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Polycarbonate/liquid crystalline polymer blend: Crystallization of polycarbonate

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Abstract

The enhanced crystallization of polycarbonate in the blend of liquid crystalline polymer/polycarbonate/(ethylene–methyl acrylate–glycidyl methacrylate) copolymer (LCP/PC/E–MA–GMA) was studied by wide angle X-ray diffraction (WAXD) and differential scanning calorimetry (DSC). The LCP/PC/E–MA–GMA 5/95/5 blends annealed at 200 °C, for 2, 4, 6, and 10 h, present an obvious crystalline structure corresponding to PC crystallization. The PC crystal obtained shows two melting temperature, T_{m1} of about 214 °C and T_{m2} of about 231 °C, with a total heat of fusion of 29 J/g (annealing time = 10 h). The preliminary results indicate that amorphous PC can be induced to crystallization by the synergistic action of LCP dispersed phase and reactive compatibilizer.

Keywords: Crystallization; Polycarbonate; Liquid crystalline polymer

1. Introduction

It is well known that the crystallization of the bisphenol-A polycarbonate (PC) is very slow because of its chain rigidity and two big methyl side groups, which retard chain diffusion [1]. Annealing for a long time above the glass transition temperature (T_g) can induce the crystallization of amorphous PC. Vonfalka and Rellensman reported that at 190 °C, one full day was necessary for the first crystallites to develop and above a week to obtain a complete spherulite [2]. Alizadeh et al. systematically studied the effect of molecular weight on the kinetics of bulk crystallization of PC. In their work, the heat of fusion of PC annealed at 185 °C gradually increased after an induction period of 50 h [3]. Organic solvents [4,5], vapors [6,7] and low melting point polymer [8,9] have been used to accelerate the PC crystallization. Recently, supercritical carbon dioxide [10,11], vapor-grown carbon fiber [12] and nano-scale filler [1,13] were also used to induce the crystallization of PC.

Many studies of the liquid crystalline polymer (LCP) blends have been carried out since the introduction of the concept of in situ composites [14–16]. Most of the studies of LCP blends deal with the morphology evolution of the LCP dispersed phase [17,18], the miscibility [19] and compatibility between LCP and the matrix [20], as well as the mechanical properties of the composites [21]. The transesterification between PC and LCP during processing, including annealing, will give a large effect on crystallization mechanism of this blend system, as well as the morphological change reported in other publications [22,23]. Few publications have addressed the PC crystallization induced by LCP dispersed phase.

In the present work, the LCP/PC dumb-bell-shaped sample was obtained by injection molding, with and without reactive compatibilization of ethylene–methyl acrylate–glycidyl methacrylate copolymer (E–MA–GMA), an effective compatibilizer for PC blends [24]. The crystallization of PC in LCP/PC/E–MA–GMA blend was detected using wide angle X-ray diffraction (WAXD) and differential scanning calorimetry (DSC). The enhanced crystallization of PC induced by the synergistic action of LCP dispersed phase and compatibilizer was observed.

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2. Experimental

2.1. Materials

The polycarbonate (PC) resin used is a commercial product of Teikoku Sanso Co. Ltd (Japan), supplied in pellets, with the trade mark K1300. The M_n is about $2.8-3.5 \times 10^4$ g mol^{-1} and the molecular weight distribution index (M_w/M_n) is 2.1. The liquid crystalline polymer (LCP), Vectra A950 from Hoechst Celanese with a melting temperature of 283 °C, is a random copolyester of *p*-hydroxybenzoic acid (73 mol%) and 6-hydroxy-2-naphthoic acid (27 mol%), with a density of about 1.4 g/cm^3. The commercial copolymer used as compatibilizer is Lotader AX8900, ethylene–methyl acrylate–glycidyl methacrylate (E–MA–GMA, 68:24:8 wt%), achieved by a high-pressure polymerization process, from Atofina, with a melt index of 6 g/10 min, and is mainly amorphous (crystallinity <5%).

2.2. Sample preparation

The PC and LCP were dried in a vacuum oven at 100 °C for 12 h and the E–MA–GMA was also dried at 50 °C for 12 h. The pellets of the components were tumbled in a drum for about 5 min before the polymers were fed into the hopper of the extruder. The extrusion of the LCP/PC 5/95 and LCP/PC/E–MA–GMA (5/95/5 and 30/70/5) blends was performed on a TSSJ-25 co-rotating twin-screw extruder made by Chengguang Chemical Institute, Chengdu (PRC) with a screw length to diameter ratio of 33. The temperature profile was in the range of 240–290 °C. The E–MA–GMA/PC 5/95 blend was blended in the same procedure with a different temperature profile of 180–250 °C. After palletizing, the extrudate was dried to remove the attached moisture during cooling and palletizing, and injected into dumb-bell samples of 4 mm thickness on a PS40E5ASE (Nissei) precise injection molding machine. The temperature profile was 255, 265, 295 and 290 °C from the feeding zone to nozzle, and both the injection and holding pressures were 50.0 MPa. The annealing of the blends was carried out in a vacuum oven at different temperatures for up to 10 h.

2.3. Characterization

The specimens for analysis were cut from the sub-skin layer of the annealed sample. Wide angle X-ray diffraction (WAXD) spectra were obtained on a Philips X'Pert Graphics & Identify at a scanning rate of 2.4 deg/min from 10 to 40 deg (2θ), operating at 35 kV, 25 mA, using Ni-filtered Cu Kα radiation. Differential scanning calorimetry (DSC) analyses of specimens were carried out on a Perkin–Elmer thermo analyzer (DSC-2) at a heating rate of 10 °C/min from 130 to 250 °C. The values of T_{m1} and T_{m2} were obtained from the differential DSC curve and the heat of fusion is the sum of T_{m1} and T_{m2} peaks.

3. Results and discussion

Fig. 1 shows the first heating DSC curves of the LCP/PC 5/95 and LCP/PC/E–MA–GMA 5/95/5 blends annealed for 2 h at 140, 160, 180 and 200 °C. It is found that the LCP/PC blend annealed at 200 °C shows only the glass transition (onset = 141.9 °C, mid = 145.2 °C and end = 148.5 °C) without any endothermic peak, the same to LCP/PC/E–MA–GMA blends annealed at 140 and 160 °C for 2 h. Noted that the middle temperature of glass transition of PC in the two specimens is 142 and 139.2 °C, both lower than that of the LCP/PC blend annealed at 200 °C, which was possibly caused by the decrease of the molecular weight due to annealing. However, an obvious endothermic peak ($T_{m2} = 230.5$ °C) and a weak shoulder ($T_{m1} = 213.4$ °C) are presented in the DSC heating curve of LCP/PC/E–MA–GMA blend annealed at 200 °C and the heat of fusion (ΔH_m) is 5.4 J/g. Similar results on the crystallization of PC had been reported by Takahashi et al. [12] ($\Delta H_m = 19.6$ J/g, $T_{m2} = 234.6$ °C and $T_{m1} = 213.1$ °C) and Alizadeh et al. [3] ($\Delta H_m = 26$ J/g, $T_{m2} = 227$ °C and $T_{m1} = 210$ °C). In these literatures, the endothermic peak was deemed to be corresponding to the crystalline structure of PC and the shoulder to the heating rate. Along with the decrease of heating rate, the shoulder will be weakened and disappear. In the LCP/PC/E–MA–GMA blend annealed at 180 °C, a relatively weak endothermic peak at 226.1 °C is observed without any shoulder at lower temperature. This implies that the PC crystallization in LCP/PC/E–MA–GMA is enhanced at appropriate annealing temperature.

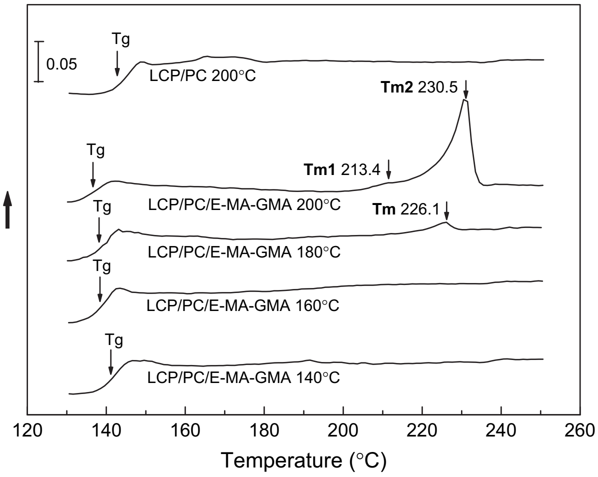
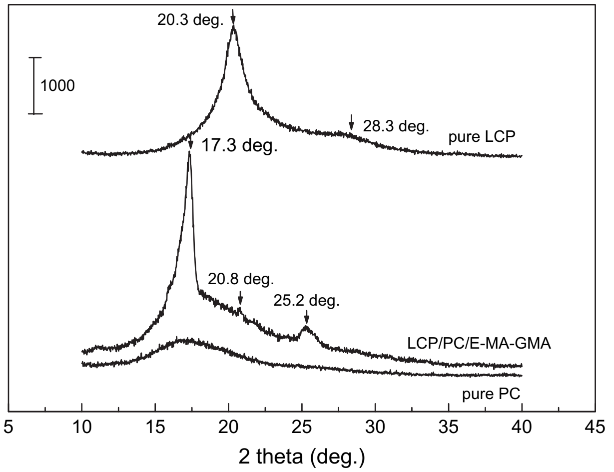


Fig. 1. The first heating DSC curves of the LCP/PC (5/95) and LCP/PC/E–MA–GMA (5/95/5) blends annealed at different temperatures for 2 h. The annealing temperature is marked under the corresponding curve.

WAXD was carried out for these blends to validate the existence of PC crystal. Fig. 2 shows the WAXD spectra of pure PC, LCP and LCP/PC/E–MA–GMA 5/95/5 blend annealed at 200 °C for 10 h. Pure PC only shows a broad reflection around 2θ of about 17 deg, which corresponds to the amorphous phase. Pure LCP presents a sharp reflection at 2θ of 20.3 deg and a broad reflection around 2θ of about 27.5 deg. Compared with pure PC and LCP, when the LCP/PC/E–MA–GMA blend has been annealed at 200 °C for 10 h, the spectra of the blend gives sharp reflections at 17.3 and 25.2 deg. The WAXD data of LCP and LCP/PC/E–MA–GMA blend annealed at 200 °C for 10 h are listed below Fig. 2. The (020) and



Sample	2θ (°)	d spacing (Å)	Assignment
LCP	20.3	4.37	110
	28.3	3.15	211/210
LCP/PC/E-MA-GMA	17.3	5.12	020/-201
	20.8	4.27	213
	25.2	3.53	-222/303/223

Fig. 2. The WAXD spectra of the pure PC, LCP and LCP/PC/E–MA–GMA (5/95/5) blend annealed at 200 °C for 10 h.

(−201) reflections are located at $2\theta = 17.3$ deg corresponding to the monoclinic unit cell [25]. These changes in WAXD spectra indicate an increase in crystallinity of PC in the annealed blend. Therefore, the DSC and WAXD results implied that PC crystallization is enhanced in the presence of LCP dispersed phase with the compatibilization of E–MA–GMA copolymer.

The first heating DSC curves of the blends annealed at 200 °C for different times are shown in Fig. 3. It is found that both the samples annealed for 30 and 60 min show only one glass transition without any endothermic peak, implying that the crystallization of PC cannot be enhanced in a short annealing time. An endothermic peak and a weak shoulder (see Fig. 1 distinctly) are observed in the sample annealed for 2 h, corresponding to the crystalline structure of PC. Here, the glass transition can also be detected, but is lower than that of those annealed for 30 and 60 min. The DSC curves of samples annealed for 4, 6 and 10 h present similar profile, a sharp endothermic peak (T_{m2} = about 231 °C) and an obvious shoulder (T_{m1} = about 214 °C). The heat of fusion of the LCP/PC/E–MA–GMA blend becomes saturated around 29 J/g, which is slightly higher than that of pure PC and PC/vapor-grown carbon fiber composite reported in the literature [3,12]. The glass transition decreases obviously owing to the enhanced crystallization of PC in all of the samples annealed for 4, 6 and 10 h. It is found from Fig. 3 that both of T_{m1} and T_{m2} are independent of the annealing time, about 214 ± 2 and 231 ± 1 °C, respectively. The result about T_{m2} in our work is similar to that of Hu and Lesser [1].

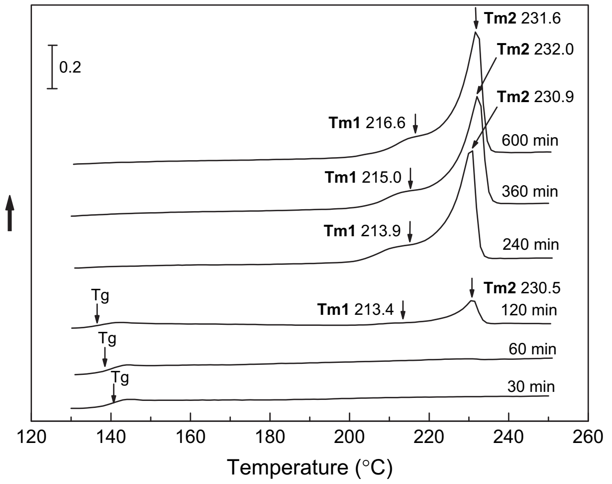


Fig. 3. The first DSC heating curves of the LCP/PC/E–MA–GMA (5/95/5) blend annealed at 200 °C for different times. The annealing time is marked above the corresponding curve.

Table 1 shows the relative crystallinity of the samples annealed at 200 °C as a function of annealing time. This relative crystallinity is a normalized crystallinity by the sum of heat of fusion which is 29 J/g in the sample annealed at 200 °C for 10 h. It is indicated that PC in LCP/PC/E–MA–GMA blend takes about 100 min for crystallization to start and 240 min to complete, and the half-time of crystallization, $t_{1/2}$, of PC is about 160 min. This indicates that PC in LCP/PC/E–MA–GMA blend has a higher rate of crystallization comparing with pure PC [3]. WAXD results also validate the crystallization process of the PC in LCP/PC/E–MA–GMA blend annealed for different annealing times.

The first DSC heating curves of the E–MA–GMA/PC 5/95 blends with and without annealing at 200 °C are shown in Fig. 4. The DSC curve shows that the blend annealed for 2 h exhibits only one glass transition without any endothermic peak, implying that E–MA–GMA copolymer cannot induce the formation of the crystalline structure in PC solely. From the DSC curve of LCP/PC 5/95 blend mentioned above, it is found that the LCP/PC blend shows no endothermic peak. So the crystallization of PC cannot be enhanced in the presence of LCP or E–MA–GMA copolymer only. It is concluded that the enhanced crystallization of the PC in LCP/PC/E–MA–GMA 5/95/5 blend is induced by the synergistic action of LCP dispersed phase and reactive compatibilizer.

Fig. 4 also shows the first DSC heating curves of the LCP/PC/E–MA–GMA 30/70/5 blend with and without annealing at 200 °C. It is observed that the crystalline structure of PC in LCP/PC/E–MA–GMA 30/70/5 blend has a very small heat of fusion (0.63 J/g) and a low melting temperature (T_{m1} = 207.4 °C, T_{m2} = 219.4 °C). The heat of fusion of 0.63 J/g from the LCP/PC/E–MA–GMA 30/70/5 blend annealed at 200 °C for 2 h is 88% less than that of the 5/95/5 blend annealed under the same conditions. This means that the

Table 1
The relative crystallinity of the LCP/PC/E–MA–GMA (5/95/5) blend annealed at 200 °C as a function of annealing time

Annealing time (min)	30	60	120	240	360	600
Heat of fusion (J/g)	0	0	5.4	25.5	27.2	29
Relative crystallinity (%)	0	0	18.6	87.9	93.8	100

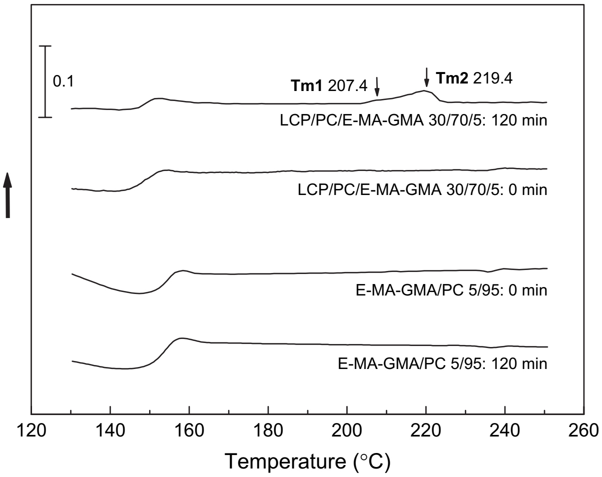


Fig. 4. The first DSC heating curves of the E–MA–GMA/PC (5/95) and LCP/PC/E–MA–GMA (30/70/5) blends with and without annealing at 200 °C.

crystallization of PC is inconspicuous with high LCP content. It seems that the LCP molecules at higher percentage have hindered PC molecules from crystallization, which results in smaller size and less perfection of the PC crystals.

The preliminary results show that the amorphous PC can be induced to the crystallization by the LCP dispersed phase with the enhanced interfacial interaction by reactive compatibilization. To investigate the mechanism of PC crystallization, the crystallization process of PC induced by the synergistic action will be studied using AFM, TEM and dynamic rheometer in the future.

4. Conclusions

The enhanced crystallization of polycarbonate in the blend of LCP/PC/E–MA–GMA was investigated in this paper, and the following conclusions were drawn:

(1) The LCP/PC/E–MA–GMA 5/95/5 blends annealed at 200 °C, for 2, 4, 6, and 10 h, show an obvious crystalline structure corresponding to PC crystallization.
(2) The PC crystal obtained in this work has two melting temperature, T_{m1} of about 214 °C and T_{m2} of about 231 °C, and has a heat of fusion of 29 J/g (annealing time = 10 h).
(3) The preliminary results show that the amorphous PC can be induced to the crystallization by the synergistic action of LCP dispersed phase and reactive compatibilizer.

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