Microstructure formation in polyblends containing liquid crystalline polymers

Jiasong He* and Wensheng Bu
State Key Laboratory of Engineering Plastics, Institute of Chemistry, Academia Sinica, Beijing 100080, People's Republic of China
(Received 23 November 1993; revised 7 April 1994)

Based on rheological data, two polyblends of poly(ether sulfone) (PES) and polycarbonate (PC) with a liquid crystalline polymer (LCP) as the dispersed phase were prepared by extrusion. The process of LCP microstructure formation was investigated by studying the morphology of the blend obtained from different sections of the extruder. The deformation of LCP domains is controlled by the viscosity ratio of the dispersed phase to the continuous phase (η_d/η_m). LCP domains in LCP/PES blend have been deformed into oriented fibrils, due to a viscosity ratio of 0.01. A quantitative comparison of LCP droplet sizes before and after the extruder die shows that the morphology of extrudates has been determined before the melt enters the die. After the die, the diameter and length to diameter ratio of LCP fibrils were increased by coalescence and further deformation by the action of extensional flow. The morphology of LCP/PES extrudates after remaining at quiescence within the die for different time intervals indicates that even after a 60 s residence, LCP domains retained their fibrillar structure in the blend and no significant recoiling and breakup of LCP fibril occurred.

(Keywords: polyblends; liquid crystalline polymers; microstructure)

INTRODUCTION

Polyblends containing thermotropic liquid crystalline polymers (LCPs) may be considered one of the most attractive research topics involving polymer blends and composites in recent years[1,2]. This group of composites, the so-called *in situ* composites, has advantages such as high performances, good processability and less abrasion on processing machines, and has shown great potential in materials application. There have been a lot of papers published on aspects of rheology, morphology, crystallization, thermal stability, compatibility and mechanical properties of these blends[3-8]. The morphology of the blend is important as it directly affects the final properties of the resultant products. For the effective transfer of stress between the reinforcement and the matrix, the LCP phase must have a fibrillar structure consisting of fine fibrils with large aspect ratios. However, from the published results it is found that not all combinations of LCP and isotropic polymers can be extruded to form a microstructure having LCP fibrils. The LCP is usually in the form of spherical droplets and short rods.

Several authors have discussed the morphology formation of blends containing LCPs in detail. Blizard *et al.*[9] studied three different polymer blends and focused on the morphology of the LCP phase. According to their results, the high degree of orientation and fibrillar structure is developed in the capillary flow and post-die drawing. They suggested that the lack of fibrillar structure in one of these blends is due to solidification during the post-die draw down. The sharp increase in viscosity of the LCP, caused by cooling and crystallization, retarded the deformation of the LCP phase.

Beery *et al.*[10] studied the structure development during capillary flow of polyblends containing LCP. The three matrices used were poly(butylene terephthalate) (PBT), polycarbonate (PC) and nylon 6. They found that long fibrillar structure developed only in the LCP/PC system at shear rates above 270 s^{-1}, when the LCP viscosity was lower than that of PC. Based on this, they concluded that elongation and orientation of the LCP phase to fibrillar structure took place when the viscosity of the matrix polymer was higher than that of the suspended LCP one.

However, most of the results in previous studies on morphology formation are based on the final morphology of extrudates after the extruder die. No detailed analysis of microstructure development within the extruder has been conducted. In the process of microstructure formation of extrudates, the deformation, coalescence, breakup and relaxation of the dispersed phase are all involved. Questions to be resolved are: how are LCP fibrils generated in the molten matrix?; and what are the conditions for LCP fibril formation?

As part of our study on the morphology formation of polyblends containing LCPs, this paper will evaluate quantitatively the size of the dispersed LCP phase, describe the processes involved in the microstructure formation and also discuss their contribution to the final structure of the extrudate.

---

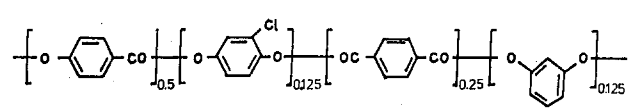
*To whom correspondence should be addressed

0032-3861/94/23/5061-06

EXPERIMENTAL

Materials

The LCP was a wholly aromatic copolyester synthesized in the laboratory[11]. It has the following structure and is in the nematic state over the temperature range 250–380°C[11]:



The two polymers used as matrices were poly(ether sulfone) (PES), obtained from Jilin University, PRC, and PC, produced by Shanghai Zhonglian Chemical Factory, PRC ($M_n = 26\,000 \pm 1000$).

Processing

Melt blending of LCP/PES and LCP/PC was performed in a single-screw extruder with a screw diameter of 20 mm and a length to diameter (*L*/*D*) ratio of 25. Before blending all the materials were dried in vacuum at 130°C for at least 7 h. The content of LCP in both blends was 10% w/w and the screw speed was fixed at 55 rev min^{-1}. The temperature profiles along the axis of the screw extruder from the feeding zone to the die were as follows:

For LCP/PES	280 to 290 to 300 to 300°C; 280 to 300 to 320 to 320°C; 290 to 325 to 340 to 320°C.
For LCP/PC	255 to 280 to 300 to 280°C; 280 to 300 to 320 to 300°C.

Samples for morphology observation were obtained at different sections as illustrated in *Figure 1*.

Measurements and observation

The rheological properties of the component polymers and their blends were measured with a Goettfert Rheograph 2001 capillary rheometer at temperatures of 300, and 320°C. A capillary die with a *L*/*D* ratio of 30 and a diameter of 1 mm was used.

The microstructure of each sample was observed by scanning electron microscopy (SEM) (Hitachi S-530). Two methods of sample preparation were used. The first involved quenching the sample in liquid nitrogen and breaking it, followed by coating the fracture with gold. The second method involved dissolving the matrix selectively for LCP/PES blend and using the remains for observation. In the latter method, typically, small samples were cut into tiny pieces, then immersed in *N*,*N*-dimethylformamide for 24 h to dissolve the PES completely. The LCP phase was separated by centrifugation and the supernatant liquid was decanted. The centrifuged LCP phase was immersed in fresh solvent and separated twice more. Finally a drop of the remaining dispersion was placed directly on an SEM sample holder, the solvent evaporated off, and coated with gold for observation. The diameter and intrinsic aspect ratio of LCP droplets and fibrils were measured with a Cambridge Instruments Quantimet 520 Image Analysis System. Typically, ~300 LCP droplets or fibrils were measured for each given sample.

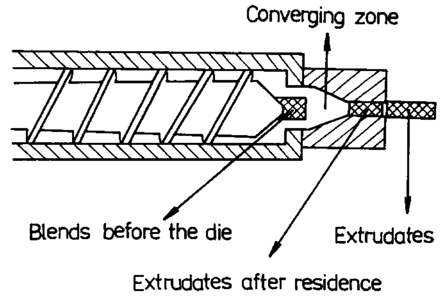


Figure 1 Schematic representation of the sections from which samples are obtained for SEM observation

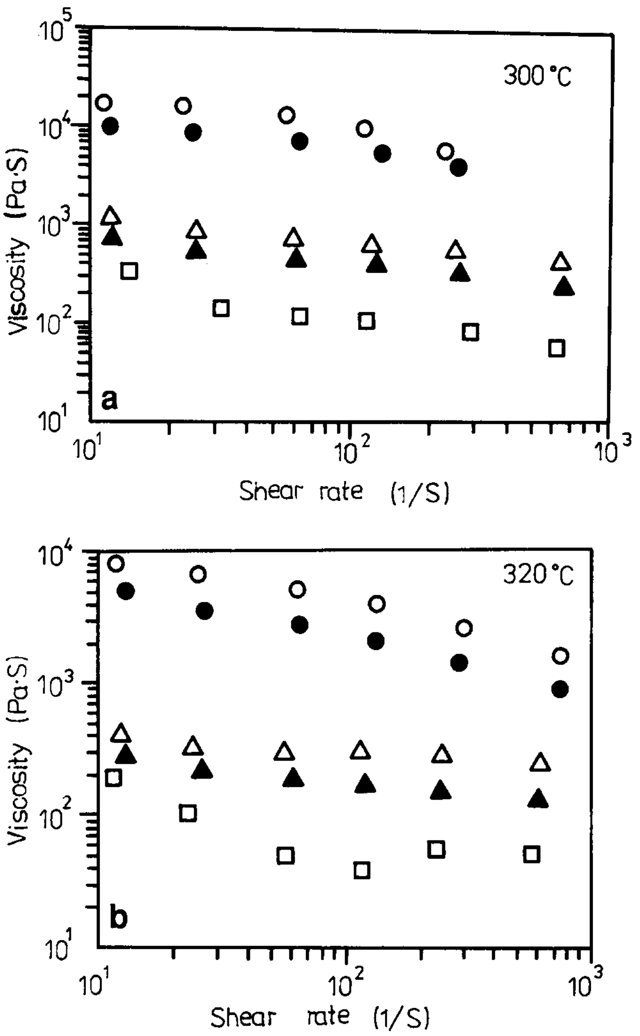


Figure 2 Viscosity of LCP (□), PC (△), LCP/PC (▲), PES (○) and LCP/PES (●) as a function of shear rate at (a) 300°C and (b) 320°C from capillary measurement

RESULTS AND DISCUSSION

Rheology

The flow curves of LCP/PES and LCP/PC blends together with their component polymers at 300 and 320°C are shown in *Figures 2a* and *b*. The viscosity ratios of LCP to the matrix polymer at their processing temperatures are obtained from these curves. The data at a shear rate of 57.6 s^{-1} are listed in *Table 1*. The viscosity of the LCP at 340°C was too low to be measured, so its value was calculated by extrapolation of the data at 300 and 320°C using the Arrhenius equation. It is noticed that all the melts exhibit non-Newtonian flow behaviour for the range of temperatures and shear rates

Table 1 Morphology of dispersed LCP phase related to viscosity ratios (in parentheses) of LCP to matrices, PES and PC (at a shear rate of 57.6 s^{-1})

	Extrusion temperature (°C)		
Matrix	300	320	340
PES	Fibrils (0.01)	Fibrils (0.008)	Fibrils (0.006)
PC	Spheres (0.16)	Spheres (0.13)	

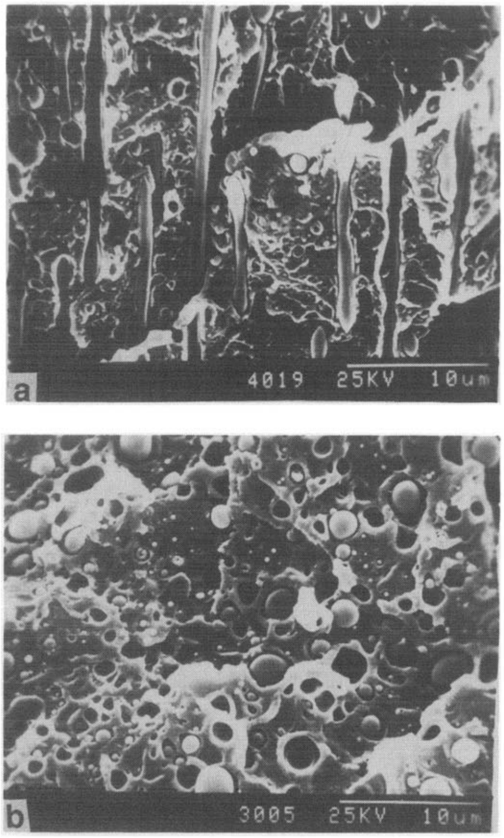


Figure 3 SEM micrographs of fracture surfaces of (a) LCP/PES extruded at 320°C and (b) LCP/PC extruded at 300°C

investigated. It should be noted that the LCP shows a stronger shear-thinning behaviour than PC and PES, especially at high temperatures. However, the viscosity of the blends shows the same shear sensitivity as PES and PC. At these temperatures, the viscosity of the LCP is lower than that of PC and much lower than that of PES. The viscosity curves of the blends lie between those of the LCP and matrix resins. This means that only a 10% concentration of LCP has led to a significant reduction of the blend viscosity.

The morphology of the LCP/PES and LCP/PC blends was observed and correlated with the viscosity ratio. *Figure 3* shows the SEM micrographs of fracture surfaces of LCP/PES extruded at 320°C and LCP/PC at 300°C. In LCP/PES extrudates long LCP fibrils with large aspect ratios and diameters of ~0.5 μm have been generated and are parallel to each other along the extrusion direction. The LCP/PES extrudates at 300 and 340°C have a similar morphology to that at 320°C. In contrast to LCP/PES, LCP/PC extrudates at 300°C show some very large deformed droplets and a lot of tiny, spherical droplets. Extrusion at 320°C resulted in a similar morphology. The morphology of LCP/PES and LCP/PC extrudates are also listed in *Table 1*. It can be seen, corresponding to the fibrillar structure, that the viscosity ratios of LCP/PES blends are <0.01, while the spherical morphology of LCP/PC correlates with a higher viscosity ratio (0.13). It is clear that viscosity ratios of <0.01 favour the fibrillation of the dispersed LCP phase. The low viscosity ratio is the origin of the viscous force necessary for the deformation of LCP droplets.

Deformation of LCP domains by shear action of the screw

In order to investigate the generation of LCP fibrils, blend melts in the screw shear zone before the die and extrudates after the die at 340°C were observed for comparison. *Figure 4a* shows the SEM micrograph of the fracture surface of LCP/PES blend obtained before the die and *Figure 4b* shows that of the extrudate. It is clear that in the extrudates very long fibrils were formed in the PES matrix. These fibrils are well oriented along the extrusion direction and all have large aspect ratios. In blended melts before the die, fine fibrils are also formed in the matrix. These fibrils are pulled out of the matrix and oriented along the extrusion direction.

Figures 5a and *b* show the SEM micrographs of the fracture surface of LCP/PC blends before the die and extrudates after the die, respectively. In contrast with LCP/PES, only spherical droplets formed in the PC matrix in the extrudates, these droplets being uniformly distributed in the matrix. In blends before the die, the LCP phase also appears to be only droplets and no deformation can be seen.

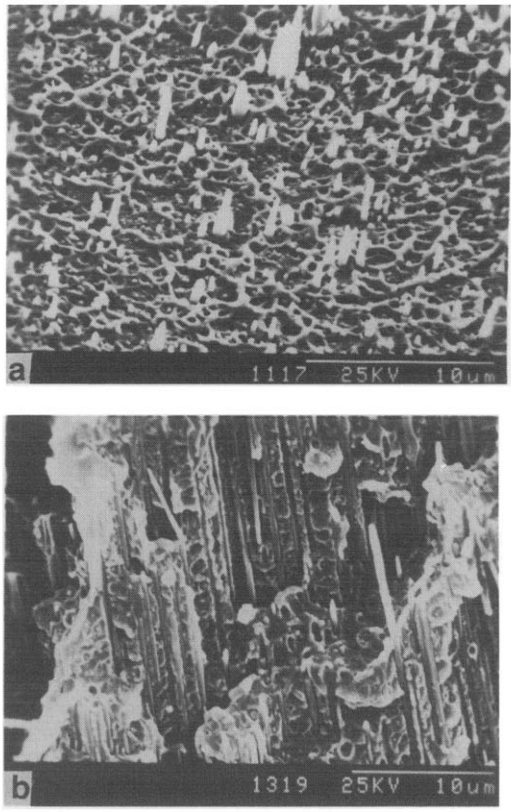


Figure 4 SEM micrographs of 10% LCP/PES blends obtained at 340°C: (a) before the die; (b) extrudates

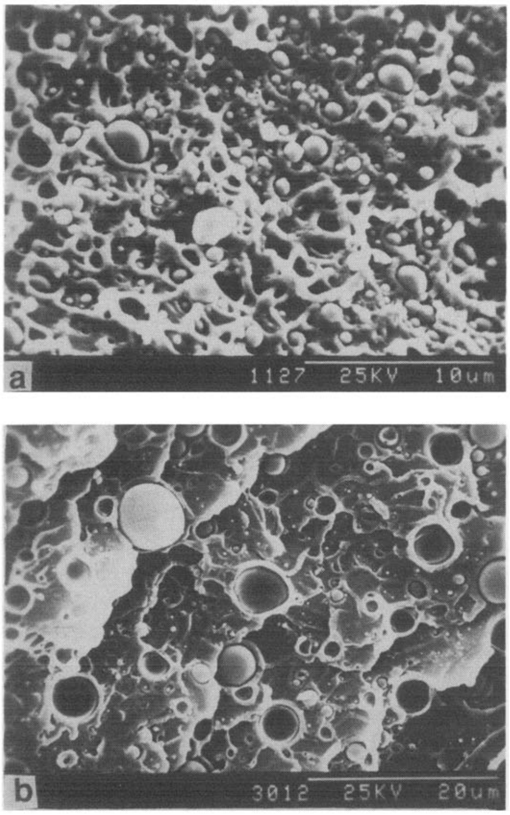


Figure 5 SEM micrographs of 10% LCP/PC blends obtained at 320°C: (a) before the die; (b) extrudates

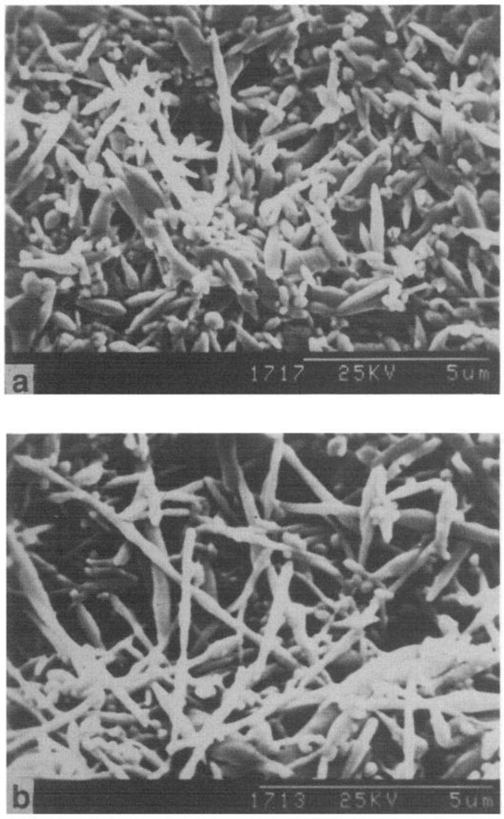


Figure 6 SEM micrographs of 10% LCP/PES blends after extraction of PES, obtained at 340°C: (a) before the die; (b) extrudates

For estimation of the size and shape of LCP domains in these two stages of extrusion, before and after the die, the matrix PES of the LCP/PES blend has been extracted by solvent. *Figures 6a* and *b* show the LCP fraction in blends before and after the die, respectively. By means of image analysis, the diameter and intrinsic aspect ratio of the LCP fibrils and droplets in blend samples were measured. *Figure 7* shows the distribution of LCP fibril diameters in LCP/PES melts before and after the die. Before the die, the largest proportion of fibrils has a diameter of 0.25 μm. The average diameter is 0.22 μm. The largest proportion of fibrils after the die has a diameter of 0.21 μm. The average diameter of LCP fibrils after the die is 0.20 μm. It is of interest to notice the distribution of LCP fibril aspect ratios shown in *Figure 8*. Even before the die the sample has LCP fibrils generated in the PES matrix. These fibrils have a maximum aspect ratio of 18. Nearly half of them have aspect ratios of ~6 and >20% of fibrils have aspect ratios in the range of 9–18. In contrast to LCP/PES, the LCP/PC sample has most LCP droplets in the form of spheres, i.e. the aspect ratio is 1.

It has been proposed by Kohli *et al.*[12] that LCP fibrils are generated in the entrance to the die, in which the extensional flow of the converging zone plays a decisive role in deforming the LCP phase. Baird and Ramanathan[13] also reported that there were no fibrils observed under conditions with no die in place, so they concluded that the die is needed for LCP fibril formation.

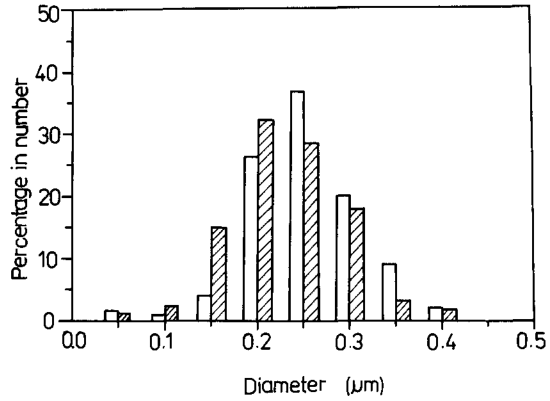


Figure 7 Diameter distribution of LCP fibrils in LCP/PES blends: (□) before the die; (▨) extrudates

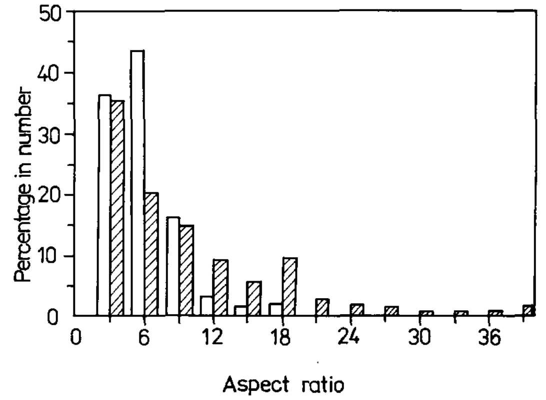


Figure 8 Distribution of the aspect ratio of LCP fibrils in LCP/PES blend: (□) before the die; (▨) extrudates

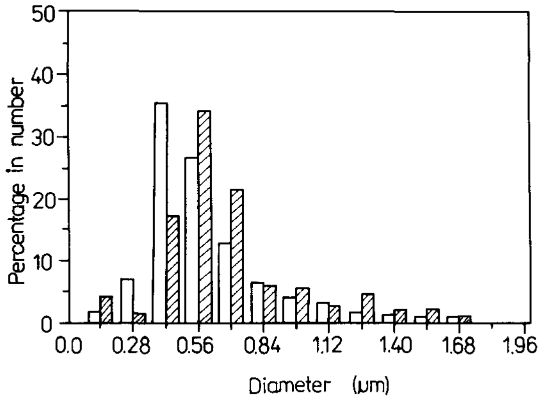


Figure 9 Diameter distribution of LCP droplets in LCP/PC blend: (☐) before the die; (▨) extrudates

In the present study, a different result was obtained in LCP/PES blends, as even in the shear flow before the die entrance the LCP domains were deformed into fibrils and well oriented. This phenomenon has also been found in a LCP/polysulfone system[14]. For LCP/PC blends, no deformation of the LCP phase is found before and after the die. The comparison of these two systems indicates that the morphology of the LCP phase in the extrudates is in accordance with that in the blends before the die. It can be thought that the general microstructure of the extrudates is determined by the shear flow before the die. In shear flow, there are many factors affecting the morphology. However, the dominant one is the viscosity ratio, as will be shown in a study to be published elsewhere. As long as the conditions favouring the LCP fibrillation are reached, the LCP phase will be deformed and elongated to fibrils by the shear flow in the barrel of an extruder.

Coalescence and further deformation of the LCP phase in die entrance

In comparing the morphology of the two samples it is found that the fibrils in the extrudate have nearly the same average diameter as those in the blend before the die. However, from the distribution of the aspect ratio, the *L/D* of fibrils after the die, we can see that there are ~35% fibrils with a *L/D* ratio in the range of 9–18 compared with ~10% in the range of 21–39. Compared with only 20% fibrils in the range of 9–18 before the die, the aspect ratio increases significantly in the flow through the die, indicating the fibril volume has increased significantly. This means that extensional flow in the converging zone of the die entrance causes further development of LCP fibrils. This results from two effects. The first effect, during extensional flow in the entrance, is the coalescence of dispersed LCP fibrils and droplets resulting in the increase in size of the LCP phase. The second effect, under the action of the extensional stress, is that the deformation has made LCP fibrils elongate further.

The coalescence of the dispersed phase in a two-phase system has been found by some authors[15,16]. In a previous paper[11], the authors have reported that during drawing the coalescence of dispersed LCP domains occurs, which accelerates the formation of LCP fibrils. In the case of extrusion, Blizard and Baird[4] suggested that the formation of LCP fibrils depends on some critical volume fraction that makes coalescence of the dispersed phase possible in a given flow field. Now, from the morphology comparison and size measurement at different stages, this coalescence has been clearly proved.

It should be pointed out that the further deformation is achieved only under certain conditions, although the coalescence occurred. For LCP/PC blends, the size of the LCP spheres increases a little, i.e. the average diameter of spheres increases from 0.55 μm before the die to 0.62 μm after the die (*Figure 9*). However, there is no morphology change after the melt flows through the die. This may be also due to the higher viscosity ratio of LCP to PC, compared with that of LCP to PES.

Ability of the LCP phase to retain fibrillar structure

The fibrillar structure of the LCP phase has been found in some extrudates of polyblends containing LCP. This indicates that LCP fibrils formed in the shear zone and die entrance have been preserved to the exit of the die. It is of interest to know how long this structure can be kept.

Figures 10a and *b* show the SEM micrographs of LCP/PES extrudates after residing in the die for 10 and 60 s, respectively. Well-oriented long and fine LCP fibrils can still be found in the PES matrix even after a 60 s residence at quiescence and they are nearly the same as those in normal extrudates (*Figure 4*), showing no obvious recoiling and breaking up of LCP fibrils. This span is usually much longer than that of extrudates through the extruder die. This means that once LCP fibrils are formed, they can retain their structure for a period of time even at a temperature as high as that of extrusion. Their relaxation and breakup are rather smaller than those in flexible polymer blends. The rigidity of LCP molecular

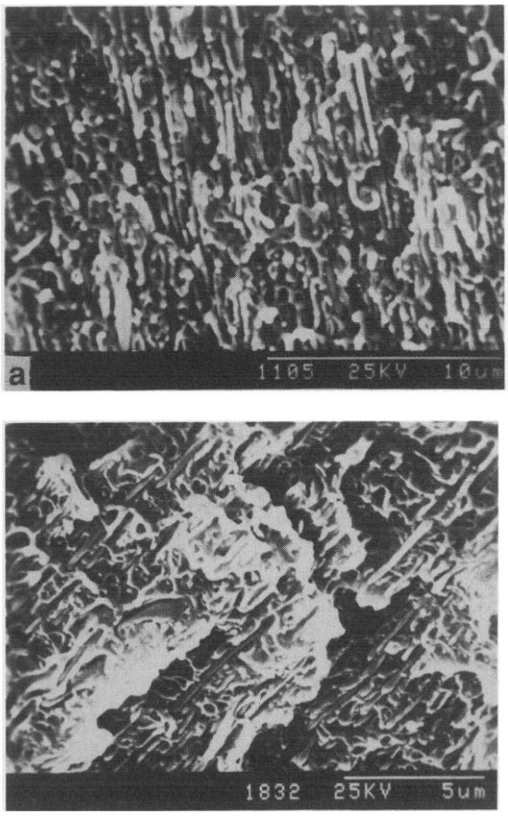


Figure 10 SEM micrographs of 10% LCP/PES blends extruded at 340°C after residence at quiescence within the die for (a) 10 s and (b) 60 s

chains results in the ability of LCP fibrils to retain their structure for a period of time in the melt. It has been pointed out by some authors[4,12] that the lack of LCP fibrils in some cases is due to the large *L/D* of the capillary which makes the fibrils relax and break up. However, from the results obtained in this study, it should be said that the long residence time in the die with a large *L/D* of the capillary would not result in the disappearance of fibrillar morphology of the LCP.

CONCLUSIONS

Based on the morphological observation of blends obtained at different stages in a single-screw extruder and quantitative analysis of the diameter and the aspect ratio of LCP fibrils and droplets, it can be concluded that the process of deformation of LCP domains in the shear flow before the die is controlled by the viscosity ratio of the dispersed LCP phase to the continuous phase. The shear flow before the die can result in the deformation and fibrillation of LCP droplets, if the viscosity ratio favours fibre formation in the LCP. The coalescence and further deformation of LCP domains in the die entrance leads to the increase in volume and aspect ratio of the fibrils. These processes together with the ability of the LCP to retain its elongated shape lead to the LCP fibrillar structure in the resultant samples of polyblends containing LCPs.

ACKNOWLEDGEMENTS

The authors are grateful to the National Natural Science Foundation of China for supporting this work.

REFERENCES

1 Kiss, G. *Polym. Eng. Sci.* 1987, **27**, 410
2 Dutta, D., Fruitwala, H., Kohli, A. and Weiss, R. A. *Polym. Eng. Sci.* 1990, **30**, 1005
3 Siegmann, A., Dagan, A. and Kenig, S. *Polymer* 1985, **26**, 1325
4 Blizard, K. G. and Baird, D. G. *Polym. Eng. Sci.* 1987, **27**, 653
5 Isayev, A. I. and Modic, M. *Polym. Compos.* 1987, **8**, 158
6 Sharam, S. K., Tendolkar, A. and Misra, A. *Mol. Cryst. Liq. Cryst.* 1988, **157**, 597
7 Apicella, A., Iannelli, P., Nicodemo, L., Nicolais, L., Roviello, A. and Sirigu, A. *Polym. Eng. Sci.* 1986, **26**, 600
8 Zhung, P., Kyu, T. and White, J. L. *Polym. Eng. Sci.* 1988, **28**, 1095
9 Blizard, K. G., Federici, C., Federico, O. and Chapoy, L. L. *Polym. Eng. Sci.* 1990, **30**, 1442
10 Beery, D., Kenig, S. and Siegmann, A. *Polym. Eng. Sci.* 1991, **31**, 451
11 He, J., Bu, W., Zhang, H., Xie, P. and Xu, X. *Int. Polym. Process.* 1993, **8**, 129
12 Kohli, A., Chung, N. and Weiss, R. A. *Polym. Eng. Sci.* 1989, **29**, 573
13 Baird, D. G. and Ramanathan, R. 'Contemporary Topics in Polymer Science', (Ed. B. M. Culbertson), Vol. 6, Plenum Press, New York, 1989, p. 73
14 Bu, W. *Master Thesis* Academia Sinica, 1992
15 Utracki, L. A., Dumoulin, M. M. and Toma, P. *Polym. Eng. Sci.* 1986, **26**, 34
16 Roland, C. M. and Bohm, G. G. A. *J. Polym. Sci., Polym. Phys. Edn* 1986, **22**, 79