The control samples expanded 3.1×10^{-3} cm^3, on average, as the typical sample increased 22.9% in weight. The slope of this expansion, the volume change per gram of water absorbed, is 2.7×10^{-4} cm^3 per g. The polystyrene–(copolymer-coated wood) composite that was exposed to water expanded 0.78% in length, 5.04% in width, and 10.5% in thickness after 263 days sub-

TABLE IV
Percent Dimensional Change in the Composites

Composite sample	Change in width (%)	Change in thickness (%)	Change in length (%)
Control	4.55	15.6	1.05
Copolymer	5.04	10.5	0.78
Ratios (control/copolymer)	0.90	1.49	1.35

merged. The copolymer samples expanded 1.7×10^{-3} cm^3, on average, as the typical sample increased 19.7% in weight. The expansion of the copolymer composite per gram of water absorbed is 1.7×10^{-4} cm^3 per g. Copolymer samples expanded only 55% as much as did the controls when immersed in water. These data show that the partial molar volume of the water is significantly lower in the control samples than in the copolymer-coated composites. A mole of water added to the control samples occupies more space than one added to the copolymer sample.

The expansion of the sample is highly dependent on the direction of extrusion. The length expands about 1%, the width expands about five times as much, and the thickness expands over 10 times as much as the length does in these extruded composites. The data for these dimension changes are given in Table IV. These data may be partially explained by the dimension and orientation changes that occur during extrusion. The plank from which these samples are cut is formed with a 22% reduction in the width of the melted extrudate at the die and a 71% reduction in thickness of the melt as it passes into and through the die. Some of the sample swelling is probably a recovery of fiber volume lost in compaction or crushing as the fibers pass through the die. The stranding plate that precedes the final orifice of the die also affects the composite.

The stranding plate forces the extrudate into tubules in a high-pressure flow through tubes parallel to the direction of flow. This also aligns the long axis of the fiber near the tube wall with the direction of flow[10] and the wall of the tubes. Since the wood is wood flour, the aspect ratio of the fiber is close to 1 but a long axis and alignment can still be detected at the strand lines in the composite. This preferred orientation of some of the flour may partially cause the differential expansion of the composites.

The changes in control dimensions are about equal to or greater than those in the copolymer formulation. The length change in the control is 1.35 times that of the copolymer, the width change is about 90% of that of the copolymer, and the thickness change in the control is 1.49 times that of the copolymer.

The copolymer coating on the wood decreases the swelling in the solid, the partial molar volume of the imbibed water, and the dimensional change in the solid. This causes the increase in the density of the copolymer composite upon imbibition of water.

CONCLUSIONS

Poly[lignin-*g*-(1-phenylethylene)] graft copolymers posses macromolecular surface activity as indicated by their capacity to form stable emulsions between incompatible fluid phases, to adhesively bond to wood surfaces, and to change the contact angle of water on coated wood. The surface activity of the copolymer changes with its composition. As the weight percent lignin in the copolymers increases beyond 20 wt %, the amount of the emulsion phase formed in the water–benzene mixture decreases. Coating birch wood (*Betula papyrifera*) with a lignin-1-ethenylbenzene graft copolymerization product increases the water contact angle. The graft copolymers change the contact angle of water on wood from 50° to 110°. Coating birch wood with the lignin-1-ethenylbenzene graft copolymerization product also increases the binding strength of poly(1-phenylethylene) plastic coatings on the wood. Lap shear strengths increased 56%, from 1826 to 2840 kPa, when the wood was coated with a grafted product containing 51.7% lignin.

Maple wood flour could be adhesively solvent-coated with the copolymer and both coated and uncoated maple flour could be extruded through a stranding plate into a wood-filled composite with polystyrene. The physical property tests show that the control samples are about 3% stiffer and less deformable than are the copolymer composites when dry and about 5 or more percent more deformable than are the copolymer composites when wet. The copolymer samples are always denser than are the controls.

The copolymer coating on the wood decreases swelling in the solid, the partial molar volume of the imbibed water, and the dimensional change in the solid. This causes the increase in density of the copolymer composite upon imbibition of water. Coating the wood component of the composite with the copolymer creates a hydrophobic barrier that produces a permanent decrease in water imbibition into the composite and lowers the water swelling of the composite. Expansion is highly dependent on the direction of extrusion. Length expands about 1%, width expands about five times as much, and thickness expands over 10 times as much as does the length. This differential expansion in water may be due to the 22% reduction in width and a 71% reduction in the thickness of the melt as it passes through the die and the alignment of the long axis of the fiber with the direction of flow through the die.

The higher wet strength and modulus of the copolymer-coated composite, its reduced dimensional change, swelling, and water uptake from water immersion, and its higher density recommend this material for high water exposure applications such as dock and pool decking.

Thermogravimetric analysis data of the reaction products of different lignin/poly(1-phenylethene) compositions show that, below 200°C, there is 1–2% weight loss. The copolymers are stable and thermoplastically moldable below this temperature. In the reaction product, there exists evident phase separation caused by homopoly(1-phenylethene) and grafted lignin, as evidenced by the two thermal absorbance peaks of some products.

Lignin-1-ethenylbenzene graft copolymers have been made by free-radical graft copolymerization of 1-ethenylbenzene on lignin in a nitrogen-saturated solvent containing calcium chloride and hydrogen peroxide. Yield and limiting viscosity number data from reactions run at the same mol ratio of the chloride ion to hydrogen peroxide but the decreasing amounts of both the chloride ion and hydrogen peroxide support the role of the chloride ion as the active site initiator and hydroperoxide as the redox energy source. Failure of polymerization in a blank reaction containing no lignin shows that lignin is a critical part of the reaction initiation. After the copolymerization of lignin and 1-ethenylbenzene, part of the original lignin was changed from a benzene-insoluble material to a benzene-soluble material, part of the original lignin was changed from a base-soluble material into a base-insoluble material, and part of the reaction product could not be dissolved in either benzene or aqueous base. The original, hydrophilic lignin had become a hydrophobic material. These solubility changes, physical changes, FTIR, and fractionation behavior of the reaction product all support graft copolymerization.

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References

1. Meister, J. J.; Chen, M. J. Macromolecules 1991, 24, 6843–6848.
2. Meister, J. J.; Patil, D. R.; Channell, H. In Proceedings of the International Symposium on Oilfield and Goethermal Chemistry, Soc. Petrol. Eng. Paper #13559, Phoenix, AZ, April 4–11, 1985.
3. Meister, J. J.; Chen, M. J.; Gunnells, D. W.; Gardner, D. J.; Milstein, O.; Gersonde, R.; Hutterman, A. Macromolecules 1996 29, 11389–11398.
4. Meister, J. J. U.S. Patent 4 940 764, 1990.
5. Zisman, W. A. Contact Angle, Wettability and Adhesion; Advances in Chemistry Series 43; American Chemical Society: Washington, DC, 1964; Chapter 1.
6. Gunnells, D. W.; Gardner, D. J.; Chen, M. J.; Meister, J. J. J Wood Chem Tech 1995, 15, 287–302.
7. Chen, M. J.; Meister, J. J.; Gunnells, D. W.; Gardner, D. J. Adv Polym Technol 1995, 11, 97–109.
8. Zhang, S. Thesis submitted for Master of Science Degree, University of Detroit, 1995.
9. Laver, T. C. U.S. Patent 5 516 472, May 14, 1996 (to Strandex Corp., 829 Huntersknoll Lane, Cincinnati, OH 45230). See commercial product list.
10. Hermanson, J. Third Quarter Progress Report, 1999; Action Item 102, Figure 2; Office of Naval Research Contract N00014-97-C-0395; Fall, 1999.