

Novel Applications of Lignin in Composite Materials

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ABSTRACT: Some exploratory work was done to look at novel applications, such as filler use and comonomers, for lignin in thermosetting unsaturated polyesters and vinyl esters. The solubility of different lignins (pine kraft, hardwood, ethoxylated, and maleinated) was determined in different resin systems (acrylated epoxidized soybean oil, hydroxylated soybean oil, soy oil monoglyceride, and a commercial vinyl ester) to give an idea of the compatibility of lignin with the resin systems that were used. Further, the use of lignin as a filler was studied. An increase in the glass-transition temperature was noticed, and the modulus at 20°C decreased because of the plasticizing effect of lignin. The lignin was modified to improve its effect on the matrix properties by adding double bond functionality, thus making it possible to incorporate the lignin molecule in the resin through free-radical polymerization. Modified lignin was introduced in several resins by a reaction with maleic anhydride and epoxidized soybean oil and was tested for its effect on the solubility, glass-transition temperature, and modulus. This modification improved the solubility of lignin in styrene-containing resins, as well as the chemical incorporation of lignin in the resin. Moreover, lignin was used to treat the surfaces of natural hemp fibers to utilize lignin's natural affinity for cellulosic fibers. The idea was to cure the surface defects on the natural fibers and increase the bonding strength between the resin and fiber. An optimum improvement was noticed that depended on the amount of lignin covering the fibers. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 323–331, 2002

Key words: modified kraft lignin; composites; natural fibers; soybean oil; affordable composites from renewable sources (natural oil-based resins)

INTRODUCTION

Lignin is one of the three most abundant renewable resources on our planet amid cellulose and natural oils. Most industrial lignin is obtained as a waste product during the paper pulping process, but it can be found in all plants like rice and straw. While cellulose is used for paper production and natural oils are mainly used in the food industry, the industrial applications of lignin are rather limited, despite its widespread availabil-

ity. In 1998 about 1% of all lignin generated in paper production worldwide was isolated and sold.¹ The remaining 99% was either burned in an energy recovery step for the pulping process or disposed of in waste streams. The global production of lignin products was reported by Lin and Zhong to amount to 138,500 tons/year in 1990.² Extrapolating these 1% numbers leads to a worldwide production of more than 10 million tons/year of available renewable raw material.

A large number of studies on lignin focused on finding a higher value application for lignin than fuel.^{1,3} An extensive review of lignin studies since its discovery in 1838 by Anselme Payen is given by McCarthy and Islam.¹ Applications of water-

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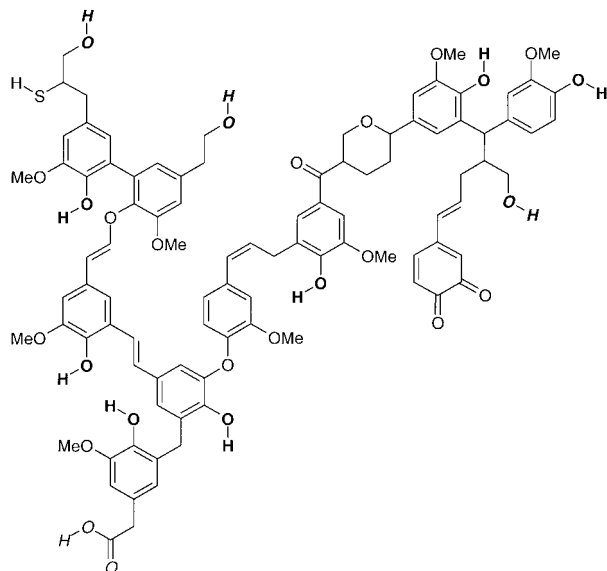


Figure 1 The proposed structure of pine kraft lignin.²⁶

insoluble kraft lignin in polymers include as fillers in thermoplastics⁴; coreactants for thermoplastics⁵; and coreactants in thermosetting phenolic,^{6,7} epoxy,⁸ and polyurethane resins.^{3,9} Lignin is a promising compound to be used in polymers because of its phenolic base structure (Fig. 1), which could lead to improvement of the mechanical properties when incorporated in a plastic. Studies concentrating on the use of lignin as a comonomer in unsaturated polyesters or vinyl esters (VEs) are very limited and deal with acrylics.¹⁰ This is largely due to the free-radical inhibiting capability of the quinonic structures in the kraft lignin molecule³ and the ability to form more of these quinonic structures by resonance stabilization from aromatic hydroxyl groups, as well as the unavailability of suitable double bonds reactive toward free-radical polymerization. Additionally, lignin is incompatible with styrene, which is commonly used as a reactive diluent in unsaturated polyester resins.

Kraft lignin has a glass-transition temperature of about 142°C,⁵ which can be increased by chain extension reactions.¹¹ Thus, the addition of lignin to existing resin systems has the potential to increase the glass-transition temperatures of both petroleum-based and natural oil-based (affordable composites from renewable sources or ACRES) unsaturated polyester resins.¹² Lignin also increases the electrical resistance in polyolefins, making them more attractive in electrical shielding applications.⁴ Lignin in wood serves to protect the cellulose fibers against biological attack, in addition to adhesion of the cellulose fi-

bers. However, lignin has been proved to be degradable by certain wood-rotting fungi¹³ such as White Rot fungi, thus making it possible to break down lignin-based materials in some environments. Using lignin in partially biodegradable ACRES resins could result in a more controlled biodegradable resin.

The ACRES resins used in this research are derived from soybean oil.¹² The unsaturated carbon-carbon bonds found in this oil are relatively nonreactive toward free-radical polymerization, and functionalization of these double bonds is therefore needed. Four chemical pathways relevant to this research are shown in Figure 2 and summarized in Table I. Reaction (1) epoxidizes the double bond to give epoxidized soybean oil (ESO),¹⁴ which then can react further [reaction (2)] with acrylic acid to give acrylated ESO (AESO).¹⁵ Following path (3) we obtain hydroxylated soybean oil (HSO). Soy oil monoglyceride (SOMG) is the reaction product using an alcoholysis reaction [reaction (4)].^{16,17} A complete description of reaction pathways and additional modification reactions of soybean oils is given by Khot et al.¹⁸ and Wool et al.¹²

The easiest way to introduce a new component in an existing resin is by adding the unmodified component to the system as a filler. The so-called filler may change certain properties (mechanical, electrical, etc.) of the matrix resin in a positive way. In thermoplastic polyolefins the addition of lignins showed no significant increase in the mechanical properties, and thermoset resins were therefore considered in this study.

The high styrene content in commercially available thermosets (ca. 50%), such as VEs and unsaturated polyesters, showed incompatibility with lignin. For this reason, only soybean oil based resins were used for this study, because of the ability to vary the styrene content.

The aliphatic and aromatic hydroxyl functional groups present in lignin structures (Fig. 1) also

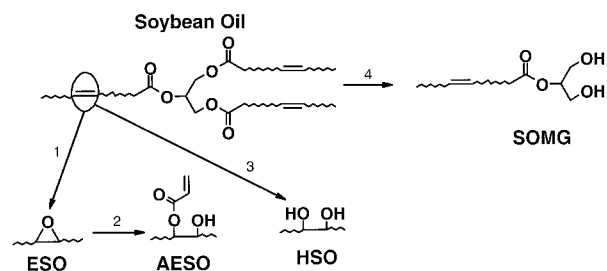


Figure 2 The relevant functionalizations of soybean oil.

Table I Relevant Functionalizations of Soybean Oil

Product Acronym	Product	Reaction No. ^a	Reaction
ESO	Epoxidized soybean oil	1	Epoxidation
AESO	Acrylated epoxidized soybean oil	2	Acrylation
HSO	Hydroxylated soybean oil	3	Hydroxylation
SOMG	Soy oil monoglyceride	4	Glycerolysis

^a From Figure 2.

provide a possibility for an esterification reaction with maleic anhydride (MA) to introduce reactive maleate half-ester groups to the molecule. The double bonds of the maleate half-esters are reactive for radical polymerization. Although homopolymerization of lignin maleates using the introduced double bond functionality seems impossible because of the limited reactivity of lignin with MA, the introduction of this product to other similar resin systems containing maleate functional groups may provide some improvements in the mechanical properties of the resulting polymers by connecting this large molecule to the resin through the maleates. In this study we explored the effect of the addition of the lignin maleates to the SOMG maleates (SOMG/MA). When copolymerized with styrene, the SOMG/MA produce rigid thermoset polymers.¹⁶ Lignin, which is a natural product and a large polyol molecule, has the potential to be used as a copolymer in the SOMG/MA resin system.

In order to make lignin more compatible with commercial VEs and unsaturated polyesters containing a high amount of styrene, the aliphatic and aromatic hydroxyl groups of lignin can also be reacted with a polyepoxy, such as ESO, as was done for the introduction of lignin in epoxy resins.⁸ The remaining unreacted epoxy groups can later be reacted with acrylic or maleic acid, for example, to provide the double bonds to anchor the lignin molecules in the resin.

The mechanical properties of polymer composites depend on the properties of the fiber, the properties of the matrix, and the interfacial strength, among other factors. A strong interface is required for efficient transfer of stress from the matrix to the reinforcing fibers. The fibers are therefore treated with sizing or bonding agents to improve the interfacial strength. This issue is especially important in natural fiber composites. Natural fibers, being cellulosic in nature, have surfaces that are highly hydrophilic. This results in poor bonding with polymeric matrices, which are organic in nature. A number of treatments to

impart bonding between natural fibers and polymeric matrices were used in the past with varying success.¹⁹ In the current study experiments were carried out to explore the application of lignin as a surface treatment agent for natural fibers. This concept is derived from nature because wood can be considered to be a natural composite in which cellulose fibers are glued together in a matrix of lignin. The hydrogen bonds provide the necessary strength and stiffness to wood. Lignin therefore has the potential to be used as a low cost surface treatment agent for composites of natural fibers with petroleum-based resins like VE, epoxy, and unsaturated polyester.

EXPERIMENTAL

Monomer Compatibility Tests

A lignin–resin compatibility matrix of four lignins in four resins was set up to understand the solubility of various lignins in different resins (see Table II).

Materials

The four resins that were used were 95+% pure AESO, (Ebecryl 860, UCB Chemicals), SOMG (prepared in our lab as described later in this article), HSO (prepared in our lab), and a VE (Derakane 411-C-50, Dow Chemical Company). The HSO was prepared by hydroxylation of soybean oil using formic acid and H₂O₂.²⁰ The four kraft lignins used in the study were pine kraft lignin, hardwood kraft lignin, ethoxylated lignin, and maleinated lignin, which were all supplied by Westvaco Corporation. The ethoxylation and maleination were performed at the Westvaco Charleston Technical Center (Charleston, SC). All kraft lignins were in powder form except for the maleinated lignin, which was a solid mass that was crushed into a fine powder before use. All chemicals were used without further purifica-

tion. Resin–lignin mixtures were made that contained a 5% weight fraction of lignin. They were mixed manually until complete dispersion of the lignin, after which they were placed on a table for several days and allowed to settle.

Lignin as Filler in AESO/Styrene Matrix

Materials

The AESO (95+% pure) was also Ebecryl 860. The kraft lignin used was the pine lignin Indulin AT (Westvaco), and the styrene was obtained as previously described. The initiator for free-radical polymerization was USP 245 from Witco Corporation. All products were used without purification.

Sample Preparation

Pure AESO was mixed with different amounts of styrene and lignin was added. Samples were made with different amounts of styrene and lignin in AESO and cured with 1% by weight initiator (USP 245) at 65°C for 1.5 h with a postcure at 120°C for 2.5 h. After curing the samples were checked for lignin–styrene separation, followed by the curing of new samples with a higher styrene content until separation was noticed. Samples were polished afterward to obtain flat parallel surfaces for dynamic mechanical analysis (DMA) testing.

Experiments

The glass-transition temperature (T_g) and the storage modulus (E') were obtained with a Rheometrics RSA II DMA apparatus. Testing was performed at a frequency of 1 Hz and a strain of 0.02% over a temperature range from –50 to 100°C at a heating rate of 5°C/min.

Use of Lignin for Reactions with MA and SOMG

The introduction of lignin to the SOMG maleates was done using two different experimental procedures. In the first approach the lignin was reacted with excess MA after which SOMG was maleinated in this mixture. In the second approach a mixture of SOMG and lignin were reacted with MA at the same time.

Materials

The soybean oil used in the preparation of SOMG was alkali refined and 100% pure (Cargill Company). The glycerol in the mixture was 99.5%

pure (Aldrich). The MA (99.5% purity, Aldrich) was in the form of briquettes and therefore powdered before use. The lignin was Indulin AT. Triphenyl antimony (99% purity, Aldrich) and 2-methylimidazole served as catalysts for maleinization. *Tert*-butyl peroxybenzoate (98% purity, Aldrich) and USP 245 were used as the radical initiators. The hydroquinone obtained from Aldrich Company was 99% pure. All the ingredients were used without further purification.

Preparation of SOMG by Glycerolysis of Soy Oil

Glycerol (250 g) was placed in a 1-L three-necked round-bottom flask equipped with a N_2 gas inlet and a temperature controller and connected to a downward condenser. The glycerol was then heated to 220°C under a N_2 atmosphere and kept at this temperature for 2 h during which time 2 mL of the water and glycerol mixture was distilled. Then 5 g of white soap and 500 g of soybean oil were added to the glycerol in four portions in 1-h intervals. The solution was heated for 5.5 h at 220–240°C with mechanical stirring and N_2 gas sparging. At the end of this time the solution was rapidly cooled with an ice and salt mixture. During the cooling of the solution some of the excess glycerol in the product was separated as a lower layer and found to weigh 102 g. The remaining SOMG mixture was a viscous oil.

Lignin–MA Reaction

In the first approach, 20 g of MA was heated to 100°C in a round-bottom flask equipped with a temperature controller. As the MA melted, 10 g of lignin with 0.15 g of triphenyl antimony as a catalyst were added. The viscous liquid reaction mixture was agitated for 4.5 h at 100°C and the reaction was followed with IR to measure the decrease in the MA characteristic peaks.^{16,21} The lignin–MA intermediate reaction product at room temperature was a dark brown solid with a very strong unpleasant odor.

Maleinization of SOMG in Lignin–MA Product

Nine grams of SOMG with 3 g of the previously prepared Lignin–MA product were heated to 100°C in a 25-mL round-bottom flask equipped with a temperature controller. Then 4.68 g of MA with 0.09 g of triphenyl antimony as a catalyst and a trace amount of hydroquinone were added to this mixture. (The weight ratio of SOMG:MA was 1.5:1 with regard to the excess MA in the lignin–MA product.) The reaction mixture was

Table II Ruling Effect for Dispersion of Lignin in Different Resins

	Pine Lignin	Hardwood Lignin	Sulfonated, Ethoxylated Lignin	Lignin-MA Adduct
AESO	Viscous dispersion	Viscous dispersion	Viscous dispersion	Viscous dispersion
HSO	Affinity dispersion	No dispersion	Affinity dispersion	No dispersion
SOMG	Affinity dispersion	Affinity dispersion	Affinity dispersion	No dispersion
VE	Partially soluble	Partially soluble	No dispersion	Partially soluble

agitated for 5 h at 100°C. The reaction product at room temperature was a dark brown viscous liquid. The SOMG-lignin-MA product weight ratio in this reaction was fixed so that the final product contains 10 wt % modified lignin.

Polymerization of SOMG/Lignin/MA with Styrene

Eight grams of SOMG/lignin/MA product were mixed with 2.8 g of styrene. A small amount (<0.5%) of an insoluble, dark brown gel precipitated down the vial with the addition of styrene. After the separation of this gel, the liquid resin was mixed with 2% of its own weight of *tert*-butyl peroxybenzoate as the radical initiator. The liquid resin was then transferred into a silicon mold after applying a vacuum to the mixture for 10 min. It was cured at 120°C for 3.5 h. The cured resin was a dark brown hard solid.

Lignin/SOMG-MA Reaction

The lignin/SOMG mixture consisted of 14 g of SOMG and 0.7 g of lignin, which meant that there was 5 wt % lignin in the mixture. After heating this sample to 85°C, 10 g of MA was added. One weight percent of 2-methylimidazole as a catalyst was added after complete mixing was attained. The reaction mixture was cooled to room temperature after 3 h and resulted in a dark brown viscous liquid.

Polymerization of SOMG/Lignin/MA with Styrene

Curing was performed as described in the first approach except the free-radical initiator USP 245 was used instead of *tert*-butyl peroxybenzoate. As styrene was introduced, it was noticed that a small amount of lignin clumped.

Experiment

The glass-transition temperature and the dynamic moduli (E' and E'') were obtained with a Rheometrics RSA II DMA apparatus. Testing was performed at a frequency of 1 Hz and a strain of

0.02% over a temperature range from -50 to 100°C while increasing the temperature at 5°C/min. Maleinization was followed on a Bruker AM250 250-MHz NMR spectrometer.

Modification of Lignin by Reaction with ESO

Materials

The ESO that was used was obtained from Witco Corporation. The three different types of lignin that were used (pine, hardwood, and ethoxylated) are the same as in Table II. The ethoxylation was performed at Westvaco with a target conversion of about 65% of the alcohol groups.²² The catalyst used for the alcohol-epoxy reaction was 99% pure 2-methylimidazole.

Reaction

The ESO and lignin were mixed in a 3.2:1 weight ratio so that 2 of the 4.4 epoxies per triglyceride could stoichiometrically react with lignin. The reaction was run for 5 h at 135°C with 2 wt % catalyst (2-methylimidazole) in a 100-mL glass beaker while constantly mixing with a magnetic stirrer. The mixture was then cooled to room temperature. The reaction product was dark brown, and the viscosity depended on the kind of lignin used in the reaction (highest for ethoxylated lignin, lowest for hardwood lignin).

Natural Fiber Surface Treatment Experiments

The composites studied in this investigation were based on hemp fibers and VE resin. Lignin was used as a surface treatment agent for the hemp fibers. Composites were made by resin transfer molding (RTM).

Materials

The hemp fibers were in the form of a random mat obtained from Hemcore Limited. The VE used was Derakane 411-C-50. Trigonox 239A from Akzo Nobel was used as the initiator. The lignin

used for hemp fiber surface treatment was the Indulin AT.

Surface Treatment of Hemp Fibers with Lignin

Two (1 and 10 wt %) solutions of Indulin AT lignin in water were prepared. Concentrated sodium hydroxide solution was slowly added to the lignin–water mixture with constant stirring until the pH reached 10, at which the lignin dissolved completely. The hemp fibers were soaked in this solution for 1 h. The excess lignin solution was drained, and the fibers were dried in air overnight followed by a vacuum at 55°C. The lignin treated hemp fibers, which had a smooth surface without any noticeable flaking of the attached lignin after drying, were used to make composites with the VE resin.

Composite Preparation

The resin was prepared by mixing the Derakane 411-C-50 with 2% by weight of Trigonox 239A. The hemp fiber random mats were weighed and placed in the RTM mold. The mold was closed, a pressure of 2.1 MPa was applied, and the resin was injected into the mold. During resin injection care was taken to ensure that all the air in the mold escaped along with a small amount of excess resin. After complete injection the resin was cured at 75°C for 2 h and postcured at 110°C for 1.5 h. The composites thus made were weighed to determine the fiber weight fractions as the ratio of the weight of the hemp fibers to the weight of the composite. The hemp fiber weight fraction was found to be approximately 20%.

Mechanical Property Measurements

A slot grinder was used to cut the composites into standard specimens for mechanical property measurements. Prior to testing, these specimens were dried in a vacuum oven at 55°C for 24 h.

Tensile Testing

The tensile tests were conducted in accordance with ASTM D3039. The 254 × 25 × 4 mm specimens were tabbed at both ends. The 38 × 25 × 2 mm tabs were made from a glass fiber composite. These were bonded to the composites using Hysol EA 9309 adhesive. The gauge length of the specimens was 178 mm. The tests were conducted on an Instron model 4484 testing machine at a constant crosshead speed of 2.0 mm/min. Three specimens of each composite were tested. Force–dis-

placement graphs plotted on a computer were used to calculate the tensile strength and tensile modulus of the composites from the peak force and the initial straight line region of the graph.

Flexural Testing

The three-point bend flexural tests were conducted in accordance with ASTM D790. The specimens were 80 × 25 × 4 mm with a span of 50 mm. The tests were conducted on the Instron 4484 testing machine at a constant crosshead speed of 1.3 mm/min. Four specimens of each composite were tested, and the flexural strength and flexural modulus were calculated from the peak force and the slope of the initial straight line region of the force–displacement graphs plotted on a computer.

RESULTS AND DISCUSSION

Monomer Compatibility Tests

Table II shows the compatibility results for the lignin dispersion in the resins. The lignin particles that did not sediment either dispersed or dissolved in the resin. The reason for dispersion can be attributed to the resin viscosity or affinity of lignin for the resin. These methods of dispersion are only important for the smaller particles because the gravitational forces are too strong for the bigger particles to be outweighed by affinity or even viscosity (i.e., in the viscosity range of the resins used here). The controlling dispersion effects via either affinity or viscosity are shown in Table II.

It should be noted that the dispersed and dissolved lignin were the only forms for which there was accounting. There was some sedimentation of lignin in all the samples. The poor dispersion of lignin–MA is mainly due to the large particle size of the ground material. It is notable that there is a lignin fraction (even though it is very small) that dissolves in the low polarity VE resin. Lignin particles were hardly visible with the naked eye. The solubility of lignin in SOMG is much better than in VE and HSO is somewhere in between. This could be seen by the dark color of the solution.

The results in Table II could be anticipated from the resin's polarity. The solubility behavior matches the relative polarity of the resins. Because lignin only dissolves in highly polar solvents, complete dissolution was not obtained in

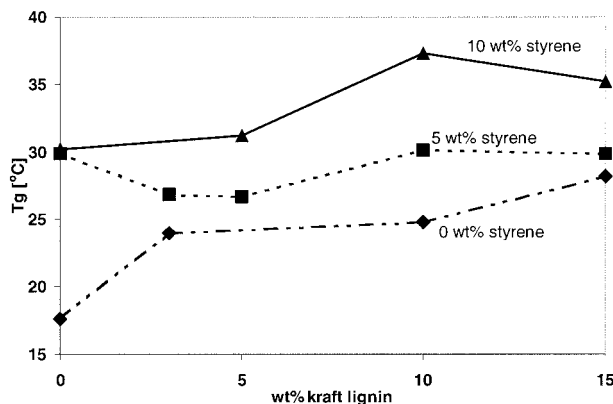


Figure 3 The glass-transition temperature (T_g) of the styrene/lignin/AESO samples.

any of the systems. To completely dissolve lignin in composite resins, lignin must be chemically modified.

Lignin as Filler in AESO/Styrene Matrix

Due to the extremely low polarity of styrene, separation of the mixture into a styrene and a lignin phase was noticed during a 4-h cure cycle. Lignin appeared to concentrate on both the top and bottom of the samples while the middle part was almost clear, suggesting that there was almost no lignin in that part of the sample. In order to be able to use kraft lignin with a styrene-containing thermoset, the maximum amount of styrene in the resin had to be determined. The amount of styrene that can be used with a maximum loading of 15 wt % lignin in AESO was found to be 12 wt % of the total resin weight. Above this amount, separation into a styrene phase and a lignin phase was noticed during curing of the samples. Therefore, only samples of 0, 5, and 10 wt % styrene were tested.

The T_g and the E' versus the lignin content are shown in Figures 3 and 4. The expected changes in T_g and E' were seen for 0 and 10 wt % styrene. Because lignin has a T_g of about 142°C,⁵ it will increase the resin T_g , which is below this value (depending on the styrene content). However, the increase is less than the value calculated with the simple mixing rules. For the maximum 15 wt % lignin, the T_g values of 36.2 and 46.8°C were obtained for 0 and 10 wt % styrene, respectively. Because lignin does not have double bonds that will participate in free-radical polymerization, the storage modulus will decrease with increasing lignin content. Introducing lignin plasticizes the polymer, thus lowering the modulus while raising the T_g a little as seen for the 0 and 10 wt %

styrene samples. This contradictory behavior can be explained by two opposite effects. On the one hand, styrene and acrylate grafting, even when very limited, will incorporate lignin into the resin, resulting in an increase in the T_g . On the other hand, the polarity of lignin will attract the polar areas inside the AESO molecule. The polar areas are residual epoxy and hydroxyl groups without grafting capacity. Positioning of these polar areas generates rubbery regions around parts of the lignin molecules, thus lowering the overall resin modulus. We did not see these effects with the 5 wt % styrene curve. A possible cause for this may be the graft copolymerization of styrene onto lignin. Phillips et al.^{11,23} showed through radiation-induced polymerization that grafting of styrene onto lignin occurs and strongly depends on the solvent (lignin accessibility). The viscosity of the sample was fairly high (compared to the solvents Phillips et al. used), thus limiting the potential of grafting. The styrene grafting should also result in a larger than expected increase in the glass-transition temperature, but that was not observed in the experiments.

Lignin-SOMG-MA Reactions

Addition of Lignin to SOMG-MA System

The DMA analysis of the cured SOMG/lignin/MA/styrene resin showed a T_g of around 136°C and an E' value of 0.9 GPa at 35°C, whereas the T_g of the SOMG/MA/styrene resin that was prepared under the same conditions (1.5:1 SOMG:MA weight ratio) without the addition of lignin had a T_g of 127°C and an E' value of 0.7 GPa at 35°C. Although there is no direct evidence for the formation of lignin maleates because of the insolubility of this product in chloroform-*d*, the ¹H-NMR anal-

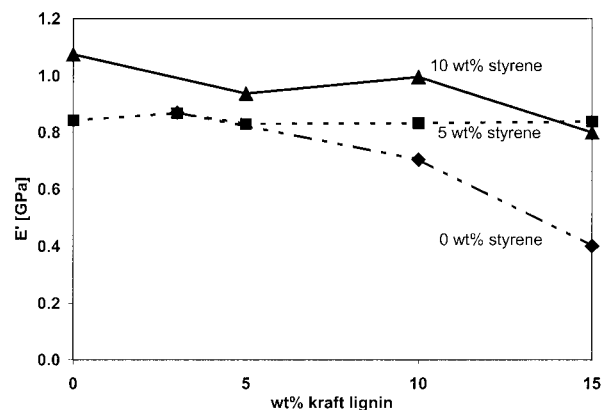


Figure 4 The complex modulus of the styrene/lignin/AESO samples at 20°C.

Table III Mechanical Properties of Hemp Composites with Lignin Surface Treatment

Composite	W_{hemp} (%)	W_{lignin} (%)	W_{VE} (%)	Density (kg/m^3)	Tensile Modulus (GPa)	Tensile Strength (MPa)	Flexural Modulus (GPa)	Flexural Strength (MPa)
Hemp/VE	20.0	0.0	80.0	1118.7 ± 2.3	3.9 ± 0.1	44.9 ± 0.9^a	4.0 ± 0.1	80.5 ± 2.9
Lignin-hemp/VE	19.1	6.3	74.6	1123.5 ± 2.4	3.7 ± 0.1	32.7 ± 0.7^a	3.9 ± 0.1	53.4 ± 1.6
Lignin-hemp/VE	19.9	0.2	79.9	1150.8 ± 2.0	4.3 ± 0.1	37.9 ± 0.4^a	4.9 ± 0.2	86.2 ± 2.5

^a Failure happened near the grips instead of in the gauge length region.

ysis of the SOMG/LIGNIN/MA product shows the formation of the maleate and fumarate half-esters. The precipitate formed in the SOMG/LIGNIN/MA/styrene product upon the addition of styrene shows that the solubility of lignin maleates in the SOMG/MA styrene mixture is critical; however, even the small amount of lignin that was soluble caused an appreciable increase ($\Delta T = 9^\circ\text{C}$) in the T_g when compared to the SOMG/MA styrene copolymer.

Addition of MA to SOMG/Lignin System

The cured samples contained too many bubbles to be tested by DMA. The samples were very rubbery, in contrast to the samples obtained by the first approach, suggesting that the maleinization reaction was not fully completed. The main consideration here is the parallel maleinization of SOMG, as well as lignin implying competition between the two. Optimization of these parallel reaction is necessary in order to obtain better samples after curing.

Modification of Lignin by Reaction with ESO

The lignin/ESO reaction product showed some remarkable differences in the reactivity of the different lignins with ESO. By following the amount of epoxies per triglyceride by $^1\text{H-NMR}$ (in chloroform-*d*), hardwood lignin showed that 0.2 of the 4.4 epoxies had reacted, which increased to 0.9 for pine lignin and 2.4 for ethoxylated lignin. The reacted epoxies per triglyceride for the ethoxylated lignin case are bigger than 2 (the maximum amount to react with lignin), which can be attributed to homopolymerization of the epoxies with the hydroxyl groups on other triglycerides formed after reaction of the oxirane ring with lignin.

ESO/Lignin/VE Matrix

As can be understood from the results for the ESO/lignin reactions, the biggest improvement of

the lignin solubility in VE came from the ethoxylated lignin. Completely insoluble unmodified, ethoxylated lignin became partially soluble after reaction with ESO. As for the other lignins, slight (with hardwood lignin) to moderate improvement (with pine lignin) in the solubilities were observed by monitoring the darkness of the solution compared to the nonmodified lignin-VE solution. The DMA test results showed a significant drop in both the glass-transition temperature and the storage modulus for all the tested lignins. This occurred because the ESO/lignin had no groups that could free radically polymerize and thus no way of incorporating into the resin. Therefore, the addition of ESO/lignin introduces weaknesses and this results in a decrease in the T_g and E . A potential solution would be to have the remaining epoxy rings react with maleic or acrylic acid.²⁴ The maleinization and acrylation reactions were already performed on pure ESO and are well known.^{15,18,25}

Natural Fiber Surface Treatment Experiments

The mechanical properties of lignin treated hemp fiber/VE composites are shown in Table III. When the hemp fibers are treated with a 10% solution of lignin, the resultant composites contain 6.3% lignin by weight of the composite. This composite has lower tensile and flexural strengths compared with the untreated hemp fiber composites. However, the tensile and flexural moduli are largely unchanged. Hemp fibers were also treated with a lignin solution of a lower concentration (1%), and composites were made. These composites were found to have 0.2% lignin by weight of the composite and showed improved properties; the tensile modulus increased by 10.0%, the flexural modulus increased by 22.5%, and the flexural strength increased by 7.0. Thus, lignin has the potential to be a useful sizing agent for natural fiber composites.

CONCLUSIONS

Several pathways for introducing lignin in unsaturated polyester and soy oil based resins were studied with varying success. A major problem was the incompatibility of the unmodified (polar) lignin with styrene, a reactive nonpolar diluent used in a large number of unsaturated polyester resin systems. However, by modification with ESO and MA, the solubility of lignin in styrene-containing liquid molding resin systems improved significantly. For the lignin-MA adduct, this also improved the mechanical properties of the cured resin. The lignin-ESO product, having no double bond functionality for free-radical reaction with the curing resin, did not show any improvement of the mechanical properties. This was expected because the lignin-ESO complex behaved as a plasticizer. Future work²⁴ will therefore concentrate on reacting lignin-ESO with an acid containing the desired double bonds. The initial results are promising because none of the results were necessarily optimized.

The fiber treatment results indicate that there is potential for the use of lignin as a surface treatment agent for natural fiber composites wherein lignin bonds to the surface of natural fibers and the irregular shape of the lignin particles provides mechanical interlocking with the matrix in composites. This mechanical interlocking improves the fiber-matrix interfacial strength, resulting in improved properties for the composites. A lower concentration of lignin at the interface is found to be more beneficial in bringing about this improvement in interfacial strength. At higher lignin concentrations the lignin particles plausibly impede the flow of resin and subsequent wetting of the fibers, resulting in a weak interface. Further research is needed to optimize the concentration of lignin at the interface to bring about an improvement in interfacial strength and to ascertain the mechanism of this interfacial bonding.

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