SECONDARY INTERACTIONS IN BLENDS OF LIGNIN AND CELLULOSE DERIVATIVES:
COMPOSITE MORPHOLOGY AND PROPERTIES

by

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(ABSTRACT)

Differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA) were used to characterize the morphology of solvent cast hydroxypropyl cellulose (HPC) films. These techniques revealed the existence of three phases in the bulk material: 1) an amorphous phase, 2) a crystalline phase, and 3) a phase of intermediate order which arises as a consequence of liquid crystal mesophase formation during solvent evaporation. Characterization of the effect of crosslinking on the tan peak temperature led to the conclusion that these relaxations (as observed by DMTA) are similar to glass transitions (T_g's) involving large-scale cooperative motions of the main chains.

This three-phase morphology presents a unique system for study with regard to the resultant morphology of binary blends with lignin. This blend system was prepared by solution blending in pyridine and dioxane, as well as melt-mixing followed by extrusion. A partially miscible system was obtained from all preparation methods; however, the injection molded and dioxane-cast materials were generally distinguished from those blends cast from pyridine solution. Their distinction is explained by an enhanced level of superstructure development in these blends as reflected by DMTA analysis and tensile
properties. The dramatic improvement in modulus and tensile strength, particularly for the injection-molded samples, leads to the conclusion that lignin serves to reinforce the amorphous matrix of the resulting composite material.

The modification of lignin's polyhydroxy character through ethylation, acetylation, and propoxylation, revealed that specific secondary interactions between the components play a minor role, if any, in determining the state of miscibility in this blend system. However, from the analysis of the interaction parameter, B, it is concluded that the extensive hydrogen bonding within the lignin influences the conformation and chain rigidity of this component which dramatically influences the development of supermolecular morphology, and subsequently the overall morphology of the polymeric blend. This is reflected by a substantial increase in the amorphous volume fraction as detected by both DSC and DMTA.

The characterization of blends prepared from the unmodified organosolv lignin with ethyl cellulose and a cellulose acetate/butyrate ester confirms the minimal role of secondary interactions between components. However, the characteristics of the second phase suggest that the formation of liquid crystal domains in the cellulose derivatives significantly contribute to the overall morphology and properties of this blend system, as was noted for the HPC/lignin blend systems.
ACKNOWLEDGEMENTS

To properly express my gratitude to my major professor, Dr. W. G. Glasser, would require another thesis. I owe him a great deal for the personal and professional development which I have experienced during my tenure at Virginia Tech.

Over the years, many friends have come and gone, but luckily some will be with me forever. To and - thank you for your friendship and support. In addition, a special debt of gratitude goes to for her technical assistance and and my committee members (Dr. G. L. Wilkes, Dr. T.C. Ward, Dr. N. G. Lewis, and Dr. F. Sebba) for their assistance in this project. This goal could never have been reached without the constant love and support from my parents - Mom and Dad, I wish there were some way to repay even a little of it.

Finally, I will take this opportunity to dedicate this work to my wife-to-be for seeing this struggle through. I love you,
PREFACE

Three of the chapters of this thesis have been prepared as manuscripts which either have been, or will be, submitted for publication. As such, each chapter has its own experimental section and literature citations. Unfortunately, a certain amount of duplication was unavoidable which could prove somewhat redundant for the reader of this work as a collection. Apologies are made if this appears inconvenient.
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LIST OF ABBREVIATIONS AND SYMBOLS

$\Delta G_{\text{mix}}$ Free Energy of Mixing
$\Delta H_{\text{mix}}$ Enthalpy of Mixing
$\Delta S_{\text{mix}}$ Entropy of Mixing
DSC Differential Scanning Calorimetry
DMTA Dynamic Mechanical Thermal Analysis
HPC Hydroxypropyl Cellulose
OSL Unmodified Organosolv Lignin
OEt(n) Ethylated Lignin
OAc(n) Acetylated Lignin
OPR Propoxylated Lignin
$T_g$ Glass Transition Temperature
$T_m$ Melting Temperature
$B$ Polymer-Polymer Interaction Parameter
$\phi_i$ Volume Fraction, component i
$V_i$ Molar Volume, component i
$\delta$ Hildebrand's Solubility Parameter, $(\text{cal/cm}^3)^{1/2}$
FTIR Fourier Transform Infrared Spectroscopy
WAXS Wide Angle X-ray Scattering
$\log E'$ Storage Modulus
$\tan \delta$ loss Tangent ($= \log E''/\log E'$)
$T_1$ $\tan \delta$ peak of amorphous HPC component (20°C)
$T_2$ $\tan \delta$ peak of liquid crystal HPC component (−80°C)
$\Delta H_u$ Heat of Melting of 100% Crystalline Material
<table>
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<tr>
<td>$C_p$</td>
<td>Heat Capacity</td>
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<tr>
<td>$\beta$</td>
<td>Secondary Relaxation Process</td>
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<tr>
<td>$E_A$</td>
<td>Activation Energy</td>
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<tr>
<td>$&lt;M_n&gt;$</td>
<td>Number Average Molecular Weight</td>
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<tr>
<td>$&lt;M_w&gt;$</td>
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<td>$T_C$</td>
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<td>$T_m^0$</td>
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<td>$H_{2u}/V_{2u}$</td>
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<tr>
<td>CAB</td>
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A. Multicomponent Polymer Systems

Over the years, multicomponent polymer materials have become increasingly visible, moving into industries as diverse as construction, automotive, appliance, and electrical to name but a few (1). The popularity of these systems can be related to a gradual narrowing of the chemical variety of polymers being produced resulting from economic, technological, and regulatory pressures (2). In order to get around this reduction in new homopolymers, multicomponent polymers have evolved as one of the favored choices. Some of the reasons for their appearance (i) the ability to economically obtain higher performance materials, (ii) the simple modification of performance as a market develops, (iii) to extend the amount of an expensive resin, and (iv) the production of a unique material in terms of either processability or performance (2). Considering this versatility, it is likely that this class of materials will maintain its popularity in the future.

The fundamental concern which must be addressed in the design of multicomponent polymer systems is the assurance of good stress transfer between the individual constituents (3). The importance of this issue is emphasized when one considers that the stress needed to break a C-C bond is about 2 million PSI, and yet the tensile strength of commercial thermoplastics lie in the range 3000-17000 PSI.
(3). This dramatic shortcoming is the result of flaws and surface cracks - the likelihood of which could increase with the addition of a second component and the formation of an interface. The approach to this concern allows a convenient means of classifying multicomponent polymer systems into three groups as follows: 1) polyblends, 2) copolymers, and 3) reinforced composites (3) (Figure 1).

While the latter two categories have most successfully addressed the issue of adequate stress transfer, polyblends continue to experience difficulties and are the subject of intensive research. The reasons for this can be arrived at from contrasting viewpoints. From practicality, the physical blending of a polymer pair requires no synthetic chemistry which keeps development costs at a minimum while providing a new polymeric material (2). Polyblends also allow the evaluation of molecular interactions in the absence of covalent bonds which may provide information in unrelated disciplines concerned with binary systems. Interestingly, both viewpoints seem to emphasize the significant role of secondary interactions between molecules, and the associated increase in the likelihood of material flaws and defects.

Obviously, polymer blends with the desired properties will be obtained only if good stress transfer between the components is assured. One solution to this problem is to find polymer pairs which are miscible with each other (4).
That is, the individual components have the ability to mix at the molecular level. Since a single phase is formed, interphase stress transfer is not a concern and the physical properties may approach, or exceed, those of a similarly composed random copolymer, i.e. the character of the individual components is lost, for example in terms of dynamic mechanical properties (Figure 2). Not surprisingly this type of system has proven to be the exception rather than the rule (5,6).

Instead, physical blends of high molecular weight polymers tend to segregate into phases containing predominantly their own kind (7). These immiscible blends typically retain the attributes of the isolated constituents with an additional loss in integrity owing to the low physical attraction forces which act across the phase boundaries (8).

It is critical to recognize that these two cases (miscible vs. immiscibility) represent the extremes in possible blend morphologies. As depicted in Figure 2, intermediate levels of miscibility are quite plausible, if not more likely to be encountered. As a result of this spectrum of possibilities, it is of considerable interest to better understand the molecular factors influencing the state of miscibility of a polyblend, a concern which is best addressed in terms of the thermodynamics of a binary polymer pair.
B. Basic Thermodynamics

The concept of miscibility and phase separation can be treated from classical equilibrium thermodynamics. In this approach, the state of miscibility of any mixture is governed by the free energy of mixing, $\Delta G_{\text{mix}}$, which is defined as

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

where $\Delta H_{\text{mix}}$ is the enthalpy change on mixing and $\Delta S_{\text{mix}}$ is the entropy change on mixing (9). For a miscible blend which forms a single, homogeneous phase the free energy of mixing is required to be negative. As is illustrated in Figure 3 (5), while this is a necessary condition for miscibility, it is not sufficient in itself, since case III also had a negative free energy over the entire composition. Here the free energy of mixing shows a maximum in the mid-composition, thus the system can develop a lower energy by separating into two phases with compositions corresponding to the two minima. Consequently, a more complete statement of the thermodynamic criteria for miscibility should include that

$$\left[ \frac{\partial^2 \Delta G_{\text{mix}}}{\partial \phi_2^2} \right]_{T,P} \tag{2}$$

be satisfied over the entire composition range (10). The implications of this fundamental treatment may become clearer if the individual terms in equation [1] are more
closely evaluated.

Unquestionably, the simplest model available for polymer blends is based on an extension of the Flory-Huggins theory of "polymer solutions" (11), and was first applied to blends by Scott (12). This treatment estimates the entropy of mixing as a combinational contribution from a lattice model to yield,

$$
\Delta S_{\text{mix}} = -R(V_A + V_B) \left[ \frac{\phi_A}{V_A} \ln \phi_A + \frac{\phi_B}{V_B} \ln \phi_B \right]
$$

where $R$ is the gas constant, $V_i$ is the molar volume of component $i$, $V_A$ and $V_B$ are the actual volumes of these components in the mixture, and $\phi_A$ and $\phi_B$ are the component volume fractions. This result provides an expression for what is intuitively apparent. The combinatorial entropy of mixing for two polymers, although favoring a miscible system, is an extremely small contribution. In the limit of very high molecular weights, the combinatorial entropy of mixing is essentially zero (5).

While the entropy of mixing is strongly dependent on molecular weight, the enthalpy of mixing, $\Delta H_{\text{mix}}$, primarily results from the energy change associated with nearest neighbor contacts during mixing and is essentially independent of molecular size (13, 14). This point is brought out in the Flory-Huggins treatment (11) to yield the expression
\[ \Delta H_{\text{mix}} = (v_A + v_B) \beta \phi_A \phi_B \] (4)

where B is a binary interaction energy density characteristic of mixing segments of components A and B. Joint consideration of these terms reveals that miscibility of polymer-pairs is greatly restricted for nonpolar systems where a small, positive enthalpy would be the norm. In general B can not be predicted from theory; however, this value can be estimated from solubility parameters for systems where strong secondary interactions are not present through the relation (15)

\[ B = (\delta_A - \delta_B)^2 \] (5)

Substitution into Eq. [3] yields

\[ \Delta H_{\text{mix}} = \nu (\delta_A - \delta_B)^2 \phi_A \phi_B \] (6)

Even a superficial inspection of this result emphasizes the dominance of immiscible polymer pairs since the solubility parameters difference must be very small to keep \( H_{\text{mix}} \) a small positive value. For example, in the region of commercially significant molecular weight around 100,000, a miscible polymer pair requires a solubility parameter match such that the difference is only about 0.1 \((\text{cal/cm}^3)^{1/2}\) (9). Obviously, this is a difficult restriction to meet.

The limitations associated with Eq. [6] and the solubility parameters approach quickly surface. This model
is only capable of predicting $H_{\text{mix}}$ for endothermic processes, and is thus restricted to non-polar systems where segmental interactions are of the weak dispersive or Van der Waals type bonding (10,15). However, when the components are polar and capable of specific interactions the mixing process may prove to be an exothermic process. Considering Eq. [1], this result would obviously provide a strong driving force for miscibility, dramatically deviating from the above mentioned restrictions. Methods for predicting polymer miscibility in these systems are limited at this stage, but some qualitative guidelines can be developed which improve the likelihood of obtaining miscible polyblends (15).

C. Secondary Interactions

In the above discussion, it became apparent that the criteria for predicting polymer miscibility in non-polar structures is not so different than those used in selecting a suitable solvent. That is, the rule-of-thumb that "like dissolves like" (16) remains an important consideration in this type of system. The discovery of miscible polymer blends such as poly(vinyl chloride) and various substituted poly(B-propiolactone) (17,18) with a solubility parameter difference of about 1.0 (cal/cm$^3$)$^{1/2}$ revealed that this approach was not as universally applicable as originally thought. At this point, it was realized that exothermic mixing provided a strong driving force for miscibility, and
prompted a number of alternative explanations based on the polymer-polymer interaction parameter $X_{23}$ (13) or the presence of favorable secondary interactions. Although these explanations have not proven to be very general, one idea has gained increasing favor from a conceptual viewpoint despite the difficulties associated with a quantitative approach.

In contrast to polyblends with nonpolar structures, when the possibility of strong secondary interactions is present, "chemical dissimilarity" between the component polymers (such as a hydroxyl containing component and a carbonyl containing component) favors a miscible, homogeneous composite (19). The rationale for this hypothesis is derived from the idea that the presence of intermolecular interactions should affect the overall balance of entropic and enthalpic contributions (particularly the latter) to the free energy of mixing (19). Consequently, it has been promoted that if the strength or number of interactions can be increased, it should be possible to prepare a miscible system from polymers showing no prior propensity toward miscibility (20).

Unfortunately, it is all too apparent why this approach cannot be carried too far. Factors such as molecular weight, concentration of interacting species, and steric considerations have not been considered. In addition, the
extent to which the intermolecular interactions will enhance self-association is a consideration which is difficult, if not impossible to predict at this point (20). While these limitations are important to recognize, the point remains that (all other factors remaining favorable) strong secondary interactions greatly enhance the potential of obtaining a compatible polyblend. Realization of this simple fact had led to the discovery of a number of miscible polymer blends, and has led to new optimism and possibilities in developing unique polymer composites (5).

The significant role played by specific secondary interactions between miscible components has not been experimentally identified in a number of polyblends. Application of analytical techniques like differential scanning calorimetry (DSC) (21) and Fourier transform infrared spectroscopy (FTIR) (20) have provided overwhelming evidence supporting the hypothesis of intermolecular hydrogen bonding between dissimilar polymer chains. One of the most dramatic examples of this behavior can be found in blends of poly(vinyl phenol) and poly(-caprolactone) (22,23). In this system, FTIR analysis showed the appearance of a new carbonyl band which was assigned to the hydrogen bonded carbonyl of the polyester. Concurrent changes in the peak wavenumber of the hydroxyl band was also observed and related to the formation of intermolecular hydrogen bonds between the two blend
components. In the case of poly(vinyl phenol), interaction is not restricted to carbonyl-containing polyesters as significant interactions were also identified between the phenolic hydroxyl and the ether oxygen of poly(ethylene oxide) and several poly(vinyl alkyl ethers) polymers (24).

Similar conclusions have been reached by Kwei, et al. (21) using thermal analysis to characterize blends of novolak resins and poly(methyl methacrylate). A positive deviation in the glass transition temperature of the blends above the weighted average was related to hydrogen bonding effects between phenolic hydroxyl and carbonyl groups of the PMMA. Subsequent work with various novolaks have identified secondary interactions between its hydroxyl functionality and ether, nitrile, sulfone, and carbonyl groups (25,26).

These examples are, at least, a limited indication of the extent to which specific secondary interactions affect the morphology of a polymer blend. There are an increasing number of accounts which continue to identify this aspect as a major factor influencing the miscibility of polymer pairs. Although most of this information is compiled on synthetic systems, the extent to which hydrogen bonding influences composite morphology is of tremendous interest in a number of biological composite systems, not the least of which is the wood cell wall.

D. Extensions to Wood Science
It has not been uncommon in the past to see analogies drawn between the wood cell wall and synthetic fiber-reinforced composites (27). Certainly, this picture cannot be disputed considering the conventional description of the cell wall as cellulosic fibers embedded in an amorphous polymer matrix (28). However, the comparison with multi-component polymer systems should be further extended in the case of wood since the amorphous matrix is in itself comprised of two components - lignin and hemicellulose. While each of these components have warranted volumes of literature as isolated materials, their consideration as a whole has been painfully neglected.

Depictions of the amorphous matrix in situ have almost exclusively considered this polymer pair to be immiscible (29) (Figure 4A). This is not particularly surprising considering that the conclusions were drawn from traditional chemical analysis on the isolated components. Consequently, these early models reflect such firmly embedded schools of thought as the three-dimensionally crosslinked structures of lignin which would favor an incompatible morphology. Also, if this polymer pair is evaluated in terms of their solubility parameter there is little reason to conclude otherwise. With a solubility parameter of 11-12 (cal/cm³)¹/² lignin is about 4 units removed from hemicellulose whose solubility parameter is
closer to 16 (30) (cal/cm³)^1/2 - a much greater difference than that required for miscibility from this treatment (11).

However, one important aspect of this consideration, which has received little attention, is the extremely polar character of this biological composite. As indicated earlier, specific secondary interactions can dramatically influence the state of miscibility in a polyblend. Hydrogen bonding has long been identified as a major determinant of solution (31,32) and solid state (33) properties for the isolated materials, but has been extended to the composite system in only a limited number of cases. Remko (34) has illustrated the possible significance of hydrogen bonding in the wood cell wall using quantum chemical calculations to evaluate the strength and stability of secondary bonds between components. Concluding that the numerous polar groups of the wood polymers are extensively chelated, he presented a new model of the cell wall (Figure 4B). Interestingly, a lamellar or sheet-like morphology is depicted which has been further advanced by Whiting and Goring (35) (Figure 4C), contradicting the traditional view of the composite morphology. Atalla and Agarwal (36) applied Raman spectroscopy to explore the molecular structure of the cell wall components. Although far from definitive, the conclusion that there exists a preferential orientation of
phenyl propane units in lignin molecules was drawn, which is conceptually in line with this lamellar morphology.

Obviously, the question of cell wall morphology has not completely eluded experimental efforts. The application of differential scanning calorimetry (37) and dynamic mechanical analysis (38) have shown only one Tg in whole wood, suggestive of a miscible lignin-hemicellulose blend. However, recent efforts in this laboratory which evaluated the influence of moisture on dynamic mechanical properties of whole wood revealed two loss peaks in the DMTA-spectrum (39). While assigned to a hemicellulose phase and a lignin phase, this result could also be explained by regions which are rich in one component or the other. These contradictions are not particularly surprising considering the complexity of this biological composite and illustrate the need to further resolve this important question.

It was Goring who (40), addressing the current direction of lignin research, said "... adopt a holistic approach. For it is when we look at the lignin polymer as itself a component that we shall elucidate the difficult riddles still unsolved." Utilization of this approach has answered a number of questions, but it has seemingly raised a number of others. Above all, studies on the cell wall composite have made it increasingly apparent that a unique relationship exists between the wood polymers. Understanding this relationship could open new avenues to
pulping schemes or novel application for this valuable natural resource - wood.

It is not possible to develop a strong analogy between the lignin-carbohydrate matrix in wood and the re-combination of these polymeric materials outside of their biological system. Features such as the polymerization of lignin in the presence of previously deposited carbohydrates, and the presence of various "additives" like tannins, fatty acids and resins extend the level of complexity far beyond the scope of this work. The point remains that a unique association exists between lignin and carbohydrates which raises an interesting question. Is the integrity of this association maintained outside of its natural environment, i.e. is a unique morphology formed upon the preparation of a binary mixture of these two polymers? If this proves to be the case, the development of new and useful polymer composites is certainly possible. Although this aspect is certainly motivation enough, addressing this concern may also lead to further insight on plausible morphologies of the amorphous cell wall matrix.

The question of lignin-carbohydrate compatibility is most conveniently investigated using cellulose derivatives. Of the numerous choices available, hydroxypropyl cellulose (HPC) is selected for several reasons. First, the secondary hydroxyl of this particular derivative most
closely simulates the functional groups which are available in the biological environment for hydrogen bonding with lignin. Also, intramolecular hydrogen bonding within hydroxypropyl cellulose stabilizes the cellulosic backbone, maintaining the relatively rigid, rod-like conformation in solution which is characteristic of unmodified carbohydrates. Finally, HPC is highly soluble in a number of solvents, an important consideration when working with unmodified lignin which has extremely limited solubility characteristics.

E. Research Objectives

It is the intention of this research effort to evaluate the role of secondary interactions in determining the state of miscibility existing in binary blends of lignin and cellulose derivatives. This concern will be addressed in several stages as outlined below.

1) To characterize the composition dependence of thermal properties in blends of hydroxypropyl cellulose and organosolv lignin prepared by casting from dioxane and pyridine, and by injection molding after melt mixing.

2) To determine the effect of lignin's hydroxy functionality on the compatibility of HPC blends as defined by the interaction energy, B. This will involve the progressive modification of lignin by 1) acetylation, 2) ethylation, and 3) propoxylolation.
3] To qualitatively evaluate the extent to which cellulose functionality contributes to the state of miscibility in blends of lignin with cellulose acetate-butyrate and with ethyl cellulose.

It is expected that this project will result in a broader understanding of the role of intermolecular interactions in determining the overall morphology of lignin/carbohydrate blends. This concern remains a critical consideration in deciphering the complex morphology of the amorphous matrix in the wood cell wall.
LITERATURE CITED


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Figure 1. Classification of the types of multicomponent polymer systems.

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Figure 3. Variation in the frequency of mixing ($\Delta G_{\text{mix}}$) with volume fraction for a completely immiscible (I), completely miscible (II), and partially miscible (III) blend of polymers.

Figure 4. Graphical models of the amorphous matrix of the wood cell wall: A) from ref. 29, B) from ref. 34, and C) from ref. 35.
Figure 1. Classification of the types of multiphase polymer systems.
Figure 2. Schematic representation of the dynamic mechanical behavior of a completely miscible (---), completely immiscible (----), and partially miscible (---) blend of a 50:50 composition of components A and B.
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Figure 4. Graphical models of the amorphous matrix of the wood cell wall: A) from ref. 29, B) from ref. 34, and C) from ref. 35.
CHAPTER 2. THERMAL AND DYNAMIC MECHANICAL BEHAVIOR OF HYDROXYPROPYL CELLULOSE FILMS.

ABSTRACT

Differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA) were used to characterize the morphology of solvent cast hydroxypropyl cellulose (HPC) films. DSC results were indicative of a semi-crystalline material with a melt at 220°C and a glass transition at 19°C ($T_1$), although an additional event was suggested by a baseline inflection at about 80°C ($T_2$). Corresponding relaxations were found in the dynamic mechanical spectrum, as well as a secondary relaxation at -55°C which was attributed to the interaction between hydroxyl groups of the polymer and the presence of residual diluent. Evaluation of the influence of casting solvent concluded that the high temperature tanδ peak ($T_2$) arises from a more highly ordered phase, presumably resulting from the formation of a liquid-crystal mesophase while in solution. Crosslinking with a diisocyanate increased the peak temperature of the two primary relaxations, and resulted in a more clearly defined peak for the $T_2$ transition. From this behavior it was concluded that both $T_1$ and $T_2$ are similar to glass transitions ($T_g$'s) associated with an amorphous component and a more highly ordered phase (due to a residual liquid crystal superstructure) in the HPC bulk.
INTRODUCTION

The development of plastics and fibers from cellulose derivatives dates back more than a century (1). The greatest growth occurred during the first half of this period, followed by a decline in commercial significance leading to the relatively stagnant market which the cellulose derivatives are caught in today. Interestingly, this lackluster period for the cellulosics coincides with the growth of polymer physical chemistry and structural characterization techniques – an area of polymer science which was not heavily emphasized in the industry. This is particularly true in the case of cellulose ethers whose market was dictated by such common properties as water solubility, physiological inertness, and high surface activity (2). Consequently, the utilization of these polymers in such applications as thickeners, binders and colloidal agents has restricted their study to, primarily, solution behavior.

The interest in extending the cellulose derivatives into new engineering plastics applications has been renewed in the last decade. This is a direct result of the discovery by Werbowyj and Gray (3,4) that hydroxypropyl cellulose (HPC) forms liquid crystal structures in concentrated water solutions. A flurry of reports soon followed extending this observation to include a wide array of cellulose and cellulose derivatives (5-8), which have
been compiled in a recent review by Gray (9). As implied above, cellulosic liquid crystals are predominantly lyotropic in character which necessarily emphasizes the solution behavior (10,11) of these polymers. However, it is necessary to understand how the solution phase behavior translates into material properties of the bulk polymer if this phenomenon is to be utilized in the development of new and improved engineering plastics.

This aspect has been greatly advanced by the recognition of the formation of liquid crystals in the bulk (i.e., thermotropic) of some hydroxypropyl celluloses (12) and various derivatives (13) of HPC. Even so, only isolated reports on the thermal behavior of HPC have occurred in the literature and have generally been concerned with the detection of the mesomorphic structures. Consequently, a comprehensive picture of the morphology of this unique cellulose derivative, and its relationship to physical properties has not yet been adequately addressed.

An extensive study on the bulk morphology of HPC by Samuels (14) first revealed the complex morphological order of this polymer, but emphasized only the crystalline melt so far as thermal properties were concerned. Similarly, later reports have dealt with fairly limited temperature ranges. A glass transition ($T_g$) was reported (15) at 10°C using inverse gas chromatography to characterize polymer-solvent interactions; and, was later substantiated
in an unrelated study using dynamic mechanical techniques. In addition, compression molded samples of HPC revealed a second-order transition by DSC at about 110°C (16), which has been attributed to a residual nematic phase in the bulk polymer. This would certainly be consistent with results by Navard and Hardins (17) which indicate that the amorphous phase of HPC is actually a low order cholesteric phase. But, it also emphasizes the ambiguous nature of HPC morphology at this time.

It is the objective of this work to further characterize the thermal and dynamic mechanical behavior of hydroxypropyl cellulose. Information regarding the phase origin of the various thermal transitions may be obtained by varying the preparation conditions to restrict, or enhance, the development of supermolecular morphology in the form of a liquid crystal mesophase. Additionally, the nature of the various relaxation processes in this material will be addressed through the evaluation of the influence of crosslinking on the temperature at which the transitions are found to occur. This is expected to provide further information on the supermolecular morphology of HPC and its relationship to the physical properties of this material.

**EXPERIMENTAL**

The hydroxypropyl cellulose used was Klucel 'L', manufactured by Hercules, Inc. This particular HPC has a nominal molecular weight of 100,000 g/mol and a molar
substitution of 4 propylene oxide groups per anhydroglucose unit (schematically presented in Figure 1). Films were prepared by solution casting from dioxane or acetone in Teflon molds. The films were left for 24 hours at ambient conditions to allow for solvent evaporation before being removed from the molds and transferred to a vacuum oven. The films were dried under vacuum at 60°C for one week and stored over P₂O₅ in a vacuum dessicator.

CROSSLINKED HPC FILMS:

Hydroxypropyl cellulose films were crosslinked out of a 10% solution of either dioxane or acetone cast into Teflon molds. Toluene diisocyanate (TDI) was used as the crosslinking agent with a dibutyl tin laureate (Union Carbide T-9) catalyst. The cure schedule included 24 hours at ambient conditions to allow for solvent evaporation, followed by 12 hours at 125°C in a forced-air oven. Formulation details are included in Table I.

DIFFERENTIAL SCANNING CALORIMETRY (DSC):

A Perkin-Elmer DSC4 interfaced to the Thermal Analysis Data Station (TADS) was used for thermal analysis with a heating rate and cooling rate of 20 deg C/min. All samples were run under a purge of dry nitrogen.

DYNAMIC MECHANICAL THERMAL ANALYSIS (DMTA):

DMTA of the HPC films was performed with the Polymer Laboratories DMTA interfaced with a Hewlett-Packard 9816 microcomputer for data acquisition. A heating rate of 4
30

deg C/min was used with a frequency of 10 Hz. Typical sample dimensions were 0.25 x 1 x 15 mm (t x 1 x w) in a single cantilever beam geometry.

SWELLING STUDIES:

The percent weight gain of diluent and the amount of soluble material of the HPC networks were determined gravimetrically. About 0.5 gram of the dry sample was placed in water until an equilibrium weight gain was reached (~5 days). After weighing the swollen samples, the material was again dried in a forced-air oven at 110°C for 3 days and re-weighed. The percent swell and percent solubles were calculated as follows:

\%
swell = [(W_s - W_2)/W_2] \times 100

\%
solubles = [(W_2 - W_1)/W_1] \times 100

where \( W_1 \) is the dry weight of the film before swelling, \( W_2 \) is the dry weight after swelling, and \( W_s \) is the weight of the diluent swollen network.

RESULTS AND DISCUSSION

SOLVENT CAST HPC:

Differential Scanning Calorimetry: The most prominent thermal event observed in HPC by calorimetry (Figure 2) is the crystalline melt which occurs over a 40 degree temperature range, from 165°C to 210°C. Using Samuel's (14) value of \( \Delta H_u = 6.44 \text{ cal} \cdot \text{g}^{-1} \), the heat of melting for this sample of 0.96 cal·g⁻¹ yields a value of 14.4% crystallinity, in excellent agreement with previous reports
Although a liquid crystal-isotropic transition has been reported for HPC of lower molecular weight (17), no evidence of this feature is found here.

The low temperature region of this scan shows a second-order transition at about 20°C, corresponding to the value reported by Aspler and Gray (15) as the glass transition \( T_g \) using inverse gas chromatography. Above this event, the material continues a relatively rapid increase in heat capacity \( C_p \) before plateauing at about 120°C. Over this same temperature region the presence of a second \( T_g \)-like event has been noted for a lower molecular weight HPC; however, in this material the identification of an additional thermal event cannot yet be made, even though there does appear to be an inflection in the baseline at about 80°C.

In an attempt to enhance the observed thermal response over this temperature range, the sample was annealed at various temperatures to induce enthalpy relaxation (18). As seen in Figure 3, after a 12 hour period at 50°C a small peak is observed in the heat capacity curve at 75°C. As the annealing temperature is increased, a small peak occurs at a constant 25 degrees higher and a relatively constant intensity. Although this is somewhat consistent with expected behavior, a peak is also induced when the sample is treated at 125°C which is above the specific event of interest. This observation would preclude the
immediate assignment of a glass transition occurring over this temperature region, seemingly indicating that the thermal response at this point is at least partially influenced by the presence of small, imperfect crystals.

Although inconclusive as to the nature of the observed thermal response in the intermediate temperature region (i.e., 60° to 130°), the results on annealed materials suggest the presence of an additional phase in bulk HPC. Further substantiation of this concern can indirectly be obtained by a more detailed consideration of the glass transition. Of particular interest is the breadth of the transition which occurs over a 50 degree temperature range, and the relatively small change in heat capacity that is associated with the T_g. While this is not particularly unusual for a semi-crystalline polymer, the amorphous phase should be much more prominent since the degree of crystallinity is estimated at only 14%. Consequently, a much sharper transition with a considerably greater change in heat capacity would be expected for this HPC. In addition, if the T_g of HPC at this composition were estimated from the Fox equation (19) using a T_g of 220°C for cellulose (20) and -60°C for propylene oxide (21) a value of -5°C is obtained. Surprisingly, this represents a 25 degree discrepancy. Although a certain degree of uncertainty lies with this approach, the implication remains that chain mobility may be restricted to a much greater degree than
would be expected. Certainly, this could not be accounted for by such a small crystalline phase component.

Dynamic Mechanical Thermal Analysis: Dynamic mechanical analysis is generally recognized as being more sensitive to molecular motion, and is, therefore, quite useful for evaluating subtle transitions in polymers. Figure 4 shows the dynamic mechanical spectra of hydroxypropyl cellulose cast from dioxane (solid line) and acetone (dashed line). Although obvious distinctions exist, the peaks or relaxation processes in the tan\(\delta\) curve at 1) \(-60^\circ C\) \((\beta)\), 2) \(10^\circ C\) \((T_1)\), and 3) approximately \(80^\circ C\) \((T_2)\) are common to both spectra. It is of considerable interest to identify the origins of these dispersions; particularly, the \(T_1\) and \(T_2\) peaks which involve large scale mobility as evidenced by the associated loss in modulus.

The low temperature, \(\beta\)-transition shows little variance between the two spectra, and can readily be attributed to a secondary relaxation process since there is no catastrophic loss in modulus. Similar relaxation phenomena have been noted in a variety of hygroscopic systems (22) and explained as a result of the interaction between diluent (e.g. water) and hydrogen bonding sites in the polymer. In line with this explanation, this process could not be detected in carefully dried samples or, for example, in a second scan of the same sample.

The influence of casting solvent becomes much more
obvious in the higher temperature relaxations of HPC. The distinction between these two solvents is that HPC forms liquid crystals in dioxane, while this degree of supermolecular order is not achieved in acetone (15). With this in mind, the differences between the observed dynamic mechanical response of these two HPC films become clearer. In the case of the dioxane cast film, the T₁ relaxation appears more as a shoulder on the low temperature side of a broad, but clearly defined, peak (T₂) centered at about 80°C. The acetone-cast film shows a more clearly resolved T₁ peak, while the T₂ relaxation is much weaker and falls off at a lower temperature. This result implies that the T₁ peak arises from an amorphous phase and should be considered as a glass transition in accord with earlier reports (15, 16).

Analogous situations with regard to T₂ in semi-crystalline polymers, i.e. a second relaxation above the material's glass transition, have often been ascribed to relaxations in the crystallites (23). However, no difference in crystallinity was observed between the two samples with estimates of 14.0% and 14.4% obtained for the acetone and dioxane cast films, respectively. The difference in the intensity and definition of this loss tangent peak has to be the result of a greater extent and higher degree of supermolecular order due to liquid crystal formation in the dioxane solvent. Interestingly, the
softening point of this HPC sample determined by thermomechanical analysis is 90°C suggesting that this residual phase may comprise a significant fraction of the system, contributing to the overall thermal behavior.

Additional information on the nature of these three (β, T₁, and T₂) relaxation processes can be gained by evaluating the effect of frequency on the peak temperature. Figure 5 shows the Arrhenius plot generated from this experiment on the dioxane cast HPC film. The activation energies derived for the three mechanisms are as follows:

$$\beta (-60^\circ) = 62 \text{ kJ\cdot mol}^{-1}$$
$$T_1 (10^\circ) = 190 \text{ kJ\cdot mol}^{-1}$$
$$T_2 (80^\circ) = 232 \text{ kJ\cdot mol}^{-1}$$

While these values are certainly in align with the previous assignments of relaxation origins, it is interesting to note the similarity of the activation energies, Eₐ, of the T₁ and T₂ peaks. The implication is that similar mechanisms are in effect. That is, both of these relaxations are like glass transitions, involving large-scale segmental mobility in two distinct phases which vary, presumably, in the degree of supermolecular order.

An additional feature of interest in the DMTA spectrum of HPC, Figure 3, is the increase in log E' that occurs at 40°-45°C. This type of behavior can only be accounted for by three effects: 1) crosslinking, 2) solvent evaporation, or 3) crystallization (for example see ref. 21). Of these
three alternatives, there is no reason to expect any contribution from crosslinking. Certainly, because of the hygroscopic nature of this system, solvent loss cannot be excluded; however, thermogravimetric analysis revealed no weight loss over this temperature range. Thus, this observation must be explained with crystallization. No event is seen in the DSC trace around this point (Figure 1) but the response could be the result of strain-induced crystallization which would not necessarily be detected by calorimetry. To further confuse the issue, the occurrence of this modulus increase was very inconsistent and the parameters influencing this type of response were not successfully isolated. It is worth mentioning that this same behavior has been observed in ethyl cellulose, ethyl hydroxyethyl cellulose, and cellulose tri-acetate in this laboratory (ref. Rials, unpubl. ms.).

CROSSSLINKED HYDROXYPROPYL CELLULOSE:

The temperature at which a polymer $T_g$ occurs can be elevated by restricting the mobility of the chains. This is typically accomplished by crosslinking the polymer such that additional energy is required to induce the cooperative motion characteristic of the glass transition (24). Some information on the nature of the relaxation processes in HPC can be gained by taking advantage of this fact. Table I summarizes the effect of crosslinking agent addition on network structure and both transition tempera-
tures, $T_1$ and $T_2$.

It is interesting to note the consistently higher swelling and sol fraction in the case of materials crosslinked out of acetone. This difference may result from a more random distribution of crosslink points in the absence of liquid crystal mesophase formation. However, as the amount of TDI increases the difference becomes much smaller. It is worth noting that in both systems the amount of light transmission when viewed through crossed-polarizers increased dramatically with increased crosslinking, but was consistently greater in the films which were prepared using dioxane as the solvent. It appears that crosslinking the HPC chain enhances the formation of an ordered phase in this system.

Dynamic mechanical analysis of these materials (Figure 6) reveals similar trends in both solvent series. As the crosslink density increases, the $T_2$ peak is shifted to higher temperatures and increased in intensity. Interestingly, in the acetone cast films the $T_1$ peak remains much more distinct with its peak maximum occurring at about $5^\circ C$ higher than that same film crosslinked out of dioxane. However, the important feature of this result is that both primary relaxations $T_1$ and $T_2$ are shifted to higher temperatures as the degree of crosslinking increases. This implies that these two relaxation processes in HPC resemble a glass transition and arise from
two different morphological phases which vary in their
degree of order.

CONCLUSIONS:

Characterization of the thermal and dynamic mechanical
behavior of hydroxypropyl cellulose revealed that this
material consists of essentially three distinct phases in
the bulk: a crystalline phase, an amorphous phase, and a
component which exhibits an intermediate level of order.
Both analytical approaches suggest that this latter phase
(arising from the liquid crystal mesophase formed in
solution) may constitute a significant volume fraction of
the overall system.

The presence of this superstructure was most clearly
reflected in the dynamic mechanical properties through two
relaxation peaks at about 10°C and 80°C, arising from the
amorphous and intermediate ordered phases, respectively. As
judged by the activation energy associated with the
relaxation of these two phases, and the effect of
crosslinking on both peak temperatures, it was concluded
that a Tg-like transition originates from both phases. This
observation is consistent with earlier reports which have
indicated the presence of a liquid crystal mesophase in
bulk HPC at room temperature.
ACKNOWLEDGEMENTS:

The author would like to thank Hercules, Inc. for providing the hydroxypropyl cellulose used in this work.
LITERATURE CITED


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TABLE I. Preparation and characterization of hydroxypropyl cellulose films crosslinked with toluene diisocyanate.

<table>
<thead>
<tr>
<th>Sample I.D.</th>
<th>Solvent</th>
<th>TDI HPC (%)</th>
<th>Swell (%)</th>
<th>Sol Fract. (%)</th>
<th>T&lt;sub&gt;1&lt;/sub&gt; (°C)</th>
<th>T&lt;sub&gt;2&lt;/sub&gt; (°C)</th>
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<td>-</td>
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<td>0.3</td>
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<td>126</td>
</tr>
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</table>
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CHAPTER 3. THE MORPHOLOGY AND PROPERTIES OF POLYMERIC BLENDS OF HYDROXYPROPYL CELLULOSE AND LIGNIN.

ABSTRACT

Polymeric blends of hydroxypropyl cellulose (HPC) and an organosolv lignin (OSL) were prepared by mixing in solutions of both pyridine and dioxane, and casting as films, and by mixing in the melt followed by extrusion. All preparations exhibited partial miscibility as evidenced by the single T\textsubscript{g} up to a composition of 40 wt. % lignin; however, above this level phase separation was found to occur. Throughout all the evaluation methods, the dioxane-cast and extruded blends were distinguished from the materials prepared from pyridine solution. Although no strong secondary interactions were found to occur between this polymer pair, a positive deviation from additivity was noted for the first two blend series while the pyridine blends were well described by this approximation. This positive deviation in T\textsubscript{g} is explained by a smaller amount of amorphous material in HPC available for interaction with the lignin component than would be expected as a consequence of the formation of a liquid-crystal mesophase. This explanation is supported through the observation of a rapid increase in modulus (~150%) with very low lignin content and an associated sharp decline in the ultimate elongation achievable. The development of morphological
features observed by scanning electron microscopy provide further substantiation of this hypothesis.
INTRODUCTION

The physical blending of polymers has become an extremely popular means of producing materials with desired properties. The technological advancement of these systems, while attributable to several factors, has primarily resulted from the relatively low investments required at the development stage (1). Interestingly, this intense technological interest has, somewhat out of turn, provided much of the motivation in the evolution of blend phase behavior as a topic of major scientific research interest. When two polymers are blended together, they may exist in a completely homogeneous state where their chain segments are mixed at the most intimate level or they may segregate into distinct regions or phases (2). Characterization of the relationships between molecular structures and blend phase behavior remains the subject of intensive research effort since the a priori prediction of blend morphology is not yet possible.

The perceived application of being able to predict the morphology of a polymer pair is primarily concerned with the selection of components which form a miscible blend, i.e. a single, uniform, homogeneous phase. Although immiscible systems are not immediately excluded from interest, the production of a novel material with unique thermal, mechanical, or optical properties requires that the polymer pair be miscible. Interestingly, the
definition of a miscible system as a homogeneous, single-phase material immediately restricts the question to amorphous polymers which have been the subject of most fundamental treatments of polymer phase behavior (3,4). Obviously, the implication is that a crystallizable component will necessarily yield an immiscible system since the definition, in its purest form, requires that a new crystal structure be formed when the system is truly miscible. Consequently, blends of semi-crystalline polymers were largely avoided in the early stages of blend phase behavior investigations. Recently, studies on binary systems containing a crystallizable component have received considerable attention from both practical and theoretical considerations. The most common, or successful, example is blends of poly(vinylidene fluoride) (5-7), the study of which has provided considerable information on polymer interactions.

The above categorization of binary blends from the standpoint of component morphology has been expanded due to the emergence of polymers composed of rigid, rod-like chains such as the aromatic polyamides which exhibit thermotropic liquid crystal behavior (8). Because of the implications of high modulus, high strength materials (9) as a result of chain orientation, these systems offer the potential for formation of unique composite materials. The synonymy between thermotropic liquid crystal polymers and
Copolyesters has prompted most of the preliminary investigations to center on these polymers as a component. Recent results by Siegmann et al. (10) using an amorphous polyamide as the second component of the blend found a dramatic increase in both modulus and tensile strength as the content of the liquid crystal component was increased. Similar results were reported by Joseph et al. (11) on blends with poly(ethylene) terephthalate, although both systems revealed a heterogeneous two-phase morphology.

The thermotropic liquid crystal nature of the synthetic polyesters makes this a particularly attractive blend component. However, the scope of liquid crystal blends is greatly expanded by considering lyotropic systems, or polymers which form liquid crystal phases above a critical solution concentration such as polypeptides, polyamides, and polyisocyanates (12). Another group of lyotropic polymer which is particularly attractive due to its abundance is that of cellulose and its derivatives (13). Most of the research effort on these systems has been on the characterization of solution behavior, with very little work on bulk properties or composite materials. For example, studies on the compatibility of mesophases in the ternary system cellulose/cellulose acetate/cellulose acetate/dimethylacetamide (14) showed incompatibility at all concentrations, a result that was further substantiated on the system cellulose acetate/hydroxypropyl cellulose/
dimethylacetamide (15) prompting the conclusion that similar mesophase structure does not necessarily favor compatibility. However, as was noted, no consideration was given to the role of the interactions based on enthalpy parameters which would, in itself, suggest phase separation of these polymers.

Of the variety of cellulose derivatives, hydroxypropyl cellulose (HPC) has been the model system of choice in the evaluation of parameters affecting liquid crystal formation. An additional boost for this polymer was provided when thermotropic liquid crystal behavior was discovered (16). However, preliminary investigations on films prepared from liquid crystals have not been particularly encouraging with only moderate increases in modulus being realized (17). Utilization of HPC as a component in polymer blends is a concept which has been largely overlooked, despite the tremendous practical and fundamental implications.

A particularly intriguing composite system for study can be found in the original source of this biological polymer. In the wood cell wall, the carbohydrate component is intimately associated with lignin - an aromatic polymer comprised of phenylpropane units (18). Conventionally described as a three-dimensionally crosslinked polymer, lignin's biological role is perceived as a structural matrix imparting strength and rigidity to the biocomposite.
However, because of the complexity of the biological system, the morphology of this biological composite has not yet been clearly defined. This is particularly evident in light of recent reports that the \textit{in situ} lignin shows a considerably more ordered structure than was originally thought (19). What is clear is that there must exist a unique relationship between lignin and the carbohydrate component with which it is so closely associated. It remains to be seen if this unique association can be re-established upon combination of the isolated components to form new and useful polymer composites.

In addressing the question of polymer blends from lignin and HPC, the effect of processing, or blend preparation, represents a prominent concern. Because of the lyotropic and thermotropic nature of HPC, the influence of solvent and temperature on liquid-crystal mesophase formation, as well as the degree of association of lignin (20) could dramatically affect the overall morphology and properties of the blend. Consequently, in evaluating blends of lignin and hydroxypropyl cellulose it is the goal of this work to characterize the extent to which blend preparation from solution (with dioxane and pyridine), and by mixing in the melt followed by injection molding determines the overall morphology and properties of this binary system as the weight fraction of the component polymers is varied.
EXPERIMENTAL

Sources and Characterization of Components:

The hydroxypropyl cellulose (HPC) used in this study was provided by Hercules, Inc. (Klucel 'L'). This material had a molar substitution of 4 propylene oxide units per anhydroglucose unit and a nominal molecular weight ($M_w$) of 100,000 as reported by the manufacturer.

An organosolv lignin (OSL) preparation, isolated from aspen wood, was obtained from the Biological Energy Corporation of Valley Forge, PA. Details of the yield and isolation conditions were not made available. Molecular weight was determined as $<M_n> = 900$ and $<M_w> = 3000$ by gel permeation chromatography. Pertinent structure and property data of the homopolymers are compiled in Table 1.

Preparation of Blends:

The HPC/OSL blends were prepared by mixing in solution and mixing in the melt. Individual solutions of the components were prepared (~5 wt.%) with both dioxane and pyridine. The solutions were then mixed together and stirred for approximately 12 hrs., after which time they were cast into Teflon molds. The films were kept at ambient conditions for 24 hours followed by further drying under vacuum at $80^\circ C$ for one week. The resultant films were stored over $P_2O_5$ in a vacuum desiccator for testing.

Extruded blends were prepared with a Custom Scientific Instruments Mini-Max injection molder. The extrusion
temperature was 170°C and the residence time was no longer than five minutes. The blended material was extruded into a warm, dog-bone mold for testing.

**Differential Scanning Calorimetry (DSC):**

Thermal properties of blends were determined on a Perkin-Elmer DSC-4 interfaced to the Thermal Analysis Data Station. All samples were scanned at a heating rate and cooling rate of 20 °C/min under a purge of dry nitrogen. The glass transition temperature (T_g) was defined as one-half the incremental change in heat capacity at the transition. The melting temperature (T_m) was determined as the temperature at which the last crystal melt was observed while crystallization temperatures (T_c) were taken as the peak maximum temperature.

**Dynamic Mechanical Thermal Analysis (DMTA):**

Dynamic mechanical properties were determined with the Polymer Laboratories DMTA interfaced to a Hewlett-Packard 9816 microcomputer. Samples were tested in a single cantilever geometry at a frequency of 10 Hz. A heating rate of 4 deg/min was employed for all samples.

**Mechanical Properties:**

Uniaxial stress-strain behavior was determined in tension with a standard Instron testing machine. A crosshead speed of 1 mm/min was employed on samples which were cut with a die in a dog-bone shape (solvent cast films), or in the case of extruded samples, a dog-bone
mold was used. Tensile characteristics were calculated on the basis of initial dimensions (gage length = 10 mm, film area = 0.71 mm$^2$ and extruded sample area = 4.2 mm$^2$).

**Fourier Transform Infrared Spectroscopy (FTIR):**

FTIR spectra were obtained in transmission mode on thin films cast on a germanium crystal with a Nicolet DXB-II spectrophotometer. Ten scans were made of each sample at a resolution of 2 cm$^{-1}$. Dry nitrogen gas was used as the atmosphere.

**Wide Angle X-Ray Scattering (WAXS):**

Wide angle X-ray diffraction patterns of the individual components and their blends were obtained in the reflection mode using a Phillips diffractometer and CuKa source. Sample thickness was approximately .010 in.

**Scanning Electron Microscopy (SEM):**

Scanning electron micrographs were taken on an Amray, Model AMR - 900 microscope. Surfaces were prepared by freezing in liquid nitrogen and fracturing. The fracture surface was sputter coated with carbon and a gold-palladium alloy.

**RESULTS AND DISCUSSION**

**Thermal Properties:**

**GLASS TRANSITION BEHAVIOR:** The variation in the glass transition temperature ($T_g$) with blend composition has been extensively applied in determining the state of miscibility of a polymer pair (2). When phase separation of the blend
components occurs the characteristic $T_g$ of the two homopolymers is observed while an intermediate value is typically observed in miscible systems. Figure 1 shows a series of thermograms of varying compositions for the blends prepared by extrusion. In this system a single $T_g$ is observed up to a lignin content of 55% where two glass transitions are observed at 70°C and about 128°C. Interestingly, the higher glass transition in the 55-85% lignin blends is slightly above that of the pure component (lignin) which is at 115°C. It appears, however, that at the higher lignin levels the blend is heterogeneous even though some miscibility of the polymer pair is evidenced by the depression of the pure lignin $T_g$. With regards to the $T_g$ behavior at lower levels of lignin addition, it is interesting to note the differences in sharpness and intensity of this event in the 40% lignin blend when compared to those blends of 20% and below. This observation may best be addressed by first considering more closely the DSC analysis of the pure HPC. In this component, an additional thermal event is apparent at 70°C-110°C. This transition has been related in earlier work to a higher ordered mesophase. Apparently, as the amount of lignin in the blend is increased, this transition is depressed in temperature and effectively masks the $T_g$ of the completely amorphous component. At the 40% blend, the mesophase structure is disrupted to the
point that the conventional step-increase associated with a glass transition becomes clearer.

Figure 2 shows a comparison between the blends prepared by solvent casting as well as extrusion. For all these systems a single glass transition is observed for blends with less than 50% lignin content. In the case of materials blended in pyridine, the $T_g$ of the blend appears to be additive falling right on the tie-line between the two pure components. However, the materials blended in dioxane and in the melt show a significant positive deviation from additivity. It should be noted that this deviation may not be as great as it appears in the dioxane cast blends as the $T_g$ of the pure lignin (cast from dioxane) was inexplicably found to be about 40° lower than that of the extruded and original lignin sample. Similarly, a 25 degree depression in $T_g$ was observed when the lignin was cast out of pyridine solution. Even with this in mind there remains an obvious distinction between the pyridine-cast blends and the other preparations in that a consistently lower $T_g$ is observed than would be expected.

The positive deviation of the $T_g$ from additivity has served as an indicator of hydrogen bonding in a number of binary polymer blends (21,22). While this behavior certainly cannot be ruled out in the present system, this observation could also be accounted for by a somewhat lower fraction of amorphous material in HPC than was counted on.
That is, if the lignin is limited to interaction with the amorphous phase of HPC, this component may represent a lower volume fraction of the system than was originally considered due to the presence of a liquid-crystal mesophase. This would result in a higher lignin fraction in the miscible portion of the blend than that calculated and an apparently higher glass transition temperature. Alternatively, if some interaction exists between lignin and a mesophase component the increased structural arrangement that exists could result in a $T_g$ above that expected as a consequence of reduced free volume.

A final feature of interest in Figure 2 is the temperature where the phase separated transitions occur. Again, in the extruded and dioxane blends the lignin-rich phase is observed at temperatures considerably higher than the pure components while the low temperature transition remains close to the tie-line. In the pyridine series, the opposite result is found which may, again, reflect variations in the level of structural ordering in the composite. Irregardless, it does emphasize the conclusion that the HPC/OSL blend is a partially miscible system as indicated by the variation in $T_g$ up to a 40% level of addition of lignin.

To further address the question of relaxation processes in these blends, dynamic mechanical analysis was applied which has proven to be more sensitive to subtle transitions
such as the higher temperature transition in hydroxypropyl cellulose. Results on the extruded series are shown in Figure 3. The tanδ spectrum for pure HPC reveals two primary relaxations at 30°C (T₁) and 85°C (T₂). Several researchers have used various methods to identify the origin of the T₁ peak as the amorphous Tg. The T₂ has been assigned to various mechanisms; however, previous results have shown it to be related to the presence of a mesophase, and this corresponds to the high temperature transition in DSC. The evaluation of the effect of lignin content provides an interesting contradiction to the observations made with DSC. This approach shows that as the lignin content is raised, the intensity of the T₂ peak increases at the expense of the T₁ peak. This observation implies a preferential association of lignin with the liquid crystal mesophase to the exclusion of the amorphous phase of the HPC.

While this case would seemingly be the most unlikely of the two, it cannot be immediately excluded as an option. Although lignin is generally regarded as a three-dimensional amorphous polymer by the scientific community of interest, evidence has been compiled to contradict this conceptual view. Specifically, monolayer film studies have indicated that lignin is essentially discotic, or planar, in character (23). Similar conclusions regarding this view have been drawn as a result
of studies on the tremendous propensity toward association in solution (20). In addition, the application of Raman spectroscopy to whole wood led to the conclusion (although weak) that lignin is much more highly oriented in situ than has been traditionally proposed (19). With the evidence suggesting a highly ordered morphology, the possibility of mesophase enhancement cannot be ignored.

Returning briefly to Figure 3, the increase in both peak intensity and peak sharpness between the 20% and 40% blends is worth noting. This point is nicely illustrated in the storage modulus curve which shows no decrease for the 40% blend until about 45°C while the lower lignin content blends exhibit a loss in modulus beginning at about 0°C. This behavior is in agreement with DSC results, and presumably reflects a modification in phase morphology.

The transition temperatures determined by dynamic mechanical analysis are summarized in Table 2 for all of the blend preparations. The most conspicuous difference between the materials is the observation of at least a shoulder for the \( T_1 \) transition at much higher levels of lignin addition in the solvent cast blends. This is particularly true for the pyridine-cast series which exhibit this shoulder even at 40% lignin content, which is somewhat consistent with the lower \( T_g \) observation made on this system using DSC. In addition, while the \( T_2 \) peak shows a consistent increase in temperature, a drop in the
$T_2$ peak temperature is found for the 20% blend in the pyridine preparations and at 10% for the extruded materials. This may be a reflection of the convoluting effect of both relaxation processes, as was suggested by calorimetry. While it cannot be definitely concluded that lignin preferentially interacts with either the amorphous phase or nematic mesophase of HPC at this point, it is apparent that a partially miscible blend is found, exhibiting compatibility with up to 40% of the lignin component.

MELTING BEHAVIOR: Table III summarizes the pertinent data related to the melting behavior of the HPC/OSL blends. In general, a fairly constant decrease in the magnitude of all the parameters with the increase in the non-crystallizable lignin component is observed. At the highest lignin level, where crystallinity could be accurately measured, the pyridine and extruded preparations show a depression of the melting point $T_m$ of about 40° while the dioxane cast blends maintained a consistently higher $T_m$ with a decrease of only 30° reflected at a 40% lignin content. However, from the heat of fusion data presented both the dioxane and extruded blends are essentially identical, as was suggested by the $T_g$ behavior of these two preparations. The pyridine cast blends are again the exception showing a slightly higher heat of melting until a decrease of 0.30 cal/gram occurs at the
maximum lignin content. This result appears to be somewhat conflicting with the lower Tg's of this blend series when compared with the other two preparations. Generally, the higher crystalline content would slightly elevate the glass transition (24) by tying up the amorphous chains and restricting mobility, as well as reducing the amount of amorphous material available for interaction with the second component.

The variation in both melting temperature and crystallization temperature is illustrated in Figure 4. As was suggested earlier, there appears to be very little difference in Tm between the various preparations. A similar conclusion can be drawn for the crystallization temperature of the materials which again show a fairly constant decrease, essentially paralleling that of Tm. Considering the influence of Tg on the kinetics of the crystallization process, it is of interest to note that while crystallinity is essentially excluded from this system at a weight fraction of 40%-50% lignin there remains a substantial crystallization window (Tm - Tg) of about 120°K in the worst case of extruded materials showing a Tg of 330°K at this composition. Typically, crystallinity would not be expected to be lost until this window is much smaller (25).

Applying a value of $\Delta H_m = 6.44 \text{ cal.g}^{-1}$ reported by Samuels (26) for a similar hydroxypropyl cellulose, the
heat of melting data in Table III were converted to percent crystallinity, the results of which are shown in Figure 5. The distinction between pyridine blends and the other two preparations is again readily apparent. At the lower levels of lignin addition there is little difference in the level of crystallinity of the blend and that of the pure component at a similar composition (dashed line). At the intermediate levels some deviation (~2%) is observed with the most significant drop in crystallinity occurring between 30% and 40%. In contrast to this behavior, both the dioxane and extruded blends show the most substantial loss in crystallinity at the onset of lignin addition. The difference then remains constant at about 4% until the two groups meet at the 40% lignin blend. It is worth mentioning, even though these differences are small, the discrepancy between this observation and the T_g of the same blends. Associated with the lower degree of crystallinity in the dioxane and extruded preparations is a positive deviation in the T_g from additivity (Fig. 2). As mentioned earlier, this is in direct contrast to the expected behavior since a slightly larger amorphous fraction is now available for interaction. Since there is little reason to believe that pyridine would restrict, or hinder, the interaction between the two components, it would appear that the lower crystallinity level does not necessarily mean an addition to the amorphous volume fraction of HPC.
This could be explained by the formation of liquid crystal mesophases which have been reported both in dioxane (27) and at the extrusion temperature (28) of 170°C. The extent of interaction between the lignin component and HPC mesophase cannot be conclusively defined at this point, however.

Figure 6 shows the WAXS pattern for several blends cast from dioxane, as well as the pure components. Pure HPC shows two peaks at $2\theta = 8^\circ$ and at $2\theta = 20.3^\circ$ which have been assigned previously (26) to the 100 equatorial reflection and a slightly oriented amorphous component, respectively. The lignin component generally shows a broad, amorphous halo centered at about $21.7^\circ$ although a small peak is also found at $2\theta = 14.8^\circ$ to which no origin has been assigned. As the amount of lignin in the system is increased, there is a small increase in the position of the low angle peak before returning to the original position with a small shoulder at $8.6^\circ$. However, because of the small magnitude of the observed shift no significance can be placed on it at this point. No effect on the high angle peak is observed with lignin incorporation into the system, although there is a shift in the minimum between the peaks at 40%. Surprisingly, this is the only instance where the lignin pattern exerts any influence on the blend. The implications of this feature are not clearly understood, but may be a reflection of the favorable interaction at
lower lignin contents.

Also included with Figure 6 is a plot of the ratioed intensities of the two peaks (I-8°/I-20°) observed in pure HPC and its blends. As is shown, a substantial decrease in intensity of the low angle peak at 5% lignin content which is followed by a steady, gradual decline in the ratio. This result substantiates the pattern observed for the degree of crystallinity determined by DSC for this series, as well as the extruded blend preparations.

As has been established by DSC and WAXS, a purely crystalline HPC phase is detectable up to a 40% lignin content. The Tg behavior then reflects the state of mixing in the amorphous phase, and ideally the melting point of the crystalline phase will be depressed by its equilibrium with the amorphous phase (29). As discussed earlier, a dramatic decrease in Tm of about 40° was observed for all the preparations. This result allows an estimation of the intermolecular interaction parameter, B (30), to be obtained through the relation

$$-\frac{B}{RT_{m2}} \Phi_2^2 = \left[ \frac{1}{T_{m2}} - \frac{1}{T_{m2}^0} \right] \frac{\Delta H_{2u}}{RV_{2u}} + \frac{\ln \phi_2}{V_2} + \phi_1 \left[ \frac{1}{V_2} - \frac{1}{V_1} \right]$$

where the subscript 2 refers to the crystallizable component, the HPC; Tm2° is its equilibrium melting temperature; ΔH_{2u}/V_{2u} is its heat of fusion per unit volume of repeat unit for 100% crystalline material; V_2 is its molar volume; and φ_2 is its volume fraction in the
blend. For blends with components whose molecular weight is above 2,000 \( V_1 \) and \( V_2 \) are large and Equation 1 can be reduced to (29)

\[
T_{m2}^0 - T_{m2} = \frac{-BV_{2u}}{\Delta H_{2u}} T_{m2}^0 \phi_1^2
\]  

(2)

from which \( B \) can be directly evaluated from the slope of a plot of \( T_{m2}^0 - T_{m2} \) vs \( \phi_1^2 \). Figure 7 shows the construction of the plot using \( T_{m2}^0 = 486.2^\circ K \) (213.1\(^\circ C\)) as estimated by extrapolation to the 0 percent lignin content. The value of \( \Delta H_{2u}/V_{2u} \) has been reported previously (26) as 7.52 cal.cm\(^{-3}\) which leads to an estimation of \( B = -3.58 \) cal/cm\(^3\) for the collective data. The negative \( B \) value provide a further indication of miscibility between this polymer pair suggesting the presence of secondary interactions. However, while the observed behavior is adequately modeled \((R^2 = 0.91)\) with the assumption of linearity, closer evaluation of the plot suggests that this may not be the case. There appears instead to be a curvilinear relationship with the slope of the line decreasing at higher lignin contents which would be consistent with the incipient phase separation observed for this system. Consequently, the observed depression in \( T_m \) may be due to a decrease in lamellar thickness of the crystallites or an additional entropic consideration, a point that is substantiated by the failure of the line to pass through the origin. Although some doubt may be cast on the
magnitude of B, the negative value (suggesting secondary interactions) is not inconceivable considering the polarity of these two polymers and warrants further investigation.

Fourier transform infrared spectroscopy (FTIR) has been used successfully in addressing the question of specific secondary interactions in a number of miscible blends (31). Its improved resolution and sensitivity over conventional infrared allow the detection of small shifts in peak position which are often associated with intermolecular interaction in polymer pairs. Utilization of this technique in the current blend system revealed no changes in the low wavenumber part of the spectrum indicating that ether or carbonyl functionality is not involved. Figure 8 shows the expanded spectra of the hydroxyl region for the two pure components and blends containing 10%, 30%, and 55% lignin cast from dioxane. For the 10% and 30% blends, there is no shift in the frequency of the hydroxyl peak which occurs at 3458 cm\(^{-1}\). At 55% the peak is shifted to a lower frequency (3446 cm\(^{-1}\)) which is intermediate to the two pure homopolymers. Rather than an indication of any hydrogen bonding between the two components, this observation presumably results from a modified environment due to phase separation which was observed at this composition. Consequently, it must be concluded that no specific secondary interactions occur in this blend system, and the partial miscibility observed at low lignin
fractions is best explained by the similar solubility parameters of 10.7 (32) and 11.2 (33) for HPC and lignin, respectively. Again, this is a somewhat surprising result considering the extremely polar character of both materials.

**Mechanical Properties:**

Results of stress-strain tests on the blends prepared by solvent casting from dioxane and pyridine, and by extrusion are presented in Figure 9. Interestingly, the extruded and dioxane cast preparations are again distinguished from those blends prepared in pyridine. In all the materials, a dramatic increase in modulus (E) is observed which is above that predicted by the simple law of mixtures (34). However, at 15% lignin content the modulus of the blends prepared in dioxane and by extrusion are about 30% higher than that of the pyridine-cast blend and about 50% higher than the predicted modulus. However, above this composition the mechanical properties of these materials begins to fall off rapidly. Interestingly, tensile strength follows a similar trend with a 150% increase at the 10% composition in the case of the extruded materials while only a moderate increase is found for the dioxane series. The tensile strength of the pyridine series is essentially unaffected by lignin content. Some caution should be exercised in comparing the extruded materials with the solvent cast blends since a significant
size difference exists between these samples. While the modulus values are not affected, the presence of micro-flaws in the material, which are known to influence ultimate properties, would exert a greater influence on the solvent cast materials because of the relatively small cross-sectional area.

The ultimate strain levels achieved by the solvent-cast blends are also illustrated in Figure 9 (extruded blends are excluded because of grip failure in many samples). Both blend series are comparable in their behavior exhibiting a very rapid decline in the ultimate strain from about 30% to 10% at a very low lignin composition. This is in direct contrast to results obtained on blends of PMMA with lignin derivatives (35) where, despite moderate increases in modulus, ultimate properties were found to decline rapidly. In this case, the relatively sharp decrease in ultimate elongation accompanied by an equally rapid increase in modulus and tensile strength (in the extruded materials) would indicate the increased orientation of HPC chains in these blends. The unusual aspect of this behavior is emphasized when the low molecular weight of the lignin component is considered. Similar results on blends of a liquid crystal copolyester and an amorphous polyamide were reported by Siegmann et al. (10) and compared to reinforced composites. This is a particularly intriguing analogy considering the biological composite from which these
components were originally isolated.

**Blend Morphology:**

There is little doubt that many of the dramatic effects imposed on the mechanical behavior of these blends by lignin are the result of the development of supermolecular morphology. To further evaluate this concern, scanning electron microscopy (SEM) was used on the freeze fracture surfaces of the blends. Figure 10 shows the results of this analysis for blends containing 15% lignin from all three preparation methods. Not surprisingly, the most dramatic difference is observed between the extruded and solvent cast blends. In the injection molded samples, a somewhat fibrous character was obtained which was not observed in the pure material. This would account for the dramatic change in mechanical properties implying orientation of the hydroxypropyl cellulose chains as a result of the extrusion process.

There are dramatic differences between the two solution cast blends with pyridine exhibiting a relatively smooth surface. Interestingly, there appears to be a sheet-like, or lamellar organization associated with this blend. While this dioxane-cast blend shows a much rougher surface, appearing more nodular. Morphological studies of HPC have indicated that the basic building-block of supermolecular structure is a rounded particle resulting from the phase separation of liquid crystal structure during solvent
removal (28). The extent to which slippage and coalescence of these domain features occurs during solvent evaporation (or an induced orientation) largely determines the film morphology. It may be that the pyridine film structure is the result of this process, and thus did not advance to the same degree in materials blended in dioxane. However, this is only speculation as the differences between the two solvent cast blends are not clear. Despite the uncertainties, it is clear that a certain degree of order is retained in the hydroxypropyl cellulose chains at low lignin compositions as reflected in the morphology and in the mechanical properties.

A final point to be made concerns the state of miscibility of the two components. There is no evidence of phase separation in the blends, at least in the classical sense, indicating the miscibility of these polymers at lower (<30%) lignin compositions. This is consistent with the observations made on the T_g behavior by DSC.

CONCLUSIONS

Blends of hydroxypropyl cellulose and lignin provide an interesting system for study, incorporating two topics of scientific interest in that this composite includes a component which is both a lyotropic and thermotropic liquid crystal polymer. Conceivably, this type of system holds considerable promise for the development of novel composite materials as a result of the possible orientation of the
liquid crystal component and the implications to high modulus, high strength materials.

Because of the interest in the development of liquid crystal superstructure, blends were prepared by casting from dioxane and pyridine solutions, and by mixing in the melt and extruding. Surprisingly, the greatest similarity in all behavioral aspects evaluated occurred between the dioxane-cast and extruded preparations rather than the two solution blended preparations as can be seen from the following specific conclusions:

1) A single Tg was observed for all preparations up to a composition of 40%. The dioxane and extruded blends showed a significant positive deviation from additivity over this range while pyridine blends were well described by this approach.

2) Composition of the phases resulting from segregation at higher lignin levels were quite variable. In the dioxane and extruded blends, a phase was found to exhibit a Tg higher than the original components from 55-85% lignin content.

3) DMTA results suggested the presence of two relaxations in the range 25°C-125°C attributable to an amorphous and residual liquid crystal phase. The amorphous phase Tg was apparent at much higher levels of lignin addition in the pyridine blend, while being masked at an earlier stage for both dioxane and extruded preparations.
4) The melting point and crystallization temperatures were not dramatically influenced by the blending method, but exhibited a paralleled, consistent decrease as the lignin component was added.

5) The percent crystallinity in the blend decreased 5% with the first 5% of lignin in the blend and only an additional 6% up to 40% lignin content for the dioxane (this was also noted in the WAXS pattern) and extruded blends while blends cast from pyridine showed the opposite result.

6) The analysis of melting point depression yielded an intermolecular interaction parameter, \( B = -3.58 \text{ cal/cm}^3 \), suggesting strong secondary interactions between the components. However, the assumption of linearity may not have been sound as an apparent change in slope could be detected at about 15% lignin content. This would be consistent with the observed phase separation at slightly higher lignin contents.

7) No evidence of hydrogen bonding was detected by FTIR in spite of the highly polar nature of the two components. The establishment of intermolecular interactions is probably limited by the propensity toward intramolecular chelation of functional groups in both components.

8) An increase in Young's modulus of about 140% was found at compositions of only 15% lignin in both dioxane
cast and extruded materials. Although not as great, pyridine-cast blends also exhibited moduli well above that predicted by the law of mixtures.

9) The tensile strength of the extruded blends also exhibited about 150% increase before falling off at a composition of 15 wt.% lignin. Although a modest increase in tensile strength was noted for the dioxane series, the solution-cast blends were not as dramatically influenced.

10) Of particular interest, the ultimate elongation decreased sharply from about 30% to 5% with a weight fraction of lignin equal to 15%.

11) The development of supermolecular morphology was most clearly evidenced in the extruded preparations which exhibited a fibrillar structure in SEM. While differences were obvious in the fracture surface of the solution-cast blends, they were not readily attributable to a given morphological feature.

As expected, this polymeric blend does exhibit some unique behavior. From the results it can be concluded that this binary pair is, at least, a partially miscible system. As evidenced by the positive deviation of the Tg in the absence of strong hydrogen bond formation, the interaction between the two components is limited to the amorphous phase of the HPC, which comprises a lower volume fraction than is readily apparent. The discrepancy in amorphous volume fraction is presumably a consequence of a residual
liquid crystal mesophase formed as the casting solution reaches a critical concentration or at temperatures appropriate for the formation of a liquid crystal mesophase. Subsequently, the ordered chains of the mesophase are dispersed in an amorphous matrix blend of lignin and hydroxypropyl cellulose. The resultant material is similar then to a reinforced composite as illustrated by the dramatic enhancement of mechanical properties. As is particularly apparent from all experiments, this is particularly true for blends below a 40% lignin composition prepared from dioxane solution and by injection molding.

It is surprising that in such a polar system as this, that secondary interactions do not seem to play a dominant role in determining the miscibility and morphology of the material. This concern will be addressed further in subsequent work.

ACKNOWLEDGEMENTS

The author would like to gratefully acknowledge the assistance of Dr. S. S. Kelley in obtaining the WAXS patterns and Mr. T. A. DeVilbiss for his assistance with the FTIR analysis.

Also, thanks go to Hercules, Inc. for providing the hydroxypropyl cellulose.
LITERATURE CITED


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Figure 6. Wide angle X-ray diffraction patterns for HPC/OSL blends cast from dioxane for compositions designated on the plot. INSET: Variation in the ratio of peak intensities ($I_{8^\circ}/I_{20^\circ}$) with blend composition.

Figure 7. Plot of $(T_{m2} - T_{m2})$ vs. $\phi_1^2$ for HPC/OSL blends prepared from dioxane (○), pyridine (△), and extrusion from the melt (□).
Figure 8. Fourier transform infrared spectrum (FTIR) in the hydroxyl region of dioxane-cast blends at the designated composition.

Figure 9. The effect of preparation method and blend composition on the mechanical properties (Young's modulus, tensile strength, and ultimate strain) of HPC/OSL blends. Pyridine-cast (•); dioxane cast (★); and melt extrusion (+).

Figure 10. Scanning electron micrographs of freeze-fracture surfaces of A) extruded, B) dioxane, and C) pyridine blends at a composition of 15% lignin. (Magnification at 2,000x).
Table I. Pertinent Structure and Property Data of Hydroxypropyl Cellulose and Organosolv Lignin.

<table>
<thead>
<tr>
<th>Component</th>
<th>Abbrev.</th>
<th>Total OH (%)</th>
<th>α-OH (%)</th>
<th>$M_n$(mol)</th>
<th>$M_w$(mol)</th>
<th>$\rho$(cm$^3$)</th>
<th>$\delta$(cm$^3$)</th>
<th>$1/2 \alpha$</th>
<th>$T_g(\circ K)$</th>
<th>$T_b(\circ K)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydroxypropyl cellulose</td>
<td>HPC</td>
<td>12.2</td>
<td>-</td>
<td>100,000</td>
<td>1.17</td>
<td>10.7</td>
<td>298</td>
<td>485</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Organo- solv lignin</td>
<td>OSL</td>
<td>8.4</td>
<td>6.1</td>
<td>900</td>
<td>3,000</td>
<td>1.24</td>
<td>11.2</td>
<td>385</td>
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1) As per information provided by Supplier (Hercules, Inc.).
Table II. Summary of transition temperatures ($T_1$ and $T_2$) from dynamic mechanical thermal analysis of hydroxypropyl cellulose/organosolv lignin blends prepared by different methods.

<table>
<thead>
<tr>
<th>Lignin Content (Wt. %)</th>
<th>Pyridine</th>
<th>Dioxane</th>
<th>Extruded</th>
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<tbody>
<tr>
<td></td>
<td>$T_1$ (K)</td>
<td>$T_2$ (K)</td>
<td>$T_1$ (K)</td>
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<tr>
<td>0</td>
<td>299</td>
<td>*B</td>
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</tr>
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<td>296</td>
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<td>298</td>
</tr>
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<td>300</td>
<td>351</td>
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<td>15</td>
<td>296</td>
<td>356 (78)C</td>
<td>302</td>
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<td>+</td>
<td>+</td>
</tr>
<tr>
<td>70</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
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</table>

A. $T_1$ peaks appeared as shoulders above 10% lignin content in both pyridine and dioxane cast blends.
B. * indicates transition was not clearly defined.
C. Values in parentheses represent peak widths at half maximum.
D. No peak was observed.
E. Materials were too brittle for analysis.
Table III. Summary of Thermodynamic Parameters for HPC/OSL Blends Prepared by Different Methods.

<table>
<thead>
<tr>
<th>Lignin Content (Wt. %)</th>
<th>Tm (°K)</th>
<th>ΔHm (gram)</th>
<th>ΔSm x 10^3 (gram.k)</th>
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<tbody>
<tr>
<td></td>
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<td>Dioxane</td>
<td>Extruded</td>
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<td>0.54</td>
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<td>40</td>
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<tr>
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<td>0.29</td>
<td>0.31</td>
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</table>
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CHAPTER 4: THE INFLUENCE OF LIGNIN MODIFICATION ON THE
COMPATIBILITY AND MORPHOLOGY OF POLYMER BLENDS
WITH HYDROXYPROPYL CELLULOSE

ABSTRACT

Ethylation, acetylation, and propoxylation were used to modify the hydroxy functionality of lignin to different extents. The resulting modified lignins were then blended with hydroxypropyl cellulose. Compatible blends were obtained for all preparations except at the higher degrees of substitution which were available in the acetylated lignins. At the intermediate degree of substitution by acetylation and ethylation, the supermolecular structure of the blend was dramatically reduced, particularly after any thermal treatment. This behavior was not noted for the blends prepared with hydroxypropyl lignin whose behavior closely resembled that of the parent lignin.

Evaluation of the polymer-polymer interaction parameter (B) through analysis of melting point ($T_m$) depression suggested favorable interactions between blend components. As the degree of conversion of lignin hydroxyl groups was increased, the interaction between the blend polymers was seen to increase, reaching a maximum at about 40% conversion, before rapidly decreasing with further reductions in the hydroxyl content. However, the propoxylated derivative revealed a much lower level of interaction even though it solubility parameter corresponds
to this maximum for the acetylated and ethylated lignins. Consequently, it was concluded that hydroxyl groups of lignin do not contribute significantly to the state of miscibility of this pair, at least not as a result of intermolecular interactions. However, the conformational stability of lignin afforded by an extensive network of intramolecular hydrogen bonds dramatically influences the overall morphology of the composite.
INTRODUCTION

New avenues to high-modulus, high-strength materials have been opened with the discovery of liquid crystal formation in polymers (1). Although not an uncommon phenomenon in biological polymers, the discovery of liquid crystal behavior in cellulose (2) and cellulose derivatives (3) is barely 10 years old. The initial report of lyotropic liquid crystals in hydroxypropyl cellulose (4) was rapidly expanded upon to include cellulose acetate, ethyl cellulose, and nitrocellulose to name but a few (3). However, because of the solvent requirement of these lyotropic systems and only minimal success in attempts to develop high-modulus materials, their application has been limited to model systems for the study of liquid crystal formation. More recently, the recognition of thermotropic character in HPC (5) and its derivatives (6) has produced a resurgence of research interest in this area. To date, these investigations have been directed more toward fundamental concerns with only a few, isolated reports extending to bulk morphology and properties (7,8).

Very few reports have dealt with the behavior of liquid crystal polymers as a component in blend systems, although the results have generally been quite encouraging (9,10). Blend studies on cellulose derivatives have generally been concerned with mesophase compatibility in solution (11,12) rather than with the development and characterization of
engineering plastics. Recent investigations into the morphology and properties of hydroxypropyl cellulose (HPC)/lignin blends (13) have reported somewhat surprising results in that a dramatic enhancement in modulus and tensile strength was generally found at relatively low lignin compositions. It was concluded, considering evidence of limited compatibility, that the lignin component acts to effectively reinforce an amorphous matrix, in which a more ordered HPC component is embedded.

The aspect of specific secondary interactions between blend components has been illustrated as a critical factor influencing the state of a polymer pair (14,15). Intuitively, one would expect this aspect to play an important role in determining the morphology of a blend with lignin and HPC as the components owing to their polar character. Of course, the opposing concern of intramolecular hydrogen bonding, which has been demonstrated as important determinant of properties in both lignin (16) and HPC (17), could conceivably be a contributing factor in the development of blend morphology.

Consequently, the objective of this work is to further investigate the influence of secondary interactions in blends of HPC and lignin on the overall morphology and properties. This will be accomplished by removing in increasing amounts the hydroxy functionality of the lignin component using three derivatizing methods: acetylation,
ethylation, and propoxylation. As a result of the different functional groups introduced upon modification (carbonyl, ether, and secondary hydroxyls, respectively) this approach is expected to provide information on the nature and propensity of hydrogen bonding between these components. In addition, the disruption of intramolecular hydrogen bonding in lignin by derivatization should provide some indication of the influence of this concern on overall blend morphology.

EXPERIMENTAL

INDIVIDUAL COMPONENTS:

The hydroxypropyl cellulose used in this study was Klucel 'L' (Hercules, Inc.). According to the manufacturer this HPC has a molar substitution of 4 propylene oxide units per anhydroglucose unit (MS=4), and a nominal molecular weight of 100,000 g·mol⁻¹.

The lignin component used for all preparations is an organosolv lignin (a representative structure is schematically illustrated in Figure 1) provided by the Biological Energy Corporation of Valley Forge, PA, and was isolated from aspen wood. The reaction conditions and yield were not made available. The number average (<Mₙ>) and weight average (<Mₘ>) molecular weight for this lignin was determined (by gel permeation chromatography) to be 900 and 3,000 g·mol⁻¹, respectively. The total hydroxyl content was determined by chemical analysis as 8.4%.
LIGNIN MODIFICATIONS:

**Acetylation:** Ten grams of lignin were dissolved in 25 ml of pyridine, and the appropriate amount of acetic anhydride was added (Table I). The reaction mixture was flushed with nitrogen, sealed, and allowed to stand at room temperature for about 24 hours with occasional stirring. The reaction mixture was then precipitated into about 500 ml of dilute HCl, filtered, and washed with water. The isolated product was air-dried for 2 days followed by additional drying at 50°C under vacuum.

The degree of conversion of hydroxyls was determined from NMR spectra. The percentage of acetate protons from the integration curve was normalized to that of a completely acetylated derivative. Additional information on the substitution of phenolic hydroxyls was provided by aminolysis according to a procedure adapted from Mansson and Samuelson (18). Approximately 10 mg of the acetylated lignin were weighed into a 5 ml reaction vial and 0.5 ml of a 1:1 pyridine:pyrrolidone mixture added. The vial was capped and allowed to stand for 30, 45, 60, and 75 minutes. At the appropriate time, 2 ml of G.C. grade CHCl₃ containing 2-3 mg of internal standard (butyryl pyrrolidone) were added. The mixture was chromatographed on a column of 10% Carbowax 20M/2% KOH on 80/100 Chromasorb W at 165°C. Extrapolation to zero time of a plot of percent acetate vs. reaction time leads to a value of the
%-phenolic hydroxy which was converted to acetoxy.

**Ethylation:** A mixture of acetone:water (9:1) was used to dissolve about 5 grams of lignin. The pH was adjusted to above 13 using 30% KOH solution and maintained throughout the reaction period. The appropriate amount of diethyl sulfate (Table I) was added and the system flushed with nitrogen, closed, and allowed to stand overnight at room temperature. The reaction product was precipitated into dilute HCl, filtered, and washed with water. The product was dried for 2 days in a pistol dryer and transferred to a vacuum desiccator for storage.

The degree of conversion of hydroxyl groups was determined using a method adapted from Hodges et. al. (19). Approximately 10 mg of the ethylated lignin was weighed into a 5 ml reaction vial to which was added an equal amount of adipic acid, 0.75 ml of 57% hydriodic acid, and 2 ml of xylene containing the internal standard (n-propyl iodide). The reaction mixture was then heated at 140°C for one hour, cooled to room temperature, and chromatographed. The degree of substitution of hydroxy functionality was determined from the integration of the ethyl iodide peak.

**Propoxylation:** The propoxylation reaction was performed in a toluene suspension with agitation at 180°C in a closed pressure reactor, using KOH as catalyst. The hydroxypropyl derivative was obtained by liquid-liquid extraction of an acetonitrile solution with hexane followed
by precipitation into water according to a procedure described previously (20). The degree of substitution and molar substitution were determined as 2.2 and 1.1, respectively from NMR analysis of the acetylated material according to a procedure described elsewhere (21). The percent hydroxy was determined as 8.6.

PREPARATION OF BLENDS:

Individual solutions of the blend components were first prepared using dioxane as the solvent. The component solutions were then mixed and stirred for about 12 hours before casting into a Teflon mold. Solvent evaporation proceeded under ambient conditions for 24 hours followed by transferral to a vacuum oven at 60°C for further removal of solvent. After 7 days the materials were transferred to a vacuum dessicator for storage over P₂O₅.

BLEND ANALYSIS:

Differential Scanning Calorimetry (DSC): A Perkin-Elmer DSC-4 interfaced to the Thermal Analysis Data Station (TADS) was used for the characterization of thermal properties of individual components and their blends. All materials were analyzed at a heating rate and cooling rate of 20 deg/min under a purge of dry nitrogen. Generally, materials were first scanned through the melt to alleviate internal stresses and subsequent scans collected. The glass transition temperature (T_g) is defined as one-half the total change in heat capacity (C_p) associated with the
transition, and the melting temperature ($T_m$) is taken as the last trace of melting unless otherwise described.

**Dynamic Mechanical Thermal Analysis (DMTA):** Dynamic mechanical properties (Log $E'$ and loss tangent) were evaluated using a Polymer Laboratories, Inc. Dynamic Mechanical Thermal Analyzer interfaced to a Hewlett-Packard microcomputer. The sample geometry used was a single-cantilever beam with typical dimensions of $1 \times 15 \times 0.1$ mm ($l \times w \times t$). A heating rate of $4$ deg/min was used typically covering a range from $-50^\circ C$ to $125^\circ C$.

**Scanning Electron Microscopy (SEM):** Fracture surfaces for morphology evaluations using scanning electron microscopy were prepared by freezing in liquid nitrogen. The samples were then coated with carbon and gold-palladium using a Denton sputter-coater. Micrographs were taken with an Amray Model AMR-900 scanning electron microscope.

**RESULTS**

**LIGNIN MODIFICATION:**

The results of the acetylation, ethylation, and propoxylation reactions of the organosolv lignin are summarized in Table I. In the case of modification with acetic anhydride, complete conversion of hydroxyls is only achieved at an excess molar ratio of about $2:1$, and below this level the phenolic hydroxyls appear to react preferentially. Surprisingly, despite the complete replacement of hydroxy functionality there is only about a $20^\circ C$ decrease
in the glass transition temperature ($T_g$) of the unmodified lignin. Ethylation of lignin resulted in only 40% conversion of hydroxyls which corresponds to the phenolic hydroxyl content of this material. However, the $T_g$ is seen to decrease from 115°C for the original lignin to 57°C at the highest level of conversion. Although data is available only for the completely substituted propoxy derivative, with a $T_g$ of 69°C this modification results in an intermediate material, at least as far as this characteristic property is concerned.

Table I also summarizes the results of solubility parameter calculations (based on the model structure of Figure 1) using the group molar contribution method advanced by Small (22). As is apparent, some overlap is afforded by the various preparations primarily at the lower levels of acetylation and higher levels of ethylation which is a reflection of the degree of substitution (DS) of hydroxy functionality. The values obtained also provide a nice range around the calculated solubility parameter of hydroxypropyl cellulose which is 10.1 (cal/cm$^3$)$^{1/2}$. However, because of the uncertainties associated with this method these should be regarded only as estimates rather than absolute values.

MODIFIED LIGNIN BLENDS:

Ethylation: The effect of lignin content on the $T_g$ of blends prepared with HPC and the ethylated lignin
derivatives, as well as the unmodified parent lignin, is shown in Figure 2. Although considerable scatter is evident, a single $T_g$ for all the materials is found up to the 40 wt. % lignin content evaluated. For the two lower levels of modification, an initial decrease in $T_g$ is observed followed by a consistent increase to a $T_g = 315^\circ K$ at the highest lignin composition. Quite the opposite trend is observed as the phenolic hydroxyls of the lignin are further removed with the blend exhibiting an initial increase in $T_g$, followed by a decline which plateaus at 15% lignin content in the case of the OEt3 lignin and a continued decrease below ambient temperatures for the highest ethylated lignin. It should be emphasized at this point that these data are collected on materials after first scanning through the melt. Considering that a single $T_g$ was found for all systems implying miscibility, the observed behavior for the blends prepared from the higher DS lignins is not readily explained. It would appear that there are two competing effects on the observed $T_g$ of the blend. In all cases, the higher $T_g$ lignin component should elevate the $T_g$ of HPC as is observed for the unmodified lignin; however, if the supermolecular structure is disrupted to a significant extent a reduction in the observed HPC $T_g$ could result. The net effect would then depend on the extent to which these factors are exerted.

Table II summarizes the crystallinity data from DSC
analysis on these blends. As a whole, there is very little difference in the percent crystallinity of these preparations all of which show a consistent decrease as the lignin component of the blend is increased. If anything, the level of crystallinity may be maintained at a slightly higher level in the ethylated lignin blends. It is interesting to note that the largest decrease in crystallinity is found in the lowest lignin composition blends, after which a much more gradual decline is observed. However, the primary point to be made is that essentially no difference in crystallinity between blends prepared from lignins with different ethyl contents exists, and therefore changes in the volume fraction of this phase cannot account for the observed discrepancies in the $T_g$ behavior.

Conspicuously absent from the previously discussed data is the blend series prepared from lignin in which the phenolic hydroxy functionality had been completely removed. As is implied by this absence and the $T_g$ behavior presented some extreme behavior which may clarify the observed variation in the glass transition of these materials, Figure 3 shows the initial DSC scan and subsequent scan for several compositions in this series. The overwhelming feature of the initial scan is the striking contrast between the pure hydroxypropyl cellulose and even the lowest lignin composition. Although all the
materials exhibit a T_g at 20-30°C, the HPC melt has been
depressed some 30 degrees and a second peak found about 15
degrees above the major melting peak. In addition, the
temperature region 80-120°C exhibits the occurrence of an
additional event which is much clearer than that observed
for the pure HPC.

Upon cooling and re-scanning these blends a tremendous
increase in the heat capacity change (\Delta C_p) at T_g is
observed which indicates a considerable increase in the
amorphous volume fraction of the system. Generally, as the
lignin component is increased the T_g occurs over a much
narrower range and exhibits a slight increase in intensity.
Obviously, the increased amorphous component occurs at the
expense of the supermolecular order as is confirmed by the
high temperature region of the scan. In all cases, there
is an extremely broad, weak endotherm, the onset of which
begins consistently at about 70°C. Attempts to
re-crystallize this material by annealing at 130°C were
unsuccessful. One final aspect which is of interest is the
exothermic behavior, which begins at consistently lower
temperatures as the lignin content is increased; unfortunately, the significance (if any) of this feature
cannot be accounted for at this time.

Unquestionably, this dramatic enhancement of the
amorphous phase cannot entirely be accounted for through
the extinction of only 16% crystallinity. However, as
reported previously (23), HPC also contains a significant phase of intermediate order as a consequence of the formation of a liquid crystal mesophase during solution casting and this may account for the additional increase in the amorphous fraction of the blend. This result is most clearly illustrated by the evaluation of dynamic mechanical properties as shown in Figure 4. Both log E' and the loss tangent clearly indicate this point for several compositions of the OEt3 series, which exhibited similar behavior, although not to the same extreme, as the higher DS lignin blends. At 5% lignin content, a relatively indistinct peak corresponding to the amorphous T_g is located at 15°-20°C followed by a broad, poorly defined transition with a tan maximum at 100°C. This is quite representative of pure HPC where this high temperature (T_2) transition has been reported to originate from a residual nematic mesophase. As the blend composition goes to higher lignin contents, the peak maximum is shifted to lower temperatures and almost doubles in intensity. Similarly, the magnitude of the loss in modulus associated with the low temperature (20°) relaxation becomes much more dramatic.

The depression in temperature of the observed tan maximum cannot be directly related to the lignin component since the peak temperature at 20% lignin content is 20 degrees below that of the pure lignin T_g determined by DSC.
Consequently, it would seem that the temperature at which this relaxation process occurs is primarily related to the degree of order of this phase. As the lignin content is increased, the level of order is decreased until an essentially amorphous material remains. Obviously, as the degree of ethylation of the lignin component is increased, the disruption of order becomes much more extensive. This is particularly true after any thermal treatment.

To summarize, over the range of compositions investigated, miscible blends were obtained as reflected by a single $T_g$. The temperature at which the glass transition occurs appears to depend on two competing factors: 1) an elevation as a consequence of the higher $T_g$ lignin component, and 2) a depression resulting from the disruption of superstructure. As the degree of ethylation increases, the second factor becomes much more critical especially after any thermal treatment. This is particularly evident with the most extensively ethylated lignin which exhibits a tremendous increase in the $C_p$ associated with the amorphous $T_g$ which indicates a predominantly amorphous material after scanning through the melt. Further evidence is provided by a decreasing peak temperature for the $T_2$ transition in the OEt3 blends as the lignin content increases, which is presumably the result of a lower extent of ordering in this phase.

**Acetylation:** The acetylated lignin derivatives provide
a much more comprehensive range of hydroxy contents as complete substitution was achieved (Table I). As a result, the increased disparity in solubility parameter between HPC and the lignin component would lead to the expectation of more dramatic morphological differences in these materials. Figure 5 provides the first indication of distinction in the morphology of these materials. Using Samuel's (17) value of $\Delta H_u=6.44 \text{ cal} \cdot \text{g}^{-1}$ the heat of melting of the various blends was converted to percent crystallinity. As is shown, up to a degree of conversion of about 65%, there is very little difference in the percent crystallinity at all blend compositions. As the hydroxy content is reduced further, the addition of lignin has a much smaller effect on the blend's crystallinity, as is strongly evidenced by the sharp upturn at this point in the higher lignin content blends. The implication of this observation is simply that as the degree of acetylation is increased, a point is reached where considerably less interaction between the lignin component and HPC, as a result regions which are rich in HPC are formed and the crystallization process is influenced to a lesser extent.

This observation is born out in the analysis of glass transition temperature as shown in Figure 6. Generally, a single $T_g$ exhibiting a moderate increase with lignin content for the OAc1 and OAc2 blends is found. In the case of the OAc3 blend preparation, in which the lignin DS is
about 80%, a single $T_g$ value is observed; however, at the higher lignin contents (particularly 30%) the observed $T_g$ is considerably lower than one would expect. As has been discussed earlier, this may be the result of an increased amorphous HPC component, or the miscibility of the polymer pair is reduced and phase separation occurs. The latter explanation would seem to be favored upon consideration of the completely acetylated lignin blend, as well as the next highest level of acetylation. As is apparent, there is a considerable gap in the $T_g$ values of these two series and those with a higher hydroxy content, especially at the lower lignin compositions. Obviously, the observed $T_g$ corresponds to an essentially pure amorphous HPC phase which is confirmed by the presence of a second $T_g$ in both of these blends at about 365°K which is essentially that of the pure lignin component. Of the two series, it would appear as though a certain level of mixing is still obtained in the OAc4 preparations as there is some increase in $T_g$ with an increasing lignin content; and, although the OAc4 lignin has a slightly higher $T_g$ than the completely acetylated derivative, this transition is seen to occur at about the same point in the blended material.

Additional evidence of phase separation is clearly presented by SEM analysis. As shown in Figure 7, presenting a series of micrographs for these blends at a 40% lignin composition, a fairly uniform surface is found
for both the OAcl and OAc2 blend preparations; however, domain morphology is exhibited in all of the blends at degrees of acetylation above this 76% level. It should be noted that at lower lignin content, the OAc3 system did not show any formation of lignin domains, which is consistent with DSC observations.

It is interesting to consider the region of overlap between the acetylated and ethylated lignins which occurs essentially at the lowest degree of acetylation. Interestingly, similar behavior is observed for both of these blends. As seen in Figure 8, the intensity of the T_g is greatly increased, (after the initial scan through the melt) as was observed for the OEt3 and OEt4 preparations, at the expense of the crystalline and mesophase components of the system. However, the same extent of disruption is not achieved, and it generally required a higher thermal treatment to obtain this effect. Although this observation would seem to confirm an enhanced level of miscibility between the components of the blend, the extent to which the supermolecular structure of hydroxypropyl cellulose is destroyed remains somewhat a surprise. While miscibility in semi-crystalline blends often reflects a decrease in crystallinity, the extent of this decrease is typically that observed in the OAcl blends, for example. Consequently, there seems to be no precedent for the behavior observed in this particular system and no
explanation other than improved miscibility can be offered at this time.

As has been discussed, a much greater perspective of morphology for the HPC/lignin blend system is afforded by the acetylation of lignin since complete removal of the hydroxy functionality of lignin is achieved. As the extent of modification is increased, the binary pair is seen to go from a miscible system to an immiscible blend as evidenced by both thermal properties and scanning electron microscopy of fracture surfaces. Again, there is a considerable disruption of HPC superstructure at acetylation levels corresponding to those in the ethylated derivatives. Presumably, this reflects an increased level of interaction at the initial modification levels, before moving to an increasingly immiscible system as the hydroxyl groups of the lignin are completely removed.

Propoxylation: The modification of lignin with propylene oxide presents somewhat of a unique case in that, although phenolic hydroxy and carboxy groups of lignin are eliminated, the hydroxy functionality remains intact. Furthermore, the similarity in side-chain structures between the two blend components may actually serve to improve their miscibility. Although it is difficult at this point to draw any conclusions regarding the enhancement of miscibility, a compatible system is again obtained as evidenced by a composition dependent Tg.
Although not presented, this particular derivative was found to yield blends which were quite comparable in all aspects ($T_g$, $\Delta H_m$, etc.) to those prepared with the unmodified lignin.

DISCUSSION

The hydroxy functionality, and particularly the phenolic hydroxyl, of lignin has generally been recognized as the predominant structural feature determining the physical properties of this wood cell wall polymer. Considering the influence of secondary interactions on the state of miscibility of polymer pairs, it is conceivable that this hydroxy functionality could significantly affect the morphology of blends prepared with lignin. This has been convincingly demonstrated for this system as a range of miscible states (from completely miscible to completely immiscible) was obtained in blends with HPC upon the incremental elimination of lignin hydroxyl groups. The extent to which the change can be attributed to the removal of hydroxyl groups is somewhat difficult to assess since the modification reactions also alter the solubility parameter of the component as well. However, some insight can be gained into this concern through the evaluation of the interaction parameter, $B$ (25). For semi-crystalline blend systems, this parameter is conveniently evaluated through analysis of the melting point depression using the following simplified expression (26):
where $T_{m2^0}$ is the equilibrium melting point of HPC, $T_{m2}$ is the melting point of the blend, $\Delta H_{2u}/V_{2u}$ is the heat of melting per unit volume of 100% crystalline material, and $\phi_1$ is the volume fraction of the amorphous component — in this case, lignin. A plot of $T_m$ vs. $\phi_1^2$ should then yield a straight line with a slope directly proportional to $B$.

All of the blend systems are sufficiently described by the assumption of linearity as is demonstrated by the correlation coefficient ($R^2$) in Table III where a summary of the model data and resultant $B$ parameters are presented. As might be expected, the greatest range of $B$ is in the series of acetylated lignins with values from -1.5 cal·cm$^{-3}$ for the completely derivatized material to -6.45 cal·cm$^{-3}$ for the OAc2 blends. For the blends prepared from the ethylated lignins, similar values are found although there is an inexplicable decrease in the interaction parameter for the OEt2 blends with a degree of conversion of 27%. The negative $B$ parameters necessarily imply a favorable interaction between the blend components in all proportions, while the magnitude of, for example, the OAc2 blend would seem to indicate the presence of strong intermolecular interactions (26). One final point is that in no system does the intercept pass through zero. This aspect has been attributed in various reports as indicative of a
melting point depression due to such factors as a reduction in lamellar thickness of the crystallite (27), rather than a difference in the established equilibrium with the changing amorphous phase composition. Consequently, since no attempt was made to obtain equilibrium melting temperature, it is possible that this effect may contribute to the magnitude of B. However, the observed trends and comparison between these blend systems should still be valid.

As noted previously, the observed onset of incompatibility could largely be expected from simple considerations of the solubility parameter. This point is further explored by plotting the interaction energy parameter against the solubility parameter of the lignin component in the blend (Figure 9), which reveals several interesting features. The most prominent aspect of this graph is the parabolic shape obtained when the ethylated and acetylated lignins are considered together with an apex at about 9.7 \((\text{cal/cm}^3)^{1/2}\). This is in reasonable agreement with the solubility parameter estimate for HPC. However, blends prepared with the propoxylated lignin, whose solubility parameter corresponds with the maximum when lignin is modified by acetylation or ethylation, is seen to interact to a much lower level with HPC. This inadequacy in the application of this simplified approach can possibly be explained from several perspectives.
Beginning with the assumption that lignin is extensively hydrogen bonded within itself, the hydroxyl groups would not be free to interact with the HPC component. Replacement of this functional group with an ethyl or acetyl group would initially disrupt the intramolecular hydrogen bonding making available more sites to interact with the hydroxypropyl cellulose. However, in the case of propoxylation, the fact that hydroxy functionality is still available for intramolecular stabilization of the lignin, may account for the reduced interaction since few hydroxyls for intermolecular interactions would be available.

An alternative consideration can be found along this same line of thought. Although lignin is typically considered as a three-dimensionally branched (or crosslinked) polymer, quantum chemical calculations on hydrogen bonding in this polymer have suggested that the lignin macromolecule is stabilized in essentially a planar conformation (28). This concept has been further advanced in light of experimental evidence which noted no change in monolayer film thickness with molecular weight (29) - advocating an essentially two-dimensional polymer. Since this conformation is presumably stabilized by the extensive intramolecular hydrogen bonding modification by acetylation or ethylation would lead to an increasingly flexible chain, and more of a three-dimensional orientation. Propoxylation
of the lignin would not result in a similar increase in flexibility since the propensity for intramolecular hydrogen bonding, and subsequent conformational stability would be retained. Consequently, the enhanced compatibility between the lignin and HPC would result more from entropic concerns rather than enthalpic considerations of intermolecular interactions. This approach could also account for the disruption of supermolecular order in the HPC, as the lignin is forced out of its normal conformation and into a more three-dimensional arrangement. To complete this hypothesis, increased substitution would result in an increase in rigidity as a simple consequence of the substituent group's added bulk. This factor, along with the increased differences in solubility parameter would ultimately lead to the immiscible state observed for the more highly acetylated lignins.

Although this conceptual picture is certainly not inconceivable, the likelihood of specific interactions between the components cannot be ruled out. Although the ethylation and acetylation reactions eliminate the hydroxy functionality of the lignin, they introduce ether and carbonyl, respectively, which may actually enhance the possibility of hydrogen bonding between the two components. A final address to the concern of specific secondary interactions is shown in Figure 10, which plots the reciprocal of $T_m$ against volume fraction for selected blend
preparations in a treatment proposed by Mandelkern and Flory (30). A linear relationship is obtained for all of the blend compositions, extrapolating to a common point which is equal to the melt of the pure HPC. The point to be noted is the linearity of the plots, which according to theory should be found only in the absence of specific interactions between blend components. Therefore, it must be concluded from this result that hydrogen bonding between HPC and lignin or its derivatives cannot be a significant contributing factor to the compatibility of this binary blend. Rather, the level of miscibility is dependent primarily on the proximity of the individual component's solubility parameters; and, although no data is presented to this end, presumably on the conformation of the lignin macromolecule as determined by the extent of intramolecular chelation of hydroxy functionality.

CONCLUSION

The modification of lignin dramatically influences the morphology of blends with hydroxypropyl cellulose. Generally, as the hydroxy content of lignin is incrementally removed the system goes from miscible to incompatible at all compositions as evidenced by both thermal properties and fracture surface analysis by SEM. Interestingly, a point is reached in both the ethylated and acetylated derivatives where the supermolecular morphology of the HPC is essentially destroyed; however, the
hydroxypropyl lignin blends, possessing a similar solubility parameter, failed to have this effect as its behavior was observed to be quite similar to that of the parent lignin.

Analysis of melting point depression data showed that a maximum level of miscibility was reached at a solubility parameter of 9.7 (cal/cm³)¹/² for the lignin which corresponds roughly to a degree of substitution equal to about 30% for the acetylated and ethylated derivatives. This value is in qualitative agreement with the estimated value of 10.1 (cal/cm³)¹/² for hydroxypropyl cellulose. Apparently a considerable contribution due to changes in crystal morphology is reflected in the experimentally obtained interaction energy parameter, B, the magnitude of which suggests strong secondary interactions. Further treatment of the data dictates the conclusion that hydrogen bonding between blend components is not a significant factor contributing to the state of miscibility of this polymer pair. However, it does appear as though the substantial hydroxy functionality of lignin does dramatically influence the overall morphology of this composite as a consequence of extensive intramolecular hydrogen bonding. As the hydrogen bonding network of lignin is dissociated by modification, the relatively rigid, planar conformation is disrupted to the extent that superstructure development in the composite is greatly
inhibited. This could have important ramifications in the development of reinforced composites prepared with liquid crystal polymers.

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LITERATURE CITED


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Figure 8. Differential scanning calorimetry curves of HPC/OAc1 blends (degree of acetylation = 23%). Weight % of lignin is given with the respective curve.

Figure 9. The variation in the interaction parameter, B, with the solubility parameter, $\delta$, of the lignin component.

Figure 10. Plot of $1/T_m$ vs $1$ for HPC blends with OAc2 (···), OEt3 (──), OPr (··×··).
Table I. Summary of hydroxyl data and physical properties for lignins derivatized with acetic anhydride (OAc), diethyl sulfate (OEt), and propylene oxide (OPr).

| Sample ID | Molar Ratio<sup>a</sup> (Reagent/OH) | Degree of Conversion, %<sup>b</sup> | OH-Groups/C<sub>9</sub> | Physical Properties<sup>c</sup> |
|-----------|-------------------------------------|-------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|           |                                     | Total-OH by NMR<sup>d</sup>   | Phenolic-OH by Aminolysis | Total Phenolic  | T<sub>p</sub> (g/cc) | p (cal/cc)<sup>1/2</sup> |
| OSL       | ***                                 | 0                             | 0                | 1.47            | 0.59            | 115             | 1.21            | 11.1            |
| OAc-1     | 29                                  | 23<sup>b</sup>               | 17               | 31              | 1.14            | 0.41            | 110             | 1.17            | 10.5            |
| OAc-2     | 61                                  | 66                            | 56               | 0.52            | 0.26            | 106             | 1.11            | 9.3             |
| OAc-3     | 80                                  | 84                            | 64               | 0.35            | 0.21            | 103             | 1.08            | 9.0             |
| OAc-4     | 100                                 | 96                            | 71               | 0.19            | 0.14            | 101             | 1.06            | 8.7             |
| OAc-5     | 192                                 | 100                           | 95               | 0.0             | 0.03            | 96              | 1.05            | 8.4             |
| OEt-1     | 23                                  | 18<sup>d</sup>               | ***              | ***             | 1.22            | 0.34            | 109             | 1.16            | 10.6            |
| OEt-2     | 50                                  | 27                            | ***              | ***             | 1.08            | 0.20            | 96              | 1.14            | 10.4            |
| OEt-3     | 67                                  | 35                            | ***              | ***             | 0.96            | 0.08            | 75              | 1.10            | 10.2            |
| OEt-4     | 172                                 | 40                            | ***              | ***             | 0.88            | 0.0             | 57              | 1.09            | 10.0            |
| OPPr-1    | -                                   | 100                           | ***              | 1.47            | 0.0             | 69              | 1.06            | 9.7             |

<sup>a</sup> Molar ratio was calculated on the basis of 1 mole acetic anhydride or 1 mole of diethyl sulfate per mole of hydroxyl as equimolar (e.g. 100%).

<sup>b</sup> The percent degree of conversion was obtained by NMR from the integration curve.

<sup>c</sup> Solubility parameters were calculated using the group contribution method of Small.

<sup>d</sup> Total hydroxyl for the ethylated lignins were determined by HI-GC as described in the experimental section.
TABLE II. Summary of percent crystallinity at different lignin contents for blends prepared with HPC and ethylated lignin and the parent organosolv lignin.

<table>
<thead>
<tr>
<th>Sample I.D.</th>
<th>Lignin Content (Wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>OSL</td>
<td>15.9</td>
</tr>
<tr>
<td>OEt1</td>
<td>-</td>
</tr>
<tr>
<td>OEt2</td>
<td>-</td>
</tr>
<tr>
<td>OEt3</td>
<td>-</td>
</tr>
</tbody>
</table>
Table III. Summary of Melting Point Depression Analysis for Blends of HPC and Lignin Modified to Different Extents by Acetylation, Ethylation, and Propoxylation.

<table>
<thead>
<tr>
<th>Sample I.D.</th>
<th>Intercept</th>
<th>Slope</th>
<th>R²</th>
<th>-R</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPC/OSL</td>
<td>9.675</td>
<td>196.8</td>
<td>0.98</td>
<td>(-3.0)</td>
</tr>
<tr>
<td>HPC/OPr</td>
<td>6.820</td>
<td>137.6</td>
<td>0.95</td>
<td>(-2.13)</td>
</tr>
<tr>
<td>HPC/OAc2</td>
<td>2.322</td>
<td>415.6</td>
<td>0.95</td>
<td>(-6.45)</td>
</tr>
<tr>
<td>HPC/OAc3</td>
<td>3.187</td>
<td>285.5</td>
<td>0.98</td>
<td>(-4.43)</td>
</tr>
<tr>
<td>HPC/OAc4</td>
<td>5.337</td>
<td>102.4</td>
<td>0.91</td>
<td>(-1.59)</td>
</tr>
<tr>
<td>HPC/OAc5</td>
<td>6.104</td>
<td>97.8</td>
<td>0.94</td>
<td>(-1.52)</td>
</tr>
<tr>
<td>HPC/OEt1</td>
<td>5.281</td>
<td>351.9</td>
<td>0.99</td>
<td>(-5.46)</td>
</tr>
<tr>
<td>HPC/OEt2</td>
<td>5.514</td>
<td>165.6</td>
<td>0.97</td>
<td>(-2.56)</td>
</tr>
<tr>
<td>HPC/OEt3</td>
<td>5.212</td>
<td>420.7</td>
<td>0.98</td>
<td>(-6.52)</td>
</tr>
</tbody>
</table>
Figure 1. Schematic Representation of an Organosolv Lignin (from aspen wood).
Figure 2. The influence of degree of ethylation of lignin on the composition dependence of $T_g$ in blends prepared with HPC/OSL (θ), OEt1 (–), OEt2 (–•), OEt3 (–.), and OEt 4 (–).
Figure 3. Differential scanning calorimetry analysis of several blends of HPC/0Et4 (degree of ethylation equals 40%) with the indicated lignin contents: (A) initial scan, (B) subsequent scan.
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Figure 7. Scanning electron micrographs of the fracture surface of blends with a 40 wt.% lignin content which vary in the degree of acetylation: A) HPC/OSL, B) /OAc1, C) /OAc2, D) /OAc3, E) /OAc4, and F) /OAc5. (2000x).
Figure 7. Scanning electron micrographs of the fracture surface of blends with a 40 wt.% lignin content which vary in the degree of acetylation: A) HPC/OSL, B) /OAc1, C) /OAc2, D) /OAc3, E) /OAc4, and F) /OAc5. (2000x).
Figure 8. Differential scanning calorimetry curves of HPC/OAc1 blends (degree of acetylation = 23%). Weight % of lignin is given with the respective curve.
Figure 9. The variation in the interaction parameter, $B$, with the solubility parameter, $\delta$, of the lignin component.
Figure 10. Plot of $\frac{1}{T_m}$ (°K$^{-1}$) vs $\phi_1$ for HPC blends with: OAc$_2$ (•••••), OEt$_3$ (———), and OPr (―X―).
CHAPTER 5. THE COMPATIBILITY OF LIGNIN WITH ETHYL CELLULOSE AND A CELLULOSE ACETATE/BUTYRATE ESTER

ABSTRACT

Polymeric blends of lignin with ethyl cellulose and a cellulose acetate/butyrate ester were prepared over the entire composition range. Fracture surface analysis revealed phase separation at a lignin content of 10% when blended with ethyl cellulose and 5% in the cellulose ester system. While this extensive level of incompatibility is in accord with empirical predictions for the ethyl cellulose blends, a higher level of miscibility was predicted for the CAB blend system. Results from both differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA) suggest that the observed separation of phases may not be entirely driven by the immiscibility of the two components since the individual phases behave quite differently from the pure components. Specifically, in the case of the lignin/ethyl cellulose system, the observed relaxation due to the addition of lignin was 35°C higher than either of the pure component transitions in the 5% lignin blend, and decreased only 25°C as the lignin content was increased to 40%. While the implications of this observation remain somewhat ambiguous, it appears as though the two phase morphology of these blend systems may be due in part to the formation of liquid crystal mesophases during solvent evaporation.
INTRODUCTION

The phenomenon of liquid crystal formation in various polyesters has been utilized through the appropriate manipulation of process parameters to develop high-modulus, high-strength materials of considerable commercial interest (1). The discovery of this same behavior in cellulose (2) and a number of its derivatives (3-5) has generated a tremendous amount of interest over the last few years in anticipation of similar advances. Unfortunately, the rate of progress with cellulosic liquid crystals has been slow compared to that enjoyed by the polyesters, primarily as a consequence of the mesophase structure (which is cholesteric) and the solvent requirement of these predominantly lyotropic systems (5). One aspect of utility which has been only superficially addressed with liquid-crystal forming polymers is their incorporation as a component in binary blend systems, although considerable promise has been demonstrated with liquid crystal polyesters (6).

While reports of polymer blends containing cellulose derivatives are not altogether absent from the literature (7-9), the aspect of supermolecular structure development in these systems has been inadequately considered. Investigations of this nature have recently been undertaken in this laboratory on blends of hydroxypropyl cellulose (HPC), which displays both thermotropic and lyotropic
liquid crystal behavior, with an organosolv lignin (10). For this system, an increase in both tensile modulus and tensile strength of about $2^{1/2}$ times was found for injection molded samples while the ultimate strain was dramatically decreased at very low lignin contents (<20%). From thermal and dynamic mechanical analysis it was concluded that the lignin component essentially served to reinforce the amorphous matrix in which a mesophase structure is embedded. That is the blend morphology was similar to that of a fiber-reinforced composite.

In polymer blends, the presence of specific secondary interactions between components has been shown to dramatically enhance the state of miscibility and subsequent morphology of the system (11). Considering the polar character of both lignin and HPC it is not unlikely that hydrogen bonding between these polymers could substantially influence the degree of compatibility, and thereby the overall morphology of the blend. Initially, this question was directed toward the functionality of the lignin component by incrementally eliminating the hydroxy groups, particularly the phenolic hydroxy through ethylation, acetylation and propoxylation (12). The results indicated that intermolecular interactions between lignin and HPC are not a dominating factor; however, the conformational stability afforded by an extensive network of intramolecular hydrogen bonds in lignin may
significantly affect the composite's morphology by restricting the development of superstructure in the system.

Alternatively, the extent of interaction in lignin blends should also be sensitive to the type of functional group associated with the cellulose component. This aspect is most conveniently addressed through the selection of an appropriate cellulose derivative which replaces the original hydroxy functionality. Consequently, it is the intent of this report to address, at a cursory level, the influence of the cellulose derivative type on the compatibility with lignin. The cellulose derivatives selected are ethyl cellulose and an acetate/butyrate ester which introduces ether and carbonyl groups, respectively, as potential sites for interaction with lignin's hydroxy functionality.

EXPERIMENTAL

Materials: The lignin component used in both blend systems was an unmodified organosolv (Biological Energy Corp.) isolated from aspen wood. The molecular weight, \( \langle M_n \rangle \), was determined by gel permeation chromatography as 800 g·mol\(^{-1}\) with a polydispersity of 3.4. The ethyl cellulose (EtC) was a Hercules, Inc. product (T150) with an ethoxyl content of 50.5%. The cellulose acetate/butyrate ester was obtained from Tennessee-Eastman Co. Structural details of this copolymer were not available.
Blend Preparation: Individual component solutions (~10 wt. %) were prepared in dioxane which were subsequently mixed and stirred for 12 hours. The blended solutions were cast into Teflon molds where the solvent was allowed to evaporate at ambient conditions for 24 hours. The films were then removed from the molds and transferred to a vacuum oven at 60°C for 1 week to remove residual solvent. The dried films were then stored over P₂O₅ in a vacuum dessicator until testing.

Differential Scanning Calorimetry (DSC): A Perkin-Elmer DSC4 interfaced to the Thermal Analysis Data Station (TADS) was used for thermal analysis. Approximately 20mg samples were scanned at a heating rate of 20 deg·min⁻¹ under a purge of dry nitrogen. The glass transition (Tg) was defined as one-half the total change in heat capacity (1/2ΔCp) associated with the transition. The melting temperature (Tm) was taken as the peak maximum.

Dynamic Mechanical Thermal Analysis (DMTA): Dynamic Mechanical properties (Log E' and tan δ) were evaluated with a Polymer Laboratories, Inc. DMTA interfaced to a Hewlett-Packard 9816 microcomputer. All samples were scanned at a heating rate of 4 deg·min⁻¹ and a frequency of 10 Hz. A single cantilever beam geometry was utilized on samples with typical dimensions of 1mm X 15mm X 0.25mm (L x W x T).

Scanning Electron Microscopy (SEM): Fracture surfaces
were prepared by submerging the samples in liquid nitrogen for about 1 minute and breaking. The samples were coated with carbon and a gold-palladium alloy. An Amray scanning electron microscope, Model AMR-900, was used for analysis.

RESULTS AND DISCUSSION

Ethyl Cellulose Blends: A summary of results obtained by differential scanning calorimetry on the ethyl cellulose blend series (EtC/OSL) is presented in Table I. Up to a lignin content of 20%, a single glass transition temperature ($T_g$) is found which shifts about 15°C to a lower temperature. The onset of phase separation is first detected by DSC at a lignin content of 30% through the appearance of a second transition which is also present in the 40% lignin blend. Although this transition is presumably related to the lignin component, the temperature at which it occurs is 35°C to 50°C higher than that of the pure material, and is even above the higher $T_g$ ethyl cellulose component. Consequently, it is difficult to assign this event to the existence of a phase comprised of lignin or even a lignin-rich region. As the weight fraction of lignin is increased further, a single $T_g$ is again observed which is apparently dependent on the composition of the blend.

Although analysis of $T_g$ behavior suggests a window of miscibility at the extremes of blend composition, a somewhat conflicting view is presented when the melting
behavior of this blend system is also considered. In the event of miscibility, a substantial decrease in the melting temperature, \( T_m \), would be expected; however, for the blend compositions analyzed there is essentially no change in the temperature at which the melt occurs. Furthermore, the observed decrease in the heat of melting, \( \Delta H_u \), does not exceed that expected as a result of the diminished weight fraction of ethyl cellulose (the crystallizable component) in the blend. This indicates that essentially no interaction occurs between the lignin and ethyl cellulose components in this blend system.

The evaluation of blend morphology by scanning electron microscopy provides further evidence of a much greater level of immiscibility than that indicated from the \( T_g \) behavior of the blend. As seen in Figure 1, at a lignin content of only 5% no indication of phase separation is present. As the lignin content is raised to 15%, phase separation is readily apparent in the form of globular domains. As the lignin component in the blend is increased further the extent of phase separation increases proportionally and changes in appearance. At the 15% lignin composition the rounded structures remain intact upon fracture while at 30% lignin, the discontinuous phase appears to have experienced a brittle fracture such that these structures appear more rod-like in character. Also, it is of interest to note the relative area of the discrete
phase in that it appears to occupy more than 30% of the surface raising the question, again, of the composition and nature of this morphological component.

In a further address of the nature and composition of the individual phases, the dynamic mechanical properties of several EtC/OSL blends are presented in Figure 2. Consistent with the phase morphology revealed by SEM, two relaxation processes are present in the tanδ spectrum at all of the blend compositions. With a lignin content of only 10% a small peak is seen at 165°C which is not present in the spectrum of pure ethyl cellulose. The temperature at which this transition occurs is seen to decrease about 25°C as the lignin content reaches 40%. Although occurring to a much lesser extent, the peak related to the pure ethyl cellulose is also shifted to a lower temperature. The intriguing aspect is the fact that the relaxation process common to the blended materials occurs at a temperature considerably higher than that of either pure component. Since it is not possible to attribute this observation to phase composition alone, the explanation may lie in the level of supermolecular order of the discrete phase. That is, the observed morphology may be the result of mesophase formation as solvent evaporation proceeds leading to a residual morphological component comprised of lignin and ethyl cellulose which is more ordered than the amorphous constituent.
An additional feature of interest in the dynamic mechanical spectra of these materials is the increase in modulus found at about 135°C in the case of the pure ethyl cellulose. It is this feature which is reflected in the prominent peak at this temperature in the loss tangent. Interestingly, this behavior has been observed for several cellulose derivatives in this laboratory (13) and is, presumably, the result of further crystallization. As seen in Figure 3, when the materials are re-scanned through this temperature region no modulus increase is observed which is in accord with the previous account of this observation as a crystallization process. This is further reflected in the diminished intensity of the $\tan\delta$ maximum (note difference in the y-axis range) at 130°C which is now more indicative of the $T_g$ of the amorphous ethyl cellulose component. Finally, it is interesting that the higher temperature relaxation is shifted to slightly higher temperatures while essentially no difference is found in the lower temperature transition when these materials are re-scanned. This may be the result of residual solvent loss or additional supermolecular organization.

In summary, a single $T_g$ is noted for blends of lignin and ethyl cellulose over a wide range of compositions by DSC. However, results by both SEM and DMTA indicate that a homogeneous material is actually obtained over a much narrower range with phase separation occurring at a lignin
content of only 10%. The exact nature of the phases, in terms of both composition and supermolecular development, remains somewhat ambiguous although it is difficult to explain the results in terms of segregation into a pure, amorphous component phase. At all compositions analyzed by DMTA the relaxation process which would be related to the lignin phase, in the classical sense of phase separation, is located at a temperature considerably above that of either pure component. No definitive explanation for this observation can be offered at this point.

**Cellulose Acetate/Butyrate Blends:** Intuitively the carbonyl functionality of this cellulose derivative presents a more favorable site for the interaction with the hydroxy groups of lignin, and as a consequence, improve the level of compatibility compared to the ethyl cellulose blends. Miscibility enhancement resulting from acetylation has been demonstrated experimentally by Erins and Gravitis (14) on blends of lignin and hemicellulose. As is shown in Figure 4, this premise would indeed appear to hold although not to a significant extent. From 30% to 70% lignin content two Tg's are found which correspond roughly to the pure components while at the extremes of blend composition a single transition is present which is adequately modeled by the Gordon-Taylor equation (15) using a value for the adjustable parameter, 'k', of 0.46. From this analysis, it would appear that the range of compositions leading to a
miscible blend is slightly greater than in the ethyl cellulose system.

Surprisingly, dynamic mechanical analysis reveals a single tan δ peak which exhibits a monotonic decrease from 143°C to 125°C (Table II) up to a 55% lignin content (representing the maximum lignin composition yielding a testable film). This may be the result simply of a lack of integrity of the material after passing through this transition, making the second transition (as observed by DSC) inaccessible. There is evidence of heterogeneity in the system as judged by the increased peak width, which essentially doubles, from 12°C for the pure CAB to 22°C at a lignin content of 55%. Also presented in Table II are the activation energies (E_a) associated with each relaxation process. Not surprisingly, the variation in this parameter essentially parallels that exhibited by the glass transition; however, the relative magnitude of change in E_a is somewhat surprising, decreasing almost 100 kJ·mol⁻¹ over only an 18°C depression in T_g.

Although results from thermal analysis imply a slight enhancement of miscibility over that observed in the ethyl cellulose system, SEM analysis of fracture surfaces again provides a contradiction to this view. As seen in Figure 5, phase separation is evident as rounded domains even at a composition of only 5% lignin. A considerable increase in domain size occurs as the amount of lignin is increased to
15% while very little change is found at 30%. Finally, the poor adhesion between particles and the matrix would suggest classical phase separation in this completely immiscible system.

**Theoretical Predictions:** Since the heat of mixing provides an approximate measure of the free energy of mixing, it is generally indicative of the degree of compatibility between two polymers. The heat of mixing for binary blend systems has been estimated by the following equation proposed by Schneier (16).

\[
\Delta H_m = \left[ \tilde{x}_1 M_1 \rho_1 (\delta_1 - \delta_2)^2 \tilde{x}_2 (1 - \tilde{x}_2) M_2 \rho_2 \right. \\
\left. + (1 - \tilde{x}_1) M_1 \rho_1 \right]^{1/2}
\]

where \( \tilde{x} \), \( \rho \), and \( M \) are the weight fraction of polymer, polymer density and the monomer unit molecular weight, respectively; \( \delta \) is the solubility parameter of components 1 and 2 as denoted by the subscripts (values are summarized in Table III). Although this approach is most generally applicable to non-polar blends, it has been successfully applied to blends of polar polymers where specific secondary interactions are not dominant.

The blends of ethyl cellulose and lignin have been shown to exhibit only a limited degree of miscibility at the extreme compositions. The calculated heats of mixing (Figure 6) are found to be above the figure considered to be the upper limit of compatibility over most of the composition range, in excellent agreement with the observed behavior. In the case of CAB blends, however, the
predicted heat of mixing remains well below the upper compatibility limit for most blend compositions suggesting a partially miscible system should result. This is in direct contrast to observations of domain formation by SEM at all levels of lignin addition that were evaluated (from 5% to 55% lignin). Obviously, the disagreement cannot be attributed to the presence of secondary interactions as their presence would lead to deviation in the opposite direction, i.e. the observed morphology would be more homogeneous over a wider range of compositions. Considering the inability to account for this observation, the nature of the phase separation in these systems remains somewhat uncertain. Both DSC and DMTA results indicate that the observed domain structure do not arise exclusively from the segregation of blend components into pure phases. Whether or not the two phase morphology is then a result of partial miscibility of the components or due to mesophase formation cannot be conclusively stated at this juncture.

CONCLUSIONS

Blends of lignin with ethyl cellulose and cellulose acetate/butyrate yielded two-phase systems over an extremely broad range of compositions as revealed by scanning electron microscopy. Thermal and dynamic mechanical analysis suggest that the phase separation deviates from classical behavior in the sense that the establishment of pure component domains do not appear to
result from this behavior. This is most strongly evidenced by the occurrence of the additional transition in ethyl cellulose blends at temperatures considerably higher than that of either pure component. An analogous situation is found for the CAB blends in that the second-component transition as determined by DSC, occurs at a higher temperature than would be expected. Consequently, it may be that the occurrence of a two phase morphology in these systems results from the entropic driving force of liquid crystal mesophase formation, rather than polymer incompatibility alone.

ACKNOWLEDGEMENTS

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LITERATURE CITED


13) Rials, T. G. Unpublished Data.


LIST OF TABLES AND FIGURES

Table I. Summary of glass transition and melting behavior of ethyl cellulose blends with lignin (EtC/OSL).

Table II. Summary of dynamic mechanical analysis results (peak temperature, peak width, and activation energy) for selected blends of cellulose acetate/butyrate and lignin (CAB/OSL).

Table III. Solubility parameter, density, and repeat unit molecular weight of blend polymers.

Figure 1. Scanning electron micrographs of freeze-fracture surfaces of EtC/OSL blends at compositions of: A) 95/5, B) 85/15, and C) 70/30. (Magnification = 2000x).

Figure 2. Variation in dynamic mechanical properties (Log E' and loss tangent) with temperature for blends of ethyl cellulose and lignin (EtC/OSL): 100/0 (---), 90/10 (-- -), 80/20 (-·-), and 60/40 (---).

Figure 3. Second scan of EtC/OSL blends shown in Figure 2: 100/0 (---), 90/10 (-- -), 80/20 (-·-), and 60/40 (---).

Figure 4. The effect of blend composition on glass transition temperature (Tg) behavior as observed by DSC of materials prepared with cellulose acetate/butyrate and lignin. The dashed line is the predicted behavior from the Gordon-Taylor model (ref. 15).

Figure 5. Scanning electron micrographs of freeze-fracture surfaces of CAB/OSL blends at compositions of: A) 95/5, B) 85/15, and C) 70/30. (Magnification = 2000x).

Figure 6. Predicted Heat of mixing vs. weight percentage of component 1 in EtC/OSL (+) and CAB/OSL (0) blends. The dashed line results from calculation using lignin as component 1 and the solid line using the cellulose as component 1.
Table I. Summary of glass transition and melting behavior of ethyl cellulose blends with lignin (EtC/OSL).

<table>
<thead>
<tr>
<th>Lignin Cont. (wt%)</th>
<th>T_gA (°C)</th>
<th>T_gB (°C)</th>
<th>T_M (°C)</th>
<th>ΔH_u (cal. g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>119.6</td>
<td>+</td>
<td>252.4</td>
<td>3.01</td>
</tr>
<tr>
<td>5</td>
<td>117.0</td>
<td>+</td>
<td>252.5</td>
<td>2.93 (2.85)C</td>
</tr>
<tr>
<td>10</td>
<td>107.0</td>
<td>+</td>
<td>251.5</td>
<td>2.66 (2.71)</td>
</tr>
<tr>
<td>15</td>
<td>106.7</td>
<td>+</td>
<td>252.1</td>
<td>2.72 (2.56)</td>
</tr>
<tr>
<td>20</td>
<td>104.9</td>
<td>+</td>
<td>251.8</td>
<td>2.42 (2.41)</td>
</tr>
<tr>
<td>30</td>
<td>94.3</td>
<td>147.3</td>
<td>250.7</td>
<td>2.61 (2.11)</td>
</tr>
<tr>
<td>40</td>
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<td>-</td>
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</tr>
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<td>55</td>
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<td>70</td>
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<tr>
<td>90</td>
<td>96.8</td>
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</tr>
<tr>
<td>100</td>
<td>95.2</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
</tbody>
</table>

A. Transition not present.
B. Could not be accurately determined.
C. Calculated values based on the heat of melting of pure ethyl cellulose and corrected for the lower weight fraction.
Table II. Summary of dynamic mechanical analysis results on selected CAB/OSL blends.

<table>
<thead>
<tr>
<th>Lignin Content (%)</th>
<th>T_p - 10 Hz (°C)</th>
<th>tan δ FWHM&lt;sup&gt;1&lt;/sup&gt; (°C)</th>
<th>E_A (kJ·mol&lt;sup&gt;-1&lt;/sup&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>143</td>
<td>11.6</td>
<td>265</td>
</tr>
<tr>
<td>10</td>
<td>138</td>
<td>13.2</td>
<td>203</td>
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<td>20</td>
<td>134</td>
<td>14.7</td>
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<tr>
<td>55</td>
<td>125</td>
<td>22.2</td>
<td>171</td>
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</table>

<sup>1</sup>Tan δ peak width at half-maximum.
Table III. Solubility parameter, density, and monomer unit molecular weight for blend polymers.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Solubility Parameter, $\delta$ (cal/cc)$^{1/2}$</th>
<th>Density, $\rho$ (g/cc)</th>
<th>MW (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lignin</td>
<td>11.1</td>
<td>1.24</td>
<td>184</td>
</tr>
<tr>
<td>Ethyl cellulose</td>
<td>10.3</td>
<td>1.18</td>
<td>246</td>
</tr>
<tr>
<td>Cellulose acetate/butyrate</td>
<td>11.6</td>
<td>1.15</td>
<td>302</td>
</tr>
</tbody>
</table>
Figure 1. Scanning electron micrographs of freeze-fracture surfaces of EtC/OSL blends at compositions of: A) 95/5, B) 85/15, and C) 70/30. (Mag.=2000x)
Figure 2. Variation in dynamic mechanical properties (Log $E'$ and tan $\delta$) with temperature for blends of ethyl cellulose and lignin (Etc/OSL): 100/0 (---), 90/10 (--), 80/20 (---), and 60/40 (----).
Figure 3. Second scan of EtC/OSL blends shown in Figure 2: 100/0 (---), 90/10 (--), 80/20 (---), and 60/40 (----).
Figure 4. The effect of blend composition on glass transition temperature ($T_g$) behavior as observed by DSC of materials prepared with cellulose acetate/butyrate and lignin. The dashed line is the predicted behavior from the Gordon-Taylor model (ref. 15)
Figure 5. Scanning electron micrographs of freeze-fracture surfaces of CAB/OSL blends at compositions of: A) 95/5, B) 85/15, and C) 70/30. (Mag.=2000x)
Figure 6. Heat of mixing vs. weight fraction of component 1 in EtC/OSL (+) and CAB/OSL (0) blends. The dashed line results from calculation using lignin as component 1 and the solid line using the cellulose derivative as component 1.
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