

# Morphology evolution of a liquid crystalline polymer confined by highly packed glass beads in polycarbonate

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## Abstract

Very long and perfectly oriented fibrils of a liquid crystalline polymer (LCP) were in situ formed in capillary flows by adding large amounts of glass beads (GB) to a polycarbonate (PC)/LCP blend. Thermodynamically the different interfacial tensions between the components made GB migrate to the LCP phase. Then the high content of GB spheres produced a confined condition, so that the LCP droplets passed through the simultaneously formed micro-capillaries, followed by being stretched into fibrils and stabilized consequently. © 2005 Elsevier Ltd. All rights reserved.

*Keywords:* Hybrid composites; LCP; Morphology

## 1. Introduction

In situ composite containing a liquid crystalline polymer (LCP) and a thermoplastic polymer is attractive in two ways: the LCP fibrillation during processing results in a ‘self-reinforced’ blend [1,2]; the LCP can sometimes act as a ‘processing aid’ reducing the melt viscosity [3]. Combining the concepts of the in situ composite and hybrid composite, in situ hybrid composite has been developed to gain better mechanical performance and processability [4–6]. These improvements strongly depend on the LCP morphology [7], which is greatly affected by the processing conditions [8–10], the viscosity ratio of the components [8, 11], LCP content [8–14], and the rheological properties of the matrix [15,16]. When additional hydrodynamic effects arise from the presence of fillers in in situ hybrid composites, the morphology evolution of LCP becomes more attractive and sometimes beyond the scope of the understanding of conventional binary blends.

Induced by different fillers, various hydrodynamic effects

affected the morphology evolution of LCP in various ways. Tjong et al. [17] described how the LCP fibrillation was prevented by the lower shear rate resulted from the presence of a higher content of whiskers in polyamide 6 (PA 6)/LCP composites. On the other hand, Lee et al. [16,18] introduced a spherical silica filler (SiO<sub>2</sub>) into polypropylene (PP)/LCP blends to serve as a viscosity thickening agent and to promote the fibrillation of LCP. Recently, the morphology evolution of polycarbonate (PC)/LCP and nylon 6/LCP blends affected by the addition of glass fiber (GF) and glass bead (GB) was investigated in our laboratory [19–22]. Interestingly, the LCP fibrillation was found promoted by the addition of certain content of GF or GB fillers. Considering the hydrodynamic effects induced by the GF and GB addition, He and coworkers suggested that LCP underwent elongational flow, which would favor the LCP fibrillation more effectively than simple shear flow. When the LCP droplets passed through the micro-capillary formed by the stacked glass fibers or the micro-rollers formed by the rotating glass beads, the elongational flow field developed. Furthermore, the stacks of glass fibers or the packing of glass beads can potentially provide confined conditions for the morphology evolution of LCP.

In this work, a series of in situ hybrid composites were prepared by adding a small amount of liquid crystalline polymer (LCP) and different volume fractions of glass beads (GB) to polycarbonate (PC). We investigate the morphology

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evolution of LCP with the presence of various contents of GB in the PC/LCP/GB composites and focus on the significant morphology evolution of the LCP resulted from the confinement of the highly packed GB spheres.

## 2. Experimental

### 2.1. Materials

Polycarbonate (PC), trade name Lexan101R with a room-temperature density of  $1.2 \text{ g/cm}^3$ , purchased from GE Plastics Shanghai Co., Ltd., China, was used as the matrix. The LCP used was a commercial thermotropic liquid crystalline copolyester (Vectra A950, Hoechst Celanese, USA), comprising of 73 mol% hydroxybenzoic acid and 27 mol% hydroxynaphthoic acid, hereafter referred to as VA. Its density in the solid state was  $1.4 \text{ g/cm}^3$ . Hollow glass beads (GB) with the trade name Cenosphere, kindly provided by Shenzhen Microspace Special Material Co., Ltd., China, were used as fillers. The average diameter and real density of GB were  $2 \mu\text{m}$  and  $2.3 \text{ g/cm}^3$ , respectively, according to the information of the manufacturer. All materials were dried in a vacuum oven at  $110 \text{ }^\circ\text{C}$  for at least 24 h before use.

### 2.2. Processing

PC was melt blended with 10 wt% VA together with 0, 5, 10, 20 and 30 vol% GB, respectively, to prepare PC/VA blend and PC/VA/GB composites. Melt blending was carried out by using a Haake RC90 Rheocord equipped with a twin-screw extruder at a fixed screw speed of 50 rpm. The temperature profile of barrel section from the feeding zone to the die was set at 240, 275, 275 and  $260 \text{ }^\circ\text{C}$ . The extruded strand was immediately water quenched, pelletized and vacuum dried at  $110 \text{ }^\circ\text{C}$  for at least 24 h.

The following equation was used to calculate the glass bead volume fraction,

$$V_{\text{GB}}(\text{in}\%) = (W_{\text{GB}}/\rho_{\text{GB}})/(W_{\text{GB}}/\rho_{\text{GB}} + W_{\text{PC}}/\rho_{\text{PC}} + W_{\text{VA}}/\rho_{\text{VA}}) \times 100\% \quad (1)$$

where  $V$ ,  $W$  and  $\rho$  represent the volume, weight and density, respectively. The VA content was fixed to 10 wt% in the present systems. For convenience, throughout the text and in the figures PC/VA/GB composites containing various amounts of GB are represented by PCVAGB $x$ , respectively, with the  $x$  as the part per hundred of GB by volume.

### 2.3. Morphological observation

First, capillary rheology experiments were conducted in a Rosand twin bore capillary rheometer, Model RH7-2 (Bohlin Instruments Ltd., UK), to measure the shear viscosity of the present systems over a wide shear rate

range ( $20\text{--}10,000 \text{ s}^{-1}$ ) at  $280 \text{ }^\circ\text{C}$ . Then the extrudates collected without any post-drawing were cryofractured and coated with a thin layer of gold. A field emission scanning electron microscope (SEM Hitachi S-4300) with an accelerating voltage of 15 kV was used to observe the fracture surface. The extrudates were also immersed in 1,2-dichloroethane for at least 24 h to dissolve the PC matrix, and the residue was collected and dried for morphological analysis.

## 3. Results and discussion

### 3.1. Formation of long LCP fibrils

Fig. 1 shows SEM images of PCVAGB30 extruded from a capillary rheometer at a shear rate of ca.  $1260 \text{ s}^{-1}$ . The extrudates were cryofractured parallel to the main flow direction (Fig. 1a). As Fig. 1a shows, there are LCP fibrils and GB spheres coexisted in the ternary composite. The lengths of these LCP fibrils are more than  $20 \mu\text{m}$  and their diameters ca.  $1\text{--}3 \mu\text{m}$ , respectively. Moreover, these LCP fibrils with large aspect ratios are found oriented in the flow direction.

The deformation and orientation of LCP droplets are more observable as shown by SEM images of the residue of PCVAGB30, centrifugally extracted from the supernatants after selectively dissolving the matrix PC, with different magnifications (Fig. 1b and c). Very long even nearly continuous LCP fibrils, with large aspect ratios  $>20$ , exist in the residue and perfectly align along the same direction. In addition, some LCP fibrils branch off and connect with each other, forming a network texture.

Such a continuous fibrous structure or network texture of LCP usually formed at higher LCP contents [8,11–14] or at very small viscosity ratio ( $<0.01$ ) of the dispersed phase to the continuous phase [23]. In the case of larger viscosity ratio, good fibrillation of the dispersed phase could be obtained by hot-drawing [13,18,24] or coextrusion method [25]. Consider the present PC/VA/GB composites. First, the LCP content in these composites was not very high (10 wt% in total and 11–18 wt% in the corresponding PC/VA system). Secondly, the viscosity ratio of these composites was larger than unity because the GB addition increased the viscosity of VA but decreased the viscosity of PC and the composites (the rheological data are not shown here). Thirdly, neither hot-drawing nor coextrusion method was used to prepare the composites and moreover, special care was taken to avoid any post-drawing during sampling. It seemed impossible to make LCP deform to long and perfectly oriented fibrils in the present composites.

Fig. 2 shows SEM images of the residues of PCVA blend and PCVAGB5, PCVAGB10 and PCVAGB20 composites extruded at  $1260 \text{ s}^{-1}$ . As expected, most LCP particles preserve the shape of ellipsoid with aspect ratios  $<5$  for PCVA blend (Fig. 2a), suggesting that the LCP droplets

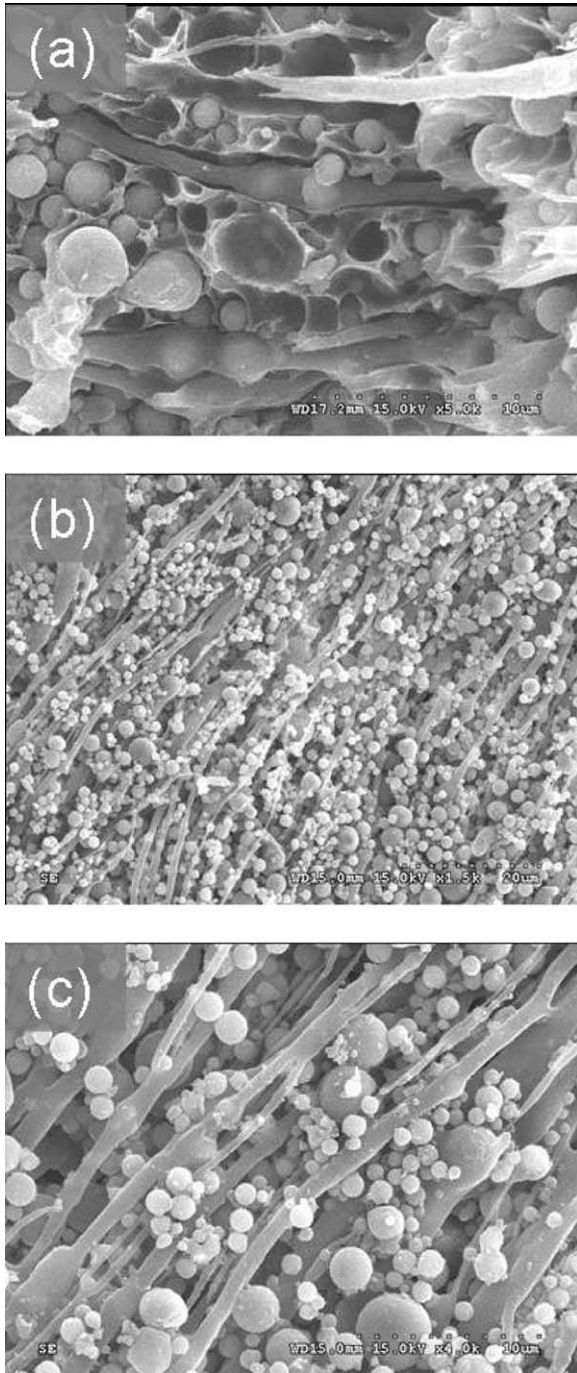


Fig. 1. SEM images of PCVAGB30 extruded from a capillary rheometer at a shear rate of ca.  $1260 \text{ s}^{-1}$ . (a) Cryofractured surface parallel to the main flow direction ( $\times 5000$ ); extracted residue under (b) lower magnification ( $\times 1500$ ) and (c) higher magnification ( $\times 4000$ ).

underwent only slight deformation without the GB addition even at a higher shear rate. With small amounts of GB added, there is promoted fibrous structure of LCP developed for PCVAGB5 composite (Fig. 2b). However, the LCP fibrils become thicker and shorter and even retract to ellipsoids for PCVAGB10 and PCVAGB20 composites, implying inferior LCP fibrillation at increased GB loadings (Fig. 2c and d).

### 3.2. Migration of GB to LCP phase

It is interesting to find that some spheres, 1–3  $\mu\text{m}$  in diameter, cling to and even enter into the LCP particles, as shown in Fig. 2d. Energy dispersive X-ray (EDX) element analysis performed on the samples identified these spheres as glass beads (the EDX element maps are not shown here).

In fact, the migration of GB spheres to LCP droplets became more frequent in the most highly filled system, PCVAGB30. This is observable in Fig. 1, but much clearer in Fig. 3, where SEM images of the residues of PCVAGB30 extruded at lower shear rates of ca. 20 and  $158 \text{ s}^{-1}$  are shown with different magnifications. It appears that the LCP particles, several microns in diameter, are enclosed by smaller GB spheres. More importantly, most of the LCP particles are spherical or ellipsoidal in shape, indicating a very limited deformation of the LCP droplets in PCVAGB30 extruded at lower shear rates.

The migration of GB spheres to LCP droplets may imply a strong affinity between the GB spheres and the LCP phase in the present PC/LCP/GB systems. Now consider the wetting coefficient,  $\omega$  [26]

$$\omega = \frac{\gamma_{\text{GB-VA}} - \gamma_{\text{GB-PC}}}{\gamma_{\text{PC-VA}}} \quad (2)$$

where  $\gamma_{\text{GB-VA}}$ ,  $\gamma_{\text{GB-PC}}$ ,  $\gamma_{\text{PC-VA}}$  are the interfacial tensions between GB and VA, GB and PC, PC and VA, respectively. If  $\omega < -1$ , the GB spheres will be of selective affinity for VA.

The interfacial tensions between the components are determined with harmonic mean equation and geometric mean equation, respectively [27]

$$\gamma_{\text{PC-VA}} = \gamma_{\text{PC}} + \gamma_{\text{VA}} - \frac{4\gamma_{\text{PC}}^{\text{d}}\gamma_{\text{VA}}^{\text{d}}}{\gamma_{\text{PC}}^{\text{d}} + \gamma_{\text{VA}}^{\text{d}}} - \frac{4\gamma_{\text{PC}}^{\text{p}}\gamma_{\text{VA}}^{\text{p}}}{\gamma_{\text{PC}}^{\text{p}} + \gamma_{\text{VA}}^{\text{p}}} \quad (3)$$

$$\gamma_{\text{A-B}} = \gamma_{\text{A}} + \gamma_{\text{B}} - 2(\gamma_{\text{A}}^{\text{d}}\gamma_{\text{B}}^{\text{d}})^{1/2} - 2(\gamma_{\text{A}}^{\text{p}}\gamma_{\text{B}}^{\text{p}})^{1/2} \quad (4)$$

where  $\gamma_{\text{PC}}$  and  $\gamma_{\text{VA}}$  are the surface tensions of PC and VA, the superscripts d and p denote the dispersion and polar components of the surface tension, the subscripts A and B denote polymers and filler, respectively. Corresponding values of the surface tension are taken from literature [28–30] and listed in Table 1.

According to Eqs. (3) and (4), the values of interfacial tensions  $\gamma_{\text{GB-VA}}$ ,  $\gamma_{\text{GB-PC}}$ , and  $\gamma_{\text{PC-VA}}$  are given in Table 2. Then a wetting coefficient of  $-6.6$  (satisfy  $\omega < -1$ ) is

Table 1  
Surface tension of polymers and glass beads [26–28]

	Surface tension (mN/m)		
	Total ( $\gamma$ )	Disperse component ( $\gamma^{\text{d}}$ )	Polar component ( $\gamma^{\text{p}}$ )
PC	24.6	18.0	6.6
VA	37.69	28.96	8.72
GB	257.7	94.7	163.0

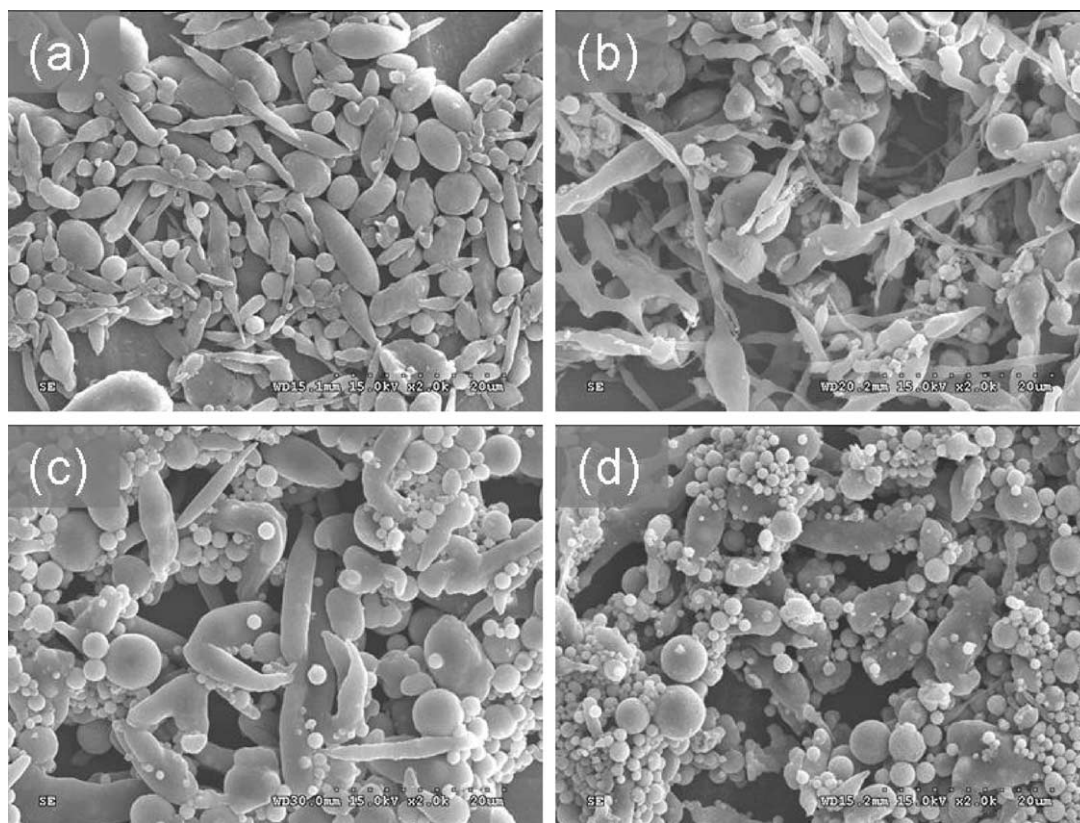


Fig. 2. SEM images of residues extracted from the binary and ternary PC composites filled with various contents of GB at a shear rate of ca.  $1260 \text{ s}^{-1}$ . The content of GB is (a) 0, (b) 5, (c) 10 and (d) 20 vol%.

obtained using Eq. (2), confirming a strong affinity between GB and the LCP phase.

It has been reported that the preferential residence of filler particles in the LCP phase would inhibit the LCP deformation [31]. This inhibition in the LCP fibrillation took place for PCVAGB30 composite at lower shear rates and for PCVAGB20 and PCVAGB10 composites even at higher shear rates in the present study. But it remains inexplicable how the LCP droplets deformed to nearly continuous and perfectly oriented fibrils in the most highly filled system, PCVAGB30, by extrusion simply at higher shear rates.

### 3.3. LCP fibrillation under confined conditions

From the viewpoint of droplet deformation mechanisms [32], the initial spherical droplets are driven to deform by an

elongational flow more effectively than by simple shear. Further, it is widely accepted that the elongational flow developed in the entry of the capillary is mainly responsible for the LCP fibrillation during a capillary extrusion [33]. In an in situ hybrid composite containing LCP droplets and filler particles dispersed in a polymer matrix, extra hydrodynamic effects arise from the presence of filler particles and act on the morphology evolution of the LCP phase.

In previous studies [21,22], we discussed two kinds of significant hydrodynamic effects promoting the LCP fibrillation: a strong extensional action of the micro-rollers of the glass beads and an enhanced local shear between the neighboring glass beads. Both effects originated from the rotation of the GB spheres in shear flow at moderate concentrations. However, the rotation of GB spheres would weaken in such a highly filled system as the present PCVAGB30 composite. In this situation, the GB spheres migrate to the LCP droplets due to the selective affinity between the GB spheres and the LCP phase. As a result, the LCP droplets were actually confined within the narrow interstices between these closely packed GB spheres.

Fig. 4 schematically illustrates the morphology evolution of LCP droplets confined by the glass beads when the highly filled system, such as PCVAGB30, was extruded through a convergent capillary die. If the GB spheres had been

Table 2

Interfacial tension between the possible polymer–polymer and polymer–filler pairs

Possible pairs	Interfacial tensions (mN/m)
$\gamma_{\text{PC-VA}}$	2.86
$\gamma_{\text{PC-GB}}$	134.13
$\gamma_{\text{VA-GB}}$	115.25

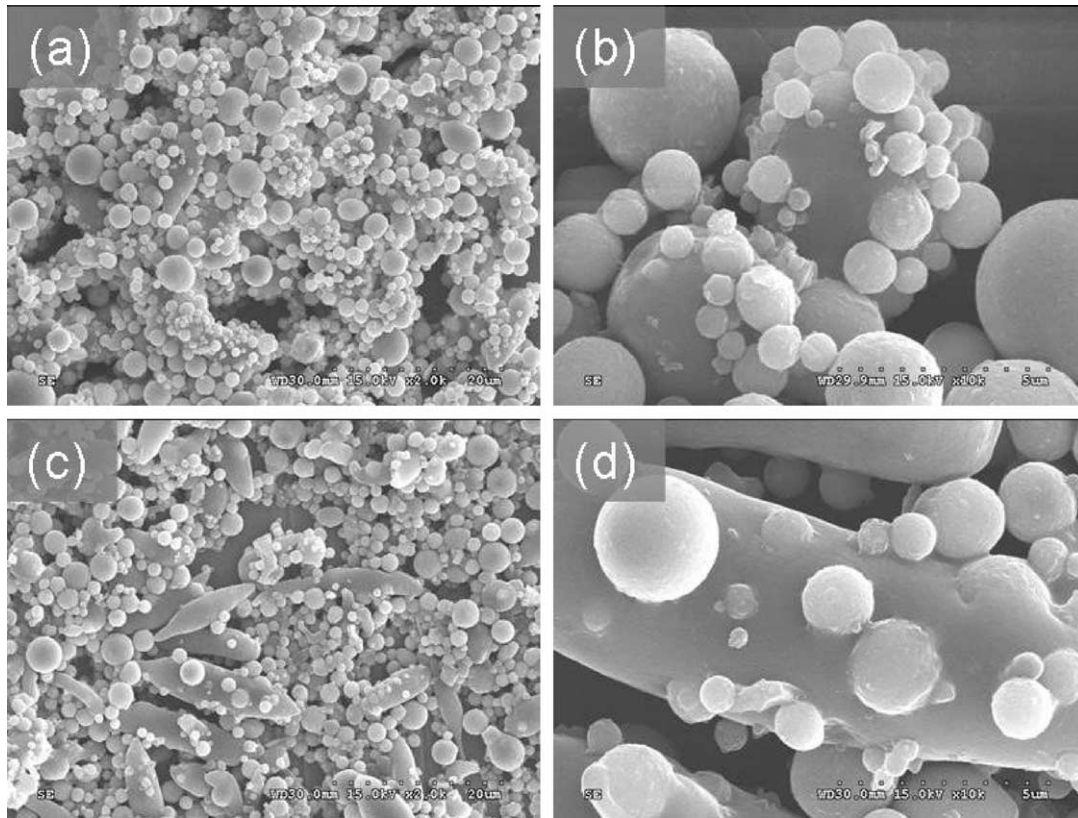


Fig. 3. SEM images of residues extracted from PCVAGB30 extruded from a capillary rheometer at shear rates of (a), (b)  $20 \text{ s}^{-1}$  and (c), (d)  $158 \text{ s}^{-1}$  under (a), (c) lower magnification ( $\times 2000$ ) and (b), (d) higher magnification ( $\times 10,000$ ).

dispersed uniformly in PCVAGB30, the average gap between them could be calculated to be ca.  $1.4 \mu\text{m}$  for cubic packing [Eq. (5)] and  $1.1 \mu\text{m}$  for hexagonal packing [Eq. (6)], respectively.

$$g_c = \left( \sqrt[3]{\frac{\phi_{mc}}{\phi} \sqrt{2}} - 1 \right) d \quad (5)$$

$$g_h = \left( \sqrt[3]{\frac{\phi_{mh}}{\phi} \frac{2}{\sqrt{3}}} - 1 \right) d \quad (6)$$

where  $g$  is the average gap between the GB spheres, the subscripts  $c$  and  $h$  denote cubic packing and hexagonal packing,  $\phi_m$  the maximum volume fraction with its value equaling to 0.524 for close cubic packing and 0.74 for close hexagonal packing [34],  $\phi$  and  $d$  the volume fraction and diameter of the GB spheres, respectively.

Therefore, the actual value of the average gap between the randomly dispersed GB spheres was ca.  $1.1\text{--}1.4 \mu\text{m}$ , being equivalent to the diameters of the stretched LCP fibrils but much smaller than the initial LCP droplets size (ca.  $3\text{--}5 \mu\text{m}$ ). Naturally, the larger LCP droplets had to deform for passing through the smaller interstices between the GB spheres. On the other hand, each interstice acted as a microcapillary, in the entry of which elongational flow prevailed and stretched the approaching LCP droplets to long and thin fibrils. It should be noted that such LCP fibrils confined within a microcapillary would be more stable than those simply dispersed in another liquid, as theoretically

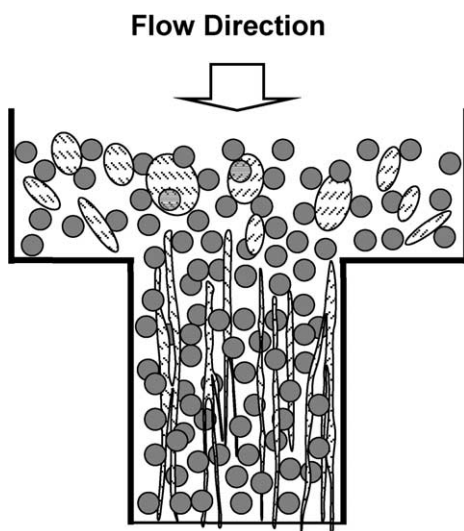


Fig. 4. Schematic diagram of the morphology evolution of LCP (⊗) confined by highly packed GB spheres (●) when passing through a capillary die.

predicted by Chin and Han [32]. From this viewpoint, it appears that the nearly continuous and perfectly oriented LCP fibrils were formed and stabilized in the present system in a way similar to the coextrusion process.

#### 4. Conclusions

This paper has presented the morphology evolution of LCP confined by highly packed GB spheres in a PC matrix. The confinement originated from the thermodynamical affinity of the GB spheres to the LCP phase and the higher GB loading. Nearly continuous and perfectly oriented LCP fibrils were obtained in the confined situation, where the LCP fibrils were formed and stabilized when passing through the micro-capillaries formed by the GB spheres at high shear rates. This phenomenon of the LCP fibrils formation and stabilization is beyond the scope of the understanding of conventional binary blends. More detailed studies of the origin and mechanism of the LCP fibrillation under such confined condition, and the mechanical and rheological properties of these highly filled in situ hybrid composites are in progress.

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