The Effect of the Viscosity Ratio of Dispersed Phase to Matrix on the Rheological, Morphological, and Mechanical Properties of Polymer Blends Containing a LCP

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SYNOPSIS

The effect of the viscosity ratio of the dispersed LCP phase to the polystyrene/poly(phenylene oxide) (PS/PPO) thermoplastic matrix on the rheological, morphological, and resultant mechanical properties of the LCP blends was investigated. The viscosity of PS/PPO is largely dependent on the blend composition, so that different levels of viscosity ratios of dispersed LCP phase to PS/PPO thermoplastic matrix are obtained by using PS/PPO premixtures of different blend ratios as a thermoplastic matrix. When the viscosity of the LCP dispersed phase is lower than that of the thermoplastic matrix, finely distributed fibril structure of LCP is obtained. Tensile modulus of injection molded specimens show a positive deviation from the additive rule when the viscosity ratio (η_{LCP}/η_{matrix}) is smaller than unity. These improvements in tensile modulus are attributed to the formation of finely distributed LCP fibrils. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The concepts of tailoring polymer properties through blending with other polymers and fillers have long been recognized as a viable method to meet specific applications. But, most polymer pairs are immiscible and form multiphase domains on mixing. 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.[1,2]

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.[3-10] Because of its lower viscosity, the LCP in these blends often form fibrous structure in the matrix of the thermoplastic polymers leading to the formation of the self-reinforced composites. In most cases, the addition of LCP increases the mechanical strength and stiffness of the thermoplastic matrix polymer. Moreover, even a relatively small amount 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.[11,12] 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 LCPs in the matrix not only improve the mechanical properties of thermoplastic material, but also make the processing free from problems associated with conventional fiber reinforced composites such as fiber breakage, abrasion of the processing machinery, increase in viscosity, energy consumption, and difficulties in uniform dispersion of fibers.[13,14]

The primary factors determining the morphology of the LCP domains in the thermoplastic matrix are the LCP content, processing conditions, and rheological characteristics of the blend components such as the viscosity ratio.[15] The morphology is also affected by the interaction between the phases, which may be modified by introduction of suitable com-

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Table I Characteristics of Polymer Samples Used in This Study

Sample	Source	$M_w{}^a$	T_g (°C)	T_m (°C)
Vectra B950	Hoechst Celanese Co.	—	—	278[b]
Polystyrene	Cheil Industries	210000	92	—
Poly(phenylene oxide)	Asahi Co.	61000	218	—

[a] Determined by GPC.
[b] Nematic transition temperature.

patibilizers.[16,17] The effects of shear rate, viscosity ratio, and interfacial tension are related to each other by the Weber number.[18,19]

The effect of viscosity ratio on the morphology of immiscible polymer blends has been studied by several researchers. Min et al.[20] found for polyethylene/polystyrene (PE/PS) blends that, when the dispersed phase had a lower viscosity, it formed long fibers in the matrix, but with higher viscosity the dispersed phase was in the form of discrete droplets. Ko and Wilkes[21] investigated the effect of processing conditions on the structures and properties of extruded films of blends of poly(ethylene terephthalate) (PET) with a liquid crystalline copolyester. The tensile modulus was considerably improved by adding of more than 30% LCP and increasing the extrusion speed. They indicated that the morphology of the LCP is dependent on processing conditions, blend composition, and viscosity ratio of the component polymers. Other studies also show that the viscosity of the dispersed LCP phase should be lower than that of matrix for good fibrillation.[15,22]

Despite the efforts related to the study of deformation of the dispersed LCP phase in polymer blends, very few attempts have been made to analyze systematically the effect of viscosity ratio on the blend morphology and mechanical properties. Thus, we examine the effect of the viscosity ratio of dispersed phase to matrix phase on the rheological, morphological, and resultant mechanical properties of blends containing a LCP. In this study, a liquid crystalline copolyester known as Vectra B950 has been chosen as a dispersed phase, and the miscible blends of polystyrene (PS) and poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) have been chosen as thermoplastic matrices. The viscosity of thermoplastic matrix could be systematically changed by varying the blend ratio of PS/PPO so that different levels of the viscosity ratio of dispersed phase to matrix are easily obtained by using PS/PPO premixture of different blend ratio as a thermoplastic matrix.

EXPERIMENTAL

Materials

The LCP used in this study is commercially known as Vectra B950 and is believed to consist of 20 mol % terephthalic acid, 20 mol % amino-phenol, and 60 mol % 2,6-hydroxy naphthoic acid. The thermoplastic matrix polymers used are pure polystyrene (PS) and polystyrene/poly(phenylene oxide) (PS/PPO) blends with different blend ratios. All the polymers used in this work are commercial grade and used as received without further purification. The characteristics of polymers used in this study are reported in Table I.

Blend Preparation

All the polymer samples were completely dried in a vacuum oven at 90°C for at least 1 day before blending. The PS/PPO premixture with different compositions were prepared at 290°C by a corotating twin screw extruder with L/D of 33. The amounts of LCP in blends were 5, 10, 20, and 30 wt % by weight. The blends with LCP were prepared at 300°C by a Brabender laboratory single screw extruder (D = 19 mm, L/D = 25). The apparent shear rate ($\dot{\gamma}$) in the extruder die was estimated by the following equation:

$$\dot{\gamma} = \frac{4Q}{\pi R^3}$$

where Q is the volumetric output and R the radius of the die. The estimated shear rate was about 50–100 s^{-1} in the extruder die.

Thermal Analysis (DSC)

The thermal properties of all samples were measured using a differential scanning calorimeter (Perkin-Elmer DSC-7). Blend samples of 11–13 mg were heated in a nitrogen atmosphere to 300°C at a heat-

ing rate of 20°C/min and then cooled to room temperature. They were then reheated at a heating rate of 20°C/min, and the second running data were accepted.

Rheological Properties

The rheological properties of component polymers and their blends were measured on a Rheometrics Mechanical Spectrometer (RMS 800) with cone and plate geometry under a nitrogen atmosphere. Dynamic experiments were performed in oscillatory shear at 10% strain and dimensions of 25 mm in diameter. The frequency sweeps were performed from 0.1 rad/s to 100 rad/s.

Morphology

The LCP blend samples for microscopy were taken from the extrudates before pelletizing for further processing. Single screw extruded strands were directly quenched in a water bath to preserve the morphology in the melt. The cryogenically fractured surface was coated with a gold sputtering unit and examined by a scanning electron microscope (SEM, JEOL JSM-35) at an accelerating voltage of 25 kV.

Mechanical Properties

Completely dried samples were injection molded at 300°C using a Mini-Max molder (CS-MMX, Custom Scientific Instruments, Inc.). The dimensions of the dumbbell type test specimens were 9 mm in length and 1.6 mm in diameter. Mechanical properties were measured at room temperature by using an Instron Tensile Tester (model 4202). 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.

RESULTS AND DISCUSSION

Thermal Properties

It is well known that the blends of polystyrene (PS) and poly(phenylene oxide) (PPO) are miscible over the entire composition range by the formation of π–π complex.[23,24] Figure 1 shows the DSC thermograms for blends of LCP and PS/PPO. All the blends showed a glass transition temperature that corresponds to the T_g of the PS/PPO matrix, and a composition independent endothermic peak at 278°C
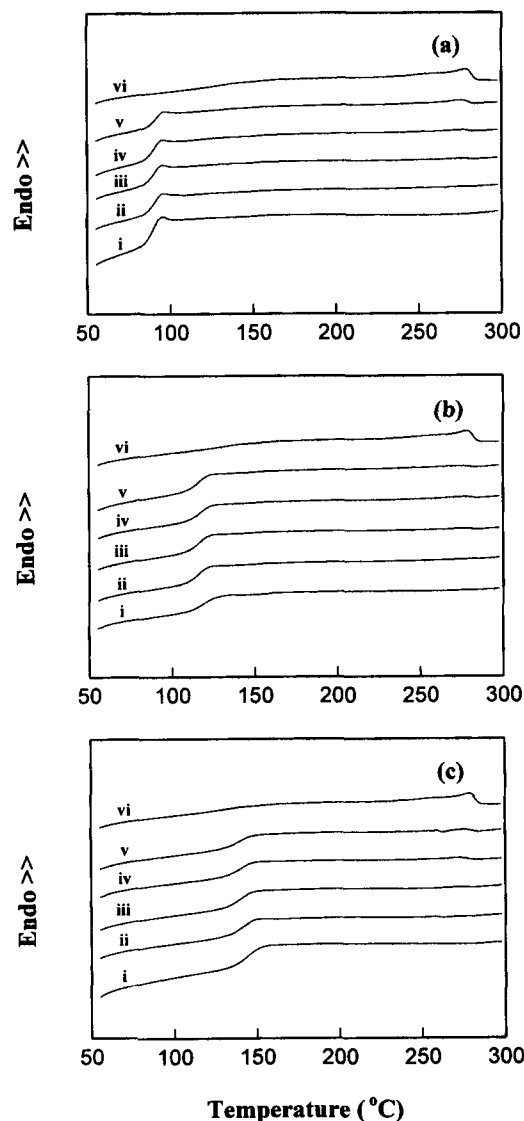

Figure 1   (a) DSC thermograms of PS/PPO (10/0) and LCP blends; (b) DSC thermograms of PS/PPO (7/3) and LCP blends; (c) DSC thermograms of PS/PPO (5/5) and LCP blends: (i) LCP 0; (ii) LCP 5; (iii) LCP 10; (iv) LCP 20; (v) LCP 30 wt %; (vi) pure LCP.

corresponding to the crystalline to nematic transition temperature of LCP. This independence of the transition temperatures on the blend ratio indicates immiscibility between the dispersed LCP phase and the PS/PPO thermoplastic matrix. Therefore, the blends of LCP and PS/PPO have two phase structure, because the PS/PPO forms a homogeneous phase.

Rheological Properties

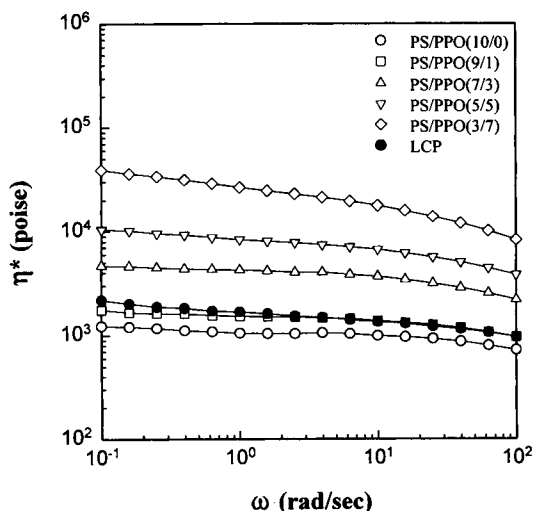The flow curves of PS/PPO blends and pure LCP under shear flow at 300°C are shown in Figure 2.

Figure 2   Shear rate dependence of the complex viscosity of PS/PPO blends and LCP at 300°C.

The PS/PPO matrix exhibits slightly non-Newtonian behavior at the shear rate range examined. This behavior is typical for the miscible polymer blends. In addition, the shear thinning effect was more pronounced for the higher content of PPO. The viscosity ratios of LCP to matrix (η_{LCP}/η_{matrix}) are shown in Figure 3. The different levels of viscosity ratios could be obtained by varying the blend ratio of PS/PPO, because the viscosity of PS/PPO is largely dependent on the blend composition.

The shear viscosity of the blends of PS/PPO and LCP are shown in Figure 4. All the blends exhibit a more or less non-Newtonian behavior, and the viscosity decreases with addition of a small amount of LCP. The LCP and blends of high LCP content show a non-Newtonian behavior at low shear rate and has higher power-law exponents. The non-Newtonian behavior at low shear rate corresponds to the first shear thinning region of flow curves for the LCPs, as proposed by Onogi and Asada.[25] In this region, piled polydomains are transformed to a dispersed polydomain system and finally to a monodomain continuous phase as the external field increases.

In all cases the viscosity of the thermoplastic matrix is reduced by adding small amounts of the liquid crystal component. Rheological properties of blends are categorized into two groups according to the viscosity behavior: one is the case that the viscosity of the blend is lower than those of the component polymers as shown in Figure 4(a) and (b), and another one is the case that the viscosity of blends is inbetween those of the component polymers as shown in Figure 4(c) and (d). It is interesting to

note that two different rheological behaviors have been observed for the blend of LCP and PS/PPO by only changing the composition of the thermoplastic matrix PS/PPO. One explanation is that the minimum in the viscosity–composition curves of the blends [Fig. 5(a) and (b)] is attributable to two main reasons: incompatibility between the two phases, and formation of elongated fibrils of the LCP that lubricate the thermoplastic matrix.

More recently, Mantia and Valenza[26] proposed a new mechanism for the prediction of minima in the viscosity–composition curves of LCP blends. 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 a minimum in these blends. As shown in Figure 5(a) and (b), the viscosity of the blends shows a minimum when the viscosity of the LCP is equal to or higher than that of the thermoplastic matrix. When the viscosity of the LCP is lower than that of the thermoplastic matrix, the lubrication effect of LCP reduces the viscosity of the blend, and the viscosity lies between those of the two components as shown in Figure 5(c) and (d).

Morphology

The fracture surfaces of the blends containing 20 wt % LCP are shown in Figures 6 and 7. The blends of LCP and thermoplastic matrices show two phase structures. In the core region (Fig. 6), the LCP domains are less elongated or in the spherical form,
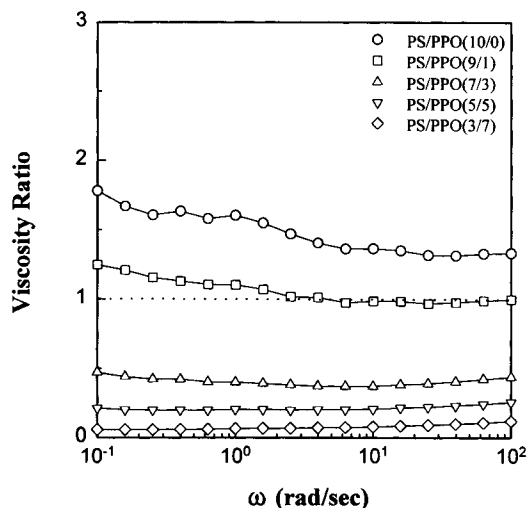

Figure 3   Shear rate dependence of the viscosity ratio (η_{LCP}/η_{matrix}) of LCP to PS/PPO at 300°C.
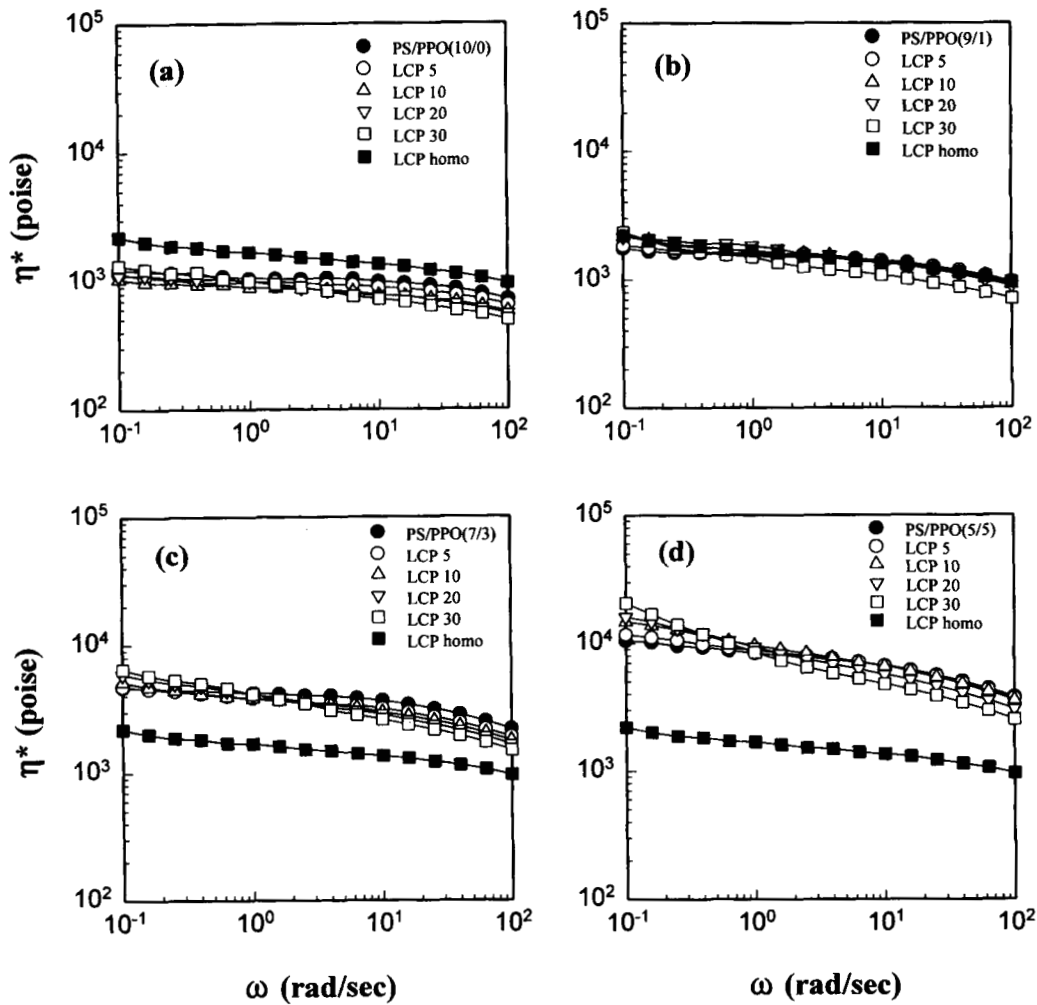
Figure 4   Shear rate dependence of the complex viscosity of PS/PPO and LCP blends at 300°C: (a) PS/PPO (10/0); (b) PS/PPO (9/1); (c) PS/PPO (7/3); (d) PS/PPO (5/5).

while in the skin region (Fig. 7), most of the LCP domains are elongated as a fibrous form. A skin/core morphology is observed for all the LCP blends. The morphology of the blends was strongly dependent upon the viscosity ratio of dispersed phase to matrix. When the viscosity ratio (η_{LCP}/η_{matrix}) is smaller than unity, the domain size of the dispersed LCP phase is finer and its distribution is more uniform as shown in Figures 6(c) and (d) and 7(c) and (d). But when the viscosity ratio is greater than unity, the LCP domains becomes larger and spherical cluster-like as shown in Figures 6(a) and (b) and 7(a) and (b).

This morphological development can be explained as follows. During mixing, the dispersed LCP particles will continue to elongate and eventually break up, when the viscous force (τ) to deform and elongate the particle is greater than the cohesive force (σ/R) of surface tension to resist the deformation.

Therefore, the ratio of the viscous force to interfacial stress determines the final equilibrium size of the LCP domains in a given flow field.

$$\frac{\tau}{\sigma/R} = \frac{\eta_{matrix}\dot{\gamma}R}{\sigma} = W_e = F(\eta_{LCP}/\eta_{matrix})$$

where W_e is Weber number related to the viscosity ratio, η_{matrix} the viscosity of the matrix, η_{LCP} the viscosity of the LCP, $\dot{\gamma}$ the shear rate, R the radius of the droplet, and σ the interfacial tension. For a viscoelastic dispersion, the critical condition for droplet break up is given by

$$W_e \geq \frac{F(\eta_{LCP}/\eta_{matrix})}{\sin(2\varphi)}$$

where $F(\eta_{LCP}/\eta_{matrix})$ is an empirical function of the viscosity ratio and orientation angle φ. Thus, the
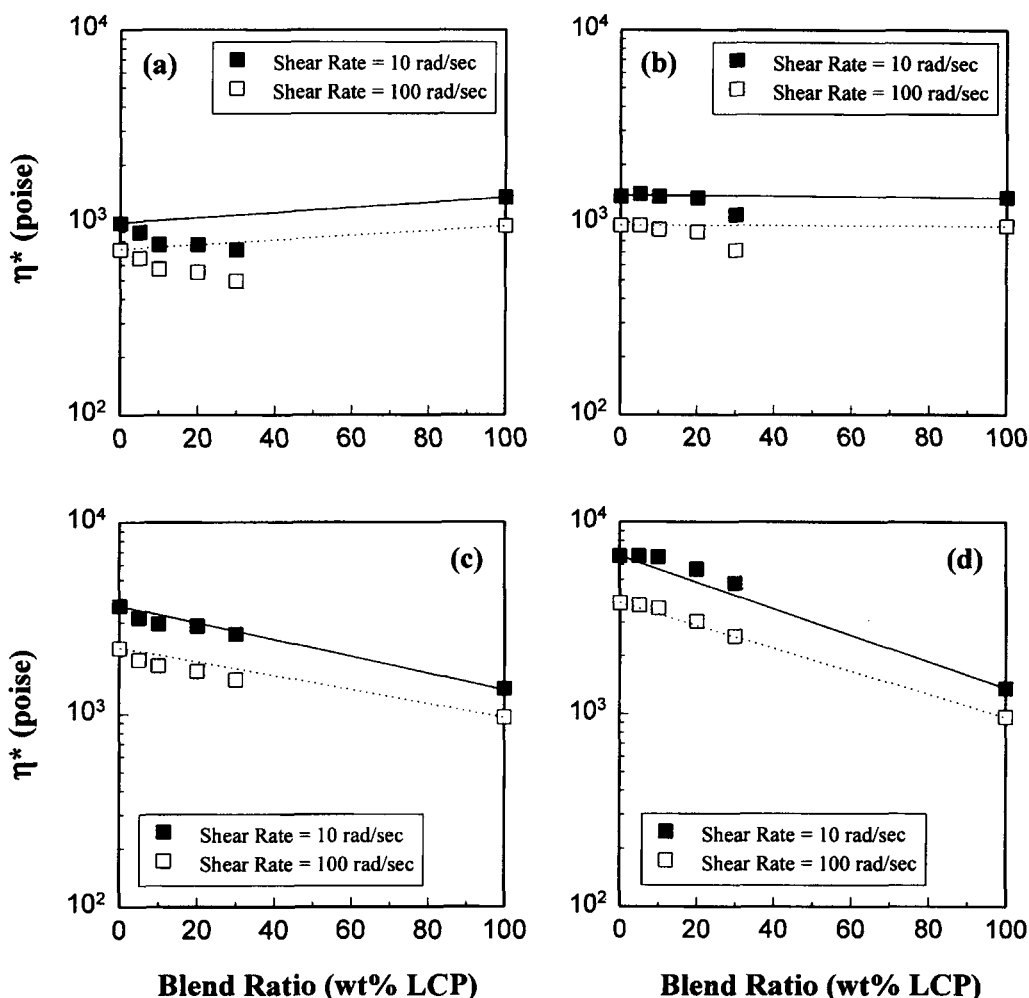
Figure 5 Viscosity versus composition of PS/PPO and LCP blends at a given shear rates at 300°C: (a) PS/PPO (10/0); (b) PS/PPO (9/1); (c) PS/PPO (7/3); (d) PS/PPO (5/5).

differences in blend morphology could be related to the viscosity ratio. The lower the viscosity ratio (η_{LCP}/η_{matrix}) is, the larger the deformation of LCP domains is. Tsebrenko[27] studied blends of flexible thermoplastics and reported that the maximum fibrillation occurs at shear rate corresponding to the intersection point, where the viscosity ratio of the components was equal to unity. However, in blends containing a LCP, the maximum fibrillation was observed at high shear rates where the viscosity of the thermoplastics is much higher than that of the LCP,[28] as observed in Figure 7.

Mechanical Properties

Tensile properties of LCP, PS/PPO, and their blends have been determined on injection molded

specimens along the machine direction. Figure 8 shows the mechanical properties of LCP blends as a function LCP content. It is found that the elastic modulus increases with LCP content over the entire composition range. This implies that the LCP serves as a reinforcing additive in PS/PPO thermoplastic matrix. It is important to note that the elastic moduli of blends of LCP and PS/PPO (7/3) show positive deviations from the simple additive rule, while the blends of LCP and PS/PPO (10/0) follow the simple additive rule. This tells us that the reinforcing effect of LCP becomes more significant when the viscosity of LCP is lower than the thermoplastic matrix polymer. This behavior can be better understood if the morphological characteristics of these materials are examined (see Figs. 6 and 7).
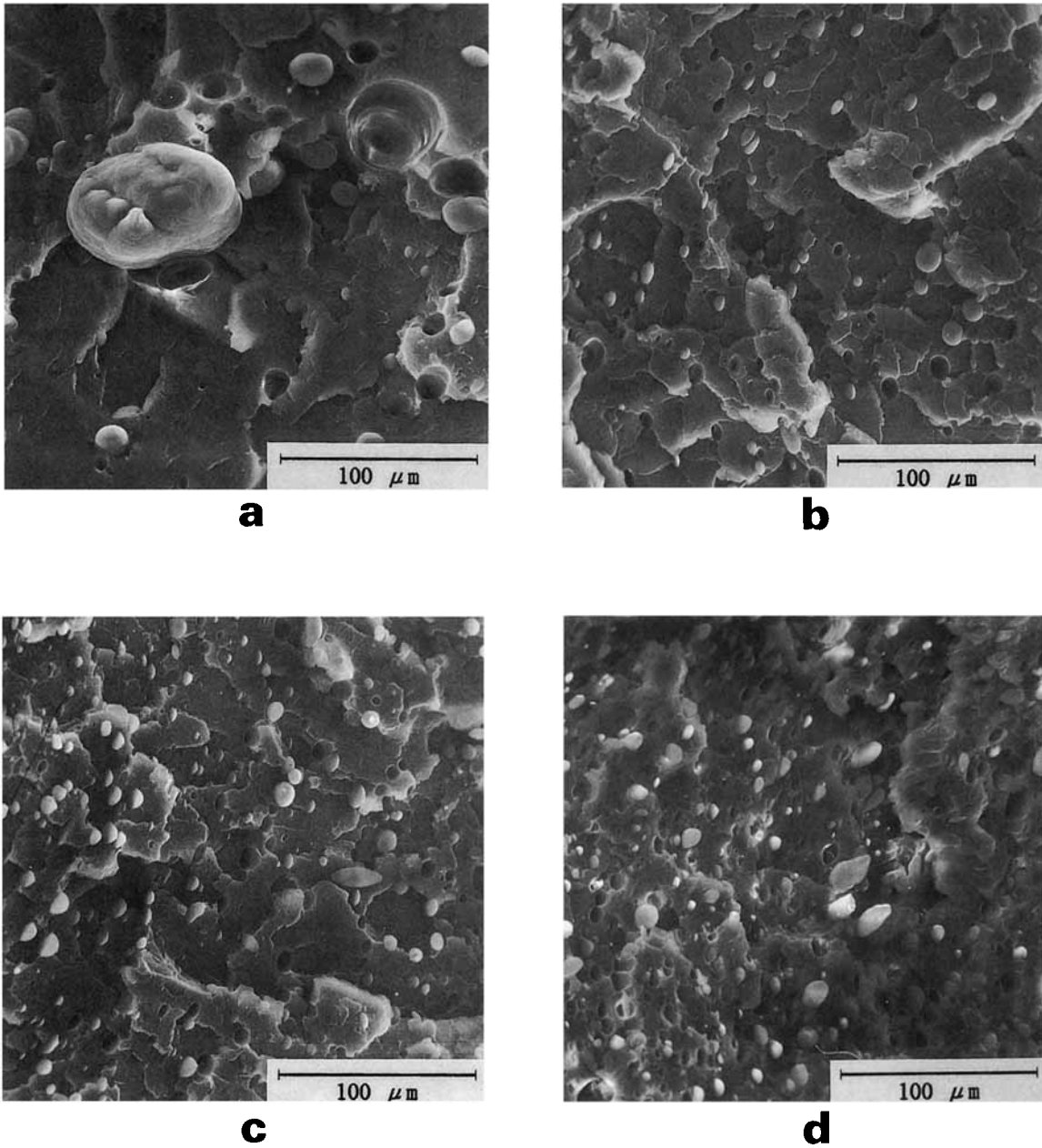
Figure 6   SEM micrographs of blends of 20 wt % LCP with different PS/PPO compositions in the core region: (a) PS/PPO (10/0); (b) PS/PPO (9/1); (c) PS/PPO (7/3); (d) PS/PPO (5/5).

Tensile strength of blends also increases with LCP content. For blends of LCP and PS/PPO (7/3), the tensile strength nearly follows the simple additive rule (Fig. 8), while the tensile strength of blends of LCP and PS/PPO (10/0) show more of a negative deviation from the simple additive rule of mixture. Elongation at break shows similar values (4–8%) over the entire composition range. This im-

plies that LCP serves as a good reinforcing additive in PS/PPO thermoplastic matrix.

CONCLUSIONS

The effect of the viscosity ratio of the dispersed LCP phase to the thermoplastic matrix (PS/PPO) on the
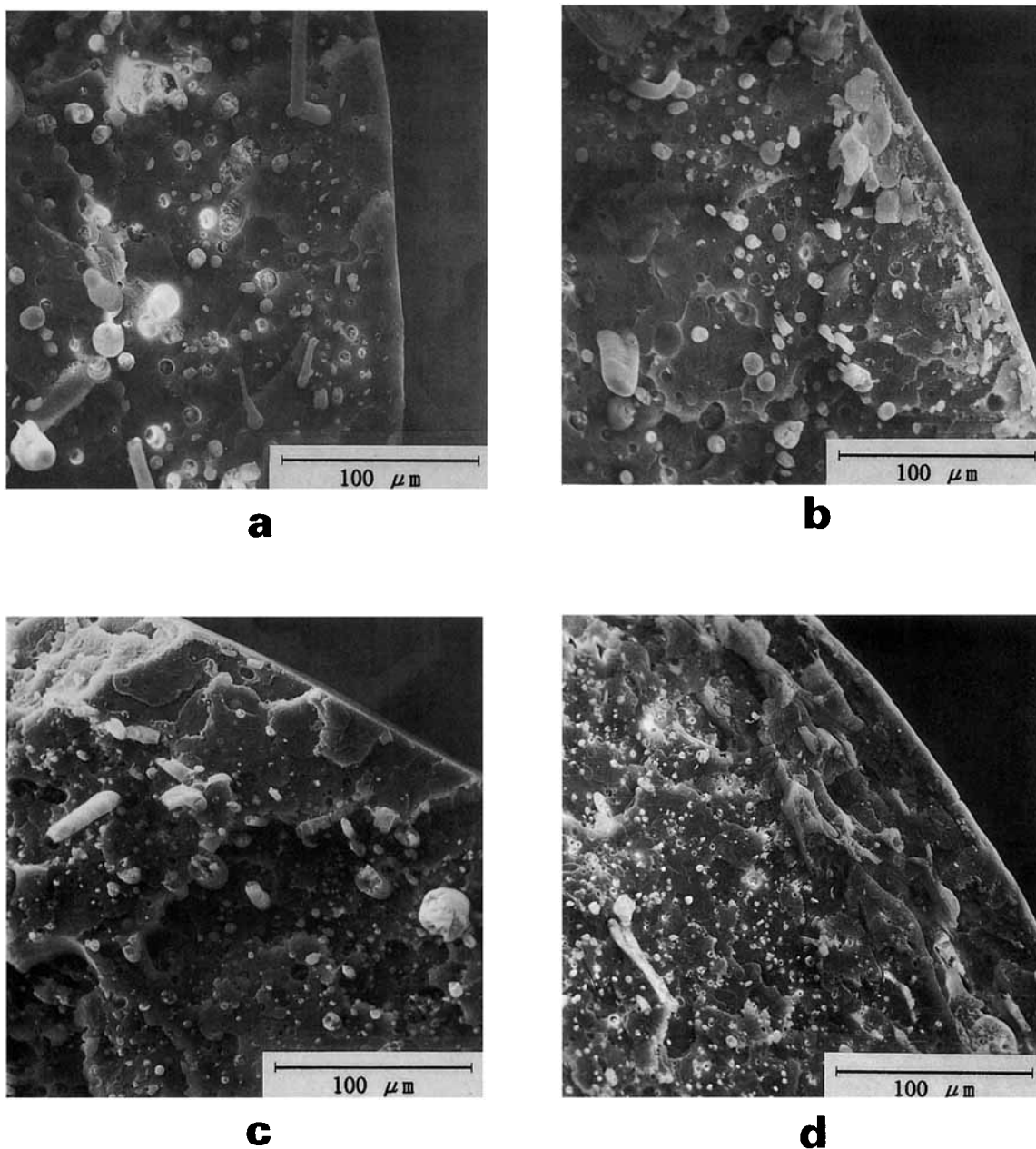
Figure 7 SEM micrographs of blends of 20 wt % LCP with different PS/PPO compositions in the skin region: (a) PS/PPO (10/0); (b) PS/PPO (9/1); (c) PS/PPO (7/3); (d) PS/PPO (5/5).

rheological, morphological, and resultant mechanical properties of the LCP blends was investigated. The viscosity ratio was varied by using a LCP and different compositions of miscible thermoplastic polymer blends (PS/PPO). The viscosity of thermoplastic matrix was systematically changed by varying the blend composition of PS and PPO, so that different levels of viscosity ratios were easily obtained. The blends were categorized into two groups according to the rheological behavior: one is the case that the viscosity of the blends is lower than those of component polymers when the viscosity of LCP is larger than that of thermoplastic matrix; another one is the case that the viscosity of blends is between those of component polymers when the viscosity of LCP is lower than that of thermoplastic matrix.
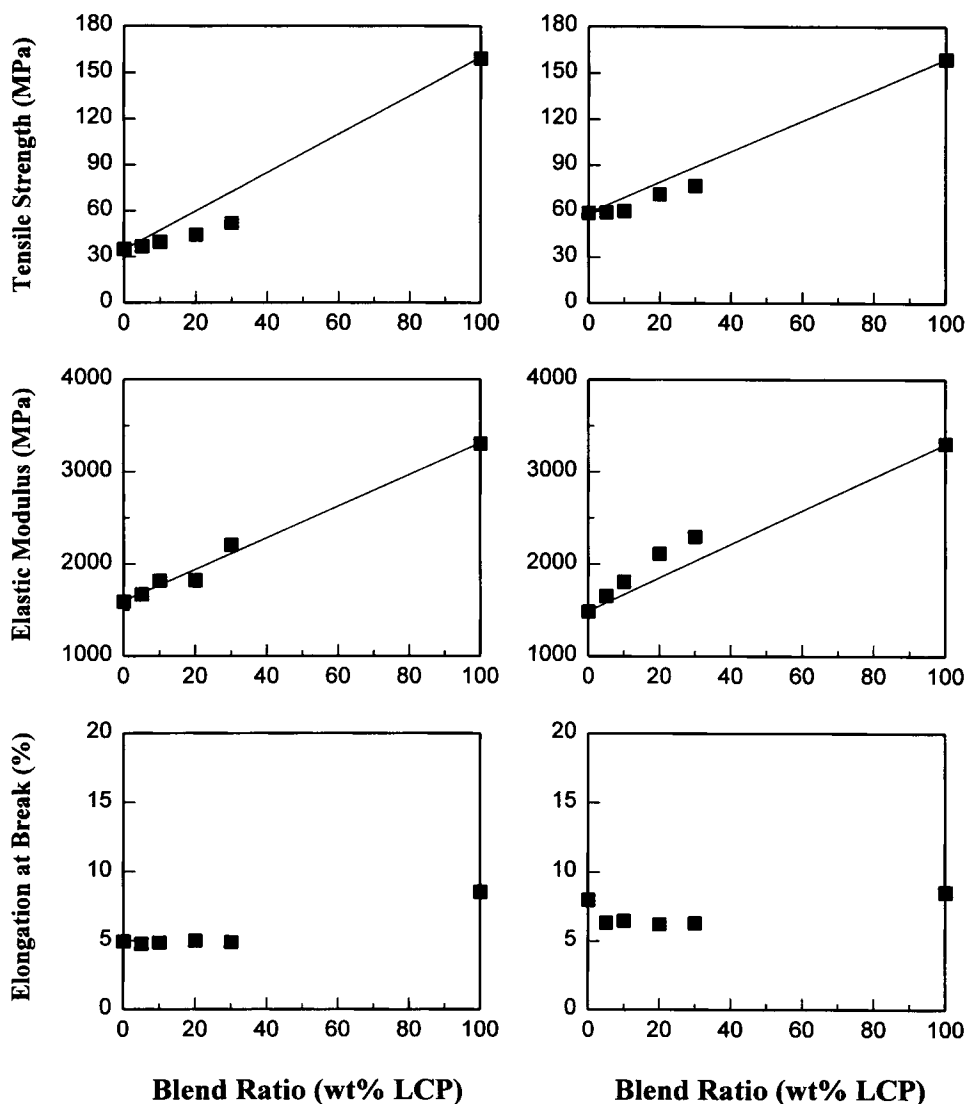
Figure 8 Mechanical properties of the LCP and PS/PPO blends injection molded at 300°C: left-hand side figures represent for PS/PPO (10/0) and LCP blends and right-hand side figures represent for PS/PPO (7/3) and LCP blends.

Morphological observations of extruded strands indicated that the finely distributed LCP fibril structure was obtained when the viscosity of the LCP dispersed phase was lower than that of thermoplastic matrix. Mechanical properties of injection-molded specimens indicated that the modulus of LCP blends showed a positive deviation from the additive rule when the viscosity of the thermoplastic matrix polymer was higher than that of LCP dispersed phase. This behavior is consistent with the morphological characteristics of the LCP blends. In summary, the viscosity ratio of the dispersed phase to the matrix is an important factor in determining the morphological and mechanical properties of LCP blends.

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