Interface Modification of PC/LCP *in Situ* Composites and its Influence on Impact Strength

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Keywords: Liquid Crystalline Polymer, Polycarbonate, Compatibilizer, Impact Strength, Interfacial Tension

ABSTRACT

The interfacial modification of the PC/LCP *in situ* composition was studied using epoxy plus DDS as compatibilizer. The interfacial tension between PC and LCP melt was estimated by a technique based on the Taylor's theory of dispersion deformation. The epoxy with DDS reduced the melt interfacial tension which affected the morphology of LCP reinforcement and the interfacial bonding between PC matrix and LCP fibrils. The impact strength of PC/LCP composites was improved by the compatibilizer.

1. INTRODUCTION

The thermotropic liquid crystalline polymer (LCP) can develop fibrillar morphology with high degree of orientation in thermoplastic matrix under appropriate processing conditions. LCP, with high stiffness and high strength, not only reinforces the thermoplastic matrix, but also serves as processing aid in extrusion or injection molding due to its low melt viscosity. Commonly, the LCP blends cannot attain their expected mechanical performance because of the poor miscibility between LCP and thermoplastics, which results in intrinsically weak interfaces. Significant work is being directed at improving the properties of polymer blends by modifying the interfaces and hence the mechanical properties by using compatibilizers.

In previous work in this laboratory, a bisphenol A epoxy resin was used to modify the compatibility between polycarbonate (PC) and LCP during injection molding [1]. It was noted that the PC/LCP interfacial morphology changed with different epoxy content which also resulted in the change of tensile properties. The observed effect of epoxy on the mechanical properties of PC/LCP however was not substantial. In the current study, a curing agent 4-Aminophenyl sulfone (DDS) has been introduced, as a step towards an improvement of the interfacial interaction, by opening the epoxy end groups for reaction with LCP. The objective is to investigate whether the interface and impact properties of PC/LCP *in situ* composites can be improved by introducing epoxy with DDS into the polymer blends.

2. EXPERIMENTAL

2.1 Materials

Liquid crystalline polymer (LCP), Vectra B950 (from Hoechst Celanese) based on hydroxynaphthoic acid (58 mol %), terephthalic acid (21 mol %), and para-aminophenol (21 mol %), was used to generate the reinforcement phase. *Polycarbonate* (PC), the thermoplastic matrix used as the continuous phase, was a bisphenol A polycarbonate, Calibre 300-15 provided by Dow Chemical. *Epoxy*, the bisphenol A epoxy resin, NPES 907, with molecular weight of 3000 was used as compatibilizer supplied by Nan Ya Plastic Corp. 4-Aminophenyl sulfone (DDS), commonly used as a curing agent, was supplied by Acros Chimica.

2.2 Processing

The PC and LCP pellets were first dried at 120 °C for at least 24 hours in vacuum of about 10 mmHg. The dried pellets of PC and LCP were mixed with weight ratio of 95 to 5. To study the effect of epoxy concentration on the compatibility of PC/LCP blends, epoxy powder was added from zero to 1 weight percent of the mixed PC and LCP pellets.

The PC, LCP pellets and epoxy powder were blended in a Haake Rheomix 600/610 mixer with banbury rotors. The temperature and the rotor speed of the mixer were set at 270 °C and 15 rpm, respectively. The mechanically mixed PC pellets and epoxy powder were added into the mixing chamber for about 30 seconds before adding the LCP pellets. After mixing the materials for about 5 min, the blend was then dried at 100 °C for at least 24 hours before further analysis.

The samples for morphological studies under a JEOL scanning electron microscope (JSM-6300F) were first blended in a Haake counter-rotating twin-screw extruder, and then injection molded into impact bars. The impact tests of the injection molded bars were performed by using Tinius Olsen impact tester (model 892). The sample size was 3.0 mm thick and 10.0 mm wide in the reduced section.

2.3 Compatibilization of PC/LCP with curing agent

The reason that epoxy serves as a compatibilizer is due to its good miscibility with PC and possible interaction with Vectra B LCP through hydrogen bonding. In order to promote the hydrogen bond with LCP the epoxy ring must be opened for hydroxylation. In the present work, DDS was used as the agent to open the ring of epoxy. The ratio of epoxy to DDS was calculated based on the molecular weight and formula of epoxy in order to have sufficient DDS to open the end group of epoxy molecules. Mixing of epoxy and DDS was a crucial step in this ring opening process. Three different mixing methods were employed:

1. Mixing epoxy and DDS with weight ratio 5:1 in hot water bath (100 °C) for 30 minutes.
2. Mixing epoxy and DDS with weight ratio 5:1 on a hot plate at about 160 °C for about 1 minute.
3. Mixing epoxy and DDS with weight ratio 4:1 on a hot plate at about 120 °C for 30 minutes.

The mixture of epoxy and DDS was pulverized and then injection molded with PC and LCP (weight ratio 95 to 5). The injection molded bars were used for impact testing and interfacial tension measurement.

2.4 Determination of Interfacial tension

A method based on the Taylor's theory [2] of melt dispersion deformation was developed to evaluate the interfacial tension between the disperse phase and the matrix in melted state. According to the theory, deformation of droplets in the melt is determined by the shear force, provided by the

viscous flow of the melts, and the resistance to deformation due to interfacial tension between droplets and surrounding melt matrix. The droplet deformation (F) is defined as :

$$F = (L - B) / (L + B)$$

where L and B are the length of the major and minor axis of the deformed droplet, respectively. The drop deformation is controlled by both the viscosity ratio of droplet to matrix (p) and the capillary number (κ).

$$p = \eta_d / \eta_m \quad \kappa = \eta_m \nu a / \sigma$$

where η_m and η_d are the viscosity of matrix and droplet, respectively, and ν is the shear rate. σ is the interfacial tension, and a is the diameter of droplet. The capillary number can be understood as the ratio between the hydrodynamic stress ($\eta_m \nu$) acting to deform the drop, and the interfacial stress (σ/a) tending to keep the drop in its equilibrium spherical shape. At steady-state, the droplet deformation is given by,

$$F = (L - B) / (L + B) = \kappa (19p + 16) / (16p + 16)$$

Interfacial tension of the melt blend can be estimated according to this equation, as long as we know the droplet size, the droplet deformation in melt and the viscosity ratio of droplet to matrix. Actually, the deformation (F) is a weak function of the viscosity ratio.

The deformation dynamics of the dispersed LCP droplets in molten PC matrix can be studied by using an optical rotational shearing rig system (CSS450-Linkam Shearing Rig, Linkam Scientific Instruments Ltd.) in which a shear stage is mounted under an optical microscope. A pair of optical windows on the shear stage allow the transmission of light through the shear stage. The gap between the optical windows is filled with the melt blends. A motor and a controlled heating system provide the blends shear force at elevated temperature. Thus the deformation of the melt droplet in the blend can be observed and/or recorded by a video tape recorder.

In this study the samples of PC/LCP blended by the Haake mixer were placed in the gap of 50 μm between the optical windows of the shear stage. The shear stage was heated to 290 °C before introducing the motion with a fixed rate of 2 s^{-1} . The droplet size was determined by measuring the diameter of spherical droplet formed after cessation of shear motion of the melt blend.

The apparent shear viscosity of PC and LCP were determined by a RMS-800 rheometer with two parallel plates of diameter 50.0 mm and gap size 0.375 mm. The temperature was kept at 290 °C and the shear rate was set at 2.0 s^{-1} . The viscosity of the matrix and droplet were 300 and 370 Pa.s, respectively.

3. RESULTS AND DISCUSSION

3.1 Morphology

Figure 1 shows the deformed and restored droplets of LCP under the shearing rig system. The deformation (F) and spherical diameter of droplets were measured from the recorded images of PC/LCP with varied epoxy addition. The corresponding interfacial tension was estimated using the aforementioned equations. Figure 2 shows the interfacial tension between PC and LCP as a function of epoxy addition. The estimated interfacial tension is in the order of 10^{-1} J/m^2 , which is reasonable. Fig. 2 shows the interfacial tension between PC/LCP melt as a function of epoxy and DDS mixture

content. The maximum reduction of interfacial tension was achieved at 0.33 weight percent epoxy and DDS mixture addition and the interfacial tension can be reduced from 0.115 to 0.06 J/m² with the mixture of epoxy and DDS. The reduction of interfacial tension with the mixture addition indicates that the bisphenol A epoxy improves the miscibility of bisphenol A PC and Vectra B LCP by interacting with both polymers at their interfaces when appropriate processing used.

Note that the Taylor's model was developed based on Newtonian flow. The PC melt is Newtonian-like but the LCP melt is not. Here, we are more interested in the comparison of interfacial tension as a function of the compatibilizer addition, instead of their absolute values. On the other hand, with small change of shear rate, the assumption of Newtonian flow in the blend might still be justified.

Fig. 1 Typical micrograph of PC/ LCP melt blend under (lower) and after (upper) shear flow.

Fig.2 The interfacial tension of PC/LCP blends as a function of compatibilizer prepared by method 3.

Fig. 3a PC/LCP with epoxy as compatibilizer

Fig. 3b PC/ LCP without epoxy

The SEM micrographs reveal the morphology change of LCP fibril surfaces due to the addition of the epoxy. As shown in figure 3, the LCP droplet surface in the blends with the compatibilizer is rougher than that pure PC/LCP. This implies a certain degree of interaction at the interface due to epoxy addition. The higher degree of interaction apparently promotes the stress transfer at the

interface and thus increases the mechanical properties of the blend. This result is also supported by Leclair and Favis' research [3]. It has been demonstrated that this epoxy is compatible with PC [4]. Whereas the hydroxylation of epoxy end group might enable the interaction with Vectra B LCP. The results imply the effectiveness of DDS in promoting epoxy as a compatibilizer of the PC/LCP blend. In order to study the correlation between the interfacial modification and the impact strength, impact testing is followed.

3.2 Impact Strength

Table I lists the impact strength of PC/LCP composites processed by different paths. As shown in the table, the impact energy of PC/LCP *in situ* composites increased from 4.87 to more than 8.60 kJ/m², whereas the interfacial tension reduced from 0.104 to about 0.06 N/m when the compatibilizer was introduced. The maximum impact energy of 10.33 kJ/m² was obtained when mixing method 3 was employed. As expected, the impact strength was correlated with the interfacial tension of melt blends. This should be attributed to the better LCP fibrillation during injection molding and the improved interface bonding between PC/LCP when the compatibilizer is used. The mixing method of curing agent (DDS) and epoxy before injection molding with PC and LCP is important. A proper mixing method will lead to a better interfacial interaction and hence a higher impact strength. The temperature of mixing might be the key factor to control the compatibility. In the method 1, the temperature was not sufficiently high for promoting the open ring reaction between epoxy and DDS, and also DDS powder was difficult to mix with epoxy resin. In the method 2, the temperature of 160 °C might already cause the cross-linking of some epoxy molecules which was severely reduced the epoxy capability to react with both PC and LCP. Apparently, method 3 gave us a better effects of compatibilization due to its intermediate mixing temperature. This preliminary investigation should be further pursued to achieve an optimal condition of compatibilization.

Table I. Impact Strength and Interfacial Tension of PC/LCP

	Pure PC/LCP	Mixed with epoxy/DDS by method 1	Mixed with epoxy/DDS by method 2	Mixed with epoxy/DDS by method 3
Impact energy (kJ/m ²)	4.87	8.60	8.97	10.33
Interfacial tension (N/m)	0.104	0.113	0.063	0.067

CONCLUSIONS

The interfacial tension of molten polymer blends can be estimated by a rotation shearing rig system based on the Taylor's theory of droplet deformation in viscous flow. The PC/LCP interfacial tension has been determined by this novel technique. Low molecular weight epoxy with DDS using as a compatibilizer reduces interfacial tension between PC and Vectra B LCP, and results in improving the impact strength of PC/LCP composites. An optimal addition of epoxy in PC/LCP can be determined by combining the interfacial tension measurement and morphology observation. The mixing techniques affect the efficiency of compatibilization of epoxy with DDS, and a better compatibilization is achieved by controlling the temperature of mixing.

ACKNOWLEDGEMENTS

The project was support by a Hong Kong UGC research infrastructure grant and Radar Company LTD in Hong Kong. Dr. Jingshen Wu in our department provided valuable suggestions. Mr. Hong Shing Chan helped in the experimental work.

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