

Multiphase materials with lignin: 5. Effect of lignin structure on hydroxypropyl cellulose blend morphology

Timothy G. Rials* and Wolfgang G. Glasser

Department of Wood Science and Forest Products and Polymer Materials and Interfaces Laboratory, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061, USA

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The incremental elimination of hydroxy functionality in an organosolv lignin by ethylation or acetylation dramatically influenced the state of miscibility and resulting morphology of blends prepared with hydroxypropyl cellulose (HPC). A maximum level of interaction between the blend components, as determined from melting point depression, occurred where 23–40% of the hydroxy groups were substituted. Above this level of modification, the interaction parameter decreased rapidly. Complete incompatibility occurred at a 90% degree of substitution with acetoxy functionality. Essentially three distinct phase morphologies could be detected in these materials. At the lowest levels of interaction, the morphology resulted from lignin domain formation and hydroxypropyl cellulose liquid crystal mesophase separation. A completely miscible, amorphous blend resulted when the polymer–polymer interaction was maximized. At intermediate levels, however, these materials were characterized by a dispersion of liquid crystal domains in an amorphous, lignin-reinforced HPC matrix.

(Keywords: hydroxypropyl cellulose; lignin; liquid crystals; polymer blends)

INTRODUCTION

Some of the more significant recent developments in materials technology have come in the area of multi-component polymer systems. These developments have been led by the success of high strength, light weight fibre-reinforced polymers, although considerable attention remains focused on polymer blends, which offer the potential of much simpler fabrication technology¹. One novel approach, hoping to combine the desirable attributes of these two material classes, has been the use of a rigid rod polymer as one component of the polymer blend, thereby replacing the macroscopic fibre with a single polymer chain². Conceptually, this would retain the inherent high strength of fibre composites and eliminate such detrimental features as a weak interface and property anisotropy.

Consistent with Flory's prediction of phase separation in a mixture of a rigid rod and a flexible polymer³, the true molecular composite has yet to be produced. The feasibility of this type of blend system has been clearly demonstrated, however, with liquid crystal (LC) copolyesters serving as rigid rod polymers in various matrices^{4,5}. Appropriate processing allowed orientation of the LC phase, resulting in dramatic strength increases in these binary systems. Surprisingly, although cellulose and its derivatives also exhibit liquid crystal phenomena⁶, their

use in such material systems has received little attention in the open literature. Ternary phase behaviour studies of cellulose/cellulose acetate⁷ and cellulose acetate/hydroxypropyl cellulose⁸ in solution have been reported, but were not extended to the bulk morphology of the blend. Consequently, the phase behaviour of these polymer systems relative to blend morphology remains an important, unanswered question.

Studies on the morphology and properties of hydroxypropyl cellulose (HPC) blends with small amounts of lignin have shown both modulus and tensile strength increases in excess of 150%⁹. For this partially miscible pair, it was shown that a fibrous HPC phase is dispersed in an amorphous matrix of lignin reinforced HPC. Considering the highly polar character of both hydroxypropyl cellulose and lignin, it is plausible that secondary interactions between the component polymers contribute to the overall state of miscibility in this binary system. The intent of this work is to address further the influence of intermolecular interactions on the phase morphology of HPC/lignin blends by modifying the hydroxy functionality of the lignin.

EXPERIMENTAL

Materials

HPC (Klucel 'L') used in this study was supplied by Aqualon Inc., Wilmington, DE, USA. The manufacturer reported a molar substitution of four propylene oxide units per anhydroglucose unit and a nominal molecular weight of 10^5 g mol^{-1} .

* Current address and to whom correspondence should be addressed: USDA Forest Service, Southern Forest Experimental Station, 2500 Shreveport Highway, Pineville, LA 71360, USA

Table 1 Hydroxy data and physical properties for lignins derivatized with acetic anhydride (Ac) and diethyl sulphate (Et)

Sample	Molar ratio (reagent/OH)	Degree of conversion (%)			OH groups/C ₉		Physical properties	
		Total OH	Phenolic OH		Total OH	Phenolic OH	T _g (°C)	δ ^a (cal cm ⁻³) ^{1/2}
			By n.m.r.	By aminolysis				
OSL	—	0	0	0	1.47	0.59	115	11.1
Ac-1	29	23	17	31	1.14	0.41	110	10.5
Ac-2	61	65	66	56	0.52	0.26	106	9.3
Ac-3	80	76	84	64	0.35	0.21	103	9.0
Ac-4	100	87	96	71	0.19	0.14	101	8.7
Ac-5	192	100	100	95	0.0	0.03	96	8.4
Et-1	23	18	—	—	1.22	0.34	109	10.6
Et-2	50	27	—	—	1.08	0.20	96	10.4
Et-3	67	35	—	—	0.96	0.08	75	10.2
Et-4	172	40	—	—	0.88	0.0	57	10.0

^a Solubility parameters were calculated using the group contribution method of Small¹¹. (HPC is estimated to have δ = 10.1 (cal cm⁻³)^{1/2}; Reference 12)

The lignin component was an organosolv lignin isolated from aspen wood, and supplied by Biological Energy Corporation of Valley Forge, PA, USA. The polystyrene equivalent number ($\langle M_n \rangle$) and weight ($\langle M_w \rangle$) average molecular weights were determined by gel permeation chromatography as 900 and 3000 g mol⁻¹, respectively. The hydroxy content of the lignin was incrementally eliminated by acetylation and ethylation according to previously described procedures¹⁰. Table 1 presents a summary of the hydroxy data, and pertinent physical properties, of the derivatized lignins.

Methods

Individual solutions of the blend components in dioxane (or tetrahydrofuran) were mixed and stirred for ≈12 h before casting into a Teflon mould. Solvent evaporation proceeded under ambient conditions for 24 h followed by transfer to a vacuum oven at 60°C for further removal of solvent. The dried films were then stored in a vacuum desiccator over P₂O₅.

The glass transition (T_g) and melting (T_m) temperatures of the component polymers and their blends were determined on a Perkin-Elmer DSC-4 interfaced to the thermal analysis data station. All materials were analysed at a heating and cooling rate of 20°C min⁻¹ under a purge of dry nitrogen. Dynamic mechanical properties (log E' and tan δ) were determined with a Polymer Laboratories Inc. dynamic mechanical analyser interfaced to a Hewlett-Packard microcomputer. The spectra were collected at a heating rate of 4°C min⁻¹ from -50 to 150°C using a single cantilever beam geometry.

RESULTS

Unmodified lignin (OSL) blends

Figure 1 presents a series of thermograms for blends prepared from HPC and the unmodified organosolv lignin. As the lignin content is increased to 40 wt%, a single T_g is observed, increasing from about 25 to 60°C. The increase in T_g is accompanied by a substantial decrease in the melting temperature of approximately 40°C. As the lignin content is increased to 55%, an increase in T_m is observed and two glass transitions are present at 65 and 130°C, indicative of phase separation of the two components. Interestingly, the higher temperature transition in the phase separated systems is slightly

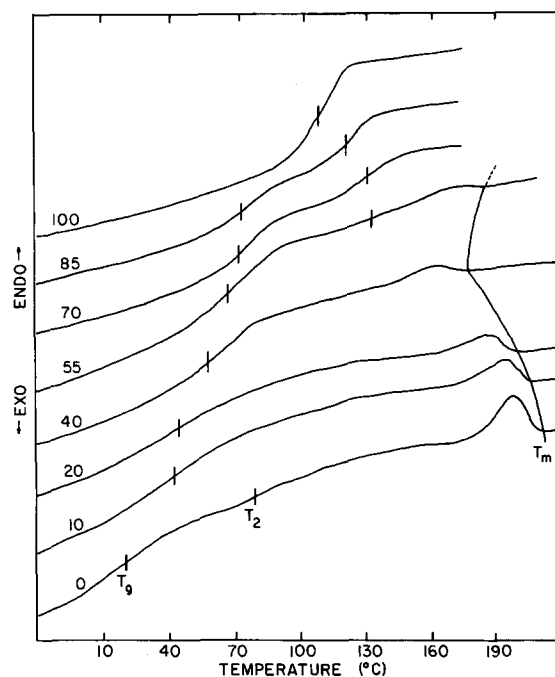


Figure 1 D.s.c. curves for HPC blends with unmodified organosolv lignin. The weight fraction (%) of lignin in the blend is shown on the curves

above that of the pure lignin component, and some composition dependence remains in the lower T_g . The above results suggest possible phase separation of the high molecular weight lignin species, and is consistent with the overall picture of partial miscibility for this polymer pair.

The evaluation of the amorphous phase behaviour for this blend system is complicated by the presence of an additional second-order transition (T_2) present in HPC. Occurring at 80°C, this transition has been attributed to a residual liquid crystal phase in the bulk polymer^{13,14}. In an effort to assess more accurately the behaviour of these two phases upon blending with lignin, dynamic mechanical analysis was used to characterize the relaxation properties. As seen in Figure 2, the tan δ spectrum of HPC consists of two primary relaxations, one at 30 and one at 85°C, which correspond to the T_g and T_2 transitions observed by calorimetry. As the lignin composition of the blend increases, the intensity of the T_2

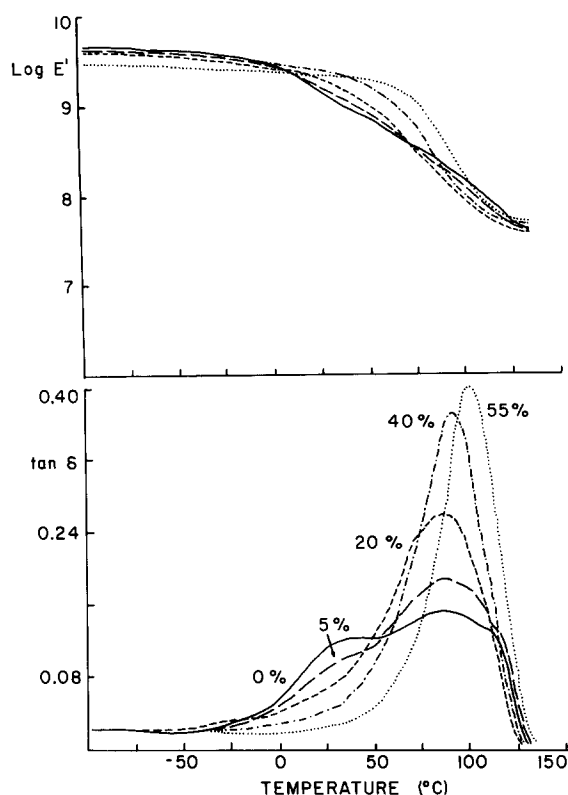


Figure 2 Dynamic mechanical properties of HPC blends prepared with unmodified organosolv lignin. The numbers represent the weight fraction of lignin in the blend

transition apparently increases at the expense of the amorphous phase relaxation. However, closer inspection reveals that this behaviour actually arises from a temperature increase in the T_g , which results in a further convolution of the two observed relaxation processes. The conclusion that can be drawn from these results is that partial compatibility exists between lignin (unmodified) and the amorphous phase of HPC without a significant effect on the formation, and separation, of a liquid crystal mesophase.

Ethylated lignin (Et) blends

The purpose of ethylation is conversion of lignin's phenolic hydroxyl groups with very little impact on the aliphatic functionality of the molecule. For HPC blends prepared from the ethylated lignins a single, unique T_g was found over the entire composition range investigated. At low levels of ethylation (Et-1 and Et-2, Table 1) the thermal behaviour of the blends was essentially identical to that of the unmodified lignin materials. In the blends prepared from the more highly ethylated lignin derivatives, however, some unusual properties were encountered. The most extreme thermal behaviour, as revealed by differential scanning calorimetry (d.s.c.), is found in the blends prepared from the highest substituted lignin, Et-4 (Figure 3a). Even the lowest lignin composition blend provides a striking contrast to pure HPC. Perhaps the most notable distinction between HPC and these blends is the apparent resolution of the K \rightarrow N and N \rightarrow I transitions, and the dramatic T_m depression of almost 30°C at only 5% lignin content. As the lignin content is increased, the melting point depression continues with the maintenance of about a 15°C window between the two first-order transitions. In addition, the T_2 transition appears much

sharper in the initial scan of this blend system. Although this is speculation, at best, this may arise as a consequence of molecular weight fractionation of HPC in these blends.

After this initial thermal treatment, d.s.c. analysis (Figure 3b) reveals an enormous increase in the heat capacity change (ΔC_p) at T_g , implying an increase in the amorphous volume fraction of the blends. While of increased intensity, the transition is seen to occur over a narrower temperature range as the lignin content increases. It is impossible to attribute the dramatic enhancement of the amorphous component to the partial extinction of a crystalline phase comprising only 16% of the pure HPC. In accordance with previous results⁹, a second HPC phase of intermediate order (i.e. related to a liquid crystal mesophase) must be invoked, and is best evaluated through the blend's dynamic mechanical properties. Figure 4 illustrates the relaxation behaviour of the HPC/Et-3 blend system, which exhibited behaviour similar to the highest ethylated lignin blends, although not to the same extreme. As the lignin content is increased to 20%, the T_2 relaxation is shifted from 100 to 50°C. The relaxation also increases in intensity while decreasing in breadth, suggesting a more homogeneous environment.

The conclusion to be drawn from this experiment is that the modification of lignin by ethylation yields blends ranging from partially miscible to miscible. As the degree of modification increases, the compatibility with HPC increases, leading to a complete disruption of supermolecular structure and an essentially amorphous blend after thermal treatment.

Acetylated lignin (Ac) blends

The acetylated lignins provide a much more comprehensive range, in that substitution levels from 23 to 100%

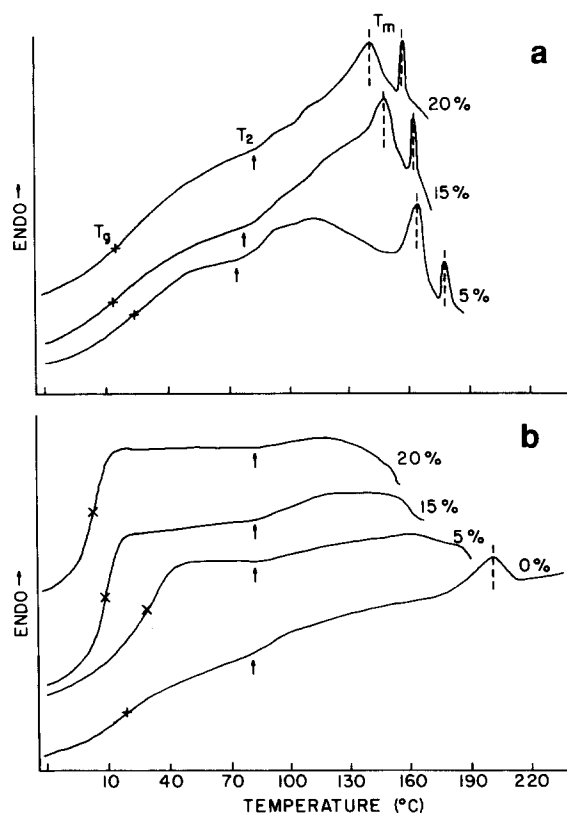


Figure 3 D.s.c. analysis of HPC/Et-4 blends: (a) initial scan; (b) immediate re-scan. The numbers represent the weight fraction of ethylated lignin in the blend

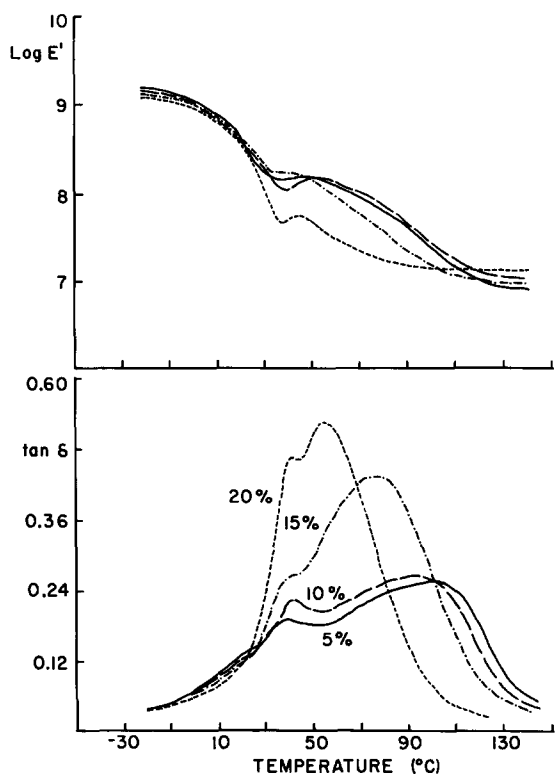


Figure 4 Dynamic mechanical properties of HPC/Et-3 blends. The numbers represent the weight fraction of ethylated lignin in the blend

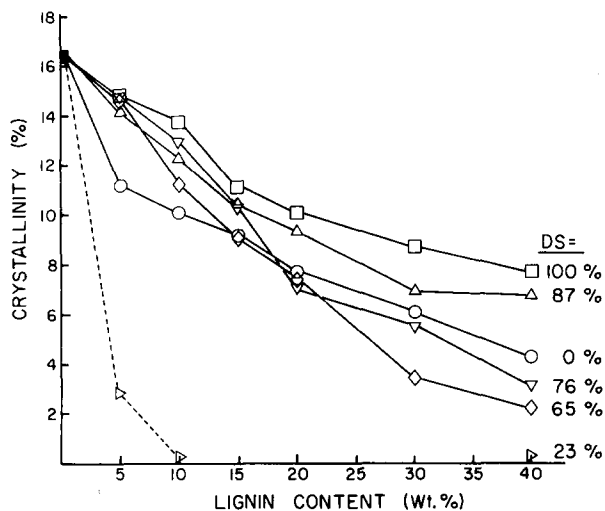


Figure 5 The variation in percentage crystallinity with lignin content for HPC blends prepared with acetylated lignin derivatives. The numbers represent the degree of substitution of hydroxyl groups

were achieved (Table 1). It is, therefore, not surprising that a much wider range of blend morphologies were obtained. Figure 5 presents the variation in crystallinity (determined by d.s.c.) of the blend as the degree of acetylation increases. At low levels of modification (23%), the crystallinity in the blends is rapidly diminished, becoming undetectable at a composition of 10% lignin. Further substitution, however, results in a greater level of crystallinity being retained in the blend until at degree of substitution $DS=87\%$ the percentage crystallinity remains higher than that of blends made with the unmodified parent lignin. Since the decrease in crystallinity of the blend may be attributable to the interaction of blend components, this information translates into an

initial increase followed by a substantial reduction in compatibility between blend components as the degree of acetylation increases. An evaluation of the T_g of these materials revealed a single transition over the blend compositions investigated until at the two highest levels of substitution the T_g s of the individual polymers were detected, indicating classical phase separation.

It is of interest to return briefly to the blends prepared with the low DS lignin (23 wt%). The analysis of this blend series by d.s.c. (Figure 6) reveals behaviour similar to the Et-3 and Et-4 blends. That is, even at relatively low lignin compositions, a tremendous disruption occurs in the development of LC superstructure. As the lignin content increases from 10 to 20% of the blend, all traces of crystallinity disappear and the T_g s become much sharper, and more classical, in their appearance. The implication is that, at this level of substitution of lignin hydroxy functionality, the increased compatibility between the two polymers leads to an essentially amorphous material with no evidence of LC mesophase formation.

Melting point depression

From the data presented thus far, it is evident that lignin modification yields polymeric blends varying widely in their morphology and properties. By inference, these differences are attributed to changes in component miscibility; however, they provide only a qualitative indication of the relationship existing between lignin structure and blend compatibility. Further insight into this question can be gained through closer inspection of the T_m depression in the blend. For semi-crystalline blends such as these, the polymer-polymer interaction parameter, B , can be determined through the following simplified expression¹⁵:

$$T_{m2}^{\circ} - T_{m2} = \left(\frac{-BV_{2u}}{\Delta H_{2u}} \right) T_{m2}^{\circ} \phi_1^2$$

where T_{m2}° is the equilibrium melting point of HPC ($=213.1^{\circ}\text{C}$, from Reference 16), T_{m2} is the melting point of the blend, $\Delta H_{2u}/V_{2u}$ is the heat of melting per unit volume of 100% crystalline material ($=7.52 \text{ cal cm}^{-3}$, from Reference 16) and ϕ_1 is the volume fraction of the amorphous blend component (i.e. lignin). A plot of ΔT_{m2}

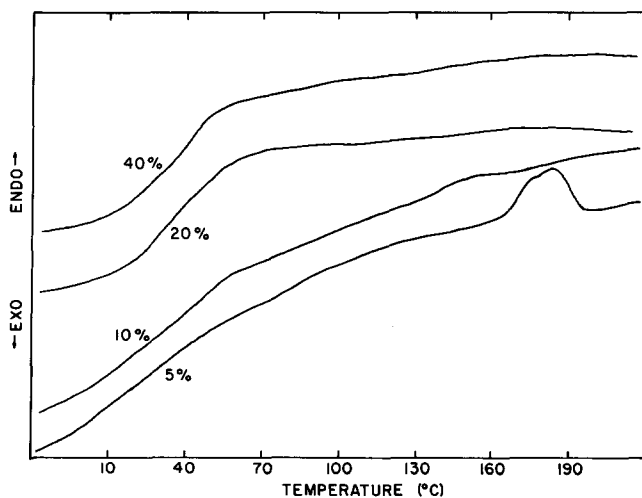
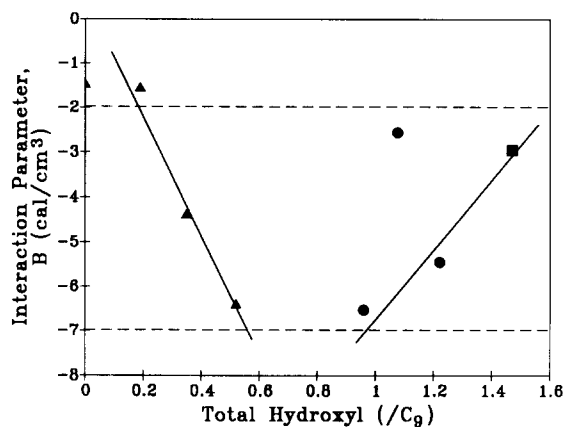


Figure 6 D.s.c. curves for HPC/Ac-1 blends. The numbers represent the lignin weight fraction in the blend

Table 2 Summary of melting point depression analysis for blends of HPC and lignin modified by acetylation and ethylation

Sample	Intercept	Slope	R^2	$-B$ (cal cm^{-3})
HPC/OSL	9.675	196.8	0.98	3.0
HPC/Ac-2	2.322	415.6	0.95	6.45
HPC/Ac-3	3.187	285.5	0.98	4.43
HPC/Ac-4	5.337	102.4	0.91	1.59
HPC/Ac-5	6.104	97.8	0.94	1.52
HPC/Et-1	5.281	351.9	0.99	5.46
HPC/Et-2	5.514	165.6	0.97	2.56
HPC/Et-3	5.212	420.7	0.98	6.52


Figure 7 Relationship between polymer-polymer interaction parameter, B , (cal/cm^3) and lignin total hydroxy content: \square , unmodified lignin; \circ , ethylated lignin; \triangle , acetylated lignin

versus ϕ_1^2 should then yield a straight line with a slope proportional to B . The results of this treatment for the HPC/lignin blends are presented in *Table 2*.

For the HPC blends incorporating the unmodified lignin, $B = -3.0$, indicating a favourable interaction between the two polymers. Upon acetylation, the magnitude of B initially increases before falling off to $-1.52 \text{ cal cm}^{-3}$ upon complete substitution, which is consistent with the observed morphologies presented earlier. With the exception of the Et-2 blends, the degree of interaction in blends of the ethylated lignins more closely resembles the low DS , acetylated materials. That is, an extremely favourable interaction is indicated, in accord with earlier conclusions regarding the miscible nature of these blend systems.

Although all of the blend systems are adequately described by this linear model ($0.91 \leq R^2 \leq 0.99$), it is interesting that the intercept fails to pass through zero, as expected, for all cases. Generally, this behaviour has been attributed to a T_m depression arising from entropic contributions such as a reduction in lamellar thickness of the crystallites¹⁵. Since no attempt was made here to obtain equilibrium melting points, this certainly may be the case; however, the discrepancy is greatest for blend systems identified either as partially compatible (e.g. unmodified lignin) or incompatible (e.g. Ac-4/5). The deviation from zero may thus be indicative of incipient phase separation of the polymer pair.

DISCUSSION

Uncertainties associated with the characterization of

both blend components make it impossible to accurately define the parameter B . Yet the assessment of melting point depression using this approach does allow the relationships existing between lignin structure and blend morphology to be clarified. As seen in *Figure 7*, a reduction in the hydroxy content of the lignin component increases the level of interaction occurring between the two polymers until a maximum is reached at a point corresponding to $DS \approx 40\%$ (represented by the Ac-1 and Et-4 blends, which were largely amorphous, making it impossible to determine the T_m depression). Further reduction of the lignin hydroxy functionality results in a diminished interaction until at complete substitution an incompatible system is found (Ac-5). It should be emphasized that this curve is generated from data on both the acetylated and ethylated lignin blends; consequently, the overlap that is encountered in this composite curve suggests that the type of modification used does not substantially influence the polymer-polymer interaction. Furthermore, this trend indicates that the hydroxy functionality of lignin does not favourably contribute to the miscibility of the two components by establishing intermolecular hydrogen bonds. This result is emphasized upon considering that the maximum interaction occurs at a degree of substitution which provides a very close match in component solubility parameters ($10.0 \leq \delta_{\text{lignins}} \leq 10.5$; $\delta_{\text{HPC}} = 10.1$).

A closer evaluation of the system as a whole provides some interesting insight into the factors contributing to the origin of supermolecular structure in this polymeric blend and, subsequently, impacting the technology related to the development of high strength composite materials. At low levels of interaction between the lignin component and HPC ($B > -2.0$), phase separation occurs due to the unfavourable energy between the polymers, as well as liquid crystal mesophase formation by HPC. This necessarily has a catastrophic effect on material properties due to the heterogeneity of the material. At the other extreme ($B < -7.0$), a miscible blend is obtained, which presumably represents the ideal situation; however, it appears as though the rigidity of the cellulosic chain is derived largely from intermolecular chain interactions. The disruption of these interactions that results upon compatibilization with a second polymer yields a much more flexible polymer, eliminating the opportunity for high strength development. In the intermediate range of polymer interaction ($-7.0 < B < -2.0$), the blend morphology originates solely from LC mesophase formation dispersed in a miscible HPC/lignin matrix. It is with this type of phase morphology that significant enhancements in both modulus and tensile strength of the HPC/lignin composite have been noted⁹.

CONCLUSIONS

The elimination of lignin's functionality significantly influences the state of miscibility that exists when it is blended with HPC. A maximum interaction between the two polymers occurs at a degree of substitution between 30 and 40%, irrespective of the type of modification (e.g. ethylation or acetylation). Continued reduction of hydroxy functionality diminishes the HPC/lignin interaction until a completely incompatible system is obtained at $DS = 90\%$. Partial miscibility of this binary system yields a compatible, amorphous phase interspersed with HPC liquid crystal domains which, upon appropriate processing,

develops high strength materials. Surprisingly, as compatibility is maximized, the rigidity of the cellulose chain is lost, as is the mechanical integrity of the polymer composite. These results directly impact the development of cellulose-based polymer composites.

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