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Graft Copolymers of Lignin with 1-Ethenylbenzene. 2. Properties

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ABSTRACT: The graft copolymerization of lignin and 1-ethenylbenzene was coinitiated by lignin, calcium chloride, and hydrogen peroxide in dimethyl sulfoxide solution. Conversion of 1-ethenylbenzene and yield of polymerized product of 90% or more were obtained. The copolymerization reaction changes the hydrodynamic radius of the product. Grafting has changed the surface properties of the original lignin from hydrophilic to hydrophobic. The copolymerization product is a thermoplastic material. White rot *Basidiomycete* were able to biodegrade styrene (1-ethenylbenzene) graft copolymers of lignin containing different proportions of lignin and poly(1-phenylethylene). The polymer samples were incubated with white rot *Pleurotus ostreatus*, *Phanerochaete chrysosporium*, and *Trametes versicolor* and brown rot *Gleophyllum trabeum*. White rot fungi degraded the plastic samples at a rate which increased with increasing lignin content in the copolymer sample. Both poly(1-phenylethylene) and lignin components of the copolymer were readily degraded. Poly(1-phenylethylene) pellets were not degradable in these tests. Observation by scanning electron microscopy of incubated copolymers showed a deterioration of the plastic surface. Brown rot fungus did not affect any of these plastics. The FTIR of the graft copolymers shows a series of characteristic absorbance peaks from multisubstituted aromatic rings and a strong poly(1-phenylethylene) (polystyrene) absorbance peak from monosubstituted aromatic rings. Subtraction of copolymer spectra taken after 50 days of incubation with the four tested fungi from spectra taken before incubation shows the loss of functional groups from the copolymer. The graft copolymer with long poly(1-phenylethylene) side chains is a macromolecular surface active material because in each graft molecule, a long hydrocarbon side chain has been grown off of a natural (oxyphenyl)propyl backbone. Surface activity of the graft copolymers is indicated by their capacity to form stable emulsions between incompatible fluid phases and to adhesively bond to wood surfaces. Dynamic contact angle measurement using the Wilhelmy plate technique shows that the graft copolymers change the contact angle of water on wood from 50 to 110°. The copolymerization product and its fractions have a coupling effect in the connection of wood to poly(1-phenylethylene). Lap shear strengths increase 56%, from 1826 to 2840 kPa, when the wood is coated with a graft copolymer containing 51.7% lignin.

Introduction

Lignin [8068−00−6], which comprises between 15 and 30 wt % of dry wood, acts as a cementing agent to bind the matrix of cellulose fibers together into a rigid woody structure. As a natural, renewable source of carbon available in a future characterized by declining petroleum supplies, lignin will play a much larger role in the synthesis of macromolecules important to society. To allow such utilization, a chemical modification method was developed to convert lignin into lignin−(1-ethenylbenzene) (styrene) graft copolymers. The properties of the copolymers can be used to design a process for forming wood−thermoplastic composites. Measurements showing solubility properties, limiting viscosity number, thermal properties, thermoplasticity, biodegradability, surface activity, wetting alteration, and phase coupling behavior are detailed in this paper.

Experimental Section

Synthesis. Dimethyl sulfoxide has been used as the solvent for the reactions reported here. This reaction can be success-

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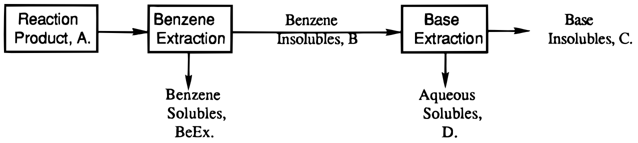


Figure 1. Flow diagram of copolymer fractionation process.

fully run with concentrations or mole ratios of the reactants in the following ranges: (1) polymerizable solids content of the reaction, 23 wt % or less; (2) hydroperoxide to calcium chloride, *0.25−32*; (3) hydroperoxide to lignin (M_n), *21−113*; and (4) weight fraction of monomer in polymerizable solids, 0.01−0.95.

Prepare sample A by placing pure ethenylbenzene in a conical flask and bubbling it with nitrogen (N_2) for 10 min. Prepare sample B by placing lignin, calcium chloride, and dimethyl sulfoxide solvent in a conical flask, stirring until dissolved, and bubbling the solution 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 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 compolymerization 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.

The fractionation of the graft copolymer is diagramed in Figure 1. The reaction product, A, is extracted with benzene for 48 h. The benzene-soluble material is recovered by evaporating the benzene and the solid is labeled fraction BeEx. The solid not dissolved in benzene is labeled fraction B and is slurried with 0.5 M sodium hydroxide for at least 16 h. This solution is filtered, and the filtrate is dialyzed against water for 3−5 days by using dialysis tubing. The solid filtered from the base is washed with 2 M hydrochloric acid, washed with distilled water, dried, and labeled fraction C. The dilute, dialyzed solution is then dried to freeze-dried to recover base-soluble, fraction D.

Solubility of the reaction products was determined in reagent grade solvents at room temperature. The limiting viscosity number of the products was determined in *N*,*N*-dimethylformamide at 30 °C using the same Cannon−Fenski viscometer for all samples.

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

The product's surface activity on wood was tested by measuring how much the materials changed the contact angle of water on birch wood (*Betula papyrifera*). The first set of treated birch samples was prepared by cleaning each wood surface with a Kimwip laboratory towel, weighing the wood strip, placing a 5 or 10 wt % solution of graft copolymer in *N*,*N*-dimethylformamide on the wood surface with an eyedropper, spreading the copolymer solution with a glass rod, drying the coated wood for 15 h in a hood and 2 h in a room temperature vacuum oven, and storing the strip in a desiccator. The second set of treated birch samples was prepared by the same general process used on the first set, but only a 5 wt % solution of graft copolymer in *N*,*N*-dimethylformamide was used to create the coating and the coating process was done twice on each specimen. Prior to testing, samples were cut and end-sealed with poly(vinyl acetate) resin.

Dynamic contact angle (DCA) measurements were performed by bringing a thin, treated or untreated slab of birch into contact with water by immersing it parallel to the grain. When the sample was exposed to the water, an increase in weight due to the absorption of water vapor began. Once this change in weight was observed, the test was started. The sample was immersed at a rate of 194 μm/s to a depth of 15 mm. The sample was removed automatically at the same rate. The test sample and test distilled water were replaced, and the test procedure was repeated. Figure 2 illustrates the main functional components of the DCA system.

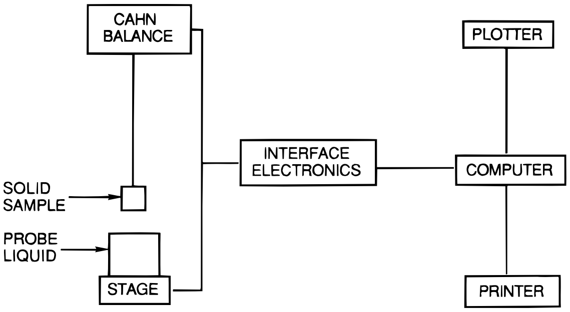


Figure 2. Schematic diagram of the Cahn dynamic contact angle tester.

The force of the liquid meniscus on the wood is measured by a force balance. Since the surface tension of water is known, the contact angle of the water and the wood can be calculated. Critical surface tension measurements were obtained using contact angle measurements obtained with a series of water−methanol mixtures. Further details on surface property measurements on wood using the dynamic contact angle method can be found in refs 3 and 4.

The surface active agents were tested as coupling agents by coating copolymer solutions onto brich sheets, made by Solon Manufacturing Co., Solon, ME 04979. The 1.75 mm thick by 15.4 mm wide by 70 mm long wood sheets were already cut into suitable sizes to match a gated steel injection mold. The solutions were 10% lignin graft copolymer in *N*,*N*-dimethylformamide. The coating was applied at room temperature by placing 2.7 g of sample solution on a weighed wood sheet and spreading it with a glass rod. The coated sheets were dried in a hood and then in a vacuum oven at room temperature for 1 h and weighed. The difference of the weight was considered the weight of the coating sample. Coated sheets were stored in a desiccator at room temperature and 50 ± 5% relative humidity until the preparation of adhesion test samples.

Wood−plastic samples for lap shear adhesion tests were prepared in a Newberry Mini-Jector, Model 50 injection molding machine. The mold was a trapezoidal steel block by which a 70 mm long supporting handle and a 12 mm wide by 27.5 mm long by 5.9 mm thick wood-contacting tongue of poly(1-phenylethylene) could be molded. The cylinder temperature was 288 °C, nozzle temperature was 171 °C, mold temperature was 25 °C, injection pressure was 3.5 MPa, pressure holding time was 12 s, and chilling time was 1−2 min. The granular poly(1-phenylethylene) used in the bonding experiments was Amoco RIPO, an additive-free poly(1-phenylethylene), and had a softening point of 107 °C and a melt flow index of 1.8 g in 10 min. The adhesion area was measured for each molded specimen after any nonadherent poly(1-phenylethylene) flakes at the edges of the wood sheet on the molded specimen were cleared off.

The wood−plastic samples were tested for adhesion by placing the injection-molded wood−plastic piece in an aluminum holder and mounting the holder in an Instron tensile strength tester (Model 4200). Figure 3 illustrates the wood−plastic piece and the aluminum holder.

The copolymerizates tested for biodegradation were supplied as a fine powder of numerically more than 100 mesh and as a compression-molded sheet of 0.15 mm thick by 5−7 cm diameter circular plastic film. The 2.5 mm diameter by 2.5 mm long cylindrical pellets of polystyrene homopolymer were tested directly for biodegradation and were compression-molded into 0.25 mm thick by 7 cm diameter circular films for testing. All compression moldings were done at 150 °C and 192 KPa pressure for 1 min.

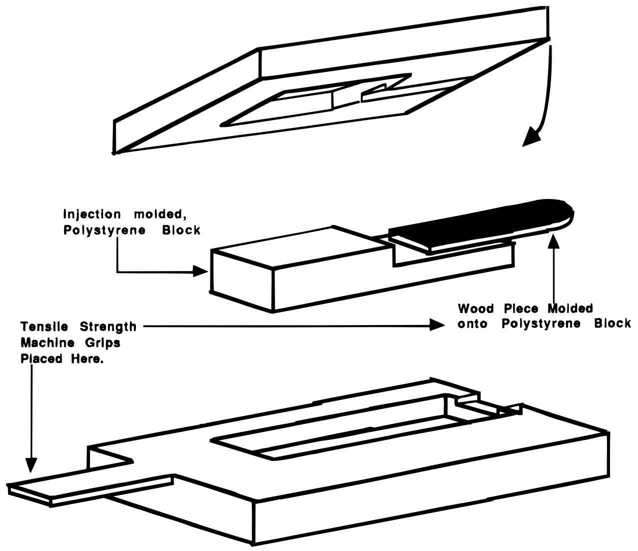


Figure 3. Aluminum brace used to hold wood−plastic samples for Lap shear, tensile strength tests.

The microorganisms used in this work were three white rot *Basidomycete* (*Phanerochaete chrysosporium*, *Trametes versicolor*, and *Pleurotus ostreatus*) and one brown rot fungus (*Gloeophyllum trabeum*). The tested fungi were cultivated on solid 2.5% agar medium. The inoculum for a copolymer sample consisted either of a piece of straw from the maintaining culture or of 2 × 5 mm plugs from a 7 day old plate culture. The plates were placed at 25 °C in a thermostated chamber at 100% humidity for 68 days.

Biodegradation was followed by weight loss, in particular by a decrease of the lignin and polystyrene components from the biodegraded complex, ultraviolet spectroscopy, infrared spectroscopy, and scanning electron microscopy of the decayed polymer. Tested powdered copolymerizates were intimately bound with the growing fungi; thus direct measurement of the loss of polymer weight was impossible. To evaluate the loss of the tested copolymerizate, the nitrogen content of the aliquot of the dry collected material from the triplicates of inoculated plates and uninoculated control was measured. The amount of nitrogen determined was converted to the amount of fungal biomass by applying the same nitrogen/biomass ratio as was found in the pure fungus from the cultures of identical age and medium. The computed fungal biomass was subtracted from the recovered material in this way. None of the recovered samples contained more than 10% fungal biomass. The quantity of separate components, lignin and polystyrene, in the treated copolymer was analyzed by UV spectroscopy using multicomponent analysis methods. Dry lignopolystyrene complexes from inoculated plates and uninoculated controls were solubilized in a dioxane−ethanol−dichloroethane (7:3:5, by volume) mixture.

FTIR spectroscopy was used to show the loss of functional groups from the copolymerization products. These tests were run on potassium bromide pellets of dried plugs from the inoculated or control plates. Salt pellets were made from 2 mg of polymer or biomass and 300 mg of potassium bromide mixed into a uniform dust and compressed at 70 MPa for 2 min. The equation for the calculation of the difference spectra is

$$\begin{aligned}&\text{missing infrared absorbance} = \{\text{absorbance spectra}\\&\quad\text{of copolymerizate from control flasks} -\\&\quad[\text{absorbance spectra of copolymerizate,}\\&\quad\text{degraded sample} - (\text{wt \% fungi in sample} \times\\&\qquad\text{absorbance spectra of fungal material})]\}\end{aligned}$$

The pieces of pressed copolymer from both the uninoculated control plates and the plates with fungi were withdrawn after 68 days of incubation and mounted on SEM stubs, sputter-coated with gold to a thickness of about 10 nm, and observed and photographed using a Phillips SEM 515.

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. 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 %. Some of the lignin used in the copolymerizations described below was extracted with benzene for 48 h at a ratio of 1 g of lignin to 10−15 mL of benzene using a Soxhlet apparatus. This removed the low molecular weight portion of the lignin (approximately 3−5 wt %) and allowed certain fractionation experiments to be done on the product to prove the existence of graft copolymer. This extraction process is not necessary to successful copolymerization of the lignin, however.

The compound ethenylbenzene was obtained from the Laboratory and Research Products Division of Kodak, Rochester, New York 14650. The ethenylbenzene was purified to remove the stabilizer by washing the monomer three times with aqueous base at a ratio of 1 g of 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 vacuum at 40 °C and 20 mmHg pressure. The central cut was collected in dark bottles and stored in a freezer at −15 °C. Polystyrene homopolymer, material RIPO, was used as received from Amoco Chemical Co., P.O. Box 400, Naperville, IL 60566. 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} equiv/g, 1.907 × 10^{-2} equiv/mL and (2) 29.86% H_2O_2 in water, 1.756 × 10^{-2} equiv/g, 1.947 × 10^{-2} equiv/mL. Reagent grade dimethyl sulfoxide and anhydrous calcium chloride 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. Weighings were done on a Mettler H6, four-decimal-place balance. All benzene extractions were done in a Soxhlet apparatus.

Results and Discussion

Synthesis. The procedure for synthesizing these materials is given in ref 1. The products prepared to test properties of the reaction products and their fractions are summarized in Table 1. Fractionation and spectroscopic analysis of several reaction products confirm the presence of graft copolymer. Mixtures formed by both mechanical mixing and solution evaporation are separated by benzene and base extraction, but reaction products cannot be separated into lignin and poly(1-phenylethylene) fractions by the same procedure. Fourier transform infrared spectroscopy of the fractions confirms the presence of lignin and poly(1-phenylethylene) in all fractions of the reaction product. The distribution of 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 poly(1-phenylethylene) homopolymer and a broad molecular weight distribution of graft copolymer.

Solubility Change. The solubility and solution properties of the reaction product, A, and all of its fractions, B, BeEx, C, or D, are changed from the properties of the staring material. After the copolymerization of lignin and 1-ethenylbenzene, the following occurred:

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 pre-extraction with benzene. However, after benzene extraction of the copolymerization product, the benzene extraction solution always had a dark-brown color. Thus, copolymer-

Table 1. Composition and Yield of the Copolymerization Reactions

	composition					yield	
sample no.	lignin (g)	1-phenylethene (g)	$CaCl_2$ (g)	H_2O_2 (mL)	DMSO (g)	g	wt %
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
1−31	2.00	18.76	2.00	2.06 g	20.00	19.24	92.68
1−32	2.01	18.78	2.00	2.02 g	20.00	19.63	94.42
1−33	2.00	18.79	2.00	2.07 g	20.00	19.19	92.30
1−34	8.00	28.15	8.00	8.0	40.02	33.16	91.73
1−35	8.04	18.76	8.00	8.0	40.03	24.14	90.07
1−36	8.01	9.39	8.00	8.0	40.10	15.45	88.79
1−37	8.01	18.74	6.00	8.0	40.04	24.59	91.93
1−38	8.01	18.76	6.00	8.0	40.02	24.36	90.99
1−39	8.04	18.75	6.00	8.0	40.05	15.96	59.57
1−40	8.00	9.38	2.08	8.0	40.08	14.56	83.77
1−41	8.03	9.38	4.04	8.0	40.09	14.98	86.04
1−42	8.01	9.38	6.28	8.0	40.00	15.89	91.37
1−43	8.00	9.38	6.00	4.0	40.00	14.86	85.50
1−44	8.01	9.39	6.00	6.0	40.00	15.13	86.95
1−45	8.01	9.39	6.00	10.0	40.00	13.30	76.44
1−47	8.03	9.38	4.03	4.0	40.00	15.41	88.51
1−48	8.07	9.38	6.03	6.0	40.00	15.60	89.40
1−49	8.00	28.1	6.0	8.0	40.14	33.02	89.04
1−50	8.02	18.76	6.02	8.0	40.00	24.93	90.14
1−51	2.02	18.76	2.02	2.0	10.01	17.26	83.06
1−52	2.00	18.76	2.01	2.0	15.02	18.16	87.48
1−53	2.01	18.77	2.01	2.0	20.04	18.65	89.75
1−54	2.00	18.77	2.01	2.0	25.02	18.92	91.09
1−55	2.00	18.76	2.01	2.0	30.03	16.97	81.74
1−56	2.00	18.78	2.04	3.0	20.06	19.13	92.06
1−57	8.06	9.38	6.00	8.0	40.05	15.59	89.39

ization 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.

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 aqueous base. After a benzene extraction solution of the copolymerization product (product A) 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 benzene and could not be extracted with 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.

3. Product fraction C could not be dissolved in either benzene or aqueous base.

4. The different solubility of fractionated products in benzene or aqueous base depended on the quantitative balance of the poly(1-phenylethene) side chain and the lignin backbone. Benzene is a good solvent for poly(1-phenylethene), but a nonsolvent for lignin. Aqueous base is a good solvent for lignin, but a nonsolvent for poly(1-phenylethene). As the amount of grafted poly(1-phenylethene) on lignin increases, the solubility of graft copolymers in benzene increases, and the solubility of graft copolymers in base decreases. Using the benzene and base extraction method given in the Experimental Section, three types of copolymers should be obtained. Product BeEx should contain a lignin with long grafted poly(1-phenylethene) side chains on it. Product C should contain a lignin with medium grafted poly(1-phenylethene) side chains on it which could not be dissolved in benzene or base. Product D should contain a lignin with short grafted poly(1-phenylethene) side chains on it. Product B would be a mixture of products C and D. Infrared spectra of the fractions showed peak intensities that reflect these composition predictions for the fractions.

Table 2. Mass Distribution of Fractions for the Reaction Product[a]

		wt % of total product in fraction			
sample no.	yield (g/wt %)	A (total)	BeEx (benzene sol)	C (base insol)	D (base sol)
2−1	17.26/83.06	100	86.3	5.46	
2−2	18.16/87.48	100	91.7	1.8	4.8
2−3	18.65/89.75	100	91.4	2.2	4.9
2−4	18.92/91.09	100	90.1	3.6	5.1
2−5	16.87/81.74	100	88.9	4.9	4.7

[a] Lignin content in the reactions (lignin/(lignin + styrene)) is 9.63%.

Data from typical separations are given in Table 2. Further, analyses by infrared spectroscopy show that all four fractions of a copolymer sample contain polystyrene and lignin while fractions from a lignin−polystyrene mechanical mixture are pure. The different solubility of the fractions of the product in benzene and aqueous base and the limiting viscosity numbers measured on each fraction reflect the different size of the grafted polystyrene chain(s) on lignin, mentioned above.

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 water. After the copolymerization, the surface properties of the original lignin added to the reaction were changed. Product B was a very hydrophobic material. When it was put into water, it would not wet or sink. It floated on the surface of water. It is evident that these wetting changes were caused by poly(1-phenylethene) side chains grafted onto the lignin. The results of wettability and infrared spectra tests show that almost all the lignin in the reaction mixture was grafted with poly(1-phenylethene).

Limiting Viscosity Number. The limiting viscosity number of kraft pine lignin in *N*,*N*-dimethylformamide at 30 °C is 0.071 dL/g. The average limiting viscosity number of six reaction products prepared with the same reaction composition and then measured in *N*,*N*-dimethylformamide is 0.190 ± 0.031 dL/g. Limiting viscosity number is therefore an imprecise but important property which supports grafting of lignin by showing an increase in hydrodynamic radius after reaction. This increase in hydrodynamic radius is roughly proportional to the percent 1-ethenylbenzene in the polymerizable material of the reaction mixture, lignin + 1-ethenylbenzene. This is shown by the data of Figure 4. As the weight percent of the polymerizable material in the reactor charge that is lignin decreases and the weight percent that is 1-ethenylbenzene rises, the limiting viscosity number of the product rises.

Limiting viscosity number also provides some mechanistic insight by its change as a function of hydroperoxide or chloride content in the reaction mixture. When the hydrogen peroxide added to the reaction mixture is

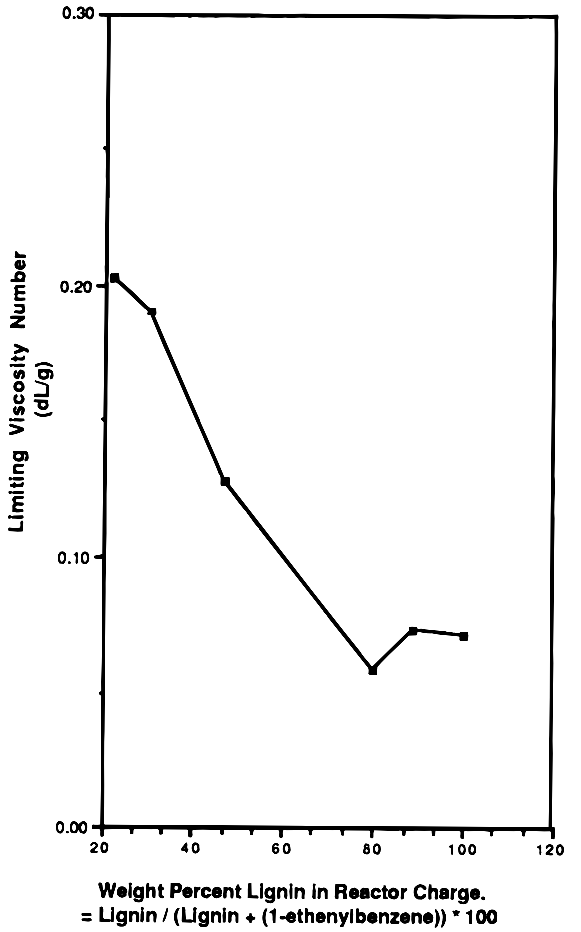


Figure 4. Influence of reaction chloride ion concentration on limiting viscosity number of the graft copolymer product: (■) η.

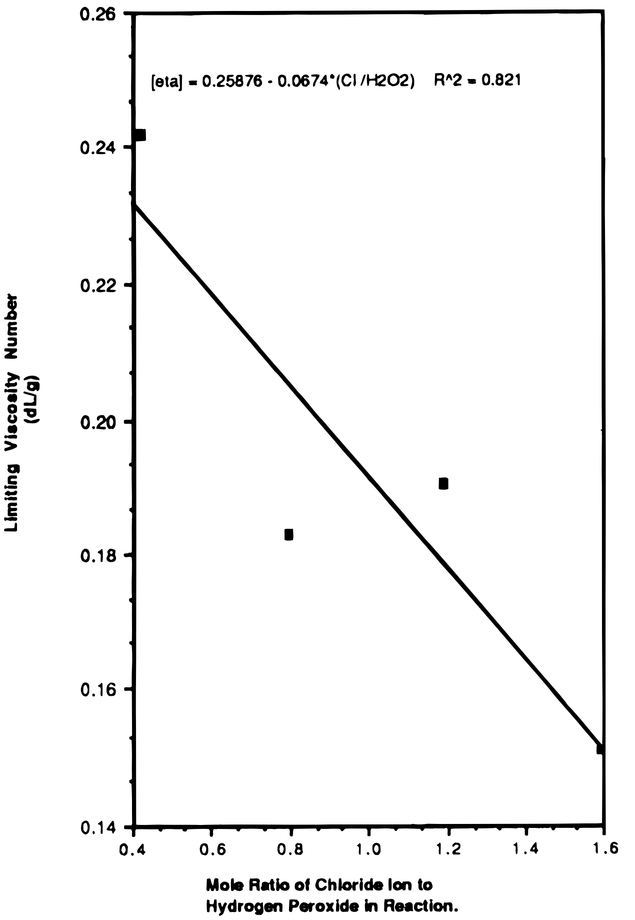


Figure 5. Change in limiting viscosity number as a function of weight percent lignin in the polymerizable materials placed in the reaction: (■) η.

changed by 25%, the limiting viscosity number of the product is essentially unchanged. However, when the chloride ion added to a fixed reaction composition increases and raises the mole ratio of chloride ion to hydrogen peroxide in a reaction, the limiting viscosity number of the product decreases, as shown by the data of Figure 5. The mole ratio of hydrogen peroxide to lignin in the reactions of Figure 5 is 108. These data imply that when the mole ratio of chloride ion to hydrogen peroxide decreases, the hydrodynamic radius of the product, and apparently its molecular weight, increase. These results would occur if the lower chloride ion content of the reaction produced fewer grafting sites and longer grafted chains on the product. This would occur if chloride ion is the active agent in producing the free radical on lignin while a hydroperoxide is the source of redox energy in the grafting reaction. Yield and limiting viscosity number data from reactions run at the same mole ratio of chloride ion to hydrogen peroxide but with decreasing amounts of both chloride ion and hydrogen peroxide support the role of chloride ion as the active site initiator and hydroperoxide as the redox energy source. At a $CaCl_2/H_2O_2$ mole ratio of 1.59, the yield is maintained above 90% and the limiting viscosity number stays at about 0.24 at mole ratios of hydrogen peroxide to lignin of 108−54. When the simultaneous reduction of chloride ion and hydrogen peroxide concentration produces a mole ratio of hydrogen peroxide to lignin of less than 50 while the $CaCl_2/H_2O_2$ mole ratio is still 1.59, yield and limiting viscosity number decrease sharply. These data imply that the $CaCl_2/H_2O_2$ mole ratio is a controlling variable for the number or lengths of grafts and that the mole ratio of hydrogen peroxide to lignin controls the yield and conversion of monomer.

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, it formed a plastic sheet in which grafted lignin was uniformly dispersed.

Thermogravimetric analysis data of reaction products of different lignin/[poly(1-phenylethene)] compositions show that, below 200 °C, there is 1% to 2% weight loss. This is possibly caused by water absorbed by the product. Product A 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 3 show that product A has two thermal absorbance peaks. This means that in product A, there exists evident phase separation caused by homopoly(1-phenylethene) and grafted lignin. The higher the lignin content in product A, the bigger the higher temperature, thermal absorbance peak. The higher temperature absorbance peak is provided by the lignin constituent in product A. 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 that of product B because there is more grafted poly(1-phenylethene) in product C than in product B.

Surface Active Properties. Emulsion Formation. The reaction product and its fractions were

Table 3. Differential Scanning Calorimetry Data for Lignin, Poly(1-phenylethylene), and Graft Copolymer

	lignin (wt %)			
sample no.	in reacn	in product A	peak (°C)	ramp (°C/min)
Amico RIPO (pure poly(1-phenylethylene))	0.0	0.0	98.9	10
30−95−1 LIG (pure lignin)	100.0	100.0	116.17	10
35−102−4BB (blank reacn lignin)	100.0	100.0	150.82	10
30−100−4A	9.6	10.32	94.82, 114.62[b]	10
35−130−3A	22.0	27.32	98.43, 133.97[b]	10
35−110−3A	30.0	32.17	98.23, 124.10[c]	10
35−120−2A[a]	30.0	34.49	102.35, 144.48[c]	20
35−113−3A	30.0	32.30	95.73, 133.25	10
35−105−3A	46.0	50.53	94.11, 125.12	10
35−120−3A[a]	46.0	51.84	101.63, 143.27	20
30−100−4B	9.6		143.40	10
35−110−3B	30.0		140.58	10
35−105−3B	46.0		146.73	10
30−87−1C	9.6		109.14	10
30−100−4C	9.6		129.47	10

[a] 1−134−4 lignin was used. [b] Very small peak. [c] Small peak.

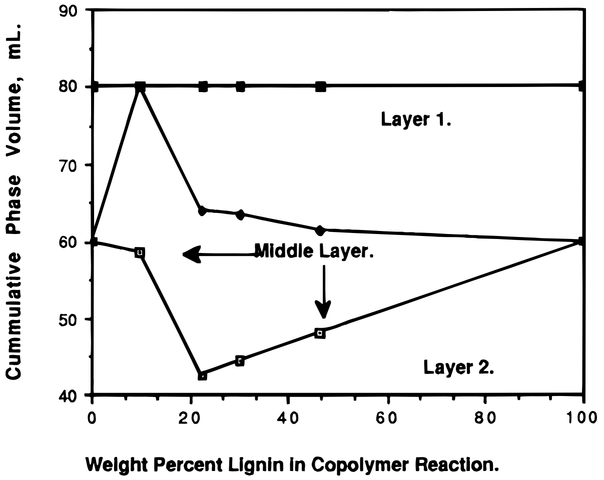


Figure 6. Volumes of each of three phases formed when a solution of copolymer in benzene is shaken with aqueous base: (⊡) aqueous phase; (♦) emulsion phase; (■) benzene phase.

Table 4. Results of Coating and Contact Angle for Birch Strips

sample no.	graft copolymer no.	DMF soln concn (%)	wt of coating (*g*)	advancing contact angles (deg)
3−1	1−50A	5	0.137	107.8
3−2	1−50B	10	0.167	99.1
3−3	1−50BeEx	5	0.083[a]	114.0
3−4	1−49A	10	0.13	110.0
3−5	1−49B	10	0.11	99.1
3−6	1−49BeEx	5	0.10	119.5
3−7	lignin	10	0.13	87.2
3−8	PPE[b]	5	0.07[a]	105.4
3−9	78% PPE + 22% lignin	5	0.093[a]	107.8
3−10	70% PPE + 30% lignin	5	0.087[a]	110.4
3−11	uncoated blank[a]			50.8

[a] There are white, poly(1-phenylethylene) flakes on the surface of these wood strips. [b] PPE = poly(1-phenylethylene) homopolymer. [c] Done in triplicate, sanded.

interfacially active. When a solution of fraction BeEx (layer 1) was well mixed with 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, base, water, and benzene with aqueous base as a continuous phase. Its appearance is the result of small droplets of benzene being dispersed in the aqueous layer by a surfactant, a "soap-like" molecule that envelopes a microdroplet or organic layer in a palisade of hydrophobic portions of the surfactant (poly(1-phenylethene)) and disperses it 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 lignin-like 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 6. 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.

Contact Angle. Contact angle measurements[4] were used in testing how well the graft copolymer allows water to wet wood. When wood is embedded in a plastic phase, the interface between the two phases is a high-energy boundary produced where the hydrophilic wood meets the hydrophobic plastic. This attempt to meld two very different phases causes the bonding across the boundary to be weak. A coupling agent can mesh these two phases together and strengthen wood−plastic composites by making the interface at the wood−plastic boundary stronger. The products listed in Table 1 could be such coupling agents, and we tested them by measuring how much the materials changed the contact angle of water on birch wood (*B. papyrifera*). The wood was coated with a solution of 5−10% copolymer in DMF and dried. Data on wood strips coated with samples 1−49 and 1−50 are given in Table 4.

The white flakes of poly(1-phenylethylene) on the surface of the birch strips could indicate that the pure polymer does not wet the wood. Under 50-fold magnification, the coatings on the birch treated with pure poly(1-phenylethylene) or mechanical mixtures of the thermoplastic and lignin appear as fine to large threads or particles with the size of the poly(1-phenylethylene) aggregate increasing with the weight percent of poly(1-phenylethylene) in the applied coating. The coating from pure poly(1-phenylethylene) or a mechanical mixture is only slightly adhesive to the surface. Large fractions of the coating break off when an analytical spatula is dragged across the coated surface under its own weight. While the polymer does change the contact angle of the surface, as shown by the data of Table 4, this is not a functional change. As soon as the surface is contacted or experiences any shear forces, this poly(1-phenylethylene) layer will cleave off. All copolymer-coated samples had smooth adherent surface coats on them, however, and the copolymer coating changed the contact angle of the wood from hydrophilic (~50°) to hydrophobic (110°). The contact angles measured on these treated and untreated birch strips are also given in Table 4. No visible leachates were observed in the test liquid after testing, indicating the copolymer formed an insoluble coat on the wood.

The lignin content in copolymers 1−50 and 1−49 is 24.2% and 32.2%, respectively. The increase in lignin content of copolymer 1−49 and its fractions by 8% produced slight increases in the contact angles of the birch coated samples. However, fractionating the reaction product (product A) into a benzene-soluble fraction (fraction BeEx) and a benzene-insoluble fraction (fraction B) sharply changes the capacity of the copolymer to alter wetting on wood. The benzene-soluble fraction (fraction BeEx) is 12% more effective in changing the water contact angle than is the complete reaction product while the benzene-insoluble fraction (fraction B) is 14% less effective in changing the contact angle. Since the capacity to change the contact angle decreases with the decreasing fraction of long-chain grafted lignin in the coating (BeEx > A > B), the most effective hydrophobic coatings are made with poly(1-phenylethylene) graft copolymers with long side chains.

Lignin gave the lowest contact angle with water, 87°, of any coating materials. A coating of poly(1-phenylethylene), though not adherent, made the birch hydrophobic, giving it a contact angle with water of 105°. This value is greater than the literature value, 93°, for the contact angle of water on pure poly(1-phenylethylene).[7] Combinations of lignin and poly(1-phenylethylene) had higher contact angles than either the pure lignin or pure poly(1-phenylethylene). Furthermore, the contact angle increased as the percentage of lignin increased. Blending lignin with poly(1-phenylethylene) should reduce the contact angle from a maximum of 105° toward 87°. Obviously, some interaction is occurring between the lignin and poly(1-phenylethylene).

Binding between Wood and Plastic. The reason the macromolecular surface active agent is applied to the wood is to allow a hydrophobic phase, such as a plastic, to bind to the wood. The increase in binding between the polymer phase and the lignin-containing materials is proven by the data which follow. This increase in binding between the phases produces stronger materials with greater tensile strengths. Coating birch wood (*B. papyrifera*) with lignin−1-ethenylbenzene graft copolymerization product increases the binding strength of poly(1-phenylethylene) plastic on the wood. Lap shear strengths increased 56%, from 1826 to 2840 kPa, when the wood was coated with a graft copolymer additive containing 51.7% lignin. Binding was tested by coating the birch with a solution of graft copolymer, drying the wood, injection molding poly(1-phenylethylene) onto the surface of the wood, and pulling the poly(1-phenylethylene) off the wood surface in a lap shear brace. The copolymers were selected so as to contrast graft copolymers of lignin and poly(1-phenylethylene) with lignin, poly(1-phenylethylene), or their mechanical mixtures. The pattern of comparison samples is

graft copolymer	contrast sample
product A (reaction product)	mixtures of lignin and poly(1-phenylethylene)
fraction B (benzene unextractable fraction)	kraft pine lignin
fraction BeEx (benzene extractable fraction)	poly(1-phenylethylene)

Coated sheets were stored in a desiccator at room temperature and 50 ± 5% relative humidity until the preparation of adhesion test samples with a lab-scale injection molding machine. Most of the copolymer-coated samples had smooth, adherent surface coats on them, but wood coated with poly(1-phenylethylene) or its lignin mixtures had a wood surface crossed with nonwetting threads or particles of polymer. Solutions prepared to test the copolymers as surface active coupling agents are listed in Table 5. The average adhesion area was 12.04 mm × 27.50 mm. The 56% increase in adhesion strength is shown by the lap shear results on the birch−plastic pieces given in Table 6.

In general, the lignin−1-ethenylbenzene graft copolymer (product A) and its two fractions (fraction B and fraction BeEx) provide stronger adhesion between wood and commercial poly(1-phenylethylene) than a mechanical mixture of lignin and poly(1-phenylethylene), pure poly(1-phenylethylene), pure lignin, or a blank. The graft copolymer is a coupling agent for the composite materials made from wood and poly(1-phenylethylene), increasing the binding strength of the two phases by, at minimum, 5% if the reaction product or its benzene-insoluble portion is used and increasing the binding strength of the two phases by, at minimum, 15% if the reaction product's benzene-soluble fraction (fraction BeEx) is used. However, when the change in adhesive strength between the two phases is plotted as a function of the weight percent lignin content of the coupling agent, there is always a minimum in the graph. This reproducible minimum implies that the lignin content of the copolymer exerts a pronounced effect on the binding between the two phases.

The most effective material for increasing adhesive strength was the reaction product containing 51.7% lignin and its fractions. As the results for untreated wood injection molded with poly(1-phenylethylene) show, this plastic has some capacity to bind to wood. This adhesion is caused by physical entrapment of portions of the injected poly(1-phenylethylene) in the pores of the wood. These coupling agents may work by increasing this entrapment.

Among the three fractions of the graft copolymer, the trend of effectiveness as a coupling agent is product A is better than fraction B and fraction B is better than fraction BeEx. The capacity of the copolymer to increase adhesive strength is apparent from the capacity of the copolymer itself to adhere to wood. Poly(1-phenylethylene) coatings on birch do not wet, and they bead into microscopic threads and particles on the surface. For the coatings prepared from mixtures, copolymer, or its fractions, the more the coating shows beading and flake formation, the less the adhesive strength.

These copolymers are surface active coupling agents which can bind wood to hydrophobic phases such as plastic. This coupling process should work best when the agent has been synthesized so that the side chain attached to the lignin has repeat units that are chemically identical to the plastic hydrophobic phase that is to be bound or connected to the wood. Thus, to bind poly(1-phenylethylene) to wood, coat the wood with poly(lignin-*g*-(1-phenylethylene)) and, to bind polyacryloni-

Table 5. Preparation of Coating Solutions[a]

A. Copolymers

sample no.	copolymer no.	wt % lignin in copolymer	wt, g		soln coating (wt %)	flakes[b]
			DMF + copolymer	concn copolymer		
5−1	1−52A	10.45	0.75	7.52	9.7	++
5−2	1−52B		1.00	10.00	10.0	no
5−3	1−52BeEx		1.00	10.02	10.0	no
5−5	1−50B		0.92	9.76	9.4	no
5−6	1−50BeEx		1.01	10.04	10.0	+
5−7	1−49A	32.17	1.00	10.03	10.0	no
5−8	1−49B		2.00	20.24	10.0	no
5−9	1−49BeEx		1.01	10.08	10.0	+
5−10	1−51A	50.41	1.00	10.00	10.0	no
5−11	1−51B		2.11	21.16	10.0	no
5−12	1−51BeEx		1.00	10.01	10.0	no

B. Mechanical Mixtures

sample no.	mixture	wt % lignin in mixture	wt, g			soln concn (wt %)	coating flakes[b]
			lig	PPE	DMF		
5−13	100% PPE	0	0	1.00	9.01	10.0	++
5−14	10% lig + 90% PPE	10	0.10	0.90	9.50	9.5	++
5−15	24% lig + 76% PPE	24	0.24	0.76	9.00	10.0	+
5−16	32% lig + 68% PPE	32	0.32	0.68	9.02	10.0	+
5−17	50% lig + 50% PPE	50	0.50	0.50	9.04	10.0	++
5−18	100% lignin	100	2.12	0	21.20	10.0	no

C. Blanks

5−19	blank (treated with DMF)
5−20	blank (treated with nothing)

[a] Five coated samples of birch were made with each solution. [b] +: Flakes seen in coating. ++: Significant flaking seen in coating.

Table 6. Adhesion Strength Determination Results[a]

sample no.	coating material	adhesion strength (kPa)	
		value	std dev
5−1	1−52A (10.45% lignin)	2464	223
5−2	1−52B	2354	497
5−3	1−52BeEx	2163	45
5−14	10% lig + 90% PPE	2247	255
5−4	1−50A (14.23% lignin)	2354	83
5−5	1−50B	2318	299
5−6	1−50BeEx	2130	217
5−15	24% lig + 76% PPE	2062	189
5−7	1−49A (32.17% lignin)	1964	309
5−8	1−49B	1944	188
5−9	1−49BeEx	2716	211
5−16	32% lig + 68% PPE	1983	270
5−10	1−51A (51.70% lignin)	2888	61
5−11	1−51B	2770	335
5−12	1−51BeEx	2754	72
5−17	50% lig + 50% PPE	1875	93
5−13	poly(1−phenylethylene)	2076	210
5−18	lignin	2160	167
5−19	blank (treated with DMF)	2057	123
5−20	blank (treated with nothing)	1857	168

[a] All breakdage occurred at the interface of poly(1-phenylethylene) and wood.

trile to wood, coat the wood with poly(lignin-*g*-acrylonitrile). However, the repeat units in the side chain of the coupling agent and the plastic do not always have to be identical. A side chain which will form a polymer alloy with the plastic phase will also act as a coupling agent between wood and that plastic.

Biodegradation. Copolymerization of lignin and 1-ethenylbenzene monomer increases susceptibility of the resulting lignin−poly(1-phenylethylene) [LPPE] product, and particularly its poly(1-phenylethylene) moiety, to fungal degradation. Procedures for the degradation tests are given in the Experimental Section.

SEM Visualization of Lignin/1-Ethenylbenzene Copolymerizates Overgrown with Fungi. Four or five days after inoculation of plates, fungal mycelia of all of the applied white rot fungi had grown over the tested powdered LPPE. The most intensive enmeshing of the LPPE was observed by the overgrown mycelial mat of *P. chrysosporium* and *T. versicolor*. Growth of *P. ostreatus* over the tested LPPE was less intensive than the other two white rot fungi. All of the applied white rot fungi and the brown rot *G. trabeum*, after 2 weeks of cultivation, completely overgrew the tested lignin powder. However, the brown rot *G. trabeum*, even after 3 weeks of cultivation, colonized only external zones of the compact mass of the LPPE powder. Growth of both white rot and brown rot fungi was sporadic in and near the applied poly(1-phenylethylene).

Mass Reduction of Lignin/Poly(1-phenylethylene) Constituents of the LPPE. All tested white rot fungi demonstrated an ability to decrease the weight of both constituents of LPPE, no matter what ratio of poly(1-phenylethylene) and lignin the plastic contained. These white rot *Basidiomycete* caused a range of weight loss of lignopoly(1-phenylethylene) copolymerizate that varied with the fungus with which the plastic was inoculated. The degrading activity of *P. chrysosporium* and *T. versicolor* toward tested LPPE exceeded the activity of *P. ostreatus*, as shown by Figure 7C,D,B. All tested LPPE have shown insignificant weight loss of its constituents after incubation with the brown rot fungus *G. trabeum*, as shown by Figure 7A. However, *G. trabeum* was able to deplete lignin applied as a natural polymer to an extent similar to that shown by white rot fungi. Degradation of poly(1-phenylethylene) incubated as a homopolymer was insignificant in all tested fungi. It appeared that the level of weight loss of poly(1-phenylethylene) component from the incubated LPPE was correlated with concentration of lignin in the copolymerizate. The higher the lignin content of the plastic incubated with the fungi, the higher the mass loss of the plastic when incubated for 68 days. *P. chrysosporium*, the most effective organism for degrading

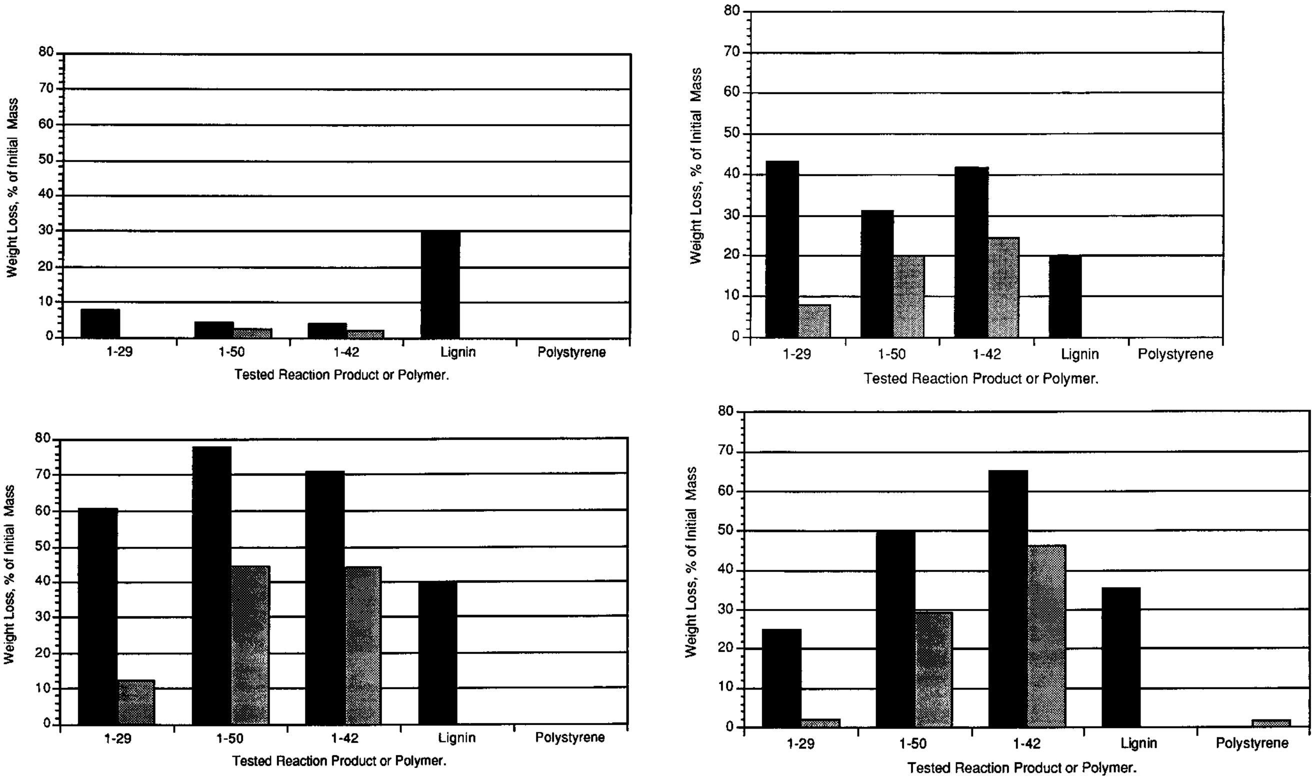


Figure 7. Mass loss of the constituents of lignin–poly(1-phenylethylene) graft copolymer induced by fungal metabolism during 68 days of cultivation on solid media. Products contained 10.3 (1–29), 32.2 (1–50), and 50.4 (1–42) wt % of lignin, respectively, and were incubated with *G. trabeum* (A), *P. ostreatus* (B), *P. chrysosporium* (C), and *T. versicolor* (D). Key: (solid bars) lignin; (shaded bars) polystyrene.

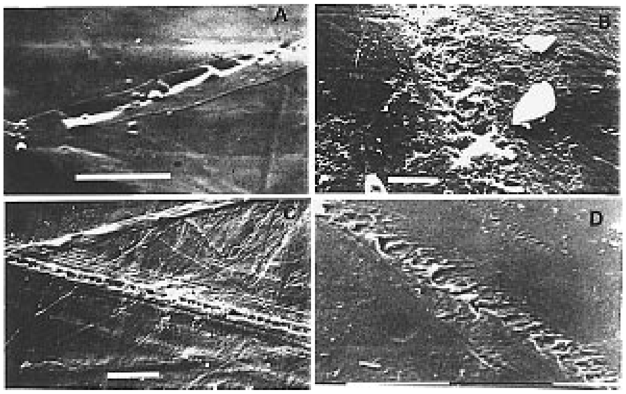


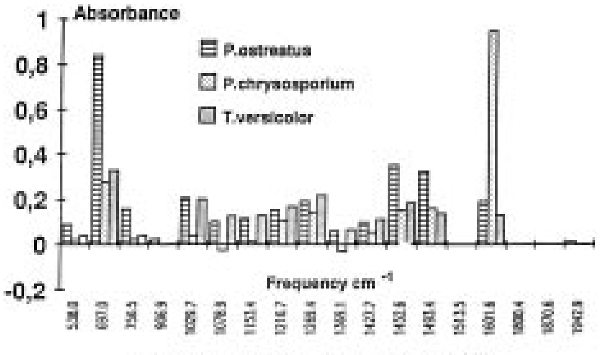
Figure 8. Scanning electron micrographs of pressed product incubated for 40 days, showing different forms of surface deterioration caused by overgrown white rot fungi: pitting (A); striating (B); pitting and decay (C). Bars, 10 μm. Micrograph 8D shows the surface of a plastic piece from a control flask that did not receive fungi.

the copolymer, degraded 16.9% of the 10 wt % lignin copolymer, 54% of the 32 wt % lignin copolymer, and 57% of the 50 wt % lignin copolymer during 68 days of incubation under areobic conditions.

Deterioration of the Plastic Surface. Additional evidence of bioconversion and degradation of the copolymers was obtained by SEM of fungi-corroded surfaces of the plastics. SEM data of the LPPE complex are shown in Figure 8. SEM data of the copolymer surface after hypeae from fungus mycelium have grown over it show obvious traces of surface corrosion. The most common types of corrosion were striating, pitting, and occasional decay. Extensive pitting and striating were observed on the surface of plastic exposed to the white rot fungi while very little deterioration of the surface of the plastic incubated with brown rot *G. trabeum* or maintained on control plates could be seen.

Qualitative Determination of Copolymer Loss by the Difference between before and after Infrared Absorbance Spectra. The infrared absorbance spectra of lignin, poly(1-phenylethylene), and a copolymerization product containing 50% lignin show a series of characteristic bands which can be assigned to specific structures in the compounds and used to monitor the loss of those structures.[8] The most obvious peaks in the spectra are the 1601, 1269, and 697 cm^{-1} peaks from the aromatic skeletal absorbance in lignin, the guaiacyl peak in lignin, and the ring hydrogens in 1-phenylethylene, respectively. The absorbance peaks of the biomass of the fungus also influence loss of functional group absorbance of infrared light. All of the mycelia show a strong, broad peak at 3450 cm^{-1} from hydrogen-bonded hydroxyl groups.

The loss of functional groups from the copolymer will show up in an infrared analysis if a spectrum of copolymer from a control flask has the mycelium-adjusted spectra of an incubated sample of the same copolymer subtracted from it. Positive values of absorbance in the resulting difference spectra will indicate a loss of functional groups from the plastic during incubation. Tests on copolymer exposed to brown rot fungus showed virtually no change in the spectra of the solid because of incubation. The data at the characteristic peaks for lignin and poly(1-phenylethylene) show significant loss of functional groups from both parts of the copolymer reaction product. Three difference spectra for copolymer 1–42 showing missing infrared absorbance after subtracting the initial copolymer spectrum from the spectra taken after the copolymer was incubated with one of three fungi are shown as Figure 9. For lignin, there is loss in the aromatic skeletal absorbance at 1601 cm^{-1} which increases from 0.05 to 0.95 absorbance units as the lignin content of the copolymer increases from 10% to 50% and the fungus attacking



Positive difference in absorbance means a loss of the infrared absorbing group during incubation.

Figure 9. Infrared absorbance missing from a 50.4 wt % lignin copolymer (1−42) after it was incubated with one of three white rot fungi and the original copolymer spectrum was subtracted from the incubated samples' spectrum.

the sample changes from *T. versicolor* to *P. chrysosporium*. There is no loss in the guaiacyl peak at 1269 cm^{-1} in the 10% lignin plastic sample, but the 32% and 50% lignin plastics show 0.1 and 0.2 absorbance unit losses, respectively. All of these data imply that lignin has been lost from the incubated copolymers. For poly(1-phenylethylene), the absorbance due to monosubstituted, aromatic ring stretch at 1493, 1452, and 756 cm^{-1} has decreased upon incubation in 11 out of 12 cases with the loss reaching 0.35 absorbance units for 50% lignin copolymer incubated with *P. ostreatus*. For the aromatic ring, C−H out of plane, bending motion at 697 cm^{-1}, the absorbance loss also appears in 11 out of 12 samples, reaching 0.83 absorbance units for 50% lignin copolymer incubated with *P. ostreatus*. Eleven out of twelve of the infrared spectra for poly(lignin-*g*-1-phenylethylene) support the biodegradation of both components to the copolymer by fungi when incubated on a solid support for 68 days.

Conclusions

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 mole ratio of chloride ion to hydrogen peroxide but with decreasing amounts of both chloride ion and hydrogen peroxide support the role of chloride ion as the active site initiator and hydroperoxide as the redox energy source. 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. Grafting increases the limiting viscosity number and hydrodynamic radius of lignin and is roughly proportional to the percent 1-ethenylbenzene in the polymerizable material of the reaction mixture. When the mole ratio of chloride ion to hydrogen peroxide in the reaction mixture decreases, the hydrodynamic radius of the product, and apparently its molecular weight, increase.

The graft products possess macromolecular surface activity, as indicated by their capacity to form stable emulsions between incompatible fluid phases, to bond adhesively to wood surfaces, and to change the contact angle of water on coated wood. The surface activity of the copolymer changes with composition. As the weight percent lignin in the copolymers increases, the amount of the emulsion phase formed in the water−benzene mixture decreases. Coating birch wood (*B. papyrifera*) with 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 lignin−1-ethenylbenzene graft copolymerization product also increases the binding strength of poly(1-phenylethylene) plastic coatings on the wood. Lap shear strengths increase 56%, from 1826 to 2840 kPa, when the wood was coated with a graft copolymer containing 51.7% lignin.

Bioconversion and degradation of lignin−1-ethenylbenzene graft copolymer was verified by weight loss, ultraviolet spectroscopy, infrared spectroscopy, and scanning electron microscopy. The most efficient degradation of lignin and poly(1-phenylethylene) constituents of the copolymer by white rot fungi was observed with the plastics with the highest lignin content, indicating that the level of weight loss of poly(1-phenylethylene) component from the incubated LPPE was correlated with the concentration of lignin in the copolymerizate. Infrared difference spectra quantifying the absorbance change from before to after incubation with white rot fungi show the copolymers have undergone significant losses of functional groups, with the highest lignin-content plastics showing the greatest functional group loss.

Poly(1-phenylethylene) is frequently used as a packaging material, and the use of this plastic will probably increase because of growing concerns about poly(vinyl chloride) in waste disposal streams. Currently, our society produces many commercial products of fully synthetic, recalcitrant materials. Copolymerization of synthetic side chains onto naturally occurring backbones should be considered as a way of producing compounds that are more easily degraded in the environment. In particular, grafting of lignin with synthetic side chains such as poly(1-phenylethylene) will form a much more biodegradable material than synthesis of a polymer from pure, petroleum-derived hydrocarbons.

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