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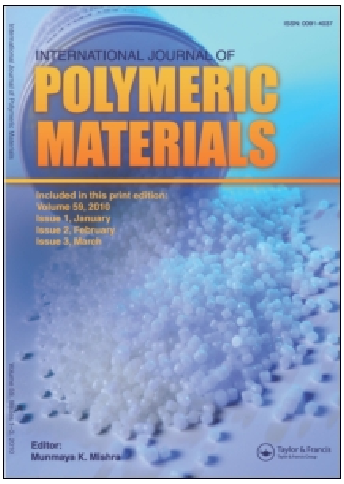

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Injection Molding of In-situ Reinforced Thermoplastic Composites Containing Thermotropic Liquid Crystalline Polymers

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Injection Molding of In-situ Reinforced Thermoplastic Composites Containing Thermotropic Liquid Crystalline Polymers

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Tensile and bending properties of blends of a polycarbonate and a polyethersulfone containing two kinds of thermotropic liquid crystalline polymers (LCPs) have been investigated. The injection molded test bars of these blends exhibit high stiffness because of the presence of in-situ formed fibers of dispersed LCP phase. The tensile and bending moduli of the LCP fibers which were shear-induced during processing were roughly estimated. The processing conditions such as melt temperature and injection molding speed have a large effect striking influences on the mechanical properties. The existence of immiscibility between LCPs and matrix polymers was detected by FTIR and DSC. The strength of the blends was found to be similar to that of pure matrix materials.

KEY WORDS Blends, liquid crystalline polymers, polycarbonate, polyethersulfone, injection molding.

INTRODUCTION

By blending thermotropic liquid crystalline polymers (LCPs) with some engineering thermoplastics, one can obtain in-situ reinforced composites, in which the dispersed LCP phase forms highly oriented reinforcing fibers in the matrix of engineering thermoplastics. Because the LCPs blend easily with thermoplastic polymers of these oriented fibers the specific surface and volume concentration in the matrix can be very high in comparison with the concentration of conventional fibers in the reinforced composites.[1-4]

In addition, the in-situ developed reinforcement due to LCP fibers can be kept or enhanced by stretching and thermoforming. Both LCPs and matrices belong to

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thermoplastics, so the processibility, toughening and recycling of LCP/resin blends have been an area of considerable interest in the last few years.[5-8]

However, despite extensive research and development, LCPs currently have a relatively small commercial market. Due to relatively high monomer costs, the materials tend to be expensive. On the other hand, it is also very difficult to prepare samples that contain fiber orientations other than uni-directional, and the properties depend strongly upon the processing conditions. Mechanical properties such as the elastic modulus, tensile strength and elongation at break of the same LCP blend reported in the scientific literature and by the producers are sometimes very different. Therefore, there is no data base to compare the mechanical properties of these blends.[3,4] This poses difficulties in finding applications. Nevertheless these systems represent new promising composite material for research and industrial applications.[8]

The investigations of the in-situ reinforced composites containing LCPs are just beginning in China.[5] In this study we investigated the mechanical behavior of injection molded test bars under various processing conditions.

EXPERIMENTAL

1. Materials

The Polycarbonate (PC) used in this study had an average molecular weight of about 38,000. The Polyethersulfone (PES) was supplied by Jilin University (China) in form of powders. The LCPs of KU 9221 and KU 9231 type were supplied by Bayer Corp. The two LCPs can be distinguished by their thermo-mechanical properties,[6] such as the relationship between shear modulus and temperature which is shown in Figure 1. The sheet of pure LCP KU 9221 was extruded using an Instron Capillary Rheometer at a constant crosshead speed of 0.3 inch/min. The melt temperature of the LCP polymer was 300°C.

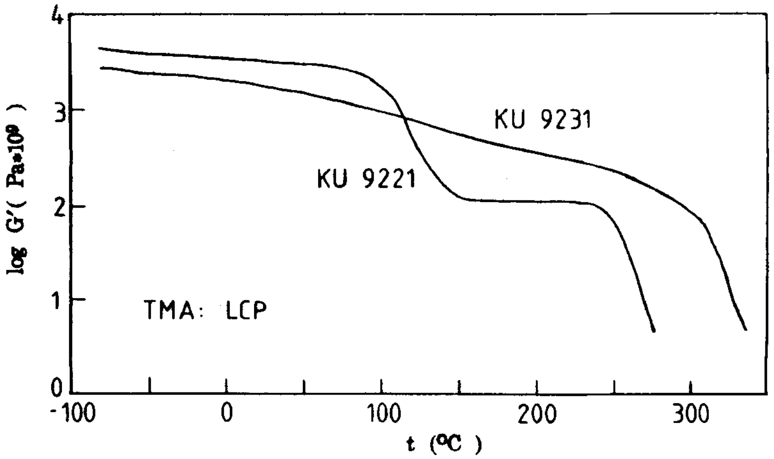

FIGURE 1 Storage modulus curve of LCP as a function of temperature by means of TMA.

TABLE I

Mechanical data of the polymers studied

	tensile			bending	
	E_p(GPa)	σ_{bt}(MPa)	ϵ_{bt}(%)	E_b(GPa)	σ_{bb}(MPa)
PC	2.2	55	100	2.0	80
PES	2.5	70	120	2.3	100
KU 9221	20	200	1.2	10	180
KU 9231	17	160	1.1	12	150

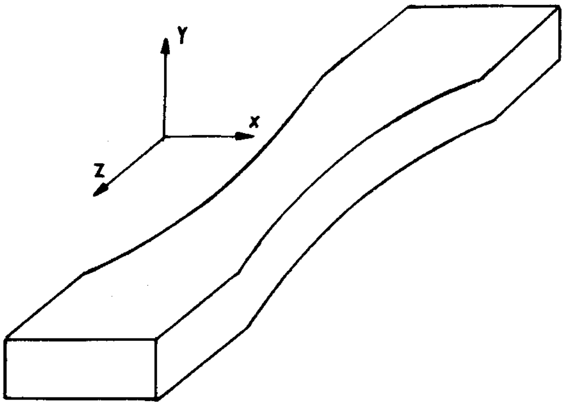

FIGURE 2 Injection molded test bar and coordinate system.

Table I lists some important mechanical properties of these materials provided by the supplier.[5,6]

2. Blend Preparation

The PC and PES were mixed with KU 9221 and KU 9231 in the weight ratio of 80:20 respectively. The mixtures were then dried at 120°C for more than 24 hours, extruded using a twin-screw extruder (L:D = 23:1) and pelletized. The pellets of two different blends were then injection molded into test bars with the dimensions of 100 × 15 × 5 mm,[5] see Figure 2. *Z* axis in Figure 2 is the flow direction. The injection molding speed can be represented by volume flux *Q*, which was 8 cm^3/s and 80 cm^3/s. The temperature of the mold was approximately 70°C.

3. Test Procedures

Thermo-mechanical analysis was done using PERKIN-ELMER DMA 7 Series. Mechanical tests were performed on Tensile Tester SHIMADZU DCS-2000 at room temperature with crosshead speed of 50 mm/min in tensile, and 1 mm/min in bending. Shear modulus was measured using Rheometrics Mechanical Spectrometer (RMS 800) in Reference 5. Microhardness was tested by Vicat-Tester HVA-10 A with test load of $P = 1000 - 1500$ g and measuring time of 30 sec. The microhardness was determined as follows[5]:

$$MH = 2*9.8*P*\sin(a/2)/d^2$$

where "a" in previous equation was constant equal to 136 and "d" was the average diagonal length. Rheological behavior was investigated on a Torque Rheometer HAAKE SYSTEM 40. Fourier Transform Infrared Spectrometer NICOLE 5DX and Perkin Elmer Co. DSC-2C was used for FTIR and DSC analyses, respectively. In DSC experiment, the heating rate and cooling rate were 10°C/min, the temperature range was 40–400°C and the experiment was conducted under the atmosphere of N_2.

RESULTS AND DISCUSSION

Curves of complex storage modulus and mechanical damping tan δ versus temperature for an extruded pure LCP sheet parallel (||) and perpendicular (⊥) to flow direction are shown in Figure 3. A pronounced anisotropy is indicated. At ambient temperature, the storage modulus in the flow direction is about four orders of magnitude higher than that in the cross-flow direction. Similarly, the mechanical damping between || and ⊥ to flow direction was about three orders of magnitude different. The anisotropy was reduced with increasing temperature. At 300°C, there were no differences in modulus and damping between the samples cut from the sheet in two flow directions.

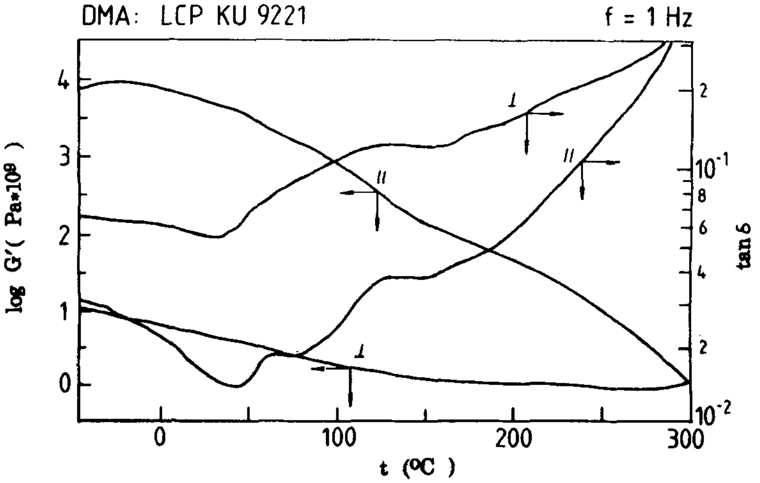

FIGURE 3 Dependence of storage modulus G' and mechanical damping tan δ on flow direction of extruded sheet by DMA (⊥ indicates transverse direction and || indicates flow direction in extrusion).

The stress-strain curves of injection molded, dumbbell shaped bars of LCP/PC and LCP/PES blends show typical behavior of brittle fracture. There was no yield point. The stress-strain curves came to an end when the ultimate stress was reached. The fracture surfaces of the blended samples had smooth appearances.

The tensile and bending properties of injection molded bars of LCP/PC and LCP/PES blends are shown in Figures 4 and 5. The processing parameters were the melt temperature T_{inj} and injection speed V_{inj} (volume flux Q). Compared to the mechanical properties of pure PC and PES given in Table I, both the PC/LCP and

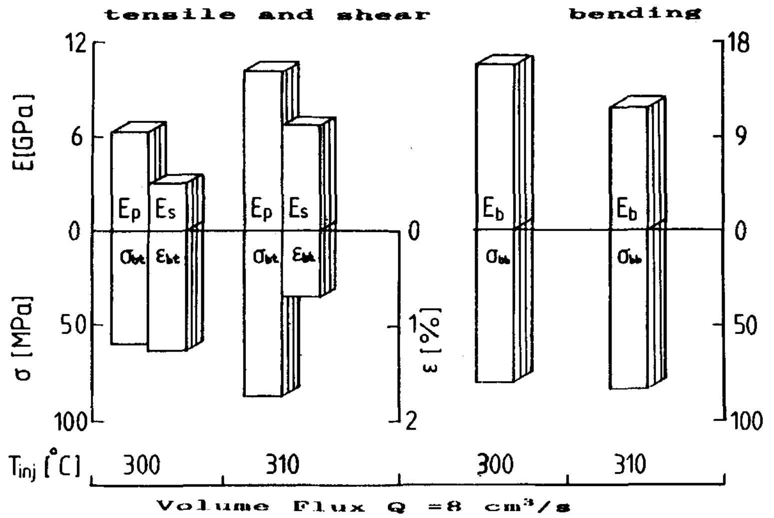

FIGURE 4 Dependence of moduli E_p, E_s and E_b; strengths σ_{bt} and σ_{bb}, elongation at break ε_{bt} on the injection molding temperature of LCP (20 wt%)/PC blends (volume flux Q = 8 cm³/s).

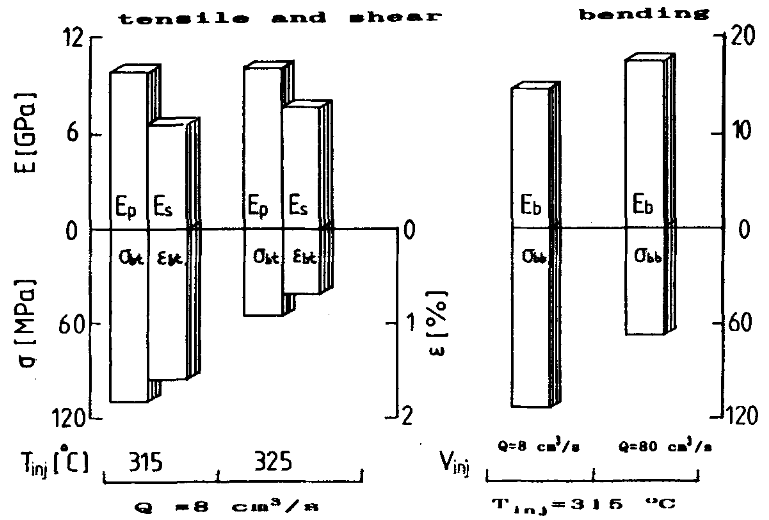

FIGURE 5 Dependence of moduli E_p, E_s and E_b; strengths σ_{bt} and σ_{bb}, elongation at break ε_{bt} on the injection molding temperature and injection molding speed of LCP (20 wt%)/PES blends.

the PES/LCP blends exhibit a many-fold improvement over the properties of pure matrix materials. This is particularly noticeable in the modulus E_p and E_b. The moduli were enhanced to E_p = 10.2 GPa, E_s = 6.7 GPa and E_b = 11.9 GPa when the LCP/PC blends were injection molded at 310°C with a volume flux Q of 8 cm^3/s. Under these processing conditions, the viscosity ratio of LCP/matrix polymer and the Weber number of the blend system (the two key factors in controlling the development of reinforcing fibers in immiscible polymer blends[9,13,14]) were such that the LCP phase was deformed and oriented into reinforcing fibers. In addition, a thick skin-layer in the skin-core structure of LCP/polymer blends and a high aspect ratio of the fibers resulted in significant reinforcing effects.[9,10,12]

On the other hand, there were only small improvements in the tensile and bending strengths of the LCP/PC blend when the bars were injection molded at 300°C or 310°C. This behavior is also shown in Figure 4. The molding temperature of 310°C resulted in higher values of the tensile strength in the LCP/PC bars. However, for the bars with the LCP/PES blend, the tensile strength decreased substantially as the injection molding temperature increased from 315°C to 325°C for Q = 8 cm^3/s. The tensile strength also decreased as injection molding speed increased from Q = 8 cm^3/s to Q = 80 cm^3/s at an injection molding temperature of 315°C. This is possibly due to the fact that at a high temperature, such as 325°C, the viscosity ratio of LCP and PES is too small for the deformation of LCP fibers. Moreover, increasing injection molding speed can result in a decrease in the thickness of skin layers due to the high shear flow.[9,10,12]

The low strengths of blends containing dispersed LCP phase is attributed to the poor interfacial adhesions between the LCPs and PC or PES indicated by Infrared-absorption Spectra and DSC. By subtracting the IR-spectra of the pure LCP from those of the blend, and by comparing the subtractively obtained PC- and PES-spectra with those of pure PC and PES, no differences could be detected (see Figure 6). The fact that no new transmittance peaks appeared in the spectra suggests that there was no significant interaction in the interface between the two components.

The same conclusion can also be drawn from Figure 7. Figure 7 shows the DSC thermograms of PC, LCP (Ku 9221) and their blend. The glass transition temperature of PC is near 148°C, the endothermal peak of LCP is near 318°C. In the DSC thermogram of LCP/PC blend, the glass transition temperature of PC and endothermal peak of pure LCP remained at exactly the same temperature as those appearing in the DSC thermograms of pure components.

The diameters of the LCP fibers are of few μm and their lengths are in the range of mm. Therefore, they generally have great specific surfaces. In the case of small strains, adhesion forces on the interface are still comparatively strong and lead to an increase in stiffness. With increasing strain, however, the weakness of the interface becomes dominating, and therefore the strengths and the strains at break point cannot be improved significantly over that of matrix.

From this investigation, it can be concluded that the dispersed LCP fibers act primarily as a stiffness-improved component due to the poor interfacial adhesions.

The fact that LCPs can under specific conditions act as a reinforcing agent in a blend has led some investigators to model the mechanical behavior of blends ac-

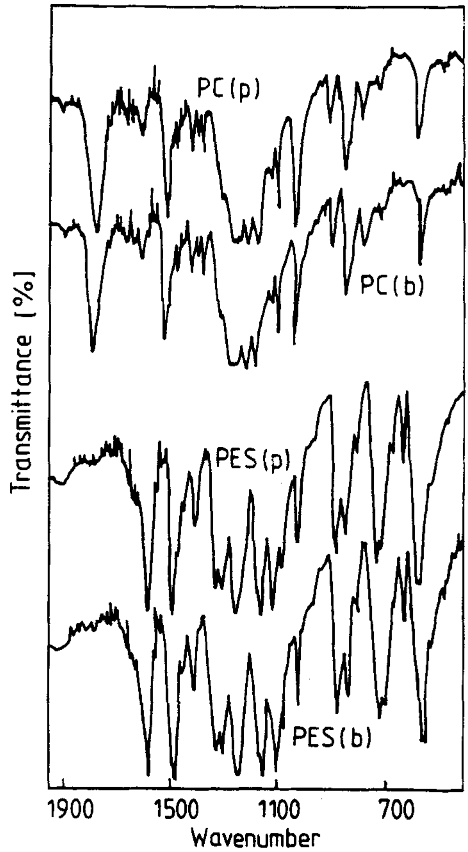

FIGURE 6 FTIR-transmittance of pure PC and PES compared with themselves in LCP-blends.

cording to composite theories.[3,4,8] Isayev and Modic[3] based their calculation on the assumption that blends of PHB/HNA and PC could be treated as unidirectional fiber-reinforced composites. Their experimental data approached the calculated properties. Kohli *et al.*[4] in their studies on blends of PHB/HNA/HQ/TA and PC showed that the modulus of highly drawn melts could be modeled effectively by the simple rule of mixtures:

$$E_c = E_1C_1 + E_2C_2$$

where E_c is the composite modulus, E_1 and E_2 are the modulus of the reinforcing LCP and the matrix, respectively and C_1 and C_2 are their volume fractions. A major reason for the agreement between the data and the model in the study of Kohli *et al.* was due to the high alignment of the LCP microfibrils in the draw direction and their high aspect ratios. In our case, the LCP fibers were shear induced during processing and the development of LCP fibers was not as perfect as that obtained from drawing. Therefore, one cannot use the rule mixture to make an accurate calculation of the mechanical properties of LCP fibers. However, according to the morphological studies given in the literature,[9,10,12] the shear induced

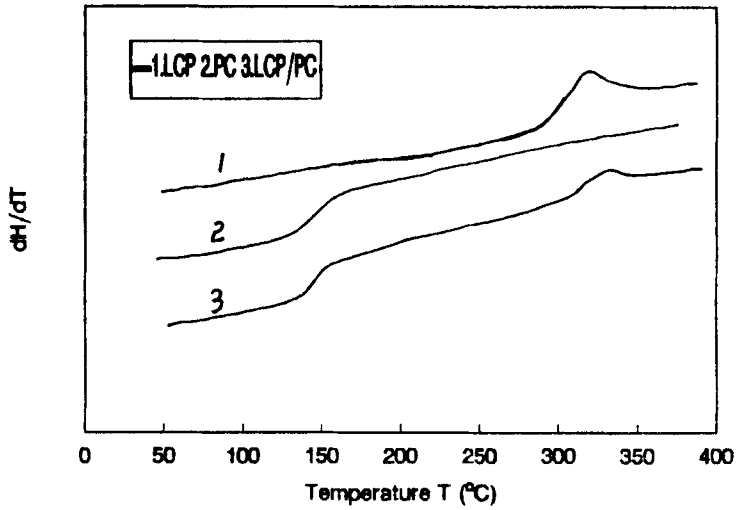

FIGURE 7 DSC thermograms of LCP, PC and LCP/PC blend.

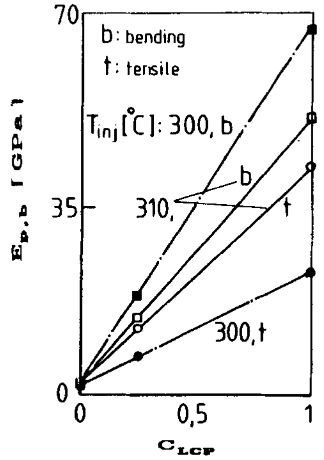

FIGURE 8 Tensile and bending moduli of LCP/PC versus LCP weight concentration.

LCP fibers could have high aspect ratio and align well along the flowing direction. This indicates that one could possibly use the rule of mixture to roughly estimate the mechanical properties of shear induced LCP fibers. For example, we applied this rule to estimate the mechanical properties of LCP/PC blend using weight fraction instead of volume fraction. The experimental and the calculated results are given in Figure 8.

It can be seen that the processing conditions can have striking influences upon the mechanical properties of LCP fibers. In the tensile test, for example, the estimated E_p of the pure LCP phase in the LCP/PC blends which were injection molded at the temperature of 310°C and with the volume flux of 8 cm^3/s could be obtained by extrapolating to $C_{lcp} = 1.0$ according to the rule of mixture and the value was 42.2 GPa, which was much higher than the value of $E_p = 22.8$ GPa obtained from the LCP/PC blends injection molded at temperature of 300°C and with the same injection molding speed.

In fact, these estimated values are higher than what can be expected according to polymer literature, which could possibly mean that the effect of using the rule of mixture to estimate the mechanical properties of LCP fibers is not very satisfactory. In our next report, we will use Cox's or Halpin-Tsai model[15,16] to calculate the modulus of LCP fibers based on our morphological studies. In any case, our present estimates, show that the different processing conditions can indeed change the mechanical properties of reinforcing phase-LCP fibers during processing.[3,4,8]

With a programmed torque rheometer, torque energy to study processability of

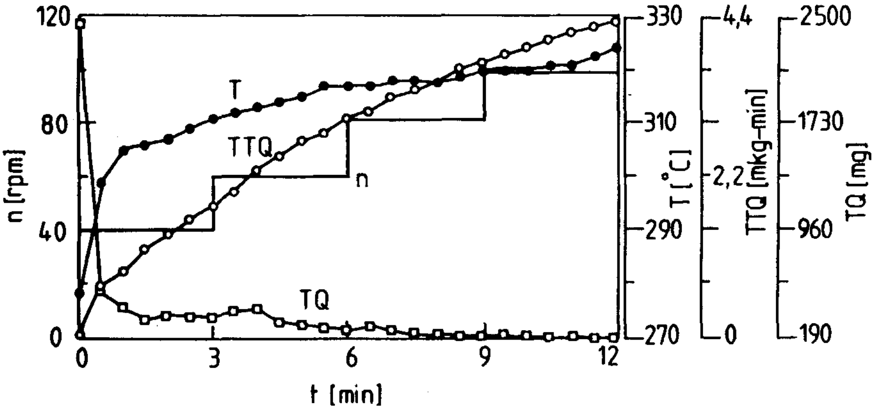

FIGURE 9 Processing behavior (rotation speed *n*, torque *TQ*, total torque *TTQ* and temperature *T*) of LCP by means of torque-rheometer.

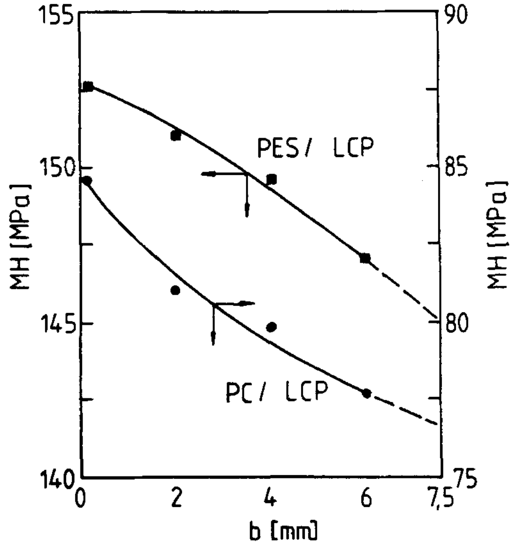

FIGURE 10 The distribution of microhardness in injection molded LCP/PES and LCP/PC blends at the halved width direction of samples.

LCP was measured, which reflects the flow behavior (viscosity) of the polymer under shear and thermal stress. The result is given in Figure 9.

The measured curves display that, at a beginning rotor speed of $n = 40$ rpm, the torque response curve TQ of the LCP sample decreased quickly during the first 1 min of processing from 3450 mkg to a level about 450 mkg, and then went down slightly until 150 mkg when the rotor speed automatically changes step by step from 40, 60, 80 to 100 rpm. Very little work was done on the melt as indicated by the area under the torque curve. Correspondingly, the melt temperature increased only slightly from 300°C to 320°C.

This result illustrates the very good processibility of LCP/polymer blends. Because of its superior flow behavior, LCP phase can lubricate the melt blend under certain processing conditions. This "internal" lubrication effect of LCP phase can decrease the viscosity while the LCP phase is deformed into reinforcing fibers. Because the interaction at the interface of LCP phase and polymer matrix is very low, the LCP phase can be distributed well in matrix. Under the influence of the flowing field, the LCP phase is oriented to form microfibers or microdomains. The LCP domains can also reduce the internal friction between molecular chains of matrix when the blended melt is deformed. Therefore, it can noticeably decrease the viscosity of LCP/polymer blends, which means that LCP works as internal lubricant in polymer matrix. Thus LCPs are often used as a processing aid.

It is well known that all of the samples made of LCP/polymers, whether injection molded or extruded, exhibit pronounced anisotropy and skin-core structure.[9–12] The anisotropy and the layer structure are still obvious even when blending relatively small amounts of LCP with thermoplastics. The microhardness measured on the cross-section of the injection molded bars of LCP/PC and LCP/PES showed that it was harder in the core area than the skin area. See Figure 10. This result indicates complex melt flow behavior during mold filling.

CONCLUSION

Using mechanical techniques, we have characterized the tensile and blending behavior of the blended LCP/PC and LCP/PES composites in the form of injection molded test bars. The modulus of LCP fibers was estimated by the rule of mixture. The results were not accurate enough and a more complicated model, such as Cox's model, should be used.

Because of the very limited miscibility and the poor interface adhesions between the LCP phase and polymer matrix, the increase in the stiffness is more obvious than the increase in strength.

Because of its superior flow behavior, the LCP phase can lubricate the blend melt under certain processing conditions. This "internal" lubrication effect of the LCP phase can decrease the viscosity of blends and deform the LCP phase itself into reinforcing fibers.

The injection molded LCP/polymer blends have pronounced skin-core structures. The microhardness in the core area is greater than that in the skin area due to the homogeneous distribution of LCP concentration caused by melt flow.

NOMENCLATURE

E_p = tensile modulus
E_s = shear modulus
E_b = bending modulus
σ_{bt} = stress at break in tensile tests
ε_{bt} = elongation at break in tensile tests
σ_{bb} = stress at break in bending tests
MH = microhardness
T_{inj} = injection temperature
V_{inj} = injection speed
C_{lcp} = LCP concentration in blend
TQ = torque
TTQ = total torque
b = halved width of test bar

Acknowledgments

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