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High pressure crystallized poly(ethylene terephthalate): high crystallinity and large extended-chain crystals

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Abstract

High-pressure crystallized poly(ethylene terephthalate) samples were investigated with differential scanning calorimetry and scanning electron microscopy. Poly(ethylene terephthalate) (PET) extended-chain crystals with thickness up to 6 μm were formed under high pressure. Calorimetric measurements showed that the highest melting point of these samples was 553.13 K without superheating, and the melting enthalpy was up to 138.2 J/g, higher than the value of ideal PET perfect crystals used by some researchers. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(ethylene terephthalate); High pressure; Extended-chain crystals

1. Introduction

Poly(ethylene terephthalate) (PET) is a semicrystalline polymer composed of crystalline and amorphous regions. A great variety of microstructures can be developed in PET by changing the crystallization conditions. The crystallization rate of PET is low at normal conditions since its molecular chain is semirigid. The crystallinity is usually lower than 60% [1]. However, Yukishige et al. obtained a PET sample with a melting enthalpy up to 131.8 J/g through long time (near to 1 year) annealing at low pressure [2].

Although Siegmann et al. reported that PET extended-chain crystals with thickness up to 100 nm can be formed under high pressure, [3] no other experimental evidence reported by following investigators confirmed this result. The results about the morphology of high-pressure crystallized PET have discrepancies, but in the view that high pressure can accelerate PET crystallization rate they are almost consistent with each other [4–7]. In this work, the differential scanning calorimetry (DSC), wide angle X-ray diffraction (WAXD), Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) were employed to characterize high-pressure crystallized PET samples. The result showed that the melting enthalpy

was up to 138.2 J/g and extended-chain crystals with thickness up to 6 μm were formed.

2. Experimental

An unoriented commercial PET (Yanshan Petrol. Chem. Co. China) was used as the original material. The molecular weight, calculated from viscosity, was about 18 000. Before high-pressure treatment, the starting material was allowed to stand at 368 K in vacuum for 36 h to eliminate moisture. High-pressure experiments were carried out with a piston-cylinder high-pressure apparatus [8]. The following procedure for crystallization was used. After loading the sample, low pressure (50 MPa) was applied and temperature was raised to 603 K. After equilibrium was established, pressure was raised to 300 MPa. The samples were kept under these conditions for 6, 12 and 24 h, respectively corresponding to samples 1–3, and then quenched down to ambient condition. This procedure ensured that the polymer temperature would not exceed the crystallization temperature so as to minimize degradation of PET at elevated temperature and also to ensure that the polymer would be in a molten state before crystallization takes place.

Calorimetric measurements were performed at atmospheric pressure by using a Perkin–Elmer DSC-2 instrument. The
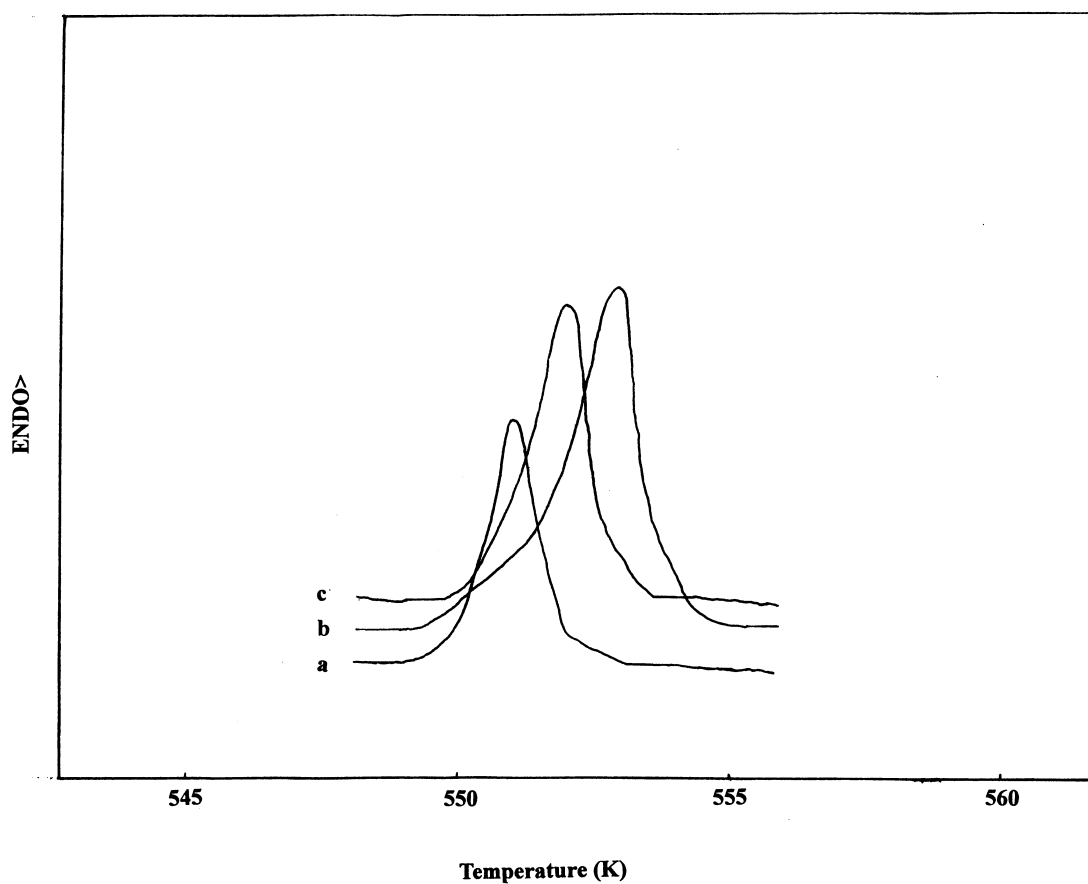
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Fig. 1. DSC measurements on PET crystallized at 300 MPa, 603 K for (a) sample 1, 6 h; (b) sample 2, 12 h; and (c) sample 3, 24 h. The heating rate was 1.25 K/min.

calorimeter was calibrated with standard substances which melt in the range of PET melting. The heating rate was 1.25 K/min to prevent superheating. 10 K/min was also used for comparison.

WAXD measurements were obtained at room temperature with a D/max-1-a instrument, crystallinities being estimated. FTIR was carried out on a Nihon Bunkou DS-402G from samples in KBr discs. SEM was performed on a AMRAY 1845FM apparatus. Fracture of specimens was carried out at liquid N_2 temperature.

3. Results and discussion

Fig. 1 shows the DSC curves for the high-pressure crystallized PET samples. The heating rate was 1.25 K/min. The melting temperature (T_m) and melting enthalpy (H_m) were listed in Table 1. Another melting enthalpy in Table 1 was obtained with heating at 10 K/min. All samples had only one melting temperature, respectively. The melting points of these samples were much higher than that of the original sample (527 K), which approximately equaled the equilibrium melting point of PET suggested by Wunderlich [9]. This possibly indicated that PET extended-chain crystals were formed in the samples. On decreasing the heating rate, the melting enthalpy had a little reduction. Nevertheless, the melting enthalpies of sample 2 and sample 3 were higher than the value (135 J/g) of ideal perfect PET crystals used by some researchers [6,7], when the heating rate was 10 K/min. Even the heating rate was 1.25 K/min, the melting enthalpy of sample 2 was higher than this value. This suggested that the crystallinities of samples 2 and 3

Table 1
The crystallization conditions and results

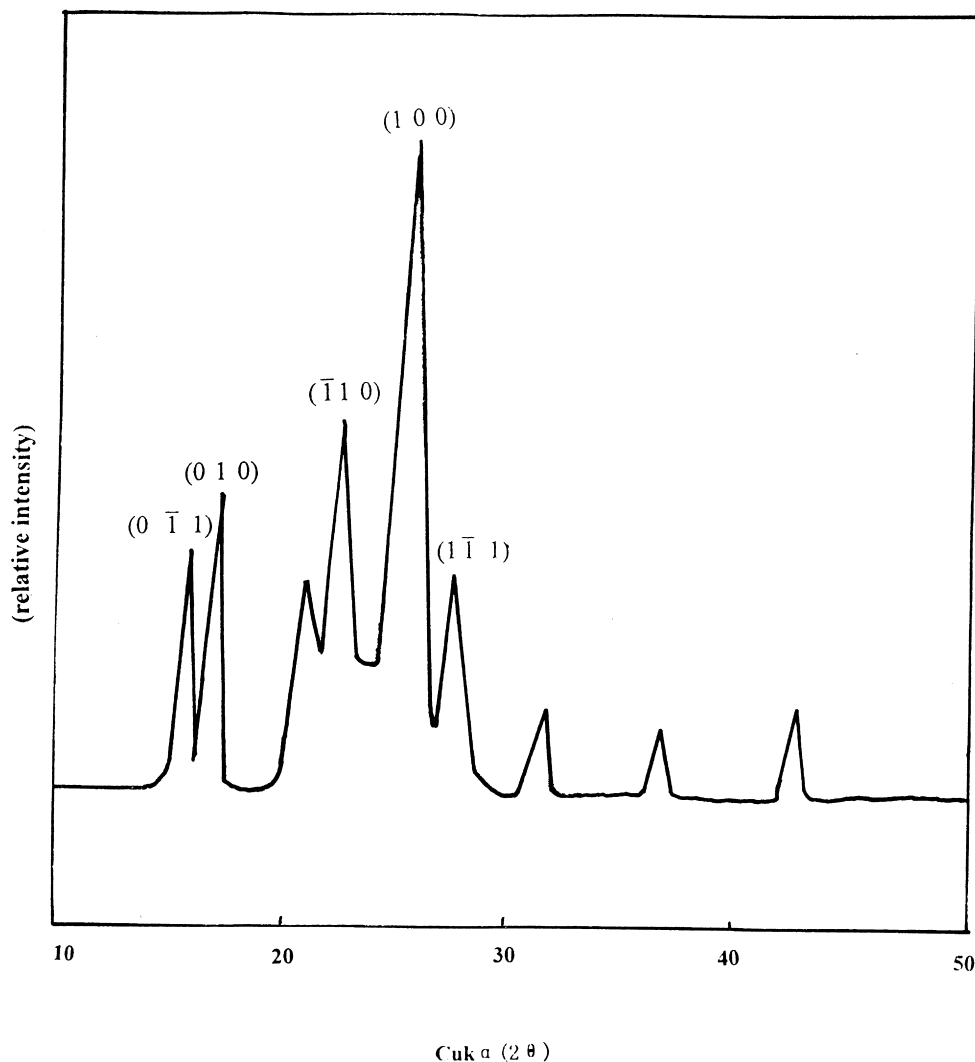| Sample	Crystallization conditions 300 MPa 603 K	Melting point T_m (K) 1.25 K/min	Melting enthalpy H_m (J/g) 1.25 K/min	Melting enthalpy H_m (J/g) 10 K/min	Crystallinity X_{cWAXD} (%)
Sample 1	6 h	551.86	90.13	93.31	64.2
Sample 2	12 h	553.13	137.41	138.20	96.7
Sample 3	24 h	552.40	133.51	136.74	94.8

Fig. 2. The WAXD pattern of sample 2 crystallized at 300 MPa, 603 K for 12 h.

were very high, possibly near 100%; on the other contrary, this also showed that the commonly used melting enthalpy of ideal perfect PET crystals is low, which should be higher than the value measured in our experiments. The result suggested that the melting enthalpy of 140 J/g reported by Wunderlich is more precise for PET ideal crystals [9].

An interesting result was that the sample crystallized for the longest time did not have the highest melting temperature and melting enthalpy, but sample 2 had the highest for both the data. This possibly originated from degradation. Both crystallization and degradation have been taking place under these experimental conditions. At the first stage of crystallization, there remained enough amorphous PET for crystal growth, the effect of crystallization, composed of thickening and lateral growth, was more important on the microstructure of PET extended-chain crystals. So the melting temperature and melting enthalpy increased along with the crystallization time. However,

when the amorphous part nearly disappeared, namely, the crystallinities were near 100%, just like sample 2, the crystal growth rate drastically slowed down. But this had little influence on the degradation, especially under elevated temperature condition. On increasing crystallization time too longer, the effect of the degradation on melting temperature and melting enthalpy emerged, because many defects were induced by the degradation in these extended-chain crystals. So the melting temperature and melting enthalpy decreased in sample 3.

The wide-angle X-ray diagram of sample 2 is displayed in Fig. 2. All diffraction lines corresponded to triclinic crystal structure, which was the same as that of the original sample. This implied that the higher melting points of the high-pressure crystallized samples were not due to a new crystal structure. The crystallinities of samples 1–3 were also estimated with WAXD and listed in Table 1. It can be seen that samples 2 and 3 had very high crystallinities and this was consistent with the result of DSC.
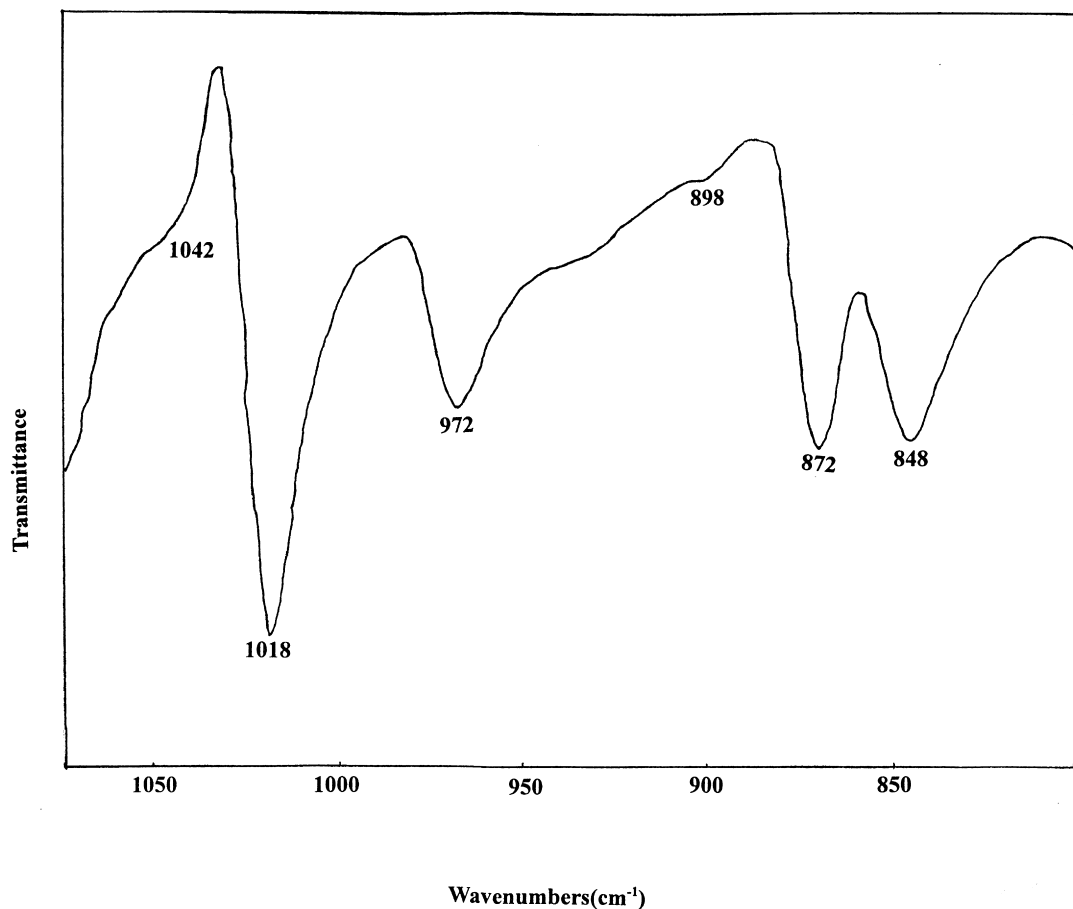
Fig. 3. The infrared spectrum of sample 2 crystallized at 300 MPa, 603 K for 12 h.

FTIR measurements showed that 988 cm^{-1} band, which has been assigned to folded chains [10], was not detected in the spectra of these samples. This suggested that crystals with chain-extended instead of chain-folded were formed in the high-pressure crystallized samples. The infrared spectrum of sample 2 is displayed in Fig. 3. It can be seen that the bands corresponding to *gauche* (898, 1042 cm^{-1})

conformation were very weak and the intensity ratio between bands corresponding to *trans* (972, 848 cm^{-1}) and *gauche* is very high. This revealed that sample 2 has high crystallinity.

Fig. 4 gives out the typical secondary electron images (SEI) of the fracture surface of sample 1(a), sample 2(b) and sample 3(c). The fracture surface reveals the striated
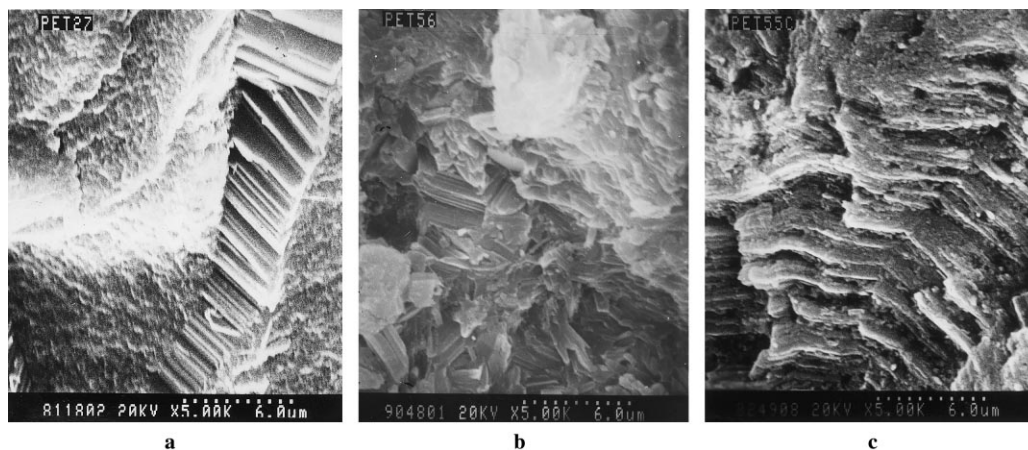

Fig. 4. The SEI of high-pressure crystallized PET fracture surface (a) sample 1; (b) sample 2; and (c)sample 3.

appearance, which is the most characteristic feature for extended-chain crystals. The thickness of these extended-chain crystals was up to 6 μm, which was much longer than the length of the original molecular chain, calculated from the average molecular weight. Although the crystallization time of sample 3 is four times of sample 1, the thickness of PET extended-chain crystals had little increase.

On the basis of the results of DSC, FTIR and SEM, it was clear that high pressure can accelerate PET crystallization and promote the formation of large PET extended-chain crystals. The crystallinity was near to 100% and the thickness of extended-chain crystals was up to 6 μm.

More details about the effect of crystallization pressure and temperature on PET will be given in future publications.

Acknowledgements

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