

Epoxy–Lignin Polyblends: Correlation between Polymer Interaction and Curing Temperature

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SYNOPSIS

A bisphenol A–polyamine hardener based epoxy adhesive (EP) was modified by polyblending with Kraft lignin (L). EP–L polyblends with an L content up to 40% by weight were cured at room temperature or above their glass transition temperature (T_g). Previous data have shown that the thermal and viscoelastic properties, as well as adhesive performance of the EP–L polyblends, are influenced by the curing temperature and by the L content in thermally cured polyblends. A reasonable explanation for the different behavior of EP–L polyblends as function of the curing temperature and their L content could be the enhanced degree of bonding between L and the EP network taking place at elevated temperature. This bonding was specifically considered to take place between L and possible unreacted amine groups of the hardener. Characterization of the EP–L polyblends was performed to search for evidence of irreversible chemical bonding between L and the EP network in thermally cured EP–L polyblends. FTIR studies, L extractibility from the crosslinked polyblends, and quantitative data concerning the reactivity of L toward the polyamine hardener are discussed.

INTRODUCTION

Previous papers in this series^{1–3} reported the effect of various amounts of Kraft lignin (L) on the adhesive performance, thermal, and viscoelastic properties of a bisphenol A-based epoxy polymer adhesive (EP) which had been modified by polyblending with L in amounts up to 40% by weight and cured at room temperature or temperatures above EP's T_g .

It was found that in EP–L polyblends which had been prepared and cured at room temperature L, in amounts between 5 and 20%, had little effect on the adhesive strength (single lap shear using tensile load). An improvement of the adhesive strength shear of both the EP and particularly of the EP–L polyblends, was obtained after a post-curing process (4 h at 75°C).¹ DSC and DMA analyses of the polyblends cured at room temperature disclosed a single T_g , which is characteristic for monophasic systems.

DMA data revealed a gradual reduction of the peak value of $\tan \delta$ in relation to the amount of L in the polyblends. This was apparent due to an increase in the tensile storage modulus and a decrease in the tensile loss modulus at temperatures close to T_g .² The significant improvement in the adhesion of the EP–L polyblends after post-curing, as well as their moduli behavior at or around T_g , suggested the formation of a bond between L and EP network, which could develop at higher temperatures.

In further studies³ the same EP–L system was cured above its T_g , i.e., for 2 h at 100°C and the amount of L was increased up to 40%. When compared with the EP control, the adhesive strength in shear of the thermally cured polyblends disclosed considerably higher values in the blends having up to 30% L content with a maxima occurring at 20% L. However, the shear strength was drastically reduced in the blend specimens having L contents in excess of 35%. Moreover, for the same volume fraction of two different fillers (L or silica), the adhesive bond strength was found to be one and a half times higher for EP-20L than for EP-40 silica, despite their very different moduli, i.e., 6.6 GPa for L⁴ and 97 GPa for silica.⁵ Moloney and Colab⁶ revealed

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that the modulus and strength of a filler is one of the principal parameters which determines the strength and toughness of a filled epoxide resin. Hence, the better adhesive performance of the EP-20L when compared with that of the EP-40 silica mixture was unexpected.

The T_g 's of the EP-L polyblends were quite close to one another and had a slight tendency to increase in both DSC and DMA analyses, mostly for EP-40L. Only one T_g was detected for blends with 20% or less L content, but two T_g 's were found in the blends with a higher L content, which depicts an L-resin miscibility up to 20% L.

Curing studies performed using the DMA scanning mode showed a damping maximum at 106°C for EP and all EP-L blends and a second damping peak above 130°C for all blends except EP. It was found that, with the exception of the EP-40L blend, pre-curing the blends at 100°C for 2 h lead to the disappearance of the second damping peak.

The beneficial effect of the thermal cure upon the mechanical properties and miscibility of the polyblends within a specific content of L was obvious. From the shape of the curves of proton spin-lattice relaxation time, $T_{1\rho H}$ (calculated from solid state NMR spectra) vs. content in L, it was reasonable to assume that a stoichiometric reaction occurred at 20% L. The extent of the reaction was probably not sufficient to mix the two components at the molecular level, but it was the highest at this composition generating homogenous properties on a macroscale, and creating the appearance of a homogenous mixture, even on a very fine scale. The proton spin-lattice relaxation time in the rotating frame ($T_{1\rho H}$) is a parameter which was suggested in 1981 as a probe of phase compositions for blends⁷ and has been used since then in various systems.

A reasonable explanation for the different behavior of EP-L polyblends as a function of their L content could be the enhanced degree of bonding between L and the EP network taking place at elevated temperatures. A chemical reaction between one of the L functional groups and some unreacted amine groups present in the hardener could be responsible for L-EP network bonding.

The occurrence of a chemical reaction involving participation of some of unreacted amine groups present in the system and one of the functional groups in L can be explained by: (i) the presence of traces of unreacted amine groups in cured EP networks; (ii) an apparently balanced EP-amine system in most of the EP-L polyblends.

(i) The amine-cured EP networks are generally assumed to result exclusively from the addition re-

actions of epoxide groups with primary and secondary amines.⁸ However, these reactions are often incomplete due to steric and diffusional restrictions and additional reaction such as epoxide homopolymerization can occur.⁸⁻¹¹ Hence the presence of traces of unreacted amines in the crosslinked EP network is generally accepted.

(ii) It appeared that L-amine reactions do not really compete with the principal addition reaction of epoxide groups with primary and secondary amines, at least in those blends having not greater than 20% L. The T_g of EP-L blends, with exception of the EP-40L blend, did not show any amine epoxy unbalance.

A possible chemical reaction between L and polyamine hardener was first postulated in relation to the determination of the curing kinetics of the same EP-hardener system. The curing kinetics data, obtained from dynamic experiments,¹² have shown that the presence of L did not significantly affect the EP curing process. However, a slight increase in activation energy and a slight reduction of the cure rate with a corresponding L content could, at a first glance, be explained by an interaction between L and the polyamine hardener. This explanation was based on the results of a further thermal analysis between L-polyamine hardener and L-EP prepolymer. In the dynamic experiments, conducted between -30 and 200°C and at a heating rate of 10°C/min, an exothermic reaction took place between L and the hardener at ca. 50°C, whereas no interaction could be detected between L and the EP prepolymer.

This paper presents the results of further investigation of the same EP-L polyblends, thermally or room temperature cured, in a search for evidence of irreversible chemical bonding between L and EP network.

FTIR studies, L extractibility from the crosslinked polyblends, and quantitative data concerning the reactivity of L toward the amine hardener were undertaken.

EXPERIMENTAL

Materials

The same epoxy prepolymer hardener system as in previous works was used. Epoxy prepolymer based on DGEBA (Ciba Geigy 1200 CA resin) was utilized without purification. It was cured stoichiometrically with an accelerated aliphatic polyamine (Ciba Geigy, HY 2992) according to their respective equivalent weights: 1200 CA: 180 g/eq; HY 2992: 55 g/eq. Both

epoxy prepolymer and hardener are liquid at room temperature.

The second polymer L is a Kraft lignin chemically extracted from a mixture of hardwoods and precipitated from the black liquor with sulfuric acid and pH adjusted to about 6.7 (Tomlinite Domtar). It has the following characteristics:

Molecular weight[†]

—Average weight molecular weight (\bar{M}_w): 2800

—Average number molecular weight (\bar{M}_n): 650

—Polydispersity (\bar{M}_w/\bar{M}_n): 4.3

Assay (%)[‡]

—C: 65.06

—H: 6.03

—S: 1.59

—Total OH: 20.7 (including phenolic and aliphatic)

—Methoxyl: 17.2

—Carbonyl: 5.0

Gel permeation chromatography was performed using a set of three columns consisting of crosslinked styrene divinylbenzene polymer (one ultrastyrigel 500 A and two ultrastyrigel linear) connected to a Universal Injector (Waters U6K), an HPLC Pump (Waters 510), and an R. I. Detector (Waters 410) were used. Tetrahydrofuran (THF) (Omnisolv BDH, suitable for chromatography) was used as the eluant at a flow rate of 1 mL/min; 100 μ L injections were made from 0.2% acetylated L solutions in THF. The column calibration for molecular weight determination was made with a set of 10 polystyrene standards (Waters).

Molecular weight averages (\bar{M}_n and \bar{M}_w) and polydispersity (\bar{M}_w/\bar{M}_n) were calculated from the retention times via a calibration curve using a computer (Waters 840 Control and Data Station) and Waters Expert GPC Software.

Similar methods for the determination of molecular weight distribution of different lignins are reported in the literature.^{13,16-18} In a typical acetylation procedure,^{14,15} water-washed and dried L (400 mg) was acetylated with a mixture of pyridine (2 mL) and acetic anhydride (2 mL). The L was dissolved in pyridine prior to the addition of acetic anhydride,

and the mixture was then allowed to stand at room temperature for 24 h. After that, methanol (2 mL) and methylene chloride (16 mL) were added to the reaction mixture; after a further 30 min, the mixture was washed three times with 2 N HCl and then washed with distilled water to pH 7, and dried on anhydrous Na₂SO₄. The solvents were evaporated under reduced pressure.

Preparation of Cured Samples

The polyblends were prepared by manually stirring the epoxy prepolymer and the corresponding quantity of L (10–40% by weight of polyblend) for 2 min; the equivalent quantity of curing agent was then added and the resulting mixture was stirred for another 5 min.

Twelve minutes after preparation, the mixtures were poured into silicone molds (65 × 12 × 1.5 mm) and then cured in an oven at 100°C for 2 h. The cured samples were then allowed to cool in a desiccator. Duplicate samples were cured at room temperature for 24 h and then stored in a desiccator.

For IR spectra and L extraction, the solid cured samples of the EP control and the EP-L polyblend were first powdered by scraping lightly with a razor blade and then the scrapings were ground in a mechanical vibrating ball mill. For IR qualitative spectra, the powder was suspended in potassium bromide and pressed into a pellet.

For determining the extractability of L from EP-L polyblends, a suitable amount of powder (to contain about 4 mg L) was weighed accurately on a Sartorius 4501 microbalance (accuracy of \pm 0.005 mg), placed in a 100 mL round-bottom flask with 20 mL dioxane–water 9 : 1 (by volume), and then refluxed under constant stirring for 10 h. The undissolved material was quantitatively filtered off and washed with dioxane–water in a 50 mL volumetric flask. The filtrate was then diluted to the mark and thoroughly shaken.

For UV analysis, a 10-mL aliquot was diluted to 25 mL with the same solvent. Extraction time was established with the same sample (EP-40L) extracted at different times and thereafter analyzed for L content by UV analysis.

Procedures

FTIR Spectroscopy

FTIR qualitative spectra were recorded on a 102 Bomen Michelson spectrophotometer between 4000 and 200 cm⁻¹. Powdered specimens were pressed

[†] The molecular weight of L was determined by gel permeation chromatography in acetylated form in order to avoid association of free hydroxyl groups and to increase the solubility in tetrahydrofuran.¹³⁻¹⁵

[‡] Data furnished by Domtar Research Center, Seneville, PQ, Canada.

into pellets with potassium bromide. The thickness of the pellets was kept approximately constant. By using a different ratio of polyblend powder to potassium bromide (i.e., 6 mg/1000 mg for EP control, 7.5 mg/1000 mg for EP-20L, and so on), the EP content was also kept approximately constant in each pellet.

The IR spectra of the thermally cured EP control sample is shown in Figure 1 and that for the L control sample in Figure 2. In the EP control spectra the characteristic bands for DGEBA epoxy polymer are easily recognizable^{8,19-21}:

- C—H in epoxy: 3060, 3005, 1410, 1435 cm^{-1}
- Aromatic ether: 1245 cm^{-1}
- Aliphatic ether: 1160, 1042 cm^{-1}
- Branched ether: 1120, 1065 cm^{-1}
- bisphenol ring:
 - C=C aromatic: 1610, 1580, 1510, 1460 cm^{-1}
 - C—H aromatic: 1185, 1010 cm^{-1}
- C—H aromatic in *p*-substituted benzene: 830 cm^{-1}
- Methyl group: 2962 cm^{-1}

—Methylene group: 2860 cm^{-1}

—Geminate methyl group: $\begin{array}{c} \text{CH}_3 \\ | \\ -\text{C}- \\ | \\ \text{CH}_3 \end{array}$: 1385, 1365 cm^{-1}

—OH group: 3500–3400 cm^{-1}

Also, barely detectable are the characteristic bands of traces of epoxy rings at 920, 870, and 760 cm^{-1} .

The FTIR spectra for EP control cured at room temperature was similar to that shown in Figure 1. The particular characteristic IR absorption bands of the L control sample (Fig. 2) come from the following:

- C=C in aromatic ring: 1610, 1510, and 1460 cm^{-1}
- Trisubstituted aromatic ring: 1150, 835 cm^{-1}
- Aromatic ring vibrations conjugated with an α carbonyl group: 1585 cm^{-1}
- Syringyl ring breathing with carbonyl stretching: 1330, 1220 cm^{-1}

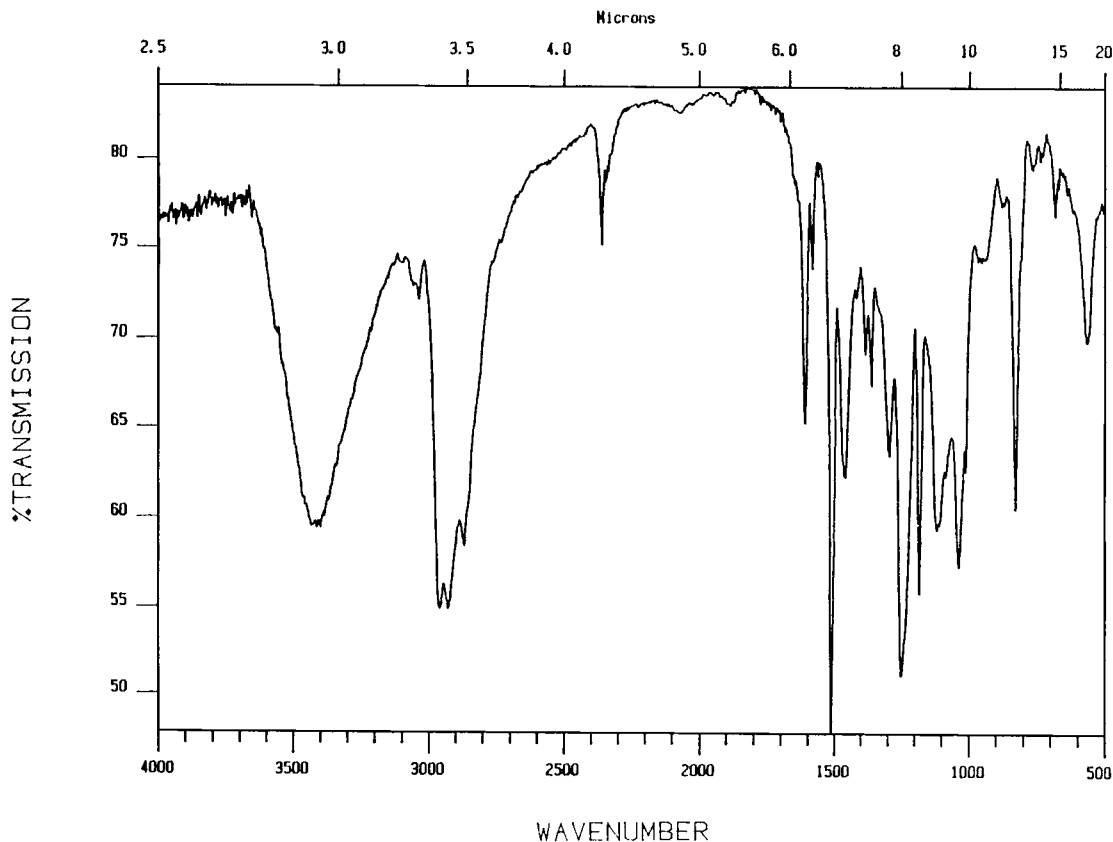


Figure 1 IR Spectrum of thermally cured EP control.

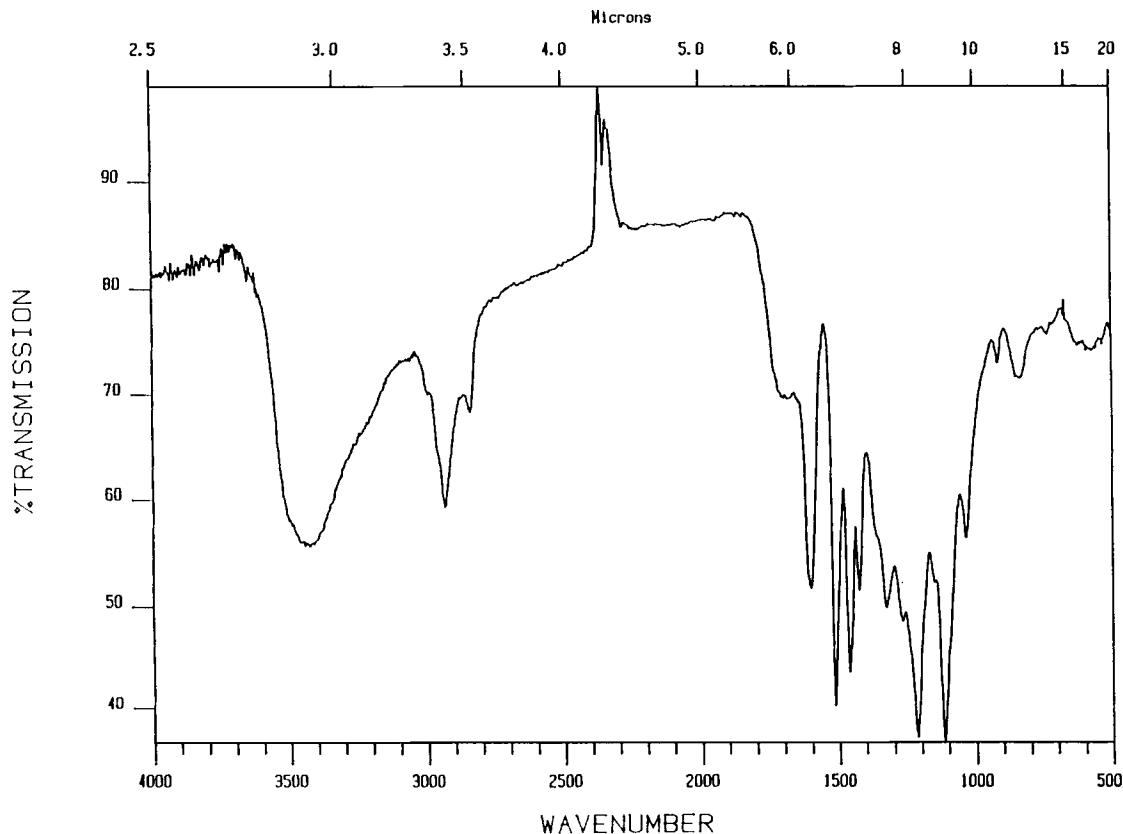


Figure 2 IR Spectrum of L control.

- Ether linkages: $1145, 1040 \text{ cm}^{-1}$
- C—H aliphatic stretching and bending in methyl and methylene groups: $2940, 2850, 1478, 1370 \text{ cm}^{-1}$
- OH groups: $3400, 1370, 1043 \text{ cm}^{-1}$

The visible broad shoulder between 1750 and 1650 cm^{-1} could result from acid or ester carbonyl groups (1725 cm^{-1}), carbonyl stretching ($1725\text{--}1650 \text{ cm}^{-1}$), nonconjugated ketone carbonyl groups ($1712\text{--}1705 \text{ cm}^{-1}$), aldehyde or ketone carbonyl (1669 cm^{-1}).^{22,23}

Ultraviolet Spectroscopy

UV spectra were recorded on a Perkin-Elmer 552 UV-VIS spectrophotometer from 400 to 190 nm in 1-cm silica cells using dioxane–water $9 : 1$ (by volume) as solvent (1,4-dioxane, Omnisolv BDH, suitable for spectrophotometry and chromatography).

First, the L characterisation in UV was done in accordance with procedures given in the extensive literature concerning the study of different kinds of L in UV.^{24–26} The UV absorption spectra of L so-

lutions in dioxane–water show a characteristic maximum at 277 nm (Fig. 3). Free and etherified hydroxyl groups contribute significantly to the

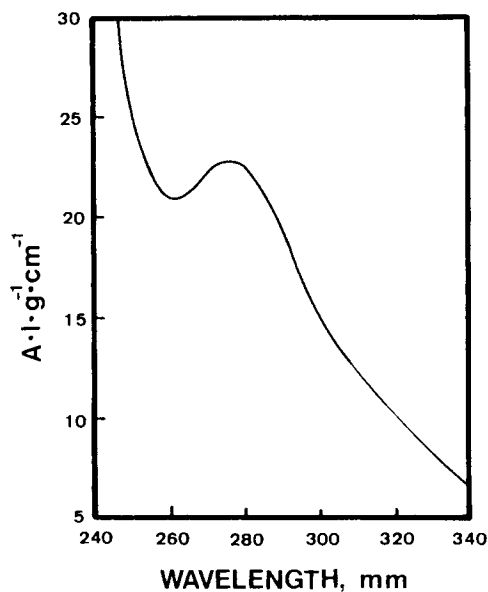


Figure 3 UV Spectrum of L.

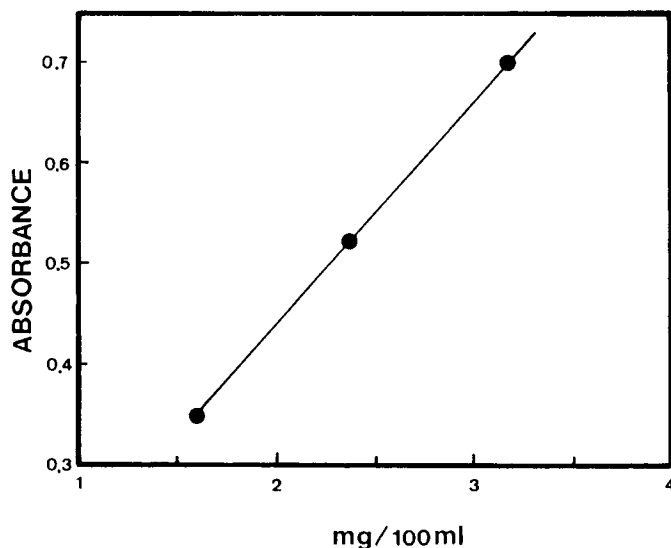


Figure 4 UV Calibration curve for L at 277 nm.

characteristic absorption maximum of lignins near 280 nm.^{24,25}

The absorbance at 277 nm was used to establish the calibration curve for L in the dioxane-water solution (Fig. 4). Its characteristic absorptivity was found to be $22.07 \text{ A L g}^{-1} \text{ cm}^{-1}$. This absorptivity value was used to determine the L concentration in EP-L polyblend solutions prepared according to the previous subsection. The solutions were scanned versus a corresponding blank solution of the EP control sample prepared in the same way as the EP-L polyblend samples. In all cases, the absorbance values recorded are averages of three determinations.

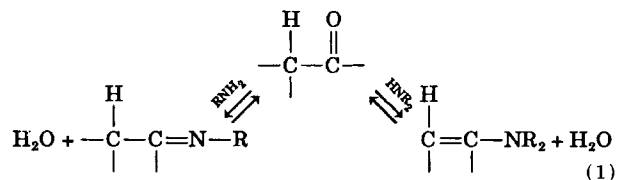
RESULTS AND DISCUSSION

FTIR Spectroscopy

EP-L polyblends with 20 and 40% L content, thermally cured or cured at room temperature, were analyzed in an attempt to establish the influence of L on the possible chemical changes occurring in EP-L polyblends during the thermal curing process. In spite of the fact that the behavior of thermally cured polyblends are different from those cured at room temperature, their FTIR spectra did not disclose visible chemical changes. However, as we suggested an L bonding to the EP network via traces of unreacted amine groups, which can occur only at elevated temperatures, is responsible for the different properties of EP-L polyblends. Therefore, the FTIR study was directed toward the detection of irreversible chemical changes in L induced by the reaction between it and polyamine hardener. It was also con-

cerned with the identification of these changes in L present in the cured EP-L network.

From all the functional groups present in L, the carbonyl groups which comprise about 5%, seem to be the most susceptible to react with amines (secondary and primary). The reaction between carbonyl compounds and amines is illustrated in the following equation:



The reaction product with primary amines having C=N-R double bond is an imine and that with secondary amines having C=C-NR₂ double bond is an enamine. Imine formation is normally an acid-catalyzed process. Reaction is very slow at both high and low pH but reaches a maximum rate at a weakly acidic pH, i.e., 4.5.²⁷

The removal of the water produced by the condensation made possible the facile preparation of enamines from ketones or disubstituted aldehydes²⁸ and the same effect should be applicable for the imines as well. The imines have IR absorptions in the double bond region $1630\text{--}1690 \text{ cm}^{-1}$ ²⁹ and in enamines they appear generally in the $1600\text{--}1680 \text{ cm}^{-1}$ region.²⁸ In enamines there is also a C-N vibration band whose frequency is similar to that found in the tertiary amines, i.e., $1310\text{--}1360 \text{ cm}^{-1}$.

The detection of the chemical changes in L induced by its reaction with the amine hardener (H) was carried out on an L-H mixture with a ratio 1.08 : 1, i.e., the same ratio as in an EP-20L polyblend. A thin film of this mixture was scanned immediately after preparation.

After scanning, the film was cured for 1 h at 100°C, cooled down, and then rescanned. The differences between the fresh and cured blends were obtained by digital subtraction of their respective absorbance spectra (Fig. 5).

When a polymer is examined before and after a chemical or physical treatment, and subtraction of the original spectrum from the final spectrum is done, positive absorbances reflect the structures that are formed during the treatment and negative absorbances reflect the loss of structure.³⁰ The difference spectra from Figure 5, which represents, in fact, the L spectra after the thermal treatment, indicates the following features:

— *Positive absorbance:*

(a) 1130 cm^{-1} : These peaks can be attributed to C-N vibrations in enamines²⁹

— *Negative absorbance:*

(a) 3360; 3290 cm^{-1} : These peaks can be attributed to N-H stretching vibrations in amines²⁹

The negative absorbance is an indication of the amine loss during the reaction with L, occurring at 100°C.

(b) 2940; 2850; 1478 and 1370 cm^{-1} : These bands designate aliphatic C-H stretching and bending in methyl and methylene groups in L with a very high degree of certitude. It is not possible to distinguish C-methyl, methoxyl, or methylene C-H in these bands. However, it seems likely that the intensities of these bands are affected by geometry and electronic effects in the case of aromatic methoxyl group.²²

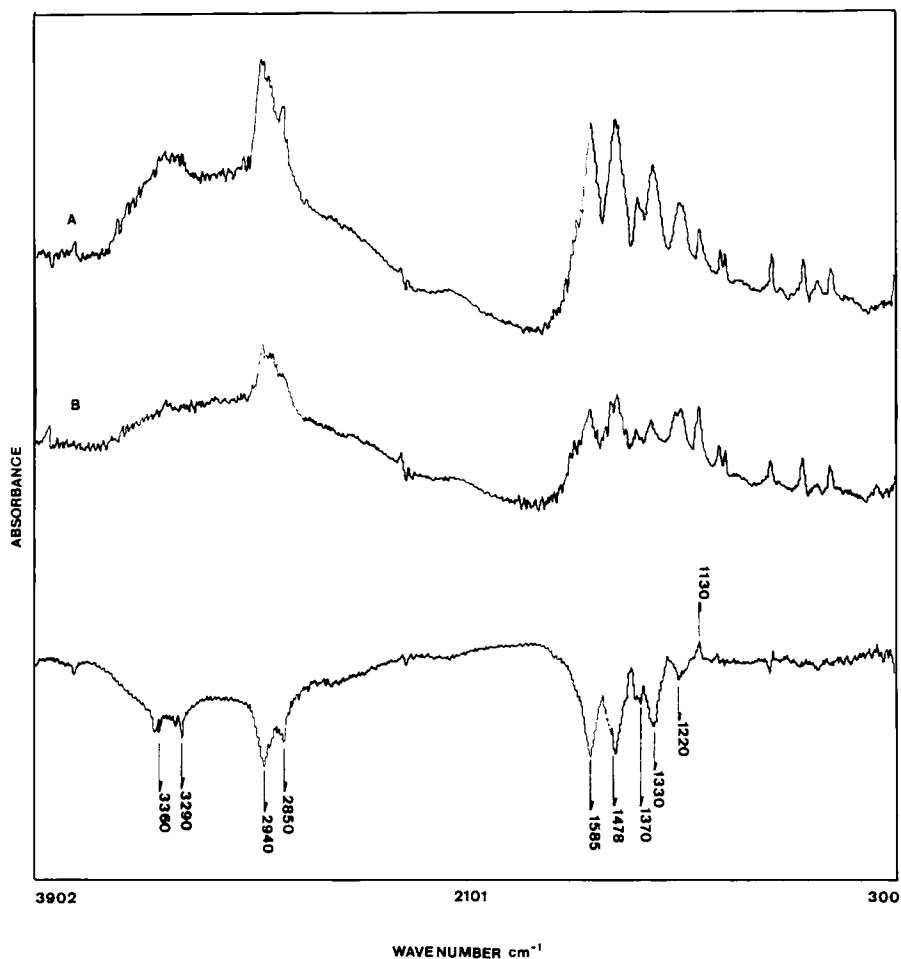


Figure 5 Difference FTIR spectra of L-H blend 1 : 1.08—(A) before and (B) after thermal treatment.

It is obvious that even a partial replacement of the carbonyl groups in basic L structure will induce changes in electronic effects and consequently changes in the intensities of the above-mentioned bands. It will be noted that methoxyl groups with a content of 17.2% count as the most abundant functional groups of L. Consequently, their IR characteristics are influenced the most by changes in L chemical structure.

(c) 1585; 1330 and 1220 cm^{-1} : The absorption at 1585 cm^{-1} is assigned to aromatic ring vibrations conjugated with an α carbonyl group. The 1330 and 1220 cm^{-1} absorbance are attributed to syringyl ring breathing with carbonyl stretching. All of these bands are indirectly related to some of the L carbonyl groups. Consequently, their negative absorbance is an effect of the carbonyl groups loss.

The spectral absence of the double bonds $\text{C}=\text{N}-\text{R}$ and $\text{C}=\text{C}-\text{NR}_2$ of imines and enamines, respectively, can be explained by the fact that both absorb in a region where different L functional groups, especially carbonyl (enumerated in the subsection on FTIR Spectroscopy) are spectrally active. Therefore, the absorptions arising from all these groups are superimposed, impeding their gain or diminution evaluation.

The difference spectra of the L-H mixture before and after thermal treatment disclosed a diminution in the amine and the carbonyl groups induced by

thermal treatment. Positive absorbance at 1130 cm^{-1} is an indication of enamine presence. The same difference spectra also suggest that the intensity of the bands related to the L aromatic methoxy groups are the one most affected by thermal treatment.

The FTIR difference spectra have provided information concerning the structural changes arising in L and confirmed that these changes are a result of L reaction with polyamine curing agent, which take place only during thermal treatment. Further quantitative data concerning L-H reaction were obtained by thermal and chemical analyses. The implications of these data will be discussed later.

Figures 6(A) and (B) shows the difference spectra obtained after digital subtraction of the EP control spectra from the EP-20L [6(A)] and also from EP-40L polyblends spectra [6(B)]. Both EP and EP-L polyblends were cured at room temperature. The EP common features in the spectra were canceled by subtraction and only the L absorbance was recorded. As expected, the spectra of L present in polyblends is similar to the spectra of the control L (Fig. 2), and one can assume that there is no interaction between L and the EP-curing agent system in the room temperature curing process.

In Figures 7(A) and (B) are presented the same difference spectra but in this case both EP and EP-L polyblends were thermally cured. The difference spectra from Figures 7(A) and (B) again is a record

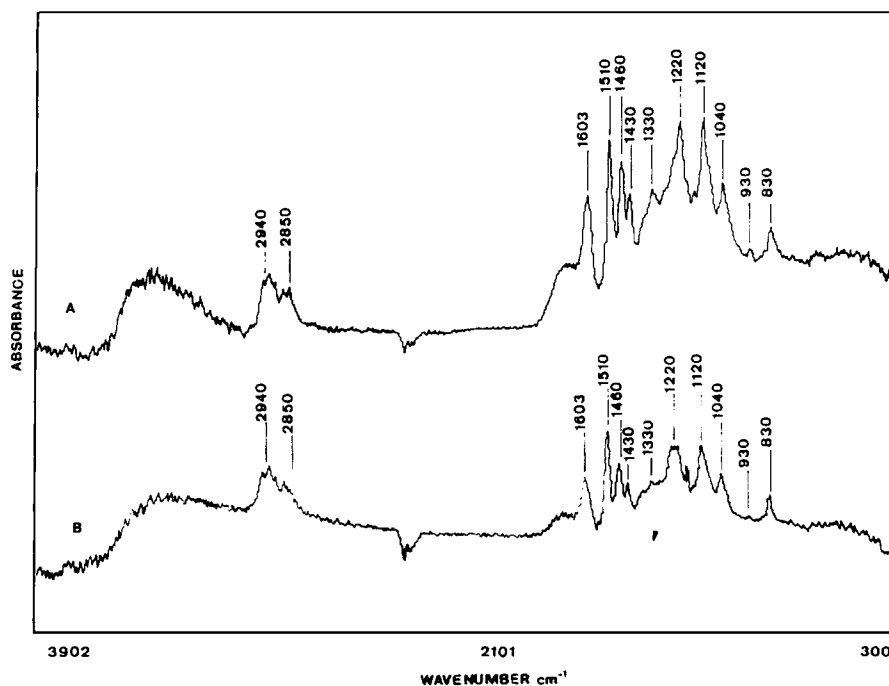


Figure 6 Difference FTIR spectra of EP-L polyblends, EP control cured at room temperature.

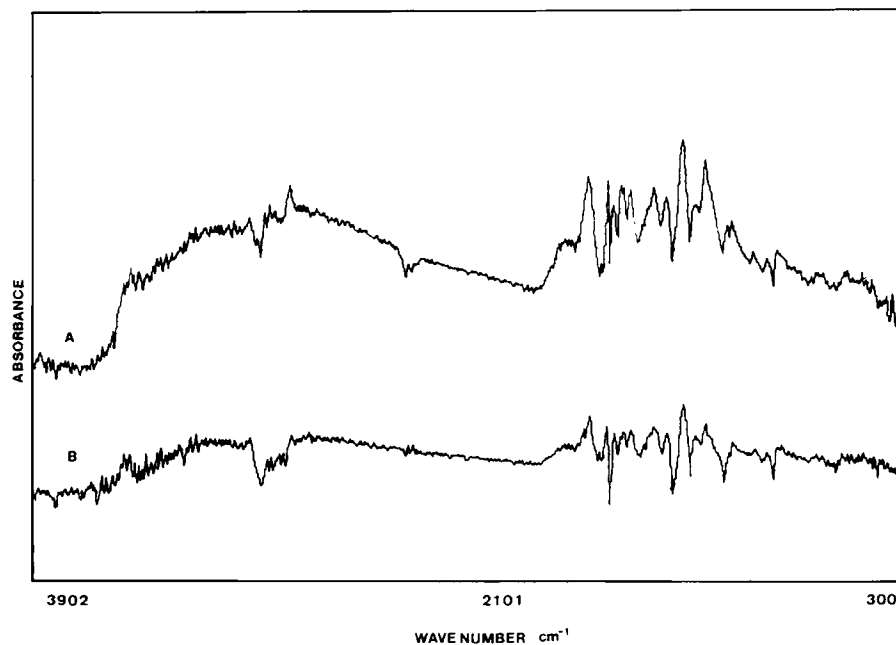


Figure 7 Difference FTIR spectra EP-L polyblends, EP control thermally cured.

of the absorbance of L which is present in the polyblends.

It is not surprising that this time its spectra is no longer similar with L control spectra. As may be seen in Figures 7(A) and (B), only a part of the spectral changes occurring in L after its reaction with polyamine curing agent (Fig. 5) can be detected easily in the spectra of L present in EP-L polyblends. The difference FTIR spectra present negative visible peaks at 2940 and 2850 cm^{-1} disclosing the same pattern as in Figure 5. In the meantime it is difficult to ascertain if there are really negative peaks at 1478 and 1370 cm^{-1} . Negative peaks at 1585, 1330, and 1220 cm^{-1} are not detectable. However, some new peaks appear at 1270 and 1191 cm^{-1} , which are difficult to link to a specific L or EP network modification.

In conclusion, the FTIR spectra clearly indicate the feasibility of a reaction between L and H through their carbonyl and amine groups, respectively, and that this can occur only at elevated temperatures. Part of the L spectral changes induced by this reaction are evident in difference spectra obtained from thermally cured EP-L polyblend and the EP control whereas none of them are identifiable in the difference spectra resulting from room temperature cured polyblends and the EP control.

Extractibility of L from EP-L polyblends

Although the extraction of L from EP-L polyblends is a time-consuming procedure, with a fairly high

degree of reproducibility, this method was used because of the ability of UV spectroscopy to detect L in very low concentrations. The degree to which L is chemically bonded to the polymer network was calculated from the L concentration in the EP-L polyblend solutions after extraction. The results are illustrated in Figure 8. These data disclosed a proportional relationship between the percentage of L bonded to the EP network during the curing process and its content in polyblends.

A small quantity of L was also extractable from the room temperature polyblends but the data scattering was too high for a reasonable interpretation.

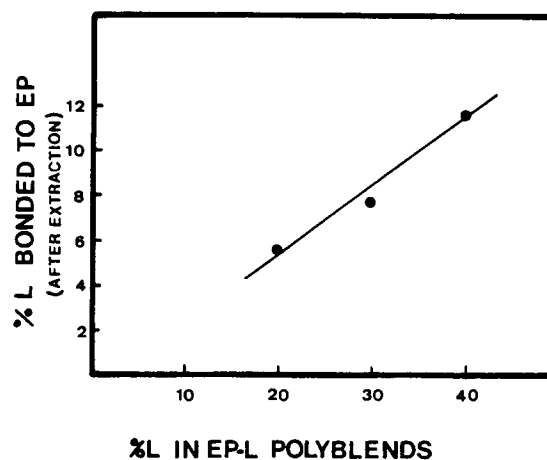


Figure 8 Extractibility of L from the thermally cured EP-L polyblends.

As can be seen from the Figure 8, the content of L irreversibly bonded to the EP network is quite modest. If one considers the bond occurring between carbonyl and amine groups, the results show that a very small quantity of amine groups is involved in bonding: i.e., ca. 0.25% in the case of the EP-20L polyblend (calculated at a content of 5% carbonyl groups in L). Consequently, one may consider with justifications that the bonding of L to the EP network occurs via unreacted amine groups.

Quantitative Data Concerning the Reactivity of L towards the Polyamine Hardener

Quantitative data concerning the reactivity of L toward the polyamine hardener (H) were undertaken in two directions:

- (i) The determination of kinetic parameters for the L-polyamine curing agent "reaction."
- (ii) The determination of the amine value of the hardener before and after its room temperature or 100°C temperature "reaction" with L.

First, the kinetic parameters of the reaction between L and H were determined. We were particularly interested in determining the activation energy (E) and the frequency factor value ($\log z$), in order to confirm that the L-H reaction does not compete with EP-H curing reaction. Several mixtures of L-H were prepared with different L-H ratios corresponding to their ratios in 10, 20, and 40% in EP-L polyblends. Then the kinetic data of each of them were investigated using the differential scanning calorimetry (DSC) technique with a single dynamic scan. A DuPont 910 differential scanning calorimeter connected with a DuPont 1090 thermal analyzer were used for the dynamic scans at a heating rate of 10°C/min. The DSC cell was calibrated with Indium.

The mixtures of the L-H for the DSC scans were prepared by thoroughly mixing the required components just before the start of the scan. About 8-10 mg of the mixture was used in each scan. The kinetic data were obtained using the DuPont, Borchard, and Daniel kinetic program. Details concerning the calculation of the kinetic parameters are discussed elsewhere.¹²

Figure 9 shows typical results of selected dynamic runs which were carried out at a single heating rate

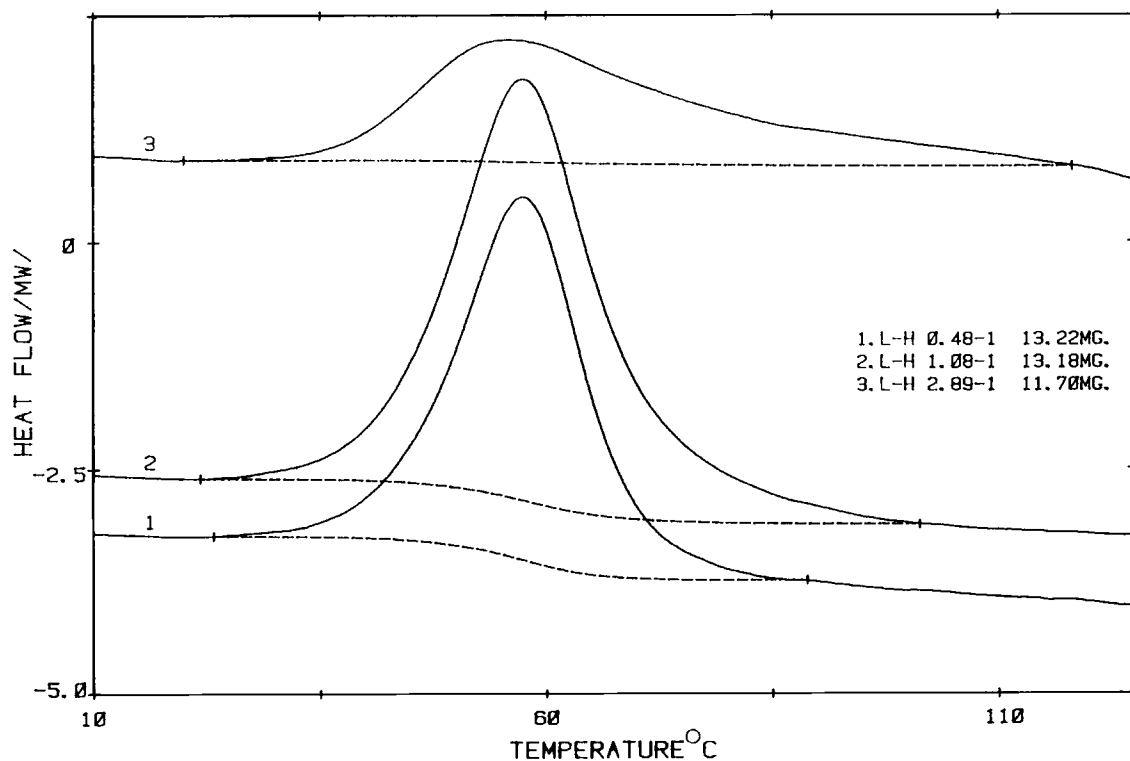


Figure 9 Typical DSC scans for L-H blends.

Table I Comparative Kinetic Parameters, for L-H Blends, EP, and EP-20L Polyblend

Kinetic Parameters	Sample Type				
	Lignin-Hardener Blend, L : H Ratio			EP Control ⁸	EP-20L Polyblend ⁸
	0.48 : 1 as in 10% L Polyblend	1.08 : 1 as in 20% L Polyblend	2.89 : 1 as in 40% L Polyblend		
Reaction order	1.33	1.82	4.97	1.34	1.51
Activation energy (kJ/mol)	153	154	177	70.3	73.4
Log Z (min ⁻¹)	24.4	24.4	28.4	9.79	10.3
Heat of reaction (J/g)	66.2	90.5	51.1	469	367
Max peak temperature (°C)	57.6	57.6	55.6	91.6	90.0

of 10°C/min, in the temperature range -10 + 180°C. The kinetic parameters which were calculated from these curves are listed in Table I. For the control, kinetic data similarly determined in a previous work for EP and EP-20L, are also shown in Table I.

As can be seen from this table, the energy of activation and the frequency factor value are more than twice as high for the L-H mixtures as the corresponding values for the EP control or EP-20L polyblend. This confirms that L-H reaction cannot compete with the EP-H curing reaction.

Another type of quantitative data related to the reactivity of the L-H system as a function of temperature was indicated by the determination of the H's amine number before and after its "reaction" with L. The amine number is represented by mg KOH equivalent to basic nitrogen of a 1 g curing agent sample. It was determined by titration with

anhydrous perchloric acid in acetic acid to the crystal violet end point.³¹

Several mixtures of L-H were prepared with L : H ratio similar to the L-H ratio in the blends for the determination of the kinetic parameters. After preparation, the blends were kept in a forced circulation oven at 100°C for 2 h. Duplicate samples were maintained at room temperature for 24 h. All the mixtures were in liquid form, except that corresponding to the L-H ratio as in EP-40L polyblend.

After preparation and the required thermal treatment, approximately 0.4-0.5 g from each blend was dissolved in 15 mL of glacial acetic acid and titrated with the perchloric acid solution.

The results are illustrated in Table II. Data from this table disclose that the reactivity of the system L-H is enhanced by thermal treatment, as the amine number of the mixture is lower than the value corresponding to the equivalent quantity of H in mix-

Table II Amine Number Data for the L-H Blends

Ratio L-H	Calculated as Function of H Content	Amine Number (mg KOH/g)					
		Without Thermal Treatment			With Thermal Treatment		
		Determined	Δ No. Toward Calculated		Determined	Δ No. Toward Calculated	
(mg)	(%)		(mg)	(%)			
0 : 1	608 ^a	—	—	—	—	—	—
0.48 : 1	410	411	+1	—	387	-23	-5.6
1.08 : 1	295	292	-3	—	257	-38	-12.9
2.89 : 1	166	—	—	—	144	-22	-13.3

^a Determined

tures. At room temperature the system appears to be chemically inactive as the amine number of the mixture is similar to those of the corresponding quantity of H.

CONCLUSIONS

The suggested reaction between L and the polyamine curing agent taking place only at elevated temperatures was confirmed by FTIR spectroscopy, thermal analysis, and determination of the amine number. FTIR spectroscopy has also substantiated the participation of some L carbonyl groups in this reaction. Kinetics data indicated that during the EP-L polyblends crosslinking process, the above reaction cannot compete with the addition reaction of epoxide groups with primary and secondary amines. The FTIR difference spectra of L present in thermally cured and room temperature cured EP-L polyblends show that L spectral changes can be induced only by the thermal crosslinking process.

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

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