

EFFECT OF DRAWING ON MORPHOLOGY, STRUCTURE AND MECHANICAL PROPERTIES OF BLENDS OF A LIQUID CRYSTALLINE POLYMER AND MODIFIED POLY(PHENYLENE OXIDE)

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ABSTRACT

Polymer strands with various draw ratios of a thermotropic liquid crystalline polymer (LCP) and modified poly(phenylene oxide) were prepared by drawing the melts leaving a slit die in open air. The morphology, structure and mechanical properties of the resulting strands were studied as a function of LCP content and draw ratio. It was found that the thermal and mechanical properties of the matrix phase did not change dramatically with the amount of LCP and draw ratio, but the orientation of LCP phase could be increased with draw ratio. The mechanical properties of the strands could be improved by moderately drawing the melts. Wide angle X-ray diffraction suggested that the improvement in tensile strength of the strands was due to the resultant fibrillation of LCP phase and enhanced molecular orientation. Morphological observation indicated that excessive drawing of the strands could lead to the break down of the microfibrils of LCP and thus resulted in the decrease of mechanical strength.

INTRODUCTION

The mechanical properties of polymers can be greatly improved by the addition of fibrous fillers, such as glass fiber and carbon fiber. However, due to numerous problems encountered during processing and fabrication, this method was restricted. The addition of fibrous materials to polymer melt increases the viscosity considerably, leading to problems of poor mold filling, longer cycle time and larger power consumption. In order to counterbalance the viscosity increase caused by the addition of filler it requires to increase the processing temperature, yet which may cause thermal degradation of the matrix. Furthermore, fibrous fillers may subject

to breakage during processing, leading to lower aspect ratio and lower effect of enhancement. Besides due to the surface hardness of the adding fibers, serious abrasion wear on the processing equipment will lead to the increase of fabrication expenses.

One way developed recently to overcome these difficult problems is to form in-situ composite by adding rigid liquid crystalline polymer (LCP) to a traditional isotropic polymer^[1]. The addition of LCP can greatly decrease the viscosity of the matrix. At processing temperature, under elongation flow field the LCP can be oriented into microfibrillar structure and then be retained after solidification because of the rigidity of LCP chains. Thus, the LCP serves as a processing aid and a reinforcing fiber as well^[2]. Blends of LCP with engineering thermoplastics have attracted much attention in recent years. Although many investigations have pointed out that the viscosity ratio between the LCP phase and matrix phase is a key factor controlling the microstructure of LCP^[3], there are still many factors affecting the fibrillation and molecular orientation of LCP, such as materials selection, compositions and processing parameters. Among these factors, the flow field was found to be extremely important for specific LCP/isotropic polymer system. Investigations indicated that simple shear flow has less effect on the fibrillation of dispersed phase^[4-6]. While the elongation flow, such as drawing, was most effective in the fibrillation and orientation of LCP phase.

In the previous study^[7], we investigated the structural properties and impact fracture behavior of injection molded blends of liquid crystalline polymer (Vectra A950) and polystyrene modified poly 2, 6-dimethyl-1, 4 phenylene oxide (denoted M-PPO). Blending of PPO with PS furnished good processability and mechanical properties. In the injection molded PPO/LCP blends, the yield stress of the M-PPO could be greatly increased with the incorporation of LCP, but the strain at break decreased. Correspondingly, the notched impact strength of the blends decreased dramatically. Little information is available on the effect of drawing on the fibrillation and orientation of polymer blends containing a LCP phase. This paper puts emphasis upon the effect of melt drawing on the microstructure and mechanical properties as well as the morphology of M-PPO/blends.

EXPERIMENTAL

1. Materials

The thermotropic liquid crystalline polymer used in this research was Vectra A950 commercially produced by Hoechst-Celanese. According to the manufacturer, Vectra A950 is a wholly aromatic copolyester consisting of 25 mol% of

2, 6-hydroxynaphthoic acid (HNA) and 75 mol% of p-hydroxybenzoic acid (HBA). Polystyrene modified poly 2, 6-dimethyl-1, 4-phenylene oxide (M-PPO) was purchased from the General Electric Company (Noryl PX1214-701).

2. *Sample preparation*

Both polymer pellets of LCP and M-PPO were dried in oven separately before blending. The pellets of blends containing 5, 10, 20, 30, 40 and 50 wt% LCP were premixed with M-PPO in a twin screw Brabender Plasticorder at a barrel temperature of 290 °C. The extrudates were cut into pellets by a pelletizer. Strands of the blends containing various contents of LCP were obtained by drawing the melt at different speed leaving a slit die of $50 \times 5 \text{ mm}^2$, the rotation speed of the screw was 20 r.p.m.. Dog-bone tensile bar were punched along the flow direction from the strands with a standard mold for plastics testing.

3. *Mechanical properties*

The mechanical properties of the specimens were determined with an Instron tensile tester (model 4206) at a crosshead speed of 1 mm/min. To avoid stress concentration at the grips and obtain better grasping of the specimen, a layer of fine sand paper was used at the grips.

4. *DSC analysis*

The differential scanning calorimetry (DSC) measurements were carried out from 50 to 200 °C under nitrogen atmosphere using Perkin-Elmer thermal analysis system (model DSC-7). Sample weights about 5 mg. The heating rate was 10 °C/min.

5. *Wide angle X-ray diffraction*

Wide angle X-ray diffraction curves were taken on a Simens D500 X-ray diffractometer. The tube voltage was 40 kV and tube current 35 mA.

6. *Morphology*

Morphology of the draw strands were observed using Zeiss reflective optical microscope and scanning electron microscope (Jeol JSM 420). To observe individual microfibrils, the matrix was dissolved with chloroform. All SEM samples were coated with a thin layer of gold before observation.

RESULTS AND DISCUSSION

Effect of drawing on the mechanical properties

In our previous study, as the viscosity ratio of LCP to matrix^[8] polypropylene was larger than unity, the LCP could not be oriented into fine microfibrils, and the adhesion between LCP and matrix was poor, the resulted blends showed poor mechanical strength. The LCP could be simply regarded as voids. The mechanical

strength of the blends could be expressed as follows when LCP phase was less than 30 wt%^[11].

$$\sigma = (1 - \Phi_2)\sigma_1 \quad (1)$$

Where σ_1 represents the strength to break of the pure matrix, Φ_2 is the volume fraction of the LCP phase. In this paper, the viscosity ratio of LCP to M-PPO is less than unity, the LCP phase can be oriented into fine microfibrils. Therefore, the mechanical properties are highly associated with the aspect ratio of the dispersed phase. The tensile modulus of blends can be calculated with a modified Tsai-Halpin equation as follows^[11]:

$$E/E_1 = (1 + AB\Phi_2)/(1 - B\Phi_2) \quad (2)$$

Where E_1 is the tensile modulus of the matrix and Φ_2 is the volume fraction of the reinforcing fiber. Constant B is represented as:

$$B = (E_2/E_1 - 1)(E_2/E_1 + A) \quad (3)$$

Where E_2 is the fiber's modulus, A is a geometry constant. For axial direction under uni-axial orientation, it is expressed as:

$$A = 2(L/D) \quad (4)$$

The calculated tensile modulus of M-PPO/LCP, as a function of aspect ratio with different LCP volume contents by equation (2), increases dramatically at low aspect ratio, and then levels off. A large LCP volume content enhances the tensile modulus. Fig. 1 and 2 show graphical representations of the Tsai-Halpin equation with different aspect ratios and experimental data at draw ratios of 1.5 and 7.9, respectively, it can be seen that at low draw ratio, LCP shows lower aspect ratio. The variations of the tensile yield strength and modulus with the content of LCP are shown in Figs. 3 and 4, respectively. It can be seen that the addition of LCP can greatly enhance the yield strength and modulus of the blend. Figs. 5 and 6 show that drawing has great influences on the tensile yield strength and modulus of M-PPO/LCP blends when the LCP content was more than 20 wt%. The yield strength and modulus of M-PPO show little change with the variation of draw ratio. Therefore, it can be concluded that drawing mainly influence the LCP phase. From Fig. 5, it should be noted that the yield strength of the blends can be greatly improved by drawing the strands when the draw ratio is less than 4.1. Further drawing the strands containing LCP more than 30 wt% results in a decrease in the yield strength. Therefore, the apparent

dependence of modulus and strength on the draw ratio indicates that fibrillation and orientation of LCP take place not only in the die, but also beyond the die. Lin^[9] et al. found that the modulus of PC/30 wt% LCP increased with draw ratio up to 30, but the strength of the system rose with draw ratio up to 15, then decreased, they ascribed the decrement in tensile strength mainly to a variance in the gripping method when the samples were tested because of the small diameter of the samples with higher draw ratio. Our morphology observation gives different explanation which will be described later. Yee^[10] reported that little dependence of modulus on the draw ratio was found for the polystyrene/Vectra B950 blends; Crevecoeur^[11] et al. reported that the modulus and tenacity of the PEI/LCP system showed no dependence of the draw ratio, and they ascribed that the LCP fibers were formed mainly before and in the die, instead of beyond the die in the drawing.

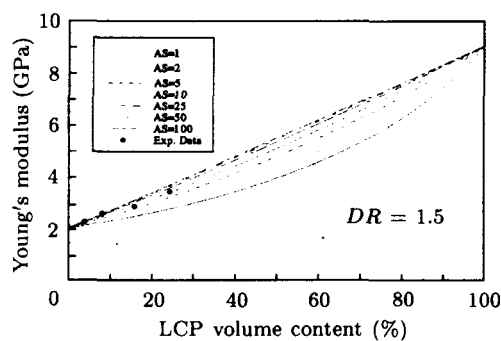


Fig. 1 Modulus-LCP volume content curves graphical representations of the Tsai-Halpin equation with different aspect ratios and experimental data at draw ratio of 1.5

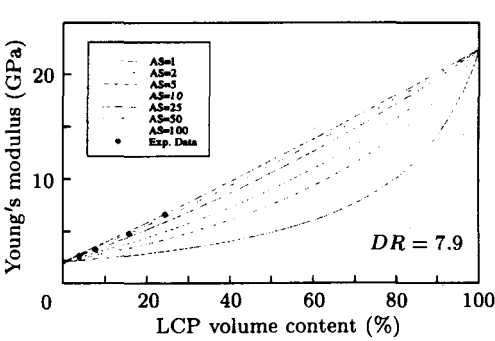


Fig. 2 Modulus-LCP volume content curves graphical representations of the Tsai-Halpin equation with different aspect ratios and experimental data at draw ratio of 7.9

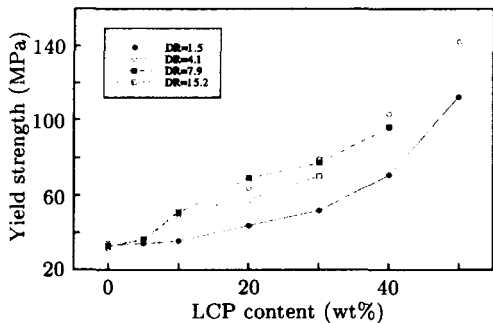


Fig.3 Yield strength as a function of the content of LCP with different draw ratios

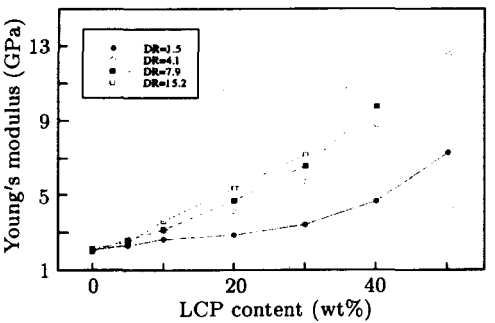


Fig. 4 Modulus as a function of the content of LCP with different draw ratios

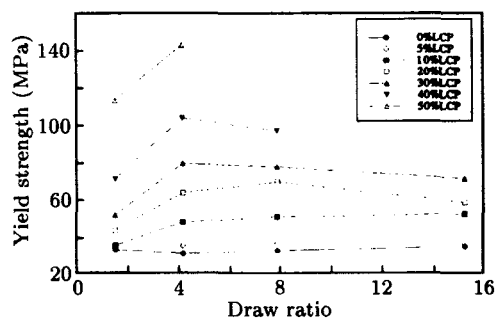


Fig. 5 Yield strength as a function of the draw ratio with different LCP contents

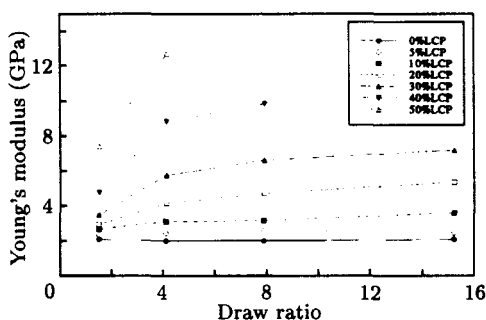


Fig. 6 Modulus as a function of the draw ratio with different LCP contents

Fig. 7 shows the effect of drawing on the glass transition temperature (T_g) of the matrix phase, M-PPO. It can be seen that, within experimental error, the T_g of matrix showed no variation with the LCP content and draw ratio. Lin^[9] et al. reported that the melting temperature of the LCP and T_g of the matrix, PC, remained constant with draw ratio in PC/LCP blend system.

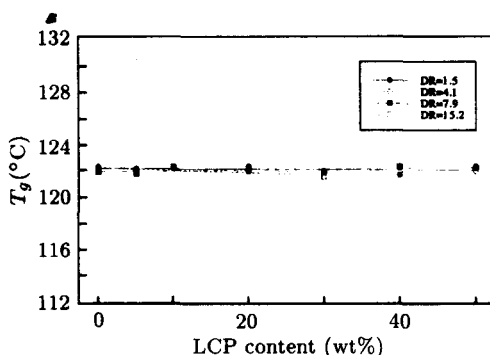


Fig. 7 The effect of drawing on the glass transition temperature (T_g) of the matrix phase M-PPO

Effect of drawing on the orientation of LCP

Crevecoeur^[11] et al. reported that, in the blends of PS/Vectra B950, the orientation factor for blend fibers, f , remained constant of 0.88 when the draw ratio increased from 5.7 to 20. The orientation factor of the pure LCP Vectra B950 also kept constant of 0.88 at draw ratios of 9.9, 30.3 and 40.4, respectively. They concluded that drawing has no influence on the orientation parameter. It would be that either the X-ray method used to determine the orientation factor is not sensitive enough to visualize the minor effects, or the small improvement in modulus that draw ratio causes, is due to other effects, such as perfection of the fibrillar structure. However, the orientation parameter increased with the LCP content. Whereas in the system of PC/LCP, Lin et. al. reported an apparent dependence of orientation parameter on drawing, in which a rapid increase of the orientation parameter was observed from 0.55 to 0.75 when the draw ratio increased from 1 to 13, and then levelled off.

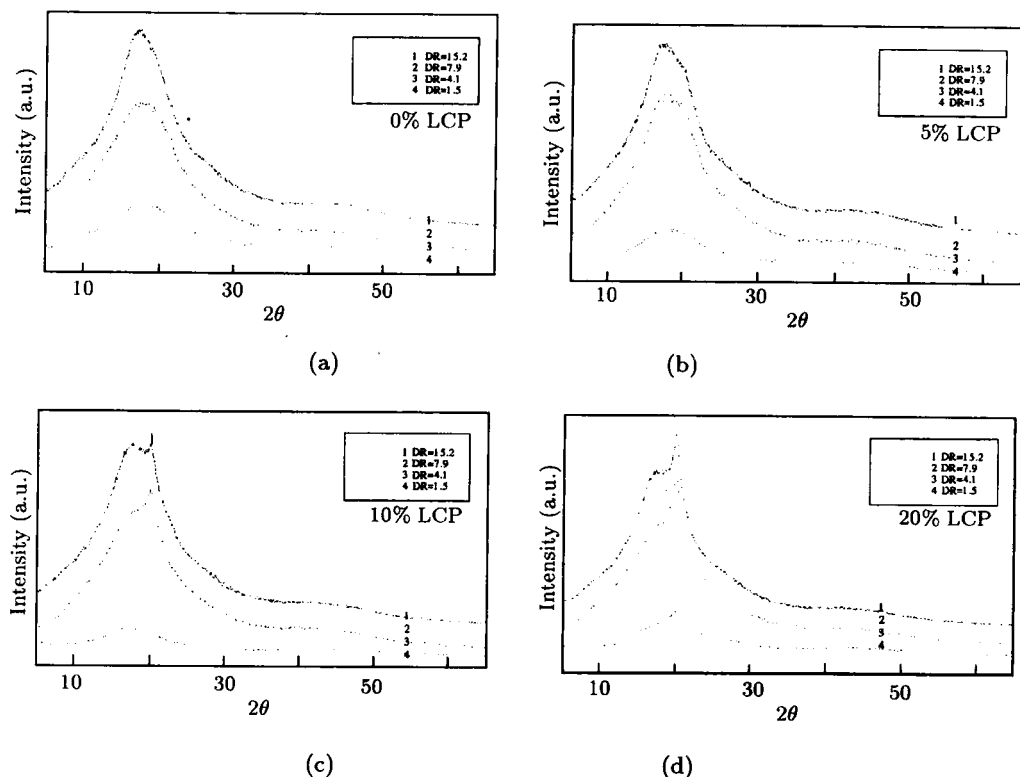


Fig. 8 The X-ray diffraction curves for M-PPO/LCP blends at various draw ratios, (a) 0 wt% LCP, (b) 5 wt% LCP, (c) 10 wt% LCP, (d) 20 wt% LCP

Figs. 8a-d are the X-ray diffraction curves for M-PPO/LCP blends at various draw ratios. It can be seen that only one diffusion peak near 20° can be found in M-PPO no matter it is drawn or not. The results in the blends containing 5 wt% LCP shown in Fig. 8b are similar to that of in pure M-PPO. Fig. 8c shows that the undrawn sample containing 10 wt% LCP has a diffusion peak similar to that of in the M-PPO sample. The drawn samples with draw ratios of 4.1, 7.9 and 15.2 have sharp diffraction peaks near 20° , and the intensity of the peak increases with the draw ratio. The blends containing more LCP have the same situations as seen in Fig. 8d for M-PPO/20 wt% LCP. The X-ray diffraction results manifest that: (1) drawing does influence the orientation and fibrillation of LCP; (2) adequate amount of LCP is needed to reflect the orientation of LCP using the X-ray diffraction method. In the blends of PEI/25 wt% LCP, Lee^[12] reported that an amorphous X-ray diffraction ring could be seen in the undrawn sample, but the ring was reduced in the blend with a draw ratio of 8. In the blends of PC/LCP, the heat of fusion of LCP phase increased with draw ratio. These results manifest that drawing can prompt the orientation and crystallization of the LCP.

Effect of drawing on the morphology

An apparent skin-core structure was observed in the injection molded blends of M-PPO/LCP^[7]. In the skin layer, LCP exhibited higher fibrillation. However, in the core part, LCP remained in the spherical structure. The average diameter of LCP microfibrils in the skin layer increased with the LCP content.

Figs. 9a-c are the micrographs of M-PPO/30 wt% LCP blends. Fig. 9a shows that LCP phase is slightly elongated, after further drawing, a fibrillar structure is developed as shown in Fig. 9b, fine LCP fibers with higher aspect ratio could be observed in the samples with a draw ratio of 4.1. However, it is noticeable that the LCP microfibrils undergo fracture when the draw ratio reaches 15.2 (Fig. 9c). Similar changes of LCP morphology is observed for the LCP phase extracted from the M-PPO/5 wt% LCP blends. The morphology evidence shows that excessive drawing would lead to the breakdown of LCP microfibrils, correspondingly, the mechanical properties of the blends with a draw ratio of 15.2 become poor as mentioned above.

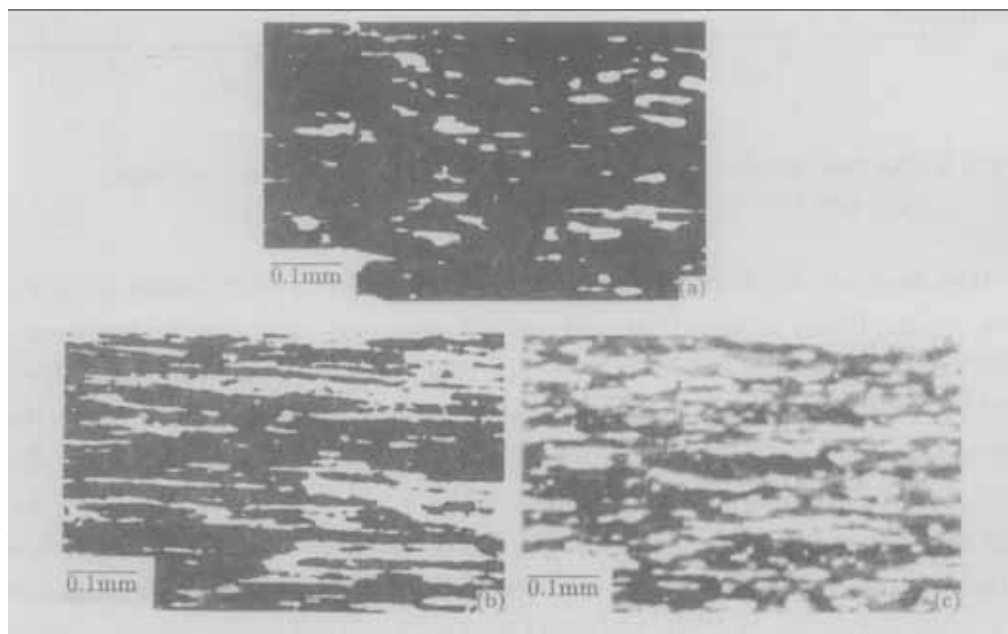


Fig. 9 The micrographs of M-PPO/30 wt% LCP blends,
(a) $DR = 1.5$, (b) $DR = 4.1$, (c) $DR = 15.2$

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Keywords:

Modified poly(phenylene oxide); Liquid crystalline polymer; Drawing of blends;

Morphology; Mechanical properties

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