

## ***In-situ* hybrid composites containing reinforcements at two orders of magnitude**

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By combining the concepts of the *in-situ* composite and hybrid composite, a concept of *in-situ* hybrid composites has been put forward. A composite structure of polyethersulfone reinforced by carbon fibres (CF) and thermotropic liquid crystalline polymer (TLCP) fibrils has been formed in injection-moulded bars by matching the characteristics and processing conditions of the TLCP and the matrix resin. These TLCP fibrils with large intrinsic aspect ratios are generated *in-situ* in the melt of the resin matrix during the processing of the ternary blends. This technique uses TLCPs to decrease the viscosity of the whole blend systems and to minimize the CF breakage as well. The improved processability is especially beneficial for the processing of advanced engineering plastics. This technique, forming reinforcements at two orders of magnitude in the resultant composites, utilizes these two reinforcements to balance the enhanced mechanical properties of the hybrid composites. © 1997 Elsevier Science Ltd.

(Keywords: *in-situ* composites; hybrid composites; fibre-reinforced plastics)

### *Introduction*

Advanced engineering plastics can be reinforced by macroscopic fibres such as carbon fibre, glass fibre and aramid fibre. These macroscopic reinforcements contribute to the large increase of the strength and modulus of the resultant composites. In order to obtain a high-strength, high-modulus and heat-resistant polymer composite, a high fibre content (up to 30%, 45% and even 60% by weight) is needed. However, the high percentage of fibre content will worsen the already bad processability of heat-resistant resins. In a sense, the processability of advanced engineering plastics determines the fulfillment of their excellent performances.

Thermoplastics can be reinforced by thermotropic liquid crystalline polymer (TLCP) fibrils generated *in-situ* during melt processing of blend systems<sup>1-4</sup>. The advantages of these so-called *in-situ* composites, attributed to the molecular rigidity of TLCPs, are indicated by the decrease of the melt viscosity and the increase of the strength and modulus of the whole blend. Although this approach to the reinforcement of thermoplastics has been a hot-spot of basic and applied researches for one decade, the prospect of these *in-situ* composites containing TLCP fibrils seems not as bright as previously expected. One of the main reasons is the limited improvement of mechanical performances achieved only by TLCP fibrils.

In the present research, a concept of *in-situ* hybrid composites is put forward. A reinforced structure in a ternary system, consisting of carbon fibres, TLCP fibrils and a heat-resistant resin, has been formed. This technique uses TLCPs to decrease the viscosity of whole blend system and to minimize the breakage of carbon fibres as well. The improved processability is especially

beneficial for the processing of advanced engineering plastics. This technique, forming the reinforcements with their diameters at two orders of the magnitude in the resultant material, utilizes these two reinforcements to balance the enhanced mechanical properties of the hybrid composites. Together with extending the area of multi-component and multi-phase polymeric materials, this technique raises new topics for material engineers and scientists.

It should be noticed that there is not barely a simple addition of TLCP into fibre-reinforced plastics in this research. Its key point is the formation of TLCP fibrils in the ternary system. Baird *et al.*<sup>5</sup> used glass fibre to decrease the anisotropy of TLCP fibril-reinforced polyetherimide. The authors<sup>6</sup> improved the processability and mechanical performances of glass fibre-reinforced polypropylene by the addition of TLCP. However, these two works did not actively and purposely generate a reinforced composite with the reinforcements having their diameters at two orders of magnitude.

### *Experimental*

The thermotropic liquid crystalline polymer used in this research was an aromatic copolyester, Rhodester (Rhone-Poulenc, France). The matrix polymer was polyethersulfone (PES), synthesized at Jilin University, China, with an *IV* of 0.38 dl g<sup>-1</sup> in *N,N*-dimethylformamide at 25°C. The carbon fibre, with tensile strengths of 232-261 kg mm<sup>-2</sup>, was produced and electrodeposited with a copolymer of styrene-*co*-maleic anhydride<sup>7</sup> at the Shanghai Carbon Works, China.

Pellets of PES and TLCP were dried in vacuum at 100°C for at least 6 h before the melt processing. Carbon fibres were cut to segments of about 1 cm in length. PES pellets and TLCP pellets were melted and mixed with chopped carbon fibres in different fractions. TLCP/CF/PES blends containing *x*wt% TLCP, *y*wt% carbon

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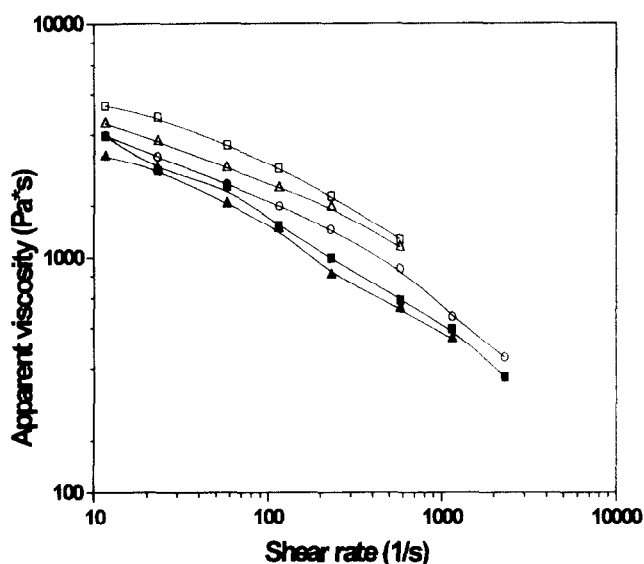


Figure 1 Apparent viscosities of PES (○), CF/PES 5/95 (△), CF/PES 10/90 (□), TLCP/CF/PES 5/5/95 (▲), and TLCP/CF/PES 5/10/90 (■) as a function of shear rate at 340°C

fibres and  $z$ wt% PES will henceforth be denoted by TLCP/CF/PES  $x/y/z$  in this article.

The melt blending of TLCP, CF and PES was conducted on a CS-194A Max Mixing Extruder (CSI Company, USA) with the rotor temperature set at 350°C, the header temperature at 340°C and the rotor speed at 50 revolutions  $\text{min}^{-1}$ . The extrudates were pelletized by a chopper and injection-moulded into cylindrical dumbbell samples with a CS-183 Mini Max Moulder (CSI Company, USA). The melt temperature was 350°C and the mould temperature 170°C. Tensile strengths and moduli of these dumbbell samples were measured with a CS-183 TE Mini Max Tensile Tester at ambient temperature. Tensile tests at an elongation rate of 1.58  $\text{mm min}^{-1}$  were performed on samples with an overall length of 22.22 mm and a diameter of the narrow section of 1.58 mm.

The rheological properties of the component polymer and its blends were measured using a capillary rheometer (Göettfert Rheograph 2001) at 340°C. A capillary die of 1 mm diameter with a  $L/D$  ratio of 30 was used. The entrance correction was not applied.

The microstructure of the injection-moulded bars was observed with a scanning electron microscope (SEM) (Hitachi S-530). *N,N*-Dimethylformamide was used to dissolve the matrix PES selectively from these bars. The TLCP and CF were separated by centrifuging the solution and decanting the supernatant liquid. The

centrifuged TLCP and CF were immersed in fresh solvent and separated twice more. Finally, a drop of the residue was observed with SEM. The diameter and intrinsic aspect ratio of TLCP droplets and fibrils, and carbon fibres were measured with a Cambridge Instrument Quantimet 520 Image Analysis System.

#### Results and discussion

Figure 1 shows the rheological behaviour of PES, CF/PES and their blends with TLCP. In the range of shear rate of  $10^1$ – $10^4$   $\text{s}^{-1}$ , all the melts show rheological behaviour of non-Newtonian fluids, indicated by the decrease of their apparent viscosities with increasing shear rate. The viscosity of CF/PES is higher than that of PES and increases with increasing CF content. However, upon the addition of 5 wt% TLCP to CF/PES 5/95 and CF/PES 10/90, the viscosities of the resultant TLCP/CF/PES 5/5/95 and TLCP/CF/PES 5/10/90 are lower than those of CF/PES blends, and even lower than that of pure PES. It is well known that with the addition of macroscopic fibres to thermoplastics the viscosity of the composites increases greatly. This usually causes many problems in melt processing, such as the fibre breakage, the wear of processing equipments. The addition of TLCP to CF/thermoplastics blends results in the viscosity reduction of the blends so that leads to a more acceptable processability of TLCP/CF/thermoplastics.

By matching the characteristics of the TLCP and PES, including the spinnability of TLCPs and the viscosity ratio of the TLCP to the matrix<sup>8–10</sup>, TLCP fibrils have been generated in injection-moulded bars of ternary TLCP/CF/PES blends. SEM micrographs in Figure 2 show TLCP fibrils and carbon fibres extracted from a TLCP/CF/PES 15/5/95 injection-moulded bar. Figure 3 shows the diameter distribution of these CFs and TLCP fibrils. It is evident that this ternary blend bar contains two kinds of reinforcements with their diameters at two orders of magnitude, i.e. the macroscopic CF with the diameter of about 7.5  $\mu\text{m}$  and the microscopic TLCP fibrils with the diameter in the range of 0.5–1.5  $\mu\text{m}$ . The resultant PES composite is named as the *in-situ* hybrid composite, which comes from its two reinforcements, carbon fibres and TLCP fibrils, with their diameters at two orders of magnitude and from the *in-situ* formation of TLCP fibrils in the melt processing of the composite.

Figure 4 shows the aspect ratio distribution of TLCP fibrils in a TLCP/CF/PES 15/5/95 injection-moulded bar. The aspect ratios of TLCP fibrils reached 30. This is achieved by using a TLCP with good spinnability and matching the processing conditions for favouring the fibrillation of TLCP. However, the major portion of

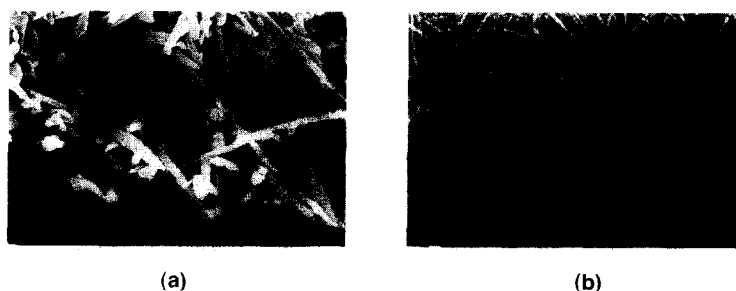


Figure 2 SEM micrographs of TLCP fibrils (a) and CFs (b) in a TLCP/CF/PES 15/5/95 injection-moulded bar after the extraction of PES matrix

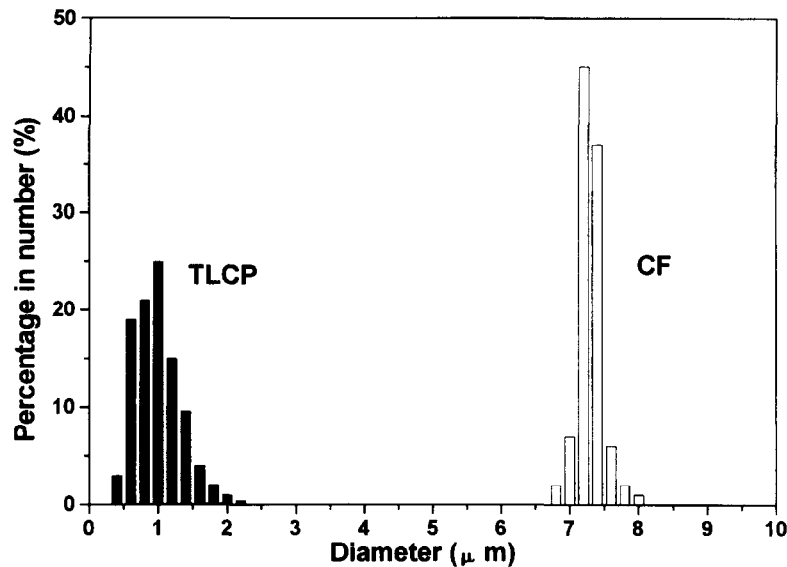


Figure 3 The diameter distribution of TLCP fibrils and CFs in a TLCP/CF/PES 15/5/95 injection-moulded bar

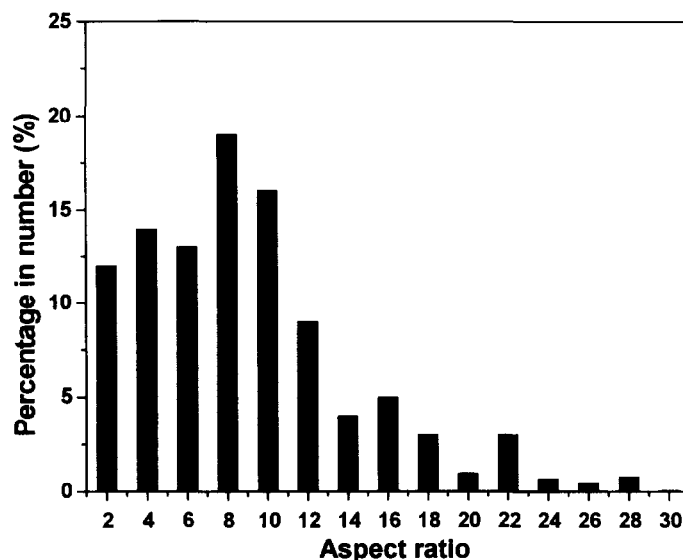


Figure 4 The aspect ratio distribution of TLCP fibrils in a TLCP/CF/PES 15/5/95 injection-moulded bar

TLCP fibrils has lower aspect ratios, which decreases the reinforcing effect of the fibrils. Larger aspect ratios can be reached by stretching the TLCP/CF/PES extrudates. But a main application of *in-situ* hybrid composites should be accomplished by injection-moulding. The difficulty of generating TLCP fibrils with much larger aspect ratios in injection-moulded bars limits the application of TLCPs in structural materials up to now.

It is known from composite mechanics when short fibres are added to the polymeric matrix, many defects such as voids, cracks, foreign inclusions and fibre misorientation are formed in the interphase between the fibre and the matrix. These original defects greatly decrease the mechanical properties of the composites. However, no such problems exist in the interphase between the TLCP and the matrix, because reinforcing TLCP fibrils are formed *in-situ* in the matrix during melt processing of extrusion or injection-moulding. In another consideration, when composite materials fracture, the cracks will propagate along the interphase between the reinforcement and the matrix and be blocked by fibres.

Based on the density of CF at  $1.8 \text{ g cm}^{-3}$  and PES at  $1.37 \text{ g cm}^{-3}$ , in a TLCP/CF/PES composite with the same weight fractions of CF and TLCP, the volume of TLCP fibrils is 1.3 times of that of CF. One order of magnitude smaller in the diameter of TLCP fibrils leads to a total length of TLCP fibrils 100 times longer than that of CF. As a result, the total surface area of TLCP may be 13 times larger than that of CF. The large surface area of TLCP phase makes TLCP fibrils play the primary role to resist the propagation of microcracks in the TLCP/CF/PES composite. So it is predicted that the mechanical properties of TLCP/CF/PES composites will be significantly improved with the addition of TLCPs. From the view-point of composite mechanics, the *in-situ* hybrid composite has an ideal structure.

The decrease of the melt viscosity of blends decreases the CF breakage. The aspect ratio distribution of CFs in TLCP/CF/PES injection-moulded bars with different CF contents is shown in Figure 5. In these composites, the weight fraction of CF is fixed, while the weight fraction of the TLCP increases from 0 to 15 wt%. From these

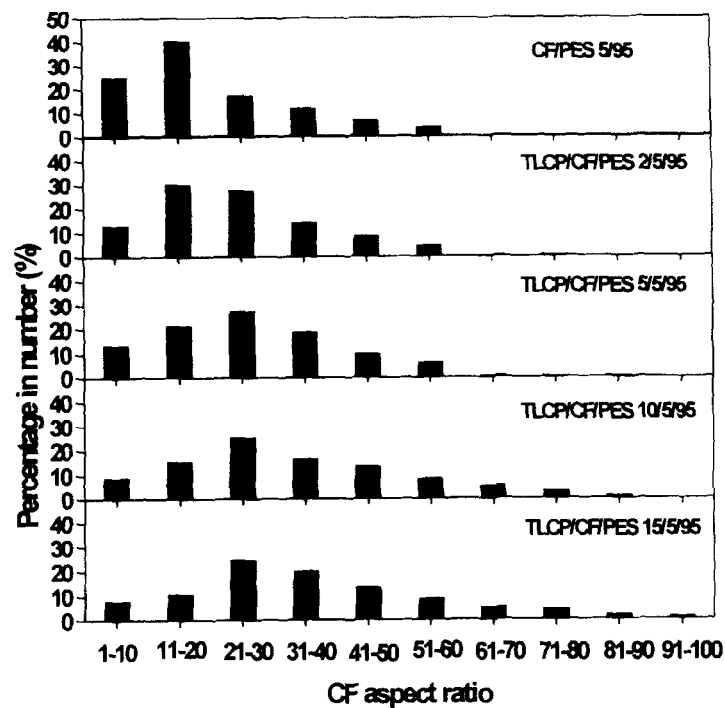


Figure 5 The aspect ratio distribution of CFs in TLCP/CF/PES injection-moulded bars with different CF contents

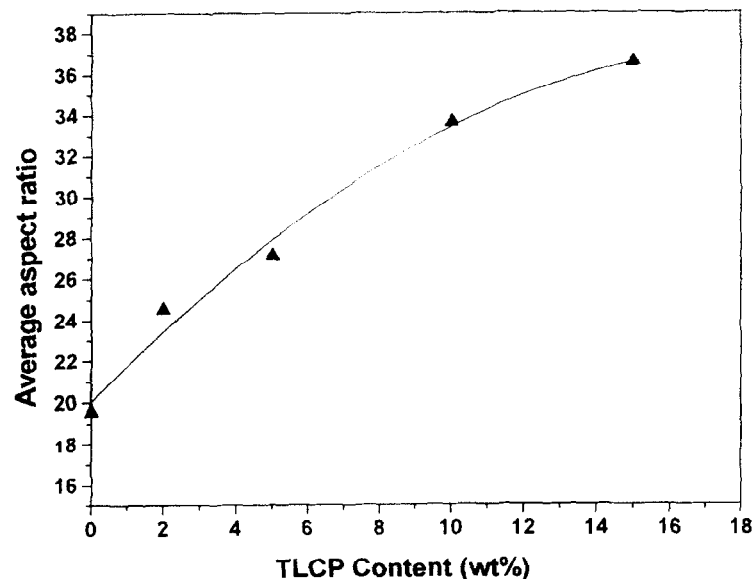


Figure 6 The number-average aspect ratio of CFs versus TLCP content in TLCP/CF/PES bars with 5 wt% CF

figures, it is clear that the fibre length depends greatly upon the TLCP concentration. Increasing TLCP content increases the number-average aspect ratio of CF in the sample (Figure 6). Higher melt viscosity with a low TLCP concentration results in the breakage and damage of carbon fibres during the processing. So in other words, the addition of the TLCP favours the processing of the ternary blend and the reinforcing effect of carbon fibres in TLCP/CF/PES composites.

Table 1 shows the mechanical properties of injection-moulded TLCP/CF/PES composites. A CF/PES 5/95 composite has its tensile strength and modulus 18% and 51% higher than those of pure PES, respectively. An addition of 5 wt% TLCP to a CF/PES 5/95 blend increases the tensile strength and modulus 11% and 22%

Table 1 Tensile properties of injection-moulded CF/PES and TLCP/CF/PES

Sample	Tensile strength (MPa)	Tensile modulus (GPa)
PES	96.0	0.925
CF/PES 5/95	113.1	1.38
TLCP/CF/PES 5/5/95	123.8	1.64
CF/PES 10/90	<sup>a</sup>	<sup>a</sup>
TLCP/CF/PES 5/10/90	167.4	1.90

<sup>a</sup> This formulation could not be injection-moulded by CS-183 due to its high viscosity

further, respectively. Due to a high melt viscosity of a CF/PES 10/90 blend, this formulation could not be injection-moulded by the CS-183 Mini Max moulder. However, with the addition of the TLCP, the TLCP/CF/PES 5/10/90 formulation can be injection-moulded and has tensile strength and modulus 74% and 104% higher than those of pure PES, respectively.

#### Conclusions

The concept of *in-situ* hybrid composites, which is put forward in this paper, has been achieved experimentally. By matching the characteristics of the TLCP and the matrix resin and matching the processing parameters of ternary blends containing carbon fibres, two kinds of reinforcements with their diameters at two orders of magnitude have been formed in the resultant injection-moulded composites, and TLCP fibrils are generated *in-situ* during the processing.

The addition of the TLCP decreases the melt viscosity and improves the processability of ternary blends. The latter function results in the decrease of the breakage of carbon fibres, which favours the reinforcing effect of chopped carbon fibres. Furthermore, the TLCP fibrils with their diameters of 0.5–1.5  $\mu\text{m}$  reinforces the matrix

and block the propagation of microcracks in the composite, although the major reinforcing effect comes from the carbon fibre.

A deep insight into this *in-situ* hybrid composite is being conducted from the aspect of material structure and composite mechanics.

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