Effect of pressure on the crystallization behaviour of polyethylene terephthalate

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Abstract
Crystallized polyethylene terephthalate (PET) samples were obtained at high pressures of 200–400 MPa at a temperature of 603 K, and another group of the samples were made at pressures of 250–350 MPa and different temperatures with a fixed supercooling. The samples were investigated by means of differential scanning calorimetry and scanning electron microscopy. Characterization results suggested that high pressure could increase the crystallization rate and promote the thickening process of PET lamellar crystals.

1. Introduction

Polymer materials usually have complex structure composed of crystalline and amorphous regions, and the former type include two kinds of crystal, folded chain and extended chain; the crystal size is very small—nanometre or micron grade. A great variety of structures and properties of the polymer can be obtained at different conditions. It is very interesting and important to synthesize large extended-chain single crystals of polymer for research not only at the fundamental level but also as regards new low-dimensional functional materials.

Many works have shown that pressure is an important factor affecting the crystallization behaviour of polymer [1–7]. Some polymers, such as polyethylene (PE) [2, 3] and poly(vinylidene fluoride) (PVDF) [4], have a loose-packed hexagonal phase at high pressure, which may induce the formation of extended-chain crystals. Reports on polyamide (PA) [5–7] did not show any new loose-packed structure to exist at high pressure, but high pressure is also a necessary condition for growing extended-chain crystals in PA.

Polyethylene terephthalate (PET) is also a typical semi-crystalline polymer composed of crystalline and amorphous regions [8]. Although some investigations of the high-pressure crystallization behaviour of PET have been reported, the results have discrepancies [9–11]. Recently we have reported that extended-chain crystals of PET with thickness up to 17 μm could be obtained through a high-pressure crystallization process [12–16]. All results on PET

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Table 1. Crystallization conditions ($t = 6$ h) and results.

Sample no	1	2	3	4	5
Pressure (MPa)	200	300	400	250	350
Temperature (K)	603	603	603	578	628
Melting temperature (K)	544.8	555.0	551.1	550.2	558.1
Melting enthalpy (J g^{-1})	86.8	118.2	122.6	93.4	123.3
Crystallinity (%)	61.9	84.4	87.5	66.7	88.1

could suggest that high pressure may promote the crystallization rate. However, no direct experimental evidence has confirmed this view or concerned the effect of pressure on the process of thickening of PET crystals.

In this work, two groups of PET samples were treated through different processes. The crystallization conditions for one group were set at different pressures and the same temperature, and those for another group were set at different pressures and temperatures for a fixed supercooling. Characterization results for the samples showed clearly that pressure could increase the crystallization rate and promote the process of thickening of the extended-chain crystals.

2. Experimental details

An unoriented commercial PET (Yanshan Petroleum and Chemical Company, China) was used as the original material. The molecular weight, calculated from the viscosity, was about 18 000. Before high-pressure treatment, the original PET material was allowed to stand for 36 h at 368 K in vacuum to eliminate moisture.

High-pressure experiments were carried out with a piston–cylinder apparatus [17]. The following procedure for crystallization was used. After loading the sample, a pressure, 30 MPa, was applied and temperature was raised to a predetermined level. After equilibrium was established, pressure was raised to a predetermined level. The samples were kept under these conditions for 6 h, and then quenched to ambient conditions. This procedure ensured that the polymer temperature would not exceed the crystallization temperature so as to minimize degradation of the PET at elevated temperature and also to ensure that the polymer would be in the molten state before crystallization took place. The crystallization conditions are listed in table 1.

Calorimetric measurements were performed at atmospheric pressure by using a differential scanning calorimetry (DSC), Perkin-Elmer DSC-2 instrument. The calorimeter was calibrated with the standard substance, which melts in the range used for PET. The heating rate was 10 K min^{-1}. The crystallinity was calculated using the following equation:

$$X_c = \Delta H_m / \Delta H_m^0$$

where ΔH_m^0 is the equilibrium melting enthalpy, which was taken as 140 J g^{-1} as suggested by Wunderlich [18].

The morphology of the samples was observed by using a scanning electron microscopy (SEM), AMRAY 1845FM apparatus. Fracture surfaces of the specimens were made at liquid N$_2$ temperature.

3. Results and discussion

Figure 1 gives the DSC curves of samples 1–3. The melting temperature, melting enthalpy and crystallinity are listed in table 1. It can be seen that the crystallinity increased with the increase of pressure.
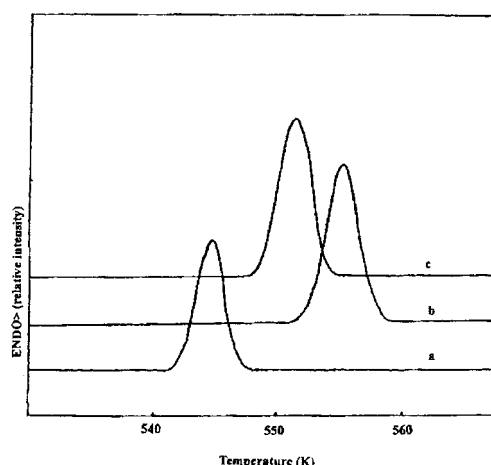
Figure 1. DSC curves of PET samples crystallized at high pressures ((a) sample 1, 200 MPa; (b) sample 2, 300 MPa; and (c) sample 3, 400 MPa).

It was considered that when the polymer was compressed the freedom of molecular chains would be decreased, and so the entropy would decrease with increase of pressure. Thus the compressibility of crystals is generally lower than that of the amorphous region, and the decrease in entropy in crystals $\Delta S_c(p)$ is less than that in the amorphous region $\Delta S_a(p)$:

$$\Delta S_a(p) > \Delta S_c(p).$$

Taking this view, it is easy to envisage that decrease of the Gibbs free energy $\Delta G(p)$ during the crystallization at high pressure could be more obvious than that at ambient conditions:

$$\Delta G(p) < \Delta G < 0.$$

This shows that high pressure can increase the driving force for the crystallization of the polymer. If the difference in compressibility between crystalline and amorphous regions is bigger, the effect of pressure on the crystallization of the polymer is more significant.

Sample 1, crystallized at the lowest supercooling, has the lowest melting temperature. This is not consistent with the crystallization law at normal pressure, because lower supercooling should correspond to a higher melting point and thicker lamellar crystals generally. Considering that the above result is brought out by both pressure and supercooling, we have not clearly revealed the effect of pressure on the crystallinity and process of thickening of polymer lamellar crystals.

In order to exclude the hindrance of supercooling, we treated samples 4 and 5 at the same supercooling as sample 2. So samples 4 and 5 were crystallized at 250 and 350 MPa respectively. Their melting enthalpies and temperatures are lower and higher than those of sample 2 respectively, indicating that the sample treated at higher pressure has higher crystallinity and thicker lamellar crystals at the same supercooling. However, the effect of pressure on the crystallization rate was less obvious, along with the increase of pressure. The reason is possibly the temperature degradation and the decreasing of compressibility of the polymer occurring along with the increase of pressure.

Figure 2 presents the secondary-electron image of the fracture surface of sample 2. The parallel striations, which are typical of extended-chain crystals in polymers [20], were clearly observed in the images. The thicknesses of the extended-chain crystals in samples 2 and 5 are about 4 and 6 μm respectively.
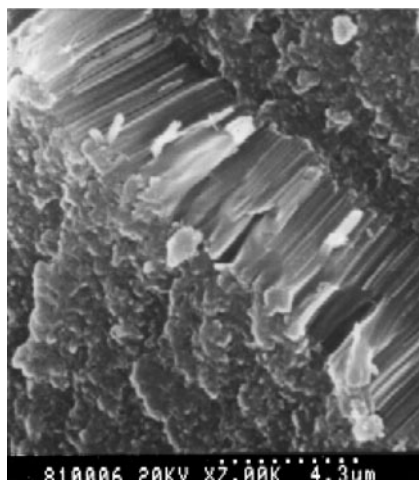
Figure 2. The secondary-electron image of a fracture surface of sample 2.

But this characteristic was not found in sample 4. It is possible that the thickness of the lamellar crystals in the sample 4 is very small that we could not detect them with our SEM. Nevertheless, it is not yet determined that extended-chain crystals did not form at 250 MPa. Therefore, we think that the sample crystallized under higher pressure has thicker lamellar crystals at the same supercooling. This suggested that high pressure could promote the process of thickening of PET crystals.

Based on the results of DSC and SEM, it could be concluded that pressure can effectively increase the crystallization rate of the PET and promote the process of thickening of the crystals under the given experimental conditions.

Acknowledgment

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