

# The Morphology and Mechanical Properties of Phenoxy/Liquid Crystalline Polymer Blends and the Effect of Transesterification

GI DAE CHOI,<sup>1</sup> SEUNG HYUN KIM,<sup>1</sup> WON HO JO,<sup>1\*</sup> and MOO SAN RHIM<sup>2</sup>

<sup>1</sup>Department of Fiber and Polymer Science, Seoul National University, Seoul 151-742, Korea;

<sup>2</sup>Fiber R & D Laboratory, Kolon Industries Inc., Kumi, Kyungbuk 730-030, Korea

## SYNOPSIS

Morphological, rheological, and mechanical properties of poly(hydroxy ether of bisphenol A) (phenoxy) and a Vectra liquid crystalline copolyester (LCP) blends were investigated. Scanning electron micrographs of fracture surfaces of injection-molded samples show that the LCP forms an elongated fibrous dispersion in the phenoxy matrix. As the mixing time increases, the tensile strength and modulus increase while the elongation at break remains almost constant. These improvements are attributed to the formation of LCP-grafted phenoxy by the interchange reaction between phenoxy and LCP. The interchange reaction was identified by DSC, a rheometer, and a FTIR spectrometer. The graft copolymer gives better adhesion between the two phases and thus improves mechanical properties of the blends. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

Most polymer pairs are immiscible and form multiphase domains on mixing. The morphology of immiscible polymer blends depends on a multitude of factors including the viscosity ratio, composition, interfacial tension, magnitude and type of flow field, and mixing time. The resultant properties of polymer blends depend on the amount and properties of the individual polymeric components as well as the mode of the dispersed material and the interaction between the phases.<sup>1,2</sup> The concept of tailoring polymer properties through blending with other polymers and fillers has long been recognized as a viable method to meet specific applications.

In particular, polymer blends containing liquid crystalline polymers (LCP) have been studied intensively to achieve a so-called *in situ* composite structure with oriented LCP fibrils in the thermoplastic matrix.<sup>3-13</sup> Because of its lower viscosity, the LCP in these blends forms fibrous structure in the matrix of the thermoplastic polymers, leading to the

formation of self-reinforced composites. In most cases, the addition of LCP increases the mechanical strength and stiffness of the thermoplastic matrix polymer. Moreover, even relatively small amounts of LCP may induce a reduction in the melt viscosity and thus make the processing easier. The LCP may also improve other properties of thermoplastics, such as dimensional stability and thermal stability.<sup>14,15</sup> When the LCP is a minor component, it is potentially capable of forming highly elongated fibrous structures parallel to the extensional flow direction. The oriented LCP in the matrix not only improves the mechanical properties of thermoplastic material, but also makes the processing free from problems associated with conventional fiber-reinforced composites such as fiber breakage, abrasion of the processing machinery, increase in viscosity and energy consumption, and difficulties in the uniform dispersion of fibers.<sup>16,17</sup>

However, many of these blends show poor miscibility between the blend components and have a heterogeneous structure. It has been reported that the apparent compatibility can be possibly increased by an interchange reaction between the blend components, as in the case of blends composed of two polyesters or of polyester and bisphenol A polycar-

\* To whom correspondences should be addressed.

bonate.<sup>18</sup> Robeson<sup>19</sup> investigated the miscibility of polyarylate/phenoxy blends under controlled time and temperature conditions. It was found that its phase behavior is strongly dependent on temperature. After heating at 270°C, the dynamic mechanical results clearly show phase separation. However, a sample molded at 320°C yielded a single phase with a dynamic modulus plateau above the  $T_g$ , indicative of cross-linking resulting from transesterification of polyarylate and phenoxy.

In this study, we report the rheological properties, morphologies, and mechanical properties of poly-(hydroxy ether of bisphenol A) (phenoxy) and LCP blends. Also, the effects of transesterification between the LCP (Vectra A950) and phenoxy on the morphological, thermal, and mechanical properties of the blends are examined as a function of the transesterification time.

## EXPERIMENTAL

### Materials

The LCP used in this study is a fully aromatic main-chain copolyester and is commercially known as Vectra A950. It is known as a random copolyester containing 75 mol % *p*-hydroxybenzoic acid (HBA) and 25 mol % 2,6-hydroxy naphthoic acid (HNA). The poly(hydroxy ether of bisphenol A) (phenoxy) used in this study is a commercial grade and was used as received without further purification. The characteristics of polymers used in this study are reported in Table I.

### Blend Preparation

The polymer samples were completely dried under vacuum at 90°C for 24 h before blending. Blends were prepared in the melt state using Mini-Max molder (CS-MMX, Custom Scientific Instruments, Inc.) at 290°C. The melt mixing time was 5 min unless otherwise specified. However, to investigate

the effects of the intermolecular exchange reaction on the morphological and mechanical properties, the mixing time was varied from 5 to 90 min.

### Rheological Properties

The rheological properties of component polymers and their blends were measured at 290°C on a Rheometrics mechanical spectrometer (RMS 800) with parallel-plate mode under a nitrogen atmosphere. Dynamic experiments were performed in oscillatory shear at 10% strain with dimensions of 25 mm in diameter and 1.8–2.0 mm in gap size. The frequency sweeps were performed from 0.1 to 100 rad/s. Steady shear viscosities were also measured in the cone-and-plate configuration with a 0.1 rad cone angle at shear rates ranging from 0.1 to 10 s<sup>-1</sup>.

### Thermal Analysis (DSC)

The thermal properties of all samples were measured using a differential scanning calorimeter (Perkin-Elmer DSC-7). Blend samples of 10–15 mg were heated in a nitrogen atmosphere to 300°C at a heating rate of 20°C/min and then cooled to room temperature. They were then reheated at a heating rate of 20°C/min, and only the second running data were accepted.

### Morphology

Melt-blended samples were injection-molded into a dumbbell-type mold and fractured at the liquid nitrogen temperature. The cryogenically fractured surface was coated using a gold sputtering unit and examined by scanning electron microscope (SEM, JEOL JSM-35) at an accelerating voltage of 25 kV.

### Mechanical Properties

Completely dried samples were melt-mixed and injection-molded into a tensile molder. The dimen-

**Table I** Characteristics of Polymer Samples Used in Blends

Sample	Source	$M_w$ (g/mol)	$T_i$ (°C) <sup>a</sup>
Vectra A950	Hoechst Celanese Co.	30,000	280 <sup>b</sup>
Phenoxy	Union Carbide Co.	82,000 <sup>c</sup>	94 <sup>d</sup>

<sup>a</sup> Determined by DSC.

<sup>b</sup> Nematic transition temperature.

<sup>c</sup> Determined by GPC.

<sup>d</sup> Glass transition temperature.

sions of the test specimens were length of 9 mm and diameter of 1.6 mm of a dumbbell type. Mechanical properties were measured by using an Instron tensile tester (Model 4202) at room temperature. The extensional crosshead speed was 1 mm/min. All the results were reported as an average of at least six measurements. The standard deviations were within 10% of the reported values.

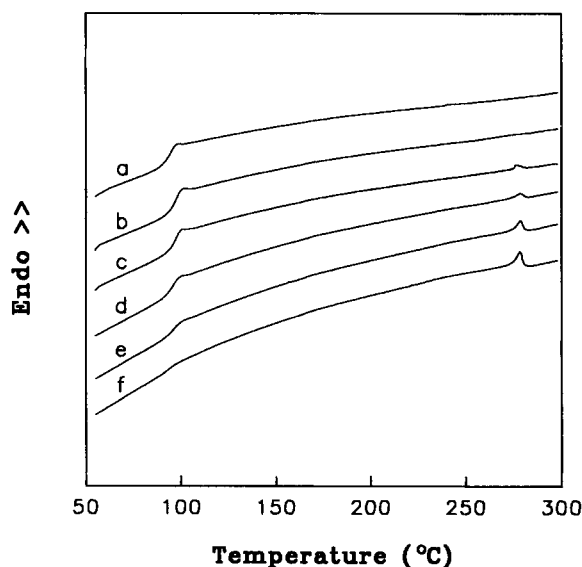
### Infrared Spectroscopy

The soluble fraction of polymer blends after transesterification was extracted by a Soxhlet with boiling tetrahydrofuran (THF) for 10 h. THF is a good solvent for phenoxy but a poor solvent for Vectra A950. Infrared spectra were obtained for extracted samples on a Fourier transform infrared spectrometer (Perkin-Elmer FTIR 1725X).

## RESULTS AND DISCUSSION

### Rheology

The blends of phenoxy and Vectra A950 copolyester are immiscible in the whole composition range. This is confirmed by the DSC thermograms as shown in Figure 1. All blend compositions showed a single glass transition temperature at 94°C, which corresponds to the  $T_g$  of phenoxy, and a composition-independent endothermic peak at 280°C, corre-



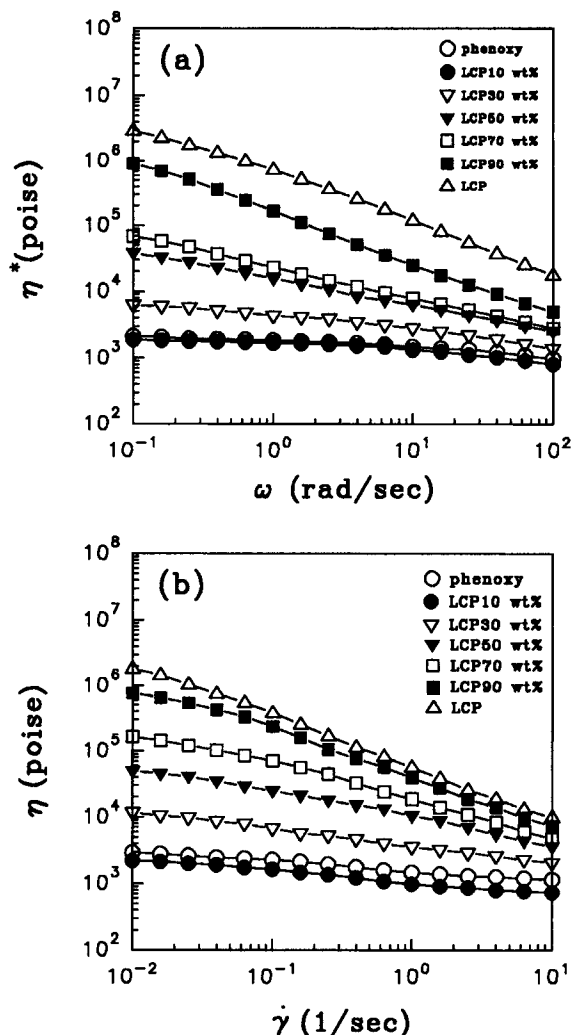
**Figure 1** DSC thermograms of LCP/phenoxy blends: (a) phenoxy; (b) LCP 10; (c) LCP 30; (d) LCP 50; (e) LCP 70; (f) LCP 90 wt %.

sponding to the nematic transition temperature of LCP. This independence of the transition temperatures on the blend composition indicates immiscibility of the two polymers.

The flow curves of pure phenoxy, LCP, and their blends measured at 290°C are shown in Figure 2. The phenoxy sample exhibits slightly non-Newtonian behavior in the shear rate range examined. This behavior is typical of thermoplastic polymers at the relatively low shear rate region. The LCP and blends of high LCP content show a non-Newtonian behavior at low shear rate and have high power-law exponents. The non-Newtonian behavior at low shear rate corresponds to the first region of flow curves for the LCPs, as proposed by Onogi and Asada.<sup>20</sup> According to their explanation, in this region for the blends of high LCP content, piled polydomains of LCP are transformed to a dispersed polydomain system and finally to a continuous phase as the external field increases. The blends with low LCP content are found to exhibit a slight non-Newtonian behavior. The variation of the viscosity with the LCP content at two different shear rates is shown in Figure 3. The blend viscosity shows a shallow minimum at about 10 wt % LCP content. Similar observations were also reported on Nylon 6/Vectra B950 blends,<sup>21</sup> where the addition of a small amount of LCP to a thermoplastic matrix resulted in a decrease in the viscosity of the blends. The viscosity of blends showed a deep minimum at a concentration range of 5–20% LCP at 290°C. The minimum in the viscosity-composition curves of the blends has been attributed to two main reasons: incompatibility between the two phases and formation of elongated fibrils of the LCP phase that tend to lubricate the melt.<sup>22</sup> More recently, La Mantia and Valenza<sup>23</sup> proposed a new mechanism for the prediction of minima in the viscosity-composition curves of LCP blends. When the viscosity of the LCP is larger than that of the thermoplastic matrix, a minimum is observed. They concluded that incompatibility and fibrillation are responsible for the reduction of the viscosity in the LCP-based blends and that the particular viscosity ratio determining the phase morphology is also responsible for the presence of minima in these blends.

### Morphology

The morphology of the phenoxy/LCP blends was studied using SEM. The fracture surfaces of phenoxy/LCP blends are shown in Figures 4 and 5. At 10 wt % LCP, the fine fibrillar structures of LCP with a diameter of about 3  $\mu\text{m}$  are well developed in



**Figure 2** Shear rate dependence of the viscosity of phenoxy, LCP, and their blends at 290°C: (a) dynamic viscosity; (b) steady shear viscosity.

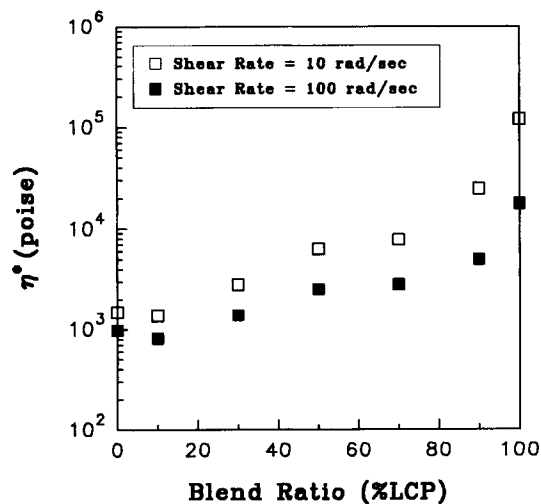
the matrix, and they appear to be distributed uniformly in the phenoxy matrix [Fig. 4(a)]. Some of the fibrils are still adhered to the matrix, and no major pullout has been observed. The fracture surface of the blend with 30 wt % LCP shows that fibrils of 5–10  $\mu\text{m}$  in diameter are formed in the phenoxy matrix [Fig. 4(b)]. However, there seems to be relatively poor adhesion between the LCP fiber and matrix, as observed by holes and open circles around fibrils. This poor adhesion may come from the differences in expansion and contraction coefficients between two polymers during cooling from the melt.

At higher LCP concentration, the “forest” of LCP fibers is clearly observed, as evident from Figure 5(a) for 70 wt % LCP and Figure 5(b) for 90 wt % LCP. These LCP fibers seem to be heavily coated with

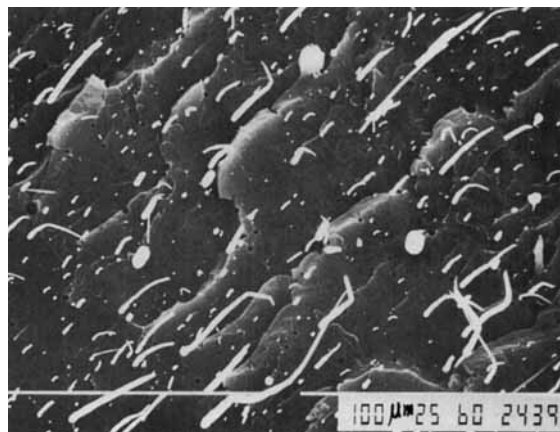
the phenoxy matrix. The micrographs illustrate the relatively good adhesion between the two phases. Similar composition-dependent adhesion properties have been reported by Limtasiri and Isayev<sup>24</sup> on poly(phenylene oxide) (PPO)/Vectra A950 blends. They reported that the addition of 5 wt % LCP resulted in holes and open circles around fibrils, indicating poor adhesion between LCP and PPO, whereas the blends with LCP contents higher than 50 wt % showed good adhesion properties.

### Mechanical Properties

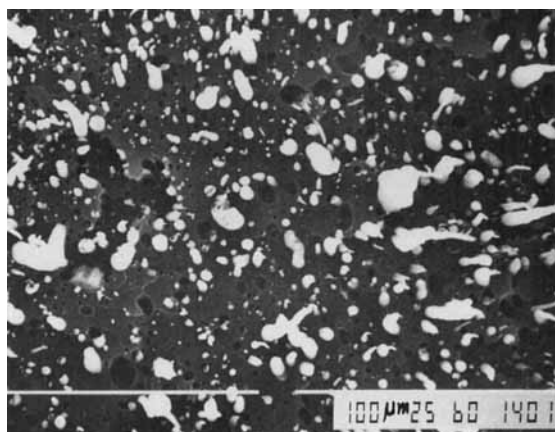
The properties of LCP and their blends are known to be highly anisotropic when processed by techniques involving one-dimensional flows.<sup>25</sup> Tensile properties of phenoxy, LCP, and their blends have been measured on injection-molded specimens along the machine direction. Phenoxy/LCP blends show brittle fracture behavior at higher than 10 wt % LCP contents. Figure 6(a) shows tensile strength as a function of composition for phenoxy/LCP blends. It is found that the breaking strength first increases with increasing LCP content and then stays at a plateau and abruptly increases again above 70 wt % LCP content. It is noteworthy that the breaking strength shows a large increase even at low LCP concentration (10 wt %). The variation of the elastic modulus of these blends with the LCP concentration is also shown in Figure 6(b). The modulus increases with LCP content. The values are comparable with the simple composite theory based on the additive rule of mixture. It implies that LCP effectively serves



**Figure 3** Viscosity vs. composition of phenoxy/LCP blends at given shear rates at 290°C.



(a)



(b)

**Figure 4** SEM micrographs of injection-molded phenoxy/LCP blends: (a) phenoxy/LCP (9/1); (b) phenoxy/LCP (7/3).

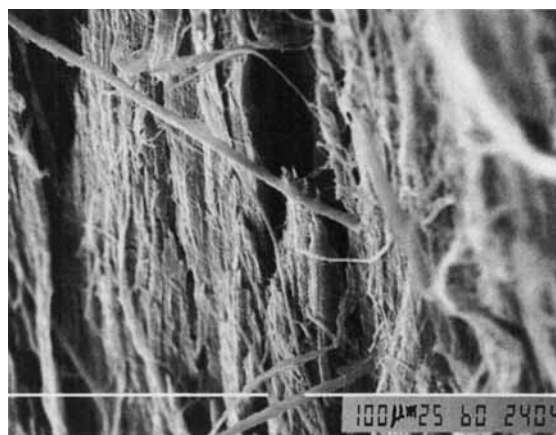
as a reinforcing additive in the phenoxy matrix. It is important to note that elastic moduli show a positive deviation from the simple additivity rule, except for blends with high LCP content. The elongation at break drastically decreases for blends with LCP concentration greater than 10 wt % and shows a typical brittle fracture behavior as shown in Figure 6(c). An increase in modulus and strength is accompanied by a dramatic drop of elongation at break even at a small amount of LCP. In fact, the low elongation at break with high tensile strength and modulus is typical for fiber-reinforced composites.

#### Thermal Modification

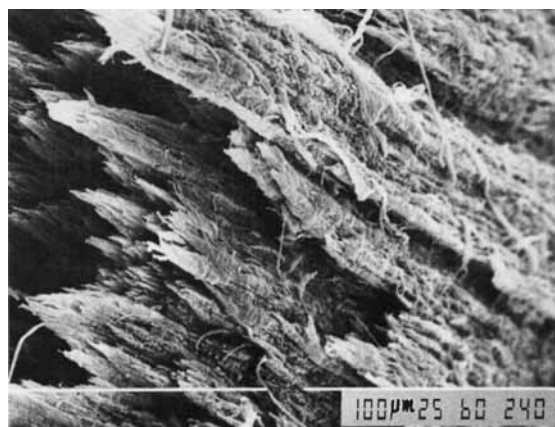
An interesting feature for blends containing polyester is the potential for transreaction, the so-called

transesterification. As in the case of blends of two polyesters, polyester and bisphenol A polycarbonate, or polyester and phenoxy, the compatibility can be possibly improved by partial transesterification between blend components. It has been reported that the intermolecular reaction between phenoxy and copolyester yields graft copolymers that are expected to exhibit an enhanced compatibilizing effect on the properties of blends.<sup>18,26,27</sup> It is noteworthy that this transesterification can be promoted by the residual catalyst remaining from polymerization. Thus, for the blend of phenoxy and liquid crystalline copolyester, a similar transesterification reaction can be expected.

The scanning electron micrographs of the injection-molded blends of 30/70 LCP/phenoxy are shown in Figure 7. When the blend is mixed for 5

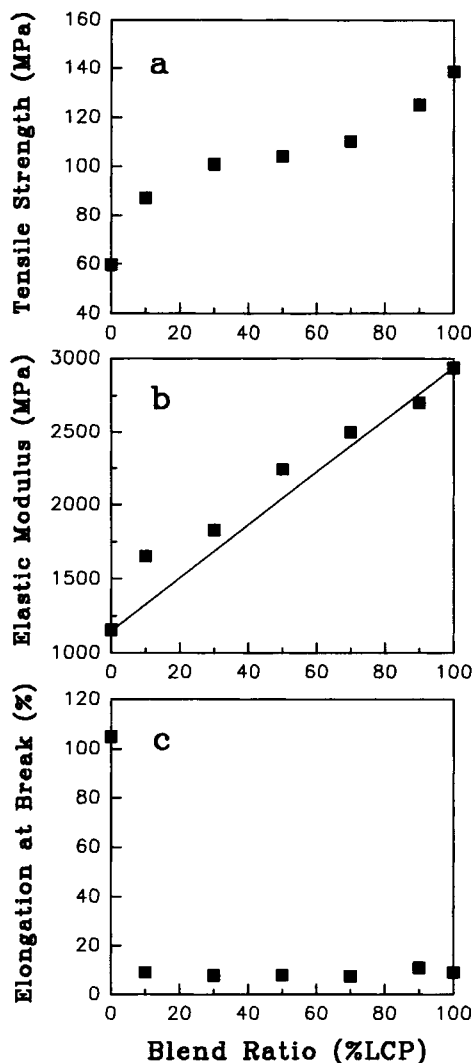


(a)



(b)

**Figure 5** SEM micrographs of injection-molded phenoxy/LCP blends: (a) phenoxy/LCP (3/7); (b) phenoxy/LCP (1/9).



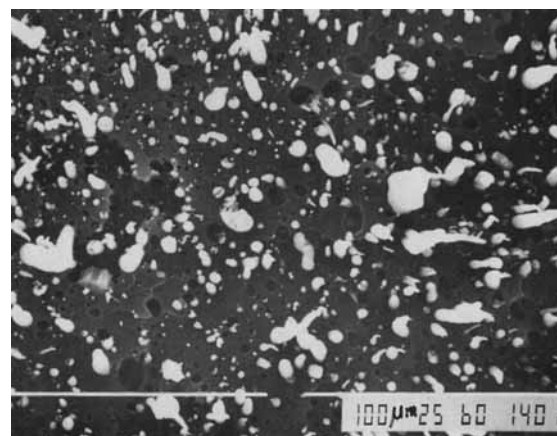
**Figure 6** Mechanical properties of phenoxy/LCP blends: (a) tensile strength; (b) elastic modulus; (c) elongation at break.

min at 290°C, slightly deformed particles of LCP are dispersed in the phenoxy matrix [Fig. 7(a)]. The figure shows that the adhesion of the LCP to the matrix is not good with circular voids around the LCP. When the mixing time is increased to 30 min, the fractured morphology becomes different as compared with the case of 5 min mixing. Figure 7(b) shows evidence of interfacial adhesion between dispersed fibrillar LCP and the phenoxy matrix, because the number of neat holes are significantly decreased and surfaces of fibrils are rough. The improvement of the interfacial property may come from the formation of graft copolymer at the interface by an intermolecular exchange reaction.<sup>28,29</sup>

The effect of mixing time on the mechanical

properties is shown in Figure 8. The longer mixing time gives higher tensile strength and modulus, but lower elongation at break. These phenomena can be better understood if the morphological characteristics of these materials are examined (see Fig. 7). The thermal modification of the phenoxy/LCP (7/3) blend gives better interfacial adhesion and thus the elongated LCP takes a greater part in the blend properties. Therefore, the property of elongated LCP (increased tensile modulus and strength, but decreased elongation at break) in the blend becomes more dominant. The good adhesion between LCP and phenoxy phases is demonstrated by the presence of many broken fibrils and the absence of visible openings [Fig. 7(b)].

The viscosity change for the phenoxy/LCP (7/3) blends with reaction times is shown in Figure 9.

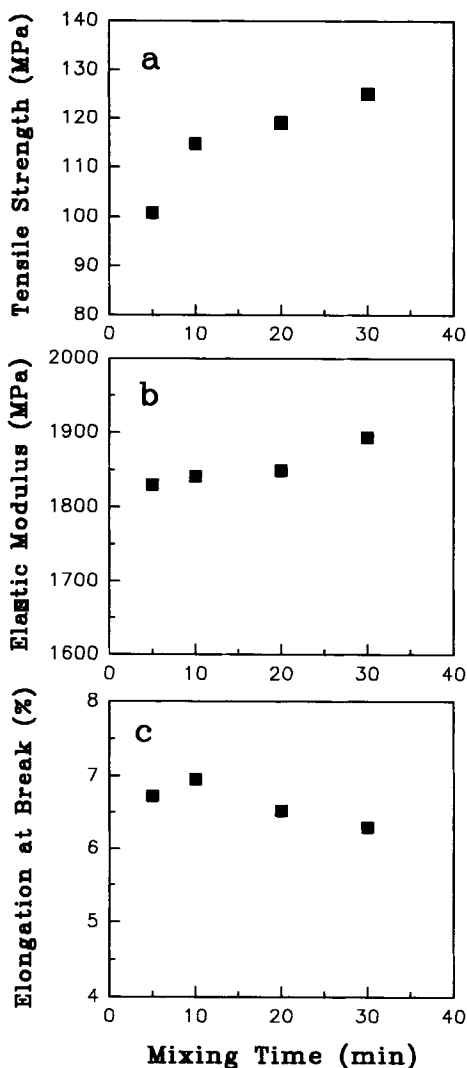


(a)



(b)

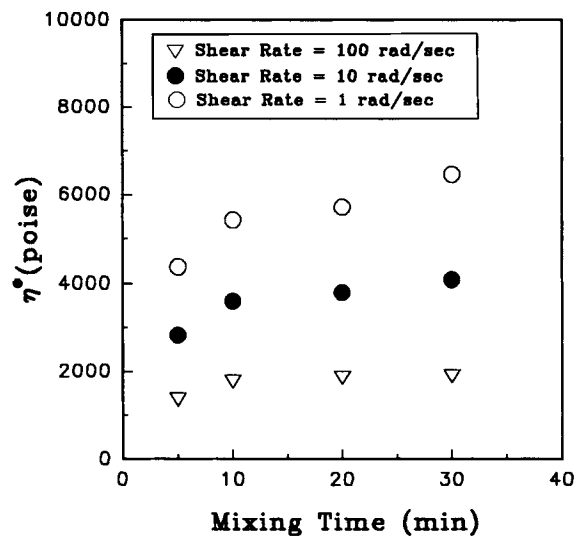
**Figure 7** SEM micrographs of the phenoxy/LCP (7/3) blends modified at 290°C for different mixing times: (a) 5 min; (b) 30 min.



**Figure 8** Effect of mixing time on the mechanical properties of phenoxy/LCP (7/3) blend: (a) tensile strength; (b) elastic modulus; (c) elongation at break.

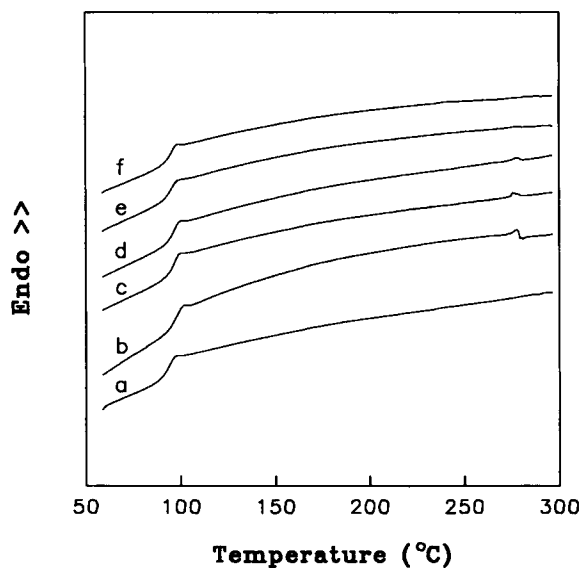
As the mixing time increases, the viscosity of the LCP blends increases. This increase in viscosity suggests that the intermolecular reaction between the phenoxy and LCP takes place in the melt mixing to yield graft copolymers. The thermal transitions of the phenoxy/LCP (7/3) blends with different mixing times are also shown in Figure 10. As the mixing time increases, the enthalpy of the nematic transition LCP ( $T_m = 280^\circ\text{C}$ ) is reduced and completely vanishes for mixing times of longer than 30 min, although the  $T_g$  of phenoxy at  $94^\circ\text{C}$  remains almost constant. These results indicate the occurrence of some molecular exchange reaction between the blend components during melt mixing at  $290^\circ\text{C}$ .

To examine more closely the possibility of a mo-

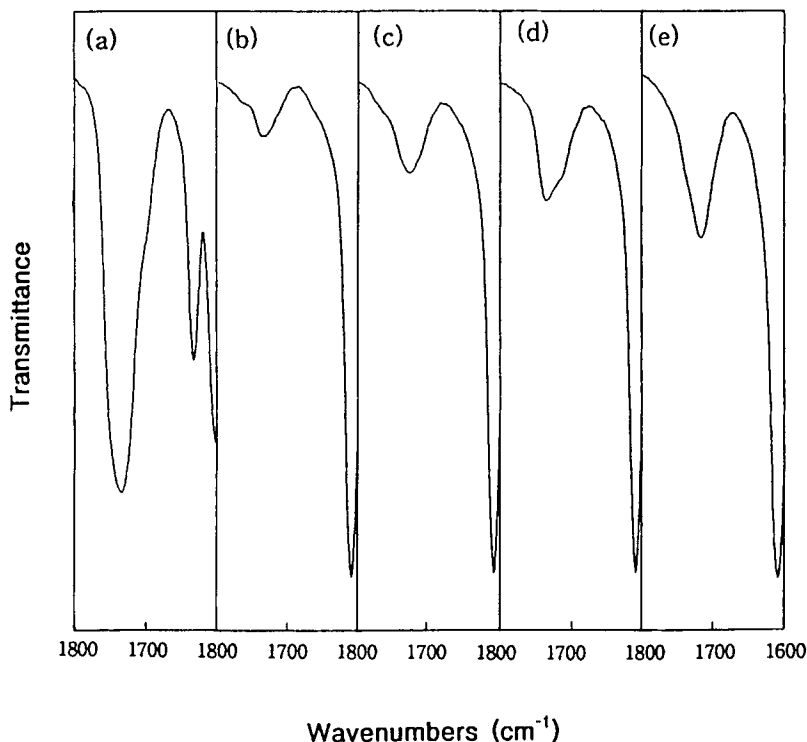


**Figure 9** Effect of mixing time on the complex viscosity at given shear rates for the phenoxy/LCP (7/3) blend.

lecular exchange reaction between phenoxy and LCP during the mixing, FTIR spectra of the soluble fraction in THF are compared to those of neat phenoxy (Fig. 11). Since LCP is not soluble in THF at all, the materials extracted by THF may be composed of phenoxy and the products of interchange reaction between LCP and phenoxy polymer. As the reaction time increases, the aromatic carbonyl absorption at about  $1740\text{ cm}^{-1}$  increases, indicating the presence



**Figure 10** DSC thermograms of phenoxy/LCP (7/3) blend modified at  $290^\circ\text{C}$  for various mixing times: (a) phenoxy; (b) 5 min; (c) 10 min; (d) 20 min; (e) 30 min; (f) 60 min.



**Figure 11** Infrared spectra of LCP and soluble fraction from LCP/phenoxy (5/5) blend modified at 290°C for various mixing times: (a) LCP; (b) 5 min; (c) 10 min; (d) 30 min; (e) 60 min.

of LCP components. In other words, the presence of LCP in the soluble fraction strongly suggests that a molecular exchange reaction has occurred during the thermal mixing.

## CONCLUSIONS

Morphological, rheological, and mechanical properties of poly(hydroxy ether of bisphenol A) (phenoxy)/LCP blends are extensively investigated. Morphological observations of injection-molded samples indicate that fibrous LCP domains are formed during processing to give a self-reinforced composite. Rheological measurements in shear flow show that the flow curves of the blends containing low LCP contents are similar to those of the unfilled phenoxy, whereas at higher content, the blends resemble the pure LCP in the flow curve. The viscosity of the blends is reduced by adding a small amount of LCP, and a shallow minimum in the viscosity-composition curves is shown at about 10 wt % LCP. The inclusion of a small amount of fibrillar LCP results in good processability and improvement in mechanical properties.

By increasing the mixing time, the mechanical properties of the blends are improved. Based on evidence collected from RMS, DSC, and the FTIR spectrometer, it is concluded that transesterification between the phenoxy and the LCP takes place during the melt mixing. The transesterification may result in the formation of LCP-grafted phenoxy, which can play a role as a compatibilizer. Consequently, in addition to fibril formation of LCP, the formation of the graft copolymer from such an interchange reaction gives better interfacial adhesion between two phases and thus improves mechanical properties of the blends.

The authors thank the Ministry of Trade, Industry and Energy of the Republic of Korea for their financial support (1991).

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Received December 16, 1993

Accepted July 22, 1994