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Growth of Spatial Dendrites in Bisphenol-A Polycarbonate Induced by Dioctyl Phthalate at High Pressure

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Bisphenol-A polycarbonate (BAPC) dendritic crystals were formed through the melt crystallization induced by dioctyl phthalate (DOP) at high pressure. The cultured dendrites belong to a three-dimensional structure with different characteristics. The dendritic growth was found to be accelerated with the increase of the applied temperature, pressure, crystallization time and DOP concentration. This finally resulted in the formation of the structures of the spatial cellular dendrites in the investigated BAPC/DOP system.

Keywords: bisphenol-A polycarbonate; blends; dendrite; growth; high-pressure crystallization

1. INTRODUCTION

With excellent optical properties, high impact resistance and high glass transition temperature, bisphenol-A polycarbonate (BAPC) has been widely used as an engineering polymer of high performance. The bulk crystallization of the polymer is extremely slow due to an

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inherent rigid nature of the molecular backbone [1]. However, the slow-rate bulk crystallization makes it easy to obtain BAPC samples of different crystallization stages in a frozen state. So the research on the crystallization of BAPC can possibly enlarge the application areas of the material and deepen the understanding about the nature of polymer crystallization [2].

Many studies on the crystallization behaviors of BAPC have been reported, including bulk crystallization [3], solvent-induced and vapor-induced crystallization [2,4], effects of nucleating agents [5–8] and supercritical carbon dioxide [9,10] on crystallinity and crystallizability in polymer blends [11]. However, to the best of our knowledge, no investigation was performed on the morphology of high-pressure crystallized BAPC samples.

In this work, wide-angle X-ray diffraction (WAXD), differential scanning calorimetry (DSC) and scanning electron microscopy (SEM) were employed to investigate the morphology of high-pressure crystallized BAPC/DOP blend samples as obtained by varying temperature, pressure, crystallization time and DOP concentration. The results showed that BAPC spatial dendrites with different characteristics were formed through the melt crystallization at high pressure.

2. EXPERIMENTAL

2.1. Materials

BAPC in pellets was a commercial product supplied by Changfeng Chem. Co., Chongqing, China. The viscosity-average molecular weight, calculated from intrinsic viscosity, was around 27500. An analytical-grade DOP used as a plasticizer was provided by Tianjin Chem. Co., Tianjin, China. By using a Haake Rheocord 90 torque rheometer equipped with a co-rotating twin screw extruder, BAPC and DOP was melt-blended as the compounding ratio listed in Table 1. The temperature profile used for the extruder was 200, 250, 265 and 220°C from hopper to die and the screw rotation was maintained at 30 rpm. The extruded rod was immediately quenched in cold water and pelletized subsequently.

2.2. Sample Preparation

High-pressure experiments were carried out with a piston-cylinder high-pressure apparatus [12]. The following procedure for crystallization was used. After loading the sample, low pressure (50 MPa) was applied and temperature was raised to a predetermined level. After equilibrium was established, the pressure was raised to the desired

TABLE 1 The Crystallization Conditions and Results for BAPC/DOP Blend Samples

Sample	BAPC/DOP (wt/wt)	Crystallization conditions	Melting point T_m (°C)	Melting enthalpy (J/g)	Crystallinity X_c (%)
1	90/10	200 MPa, 250°C for 48 h	225.58	25.24	25.56
2	90/10	200 MPa, 290°C for 48 h	217.12; 247.19	38.43	38.92
3	90/10	400 MPa, 290°C, 24 h	217.17; 222.41	36.17	36.64
4	90/10	600 MPa, 290°C, 24 h	221.85	30.89	31.29
5	90/10	200 MPa, 240°C, 6 h	223.95	29.53	29.91
6	90/10	200 MPa, 240°C, 48 h	221.42	29.00	29.37
7	90/10	200 MPa, 240°C, 72 h	219.92	29.08	29.45
8	95/5	200 MPa, 250°C, 6 h	218.83	3.077	2.953
9	80/20	200 MPa, 250°C, 6 h	221.55	27.63	31.48

value. The samples were kept under these conditions for a predetermined time, and then quenched down to ambient condition. This procedure ensured that the temperature of the polymer would not exceed the crystallization temperature so as to minimize the degradation of BAPC at elevated temperature. This also assured that the polymer would be in a molten state before crystallization took place. The crystallization conditions are listed in Table 1.

2.3. Characterization

DSC measurements were performed at atmospheric pressure by using a Netzsch DSC-204 instrument. The weight of sample was 10 mg. The melting behavior of crystals was investigated through a heating scan with a heating rate of 10°C/min at N_2 atmosphere. The crystallinity X_c was calculated from the melting enthalpy ΔH_m by means of the following equation:

$$X_c = \Delta H_m/(\Delta H_m^o \omega(PC)), \quad (1)$$

where ω (PC) is the weight ratio of BAPC in the blends, and (ΔH_m^o is the melting enthalpy of the ideal crystal, which was assumed to be 109.7 J/g according to Legras *et al*. [5].

WAXD results were obtained at room temperature with an X' Pert Pro MPD apparatus. SEM observations were carried out on a JEOL-JSM-5900LV instrument. The fresh surfaces of the samples were obtained through fracture at liquid N_2 temperature, which were further coated with gold for the detections. Prior to the gold treatment, the surfaces were etched by dimethylacetamide at 25°C for a given

time, which was capable of dissolving only amorphous, but not crystalline BAPC [13].

3. RESULTS AND DISCUSSION

3.1. WAXD Results

WAXD was employed to determine the crystal structure of the BAPC crystals obtained in the high-pressure crystallized BAPC/DOP blend samples. Figure 1 gives out the WAXD pattern of a sample crystallized at 200 MPa, 290°C for 48 h, which is typical of the obtained profiles for such characterization. All main diffraction lines should be assigned to monoclinic form, which can be crystallized from melt at normal pressure [14]. This indicated that no new crystal structure was formed in the presence of DOP at high pressure.

3.2. DSC Measurements

The starting materials of the BAPC/DOP blends were all in an amorphous state, as revealed by WAXD and DSC. The melting temperature (T_m), melting enthalpy (ΔH_m) and crystallinity (X_c) of these pressure-treated BAPC/DOP samples, obtained with DSC, are listed in Table 1. Other conditions being the same, the blend samples with larger values of melting enthalpy were obtained at higher temperature (sample 2: 38.43 J/g) and lower pressure (sample 3:

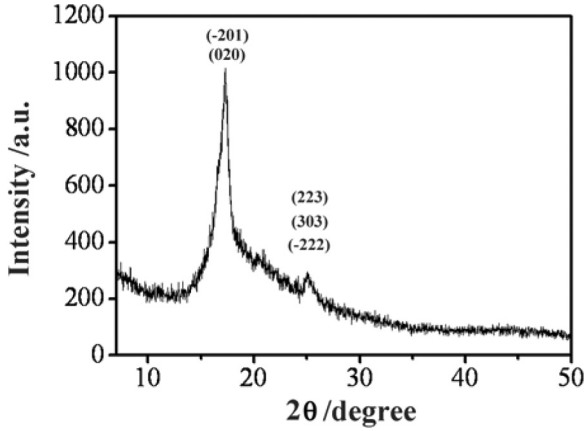

FIGURE 1 The WAXD pattern of BAPC/DOP blend sample 2 crystallized at 200 MPa, 290°C for 48 h.

36.17 J/g). The crystallinity for sample 5 crystallized at 200 MPa, 240°C for 6 h attained a value of 29.91%. However, the melting enthalpy remained more or less the same for the samples 6 and 7 crystallized at the parallel pressure and temperature for 48 and 72 h respectively, which was even slightly lower than that of the sample 5 due to long-time degradation [15]. This revealed that longer crystallization time was unnecessary to obtain a fully-crystallized BAPC/DOP blend sample. The results also showed that the growth of BAPC crystals was hastened in all these blends, and the sample with a higher DOP concentration was endowed with a larger value of crystallinity after the same high-pressure treatment (sample 9). Two melting temperatures were detected for both the samples 2 and 3, and the low (sample 2: 217.12°C; sample 3: 217.17°C) and high (sample 2: 247.19°C; sample 3: 222.41°C) melting points should correspond to the melting of two distinct populations of BAPC crystals [3]. On the other hand, the observed melting points for the samples 1–9 were in accord with the normal-pressure crystallized BAPC samples [3,11], which indicated that only folded-chain crystals were obtained in the BAPC/DOP blends.

3.3. SEM Observations

All fracture surfaces of the BAPC/DOP blend samples were observed with SEM measurements. Figure 2a gives out a representative morphology of BAPC crystals obtained in the samples of high-pressure crystallized BAPC/DOP blend. We could observe a spatial dendrite appeared and clustered on the fracture surface of sample 1 crystallized at 200 MPa, 250°C for 48 h. A higher temperature will hasten the dendrite propagation, which finally resulted in the dense dendritical

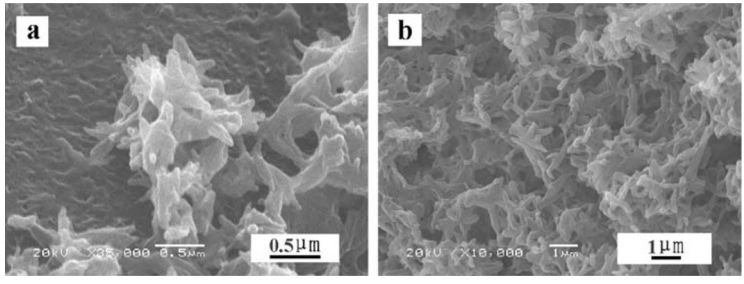

FIGURE 2 Secondary electron images of the BAPC/DOP (90/10, wt/wt) blend samples 1 and 2 crystallized at 200 MPa, different temperature for 48 h: (a) sample 1, 250°C; (b) sample 2, 290°C. The fracture surfaces were etched by dimethylacetamide at 25°C for 4 h.

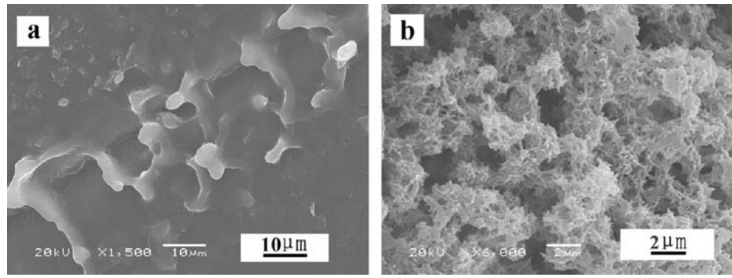

FIGURE 3 Secondary electron images of the BAPC/DOP (90/10, wt/wt) blend samples 3 and 4 crystallized at different pressure, 290°C for 24 h: (a) sample 3, 400 MPa, no etching technique was applied; (b) sample 4, 600 MPa, the fracture surface was etched by dimethylacetamide at 25°C for 6 h.

structure as designated in Figure 2b (sample 2: 200 MPa, 290°C for 48 h). Arborescent crystals with the morphology as designated in Figure 3a were detected in sample 3, which was crystallized at a higher pressure within a relative short time (400 MPa, 290°C for 24 h). Without the etching treatment, we could clearly observe the bold fibrils diverged infrequently during the growth in the amorphous matrix. Raising pressure further could accelerate the dendrite growth such that that the spatial cellular dendrites with the morphology shown in Figure 3b were observed on the etched fracture surface of sample 4 crystallized at 600 MPa for the same other conditions. Although high temperature and elevated pressure can in principle hasten dendrite propagation in the BAPC/DOP blends, a longer crystallization time was also found to be necessary for the growth of dendritical crystals of BAPC with denser structures in such blend. Figure 4a displays a secondary electron image of the fracture surface of sample 5 crystallized at 200 MPa, 240°C for 6 h, from which we could only observe a slightly-branched spatial dendrite. However, as shown in Figure 4b, the secondary electron image revealed that the spatial cellular dendrites with highly-branched structures were formed on the fracture surface of sample 7 when the crystallization time was prolonged to 72 h. BAPC/DOP blend sample 8 and 9 were prepared through the same crystallization process, and the only difference for the two samples was the concentration of incorporated DOP in the original materials. As shown in Figure 5a, the spatial dendritical crystals could still be detected on the etched surface of sample 8 with a lower DOP concentration. With the increase of the compounding ratio of DOP in the blends, the crystals of BAPC became more open and coarse. This can be revealed by a representative SEM photograph

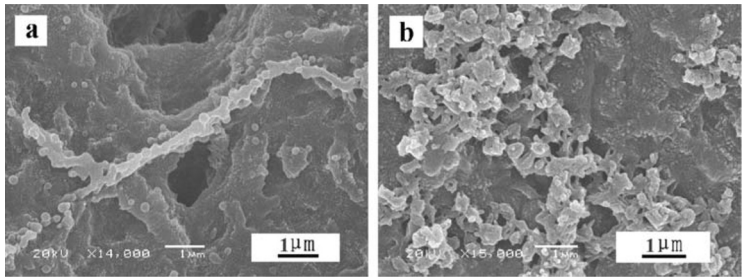

FIGURE 4 Secondary electron images of the BAPC/DOP (90/10, wt/wt) blend samples 5 and 7 crystallized at 200 MPa, 240°C for different time: (a) sample 5, 6 h, the fracture surface was etched by dimethylacetamide at 25°C for 6 h; (b) sample 7, 72 h, the fracture surface was etched by dimethylacetamide at 25°C for 8 h.

obtained from the fracture surface of sample 9 with 20wt.% DOP (Fig. 5b).

The morphologies in Figures 2–5 give some interesting indications on the growth of dendrite of polymer as well as new material design. Through delicate etching techniques, the internal organization of the dendritical crystals grown from bulk materials, which belongs to a three-dimensional structure, was disclosed clearly by SEM. The dendritic growth was accelerated with the increment of the applied temperature, pressure, crystallization time and DOP concentration. This finally resulted in the formation of the structures of the spatial cellular dendrites in the polymer blends. Another astonishing point on the revealed dendritic crystals is that they can keep their entity

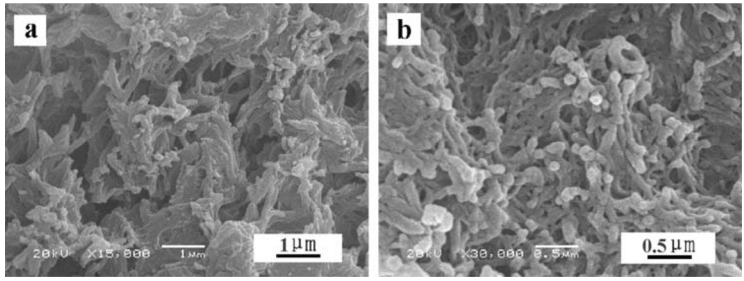

FIGURE 5 Secondary electron images of the BAPC/DOP blend samples 8 and 9 with different compounding ratio crystallized at 200 MPa, 250°C for 6 h: (a) sample 8, 5 wt.% DOP; (b) sample 9, 20 wt.% DOP. The fracture surfaces were etched by dimethylacetamide at 25°C for 6 h.

without being broken though the amorphous region is etched away. As shown in Figures 2–5(b), the disclosed crystalline-branched frames of such crystals with denser structures, due to their large specific surface area, can possibly identify a niche functional application in the field of chemical engineering such as filler layers in packed towers, catalyst supports and effluent treatment units.

According to the model developed by Strobl for polymer crystallization [16], it is proposed that the initial step is always the creation of a mesomorphic layer which spontaneously thickens, up to a critical value, where it solidifies through a cooperative structural transition. The transition produces a granular crystalline layer, which transforms in the last step into homogeneous lamellar crystallites. A typical secondary electron image of the fracture surface of sample 6 crystallized at 200 MPa, 240°C for 48 h is displayed in Figure 6, from which a granular substructure of the lamellae of BAPC can be clearly observed. The image obtained by us presented directly not only the size of single granules but also the final homogeneous lamellar crystallites that obviously evolved through a merging process. The SEM measurement may possibly indicate that the growth of the BAPC spatial dendrites in the multiphase system is compatible with the above-mentioned model, whereas similar observations were commonly obtained by transmission electron microscope (TEM) and atomic force microscope (AFM) on such homogeneous polymer systems as polyethylene (PE) [16,17], syndiotactic polypropylene (s-PP) [18], isotactic

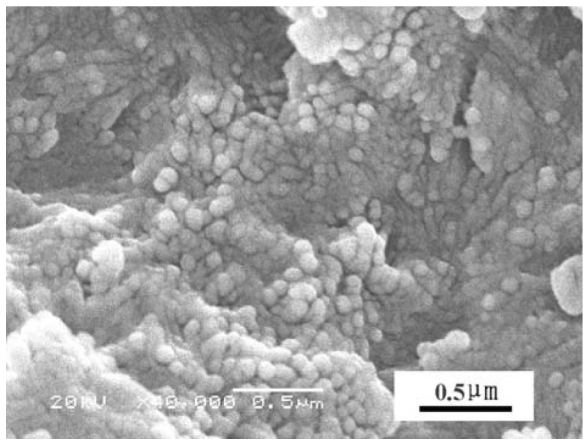

FIGURE 6 Secondary electron image of the BAPC/DOP (90/10, wt/wt) blend sample 6 crystallized at 200 MPa, 240°C for 48 h.

polypropylene (i-PP) [19], poly (vinylidene fluoride) (PVDF) [19] and poly (ethylene oxide) (PEO) [19].

4. CONCLUSION

Based on the WAXD, DSC and SEM results, it is concluded that BAPC dendrites with different characteristics were formed through the melt crystallization induced by DOP at high pressure. With the increase of temperature, pressure, crystallization time and DOP concentration, the dendritic growth was hastened and finally resulted in the formation of the structures of the spatial cellular dendrites. The SEM observations presented a granular substructure of the lamellae in the prepared samples, which suggested that the crystallization of BAPC in the heterogeneous system was compatible with the major route followed in polymer crystallization proposed by Strobl. The revealed crystalline-branched frames of such crystals may have functional application in the field of chemical engineering due to their large specific surface area.

SUMMARY

Bisphenol-A polycarbonate dendritic crystals of different characteristics were formed through the melt crystallization induced by dioctyl phthalate (DOP) at high pressure. The cultured dendrites belong to a three-dimensional structure, and can be easily exposed with the technique of selective etching. The dendritic growth was accelerated with the increment of the applied temperature, pressure, crystallization time and DOP concentration, which finally resulted in the formation of the structures of the spatial cellular dendrites. The disclosed crystalline-branched frames of such crystals, due to their large specific surface area, can possibly identify a niche functional application in the field of chemical engineering.

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