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LIGNIN AND ITS POLYBLENDS

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ABSTRACT

Lignin, one of the most abundant biopolymers, is a renewable, cheap source with great possibilities for use as a component in polymeric systems. In spite of many research efforts, its potential hasn't been exploited. Recent developments in the domain of lignin and its derivatives focus on the possibilities of their use in polymeric systems. This paper shows some recent data obtained by using lignin in polyblends with silicones, acrylics, polyurethanes, epoxy, and PVC.

INTRODUCTION

Studies on the utilization of lignin are among the most challenging and promising in the area of natural polymers. One of lignin's main properties is the fact that it is very stable in nature and acts as a stabilizer toward various stresses to which the plant is subjected, e.g., as shown by the inhibiting effect of lignin on the rate of enzymatic hydrolysis of wood.

The lignin content in North American woods varies from 26.3 to 29.3% in coniferous and from 19.3 to 24.3% in deciduous trees. The amount in plants generally varies over a very wide range.

It is well known that lignin is a polydisperse biopolymer made of phenylpropane units and that some differences regarding the molecular mass and the nature of functional groups do exist between the lignins of softwoods and hardwoods.

The most recent model [1, 2] shows that lignin comprises 94 units, corresponding to a total molecular mass of more than 17,000. This is based on a wide array of analytical determinations with H-NMR spectroscopy, gel permeation chromatography, C-13 NMR, distortionless enhancement by polarization transfer techniques, etc.

In his paper entitled "The Challenge of Lignin," Kringstad [3] presents the current and suggested application of lignin in thermosetting systems and polyblends as well as antioxidant and filler for elastomers besides other useful data regarding the upgrading of this biopolymer. More recently, data on the use of lignin in blends with thermoplastics were reported [4, 5].

Lignin can be incorporated into rubber latex masterbatching in order that its reinforcing properties can be used. Alkali-lignin was proved to be an excellent reinforcing agent for SBR when coprecipitated with rubber from latex.

EXPERIMENTAL

Materials

Different kinds of commercial kraft lignins such as Tomlinite (hardwood), Indulin AT (softwood), and Eucalin (Eucalyptus wood) were used in some polyblends in amounts up to 40% with:

1. A siliconic Dow Corning sealant based on polydimethylsiloxane which was selected because of its excellent blending properties
2. An acrylic copolymer used in a commercial sealant (Mulco)
3. A two-component flexible polyurethane made of an isocyanate polymer (Bayer) and a polyester (Bayer) with an OH content of 0.85% and an equivalent weight of 2000
4. An epoxy product based on the diglycidyl ether of bisphenol A (Ciba-Geigy) cured with an aliphatic polyamine in a weight ratio of 3.3 to 1
5. A commercial unplasticized PVC resin (BF Goodrich) having K-67

Polyblends with lignin were studied from the point of view of mechanical and thermal properties, adhesion, and durability by using mechanical testing techniques, DSC, DMA, SEM, NMR, statistical estimation, IR, FT-IR, curing kinetics, and surface analysis.

RESULTS AND DISCUSSION

L-Polydimethylsiloxane Blends

Introduction of lignin (L) into a silicone doesn't improve its adhesion or mechanical properties, but a small amount of PVC (10%) and the use of some primers showed an improvement of these properties [6].

L-Acrylic Copolymer

Although DSC data proved the incompatibility of these two polymers, the addition of L appears generally beneficial in improving the mechanical properties and durability of an acrylic sealant [7].

L-Polyurethane (PU) Blends

SEM confirms both the uniform distribution of L particles and the different morphologies of the constituent phases. SEM also clearly shows the erosion of the PU surface brought about by an artificial weathering process. This degradation process modifies the smooth surface characteristic of neat PU to a fibrillar one. DSC analysis and CP-MAS NMR confirm the immiscibility of L with PU [8-10].

Surface analysis showed that the interaction potential of different lignins decreases in the following order: Tomlinite > Indulin AT > Eucalin [11]. L as a filler was found to be less restrictive of the degree of swelling of PU than a siliceous clay-TiO_2 mixture. Hence, it is seen that lignins do not interact with an elastomer matrix to as great extent as the above-mentioned mineral filler [12].

The addition of different types of lignin increases the modulus of elasticity of the formulations investigated [13]. The curing kinetics of various PU formulations at 15% volume loading with different types of lignin and mineral filler (Sillitin/Titanox) are presented in Fig. 1.

L-Epoxy (EP) Blends

Thermally cured EP-L polyblends having up to 40% L content were investigated. Adhesive shear tests, DSC, DMA, solid CP-MAS NMR, and FT-IR were performed to establish the effect of L on the mechanical properties of the polyblends and on the morphology of these crosslinked structures.

Adhesive shear tests in tension disclosed a considerable improvement in adhesion in blends having up to 30% L content, with a maxima occurring at a 20% L loading. However, the shear strength is drastically reduced in specimens of blends having an L content in excess of 35%.

The T_gs of EP-L polyblends were close to one another, with a slight increasing trend shown by both DSC and DMA analyses, mostly for EP-40L (40% lignin). Only one T_g was detected for blends having an L content up to 20%, but blends having higher L contents showed two T_gs. Hence, EP-L blends are *miscible up to*

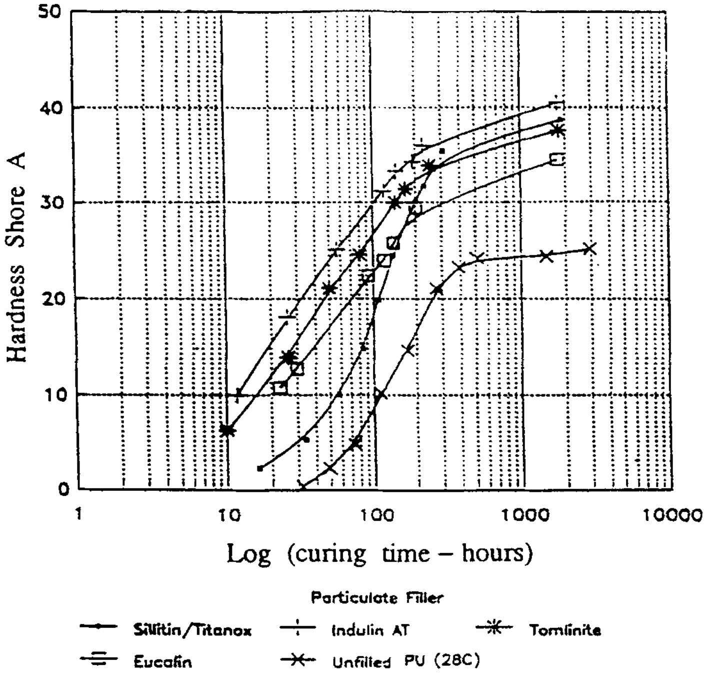

FIG. 1. Curing kinetics of various filled formulations at 15% volume loading in relation to the base unfilled formulation (stoichiometric ratio = 1.062, Baylith paste-polyol ratio = 1.0, plasticizer content = 40%).

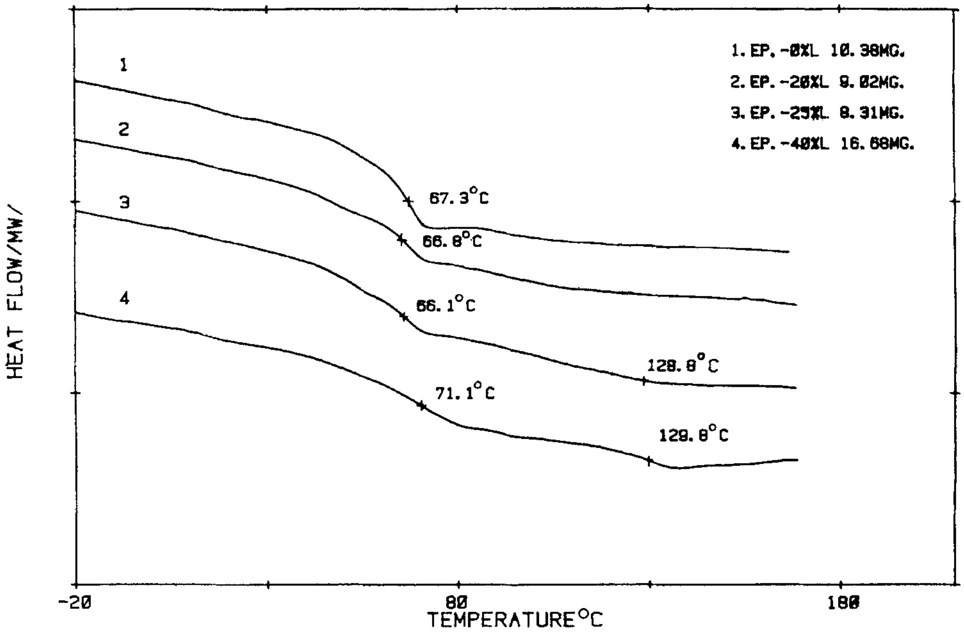

FIG. 2. DSC diagrams for EP and EP-L polyblends, Run 1.

L contents of 20% [14–17]. Figure 2 presents DSC diagrams for EP and EP–L polyblends.

A reasonable explanation for the different behaviors of EP–L polyblends as a function of their L content could be the enhanced degree of bonding between L and the EP network at elevated temperatures. This bonding can arise by a chemical reaction between L and some unreacted amine groups present in the hardener. A possible lignin–amine reaction was postulated in an earlier work based on curing kinetics evaluated using the DSC technique [17].

The above suggested reaction between L and the polyamine curing agent at elevated temperatures was confirmed by FT-IR spectroscopy and determination of the amine number. It was evident that some L carbonyl groups participate in this reaction. Kinetic data indicated that during the curing of EP–L polyblends the above reaction cannot compete with the addition reaction of epoxide groups with primary and secondary amines. The FT-IR difference spectra of L present in thermally cured and room-temperature-cured EP–L polyblends show that spectral changes can be induced only by a thermal crosslinking process.

Figure 3 shows the difference spectra obtained after digital subtraction of the EP control spectra from EP–L (20% lignin) (A) and from EP–L (40% lignin)

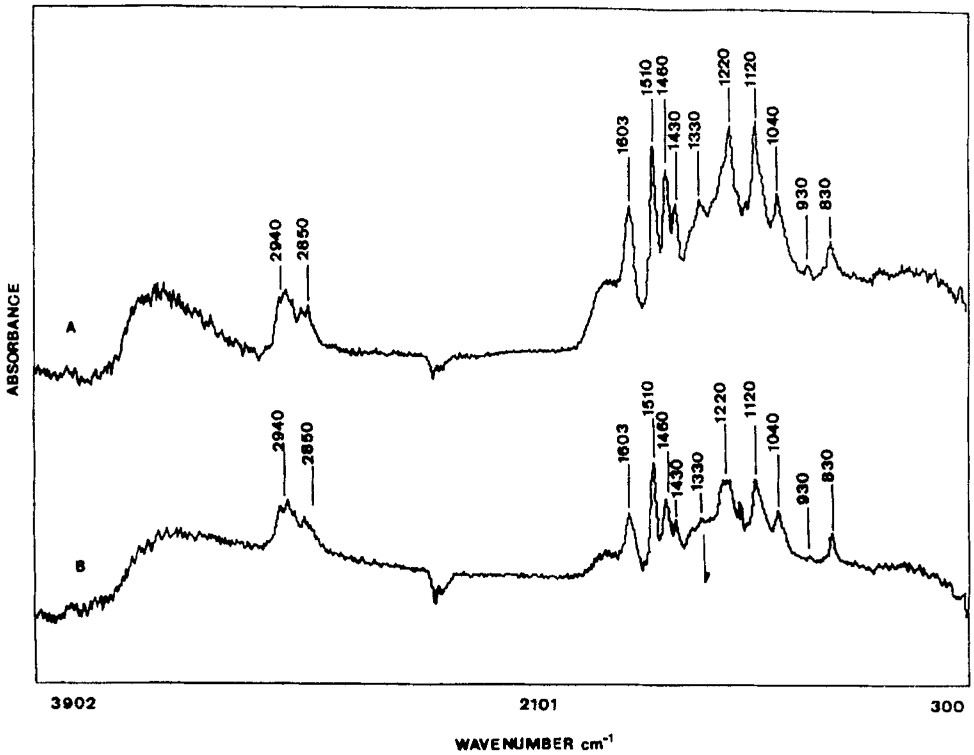

FIG. 3. Difference FT-IR spectra of EP–L polyblends, EP control cured at room temperature.

(B) polyblends spectra. Both the EP and EP-L polyblends were cured at room temperature.

From the shape of the proton spin-lattice relaxation time curves calculated from solid-state NMR spectral showing $T_{ip}H$ as a function of L content, it seems reasonable to assume that a stoichiometric reaction occurred at a blend loading of 20% L. The extent of the reaction was probably not sufficient for the two components to combine at the molecular level, but it was significant enough to generate homogeneous properties at the macromolecular scale. This was also disclosed by the results of DSC and DMA measurements [18].

Solvent extraction data support the supposition of L bonding to the EP network via unreacted amine groups of the hardener.

The adhesive shear strength of EP-L10 (10% lignin) both in air and in water is significantly improved by introducing organosilanes (2% by weight) into the blend. Among the silanes used, epoxyalkylsilane (A187) gave the best results in terms of increased shear strength in relation to the unmodified blend. The contact angle measurements are shown in Table 1. As can be seen, the wettability is improved by adding L and organosilane to the EP polymer [19]. Besides EP and L, a polymeric component such as PVC or phenoxy resin as a third partner contributes to better adhesive properties [20].

L-PVC Blends

The presence of L did not affect the thermal stability of PVC and its rheological properties during melt mixing. The obtained data show that the interaction of L with PVC can take place at temperatures above the T_g of the high molecular weight fraction of L. The partial or total replacement of TiO_2 (pigment and stabilizer) by

TABLE 1. Comparison of the Surface Parameters of EP, EP-L10, and A187

		EP	EP-L10	EP-L10-A187
Contact angle (degrees)	$\theta_w{}^a$	81	75	69
	$\theta_m{}^b$	50	38	18
Work of adhesion (mJ/m^2)	$W_a(w)^a$	84.2	91.6	97.7
	$W_a(m)^b$	83.5	90.8	99.1
Surface free energy (mJ/m^2)	γ_s	37.9	43.7	50.8
	γ_s^d	26.9	31.6	37.8
	γ_s^d	11.0	12.1	13.0
Interfacial free energy (mJ/m^2)	$\gamma_{sl}(w)^a$	26.5	24.9	24.7
	$\gamma_{sl}(m)^b$	5.2	3.7	2.5
Spreading coefficient (mJ/m^2)	$S_c(w)^a$	−61.4	−54.0	−46.7
	$S_c(m)^b$	−18.1	−10.8	− 2.5
Interaction parameter	$\phi(w)^a$	0.801	0.812	0.813
	$\phi(m)^b$	0.951	0.964	0.976

[a] To water.
[b] To methylene iodide.

L in different blends did not greatly affect the tensile stress-strain properties of the blend in comparison to PVC [21].

CONCLUSION

The above data demonstrate that lignin may serve as a highly competitive component for the production of different polymeric systems such as adhesives, sealants, plastics, and elastomers.

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