Effects of the Addition of a Liquid Crystalline Copolyester to Polystyrenes on Blending Torque and Mechanical Properties of Blends

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SYNOPSIS

Blending of polystyrenes (PS) with a thermotropic liquid crystalline polymer (LCP) was performed by using a continuous corotating twin screw extruder. The influence of LCP content on the blending process was studied by changing the barrel heater temperature and the screw speed. The torque of screw shafts, generated during the blending process, was influenced by LCP content and its influence was not simple. The torque generated during the blending process was not directly related to the apparent melt viscosity of blends. Further, the effects of the matrix viscosity on the morphology and mechanical properties of the PS/LCP blends were studied using three grades of PS as matrix resins. It was found that the size of the LCP dispersed phase decreased with increasing matrix viscosity. Consequently, the mechanical properties of the PS/LCP blend were improved. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Blending of polymers was an outstanding method for exploiting many of the polymers' desirable characteristics. Thermotropic liquid crystalline polymers (LCP) have been studied because of their inherent high stiffness and strength, high use temperature, excellent chemical resistance, low melt viscosity, and low coefficient of expansion. Because of these excellent properties, the blending of LCP with traditional polymers could result in materials that can be used as an alternative for short fiber reinforced thermoplastic composites; the *in-situ* composites have many potential advantages as compared with short fiber reinforced polymers.[1]

Continuous kneading is an efficient method for the melt-blending of polymers, which is widely used for industrial production. The materials in a continuous kneading extruder are subjected to complex shear and elongational deformations, and complex temperature profiles along the extruder barrel. Since many complicated factors may affect the torque of the screw in the extruder, the theoretical study of the torque being generated during the kneading process may be difficult. The value of the torque is an indispensable processing factor in determining the efficiency of a blending process. Therefore, it is necessary to investigate the cause for the generated torque by an experiment. Despite a large number of investigations concerning the effects of LCP content on the morphology and on the mechanical properties of blends,[2-8] relatively few studies[9-10] have appeared discussing the influence of LCP content on a continuous kneading process.

In this work, we have investigated the influence of the addition of LCP on the continuous kneading process of polystyrene (PS) by measuring the torque for extrusion. Furthermore, the effects of kneading conditions on the morphology and mechanical properties of the blends have been studied.

EXPERIMENTAL

The materials used in this work were three commercial grades of polystyrene with different melt

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flow rate values (MFR) and an aromatic copolyester. The polystyrenes were STAIRON 605, 681, and 666, Asahikasei (Japan), with MFR values of 1.5, 3.0, and 7.5, respectively, following ISO R1133. In the following discussion, STAIRON 605, 681, and 666 will be referred to simply as PS1, PS2, and PS3, respectively. The copolyester (LCP) used was Vectra A950, Polyplastics (Japan); its chemistry and structure have been reviewed by many authors.[11–13]

Melt-blending of the PS with the LCP was carried out using a continuous kneading extruder (S1KRC kneader) manufactured by Kukimoto, Ltd. Figure 1 shows the schematic diagram of this corotating twin screw extruder, which had a trough length of 255 mm. The twin screw assemblies in the trough can easily be rearranged by changing screw elements, such as the screw with different pitch, reverse screw, and kneading disc; the shape of the elements resembled an ellipse with a 25 mm major axis. These screw elements, which are fitted to the screw shaft, have a self-cleaning effect. The channel depth between the screw element and the trough was 0.4 mm. Furthermore, the channel depth between the twin screw assemblies was 0.4 mm; this depth was the idealized lowest value and depended on the kind of screw element used. A given amount of pellets of PS and LCP was fed into the extruder through a hopper by the use of two feeders (Accurate 102, Kuma Engineering Co.); a total feed rate was 1080 g/h. The pellets were transported through the solid-conveying, melting, melt-conveying, and mixing zones of the extruder and were extruded through a capillary die having a diameter of 4 mm. Finally, the strand leaving the extruder was directly quenched in a water-bath and was collected by a take-up device; the draw ratio was determined by the diameter of the die, S_o, and the diameter of the fiber, S_f, which were measured by a dial gauge. The temperature of the barrel, T_d, and the screw speed, N_d (max 360 rpm), could be accurately controlled; T_d was 300°C and N_d was 101 rpm unless indicated otherwise. Although this processing temperature was high for PS, the degradation was considered to be small due to the short (3 min) residence time. A transparent colorless sample was obtained after kneading of the neat PS. The melt temperatures at three sections of the trough, the torque of the twin screw shafts, and the screw speed could be monitored and fed to a computer (see Fig. 1). The torque at a steady state will be discussed. The weight content of LCP in the blends will be referred to as ϕ_L.

Shear viscosity measurements were made with a Toyoseiki capillary viscometer (Capillograph B1). All experiments were done at 300°C and at least three experiments were made for each composition. A capillary with $L/D = 10$ and $D = 1$ mm was used.

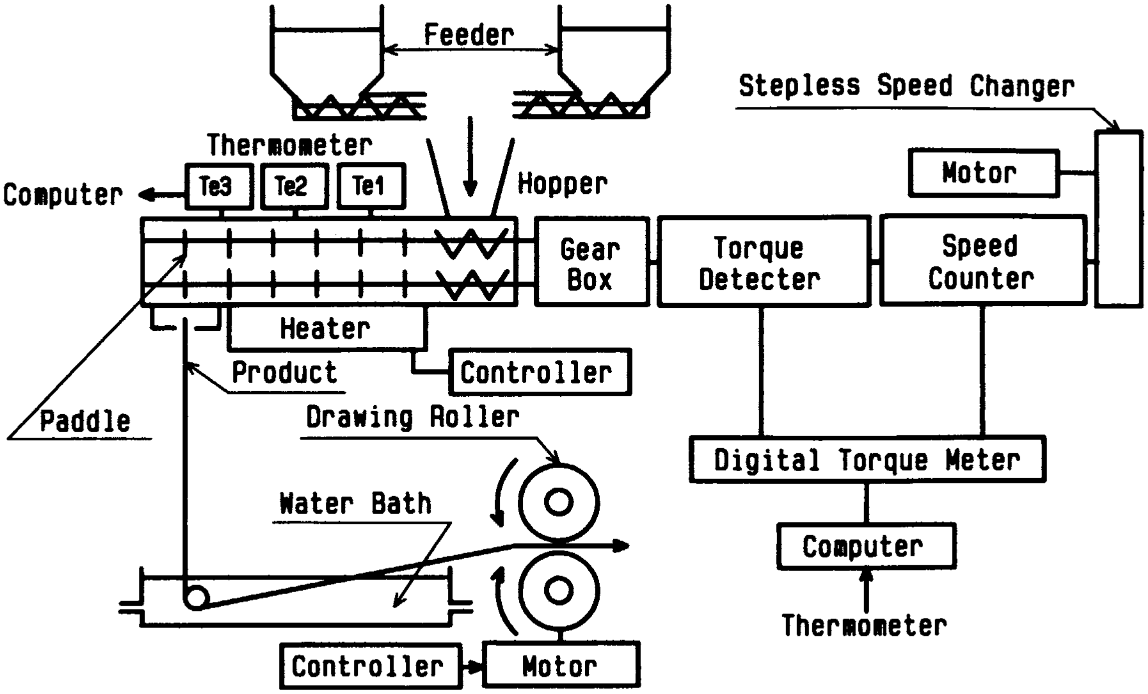


Figure 1 Schematic diagram of the kneading system used in this work.

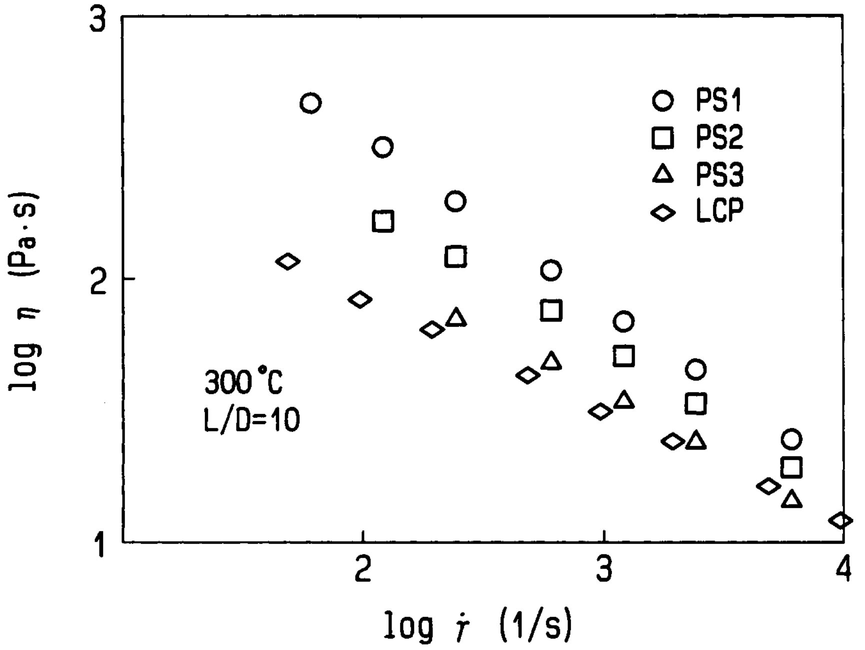


Figure 2 Apparent viscosity curves for the three polystyrenes and LCP at 300°C.

The Bagley and Rabinowitch corrections were not made. That is, the apparent viscosity of blends will be discussed in this study.

For the estimation of the size and shape of the LCP phase in the blends, the PS in a strand of the blend was selectively leached for 24 h with toluene. After being dried, the remaining LCP was sputter-coated with gold and then was examined in a Hitachi S-530 scanning electron microscope (SEM).

The change in length of the strand samples with temperature was measured using a thermal mechanical analyzer (Seikodensikogyo TMA/SS100); the gauge length was 10 mm, the heating rate was 10°C/min, and the applied stress was zero.

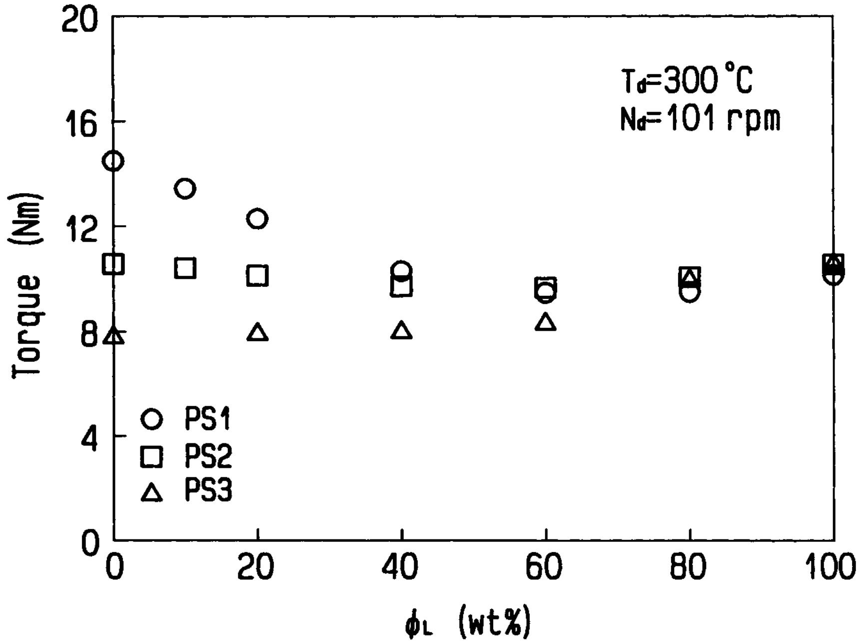


Figure 3 Effect of LCP content on kneading torque.

The tensile tests for the strand samples were performed at 30°C on a Tension UTM-III tensile tester; the crosshead speed was 0.4 mm/min and the initial gauge length was 40 mm. Since jaw breaks were often encountered, both ends of strands were reinforced by an epoxy adhesive. In this work, only the strength will be discussed.

RESULTS AND DISCUSSION

Figure 2 shows the relationship between the apparent viscosity η and shear rate $\dot{r}$ for the starting materials. All the melts exhibited non-Newtonian flow behavior in the shear rate range studied. At a given shear rate, the viscosity of PS decreased with in-

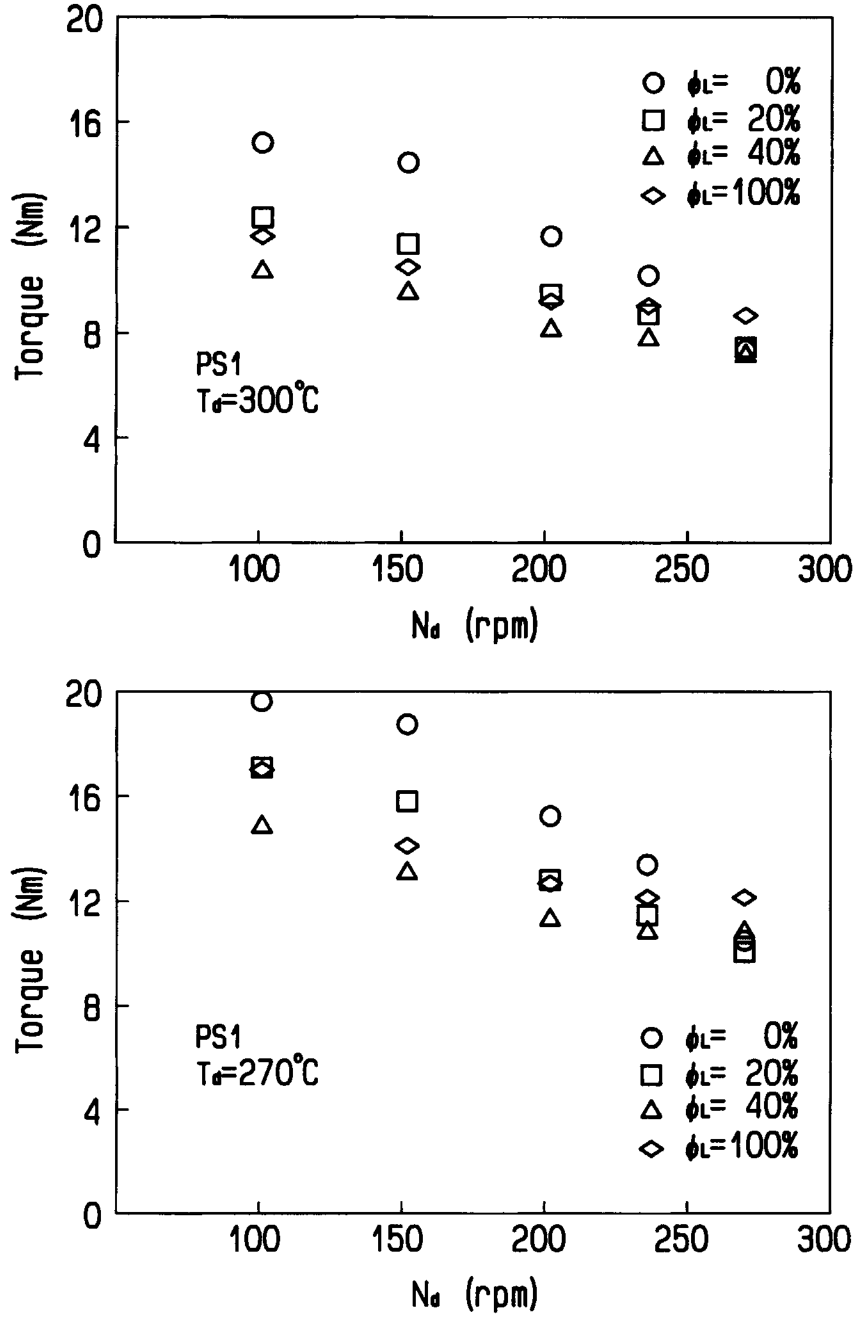


Figure 4 Effect of screw speed on kneading torque. (a) T_d = 300°C, (b) T_d = 270°C.

creasing value of MFR. The viscosity of LCP showed the lowest value at a given shear rate, except for the extremely high shear rate range. Figure 3 shows the effect of LCP content on the resultant torque of the two screw axes recorded during extrusion. The torque recorded for PS1 decreased initially and increased slightly with increasing LCP content after attaining a minimum. There is no linear relationship between the torque and LCP content. Although the torque at a low LCP content was influenced not only by the amount of LCP content, but also by the kind of PS used, the torque at a high LCP content was almost independent of the LCP content and the kind of PS used.

The torque was plotted as a function of screw speed in Figure 4(a). The torque of the neat LCP ($\phi_L = 100\%$) decreased with increasing screw speed up to about 200 rpm, above which it remained almost constant. On the other hand, the torque of the neat PS1 ($\phi_L = 0\%$) decreased with increasing screw speed, more significantly at higher screw speeds. The blends exhibited intermediate variations between these two extremes, corresponding to their LCP content. It is to be noted that the torque of the 40% LCP blend showed the lowest value at each screw speed. Figure 4(b) showed the dependence of torque on the screw speed at the barrel temperature of 270°C. Since this barrel temperature was relatively low, the torque of each blend was high as compared with that measured at the barrel temperature of 300°C. Otherwise, the variation of torque with screw speed was similar to that measured at 300°C. In order to investigate the causes for the variation of torque, we measured the apparent melt viscosities of the blends (Fig. 5). The viscosities decreased with increasing shear rate. Since the increase in screw speed is assumed to correspond to the increase in shear rate, the variation of torque with the screw speed observed for the neat LCP sample cannot be simply explained in terms of its melt viscosity. Since the viscosity of the blend at a given shear rate seemed to decrease monotonously with increasing LCP content, the phenomenon in which the $\phi_L = 40\%$ blend indicates the lowest torque cannot be simply explained in terms of the melt viscosity. These results mean that the kneading torque does not directly correlate with the apparent melt viscosity of the blends. Another mechanism must be taken into account to explain the cause for the generated torque.

The quenched samples were immediately collected after extrusion from the die. The undrawn samples were prepared for observation of SEM. Figure 6 shows the effect of LCP content on the size and shape of the LCP dispersed phase. The LCP dispersed phase in the $\phi_L = 20\%$ blend exhibited an

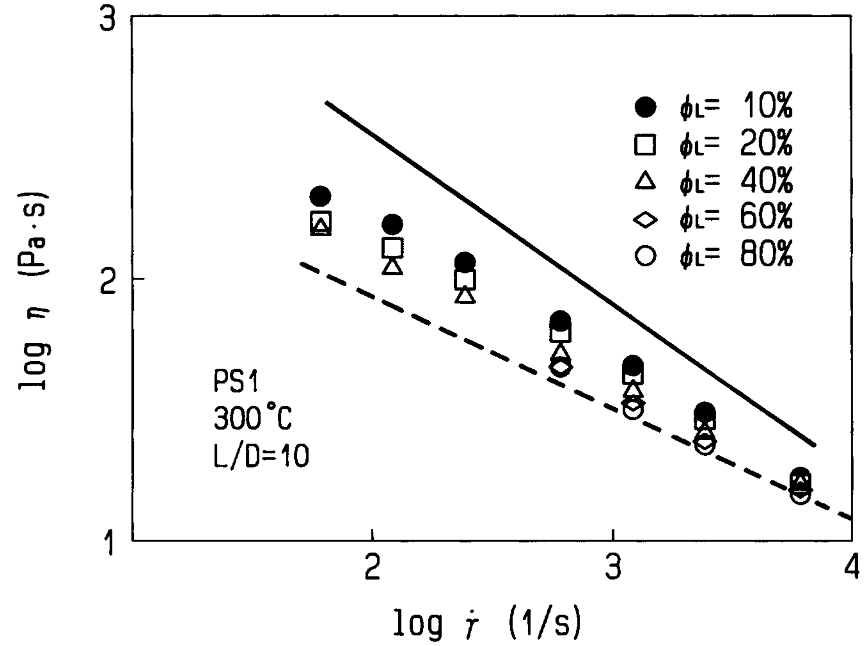
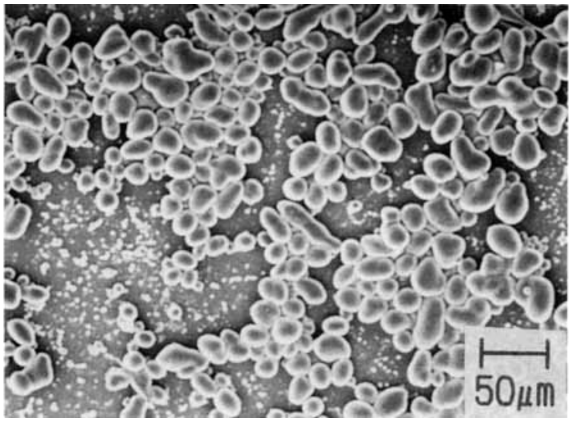
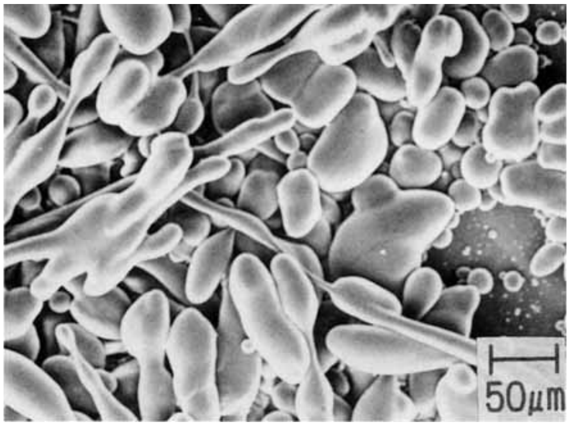


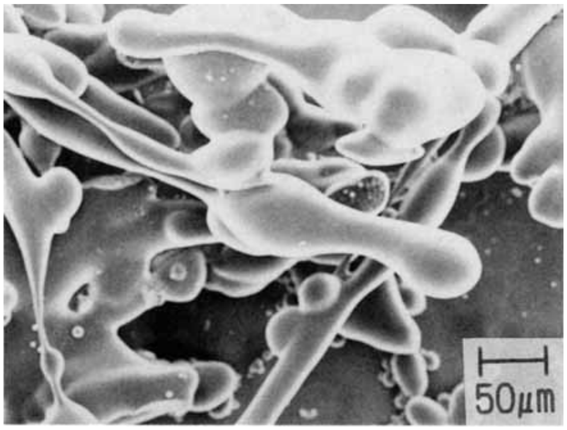
Figure 5 Effect of LCP content on the apparent viscosity curves for PS1/LCP blends at 300°C; solid line and dotted line correspond to the neat PS1 and to the neat LCP, respectively (see Fig. 2).



ϕ_L=20%, N_d=270rpm



ϕ_L=40%, N_d=270rpm

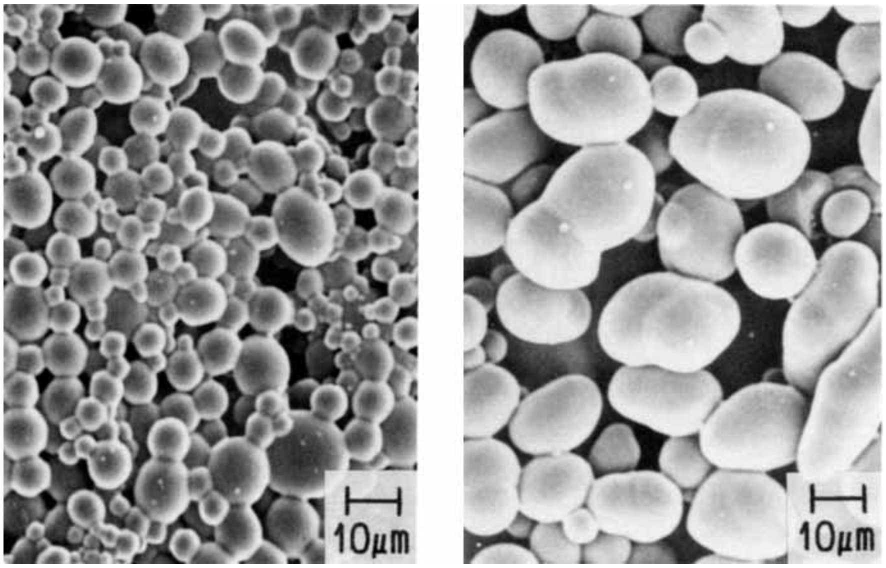


ϕ_L=60%, N_d=270rpm

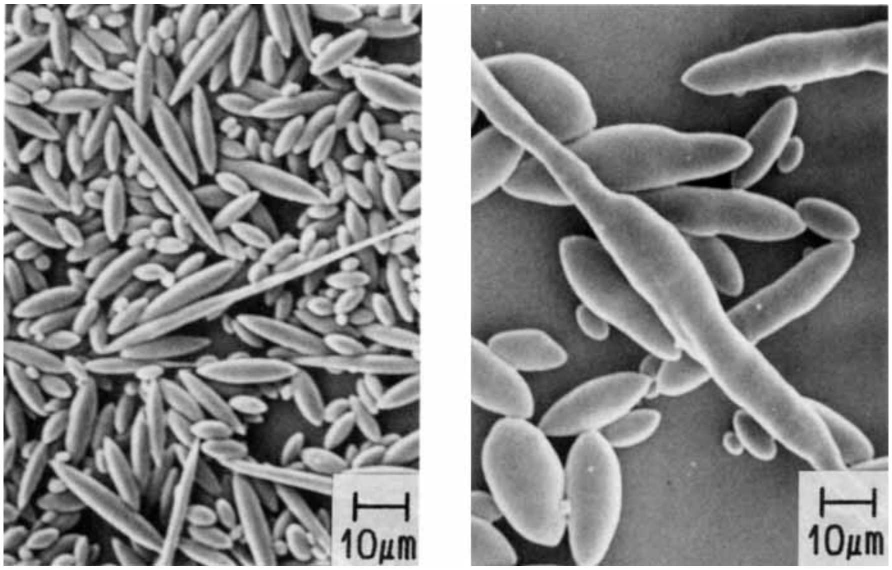
Figure 6 Effect of LCP content on the size and shape of the LCP-dispersed phase, produced in the PS1 blend.

almost spherical shape. The size increased with increasing LCP content and the aggregation of the LCP phase due to the coalescence effect can be seen in the blend with a high LCP content. Figure 7 shows the effect of matrix viscosity of PS on the size and shape of the LCP dispersed phase. The size of the LCP phase, formed in the PS1 matrix, was smaller than that formed in the PS3 matrix. This result means that the size of the LCP dispersed phase decreases with increasing matrix viscosity; this conclusion is supported by the works of other researchers.[14-15] Further, the shape became an ellipse with increasing S_0/S_f. The size of the ellipse was influenced by the size of the LCP particles formed during the kneading process. This result implied that the LCP particles with a small size should be produced during the kneading process in order to make fine LCP fibrils during the melt-drawing process. However, the LCP particles should have had a certain size to change into the well-developed LCP fibrils during the melt-drawing process, because effective stress transfer from the matrix to the particles was required. Therefore, the LCP particles with an optimum size should be produced during the kneading process in order to produce well-dispersed and well-developed LCP fibrils in the matrix by a small addition of LCP. The effects of the barrel temperature and the screw speed on the size and shape of the LCP dispersed phase were also investigated. However, a clear result was not obtained.

Figure 8 shows the effect of LCP content on the TMA curves. The sample length of the neat PS1 (ϕ_L = 0%) increased initially with increasing temperature, but started to decrease above 80°C. Similar change could be seen in the ϕ_L = 20% blend, except that the increment of the sample length was smaller and the temperature at which the sample length started to decrease was higher. On the other hand, the blends with more than 40% LCP content showed only continuous shrinkage with increasing temperature; the temperature showing a peak of maximum shrinkage was constant, regardless of LCP content. It is obvious that the TMA curves are influenced by the phase inversion. Namely, the TMA curves with more than 40% LCP content were strongly influenced by the presence of LCP. The temperature at which the neat PS1 started to shrink corresponded to its glass transition temperature. Furthermore, the blends with more than 40% LCP content indicated a peak of maximum shrinkage at about 260°C, which may be correspond to the transition temperature of LCP; the DSC curve did not clearly show the transition. The degree of shrinkage, at about 260°C, increased with increasing LCP content. Well-developed fibrils were observed in blends with more than 40% LCP content by SEM. On the other hand, undeveloped fibrils with a low aspect ratio were ob-



PS1, $S_o/S_f=2$ **PS3, $S_o/S_f=3$**



PS1, $S_o/S_f=60$ **PS3, $S_o/S_f=207$**

Figure 7 Effect of viscosity of the PS matrix on the shape and size of the LCP-dispersed phase, ϕ_L = 10%.

served in the ϕ_L = 20% blend by SEM. In addition, it is to be noted that the thermal stability of PS matrix is improved even by a small addition of LCP.

Figure 9 showed the effect of LCP content on the strength, F, of blends. There was a difference between the PS1/LCP and PS3/LCP blends in the variation of strength with ϕ_L. The strength of the PS1/LCP blend did not increase initially with the addition of LCP, but started to increase above 20% LCP content. On the other hand, the strength of the PS3/LCP blend started to increase above 40% LCP content. This difference meant that the strength of the PS3/LCP blend was not enhanced by a small addition of LCP. In the PS1/LCP blend, well-developed LCP fibrils with an infinite aspect ratio may be easily formed during the melt-drawing

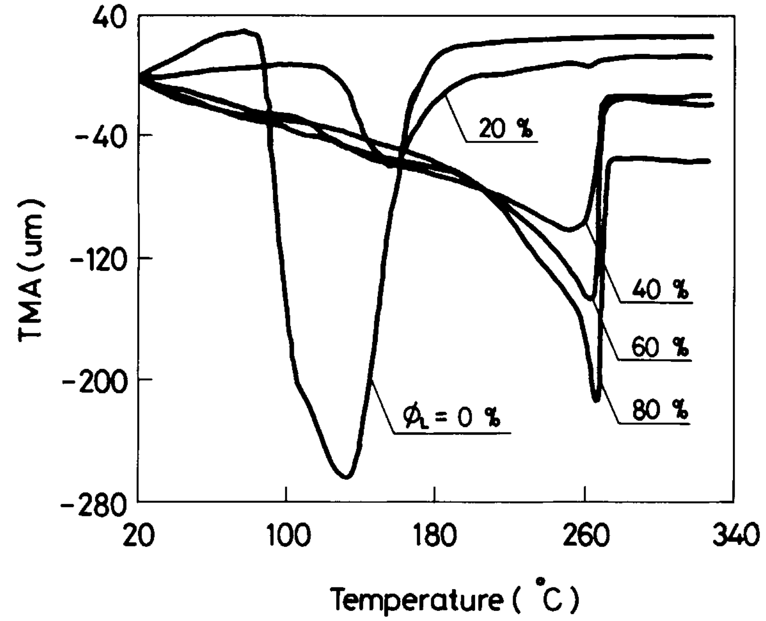


Figure 8 Effect of LCP content on TMA curves of PS1/LCP blend, $S_0/S_f \approx 100$.

process, because the matrix viscosity is relatively high. This structure may lead to the improvement of mechanical properties; the effects of matrix viscosity on the size of the LCP dispersed phase and the mechanical properties will be reported and discussed in detail elsewhere.[16]

In conclusion, a good reinforcing effect on mechanical properties seemed to be a result of a small

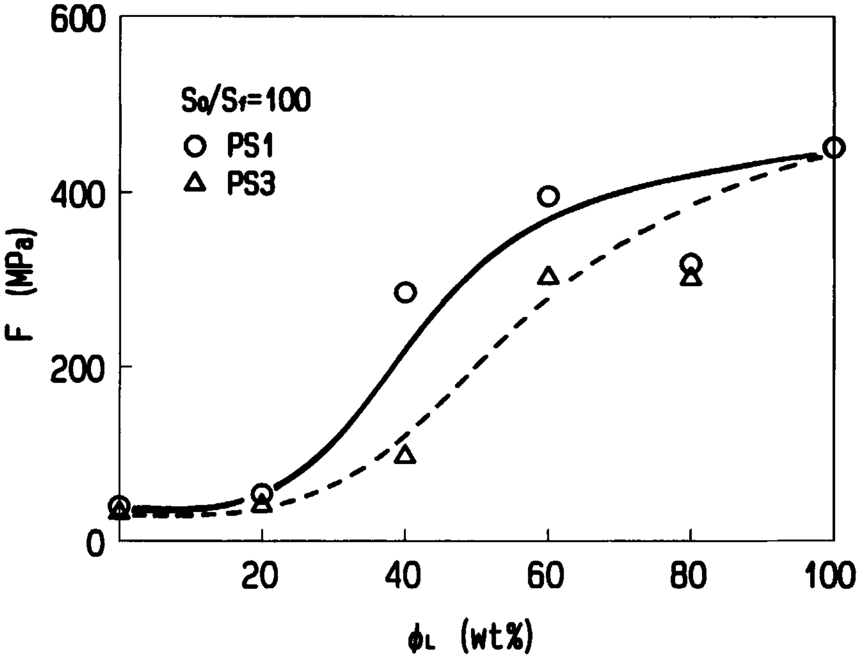


Figure 9 Effect of LCP content on the strength, F, of the PS1/LCP and PS3/LCP blends.

addition of LCP to conventional polymers when the polymer having high viscosity was used as a matrix resin.

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