Multiphase materials with lignin: 2. Blends of hydroxypropyl lignin with poly(vinyl alcohol)

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Polymer blends consisting of hydroxypropyl lignin (HPL) and poly(vinyl alcohol) (PVA) hydrolysed to the extent of 75, 88 and 96% were prepared by casting from dimethylformamide solution. The resulting films were studied with regard to their morphology by scanning electron microscopy, differential scanning calorimetry and dynamic mechanical thermal analysis. Results suggest that HPL/PVA blends form homogeneous and at least partially miscible materials (with separated phases of <2000 Å) at any composition. This is attributed both to similarity in solubility parameter and to the formation of hydrogen bonds. Supporting evidence is derived from scanning electron microscopy of freeze-fractured surfaces, from quantitative melt endotherm measurements, and from measurements of the position and range of glass transition temperatures.

(Keywords: lignin; lignin derivatives; blends; hydrogen bonding; thermal analysis; dynamic mechanical analysis)

INTRODUCTION

Polymer blends constitute a group of materials that are simple to fabricate, do not corrode and have lower weight than the conventional materials they replace[1-6]. Blend properties are governed by type and extent of interaction between component polymers. Two macromolecules may be considered 'miscible' if they form a single, homogeneous phase and intimate mixing is achieved on a molecular level. On the other hand, 'compatibility' indicates the usefulness of a blend. Thus, immiscible blends do in certain cases exhibit good mechanical properties and are said to be mechanically compatible[7]. Mechanical compatibility in immiscible blends is generally related to good interfacial adhesion between the phases of the blend constituents.

The basic thermodynamic equation describing the state of miscibility of a two-component system is given by the Gibbs free-energy equation:

$$\Delta G_{\mathrm{mix}} = \Delta H_{\mathrm{mix}} - T\Delta S_{\mathrm{mix}} \tag{1}$$

where ΔG_{mix} is the Gibbs free energy of mixing, ΔH_{mix} is the enthalpy of mixing, ΔS_{mix} is the entropy of mixing and T is the absolute temperature. In order for a mixture to be miscible ΔG_{mix} must be negative. Thus, the miscibility of a two-component mixture depends on the sign and magnitude of ΔH_{mix} and ΔS_{mix}. When dealing with polymer blends, three important parameters affect the magnitude and sign of ΔH_{mix} and ΔS_{mix}: (1) solubility parameter, (2) specific interactions, such as hydrogen bonds, and (3) molecular weight. This study focuses on solubility parameter and specific interactions of hydroxypropyl lignin (HPL) with poly(vinyl alcohol) (PVA).

The solubility parameter δ is a measure of the cohesion of a material, or of the strength of molecular attractive forces between like molecules. The relationship between the solubility parameter and the enthalpy of mixing is given by the Hildebrand equation[8]:

$$\Delta H_{\mathrm{mix}}/V = (\delta_1 - \delta_2)^2\phi_1\phi_2 \tag{2}$$

where V is the molar volume of the mixture, $\delta_{1,2}$ are the solubility parameters of components 1 and 2, and $\phi_{1,2}$ are the volume fractions of components 1 and 2. This equation expresses the concept that two polymers are miscible when their solubility parameters become perfectly matched. Equation (2) indicates that the predicted ΔH_{mix} is always positive or at best zero (in the absence of other attractive forces). Thus the Hildebrand equation suggests that phase separation rather than miscibility is favoured. However, many polymers have been reported to be miscible[1,4]. The mechanisms responsible for polymer–polymer miscibility are attributed to such specific interactions between two macromolecules as hydrogen bonding, nπ and π–π complex formation, charge transfer and ionic interactions. They have all been found to be responsible for miscibility in polymer blends[9]. Considering that ΔH_{mix} values are the net result of breaking solvent–solvent (1–1) and polymer–polymer (2–2 and 3–3) bonds and creating new polymer–polymer (2–3) bonds, the importance of the solubility parameter and specific interactions between two polymers is clearly understood[10,11].

A previous study[12] dealt with the properties of HPL/poly(methyl methacrylate) (PMMA) blends in relation to blend ratio and molecular-weight effects. This study is to formulate new materials from hydroxypropyl lignin by exploring the effect of solubility parameters and specific interactions between polymers. HPL and four types of PVA, hydrolysed to the extent of 0, 75, 88 and 96%, represent the components of the model system. By

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using the three different PVAs, the number of hydroxyl groups available for hydrogen bonding, and the difference in solubility parameter, can be regulated. The morphology, and the thermal and mechanical properties of these novel polyblends are to be described in terms of miscibility in relation to solubility parameter, and in terms of interaction in relation to volume fraction.

MATERIALS

Hydroxypropyl lignin (*HPL*)

HPL was prepared in the normal manner[13] from a commercially available kraft lignin (Indulin-AT from Westvaco Corporation, Charleston, South Carolina). It had a hydroxyl content of 6.5% and a glass transition temperature (T_g) of 63.5°C.

Poly(*vinyl alcohol*) (*PVA*)

Four commercially available (Scientific Polymer Products, Inc.) PVAs were used in this study. Important parameters for each were as shown in *Table 1*.

METHODS

Solution casting of blends

Separate 10% (w/w) solutions of each component were prepared using dimethylformamide (DMF). In order for the PVAs to dissolve fully, heating to 80°C was required. The solutions containing the two components were mixed together and allowed to stir at 80°C for 2 h. This solution was poured into Teflon moulds and the solvent was allowed to evaporate at room temperature for 2 days. The resulting films were then dried in a vacuum oven at 100°C for one week, and stored in a desiccator containing P_2O_5.

Scanning electron microscopy (*SEM*)

Freeze-fractured surfaces were observed using an AMR 900 scanning electron microscope. The samples were coated with 100 Å of gold–palladium to prevent charging. Samples were then observed at magnifications ranging from 500 to 5000 times.

Differential scanning calorimetry (*d.s.c.*)

Thermograms were obtained with a Perkin–Elmer DSC-4 instrument on samples weighing ~20 mg. Scans were started at a temperature of 30°C and heated at a rate of 10°C min^{-1} to a final temperature of 210°C. They were quenched and rescanned under the same conditions. All scans were run under a dry nitrogen atmosphere. The glass transition temperature (T_g) was defined as one-half the total change in heat capacity (C_p) occurring over the transition region. This method was used for both starting materials and polyblends.

Dynamic mechanical thermal analysis (*d.m.t.a.*)

Dynamic mechanical properties of the polyblends were determined using a Polymer Laboratories d.m.t.a. Samples were tested in the bending mode as single cantilever beams with a free length of 1 mm. The sample dimensions varied in order that the log k value remained between 3.5 and 4. All samples were run at a heating rate of 5°C min^{-1} and a frequency of 1 Hz.

Table 1 Poly(vinyl alcohol) characteristics

PVA type	T_g (°C)	δ ($\text{cal}^{1/2}\ \text{cm}^{-3/2}$)	$\bar{M}_w$
96% hydrolysed	77	12.6	96 000
88% hydrolysed	70	11.8	96 000
75% hydrolysed	60	10.6	3 500
0% hydrolysed	32	9.6	unknown

RESULTS AND DISCUSSION

Blend structure

A common qualitative technique for estimating blend miscibility consists of visual inspection. A miscible or compatible blend produces a clear and transparent film, while films of immiscible blends are usually diffuse and opaque. Although optical transparency provides some measure of compatibility, it fails to assure miscibility since blend constituents may have matching refractive indices[14]. All blends made with HPL and all three (hydrolysed) PVAs had the characteristically brown colour, but they were fully transparent and clear. This represents a symptom of compatibility.

SEM micrographs of 25% HPL/PVA* blends (*Figure 1*) reveal distinct phase separation and domain structure for PVA(0)* (*Figure 1a*). By contrast, *Figures 1b*, *c* and *d* show that 25% HPL/PVA(96), PVA(88) and PVA(75) blends have smooth fracture surfaces, and represent a homogeneous material. No sign of phase separation or domains can be detected. (The limits of detection are ~1500–2000 Å.) Therefore, under the conditions given, SEM results for HPL/PVA blends suggest that at least a partially miscible system exists. It is interesting to note that the solubility parameters of the PVAs used ranged from 12.6 to 10.6 $\text{cal}^{1/2}\ \text{cm}^{-3/2}$, yet all blends containing these alcohols showed the same homogeneous morphology. This is surprising since miscibility is limited to polymers having solubility parameters within 0.5 $\text{cal}^{1/2}\ \text{cm}^{-3/2}$. The results demonstrate that only PVA(0), which has a solubility parameter of 9.6, exhibits distinct phase separation. The method of matching solubility parameters would suggest that HPL with a solubility parameter of ~11.1 $\text{cal}^{1/2}\ \text{cm}^{-3/2}$ is just as miscible with PVA(96) ($\delta = 12.6\ \text{cal}^{1/2}\ \text{cm}^{-3/2}$) as with PVA(0) ($\delta = 9.6\ \text{cal}^{1/2}\ \text{cm}^{-3/2}$). However SEM results indicate phase separation with PVA(0) and miscibility (or compatibility) with PVA(96). This difference is explained with secondary association based on hydrogen bonding that can occur between the hydroxy groups found in both HPL and PVA(>0) but is not present in PVA(0).

Thermal properties

Differential scanning calorimetry (*d.s.c.*). A typical d.s.c. thermogram of an HPL/PVA blend (*Figure 2*) indicates a T_g at 75°C, and a T_m at 201°C. Blends containing 5, 25 and 40% HPL all showed single T_g and T_m (for PVA). However, differences in the shape of the melting endotherms of PVA(96), PVA(88) and PVA(75) were noticed. Whereas PVA(96) produced a sharp melt endotherm, PVA(88) and PVA(75) displayed more gradual, broader endotherms, which broadened as OH content declined. This difference is attributed to the different degrees of crystallinity found in the three polymers[15]. PVA(96) has a more uniform chemical

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*The number preceding the designation of blend components represents the weight fraction of the first-mentioned component; and the figure in parentheses following 'PVA' designates the extent of hydrolysis

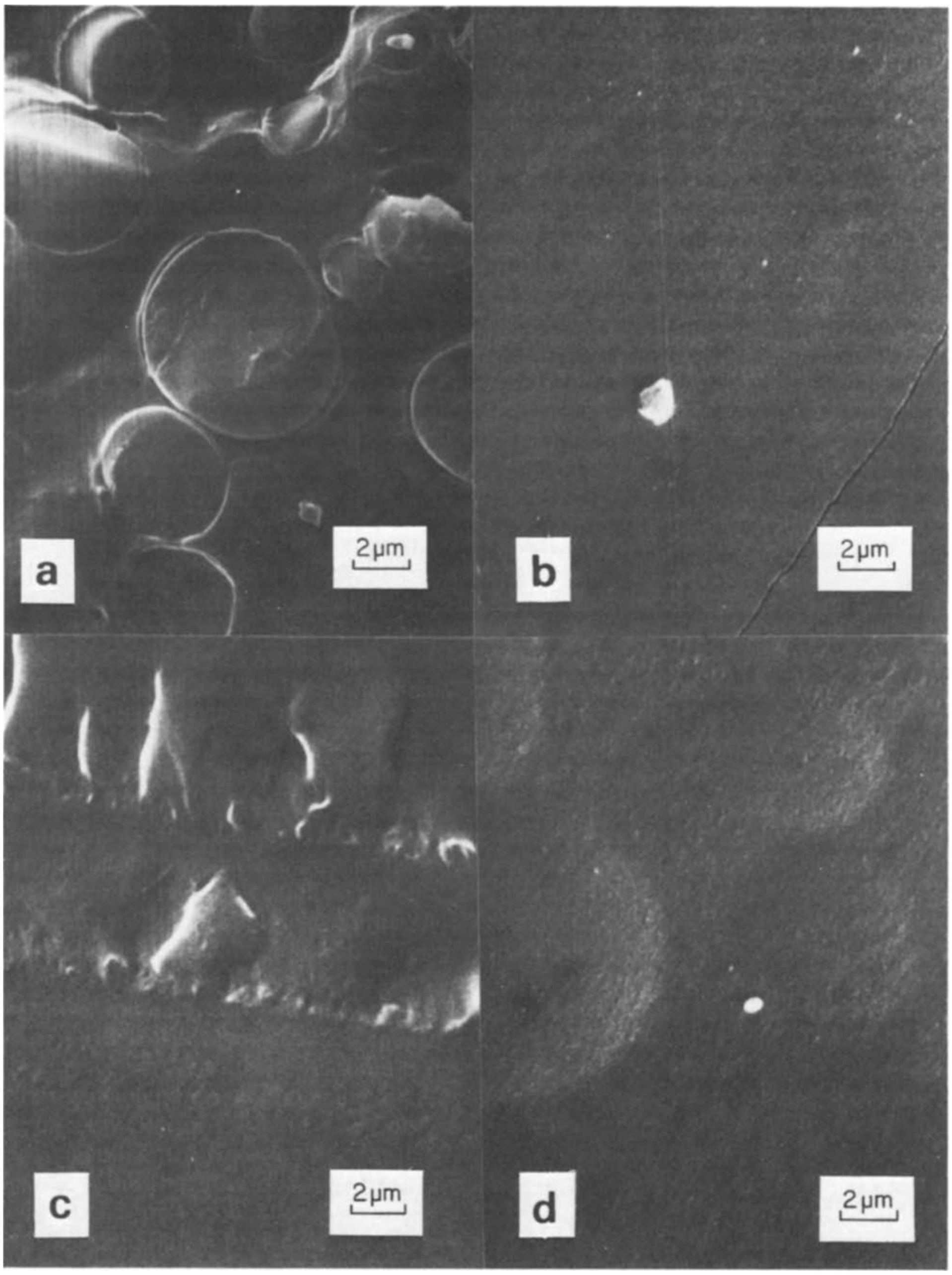

Figure 1 Scanning electron micrographs of 25% HPL/PVA blends in relation to degree of PVA hydrolysis: (a) blend with PVA(0); (b) blend with PVA(75); (c) blend with PVA(88); and (d) blend with PVA(96)

structure and thus forms crystals that melt over a narrower range than do PVA(88) and PVA(75).

The area under the melt endotherm of a d.s.c. thermogram (i.e. heat of fusion), in calories per gram of PVA, is plotted against HPL content (*Figure 3*). In blends of PVA(96) a decrease in peak area is observed at 5% HPL content. At 25% HPL the peak area returns to that of pure PVA(96), and it remains constant at 40% HPL content. Blends of PVA(88) and PVA(75) on the other hand show no change at a 5% HPL content, but a decrease at 25% HPL content. As with PVA(96), blends of PVA(88) and PVA(75) containing 40% HPL had peak areas equal to that of their respective unblended parent PVAs. A reduction in peak area indicates a change in the organization or the extent of crystallinity in that material. In the case of polymer blends changes in crystalline structure can result from polymer–polymer interactions in the amorphous phase. Such interactions create disorder in the crystal, thereby reducing the enthalpy of the phase change[16,17]. The observed reductions in melt endotherm area (*Figure 3*) may therefore indicate the existence of polymer–polymer interactions between HPL and PVA molecules.

Analysis of the glass transitions for the HPL/PVA blends was made difficult by the fact that the HPL had a T_g of 63.5°C and the PVA(96), PVA(88) and PVA(75) had T_g values of 77, 70 and 60°C, respectively. This difference in T_g between two blend components is insufficient to support homogeneous blend morphology by thermal analysis and to rule out that transitional smearing or overlapping will not hamper the observation of two separate T_g[18]. Since the maximum difference in the T_g values of the HPL/PVA components is only 13.5°C, it was not expected that two separate transitions were resolved. But analysis of the actual transition temperatures rather than the shape of the transitions can

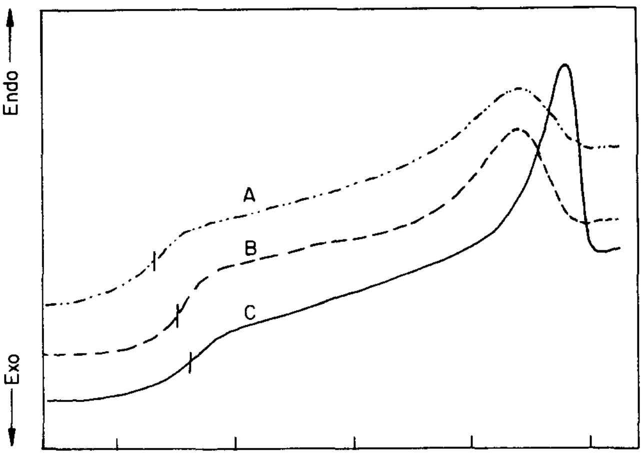

Figure 2 D.s.c. thermograms of 25% HPL/PVA(75) (A), PVA(88) (B) and PVA(96) (C)

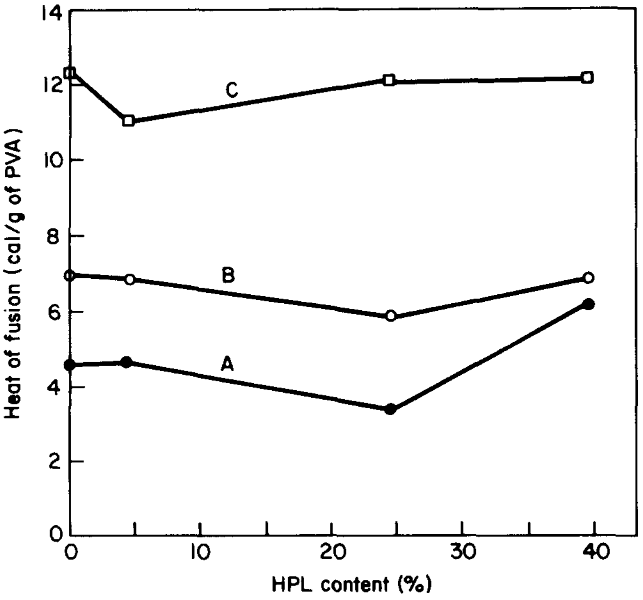

Figure 3 Relationship between heat of fusion and HPL content for PVA(75) (A); PVA(88) (B) and PVA(96) (C)

still provide information concerning the state of the HPL/PVA blends.

Theoretically miscible polymer blends will show T_g values that are intermediate between those of the parent polymers. They follow such models as the Fox or Gordon–Taylor relationships[19,20]. However, in the case of HPL/PVA blends the T_g data did not follow any of these well known models, and T_g values above those of the parent polymers were observed. In order to describe this phenomenon, the quotient of the experimental blend T_g divided by the predicted (Fox) T_g was related to HPL content (*Figure 4*). The data indicate that PVA(96) and PVA(88) display almost identical trends with virtually all of their data points having values above unity. This suggests that the experimental T_g values are higher than those predicted by the Fox equation. It is also apparent that the greatest deviation from the predicted T_g is seen at 25% HPL content. Deviations from linear models, such as Fox, have been reported in blends that are miscible or partially miscible, and these have been described as the result of strong specific interactions[21–23]. Therefore it is believed that interactions between HPL and PVA are responsible for the observed increase in T_g quotient, and that the greatest interactions are observed at 25% HPL for PVA(96) and PVA(88), and at 40% HPL content for PVA(75). For the PVA(88) blends this result correlates well with that observed with the melt endotherm data, which indicated a reduction in the energy needed to disrupt the crystalline structure of PVA at the 25% HPL level. However, it should be noted that the PVA(75) blends followed the PVA(88) blends in terms of melt endotherms yet they did not follow the trend of the PVA(96) and PVA(88) blends seen in *Figure 4*. The reason for this discrepancy may be attributed to molecular-weight differences between PVAs. The PVA(96) and PVA(88) samples had molecular weights (M_w) of 96 000 whereas PVA(75) had a molecular weight (M_w) of 3500. On the other hand, at a HPL content of 40%, the PVA(75) blend had a T_g above that predicted, which once again is believed to be due to strong specific (secondary) interactions.

These interactions are also believed to result in blend T_g values that are higher than those of the parent polymers. The presence of strong interactions could result in an amorphous component that coexists in a more closely associated state with another polymer, thereby reducing free volume and raising T_g. Another possible explanation for the observed increase in T_g is suggested in studies on PVA gels. These gels are not gels in the classical sense since their crosslinks are formed not by primary chemical (covalent) bonds, but rather by secondary bonds such as hydrogen bonds[24]. If such quasi-crosslinks were formed in HPL/PVA blends in large enough numbers, they could severely restrict Brownian motion of the long-chain molecules, thereby raising T_g.

Dynamic mechanical thermal analysis (*d.m.t.a.*). The tan δ curve for pure PVA(96) (*Figure 5*) shows a sharp α transition at 88°C, which signifies large-scale molecular motion in the amorphous phase. Also present is a shoulder centred at 130°C, which has been reported by several investigators, and is attributed to torsional or

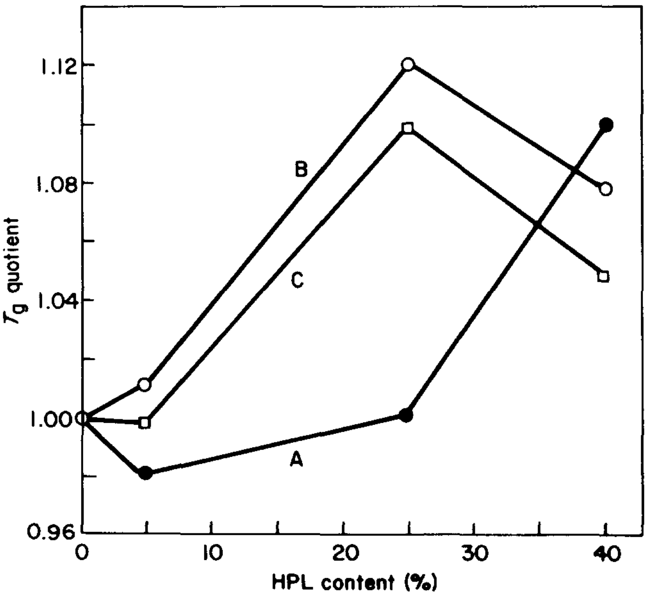

Figure 4 Relationship between T_g quotient and HPL content for PVA(75) (A); PVA(88) (B) and PVA(96) (C). ('T_g quotient' is the ratio between the experimental blend T_g and the T_g predicted by the Fox equation for the same blend)

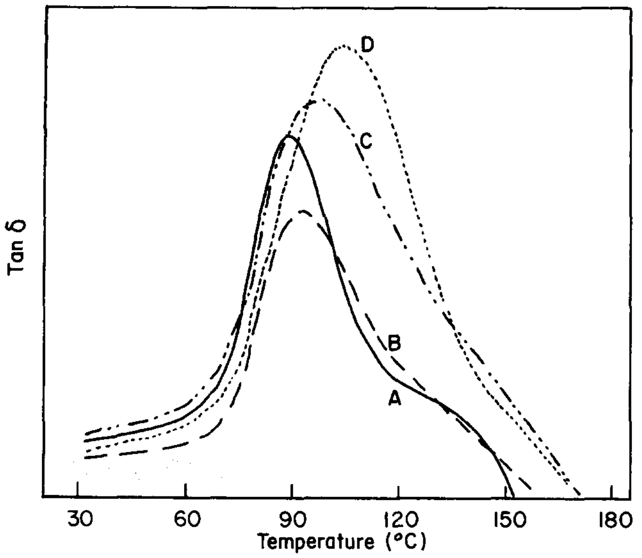

Figure 5 Relationship between tan δ of the HPL/PVA(96) blends and HPL content: A, 0% HPL; B, 5% HPL; C, 25% HPL; and D, 40% HPL

rotational motion of chains closely associated with the crystal lattice of PVA[25–27]. The PVA(96) blend containing 5% HPL displays an α transition that has shifted from 88°C (for pure PVA(96)) to 92°C for the blend (*Figure 5*). The peak width at one-half peak height has become greater during blending. This increase in peak width causes the distinct shoulder that was seen with pure PVA(96) to become non-distinct. Likewise blends consisting of 25 and 40% HPL also experience peak broadening and increases in tan δ transition temperature to 96 and 105°C, respectively. These non-typical increases in tan δ transition temperatures, which represent glass transitions, can be explained by the same mechanisms used to explain the T_g data produced by d.s.c. That being so, the presence of strong interactions causes the amorphous components to coexist in a more closely associated state, and this enables these interactions to act as quasi-crosslinks which limit molecular mobility. This possibly explains the existence of a blend T_g above that of the parent polymers.

The presence of peak broadening with the addition of HPL suggests that varying degrees of miscibility possibly exist between HPL and PVA(96). A narrow tan δ transition would indicate that a polymer experiences a uniform environment and thus relaxes over a narrow temperature range. However, in the case of partially miscible blends, a polymer can experience environments associated with polymer (1–1) interphases and varying degrees of polymer (1–2) interphases. These different environments stand to induce polymer relaxations occurring over a broader temperature range and resulting in a broadening of the tan δ transition[2].

The behaviour of the log E' curves for pure PVA(96) and for blends consisting of PVA(96) and 5, 25 and 40% HPL (*Figure 6*) illustrate a consistent broadening of the glass–rubber transition with HPL content, and this is classical behaviour for partially miscible blends[28]. Conversely, at 40% HPL content the modulus transition occurs over a narrower range than that experienced by blends consisting of 5 and 25% HPL. This indicates that the blend consisting of 40% HPL may be more miscible than the blends containing 5 and 25% HPL.

HPL/PVA(75) blends showed the same trends that were observed with PVA(96) blends, namely an increase in blend T_g as well as in tan δ transition width with increasing HPL content. However, blends consisting of PVA(88) did not follow the same trends as those found with PVA(96) and PVA(75). This is illustrated in *Figure 7* where the T_g do not vary consistently with HPL content. However, the relatively small changes in T_g that occurred between pure PVA(88) and blends containing 5 and 25% HPL may make this difference insignificant. The major difference between the blends containing PVA(88) and those containing PVA(96) and PVA(75) rests in their relationships between the tan δ transition width and HPL content (*Figure 8*). In order to normalize the data to those of the respective starting materials, the ordinate in *Figure 8* indicates the quotient of the blend tan δ transition width divided by that of the pure PVA of that blend. Therefore, a value of 1.0 on the ordinate indicates that the tan δ transition width of the blend is the same as that of the pure PVA used in that blend; and a value of < 1.0 indicates a tan δ transition width that is smaller than that of the pure

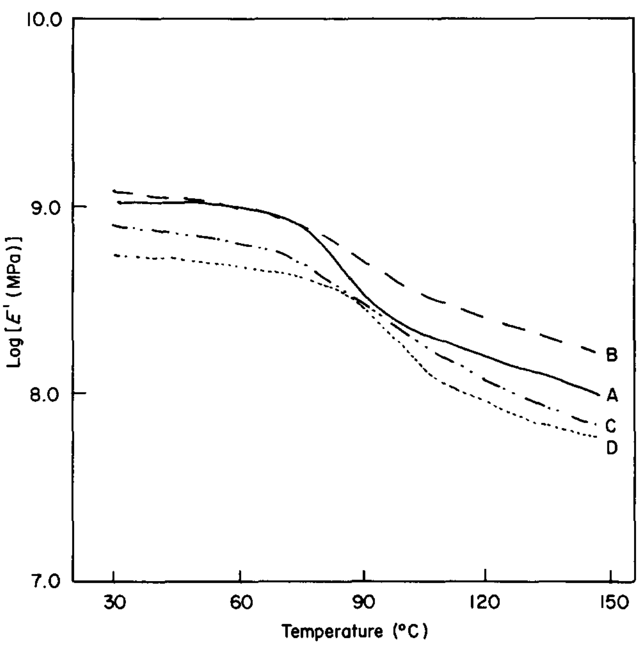

Figure 6 Relationship between storage modulus (log E') and temperature for HPL/PVA(96) blends in relation to HPL content: A, 0% HPL; B, 5% HPL; C, 25% HPL; and D, 40% HPL

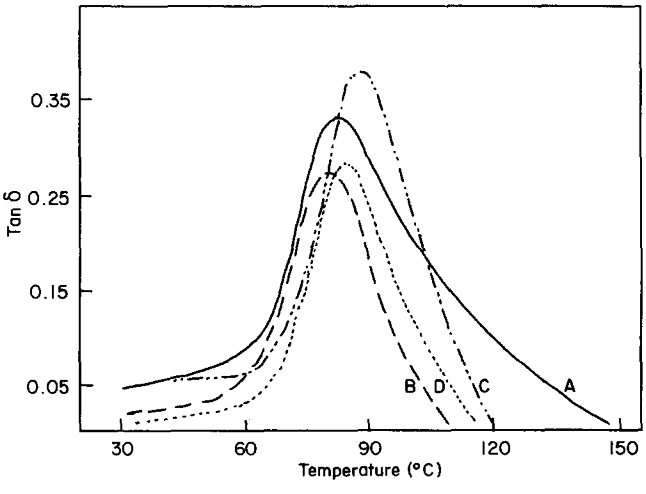

Figure 7 Relationship between tan δ of the HPL/PVA(88) blends and HPL content: A, 0% HPL; B, 5% HPL; C, 25% HPL; and D, 40% HPL

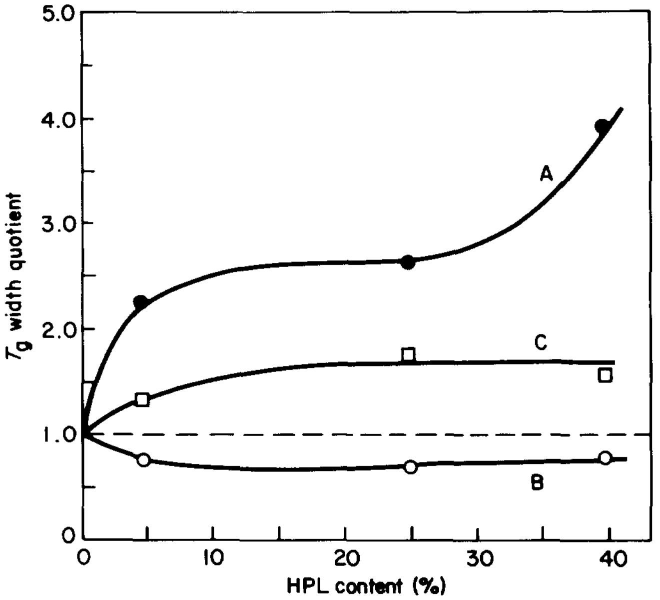

Figure 8 Relationship between T_g width quotient and HPL content for PVA(75) (A), PVA(88) (B) and PVA(96) (C). ('T_g width quotient' is the ratio between the experimental blend T_g width and the T_g width of the corresponding parent PVA)

PVA used in that blend. The minimum and maximum T_g ranges are indicated by actual data points.

Blends consisting of PVA(88) and HPL had tan δ transitions that were consistently more narrow than that of pure PVA(88) (*Figure 8*). By contrast blends containing PVA(96) and PVA(75) had tan δ transitions that were consistently broader than those of their respective parent PVAs. This fact indicates that these blends had a greater degree of miscibility than that for PVA(96) and PVA(75) blends. The mechanism responsible for this increased miscibility is believed to be related to both solubility parameter and increased polymer–polymer (1–2) interactions.

The solubility parameter of HPL is close to that of PVA(75) and PVA(88). If it were assumed to be within a few tenths of matching the solubility parameter of either partially hydrolysed PVA sample, at least a partial miscibility for PVA(75) and/or PVA(88) blends would result. With the combination of closely matched solubility parameters and the ability to form hydrogen bonds, a high degree of miscibility would be predicted for blends consisting of PVA(75...88) and HPL. Outside of this solubility parameter range, very limited miscibility would be predicted. However, the ability of these polymers to associate with each other, and to form hydrogen bonds, is believed to create an at least partially miscible system. The ability of PVA(96) to form more hydrogen bonds than PVA(75) is the reason for the consistently narrower tan δ transitions as compared to PVA(75) blends, thus indicating greater miscibility.

CONCLUSIONS

Polymer blends composed of HPL and PVA hydrolysed to the extent of 96, 88 and 75% formed homogeneous materials with no sign of phase separation. Therefore HPL/PVA blends are concluded to form at least partially miscible systems.

The PVAs used in this study had solubility parameters that ranged from 12.6 to 10.6 cal$^{1/2}$ cm$^{-3/2}$, yet all blends containing these alcohols showed the same homogeneous morphology. Hydroxypropyl lignin has been assigned a solubility parameter of roughly 11.1. This exceeds the normal limit of $\Delta\delta$ of 0.5 that determines miscibility. Therefore, it is believed that hydrogen bonds on both polymers allow HPL to form at least partially miscible systems over a wider-than-expected range on the basis of solubility parameters.

The presence of secondary interactions, such as hydrogen bonds, was indicated by a decrease in the melt endotherm area observed with a number of HPL/PVA blends. A reduction in melt endotherm area indicates a change in the organization or extent of crystallinity. In HPL/PVA blends changes in the crystalline structure are believed to result from polymer–polymer interactions in the amorphous phase.

The glass transition temperatures of HPL/PVA blends increased as HPL content increased. Uncharacteristically, these blend T_g values were found to be higher than those of the parent polymers. This unusual trend was explained by the presence of hydrogen bonds between the hydroxyl groups of HPL and PVA. These secondary bonds act as quasi-crosslinks, resulting in higher T_g values.

Changes in the shape of the tan δ transitions of the d.m.t.a. thermograms of HPL/PVA blends indicated that blends containing PVA(96) and PVA(75) represented partially miscible systems. Blends containing PVA(88) showed narrower or more constant tan δ transitional breadths with increasing HPL content, and this was attributed to a greater degree of miscibility. The mechanism responsible for this increased miscibility is believed to be a combination of closely matched solubility parameters and polymer–polymer interactions.

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