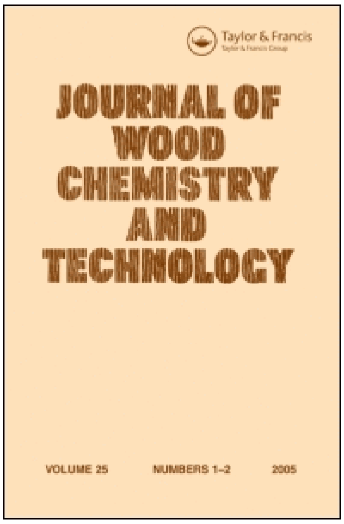

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ALTERATION OF THE SURFACE ENERGY OF WOOD USING LIGNIN-(1-PHENYLETHENE) GRAFT COPOLYMERS

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ABSTRACT

Graft copolymers of lignin, made by free radical graft copolymerization of 1-phenylethene on lignin, increased the contact angle of water on birch wood (*Betula papyrifera*) and decreased the critical surface tension of the wood when coated onto the wood surface from an N,N-dimethylformamide solution. The coating of copolymer changed the wood from hydrophilic (~50°) to hydrophobic (110°).

The most pronounced change in contact angle was produced by benzene-soluble extracts of the reaction product. These extracts contained lignin with long poly(1-phenylethylene) sidechains and pure poly(1-phenylethylene). They produced surfaces with the numerically highest contact angles with water and changed the wetting behavior of the surface more than physical mixtures of lignin and poly(1-phenylethylene) or either of the pure polymers.

Despite coating weights of less than 100 mg/cm, the critical surface tension of the birch wood coated with the various lignin-(1-phenylethylene) graft copolymers ranged from 26.9 to 44.9 dynes/cm while the uncoated birch had a critical surface tension of 49.6 dynes/cm.

INTRODUCTION

Lignin [8068-00-6], which comprises about 25 weight percent of dry wood, acts as a cementing agent to bind the matrix of cellulose fibers together into a rigid woody structure. A chemical modification scheme using 1-phenylethene ([100-42-5], styrene) has been developed to convert various lignin preparations into macromolecular surface active agents. The products of these reactions are poly(lignin-g-(1-phenylethylene))-containing polymers (lignin-styrene graft copolymers) and are shown to have 90 weight percent lignin grafting efficiency by solubility and extraction tests. These copolymers can be processed in a manner similar to polystyrene. Surface activity of the graft copolymers was indicated by their capacity to form emulsions between incompatible fluid phases and to adhesively bond to wood surfaces. When wood is embedded in a plastic phase, the interface between the two phases is a high energy boundary produced when the hydrophilic wood meets the hydrophobic plastic. This attempt to meld the two very different phases causes the bonding across the boundary to be weak. A coupling agent that can mesh these two phases together can strengthen wood-plastic composites by making the interface at the wood-plastic boundary stronger. Dynamic contact angle measurements using the Wilhelmy plate technique were used as an indicator of how well the graft copolymer acts as a coupling agent between wood and plastic.

The contact angle is a phenomenon resulting from forces present at equilibrium in the solid-liquid-vapor interface. This interface is quantified by Young's equation:

$$\text{cosine}\ \theta = \frac{\gamma_{sv} - \gamma_{s\ell}}{\gamma_{\ell v}}$$

where: θ = contact angle,

γ_{SV} = surface tension of solid-vapor,

$\gamma_{s\ell}$ = surface tension of solid-liquid, and

$\gamma_{\ell v}$ = surface tension of liquid-vapor.

No methods exist for directly measuring the surface tensions of the solid-vapor or the solid-liquid. A quantity that is measurable is the reversible work of adhesion. The work of adhesion is the work done as a clean, dry solid is immersed in a liquid. It is the work done as the solid-liquid surface is created and the solid-vapor surface is destroyed. It is quantified by the Dupre equation:

$$W_A = \gamma_{sv} + \gamma_{s\ell} - \gamma_{\ell v}$$

where: W_A = reversible work of adhesion. Dynamic contact angle (DCA) measurement is based on the Wilhelmy Plate technique for measuring the surface tension of liquids. A thin plate is brought into contact with and immersed in a liquid. The force increase caused by the weight of liquid in the meniscus formed is related to the liquid surface tension and the contact angle. The Wilhelmy equation is:

$$W_A = P\,\gamma_{\ell v}\cos\theta - V\rho g$$

where: **P** = sample perimeter at interface, **V** = volume of liquid in meniscus, ρ = density of liquid, and g = force due to gravity. By using a liquid of known surface tension the contact angle can be measured. The volume, density, gravity portion of the equation is the buoyancy force. By plotting a graph of the force versus the depth of immersion the slope of the buoyancy can be calculated. If the slope is extrapolated to a zero immersion depth, the force change at zero immersion can be calculated. This eliminates the buoyancy portion of the equation as well as the depth of immersion. This leaves:

$$F = P\,\gamma_{\ell v}\cos\theta$$

where: **F** = force at zero immersion depth. Dynamic contact angle analysis has been successfully applied to textile fibers[1], wood fibers[2], and solid wood[3,4].

Dynamic contact angle analysis compensates for the chemical and physical complexity of wood that make static contact angle measurement techniques inaccurate[3]. The two measurements obtained during DCA analysis are the advancing angle and the receding angle. The advancing angle is measured as the clean, dry solid is immersed in the test liquid. The receding angle occurs as the wetted solid is removed from the liquid. Wood has different advancing and receding angles. This is termed contact angle hysteresis and it is caused by chemical heterogeneity on the solid surface, surface roughness, or liquid-solid interaction. The chemical composition of the wood surface depends upon the processing and conditioning of the sample[5] but the effect of the chemical composition on the contact angle of the wood surface is not clear. The surface of wood is also rough. The degree of roughness depends upon the grain orientation and processing of the sample. Experimentally, roughness has been shown to have only a small effect on the contact angles on wood[6]. Wood also interacts with most test liquids. It is a hydroscopic material that absorbs liquids through its gross structure (capillary flow) and through chemical absorption.

Graft copolymers are molecules in which a synthetic sidechain has been grown off of an existing polymeric backbone. In this study, a 1-phenylethylene ([9003-53-6], polystyrene) chain has been grown off of lignin. Since the graft copolymers have two parts of differing structure and composition, they are surface active materials.

EXPERIMENTAL

The preparation of lignin graft copolymers was accomplished, in general, under oxygen-free conditions by combining a redox initiator; a halide salt; one or more monomers polymerizable by free radical reaction; and, possibly, a suitable solvent; with lignin or a lignin-containing material to create a dispersion and allowing time for graft polymerization to occur. This reaction can be successfully run with concentrations or mole ratios of the reactants in the following ranges; 1. polymerizable solids content of the reaction: 23 weight percent or less, 2. hydroperoxide to calcium chloride: 0.25 to 32, 3. hydroperoxide to lignin (M_n): 21 to 113, and 4. weight fraction of monomer in polymerizable solids: 0.01 to 0.95.

Prepare solution A by placing pure 1-phenylethene in a conical flask and bubble it with nitrogen (N_2) for 10 minutes. Prepare solution B by placing lignin, calcium chloride, and dimethylsulfoxide solvent in a conical flask, stir until dissolved, and bubble the solution with N_2 for 10 minutes. Solution A and B are stirred while being purged with nitrogen. Add H_2O_2 to solution B, and bubble it with N_2 for 20 minutes. Add solution A to solution B. After 5 minutes of stirring and bubbling N_2 through the reaction mixture, the flask is stoppered, placed in a 30°C bath, and stirred for 48 hours. The preferred stirring rate in the conical flask used in laboratory synthesis is 2 to 5 Hertz. This produced a shear rate of approximately 10 to 200 per second in the reaction mixture and this is the preferred shear rate for high yield synthesis. All reactions are terminated by opening the reaction vessel. This terminated slurry can then be added to 10 times its volume of acidified water (pH = 2) and the polymer recovered by filtration. Examples of synthesis are given in reference 7.

Proof of formation of graft copolymer was completed by mass balance of fractionated reaction product, solubility tests, wetting tests, phase partitioning tests, and FTIR analysis.

The fractionation of the graft copolymer is diagramed in Figure 1. The reaction product, A , is extracted with benzene for 48 hours. The benzene-soluble material is recovered by evaporating the benzene and the solid is labeled fraction BeEx (grafted lignin with long polymer sidechain and homopolymer). The solid not dissolved in benzene is labeled fraction B (grafted lignin with medium and short polymer

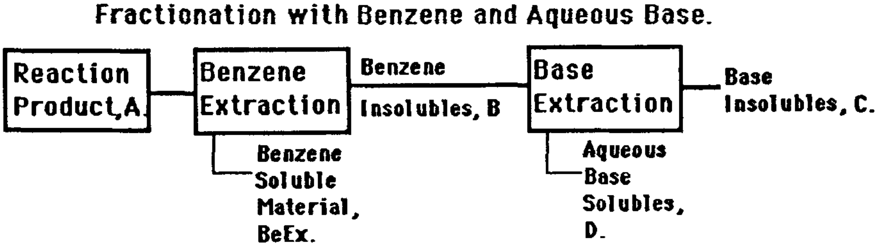


Figure 1. Flow Diagram of Copolymer Fractionation Process

sidechains) and is slurried with 0.5 M sodium hydroxide for at least 16 hours. This solution is filtered and the filtrate is dialyzed against water for 3 to 5 days using dialysis tubing. The solid filtered from the base is washed with 2M hydrochloric acid, washed with distilled water, dried, and labeled fraction C (grafted lignin with medium polymer sidechain). The dilute, dialyzed solution is then dried or freeze dried to recover base-soluble fraction D (grafted lignin with short polymer sidechain).

The products were 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 weight percent 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 hours in a hood and 2 hours 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 weight percent 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 polyvinyl acetate resin.

Dynamic contact angle measurements were performed by bringing a thin, treated or untreated slab of birch into contact with water

Table 1. Composition and Yield of Copolymerization Reactions

	Composition (g)					
Sample Number	Lignin	1-Phenyl ethene	$CaCl_2$	H_2O_2 (mL)	Solvent	Yield (g) / (wt. %)
1-1	8.00	28.1	6.00	8.0	40.14	33.02/91.47
1-2	8.02	18.76	6.02	8.0	40.00	24.93/93.09
1-3	2.00	18.76	2.07	3.0	19.99	20.37/98.12
1-4	2.01	18.77	2.02	4.0	20.02	19.10/91.92

by immersing it, parallel to the grain, at a rate of 194 microns per second. 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 references 8 and 9.

RESULTS AND DISCUSSION

Synthesis data for the graft copolymers used as coupling agents are given in Table 1. Samples 1-1 and 1-2 contained 22 and 30 weight percent lignin in the reaction mixture, respectively. All four samples were fractionated by the benzene/base extraction process to form fractions B, C, D, and BeEx.

Data from typical fractionations are given in Table 2 and these results imply that the amount of ungrafted lignin is virtually zero. Further, analysis by infrared spectroscopy shows that all four fractions of a copolymer sample contain poly(1-phenylethylene) while fractions from a lignin-(poly(1-phenylethylene) mixture are pure.

Table 2: Mass Distribution of Fractions for Reaction Product*

Sample Number	Yield (g/wt.%)	Weight Percent of Total Product in Fraction A	BeEx	C	D
2-A	17.26/83.06	100	86.3	5.46	-
2-B	18.16/87.48	100	91.7	1.8	4.8
2-C	18.65/89.75	100	91.4	2.2	4.9
2-D	18.92/91.09	100	90.1	3.6	5.1
2-E	16.87/81.74	100	88.9	4.9	4.7

* Lignin content in the reactions (lignin/(lignin+1-phenylethene)) is 9.63 wt. %.
A = The complete reaction product.
BeEx = Fraction of product soluble in benzene.
C = Fraction of benzene extraction residue insoluble in base.
D = Base soluble fraction.

Spectra were obtained by Fourier transform, infrared spectroscopy from reaction product fractions, pure poly(1-phenylethylene), and treated lignin. Data from the infrared spectra of the materials are presented in Figure 2. Lignin was treated in a blank reaction containing no 1-phenylethene, mixed with poly(1-phenylethylene), extracted with benzene, and tested for infrared absorbance. The lignin shows a characteristic absorbance peak at 7.88 micrometers wavelength. Poly(1-phenylethylene) shows a strong absorbance peak at 14.35 micrometers wavelength. The absorbance peaks are distinct and allow the materials to be distinguished. Spectra on all the fractions of reaction product 1-3 show both peaks, as shown by the spectra for the fractions plotted in Figure 2. The spectrum for fraction D is that of reaction 1-4 since fraction 1-3D was too small to analyze. Measurements on other samples of Table 2 show the same distribution of both components of the copolymer in all product fractions. The infrared spectroscopy results show that the two components of the reaction product, lignin and poly(1-phenylethylene), are distributed throughout the product's fractions and must be chemically bound. This would only be possible for a graft copolymer since mechanical and solution mixtures are readily separated by the extraction process. Peak height ratios from the infrared spectra support the long,

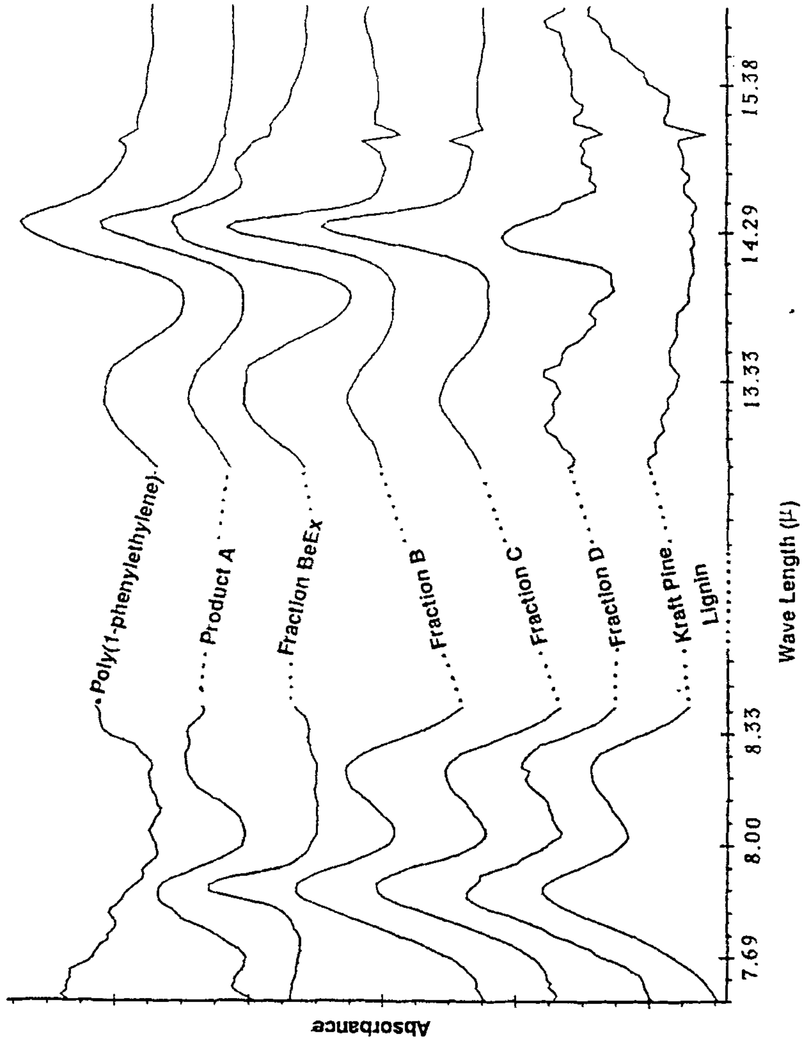


Figure 2. FTIR Spectra of Reaction Product, Its Fractions, Pure Poly(1-phenylethylene) and Lignin

medium, and short extents of grafting stated in the EXPERIMENTAL Section. In addition to the infrared data, the following chemical and physical properties of the reaction product also support the hypothesis of copolymer formation:

1. The lignin component in fraction BeEx has been changed from benzene-insoluble to benzene-soluble, and at the same time, from base-soluble to base-insoluble.

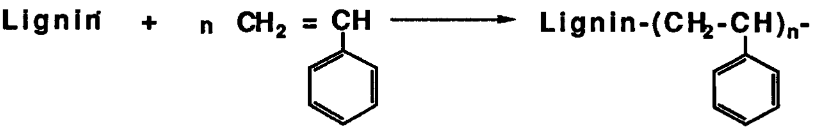
2. A large amount of stable emulsion is always formed when a benzene solution of fraction BeEx is fully mixed with aqueous base or water.

3. The lignin component in fraction B has been changed from water-wettable to water-nonwettable.

4. Fraction C can not be dissolved in benzene or aqueous base.

Of course, a mechanical mixture of lignin and poly(1-phenylethylene) does not have the above properties. 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 poly(1-phenylethylene) chain(s) on lignin, as mentioned in the EXPERIMENTAL Section.

These data show that the reaction being run is the grafting reaction given in the following equation:



Solutions of the reaction products or the fractions obtained from them were applied to birch strips as described in the EXPERIMENTAL Section. Pure solutions of the two components contained in the grafted product; lignin and poly(1-phenylethylene); and physical mixtures of these two components, were prepared and applied to birch strips. Data on the preparation of the coated wood samples are given in Tables 3 and

Table 3. Coating Results for Birch Strips

Sample Number	Graft Copolymer Number	DMF Solution Concentration (%)	Weight of Coating (g)
3-1	1-1A	5	0.137
3-2	1-1B	10	0.167
3-3	1-1BeEx.	5	0.083*
3-4	1-2A	10	0.13
3-5	1-2B	10	0.11
3-6	1-2BeEx.	5	0.10
3-7	Lignin	10	0.13
3-8	PPE	5	0.07*
3-9	78%PPE+22%lignin	5	0.093*
3-10	78%PPE+30%Lignin	5	0.087*

* There are white poly(1-phenylethylene) flakes on the surface of these wood strips. All copolymer-coated samples had smooth, adherent surface coats on them. PPE = pure, poly(1-phenylethylene) homopolymer.

Table 4. Contact Angle Results For Birch Strips

Sample Number	Copolymer Number	Advancing Contact Angle (°)
3-1	1-1A	107.8
3-2	1-1B	99.1
3-3	1-1BeEx.	114.0
3-4	1-2A	110.0
3-5	1-2B	99.1
3-6	1-2BeEx.	119.5
3-7	Lignin	87.2
3-8	PPE	105.4
3-9	78%PPE+22%lignin	107.8
3-10	70%PPE+30%Lignin	110.4
3-1 1	Uncoated Blank (3)#	50.8

= Done in triplicate. Sanded.

Table 5. Dynamic Contact Angle and Critical Surface Tension Results For Birch Strips

Sample Number	Copolymer Number	Weight of Coating (g)	Advancing Contact Angle (°)	Critical Surface Tension, γ_c dynes/cm
3-1	1-1A	0.170	92.8	44.8
3-2	1-1B	0.160	100.7	38.6
3-3	1-1BeEx.	0.137	107.4	30.8
3-4	1-2A	0.150	100.4	44.9
3-5	1-2B	-	95.2	38.7
3-6	1-2BeEx.	0.127	115.1	26.9
3-7	Lignin	0.120	84.5	45.6
3-8*	PPE	0.127	92.0	40.8
3-9*	78%PS+22%lignin	0.113	94.5	46.5
3-10*	70%PS+30%Lignin	0.117	98.4	43.0
3-12	Uncoated Birch@	0.0	96.2	49.6

* There are white poly(1-phenylethylene) flakes on the surface of these wood strips.
All copolymer-coated samples had smooth, adherent surface coats on them.
@ = Unsanded.

5. Data from the dynamic contact angle study and critical surface tension study are given in Tables 4 and 5. Blanks for the contact angle study of Table 3 were freshly sanded before testing. Blanks for the study of critical surface tension were aged wood with no surface treatment. Wood samples treated with only N,N-dimethylformamide showed no change in surface properties when compared to original birch. Contact angle measurements on samples after 72 hours of exposure to laboratory conditions or repetition of the contact angle measurements on the same samples after 6 hours show no change in contact angle other than would be expected for increase in the water content of the wood.

The white flakes of poly(1-phenylethylene) on the surface of birch strips coated with lignin/poly(1-phenylethylene) mixtures show that the pure polymer can 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°). Thus, these copolymers are surface-active, coupling agents which can alter the contact angle of the surface of wood.

Critical surface tension is the number obtained by extrapolating to zero contact angle, a plot of contact angle with a specific solid versus fluid surface tension for a series of fluids. It is a property of the surface which can be crudely correlated with surface chemical composition. The critical surface tension of lignin-coated birch wood was 45.6 dynes/cm, as shown by the data of Table 5. This was somewhat higher than the literature values for lignin critical surface tension of 36 to 37 dynes/cm found by Lee and Luner[10]. The critical surface tension for the neat birch wood was 49.6 dynes/cm. Despite low coating weight, the critical surface tension of the birch wood coated with the various lignin-(1-phenylethylene) graft copolymers ranged from 26.9 to 44.9 dynes/cm. This result is in agreement with the work of Zisman[11] who showed that even a single monolayer of molecules on a solid surface can alter its wetting properties. The surface tension obtained by lowering the birch wood critical surface tension with poly(lignin-g-(1-phenylethylene)) copolymers is consistent with literature values for the critical surface tension of unswollen poly(1-phenylethylene), 40 to 44 dynes/cm[12]. Pure poly(1-phenylethylene) coated birch wood had a critical surface tension of 40.8 dynes/cm. The critical surface tensions found for the copolymer coating are also consistent with values for polymeric alkylaromatic surfaces, 33 dynes/cm, and aliphatic monolayers, 24 dynes/cm[13].

Samples 3-3 and 3-6 were the benzene soluble (BeEx fraction, nonpolar) components of the poly(lignin-g-(1-phenylethylene)) copolymer and exhibited the lowest critical surface tensions, 30.8 and 26.9 dynes/cm . Wood coated with benzene insoluble fraction B, samples 3-2 and 3-5, had critical surface tensions of 38.6 and 38.7 dynes/cm, respectively. The water insoluble material, samples 3-1 and 3-4, had critical surface tensions of 44.8 and 44.9 dynes/cm. Physical mixtures of poly(1-phenylethylene)) and lignin, samples 3-9 and 3-10, had critical surface tensions of 46.5 and 43.0 dynes/cm. In most instances, the lower critical surface tension values exhibited correspondingly larger water advancing contact angles, indicating a hydrophobic surface.

The most interesting aspect of the critical surface tension data for the poly(lignin-g-(1-phenylethylene)) copolymers is that the combination of the two polymer materials produces copolymers with critical surface tensions that are lower than either of the individual components alone. This result should be investigated further since it suggests that the poly(lignin-g-(1-phenylethylene)) copolymer coatings tend to orient the hydrophobic portion of their structure towards the air. Other polymer materials have been shown to exhibit particular surface orientations in air[14].

CONCLUSIONS

Graft copolymers of lignin, made by free radical graft copolymerization of 1-phenylethene on lignin, increased the contact angle of water on birch wood (*Betula papyrifera*) and decreased the critical surface tension of the wood when coated onto the wood surface. All copolymer-coated wood strips had smooth, adherent surface coats on them while physical mixtures of lignin and poly(1-phenylethylene) produced surfaces covered with threads or particles that partially lifted off of the wood. This shows that the pure polymer can not wet the wood and will not form an adherent interface with it. The most pronounced change in contact angle was produced by benzene-soluble extracts of the reaction product. These extracts contained lignin with long poly(1-phenylethylene) sidechains and pure poly(1-phenylethylene).

Despite coating weights of less than 100 mg/cm, the critical surface tension of the birch wood coated with the various lignin-(1-phenylethylene) graft copolymers ranged from 26.9 to 44.9 dynes/cm while the uncoated birch had a critical surface tension of 49.6 dynes/cm. The critical surface tensions found for the copolymer coating are consistent with values for polymeric alkylaromatic surfaces, 33 dynes/cm, and aliphatic monolayers, 24 dynes/cm.

Acknowledgement

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