

# Multiphase Materials with Lignin. XII. Blends of Poly(vinyl Chloride) with Lignin–Caprolactone Copolymers

WILLER DE OLIVEIRA and WOLFGANG G. GLASSER\*

Department of Wood Science and Forest Products, and Biobased Materials Center, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061

## SYNOPSIS

A previously described starlike copolymer consisting of a lignin derivative (hydroxypropyl lignin) and caprolactone has been blended with poly(vinyl chloride) (PVC) over a composition range of 0–100%. Solvent-cast films of the blends were examined with regard to thermal, mechanical, crystallinity, and morphological characteristics. In addition, the blends were examined with regard to aging effects. The results suggest that the lignin/caprolactone copolymer forms either a miscible (by thermal analysis) or a nearly miscible (with phase dimensions in the order of 10–30 nm) system in which physical properties are modified over a wide range of modulus and elongation. Blends with copolymer content exceeding 50% reveal partial caprolactone crystallinity that increases with age. Lignin derivative not copolymerized with caprolactone, by contrast, produces macrophase-separated structures with exceedingly poor properties. Lignin caprolactone starlike copolymers are materials ideally suited as plasticizers for PVC. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

Multiphase polymeric materials based on miscible systems have become an important subject for scientific investigation. Industrially, many plastics manufacturers are turning to polymer blends because the mixing of polymers offers a convenient and inexpensive alternative to developing totally new materials.<sup>1</sup> Multiphase polymeric systems have been primarily used in the production of impact-resistant rigid plastics and thermoplastic elastomers. Morphologically, they consist of a continuous phase that dictates most of the characteristic properties of the final product and a dispersed phase that introduces certain unique properties (i.e., impact strength). In the present work, poly(vinyl chloride) (PVC) has been selected as the polymer for studying the compatibility with a lignin-derived block copolymer.

Blends of PVC and polycaprolactone (PCL) have received much attention in the past two decades be-

cause these two polymers form a truly compatible system over the full range of composition.<sup>2–8</sup> Specific interaction through hydrogen bonding between the components is suggested to be the basis of miscibility.<sup>8,9</sup>

PVC is known for its efficiency to form miscible systems with several other low and high molecular weight substances acting as plasticizers.<sup>9,10</sup> PVC is a brittle, hard, and semicrystalline polymer unless modified. Lignins (and hydroxyalkyl lignin derivatives) are known to be immiscible with PVC and with many other polymers.<sup>11</sup> However, by copolymerizing lignin with caprolactone, the copolymer can be expected to exhibit improved compatibility or miscibility with PVC. It is expected that the role of the PCL segments covalently attached to lignin will act as “surfactants” that improve the adhesion of the lignin phase to the PVC matrix. Recently, the synthesis of lignin–caprolactone copolymers (LCL) has been described.<sup>12</sup> This is achieved by either anionic polymerization or by grafting of PCL segments onto the lignin backbone.<sup>12</sup>

In this article, the analysis of polymer blends of LCL copolymer with PVC is investigated. The study focuses on the determination of compatibility and

\* To whom correspondence should be addressed.

the evaluation of the blends' morphology and mechanical properties.

## EXPERIMENTAL

### Materials

PVC was obtained from Aldrich Chemical Co. and it was used as received. It had number- and weight-average molecular weights of 28,800 and 52,600 daltons, respectively. The LCL starlike copolymer was prepared by the bulk copolymerization of freshly distilled  $\epsilon$ -caprolactone monomer initiated by the hydroxyl groups of a lignin derivative, according to the procedure outlined elsewhere.<sup>12</sup> The number- and weight-average molecular weights of the copolymer were 9800 and 26,500 daltons, respectively. The seven-armed star copolymer was composed of 20 wt % lignin derivative, and the molecular weight of the PCL blocks averaged 1100 daltons per arm. Hydroxypropyl lignin (L) ( $M_n = 1900$ ;  $M_w = 12,000$ ) was obtained by propoxylating commercial kraft lignin (Indulin AT, Westvaco Corp.) in accordance with earlier publications.<sup>13,14</sup>

### Methods

#### Blend Preparation

All blends were prepared by solvent casting from solution. Approximately 3 g of polymer of a particular blend composition were dissolved in 50 mL of tetrahydrofuran and stirred for 2 h to ensure complete solubilization of the polymers. The solution was transferred into an evaporation Teflon dish covered by perforated aluminum foil, and the solvent was allowed to slowly evaporate at room temperature for 2 days. The films were then transferred to a vacuum desiccator for further drying for at least 1 week. Dog-bone-shaped samples with a gauge length of 10 mm and a gauge width of 3.2 mm were cut from the thin films using a die.

#### Characterization

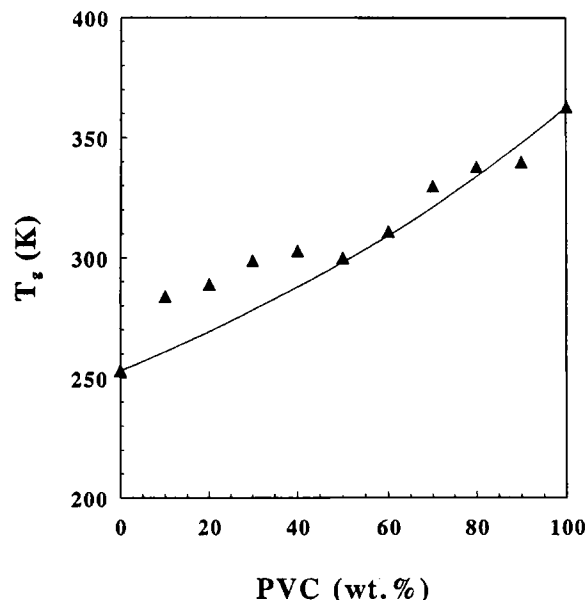
The dynamic mechanical properties of the blend systems were determined using a dynamic mechanical thermal analyzer made by Polymer Laboratories Ltd., Shropshire, England. Standard tensile stress-strain measurements were done on dog-bone specimens with a MINIMAT testing machine of Polymer Laboratories Ltd., at room temperature. Thermal properties were analyzed on a Perkin-Elmer Model DSC-7. The temperature was scanned from  $-100$  to

$100^\circ\text{C}$  at a heating rate of  $10^\circ\text{C}/\text{min}$ . The percent of crystallinity was calculated on the basis of measured heat of fusion per gram of pure copolymer in the sample to the heat of fusion per gram of 100% crystalline PCL, 32.4 cal/g.<sup>15</sup> Scanning and transmission electron microscopy were operated both on a Phillips EM-420 STEM. For SEM analysis, films were first immersed in liquid nitrogen and then fractured and analyzed at their fractured surface. For TEM analysis, ultrathin films were microtomed using a Reichert-Jung ULTRACUT System FC-4 at  $-70^\circ\text{C}$ . The microtomed samples were then mounted on a copper TEM grid and stained with ruthenium tetroxide for 15–45 min.

## RESULTS AND DISCUSSION

### Thermal Analysis

The thermal analysis data, by DSC, for the binary blends of PVC and LCL-copolymer reveal single glass transition temperatures for all blend compositions. This single  $T_g$  is consistently intermediate between the  $T_g$ 's of the individual blend components. The data agree well with the relationship of Fox<sup>16</sup> up to copolymer contents of approximately 50% (Fig. 1). At higher copolymer contents (i.e., lower PVC contents, Fig. 1), the blend morphology is no longer purely amorphous. The partial crystallinity



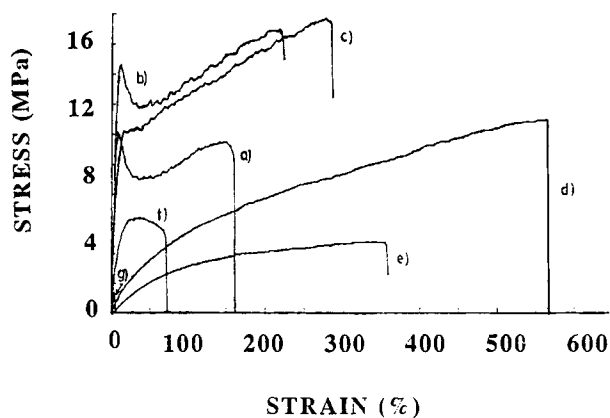
**Figure 1** Relationship between  $T_g$  and PVC content for LCL/PVC blends. (▲) Experimental values. The relationship according to the Fox equation<sup>16</sup> is given as a continuous line.

of the copolymer (evidence to be presented below) is now responsible for the shifting of the  $T_g$  above that predicted by the Fox relationship. If this crystalline copolymer phase is taken into consideration, and if blend composition is expressed for the amorphous phase only, the  $T_g$  values of the blends having 0–50% PVC content also fit the Fox equation (Fig. 1). The single  $T_g$  is an indication, by thermal analysis, for compatibility between PVC and LCL-copolymer.

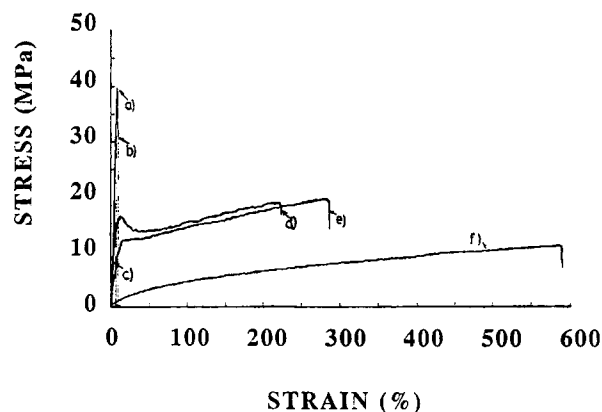
The dynamic mechanical thermal analysis data (not shown) reveal up to four (in part exceedingly subtle) transition processes in the temperature range between  $-110$  and  $110^\circ\text{C}$ . These can be attributed to secondary relaxations of the PCL component ( $-110^\circ\text{C}$ ) and of PVC ( $-50^\circ\text{C}$ ); to the single  $T_g$  of the amorphous blend components (located between  $16$  and  $67^\circ\text{C}$  depending on composition); and to the melting transition of the crystalline PCL phase (ca.  $60^\circ\text{C}$ ). These data (not shown) support the conclusion of compatibility by DSC (Fig. 1).

### Tensile Properties

The tensile-strength characteristics of solution-cast films of PVC/LCL blends over the entire composition range (i.e., 0–100% PVC and, conversely, 100–0% LCL copolymer) indicates that LCL significantly contributes to either or both maximum stress at break or elongation (Fig. 2). The ability to “elongate,” or plastically deform, rises quickly with increasing LCL copolymer content, up to about 50%. At higher copolymer contents, the blends reveal rising modulus that must be attributed to the crystallinity of the PCL component. These results suggest that PVC is effectively plasticized by the LCL-co-



**Figure 2** Effect of copolymer content on tensile properties of LCL/PVC blends: (a) 0%; (b) 10%; (c) 20%; (d) 40%; (e) 60%; (f) 80%; (g) 100% LCL copolymer.

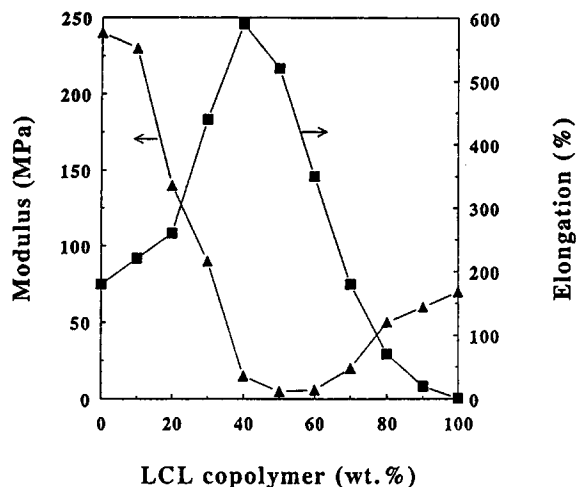


**Figure 3** Comparison of the tensile properties of PVC blended with lignin derivative not copolymerized with caprolactone (L) and PVC blended with lignin-caprolactone starlike copolymer (LCL): (a) 10% L; (b) 20% L; (c) 40% L; (d) 10% LCL; (e) 20% LCL; (f) 40% LCL copolymer content.

polymer and that a miscible amorphous phase is formed in blends where the copolymer concentration is less than 50%. At higher copolymer contents, partial caprolactone crystallinity is responsible for a renewed rise of modulus (Fig. 2). This is in agreement with the results obtained by DSC (Fig. 1).

A control experiment involving blends between PVC and the lignin derivative (L) not copolymerized with caprolactone produces data indicative of complete macrophase separation (Fig. 3). Solvent-cast films could only be obtained with blends containing up to 40% lignin. Above 40%, macrophase separation was observed without magnification. Tensile stress vs. strain results (Fig. 3) reveal complete loss of all elongation properties of PVC when L is added. This is in striking contrast to the data obtained with the corresponding LCL containing blends (Fig. 2). This provides conclusive evidence that L/PVC blends have poor mechanical properties by suffering embrittlement whereas LCL/PVC blends experience plasticization of PVC. The results support the basic premise of this study, namely, that copolymerization of lignin with caprolactone results in copolymers with superior compatibility with PVC.

The impact of LCL copolymer content on the modulus and elongation behavior of PVC, over the entire composition range, reveals that modulus declines from ca. 250 to ca. 10 MPa as LCL content rises from 0 to 50%. At the same time, elongation increases from approximately 200 to 600%. The loss of elongation properties, and the rise in modulus at LCL copolymer contents exceeding 50%, is again consistent with partial crystallization of PCL component in the blend (Fig. 4).



**Figure 4** Effect of copolymer content on (▲) modulus and (■) elongation properties of PVC/LCL blends.

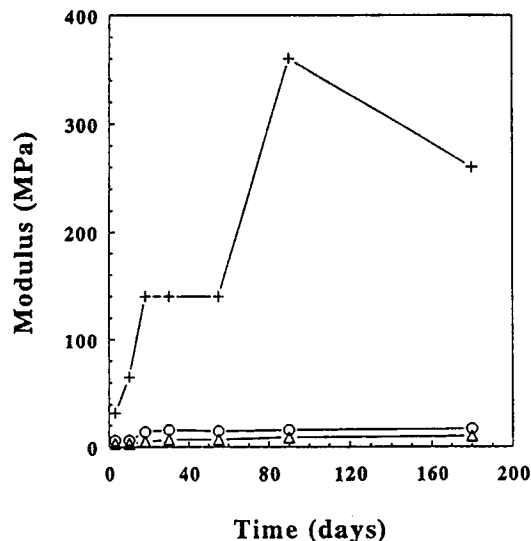
### Aging Studies

PCL is known to develop crystallinity when the polymer is annealed for appropriate periods of time, at temperatures intermediate between melting point and glass transition temperature. LCL copolymers have similar aging behavior as shown elsewhere.<sup>12</sup> In the case of blends of LCL-copolymer and PVC, the crystallization process proceeds slowly at room temperature. Therefore, it was of interest to determine to what extent blend crystallinity is affected by aging at room temperature. The modulus data of LCL/PVC blends aged for up to 6 months (Fig. 5) indicate a change in modulus with aging time for three different blend compositions. For the blend rich in PVC, there is a dramatic increase in modulus with time. The opposite happens in those blends where the copolymer content is high. Low and relatively constant moduli are seen during the 6 month period. The increase in modulus in samples with low copolymer content can be explained with antiplasticization arguments presented by Sundgren et al.<sup>17</sup> since crystallinity factors (presented later) can be ruled out.

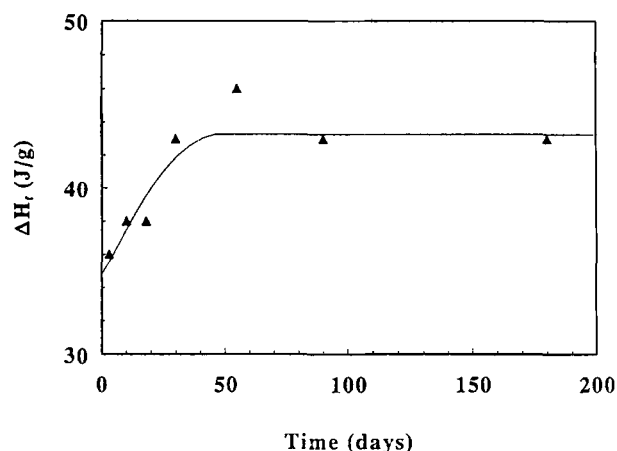
Antiplasticization describes the observation of increased modulus and decreased elongation upon the addition of a blend component. This may result when relatively small amounts of a plasticizer are used. Several factors are involved, and many theories have been proposed, to explain this phenomenon. Among the most popular is the so-called hindered molecular motion theory.<sup>7,18</sup> It is well known that the secondary transitions, particularly the  $\beta$ -transition, are associated with ductility and increased impact strength. If such transitions do not occur, the resin is brittle at room temperature. Small

amounts of antiplasticizers in PVC reduce and even eliminate its  $\beta$ -transition, as shown in the work of Sundgren and co-workers with PVC antiplasticized with PCL.<sup>17</sup> Impact energies of these PVC compositions decreased with the PCL content, rising to about 12%, and then rose with further increases in plasticizer content. The small amount of LCL copolymer in the 90% PVC blend (Fig. 5) may cause immobilization of the PVC chains through a type of polar cross-linking mechanism. The resulting loss of freedom of motion is responsible for the embrittlement of the PVC matrix. On the other hand, in high copolymer-containing blend systems, there are enough PCL segments to be dispersed, and therefore dissolved in the PVC, which then produces a flexible and ductile material. When the copolymer is the matrix (> 60% copolymer), there is a slight gain in modulus owing to the crystallization of the copolymer, as detected by DSC.

Heat of fusion data by DSC indicated that only the blend with 60% copolymer exhibited an endothermic peak throughout the aging period. For this material, there is indeed an increase in the measured heat of fusion during the time period (Fig. 6). Since this rise in heat of fusion does not suggest a dramatic gain in crystallinity with aging (only about 25%, from 12 to 15% of the caprolactone component), this demonstrates once more that it is not crystallinity that affects the embrittlement of the matrix, but rather a lack of enough PCL segments to promote plasticization of PVC.



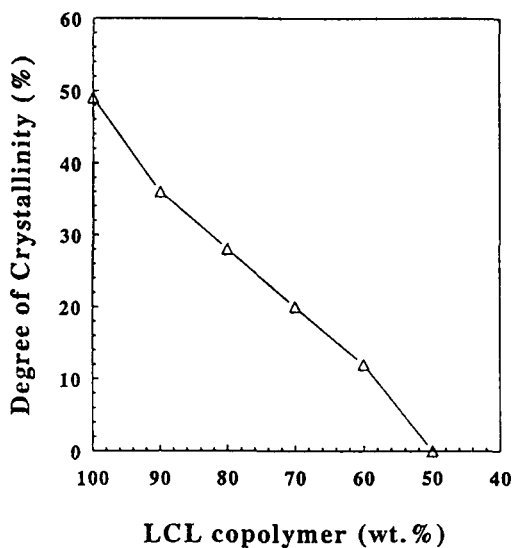
**Figure 5** Effect of aging at room temperature on the modulus of PVC blended with LCL-copolymer in the following compositions: (+) 10%; (Δ) 40%; (○) 60% LCL copolymer.



**Figure 6** Effect of aging at room temperature on the heat of fusion of 10% LCL-copolymer blends with PVC.

### Crystallinity Properties

The degree of LCL crystallinity of aged (> 6 months) blend samples was found to be related to blend composition (Fig. 7). The degree of crystallinity was calculated from the area under the heat of fusion peak in the DSC thermograms. Since the LCL-copolymer crystallizes at room temperature, the amount of crystallinity present increases with time. Therefore, all data were obtained using samples annealed for at least 6 months at room temperature in a desiccator. The results show a decrease in degree of crystallinity as the LCL copolymer content declines. At concentrations below 50% copolymer content, there is no more crystallization of



**Figure 7** Relationship between degree of crystallinity and copolymer content of LCL/PVC blends aged for > 6 months at room temperature.

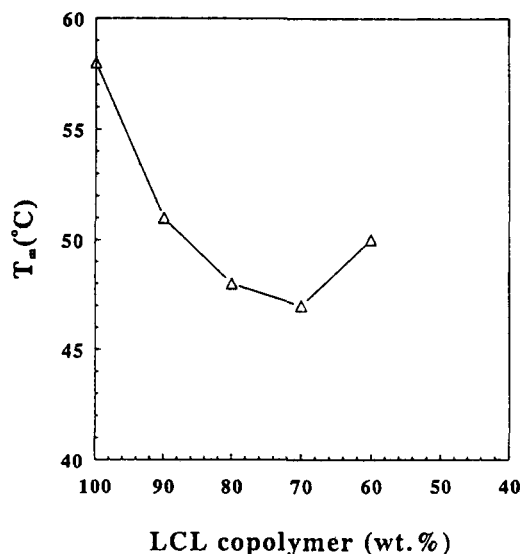
PCL segments. This can be attributed to the dilution of PVC chains within the blend, and this restricts the rearrangement of PCL segments to induce crystallization.

The melting point of the caprolactone crystalline phase is a function of the LCL copolymer content in the blend (Fig. 8). There is a decrease in melting point as the blend is enriched with PVC. Such a decrease in  $T_m$  was also reported by Ong<sup>4</sup> in his studies on PVC blends with PCL.

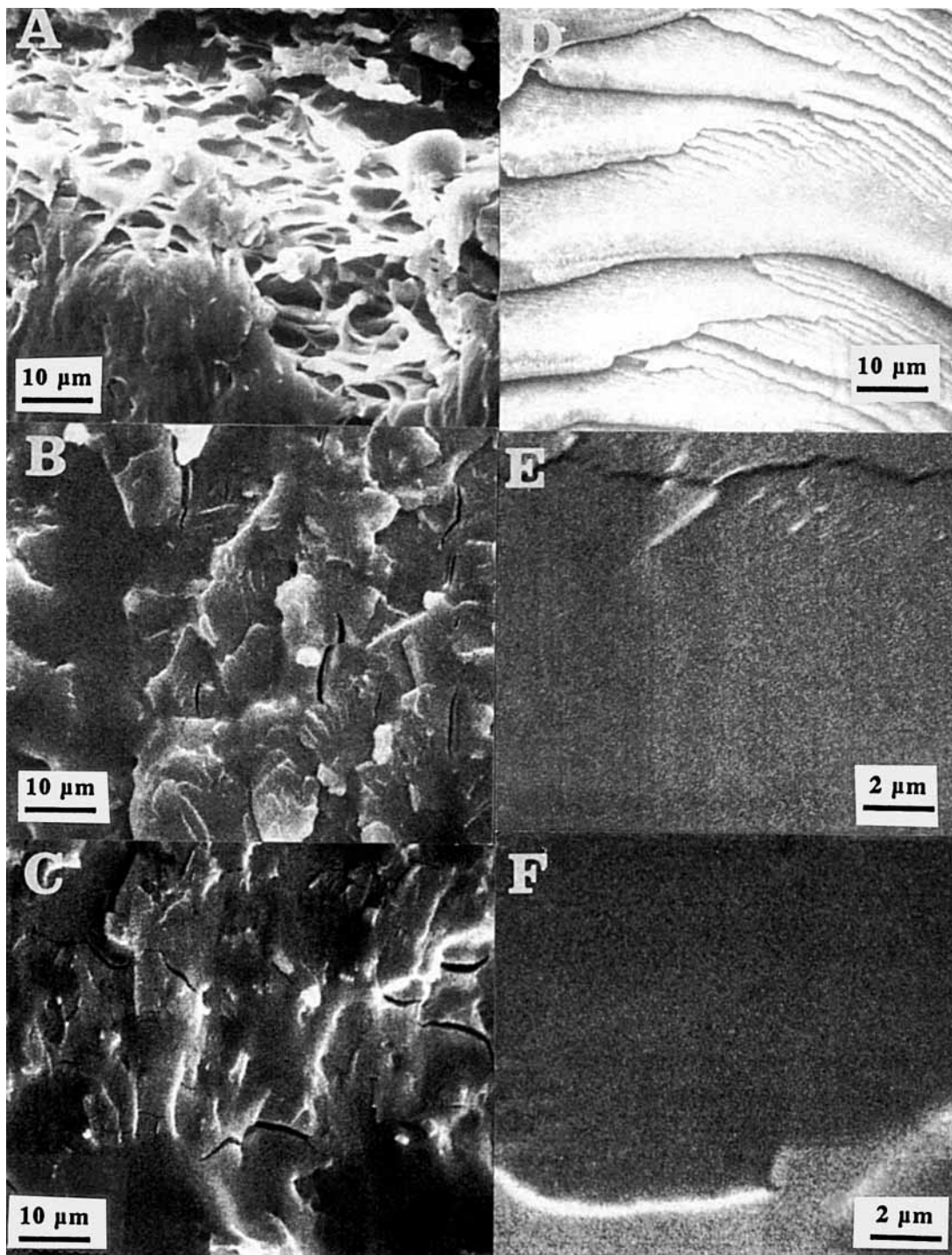
The effect of crystallinity on thermal (Fig. 1) and tensile properties (Figs. 2 and 4) has been pointed out in earlier sections. With LCL-copolymer concentrations of > 60%, the copolymer blend component crystallizes, and this results in a rise in  $T_g$ , in a strengthened matrix, and in reduced elongation.

### Morphology

Transmission and scanning electron microscopy were employed for studying the morphology of LCL/PVC blends. Staining with  $\text{RuO}_4$  was used for TEM analysis. The changes in morphology of polymer blend samples with composition are illustrated in the SEM micrographs of fracture surfaces of both types of blends, L/PVC (control) and LCL/PVC (Fig. 9). The micrographs reveal two-phase morphologies for all L/PVC blends with L-particle sizes increasing as L-content rises and single-phase morphologies for the LCL/PVC blends in which it is almost impossible to detect phase separation. The copolymer particles were submicron in size, and they were evenly distributed in the PVC matrix. This



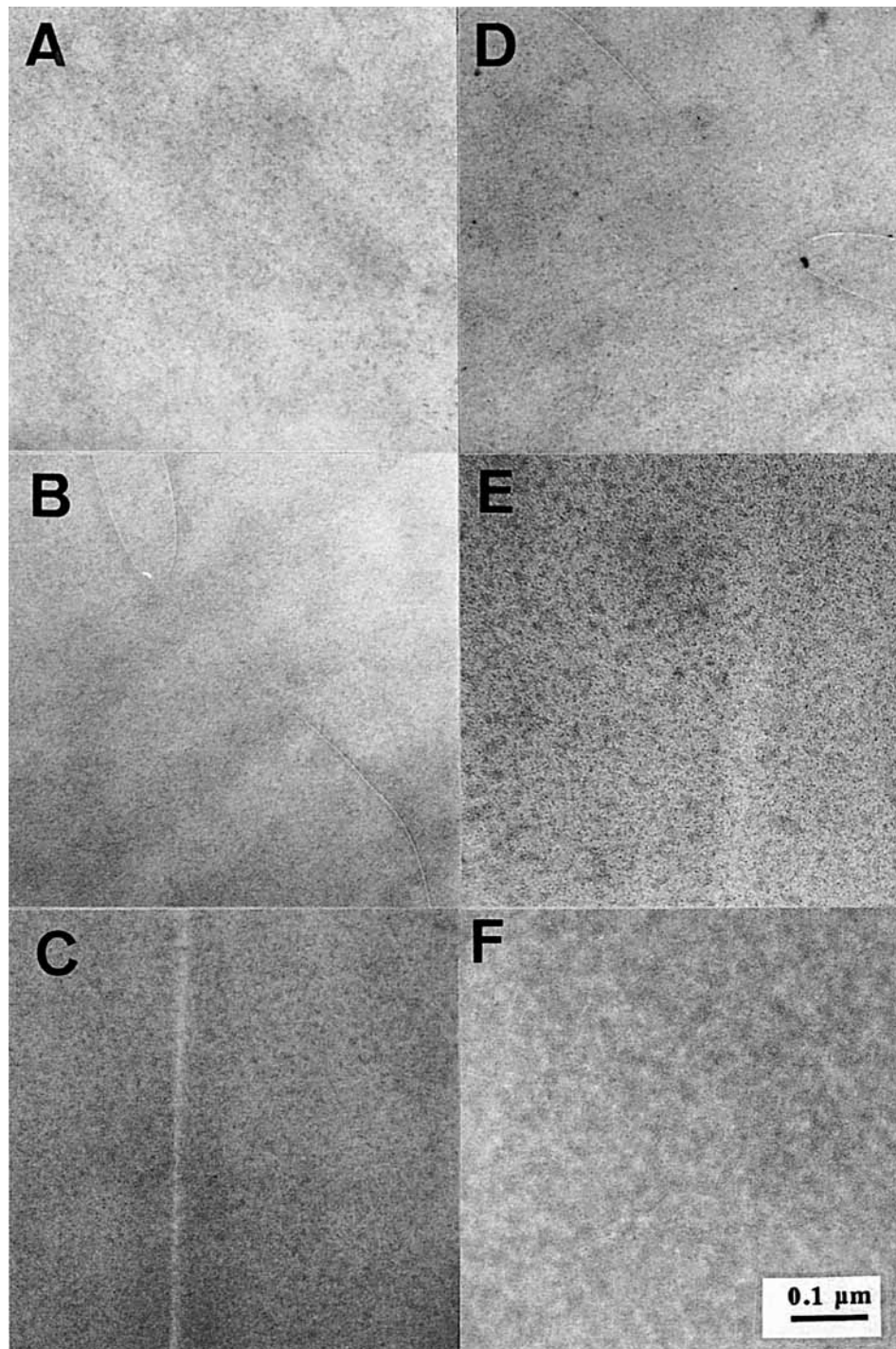
**Figure 8** Effect of copolymer content on the depression of the melting point in LCL/PVC blends.



**Figure 9** Comparison of morphologies, by scanning electron microscopy, of fractured surfaces of PVC blended with lignin derivative not copolymerized with caprolactone (L) and PVC blended with lignin-caprolactone copolymer (LCL): (A) 10% L; (B) 20% L; (C) 40% L; (D) 10% LCL; (E) 20% LCL; (F) 60% LCL-copolymer content.

type of morphology can be described as a coarse structure with a fine dispersion of phases, which can be interpreted as a blend of two miscible polymers.

Although solution blending provides mixing of the two components at the molecular level in a common solvent, phase separation is evident for the L/



**Figure 10** Transmission electron micrographs of solvent-cast films of LCL/PVC blends: (A) 5% LCL; (B) 10% LCL; (C) 20% LCL; (D) 40% LCL; (E) 60% LCL; (F) 80% LCL-copolymer content. Magnification 105,000 $\times$ . LCL-copolymer phase stained with ruthenium tetroxide.

PVC blends (Fig. 9). There is clear evidence of macrophase separation, and this agrees with the tensile test results. The way in which the samples fractured

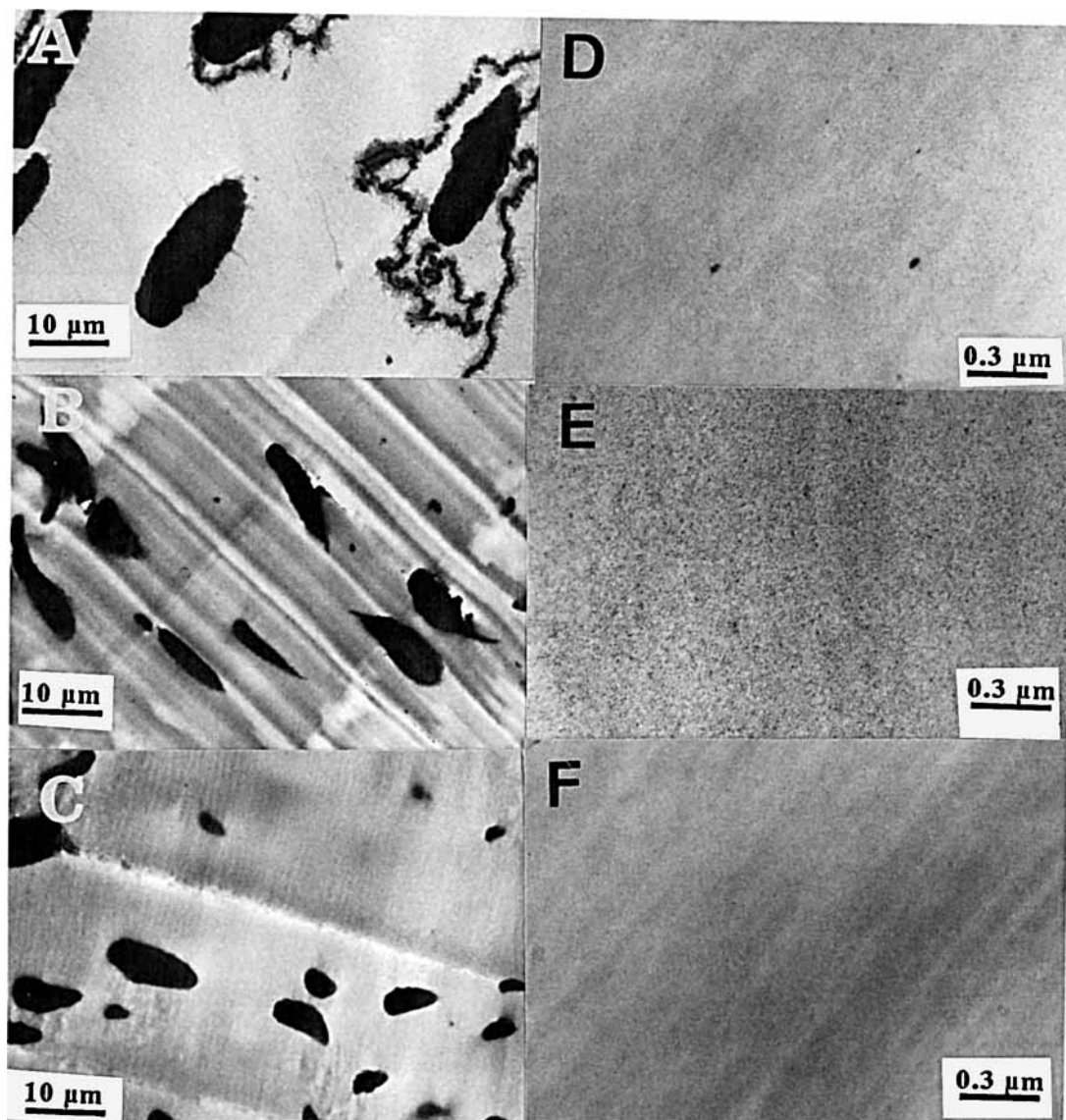
is another indication of poor adhesion between the components. The L/PVC system seems to fail in a macroscopically brittle fashion, whereas the LCL/

PVC system fails ductilely as evidenced by the smooth fracture surfaces seen in the micrographs of Figure 9.

TEMs of thin films of LCL/PVC blends cast from dilute solution, stained with  $\text{RuO}_4$ , reveal copolymer domains in sizes ranging from 10 to 30 nm (Fig. 10). The matrix is formed by the major component, and there is a transition at about 50% composition. Phases are small, but clearly visible, with defined boundaries at high copolymer content. The small size distribution observed in all compositions

is another indication of significant miscibility between blend components.

Transmission electron microscopy was also applied to the L/PVC blends (Fig. 11). A comparison of TEM micrographs containing various concentrations of L and LCL copolymer reveals two-phase and macrophase-separated structures for the control and nearly single-phase structures for blends with the copolymer. Stained L-particles are irregular in shape and vary within a wide size range (0.1–1.0  $\mu\text{m}$ ). They are unevenly distributed. On the other



**Figure 11** Comparison of morphologies, by transmission electron microscopy, of solvent-cast films of PVC blended with lignin derivative not copolymerized with caprolactone (L) and PVC blended with lignin-caprolactone copolymer (LCL): (A) 10% L; (B) 20% L; (C) 40% L; (D) 10% LCL; (E) 20% LCL; (F) 40% LCL-copolymer content. The contrast was enhanced by either stained L or LCL phase with ruthenium tetroxide.



hand, in the LCL/PVC system, TEM micrographs show that the compatibility of the copolymer with PVC is far superior to that of the lignin derivative. The copolymer particle sizes are very small (10–30 nm) and evenly distributed in the PVC, forming an almost single-phase system.

## CONCLUSIONS

Blends of LCL copolymer with PVC were prepared by solvent casting from solution. The blends were shown to exhibit single glass transition temperatures intermediate between those of the blend components. With exception of the blends with high copolymer concentration (above 50%), the blends'  $T_g$  followed the Fox equation.

The morphology of the blends was investigated by DSC and electron microscopy. The presence of PVC plays a major role in depressing the  $T_m$  of the PCL segments. Copolymer crystallinity was found to exist in blends having > 50% copolymer content.

Stress-strain properties showed a decrease in modulus and increased ductility as the PVC was plasticized with copolymer. This trend was reversed at high copolymer contents where, due to crystallization, an increase in modulus and a reduction in elongation was observed.

The mechanical properties of the blends were affected by aging, especially at low copolymer content due to an antiplasticization effect. Modulus and tensile strength increased, and elongation decreased with time. Blends rich in copolymer were not affected by aging.

Electron microscopy revealed a significant miscibility between PVC and LCL copolymer, over a wide composition range (from 10 to 90% copolymer). TEM illustrated a two-phase structure that was microscopically phase-separated with domain sizes ranging from 10 to 30 nm, approximately. This was not observed for L/PVC blends that exhibited distinct macrophase separation.

Copolymerization with caprolactone was recognized as a promising method for incorporating lignin into PVC blends.

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