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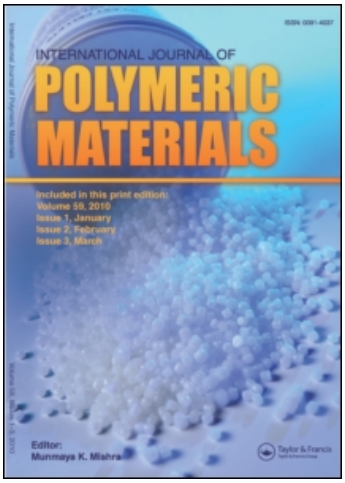

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The Processing and Mechanical Properties of In-situ Thermotropic Liquid Crystalline Polymer Composite Materials

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By blending the thermoplastics (TPs): polycarbonate (PC) and polyethersulfone (PES) with thermotropic liquid crystalline polymers (TLCPs): KU9221 and KU9231, and then extruding the blends to form fibers, the in-situ reinforcing characteristics were studied. The injection experiment of blends was compared with the extrusion experiment. According to the experimental results, in-situ reinforcing characteristics of these processes were analyzed in theory. These researches have come to some important conclusions. TLCP domains can be transformed to form fibers and orientated in the direction of shear flowing during processing, these TLCP microfibers result in improved mechanical properties of the TP/TLCP blends. The extruding flow is easier to orientate TLCP domains and results in better in-situ reinforcement than that of injection moulding, and the extruded fibers have better mechanical properties. The mechanical properties of the blend fibers are improved with increasing tensile ratio of melt drawing and the content of TLCPs.

KEY WORDS Processing, polymer blends, liquid crystalline polymers, mechanical property

INTRODUCTION

In the last few years, a lot of polymer scientists have paid considerable interest in a new kind of reinforcing materials: Thermotropic Liquid Crystalline Polymers (TLCPs) due to their specific chemical structures, high strength, high modulus, low viscosities and other good mechanical properties. By blending TLCPs with some engineering thermoplastics, one can obtain so-called in-situ reinforcing composites. These polymer composites overcome the defects of difficult processability and poor mechanical properties of classical composite materials. When processed with resin matrix at high temperature, TLCP's microdomains can be transformed and orientated to form microfibers in the matrix. When cooled, these microfibers behave as reinforcing phase of the resin matrix.[1,2]

TLCPs have good mechanical properties and processability. Generally, the mechanical properties of TLCP blends are sensitive to the processing technical conditions[1-9] and little added TLCP can improve the mechanical properties of the blends.[3,4,7] The matrix of blends can be thermoplastics, thermosetting plastics and

even TLCPselves. Now the main research interest concentrates on thermoplastics (TP)/TLCP blend system.

EXPERIMENTS

Materials

The TLCPs (marked as KU9221 and KU9231) used in this study were supplied by Bayer (Germany). Two kinds of polycarbonate (PC) were used: PC-A and PC-B (domestic products with average molecular weight of 38,000 and 29,800 respectively). The polyethersulfone (PES) was supplied by Jilin Univ. (PRC) in the form of powders. Table I lists some important mechanical properties of these materials. In this work, KU9231 and PES were blended with weight ratio of 1:9 and 3:7, KU9221/PC-A was 1:4, KU9221/PC-B was 1:9 and 1:4. All experimental materials were dried at proper temperature before experiments.

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Measurements of Plasticized Curves

The plasticized curves of PC-B/KU9221 and pure KU9221 were also measured by the capillary rheometer of XLY-II under these conditions: pressure: 4 MPa; graduation: 5°C/min.; the temperature range was 80–350°C.

Injected Samples

All samples were injected by the injection mold of ARBURG (Germany). Table II lists the injection technical parameters.

Extruding and Drawing

All experimental materials (the pures and blends) extruded by a twin-screw extruder were drawn directly in melting state.

TABLE I

Mechanical date of the polymer studied

	tensile		bending	
	E_p(GPa)	σ_{bb}(MPa)	E_p(GPa)	σ_{bb}(MPa)
PC-A	2.2	55	2.0	80
PC-B	/	68	/	98
PES	2.5	70	2.3	100
KU9221	20	200	10	180
KU9231	17	160	12	150

TABLE II

Injection technical conditions

blends	injec.T°C	mould T°C	P MPa	injec.t sec	pressure t s
PC-B/KU9221	300	80	0.5	20	30
PC-B/KU9221	310	80	0.5	20	30
PES/KU9231	335	80	0.5	20	30

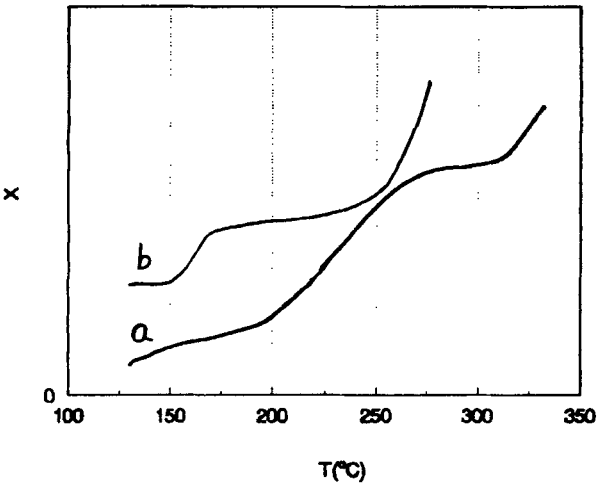

FIGURE 1 Plasticized curves of pure KU9221 and PC-B/KU9221 (4:1). (a) the pure KU9221; (b) the blend of PC-B/KU9221 (4:1)

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Mechanical Measurements

Mechanical measurements of extruded composite fibers and injected samples were tested under the standard conditions with the drawing rate of 50 mm/min in tensile and 1 mm/min in bending.

RESULTS AND DISCUSSION

1. Plasticized Properties

Figure 1 shows the plasticized curves of pure KU9221 and PC-B/KU9221 (4:1). X (ordinate) is the relative value of the displacement of the piston (change of the volume). T (abscissa) is the temperature of the materials. The figure indicates that there are three transitions for each curves (195°C, 260°C and 307°C for the pure, 154°C, 167°C and 240°C for the blend). They possibly correspond to softening point, melting point and flowing point respectively. We know that the softening point of PC-B is near 148°C, so the softening point of the blend PC-B/KU9221 is between the two pures (PC-B and KU9221). Similarly to the flowing point. 167°C

is by no means the actual melting point of the blend, but is relative to the flowing point of PC-B. Since the melting points of the TLCPs are generally over 260°C, the processing temperature of blends must be over 260°C in order for TLCPs to transform largely, no matter blends can flow over 240°C.

2. Mechanical Properties of Injected Samples

Tables III and IV list the mechanical properties of the injected samples (data with * are from references). According to the lineal additive law, the contribution of TLCPs:

$$\sigma_{c-\mathrm{lcp}} = (\sigma_c - \sigma_p\omega_p)/\omega_{\mathrm{lcp}} \tag{1}$$

the percent of the contribution of

$$\mathrm{TLCPs} = \sigma_{c-\mathrm{lcp}}/\sigma_{\mathrm{lcp}} \tag{2}$$

$$\omega_p + \omega_{\mathrm{lcp}} = 1 \tag{3}$$

where, c: blends; p: resin matrix; lcp: pure TLCP; c-lcp: TLCP in blends.

The systems PC are easy to be injected due to their low viscosities.[20] From Table III, for PC-B system, the strength and modulus of the samples injected at 310°C are higher than those injected at 300°C. It indicates that the contribution percent of TLCPs is higher at 310°C than at 300°C. So the TLCP can bring their properties of high strength and modulus into full play under proper processing conditions. On the other hand, the strength and modulus may be even lower than those of the matrix under unproper conditions (for example 300°C).[9]

Due to the two reverse action of temperature on the orientation of the molecular,[15,16] there is an optimal injection temperature for highly orientated samples.

TABLE III

Mechanical properties of PC system injected samples

mat.	injection T °C	σ_{bt} MPa	σ_{bb} MPa	E_b GPa
PC-B *		68.	98.4	
KU9221 *		200.	180.	10.
PC-B/KU9221(4:1)	300	58.4±7.0		
contribution % of TLCP		10.		
PC-B/KU9221(4:1)	310	82.0±1.6	101.±1.	3.6±0.2
contribution % of TLCP		69.	62.	
PC-B/KU9221(9:1)	300	62.4±4.0		
contribution % of TLCP		8.		
PC-B/KU9221(9:1)	310	73.9±1.2	11.7±3.	2.9±0.1
contribution % of TLCP		63.5	158.	

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TABLE IV

Mechanical properties of PES system injected samples

mat.	injection T °C	σ_{bt} MPa	σ_{bb} MPA	E_b GPa	σ_i KJ/m
PES *		70.	100.	2.3	
KU9231 *		160.	150.	12.	
PES/KU9231(9:1)	355	87.9±0.1	136.±2.	3.5±0.2	6.3±1.4
contribution % of TLCP		156.	306.7	119.2	
PES/KU9231(7:3)	355	72.0±2.5	100.±5.	4.8±0.3	3.3±0.1
contribution % of TLCP		47.9	66.7	88.6	

For system PC, not 300°C (too low for TLCPs to stretch), but 310°C. This temperature is little above the flowing point of TLCPs according to the plasticized curves and is proper for TLCPs to transform, orientate and to form obvious fiber structure.

The tensile strength and bending modulus of system PC-B/KU9221 (9:1) are lower than those of system 4:1, but on the contrary to the bending strength. It indicates that under the same injection conditions, some mechanical properties of blends will increase with the increase of content of TLCPs, but as to strength, it increases limitedly.

In this work, we did not obtain pure PES samples at injection temperature of 290–350°C and obtained samples of PES/KU9221 at injection temperature of 335°C with difficulty. It was due to the high viscosity, poor flowing property and decomposition at high injection temperature of PES.

System PES is different from system PC, the mechanical properties (except for bending modulus) of its 9:1 system are better than those of its 7:3 system. And its reinforced effect is also much better than the later, the former exceeds 100, even reaches 300, while the latter only 90. One reason of this result is due to the poor injection of samples (at 335°C, PES begins to decompose). But the main reason is that system PES/TLCP has poor miscibility,[20] and the increase of TLCP content will result in the worsening of the interface properties of two phases, so the mechanical properties will worsen.

Obvious skin core structure at the fractures of samples after mechanical testing can be seen with naked eyes. The surfaces of samples are mainly composed of fiber structure (TLCP fibers on surface layer are of 10% of total TLCP[8]). It is mainly relative to fluid field and cooling rate.[17] This structure has been extensively reported and is more obvious in system PES than in system PC. That is why the reinforced effect of system PES is better than that of system PC. From the fractures of samples, we saw the distinct layering structure which corresponded to the distribution of the rectangular fluid field. It indicates that the fluid field can strongly affect the microstructures and the macroproperties of injected samples.

General speaking, it is difficult to obtain good tensile strength and reinforced

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effect by injection. In this work, the tensile strength of system PC did not reach the due strength of TLCPs, but the reinforced effect of bending strength is notable.

3. Properties of Extruded Composite Fibers

We determined the technical conditions of blending and extrusion according to the data of melting point from References 9 and 20. We found under these technical conditions, the melts of system PES were suitable to be spined due to their proper viscosities. They still had enough supporting strength when spined largely. The surfaces of the fibers were smooth and their diameters were even. But finding proper processing technical conditions for system PC is very difficult. If the processing temperature increases, the viscosities of melts will decrease and the fibers have not enough supporting strength, they fracture easily. If the temperature decreases, the TLCPs will melt poorly and its microdomains cannot transform effectively. The TLCPs even can form grains in matrix. The composite fibers of system PC obtained difficulty with knods on their surfaces (possibly TLCP grains) have poor reinforced effect. This phenomenon was also shown at Reference 18. The reason for these different results is mainly dependent on that if the viscosities and melting points of the two components in blend system match well and if they have a common window of processing temperature. According to Reference 20 and plasticized curves, the absorptive peak of PES (233°C) is nearby the TLCP's (267–355°C). At 310°C, their viscosities are also approximate (viscosities of TLCP decrease when $\dot{r} > 16$ 1/sec). On the other hand, the softening point of PC (148°C) is far from the melting point of TLCP (260°C) and over 260°C, the viscosity of PC is much less than that of TLCP.

The difference between the processing effects of system PC and system PES indicates that in the study of TLCP in-situ reinforced blending, it is very important to choose the proper TLCP which can match the matrix well. Approximate viscosities and common window of processing temperature are the main preconditions of using this reinforced method.

Figure 2 shows the strength as a function of the tensile ratio of composite fibers. It indicates: 1. The strength of composite fibers increases with the increase of the TLCP content. This result possibly can be explained by the additive law. But the brittleness of fibers also increases. 2. The strength of pure PES and PES/KU9231 (7:3) increases with the increase of tensile ratio DR (the square of D/d. D: the diameter of mold, d: the diameter of fibers). But on the contrary to system PES/KU9231 (9:1). All strength has lineal relationship with the logarithm of DR. The former can be explained by the fact that high tension of melts results in the large orientation and transformation of TLCP as well as good reinforced effect. But the later reason is not clear now. 3. The strength of fibers made at high spining rate (80 rpm) is lower than that made at low spining rate (50 rpm) with the same content of TLCP. The reason is that TLCP has strong property of shear-diluting, but this property is weak for PES. With the increase of spining rate, the viscosities of PES and TLCP no more match, the intermolecular force in TLCP microdomain causes TLCP to orientate poorly. So the strength decreases.

In this work, we found for system PES/KU9231 (7:3) (50 rpm), when the DR was over 8, the strength of the composite fibers exceeded that of pure TLCP (160 MPa). For example, the strength of fibers with diameter of 1.02 mm (DR = 8.65) was 201 MPa, as much as 2.87 times that of matrix (70 MPa). The percent of TLCP

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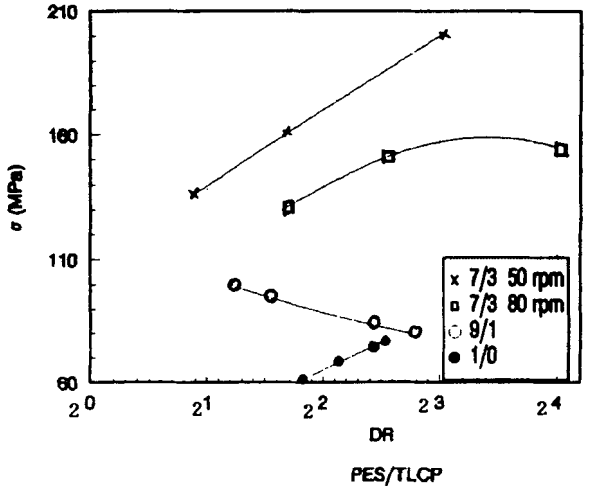

FIGURE 2 The tensile strength as a function of the tensile ratio of composite fibers

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contribution was 317%, the reinforced effect was very notable. If the DR increased more, the effect possibly also increased.

CONCLUSION

The difference of the processing effects between system PC-B and system PES indicates the importance of the TLCPs which match the matrix well. Approximate viscosities and the common window of processing temperature are main preconditions to select the reinforced method for a system.

PES's high viscosity and decomposition at high temperature of results in the difficulty for injecting system PES. The strength of system PC-B injected at 310°C is higher than that injected at 300°C. So the proper injection temperature is precondition of good reinforcement.

The mechanical properties of blends are greater than that of either pure component, PES and PC. With increasing TLCP content, the strength, modulus and brittleness of the blends will increase.

Shear flowing results in the TLCP orientation and the formation of TLCP microfibers which is the reinforcing phase. The distribution of fluid field results in the skin-core structure in extruded samples.

By blending with PC and PES, KU9221 and KU9231 express their potential high strength and modulus. Their strength is as high as 2.87 times of that of matrix. The contribution percent of TLCP is 317%. Increasing tensile ratio also can result in the increase of strength.

NOMENCLATURE

DR = tensile rate
E_b = bending mouldus

P = pressure
T = temperature
t = time
σ_{hh} = tensile strength
σ_{hl} = bending strength
σ_i = impact strength

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