

Effects of Convergent Flow on *In Situ* Fibrillation of TLCP in PEN

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ABSTRACT: A polymer melt entering a capillary die from a cylinder undergoes a convergent flow in which there is a complex combination of extensional and shear flows. The convergent flow plays an important role in controlling the *in situ* fibrillation of thermotropic liquid crystalline polymer (TLCP) in a thermoplastic matrix melt. This study examines effects of the convergent flow on development of TLCP fibrils in a TLCP/poly(ethylene naphthalate) (PEN) blend. A capillary rheometer was used and the extent of the convergent flow was varied by changing capillary dimension and shear rate. With a given capillary die, the TLCP fibrillation was found to increase with increasing shear rate because of

the increased deformation of TLCP droplets. The establishment of a fully developed shear velocity profile by using a relatively long die is considered to be necessary to retain the TLCP fibrils initiated in the convergent flow region. At a given high shear rate, TLCP fibrillation improves with increasing capillary diameter (≤ 2 mm) because of the increased difference in velocity between the capillary and the cylinder. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 1505–1513, 2004

Key words: blends; liquid-crystalline polymers; polyesters; shear

INTRODUCTION

Blending of thermotropic liquid crystalline polymers (TLCP) with commercial thermoplastics is attractive,^{1–26} mainly because of two advantages. First, because TLCP often exhibits low melt viscosity, they can be used as a processing aid to reduce viscosity of a thermoplastic matrix so that the processibility of the plastics will be improved. Second, because TLCPs can intrinsically exhibit a high degree of molecular order in the melt state, TLCPs, under appropriate processing conditions, can be deformed into fibrils; these fibrils then act as a reinforcement component for the thermoplastic matrix. Since the 1990s, there have been a great number of studies of TLCP blends with commercial thermoplastics.^{1–26} Many kinds of commercial plastic polymers have been used as a matrix to make blends with TLCPs, which included polypropylene,^{9–11,13,14,18,20,26} polyethylene,²⁴ nylon,^{3,19,21,22} polycarbonate,^{12,25} polyesters [poly(ethylene terephthalate) (PET), poly(butylene terephthalate) (PBT), and poly(ethylene 2–6 naphthalate) (PEN)],^{4,5,23,27} polystyrene,¹⁷ poly(methyl methacrylate),⁷ epoxy,⁶ and others.^{8,12,15,16} Among these studies, polypropylene (PP) was the most frequently used plastics for making blends with TLCP, but because PP has a poor immiscibility with TLCP and low melt viscosity, it was found for *in situ* fibrillation of TLCP in a PP matrix to

be very difficult.^{13,14,20,26} This difficulty can be improved by adding a compatibilizer to the blend^{9,13,14,20} or by adding a viscosity thickening agent to the PP phase.²⁶

The fibrillation of TLCP in a thermoplastic melt is a complex process, which can be affected by many factors such as miscibility between TLCP and the matrix, TLCP content, viscosity ratio of TLCP to the matrix, processing temperature, shear and elongational flows, as well as processing history. Most pairs of TLCP and thermoplastics are immiscible so that there is an interface separating the two phases. The poor interfacial tension (or in other words, the lack of interactions) between the two phases is considered to be the main reason for the melt slip that often results in a negative deviation from the rule of mixture.^{23,27–29} The shear viscosity ratio of TLCP to the polymer matrix is well known to be important in governing fibrillation of TLCP. It is often observed that a shear viscosity ratio ($\eta_{\text{TLCP}}/\eta_{\text{matrix}}$) between 0.01 and 1.0 favors TLCP droplet deformation.^{12,17,25,26} Here, the matrix viscosity is required to be greater than that of TLCP to allow efficient transfer of shear stress from the matrix to the dispersed TLCP domains for deformation of TLCP droplets. For example, He and Bu studied the effect of viscosity ratio on the fibrillation of TLCP in poly(ether sulfone) and observed that the deformation of TLCP domains was controlled by the viscosity ratio.¹² When the viscosity ratio was very low (0.01), TLCP fibrils were formed.¹² Choi et al. used two TLCPs with different viscosity behaviors to make TLCP blends with polystyrene (PS).¹⁷ They found that when the viscosity

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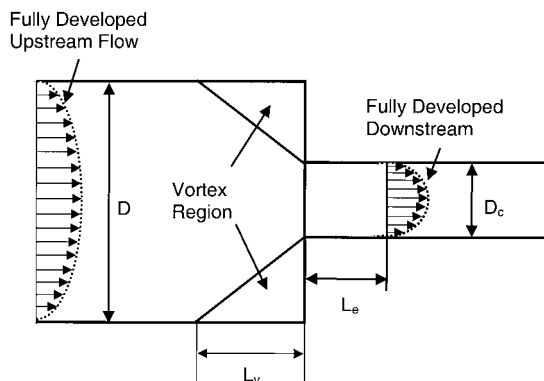


Figure 1 A schematic description of a convergent flow when a fluid in a large tube of diameter D enters a small tube (capillary) of diameter D_c . The region indicated by the length of $L_v + L_e$ is the convergent flow region beyond which the flow is fully developed.

of one liquid crystalline polymer (LCP) was lower than that of PS, fine LCP fibril structure was formed, whereas the spherical form of LCP was observed when the viscosity of the other LCP was higher than that of PS.¹⁷

However, when some commercial TLCPs such as Vectra A950 or B950 are used as a dispersed phase and blended with a low melt viscosity polymer such as PP or nylon, it often results in a viscosity ratio of TLCP to the matrix to be greater than 1.^{18,19,22} In this case, fibrillar structures of LCP could be formed at relatively high shear rates, as reported by Postema and Fennis for the blends of PP and Vectra A950.¹⁸ Thus, the criterion for determination of the LCP fibrillation by using the low viscosity ratio (i.e., $\eta_{\text{TLCP}}/\eta_{\text{matrix}} < 1$) becomes invalid. Here, to avoid the conflict, one may have to consider the original characteristics of a given TLCP. For example, the rigid chains of Vectra LCPs give much higher viscosity than the relatively flexible chains of Rodrum LCPs (e.g., LC3000 and LC5000). It also seems that the former tends to form fibrillar structures more easily in the nematic state under appropriate shear flow conditions than the latter.

No reports have been found on effect of elongational viscosity ratio on TLCP fibrillation in a thermoplastic matrix. In fact, compared to a shear condition, TLCP fibrillation should be more favored by extensional conditions. This is because similar to a fiber spinning process, an extensional flow is more effective at elongating the TLCP droplets into fibrils rather than a shear flow.

A convergent flow field can be generated in an extrusion flow process through a contraction, as illustrated in Figure 1.³⁰ Because of the flow contraction at the entrance of an extrusion die, the flow velocity must be increased in the capillary to retain a constant flow rate in volume. In this process, the melt will experience an extensional deformation because of the velocity difference in between the cylinder and the

capillary. Furthermore, in the capillary, there is a shear flow across the capillary radius. Therefore, a polymer melt entering a capillary die or any contraction will be forced to undergo both stretching and shearing due to the change in the cross-sectional area. A velocity profile in the converging flow confirms that the majority of extension occurs in the core region, and shear predominates in the outer regions of flow.³¹ After flowing through a critical length L_e of the capillary die, a shear flow profile will be fully developed and beyond L_e the shear flow profile remains unchanged.²⁷ The convergent flow region can be defined as the volume between the termination plane of the fully developed upstream flow in the cylinder and the starting plane of the fully developed downstream flow in the capillary (i.e., which is the region indicated by the length of $L_v + L_e$ in Fig. 1). In the downstream region of a constant diameter die, the shear flow predominates wherein the flow velocity becomes constant in the axial direction, and the flow is rearranged into a modified shear profile in the radial direction. The fluid on the die wall is highly sheared, whereas the fluid in the core flows is relatively unsheared. The velocity rearrangement occurs in the transition region from the extensional flow to the shear flow.

In this study, we examine effects of a convergent flow on development of TLCP fibrils in a thermoplastic matrix of PEN. PEN is a high-melt viscosity material so that it is difficult to be injection molded. Blending of a TLCP with PEN may reduce the melt viscosity and potentially result in interesting materials through the *in situ* reinforcement of TLCP.²³ In this work, a blend of 20 wt % TLCP and 80 wt % PEN is prepared by using a twin-screw extruder. Then, various flow conditions are obtained on a capillary rheometer by changing capillary diameter, extrusion temperature, or shear rate.

EXPERIMENTAL

Materials

TLCP used in this study is a copolymer of 4-hydroxybenzoic acid (HBA) and ethylene terephthalate (ET), with a proportion of 80% HBA to 20% ET. The material is produced by Unitika Ltd. (Japan) with a trade name of Rodrun LC 5000. The main chain of this TLCP contains the short aliphatic spacers in the backbone, which lead to a dramatic decrease in the melting point. The HBA/ET liquid crystalline polymer does not have a sharp transition temperature from a solid-crystalline state to a nematic one. Instead, there is a broad and relative low melting temperature range between 270 and 290°C for this polymer.

A commercial thermoplastic polymer, PEN, was chosen as the matrix for the TLCP/polymer blend because PEN has a melting temperature close to the nematic transition temperature of the TLCP. This

semicrystalline polymer, with a trade name of Eastman PEN Homopolymer 14991, was supplied by Eastman Chemical Co. The PEN polymer has a glass transition temperature of 120°C and a melting temperature of 250°C. It is confirmed by its thermal decomposition properties that this polymer is suitable for melt processing below 350°C.

Preparation of TLCP/PEN blends

The blends of TLCP and PEN were prepared by melt extrusion. Initially, the TLCP and PEN pellets were dried in a vacuum oven at 100°C for at least 12 h. A mixture of TLCP and PEN pellets with a weight ratio of 20% TLCP to 80% PEN was prepared at room temperature and then melt-blended by using the Haake Rheocord 90 twin-screw extruder. The temperature settings in the heating zones of the extruder were 280, 290, 295, 290, and 260°C from the hopper to the orifice, and the rotor speed was kept at 20 rpm. The blend extrudates from the orifice were quenched in a water bath and subsequently cut into small pellets.

Rheological characterization

In this study, a capillary rheometer (Rheograph 6000) was employed to determine the rheological properties of individual TLCP and PEN and the blend at different temperatures and shear rates. The viscosity ratios of the PEN matrix to the dispersed TLCP phase were then derived from the rheological results. The measurements of apparent viscosity were carried out by using a capillary die of $L/D = 20$ where L/D is the ratio of die length to diameter. A relatively long length die ($L = 20$ mm) was used to minimize the possible die end effects. The shear rate was varied from 50 to 5000 s^{-1} at each extrusion temperature of 275, 280, 290, and 300°C, respectively. In some cases, the shear rate was applied up to 8000 s^{-1} .

Convergent flow

Various convergent flow conditions were obtained by using different capillary diameters and shear rates. Three capillary diameters (0.5, 1, and 2 mm) were used. Because the internal diameter of the cylinder was 12 mm, the use of these capillary diameters gave area ratios of 576, 144, and 36 between the cylinder and the capillary, where a constant die length of 10 mm was used for all the three die diameters. In addition, the shear rate was varied from 50 to 5000 s^{-1} at the extrusion temperature of 290°C.

Morphological characterization

The blend melts extruded from the capillary rheometer were immediately quenched in ice water to freeze

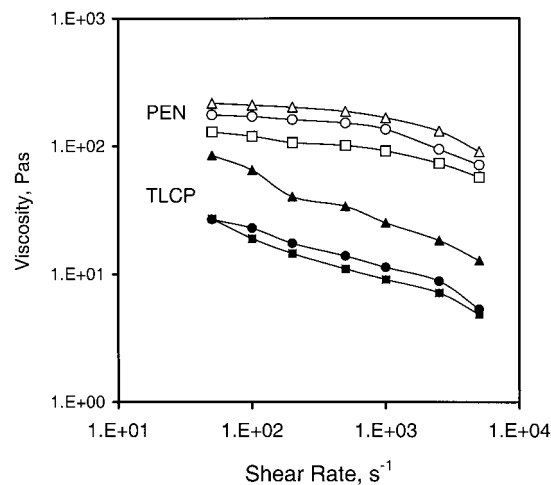


Figure 2 The apparent viscosity as a function of shear rate at various temperatures for individual TLCP (filled triangles: 280°C; filled circles: 290°C; filled squares: 300°C) and PEN (open triangles: 280°C; open circles: 290°C; open squares: 300°C). A capillary of 1 mm in diameter and 20 mm in length was used.

the morphology of the extrudate. The extrudates were directly fractured longitudinally (in the axial direction) into two halves at room temperature. For the specimens used for scanning electron microscopy (SEM Leica S360), they were then platinum sputter (Polaron SC7640) coated for electron conductivity.

RESULTS AND DISCUSSION

Viscosity ratio and blend viscosity

The apparent viscosity was measured at 275, 280, 290, and 300°C for each individual component: TLCP (LC5000) and PEN (14991). A capillary with a length of 20 mm and a diameter of 1 mm was used. As shown in Figure 2, at three temperatures (280, 290, and 300°C), PEN exhibits a shear-thinning behavior at high shear rates, whereas TLCP shows the shear thinning over the range of shear rate. The apparent viscosity of the TLCP is lower than that of the PEN in the whole range of shear rate (from 50 to 5000 s^{-1}) measured and TLCP is more shearing sensitive than PEN. As a result, the viscosity curves of the individual polymers do not cross over in the shear rate range to give a viscosity ratio of unity at any temperature applied. The viscosity ratio was directly calculated from the viscosity curves and given in Table I.

As shown in Table I, at each temperature, the viscosity ratio increases with shear rate, but its dependence on shear rate becomes weaker at higher shear rates. However, with increasing temperature, the viscosity ratio tends to increase too. At 290 and 300°C, the traces of the viscosity ratio are quite similar. From Table I, it is shown that the viscosity ratio of PEN to TLCP in the ranges of shear rate and temperature

TABLE I
Viscosity Ratios of PEN to TLCP Determined at Various Temperatures and Shear Rates Using a Capillary of Length 20 mm and Diameter 1 mm

$\dot{\gamma}$, s^{-1}	275°C	280°C	290°C	300°C
50	1.6	2.6	6.6	4.8
100	2.1	3.2	7.5	7.8
200	2.9	5.0	9.3	7.4
500	3.9	5.5	11.0	9.2
1000	5.0	6.6	12.0	10.1
2500	4.8	7.2	10.7	10.3
5000	5.2	7.1	13.4	11.8

varies between 1.6 to 13.4 so that the viscosity ratio is always greater than unity.

When these two polymers were melt blended with the fixed composition of 20 wt % TLCP and 80 wt % PEN, we compared the viscosity of the blend with that calculated by using the rule of mixture³²

$$\frac{1}{\eta_{\text{Blend}}} = \frac{w_{\text{TLCP}}}{\eta_{\text{TLCP}}} + \frac{w_{\text{PEN}}}{\eta_{\text{PEN}}} \quad (1)$$

where η_i is the viscosity of the component i or the blend as indicated, and w_i is the weight fraction of the component i . Two examples for the blend viscosity at 280 and 290°C are illustrated in Figures 3 and 4, respectively. As shown in Figures 3 and 4, the blend viscosity is considerably lower than that predicted by the mixing rule over the entire range of shear rate, indicating the negative deviation of the blend viscosity from the mixing rule. Furthermore, the blend viscosity is located between those of the component polymers only when the shear rate is higher than 500 s^{-1} at

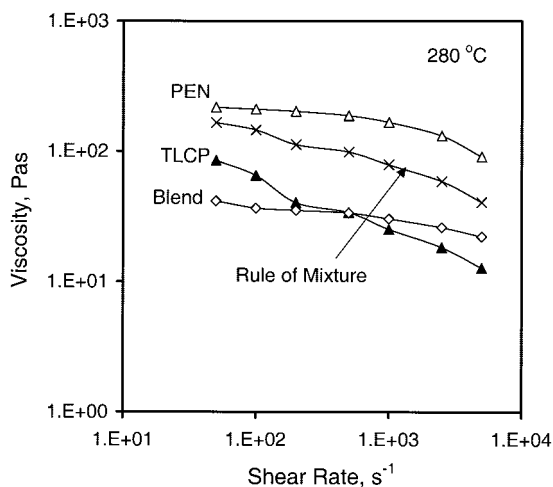


Figure 3 Apparent viscosity of the blend of TLCP/PEN at 280°C as a function of shear rate, indicated by open diamonds. The curve with cross marks was calculated by using the rule of mixture (eq. 1). The viscosity curves of individual components PEN (open triangles) and TLCP (filled triangles) are also presented here for comparison.

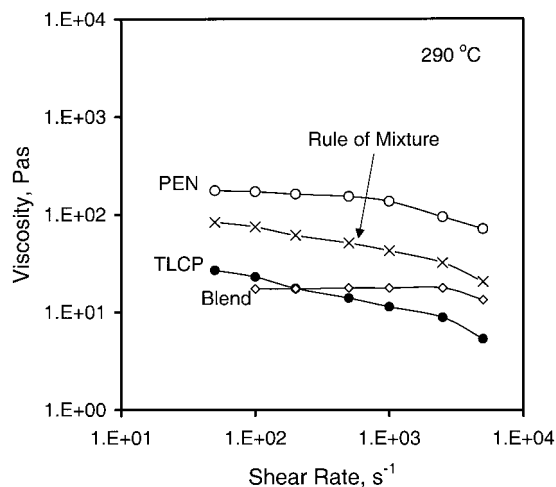


Figure 4 Apparent viscosity of the blend of TLCP/PEN at 290°C as a function of shear rate, indicated by open diamonds. The curve with cross marks was calculated using the rule of mixture (eq. 1). The viscosity curves of individual components PEN (open circles) and TLCP (filled circles) are also shown for comparison.

280°C or 200 s^{-1} at 290°C. The viscosity curve of the blend crosses over the viscosity curve of TLCP to separate them into two regions by a critical shear rate (500 s^{-1} at 280°C and 200 s^{-1} at 290°C). Below each critical shear rate, the blend viscosity is even lower than that of TLCP. The negative deviation from the mixing rule has been observed for many LCP/polymer blends.^{3,19,21,22} It was reported by Mantia et al. that the blend of nylon-6 and LCP showed similar viscosity to that of LCP at low shear rates but the blend viscosity became lower than that of each component at high shear rates.³ Their observation was explained to be due to the lack of interactions between the two phases and the formation of LCP fibrils at high shear rates.³ Similar results can also be found for other nylon/LCP blends.^{19,21,22} Except for these two factors, one may consider the effect of wall slip on the viscosity reduction during the capillary extrusion, especially at high shear rates. However, Chan et al. has concluded from the study of LCP/high-density polyethylene (HDPE) blends that the contribution of the wall slip to the viscosity reduction was negligible.²⁴

In general, if an immiscible polymer blend shows a negative deviation from the mixing rule of eq. (1), interfacial slip can be considered as one of the main causes for the negative deviation. Lam et al. recently developed a simple theoretical model to depict the interfacial slip between two layers each made of one polymer.^{28,29} It has been proven by them that the negative deviation from the mixing rule occurs only when there is an interfacial slip.²⁷⁻²⁹ On the other hand, however, for TLCP/thermoplastic blends, one has to consider other factors such as the flow-induced TLCP orientation that may promote the ease of flow (often referred as the *lubricating effect*^{7,18}) to result in a

lower blend viscosity. When the viscosity of the matrix polymer is higher than that of the dispersed TLCP, this effect would be more important because of more efficient transfer of shear deformation from the higher viscosity matrix phase to the lower viscosity dispersed phase, leading to more significant orientation of TLCP molecules.¹⁶

Effect of shear rate and shear strain

Shear rate plays a vital role in promoting fibrillation of LCP. When a polymer melt enters the capillary from the convergent region, the melt flow will be rearranged into a shear velocity profile, and this shear velocity profile is dependent on shear rate. Here, it is worth noting that the shear rate changes from a maximum value at the wall to a zero value at the center of the capillary. The dispersed TLCP fibrils or small droplets closest to the die wall will be highly sheared and aligned in the flow direction. Depending on shear rate, the state of the dispersed TLCP phase may vary between ellipsoids and microfibrils at a temperature in the nematic temperature range. The typical skin-core morphology is a result of shear rate effect, where LCP fibrils are formed only in the skin region and spherical and/or ellipsoidal forms of LCP exist in the core or center region.^{16,25} Many works have been carried out on effects of shear rate on *in situ* fibrillation of TLCP.^{3,4,16,18,21,25} For example, it was observed by Postema and Fennis from the PP/Vectra blends that at shear rates of 133 s^{-1} and higher the dispersed droplet phase of LCP was transferred into a fine fiber phase.¹⁸ Tan et al. recently reported for the blends of PC and Rodrum LC5000 that the shear rate had a significant effect on the fibrillation of the LCP phase and this effect was more prominent when the viscosity ratio ($\eta_{\text{TLCP}}/\eta_{\text{matrix}}$) was low.²⁵

In this work, Figure 5 illustrates the effect of shear flow on fibrillation at 290°C . At low shear rates (50 and 250 s^{-1}), there are only droplets dispersing in the matrix. With increasing shear rate, the fibrillar structures begin to appear at 1000 s^{-1} and they become pronounced at 2500 s^{-1} . Note that all the SEM micrographs presented in this article were taken from the longitudinal skin regions of extrudates.

At a given flow rate, the capillary length determines the time for the melt to pass through the capillary die. If there were not a shear flow profile in the capillary, the melt would not be well shear-deformed. When there is a shear flow profile, the capillary length will determine the shear strain experienced by the melt when it passes through the capillary (because shear strain = shear rate \times time). The TLCP fibrillation appears to develop only when the die length is beyond a critical length. For example, as proven in Figure 6, large droplets of 10 to $14 \mu\text{m}$ in diameter and no fibrous structures are observed at 290°C with the shortest capillary of 5 mm , regardless of the high shear

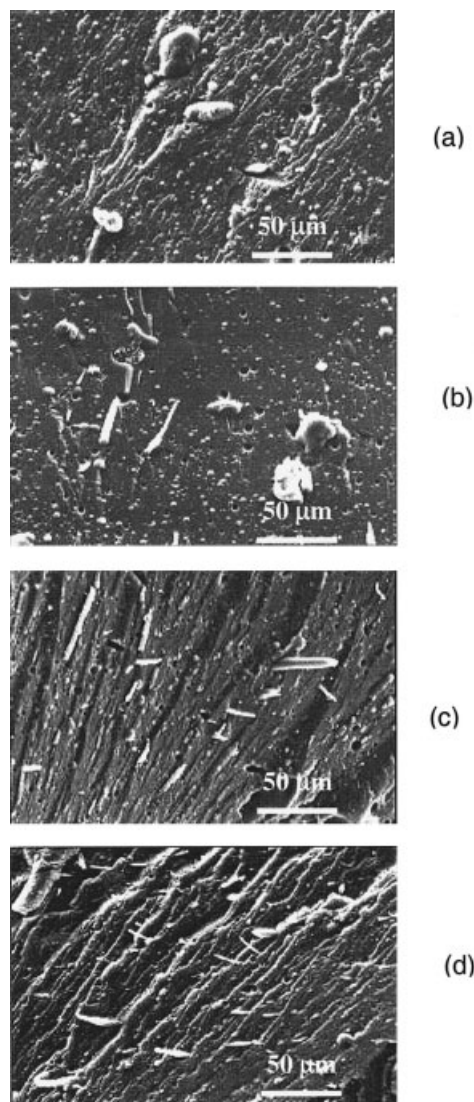


Figure 5 SEM micrographs for the fractured extrudates of TLCP/PEN blends, prepared at 290°C by using a capillary die of 1 mm in diameter and 30 mm in length and at various shear rates: (a) 50 s^{-1} , (b) 250 s^{-1} , (c) 1000 s^{-1} , and (d) 2500 s^{-1} .

rate of 5000 s^{-1} . It is also observed that with the die length of 5 mm no fibrillar structures of TLCP could be obtained. When a longer die length (10 – 30 mm) was used at similar processing conditions (temperature and shear rate), TLCP fibrils were produced [see Fig. 6(b–d)].

To explain this result, we here propose a concept about the necessity of establishment of a shear flow profile within the capillary geometry. When the capillary length is too short, a steady-state shear flow may not be reached within the capillary to allow establishment of a shear velocity profile. This means that within the short capillary the entrance effect has not dissipated and the elongated droplets by the convergent flow could not be rearranged by a steady-state flow to be well oriented in the flow direction. There-

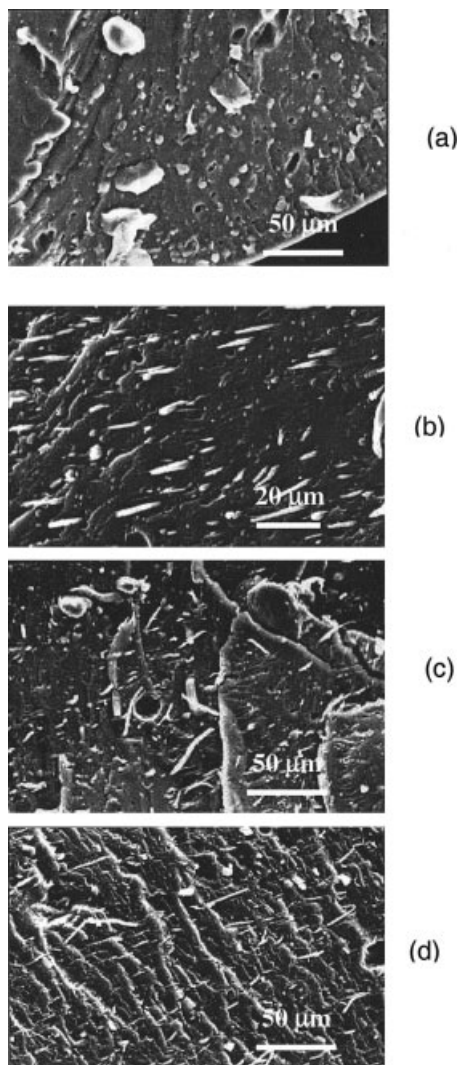


Figure 6 SEM micrographs for the fractured extrudates of TLCP/PEN blends, prepared at 290°C, and a shear rate of 5000 s⁻¹ using a capillary die of 1 mm in diameter and various lengths: (a) 5 mm, (b) 10 mm, (c) 20 mm, and (d) 30 mm.

fore, there should be a minimum capillary length (L_{cr} as shown in Fig. 1) for establishment of a steady-state shear flow profile and the minimum length should be dependent on flow rate.

When the capillary length is longer than the critical length, shear strain will play a major role both in rearranging the elongated TLCP particles to be oriented in the flow direction and in deforming them further into smaller particles and/or finer fibrils. However, to stay in the capillary for a longer time may not necessarily be better for further fibrillation of TLCP because of melt relaxation that may cause the fibrils to lose their shapes to become spherical again. Another factor that we have to take into consideration would be shear-induced coalescence. The longer the capillary length, the higher the probability of coalescence. It was proven by Mantia et al. from the blends of nylon and TLCP that fibrils of the LCP phase were

produced at high shear rates but they were lost during the shear flow in the long capillary.³

As illustrated in Figure 6, for a capillary die of diameter 1 mm, a length of 10 mm might be sufficient to allow the flow to arrange itself into a shear-velocity profile following the convergence. However, for the longer lengths ($L = 20$ and 30 mm), the orientation and fibrillation does not seem to improve very significantly compared to the case of 10 mm. This would be due to a balance between the shear-induced TLCP fibrillation and the melt relaxation or coalescence. In this work, unfortunately, extremely long capillary dies (e.g., 50 mm or longer) were not available to allow us to confirm the hypothesis.

Convergent flow and its effects

To examine effects of the convergent flow on TLCP fibrillation, three capillary diameters (i.e., 0.5, 1, and 2 mm) were used with a fixed capillary length of 10 mm. This allowed us to have three ratios of flow contraction (defined by the ratio of the cylinder cross-sectional area to that of the capillary), namely 576, 144, and 36, for the diameters of 0.5, 1, and 2 mm, respectively. Specimens were prepared at 280, 290, and 300°C and a high shear rate of 5000 s⁻¹ by using these three capillary dies. The morphological results are shown in Figures 7-9.

From these micrographs, it can be observed that the TLCP fibrillation and the fibril orientation are significantly improved with increasing capillary diameter at the same high shear rate. The use of the largest capillary diameter (2 mm) always produced the best fibrillation of TLCP in the matrix, regardless of the processing temperature. Interestingly, it is noted that even at the high temperature of 300°C, at which the TLCP fibrillation should be extremely difficult, the fine and well-oriented fibrils were still formed by using the 2 mm capillary diameter.

The above results seem to prove that the highest ratio of contraction (576) of cross-sectional area gave the poor fibrillation of TLCP, whereas the lowest ratio (36) promoted the fibrillation. At a constant volume flow rate, it is true that the extent of convergence or contraction is increased by decreasing the capillary diameter so that TLCP fibrillation should be promoted by increasing the extent of convergence. Under this circumstance, shear rate is increased when the capillary diameter is decreased. To help for understanding of the above arguments, we now provide some theoretical analysis.

Assuming that the fluid (polymer melt) is incompressible when undergoing a convergent flow and the subsequent shear flow in the capillary die, the volume flow rate Q should be the same through the cylinder and the capillary,

$$Q = \pi \frac{D^2}{4} V = \pi \frac{D_c^2}{4} V_c \quad (2)$$

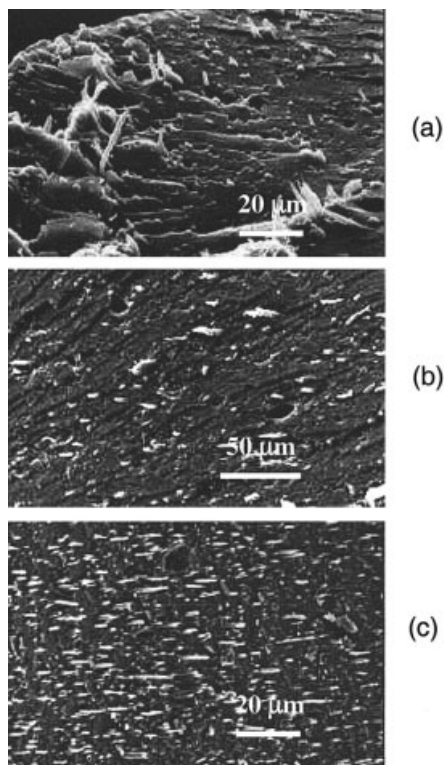


Figure 7 SEM micrographs for the fractured extrudates of TLCP/PEN blends, prepared at 280°C, and a shear rate of 5000 s⁻¹ using a capillary die with a fixed length of 10 mm but three different diameters: (a) 0.5 mm, (b) 1 mm, and (c) 2 mm.

where D and D_c are the diameters of the cylinder and the capillary, respectively, and V and V_c are the mean flow velocities in the cylinder and in the capillary, respectively. With an assumption of a Newtonian fluid, the apparent shear viscosity at the wall, $\dot{\gamma}_w$, is given by

$$\dot{\gamma}_w = \frac{D_c \Delta P}{4L\eta} = \frac{32Q}{\pi D_c^3} \quad (3)$$

where ΔP is the pressure drop, η is the fluid viscosity, and L is the capillary length. From eqs. 2 and 3, one obtains

$$\dot{\gamma}_w = \frac{8V_c}{D_c} \quad \text{or} \quad V_c = \frac{\dot{\gamma}_w D_c}{8} \quad (4)$$

and

$$V = \frac{\dot{\gamma}_w D_c}{8} \left(\frac{D_c}{D} \right)^2 \quad (5)$$

Therefore, the velocity difference between the cylinder and the capillary is

$$V_c - V = \frac{\dot{\gamma}_w D_c}{8} \left[1 - \left(\frac{D_c}{D} \right)^2 \right] \quad (6)$$

Equation 6 indicates that the velocity difference is only a function of shear rate $\dot{\gamma}_w$ for given D and D_c . Figure 10 shows plots of the velocity difference as a function of shear rate with three capillary diameters (0.5, 1, and 2 mm). The velocity difference becomes more significant when the shear rate is higher or the capillary diameter is larger. At a given shear rate, it is apparent that the larger the capillary diameter, the bigger the velocity difference when the capillary diameter D_c is smaller than a critical capillary diameter D_c^* . We derive D_c^* as follows.

To obtain the critical capillary diameter D_c^* at which the maximum velocity difference is given, the partial differentiation of $\Delta V (=V_c - V)$ is taken against D_c :

$$\frac{\partial(\Delta V)}{\partial D_c} = \frac{\dot{\gamma}_w}{8} \left[1 - 3 \left(\frac{D_c}{D} \right)^2 \right] \quad (7)$$

At $\partial(\Delta V)/\partial D_c = 0$, the following relation is obtained

$$D_c^* = \frac{D}{\sqrt{3}} \quad (8)$$

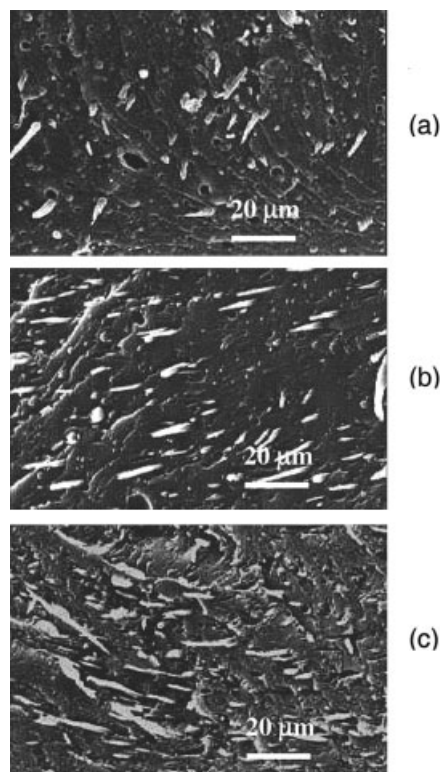


Figure 8 SEM micrographs for the fractured extrudates of TLCP/PEN blends, prepared at 290°C, and a shear rate of 5000 s⁻¹ using a capillary die with a fixed length of 10 mm and three different diameters: (a) 0.5 mm, (b) 1 mm, and (c) 2 mm.

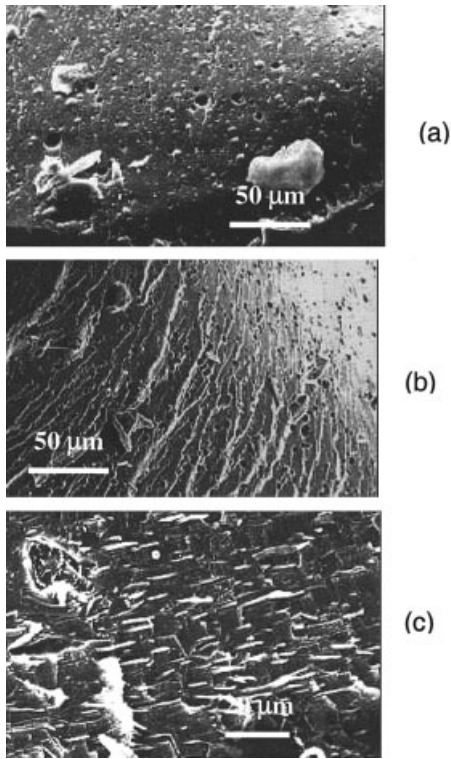


Figure 9 SEM micrographs for the fractured extrudates of TLCP/PEN blends, prepared at 300°C, and a shear rate of 5000 s^{-1} using a capillary die with a fixed length of 10 mm and three different diameters: (a) 0.5 mm, (b) 1 mm, and (c) 2 mm.

Therefore, for D is 12 mm, and D_c^* is 6.93 mm. This is clearly illustrated in Figure 11.

The curves in Figure 11 were obtained by using eq. 6 when the velocity difference was varied as a function of the capillary diameter D_c at each given shear rate. Figure 10 or 11 provides a map for choosing optimal conditions for TLCP fibrillation. For example, as it has been known that the condition of $D_c = 2 \text{ mm}$ and $\dot{\gamma}_w$

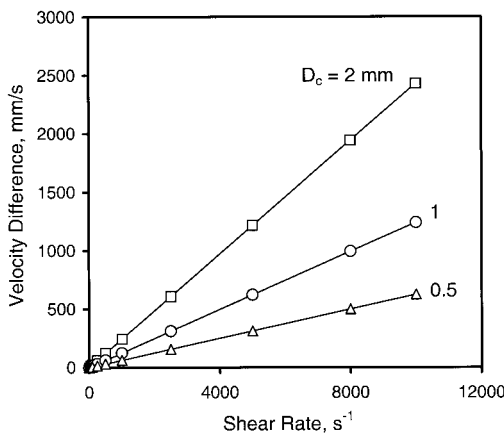


Figure 10 Flow velocity difference as a function of shear rate for three capillary diameters (0.5, 1, and 2 mm). The diameter of the cylinder is 12 mm.

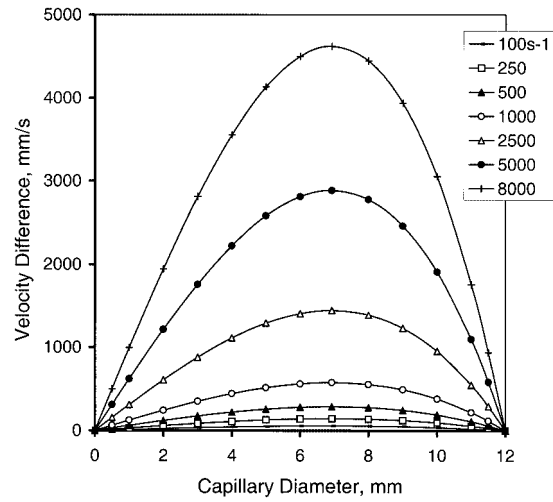


Figure 11 Flow velocity difference as a function of capillary diameter at various shear rates. The diameter of the cylinder is 12 mm.

$= 5000 \text{ s}^{-1}$ was favorable for the TLCP fibrillation, which had a velocity difference of 1215 mm/s, the shear rate has to be higher than $10,000 \text{ s}^{-1}$ to have the same level of velocity difference if a capillary diameter of 1 mm is used.

The effect of velocity difference is further considered by using a schematic description shown in Figure 12, where t is the time interval for the extensional deformation from the initial size X_0 to the stretched size X and ϵ is defined as the extensional strain. From the expression $\epsilon = \ln(1 + \Delta V t / X_0)$, one knows that the extensional strain is determined by three factors: the velocity difference, the time interval, and the initial size of the droplet. Thus, the extensive strain ϵ is increased by increasing the velocity difference or by increasing the time for the deformation.

Extensional deformation is considered to occur only in the convergent region that is between the termina-

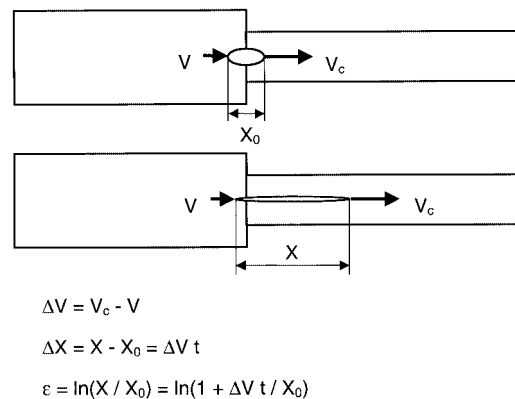


Figure 12 A schematic description on how a dispersed droplet at the capillary entrance is stretched by the flow velocity difference between its two sides, where V and V_c are the flow velocities in the cylinder and the capillary, respectively.

tion plane of the steady shear flow in the cylinder and the start plane of the steady shear flow in the capillary as shown in Figure 1, which has the length of $L_v + L_c$. The length of this region should be dependent on viscoelastic properties of the fluid, flow rate, and capillary diameter. In this convergent flow region, the velocity gradient possibly exists in the direction perpendicular to the flow direction so that there would be a shear flow in the region. Although it is extremely difficult to distinguish between the elongational effect and the shear effect on the TLCP fibrillation in the region of flow convergence, it would be reasonably assumed that extensional flow plays a vital role in stretching big spherical droplets into thin ellipsoids or fibrillar structures.

On the other hand, the major contribution of the subsequent shear flow is to align the stretched structures in the flow direction and/or to shear the dispersed domains further into smaller ones. Although this shear effect is pronounced in the region near the capillary wall, there would be no effects on TLCP fibrillation in the core region. Thus, in contrast, in the core region, as the dispersed domains are moving at similar rates and no further deformation is applied to them, the shape relaxation of deformed TLCP droplets could take place most pronouncedly. This may explain why it is extremely difficult to obtain the TLCP fibrillation in the core region.^{16,25} Therefore, it could be concluded that the optimal combination of an extensional flow and a shear flow is a necessary condition for the transformation of TLCP dispersed droplets into fibrils. This optimal combination of extensional and shear flows can be achieved by choosing an appropriate convergent flow.

CONCLUSION

The *in situ* fibrillation of TLCP in a PEN matrix has been investigated by varying capillary geometry (diameter and length), extrusion temperature, and shear rate. The effects of convergent flow on the TLCP fibrillation were examined experimentally and also analyzed through a simple theoretical approach.

It is considered that the complex combination of extensional and shear flows in a capillary extrusion process initiated the *in situ* fibrillation of TLCP. The shear rate played an important role in controlling the LCP fibrillation. For the blend studied in this work, no fibrillar structures of TLCP could be obtained when shear rates were below 1000 s^{-1} . At the high shear rate of 5000 s^{-1} , the LCP fibrillation could be obtained in most cases of capillary geometry, temperature, and shear rate, but it was important to find that the fibril-

lation was significantly improved with an increase in the capillary diameter. This was explained to be due to the increase in velocity difference between the flows in the cylinder and the capillary. Within the experimental range used in this work, it was found that the best fibrillation of TLCP could be obtained at temperatures from 280 to 300°C and at shear rates of 5000 s^{-1} or higher by using the capillary diameter of 2 mm with a length of more than 10 mm.

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