Epoxy–Lignin Polyblends. III.
Thermal Properties and Infrared Analysis

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Synopsis

Differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA) and IR analysis were performed on a nonviscous epoxy polymer system (EP) with Kraft lignin (L) up to 20%. Mixtures of EP with similar amounts of silica (S) as in EP–L polyblends were used as a reference system for the analyses performed. EP–L polyblends cured at room temperature exhibit a single T_g, a fact characteristic for the monophasic systems. One-step tensile storage modulus vs. temperature curves, and related one-peak tensile loss modulus vs. temperature curves were found for all the EP–L polyblends. At about 30°C the tensile storage modulus of EP does not change in the presence of lignin in amounts up to 20% by weight. All these showed that L is miscible with EP and it does not affect the crosslinking at room temperature. IR spectra led to similar conclusions. The gradual decrease of the peak values of tan δ with the amount of L in polyblends is due to an increase in the tensile storage modulus and a decrease of the tensile loss modulus at temperatures close to T_g. This fact is explained by a stronger bond between EP and L, which could be formed at higher temperatures. The DSC and DMA data are in agreement with the mechanical properties of EP–L polyblends, which were reported previously.

INTRODUCTION

In a previous paper,[1] the authors reported the effect of an alkali lignin in amounts up to 20% by weight on the adhesive behavior and weathering of a bisphenol-A-based epoxy prepolymer cured with an aliphatic polyamine.

Next to cellulose, lignin is the most abundant macromolecular compound in the plant world. The biosynthesis of lignin from the monomeric phenyl–propane units is generally considered as a dehydrogenative polymerization.[2] Lignin has an aromatic nature, and functional groups such as hydroxyl, methoxyl, and carbonyl are contained within all kinds of lignins. Chemical delignification in the broadest sense includes all processes which result in partial or total removal of lignin from wood- or lignin-containing pulps, by the action of appropriate reagents.[3]

Kraft lignin used in the present study is a technical product, a byproduct of the forest products industry based on an alkaline delignification. In 1980, 20 million tons of Kraft lignin were generated from the pulping process in the U.S. pulp and paper industry alone.[4] A very small amount was used worldwide in thermosets, as antioxidants or fillers in rubber and as a component in polyblends with thermoplastics.[5]

Polyblending of epoxy polymer with Kraft lignin (10–20% by weight) improves the adhesive strength in tension and could reduce formulation cost without adversely affecting its adhesive strength in shear. An important

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improvement of this characteristics of both epoxy and epoxy–lignin poly-
blends is produced by a post-curing (4 h at 75°C). At elevated temperatures,
epoxy–lignin polyblend joints behave like epoxy adhesive joints. The addition
of up to 20% lignin does not change the durability of the epoxy adhesives.[1]

In the present study, results of dynamic mechanical analysis (DMA),
differential scanning calorimetry (DSC), and IR spectra are reported for the
epoxy polymer system (EP) and epoxy–lignin (EP–L) polyblends to obtain a
better knowledge of the curing process and the final network structure. As a
reference system, mixtures of EP with similar contents of silica (S) as in
polyblends were analyzed.

The glass transition temperature (T_g) as determined by DMA and DSC
provides the required information concerning the miscibility of the two
polymers and possible interaction of lignin with the epoxy system, since the T_g
is affected by degree of crosslinking and structure of the final network.[6-8]

The variation with temperature of the tensile and loss moduli, as deter-
mined by DMA, are also discussed. This investigation also provides informa-
tion on the miscibility of the polymers.[9,10]

Lastly, results of IR analysis, which were used to determine any possible
effects of L on the curing of the EP–L polyblends, are discussed.

EXPERIMENTAL

Materials

The epoxy prepolymer is a commercial modified diglicidyl ether of bisphe-
nol-A (Ciba-Geigy 1200 CA resin), and its low viscosity facilitated a good
dispersion of L; it was cured with a commercial accelerated aliphatic polyamine
(Ciba-Geigy 1200 CA hardener), using a stoichiometric weight ratio of 3.3 to 1.
The second polymer, Kraft lignin (L), is a commercial lignin (Tomlinite-
Domtar) extracted from a mixture of hardwoods and precipitated from the
black liquor with sulfuric acid, with the pH adjusted to a level of 6–7 with
carbon dioxide.

A crystalline silica (S) was used in the same amounts as L in the reference
samples. All samples were cured for 21 days at room temperature. The
polyblends and reference mixtures were prepared by manually mixing EP with
L or S for 5 min at room temperature; L or S were used in amounts of 5, 10, 15
and 20% by weight.

Procedures

A DuPont 910 differential scanning calorimeter was used to determine the
T_g's of the epoxy system, the polyblends, and L. Samples were heated at a
constant rate of 20°C/min, from 0 to 150°C, under a nitrogen atmosphere. A
preliminary thermal cycle was performed to erase previous thermal history.

A DuPont 982 dynamic mechanical analyzer was used to measure the
variation of tensile storage and tensile loss moduli with temperature. Samples
were set into oscillation at a constant amplitude of 0.2 mm and heated at a
constant rate of 5°C/min from 20 to 90°C under a nitrogen atmosphere.
Higher temperatures would not be used because the decrease of frequency was
below the sensitivity of the apparatus. DMA cannot be applied to powderlike

materials such as L which cannot be transformed without a substantial modification of their structure in the necessary solid specimens for this kind of testing.

The IR spectra were recorded with an infrared spectrophotometer (Beckman Model 4240); potassium bromide discs were used.

RESULTS AND DISCUSSIONS

DSC

In the preliminary thermal cycles, endotherms were observed for all samples due to volume relaxation caused by short range ordering of the polymers. From these endotherms one may find the relaxation energy by superposing the first and second DSC scan for each sample and measuring the area between them.[11,12]

In Figure 1 the relaxation energy of the EP–L polyblends is compared with that of the EP–S systems. It was found that the area between the two scans corresponds to the percentage of EP in the EP–S mixtures (Table I). This is about 5–6% lower than the corresponding percentage of EP in the polyblends with L the lowest being that with 10% L (6.7%).

Sub-T_g annealing studies of rubber-modified and unmodified EP disclosed that the relaxation energy is directly related to the time and temperature of annealing. This relationship between relaxation energy and time is in good agreement with time dependent changes of the mechanical properties in the epoxy matrix below T_g.[11]

Similarly, in terms of relaxation energies decrease, one may also explain the decrease of the adhesive strength in shear for the polyblends with 10% lignin after a curing of 3 and 115 days at room temperature, which was reported in our previous paper.[1] Unfortunately, the increase in tensile strength during this period cannot be explained in this way.
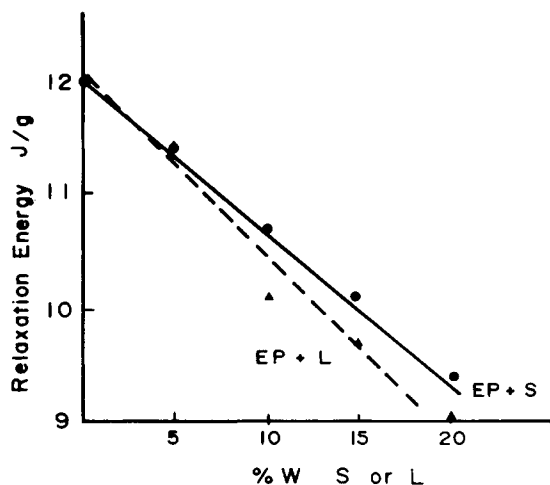

Fig. 1.   Relaxation energy variation vs. L or S content in EP.

TABLE I
Variation of the Relaxation Energy with the Amount
of Silica or Lignin in Epoxy Polymer

No.	Wt % of silica or lignin	Relax. energy according with 1 DSC scan (J/g)	Relax. energy in relation to 100% epoxy (J/g)
1	0	11.7	—
2	0	12.0	—
3	0	12.2	—
	Average	12.0	—
4		11.3	11.9
5	5 silica	11.2	11.8
6		11.4	12.0
	Average	11.3	11.9
7		10.6	11.8
8	10 silica	10.8	12.0
9		10.7	11.9
	Average	10.7	11.9
10		10.2	12.0
11	15 silica	10.4	12.2
	Average	10.3	12.1
12			
13	20 silica	9.5	11.9
14		9.4	11.8
		9.5	11.8
	Average	9.5	11.8
15			
16	5 lignin	11.5	12.1
17		11.5	12.1
		11.2	11.8
	Average	11.4	12.1
18		10.1	11.2
19	10 lignin	10.3	11.4
20		9.9	11.0
	Average	10.1	11.2
21		9.9	11.6
22	15 lignin	9.7	11.4
23		9.6	11.4
	Average	9.7	11.4
24		9.2	11.5
25	20 lignin	8.9	11.1
26		8.9	11.1
	Average	9.0	11.3

Figure 2 shows the typical DSC diagrams (second thermal cycle), for the cured EP, EP–20% S mixture, EP–20% L polyblends, and L. One can see that the DSC profile curves remain unchanged, even after polyblending with 20% L or mixing with 20% S.

Figure 3 shows the variation of T_g with the amount of L or S as determined with both DSC and DMA. The data represent an average of at least three tests with a variation of max. $\mp$ 0.3°C. The T_g values were determined as the midpoint temperature on the slopes of the heat curves and verified with the maximum peak temperature on the derivative of the heat flow curves. Com-
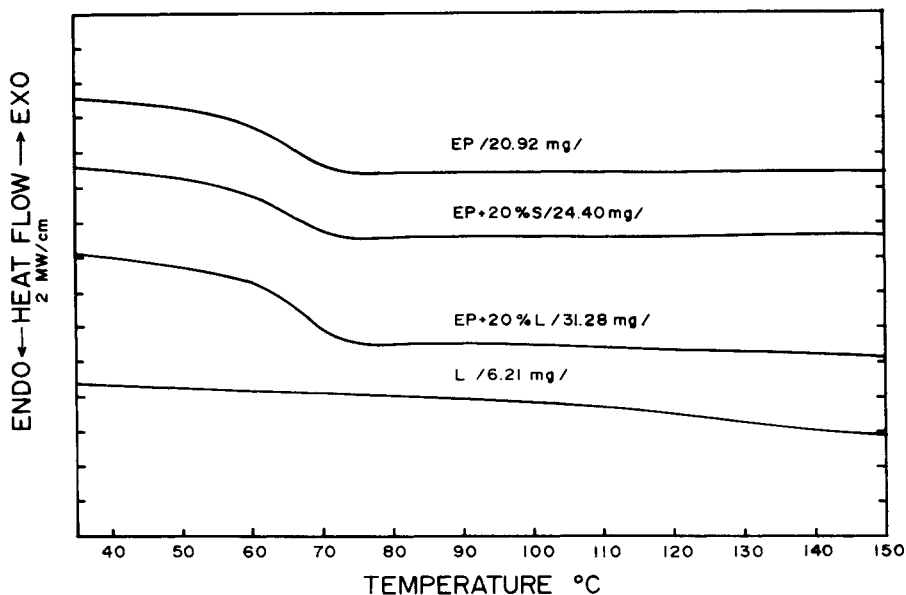
Fig. 2. DSC scans for EP, EP–20% S mixture, EP–20% L polyblend, and L.

ments concerning this data are as follows:

(1) Apparently the polyblends exhibit a single T_g characteristic for monophasic systems.

(2) The T_g's of the polyblends are very close to that of the EP with a very slight tendency to increase with the L content. In the case of S the T_g's are also very close to that of the EP but with a very slight tendency to decrease as the S content increases.

According to extensive experimental evidence existing in the literature, Theocaris and Spathis[12] explain that the increase or the decrease of the T_g of a filled polymeric matrix is due to the presence of a reinforcing agent. Based on a model for the definition of the modulus of elasticity of the composites, an
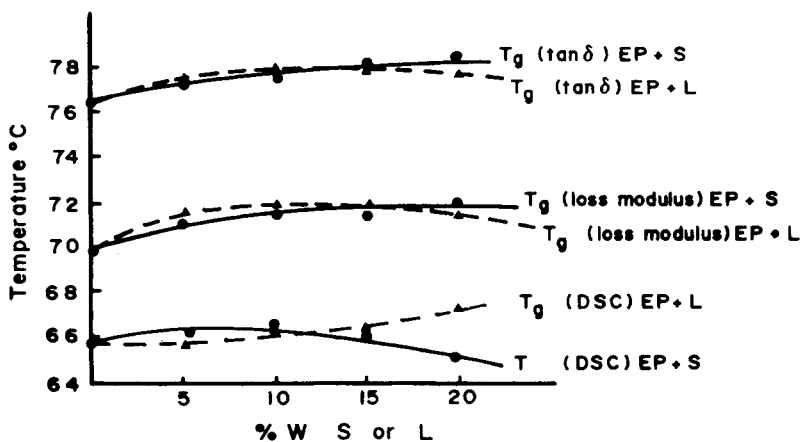

Fig. 3. T_g variation with the content of L or S in EP, as determined by DSC and DMA.

explanation of the modulus behavior was given. The basic consideration of this model was the concept of the existance of an interphase, i.e., a phase created by the matrix phase around each particle of the filler phase with different properties than the matrix itself. This difference leads to two well-separated regions of the composite with two different T_g's. The combination of two T_g's determines the resulting T_g of the composites. When the T_g of the interphase is larger than that of the matrix, the resulting T_g of the composite increases, compared to the respective matrix and vice versa.

According to this interphase concept in the case of DSC analysis, the phase created by the EP matrix around the L particles is more strongly bonded (e.g., a higher T_g) than that produced around the silica particles. The higher temperatures applied for running, i.e., 0–150°C in two consecutive DSC scans, may favor the formation of these stronger bonds, when compared with 30–90°C in the DMA scans. In the same way, one can explain the increase of adhesive strength in shear for the polyblends cured at elevated temperatures as reported earlier.[1]

(3) The T_g determined for L varied between 132 and 136°C, and these differences are explained by taking account of the heterogeneity (MW and microstructure) of this commercial product.

Our value is in agreement with some published data, i.e., 135–138°C for milled wood lignin[13] determined by DTA analysis and Kraft lignin, 154°C, determined on paper strips by torsional pendulum analysis.[14]

Even in the case of 20% L in EP–L polyblends, its T_g does not seem to be detectable on heat flow curves or on their derivatives. It is impossible that the incidence of L–EP bonding in polyblends due to the OH groups of L is high enough to effectively restrain the segmental motion characteristics of L without affecting that of the EP matrix to the same extent.

(4) The ratios between slopes (or sharpness) of the transitions (Fig. 2) and the weights of the samples are similar in all cases.

These observations are essential criteria for determining the miscibility of two polymers.[15]

DMA

Figures 4–6 show the variations of the tensile storage modulus at 30°C, maximum tensile loss modulus, and maximum tan δ for EP–L polyblends and EP–S reference mixtures. It can be seen that there is very little change in the shape of the tensile storage modulus and maximum tensile loss modulus curves for the EP–L polyblends.

The variation of tensile storage modulus for EP–S mixtures as function of S concentration fits well with the simplest theoretical equation attributed to Einstein and discussed by Nielsen,[17] i.e.,

$$G = G_1(1 + 2.5\phi_2)$$

where G_1 = modulus of the matrix, G = modulus of the reinforced matrix, and ϕ_2 = volume fraction of the reinforcing material.

As can be seen from Figure 6, max tan δ practically does not change for the EP–S mixtures in the selected interval of concentrations, but for the EP–L
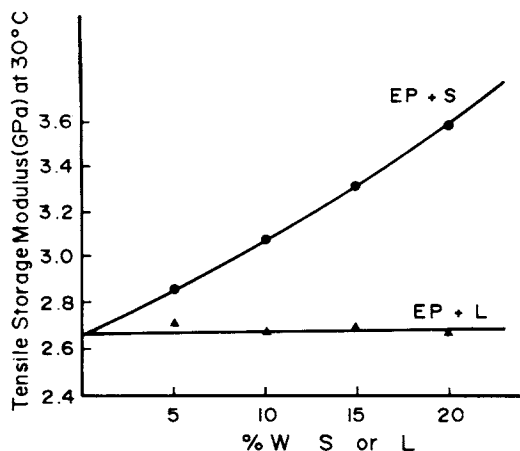
Fig. 4.   Tensile storage modulus variation at 30°C vs. L or S content in EP.

polyblends there is an orderly decrease in the values of tan δ from the pure EP to the polyblend with 20% L. As can be seen from Figure 7, (tensile storage modulus and tensile loss modulus at T_g vs. L or S content in EP), the orderly decrease of tan δ, for EP–L polyblends is due to an increase of the tensile modulus and a decrease of the tensile loss modulus.

This phenomenon might be explained also by a stronger bond between EP matrix and L at higher temperatures than the ambient one.

The T_g's obtained by DMA were determined from the peak values in the tensile loss modulus profiles and tan δ. The T_g's of the EP–L polyblends and EP–S mixtures are again very close to that of the EP, with a very slight tendency to increase with the amount of S and a very slight tendency to decrease from the pure EP to the polyblend with 20% L (see comment on DSC analysis).

A one-step tensile storage modulus vs. temperature curve and a related one-peak tensile loss modulus vs. temperature curve (as determined in our
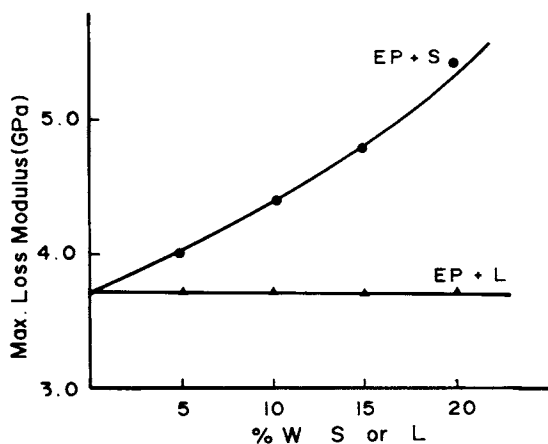

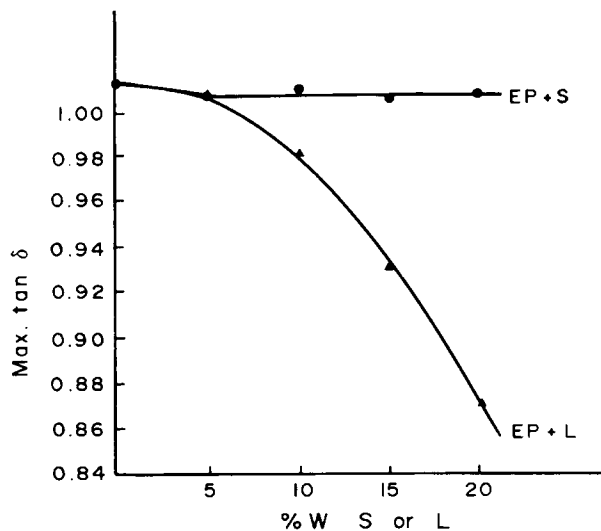Fig. 5.   Maximum loss storage modulus variation vs. L or S content in EP.

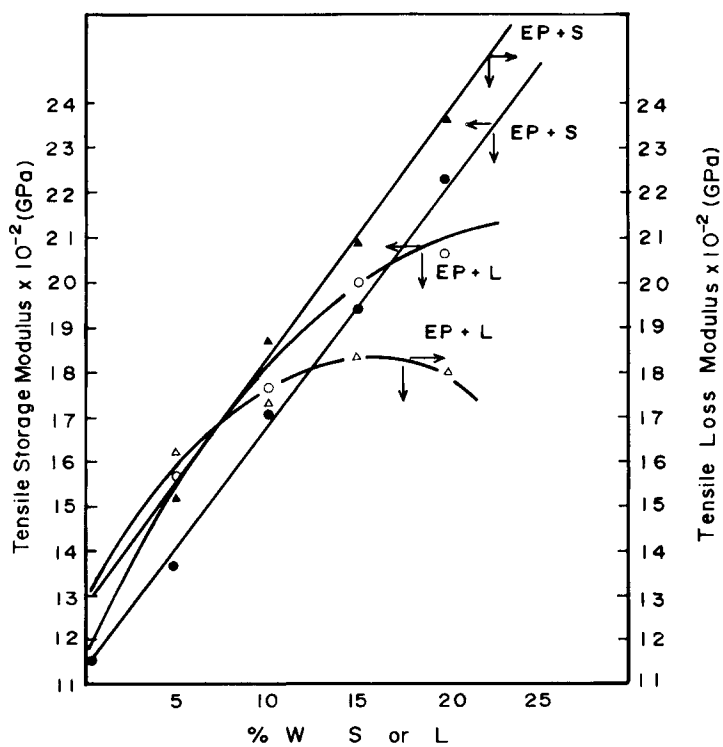Fig. 6. Maximum tan δ peak vs. L or S content in EP.

Fig. 7. Tensile storage modulus and tensile loss modulus at T_g vs. L or S content in EP.

DMA tests), both characteristics of miscible polymers, were observed for the EP, EP–L, and EP–S systems.

In the case of DMA, the presence or absence of T_g of lignin could not be detected due to the important drops in frequencies at temperatures above 90°C, which were below the frequency limits detectable by the apparatus.

From DMA data it seems that the L up to 20% in polyblends does not react with EP and consequently does not significantly affect the crosslinking process at room temperature.

It was demonstrated[8,18] that, with higher or lower quantities of hardener (or epoxy) than the stoichiometric amount, both the tensile storage modulus and max tan δ peak are shifted below or above the data corresponding to the stoichiometric amounts.

Infrared Analysis

Figure 8 presents the IR spectra of EP system before curing (spectrum A), cured EP (spectrum EP), and cured EP–20% L (spectrum EP–L20), all three
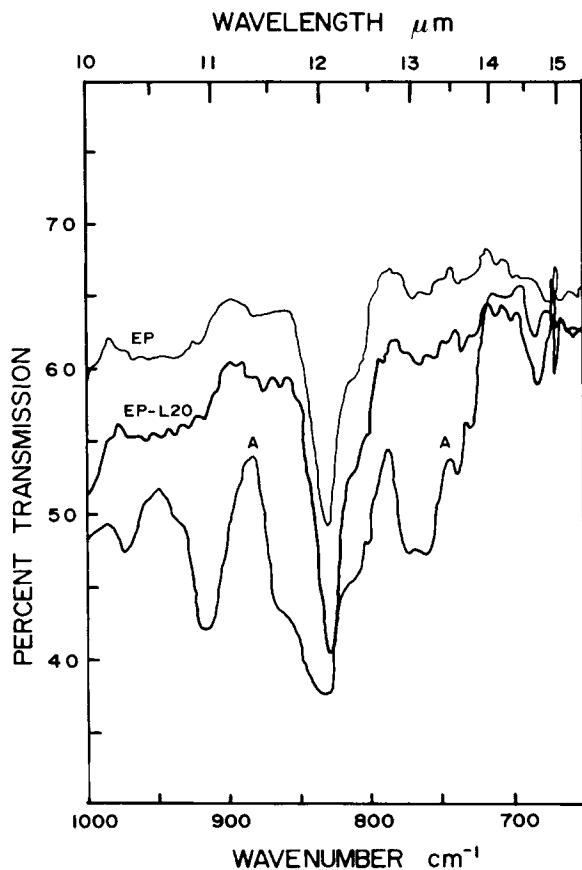

Fig. 8. IR spectra changes in the range 650–1000 cm^{-1}: (A) epoxy; (EP) unmodified epoxy polymer system; (EP–L20) epoxy–lignin polyblend with 20% L by weight.

spectra in the frequency range 650–1000 cm^{-1}, where main modifications of the EP spectrum take place during curing.

After curing, the most obvious changes in spectra are those due to the disappearance of the bands characteristic for the epoxy ring at 920, 870, and 760 cm^{-1}.[19] As can be seen from Figure 8, the disappearance of these bands is similar for both cured EP and EP–20% L polyblend.

The increase of the absorption band from the 830 cm^{-1} characteristic for the aromatic C—H band in p-substituted benzene ring is due to the aromatic character of L.

The other changes in IR spectra are also characteristic for the epoxy curing process, i.e., the bands of saturated ether at 1160 and 1140 cm^{-1} (not presented in this paper) are also similar to the case of the cured EP and cured EP–20% L polyblend.

IR data permit the conclusion that L does not participate in the curing of EP.

CONCLUSIONS

DSC, DMA, and IR data show that no reaction takes place between EP and L during the curing of EP.

A single T_g of EP–L polyblends, a one-step tensile storage modulus vs. temperature curve and a related one-peak tensile loss modulus vs. temperature curve indicate the miscibility of EP with L.

The orderly decrease of tan δ for EP–L polyblends from the pure EP to EP–20% L polyblend is due to an increase in tensile storage modulus vs. tensile loss modulus at temperatures close to T_g and is an indication of a stronger bond between EP and L, at an elevated temperature.

The slight tendency of the T_g's to increase in the DSC scans and a tendency to decrease in the DMA scans, proportional to L content, lead to the same conclusion of a stronger bond between EP and L at higher temperatures.

These conclusions are in agreement with the important improvement of the adhesive strength in shear produced by post curing EP–L polyblends at 75°C as reported previously.

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