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Blending of modified polyphenylene ether with a liquid crystalline copolyester

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Blending of poly (2,6-dimethylphenylene ether) (PPE), polystyrene (PS) and a thermotropic liquid crystalline polymer (LCP) was performed using a continuous co-rotating 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 the screw shafts generated during the blending process was influenced by LCP content; its influence was not simple. The generated torque was found to depend not only on the melt viscosity of LCP but also on its distortion temperature. Further, the effects of matrix viscosity on the morphology and mechanical properties of the PPE/PS/LCP blends were studied. Well-developed fine LCP fibrils were formed during the melt-drawing process when the matrix viscosity was high. The formation of well-developed fine fibrils was found to improve the mechanical properties of the PPE/PS/LCP blend. Two mechanisms are proposed for the formation of well-developed fine LCP fibrils.

1. Introduction

Blending of polymers is a useful method to obtain desirable characteristics which could not be realized by conventional polymers. Recently, thermotropic liquid crystalline polymers (LCP) have received attention due to their inherent high stiffness and strength, high use temperature, excellent chemical resistance, low melt viscosity, and low coefficient of expansion. Owing to these excellent properties, blending of LCP with traditional polymers might result in materials which can be used as an alternative for short fibre-reinforced thermoplastic composites; *in situ* composites have many potential advantages compared with short fibre-reinforced polymers [1].

Poly (2,6-dimethylphenylene ether) (PPE) has excellent properties but poor processability due to its high melt viscosity. To improve the processability, blending of PPE with polystyrene (PS) has been performed. The blend has also good properties and the two components are believed to be miscible at all compositions. Recently, the structure of the PPE/PS blend has been investigated in detail [2].

Continuous kneading is an efficient method for melt-blending techniques of polymers and is widely used in industrial production. In a previous work [3], blending of PS with LCP was performed and the influence of addition of LCP on the continuous kneading process was studied by measuring the torque for extrusion. Furthermore, the effects of the kneading process on the morphology and the mechanical properties of the blends were studied.

Despite a large number of investigations concerning the blend of polycarbonate with LCP [4–8], relatively few studies have appeared on the blend of PPE/PS with LCP [9]. Furthermore, there are few studies on the influence of LCP content on a kneading process [10, 11]. In this work, blending of PPE, PS and LCP was performed using a continuous kneading extruder and the influence of LCP content on the blending process was investigated. In addition, the effects of the matrix viscosity on the morphology and mechanical properties of the blends have been studied.

2. Experimental procedure

The materials used in this work were PPE (General Electric Company (Japan), PS (Asahikasei, Japan, trade name is Stairon 666, melt flow rate of the polymer 7.5 following ISO R1133), and an aromatic copolyester (LCP, Polyplastics, Japan, commercially known as Vectra A950; its chemistry and the structure have been reviewed by many authors [12–14]).

Melt-blending of PS, PPE and LCP was carried out using a continuous kneading extruder (S1KRC kneader, Kurimoto, Ltd). The experimental apparatus is shown in Fig. 1; the main part of this apparatus is the co-rotating twin extruder. The screw elements which are fitted to the twin screw shafts will be simply referred to as paddles. Details of the extruder can be found in the previous work. A given amount of pellets of PS, PPE and LCP was fed into the extruder using three feeders (Accurate 102, Kuma Engineering Co.);

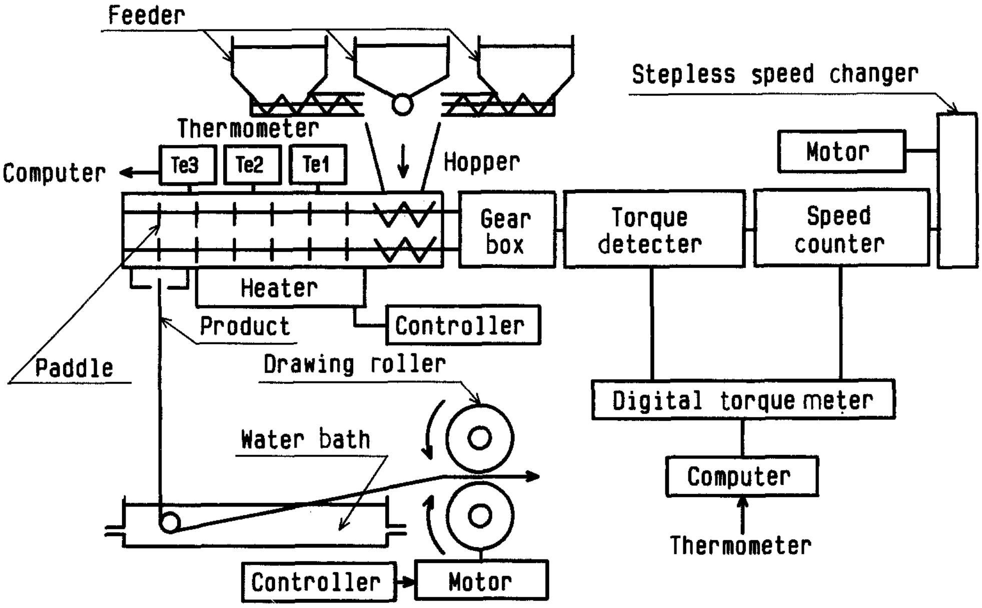

Figure 1 Schematic diagram of the kneading apparatus used.

the total feed rate was 960 gh^{-1}. These 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 rate was determined by the ratio S_0/S_f, where S_0 is the diameter of the die and S_f is the diameter of the fibre measured by a dial gauge. The temperature of the barrel, T_d, was usually 300 °C. The temperatures of the material in the three sections of the trough having a length of 255 mm, were measured. The change in the melt temperature near the hopper, T_{e1}, will be discussed (Fig. 1). The torque of the twin-screw shafts and the screw speed, N_d, was also monitored, and these data were fed into a computer; N_d is usually 101 rev. min^{-1} unless otherwise noted. The torque and the value of T_{e1} at a steady state will be discussed. The blends are described by their composition. For example, the PPE/LCP blend represents the blended sample consisting of PPE and LCP, and the PPE/PS = 6/4/LCP blend represents the blend consisting of PPE, PS and LCP; the weight ratio of PPE to PS is maintained at 6:4 regardless of the amount of LCP content. The weight content of additive in the blend is referred to as ϕ; subscripts L and S are used to denote LCP and PS, respectively.

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 performed for each composition. A capillary with $L/D = 10$ and $D = 1$ mm was used. The Bagley and Rabinowitch corrections were not applied, that is, the apparent viscosity was measured.

The thermal behaviour of the blends was studied using a Seiko Densikogyo DSC200 differential scanning calorimeter (DSC) at a heating scan rate of 10 °C min^{-1}.

For estimation of the size and shape of the LCP phase in the blends, a strand of the blend was placed in a Petri dish with toluene as solvent, for about 24 h. The PPE/PS material was dissolved and the insoluble LCP remained. The remaining LCP was placed on a cover glass with a spatula. After being dried, the remaining LCP was sputter-coated with gold and then examined in a Hitachi S-530 scanning electron microscope (SEM).

The change in length of the strand samples with temperature was measured by use of a thermal mechanical analyser (Seikodensikogyo TMA/SS100); the gauge length was 10 mm, the heating rate was 10 °C min^{-1}, and the applied stress was zero.

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^{-1} and the initial gauge length was 40 mm. Because jaw breaks were often encountered, both ends of the strands were reinforced with an epoxy adhesive. In this work, only the strength will be discussed. The variation of diameter of the strand was observed, although the take-up velocity was constant. Therefore, the strength of the sample with a given diameter was evaluated from the data on the strength versus diameter. The fracture surface was also observed by SEM.

3. Results and discussion

The apparent viscosity versus shear rate for the starting materials of PS and LCP was preliminarily measured at 300 °C (see Fig. 6). The two samples exhibited non-Newtonian flow behaviour in the shear-rate range studied (10–10^4 s^{-1}) and the viscosity of LCP was lower than that of PS up to a shear rate of about 7000 s^{-1}. The viscosity of PPE was so high that it could not be measured. The DSC curves of the PPE/PS blends exhibited a single glass transition temperature, T_g. Fig. 2 shows the effect of PS content on T_g of the PPE/PS blend: it can be seen that T_g decreases with increasing PS content. This indicates that PPE and PS are miscible in all compositions and

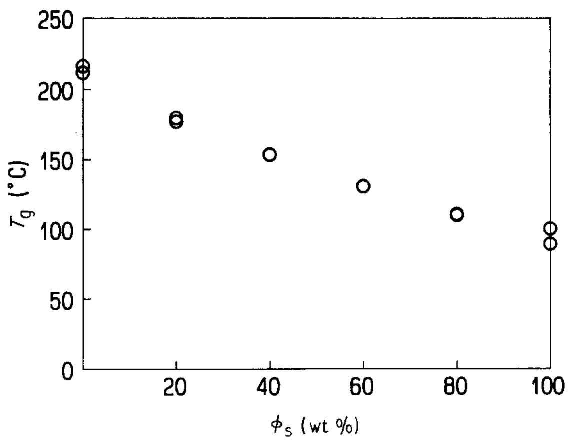

Figure 2 Plots of T_g versus the composition of the PPE/PS blend.

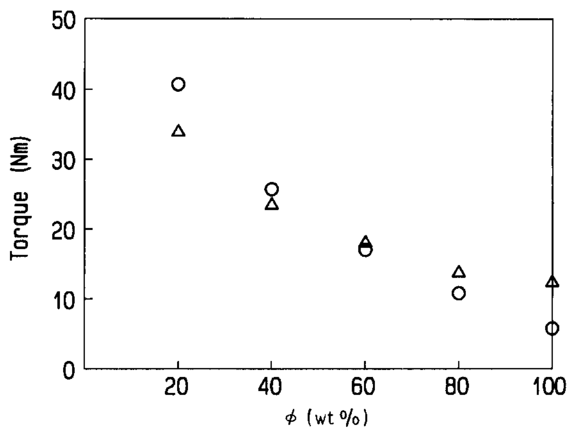

Figure 3 Variation of kneading torque with the blend composition: (○) PPE/PS blend; (△) PPE/LCP blend. $T_d = 300\,°C$, $N_d = 101$ rev. min^{-1}.

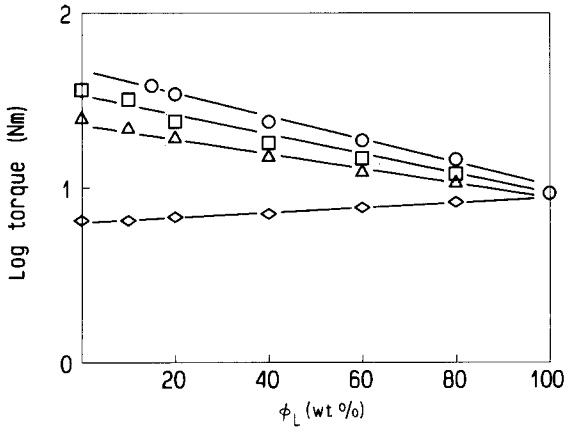

Figure 4 Effect of LCP content on the kneading torque of various PPE/PS/LCP blends. (○) 10/0, (□) 8/2, (△) 6/4, (◇) □/10. $T_d = 300\,°C$, $N_d = 101$ rev. min^{-1}.

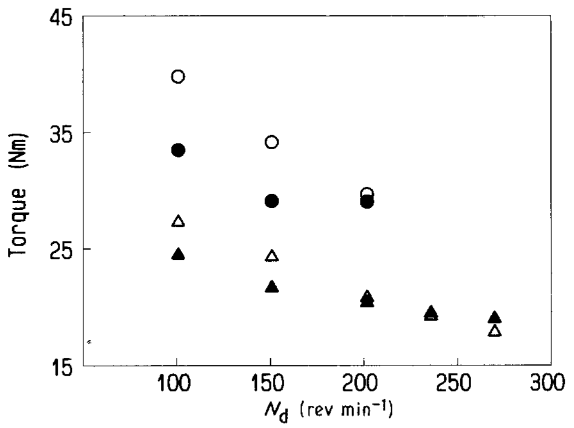

Figure 5 Effect of screw speed on the kneading torque of blends: (○, △) PPE/PS blend; (●, ▲) PPE/LCP blend. ϕ: (○, ●) 20%, (△, ▲) 40%.

that a mixture which shows complete miscibility can be made by the extruder used in this study.

The blend of PPE with LCP and blend of PPE with PS were performed. The torque of twin screw shafts generated during extrusion was measured as a function of ϕ. The results are shown in Fig. 3: the torque decreases with increasing PS or LCP contents. It can be seen that LCP reduces the torque effectively at a low content, although PS is more effective at a high content. The torque of the neat LCP ($\phi = 100\%$) is higher than that of the neat PS, although the viscosity of the neat LCP is lower than that of the neat PS over a wide shear-rate range, as described above. This indicates that the variation of torque cannot be simply explained in terms of the melt viscosity. Fig. 4 shows the effect of LCP content on the kneading torque, T, of the PPE/PS/LCP blends. Despite the weight ratio of PS to PPE, there is a linear relation between log T and ϕ_L. This result indicates that T can be represented by the logarithmic rule of mixtures.

The blending process of PPE with PS and that of PPE with LCP were studied by changing the screw speed. The torque generated during the kneading process is shown in Fig. 5. The torque of the PPE containing 20% PS decreases with increasing screw speed; on the other hand, the torque of the PPE containing 20% LCP decreases with increasing screw speed up to 150 rev. min^{-1}, above which the torque becomes constant. Similar trends can be seen in the $\phi = 40\%$ blends, that is, the torque of the PPE/LCP blend indicates relatively constant value above 200 rev. min^{-1} and that of the PPE/PS blend decreases with increasing screw speed. In the previous work, the torque of the PS/LCP blends was found to become constant with increasing screw speed. It should be noted that there is a difference between the PPE/LCP and PPE/PS blends in the variation of torque with the screw speed. In order to investigate the causes for the variation of torque, we measured the melt viscosities of the PPE/PS and PPE/LCP blends. The result is shown in Fig. 6. Both viscosities decrease with increasing shear rate and decrease with increasing ϕ. The melt viscosity of PPE is effectively decreased with the addition of LCP, more than with that of PS. Because an increase in screw speed is assumed to correspond to an increase in shear rate, the reason for the torque of the PPE/LCP blend exhibiting a constant value at high screw speeds cannot be simply explained in terms of the melt viscosity of the blend. Another mechanism must then be taken into account to explain the cause for the torque generated in the PPE/LCP blend.

A rough approximation for the shear rate, $\dot{r}$, of completely molten polymers in the trough is given by

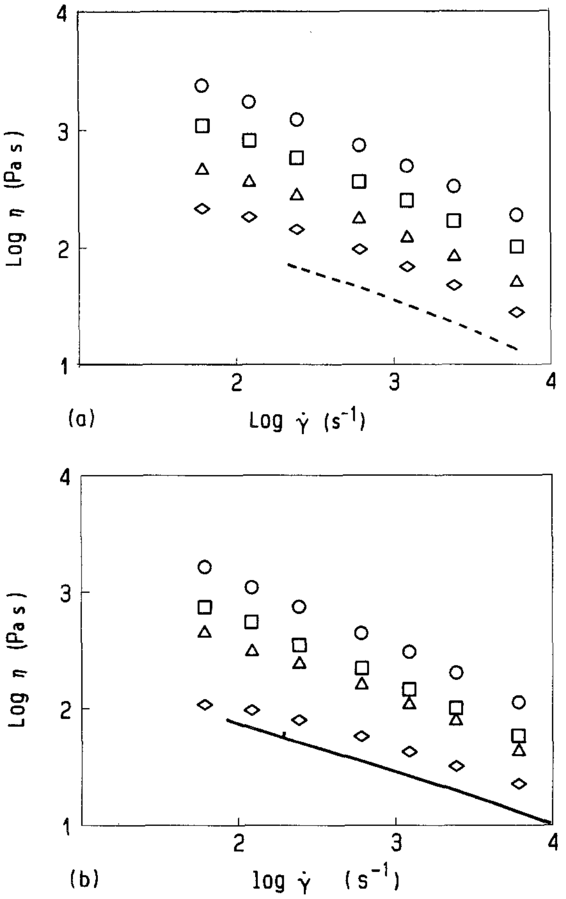

Figure 6 Flow curves of the blends at 300 °C, $L/D = 10$: (a) PPE/PS blends, (b) PPE/LCP blends. (– – –) Neat PS, (———) neat LCP ϕ_s: (○) 20%, (□) 40%, (△) 60%, (◇) 80%.

the following relationship [11, 15]

$$\dot{r} = \frac{\pi D N}{t60} \qquad (1)$$

where D is the length of a major axis of the paddles (25 mm), t is the channel depth between the paddle and trough (0.4 mm), and N is the rotational screw speed (rev. min^{-1}).

The melt viscosities of the PPE/PS and PPE/LCP blends at a given screw speed were estimated from Fig. 6 using Equation 1. Fig. 7 shows the re-plots of the kneading torque (Fig. 5) versus the estimated viscosity, η. At a given η, the torque of the PPE/LCP blend is higher than that of the PPE/PS blend. If we assume that the contribution of the flow properties to the torque is proportional to melt viscosity and shear rate, the contribution seems to be relatively small in the case of the PPE/LCP blend because the shear rate of the PPE/LCP blend is lower than that of the PPE/PS blend at a given viscosity, as seen in Fig. 6. However, the effect of this contribution cannot be seen in the variation of the torque measured. This means that the torque is not directly dependent on the melt viscosity. Because the temperature profile along the trough is complex, it seems that there is a variation in viscosity along the trough. This is not taken into account in the above discussion, that is, the above discussion appears somewhat doubtful. However, we can say at least that the kneading torque of blends is not predicted only by its melt viscosity, which is

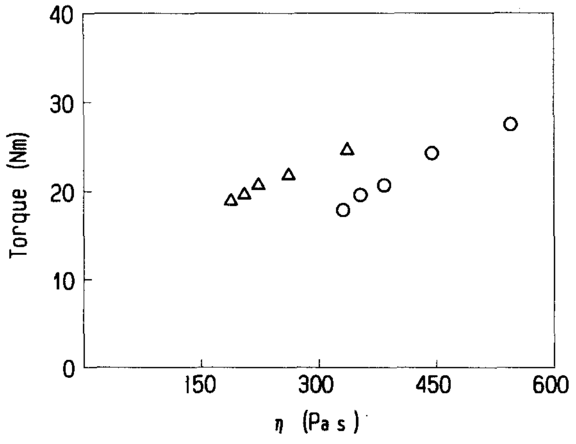

Figure 7 Relation between kneading torque and the calculated viscosity in the extruder: (○) PPE/PS blend, (△) PPE/LCP blend. $\phi = 40\%$.

measured by a capillary viscometer, from the discussions previously described.

Fig. 8 shows the effect of the screw speed on the melt temperature, T_{e1}, which is measured in the vicinity of the hopper (Fig. 1). The temperature increases slightly with increasing screw speed. It should be noted that T_{e1} of the PPE/PS blend is always lower than that of the PPE/LCP blend at a given screw speed and this difference increases with increasing ϕ. Because the distortion temperature of Vectra is high (about 250 °C) [16], it takes a long time to melt completely in the trough. The higher value of T_{e1} in the PPE/LCP blend is caused by the higher frictional forces between the polymer and the metal of the extruder and between polymers in the zone of transport of solids in the extruder. For this reason, the higher torque is observed in the PPE/LCP blend. There are two effects of the addition of LCP on the kneading torque: one is the decrease in torque caused by the reduction of viscosity of the blends, the other is the increase in torque caused by the increase in the frictional force. It would seem reasonable to suppose that the kneading torque of the blends is determined by these two mutually competing effects. Consequently, the torque of the blends exhibits anomalous behaviour described previously. When LCP is blended

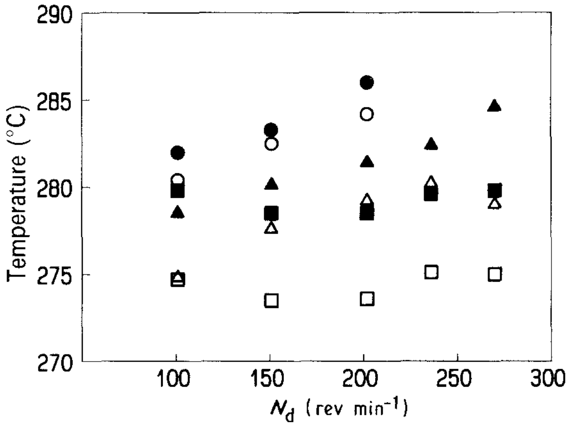

Figure 8 Effect of kneading speed on temperature, T_{e1}; (○, △, □) PPE/PS, (●, ▲, ■) PPE/LCP blends. ϕ: (○, ●) 20%; (△, ▲) 40% (□, ■) 80%.

with conventional polymers using a continuous kneading extruder, the increase in torque caused by the addition of LCP cannot be particularly ignored because its distortion temperature is high, considering its low melt viscosity.

Fig. 9 shows the effect of composition of the PPE/PS matrix on the size and shape of the LCP dispersed phase. The size of the LCP phase formed in the PPE/PS = 6/4 matrix is smaller than that formed in the PPE/PS = 2/8 matrix; the size is markedly

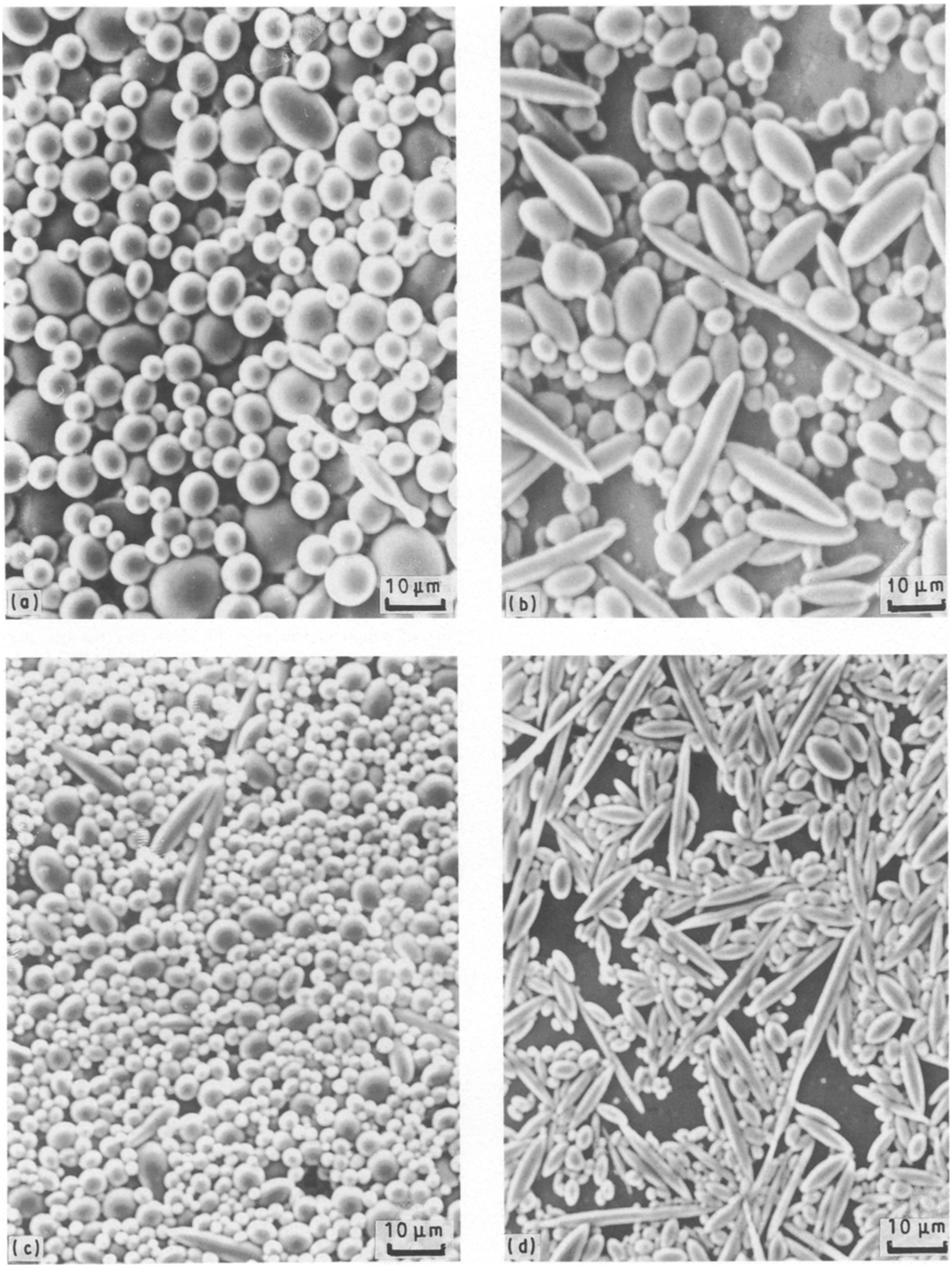

Figure 9 Effect of matrix composition on the size and shape of the LCP phase: $\phi_L = 10\%$. (a) PPE/PS = 2/8, $S_0/S_f = 2$. (b) PPE/PS = 2/8, $S_0/S_f = 17$. (c) PPE/PS = 6/4, $S_0/S_f = 1$. (d) PPE/PS = 6/4, $S_0/S_f = 10$.

small compared with that formed in the PS matrix [3]. This result indicates that the size of the LCP dispersed phase decreases with increasing matrix viscosity. It is thought that the viscosity ratio of the dispersed phase to the matrix, p, is an important factor determining the size of the dispersed phase [15]. From Fig. 6, the value of p of the PPE/PS = 6/4/LCP blend seems to be smaller than that of the PPE/PS = 2/8/LCP blend at a given shear rate; the values of p of both blends are smaller than unity. This means that the size of the LCP dispersed phase decreases with decreasing p ($p < 1$). In our study, the smallest particles of LCP are not observed when $p \approx 1$, although there is a case where the smallest particles are obtained when $p \approx 1$ [15]. The LCP particles become elliptical in form with increasing S_0/S_f. It is to be noted that the size of the elliptical form observed after the draw, is correlated with the size of the LCP particles formed before the draw. This result suggests that we should produce the LCP particles with a very small size during the kneading process in order to make well-dispersed fine LCP fibrils in the matrix during the drawing process. However, the LCP particles should have a certain size to change into the well-developed LCP fibrils during the drawing process, because effective stress transfer from the matrix to these particles is required. Therefore, we should produce the LCP particles with an optimum size during the kneading process in order to produce well-dispersed and well-developed fine LCP fibrils in the matrix by a small addition of LCP. Although the surface tension also seems to be an important factor determining the size of the dispersed phase, the effect is not considered in this work.

Fig. 10 shows the effect of LCP content on the TMA curve. The sample length of the neat PS (ϕ_L = 0% blend) and that of the ϕ_L = 20% blend increase initially and then decrease with increasing temperature; the temperature at which shrinkage commences increases with increasing ϕ_L. On the other hand, the blends with more than 40% LCP content show continuous shrinkage with increasing temperature. A marked contraction of the ϕ_L = 0% blend occurs at about 90 °C which corresponds to its glass transition temperature. The blends with more than 40% LCP content exhibit a maximum peak of shrinkage at about 260 °C, which corresponds to the transition temperature of LCP. Well-developed fibrillar structure was observed in the blends with more than 40% LCP content by SEM. On the other hand, undeveloped fibrillar structure was observed in the ϕ_L = 20% blend. It is obvious that the morphology of the LCP phase affects the shrinkage of blends. Further, it should be noted that the dimensional stability of the blend is improved by the presence of LCP, even in small amounts.

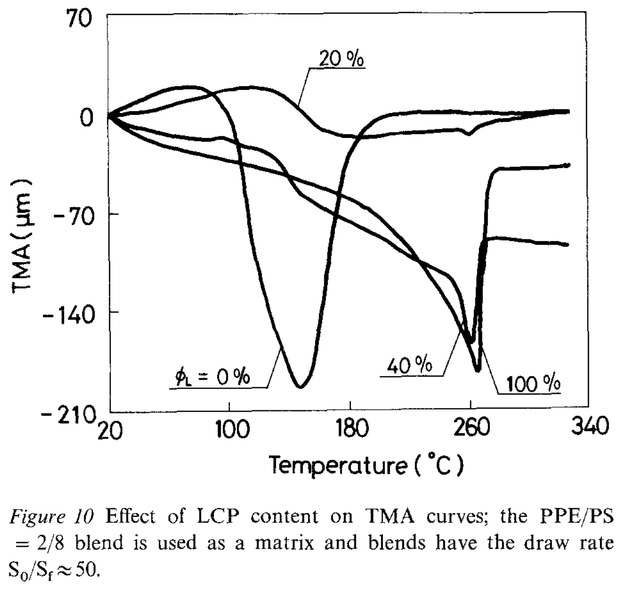

Figure 10 Effect of LCP content on TMA curves; the PPE/PS = 2/8 blend is used as a matrix and blends have the draw rate $S_0/S_f \approx 50$.

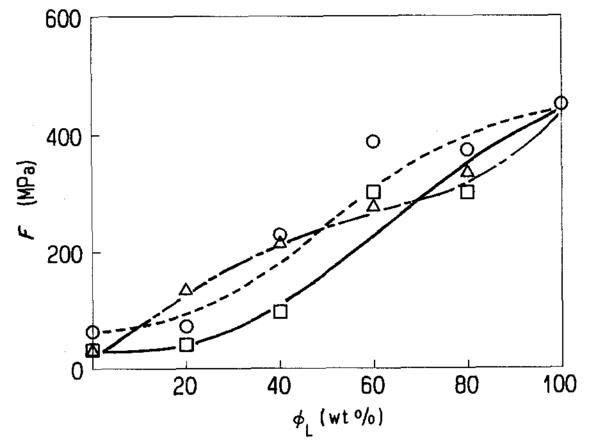

Figure 11 Effect of LCP content on the strength of blends; (○) PPE/PS = 2/8, (△) PPE/PS = 6/4, and (□) PPE/PS = 0/10 blends are used as matrices. S_0/S_f = 100.

Fig. 11 shows the effect of LCP content on the strength, F, of the blends. In both PS/LCP and PPE/PS = 2/8/LCP blends, the value of F does not increase with increasing LCP content up to 20% above which F increases steeply. On the other hand, the value of F of the PPE/PS = 6/4/LCP blend increases almost linearly with increasing ϕ_L. This result indicates that the strength is enhanced by a small addition of LCP in the PPE/PS = 6/4/LCP blend. The difference between the samples in the variation of strength with ϕ_L seems to be caused by the difference in morphology of the LCP phase formed in the matrix. Fig. 12 shows the fracture surfaces of the three blends having ϕ_L = 20%. In the PPE/PS = 6/4/LCP blend, well-developed fine LCP fibrils can be seen. On the other hand, the undeveloped LCP fibrils can be observed in the PS/LCP blend. Because the matrix viscosity of the PPE/PS = 6/4/LCP blend is rather high, the LCP dispersed phase with a small size is produced during the kneading process and sufficient stress is transferred from the matrix to this LCP dispersed phase during the melt-drawing process. Consequently, these two mechanisms lead to the formation of well-dispersed and well-developed fine LCP fibrils. It is obvious that such a structure of LCP fibrils improves the mechanical properties of the blends. In conclusion, a good reinforcing effect on mechanical properties is expected by a small addition of LCP to conventional polymers when the polymer having a high viscosity is used as a matrix resin.

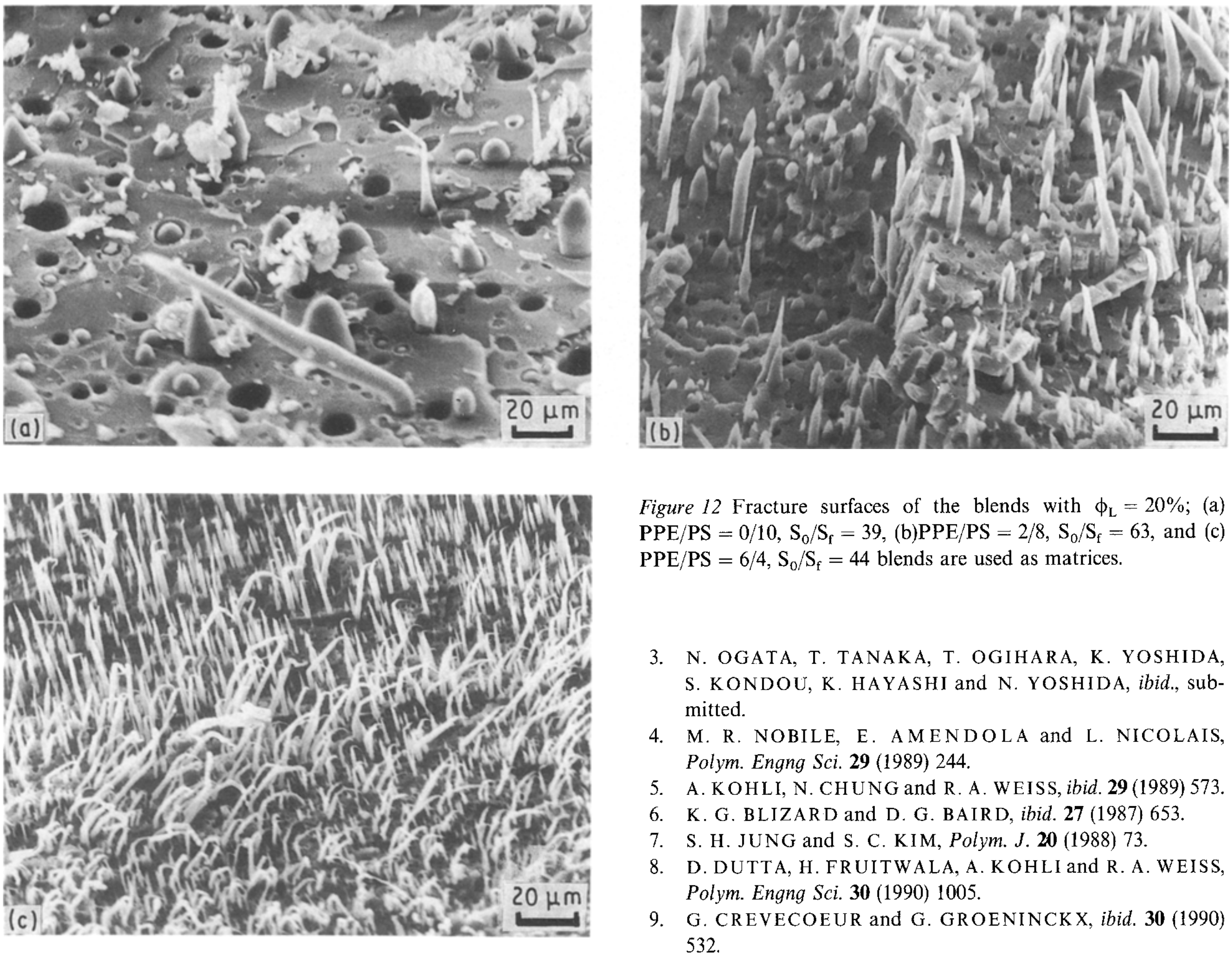

Figure 12 Fracture surfaces of the blends with $\phi_L = 20\%$; (a) PPE/PS = 0/10, $S_0/S_f = 39$, (b)PPE/PS = 2/8, $S_0/S_f = 63$, and (c) PPE/PS = 6/4, $S_0/S_f = 44$ blends are used as matrices.

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