

Notes

EFFECT OF PAN-MILLING STRESS ON CRYSTAL STRUCTURES OF HIGH DENSITY POLYETHYLENE*

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Abstract A detailed study was performed on the crystal structures of pan-milled high-density polyethylene (HDPE) using differential scanning calorimetry (DSC) and X-ray diffraction. The crystallinity of HDPE first decreased slightly, followed by a gradual increase with increasing milling times. Monoclinic crystals appeared after 4 cycles of milling. With increasing times of milling, the proportion of monoclinic crystals increased significantly while the proportion of orthorhombic crystals decreased gradually. With increasing times of milling, the crystallite size of orthorhombic form decreased greatly, while the size of monoclinic crystallites kept almost constant during milling.

Keywords High-density polyethylene, Pan-milling, Crystal structure

INTRODUCTION

Changes in the crystal phase of drawn semicrystalline polymers have attracted much attention. When a material is drawn, deformation is substantially localized in a “neck” region and it is there that discontinuous changes occur from the normal lamellae structure to a fibrillar one. How these discontinuous changes progress is a key question for research on the deformation mechanism of semicrystalline polymers.

Many different opinions exist on the deformation mechanism of semicrystalline polymers. Among them, two models are prevalent. Peterlin^[1-3] has suggested a model, based on lamella tilting and crystal shearing along the chain axis, to explain the lamellar-to-fibrillar transformation during the deformation of polymers. Peterlin's model was supported by the results obtained from vibrational spectroscopy, electron microscopy and X-ray studies on the deformation of semicrystalline polymers^[4-8]. The model proposed by Harrison^[9, 10] is of a very different nature. In Harrison's view, deformation of polymers is a quasi-melting of the crystal (below the thermodynamic melting temperature) followed by recrystallization. Melting and recrystallization is implicated in wide angle X-ray diffraction and small angle neutron scattering studies^[11, 12].

Linear polyethylene is a highly crystalline polymer whose crystallization from the melt normally produces an orthorhombic crystal structure with two chains per unit cell. However, Seto *et al.*^[13] suggested that a single chain per unit cell structure, which they designated as monoclinic, could be produced from orthorhombic materials by phase transformation involving a diffusionless process similar to twinning. Hendra *et al.* studied the phase transformations in drawn HDPE and concluded that the proportion of monoclinic crystal and its dependence on draw ratio were determined by the draw temperature, rate and medium^[14].

Till now, research has been mainly focused on changes of crystal phase caused by drawing processes. Change of crystal structures under shear stress in the solid state has rarely been studied.

* The author acknowledges the financial support for this project by the National Natural Science Foundation of China and the State Education Commission of China, and is grateful to the Analysis & Testing Center of Sichuan University for technical support of this work.

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An inlaid pan-mill^[15, 16] is a kind of mechanochemical reactor designed on the basis of stone pan-mill formerly used in China which can produce strong shear stress. In this paper, HDPE was processed in a pan-mill, its crystal structures after different times of milling were investigated using DSC and X-ray diffraction.

EXPERIMENTAL

Materials

HDPE used was HDPE6098 with a melt flow index of 0.1 dg/min and a density of 0.948 g/cm³, supplied by the Qilu Petrochemical Company.

Pan-Milling

An inlaid pan-mill type mechanochemical reactor^[16], equipped with a water cooling device with a rotating speed of 25 rpm, was used. HDPE was milled for different times (cycles). The process from the beginning of feeding to the end of material discharge was considered as one cycle.

Characterization

Melting and crystallization behavior was investigated by using a Perkin-Elmer DSC-7 differential scanning calorimeter.

Wide angle X-ray diffractograms were recorded by using a D/Max IIA diffractometer with CuK α radiation incident perpendicularly to the sample plane and the draw axis.

RESULTS AND DISCUSSION

Effect of Pan-Milling on Crystallinity

The DSC results of milled and unmilled HDPE are given in Table 1. Melting points for HDPE samples milled for different times were found to be in the range of 130~132°C. The crystallinity of HDPE first decreased with increasing milling times, but increased with increasing milling times after 2 cycles of milling. Nevertheless, the change in crystallinity was only about 4%, which is rather small considering the high stress applied to the polymer in the pan-mill.

Table 1. DSC analysis results of milled and unmilled HDPE

Milling times (cycles)	Melting point (°C)	Enthalpy (J/g)	Crystallinity (%)
0	130.2	153	53.6
2	130.2	145	50.9
4	130.2	148	51.9
6	132.0	149	52.0
8	131.3	155	54.4
10	131.0	157	54.9
15	130.3	157	55.0

Effect of Pan-Milling on Crystal Structures

Crystal forms of PE include stable orthorhombic [$P_{nam}(D_{2h}^{16})$] with cell dimensions of $a = 0.7417$ nm, $b = 0.4945$ nm, $c = 0.2547$ nm, metastable monoclinic [$C2/m(C_{2h}^3)$] with cell dimensions of $a = 0.809$ nm, $b = 0.253$ nm, $c = 0.479$ nm, $\beta = 107.9^\circ$ and high pressure orthohexagonal. Both orthorhombic and monoclinic phases have the planar zigzag chain configuration. Orthorhombic forms have two distinct diffraction peaks at $2\theta = 21.4^\circ$ (110, $d_{110} = 0.41$ nm) and $2\theta = 23.65^\circ$ (200, $d_{200} = 0.37$ nm), while monoclinic forms have a strong diffraction peak at $2\theta = 19.5^\circ$ (001, $d_{001} = 0.46$ nm) and two weak peaks at $2\theta = 14.1^\circ$ (110, $d_{110} = 0.63$ nm) and $2\theta = 17.1^\circ$ (040, $d_{040} = 0.52$ nm), respectively. Since the amorphous phase has a wide diffraction band at $2\theta = 19.5^\circ$ ($d = 0.46$ nm) which overlaps with the diffraction to the monoclinic phase, therefore, diffraction at $2\theta = 19.5^\circ$ must be used together with the other two diffraction peaks to confirm the presence of monoclinic crystals.

Figure 1 shows the X-ray diffraction curves of milled and unmilled HDPE. At milling times of 4 cycles, the

characteristic diffraction peaks of monoclinic crystals appeared clearly. The intensity of the peaks became stronger at milling times of 15 cycles. Therefore, it may be concluded that monoclinic crystals were formed during pan-milling.

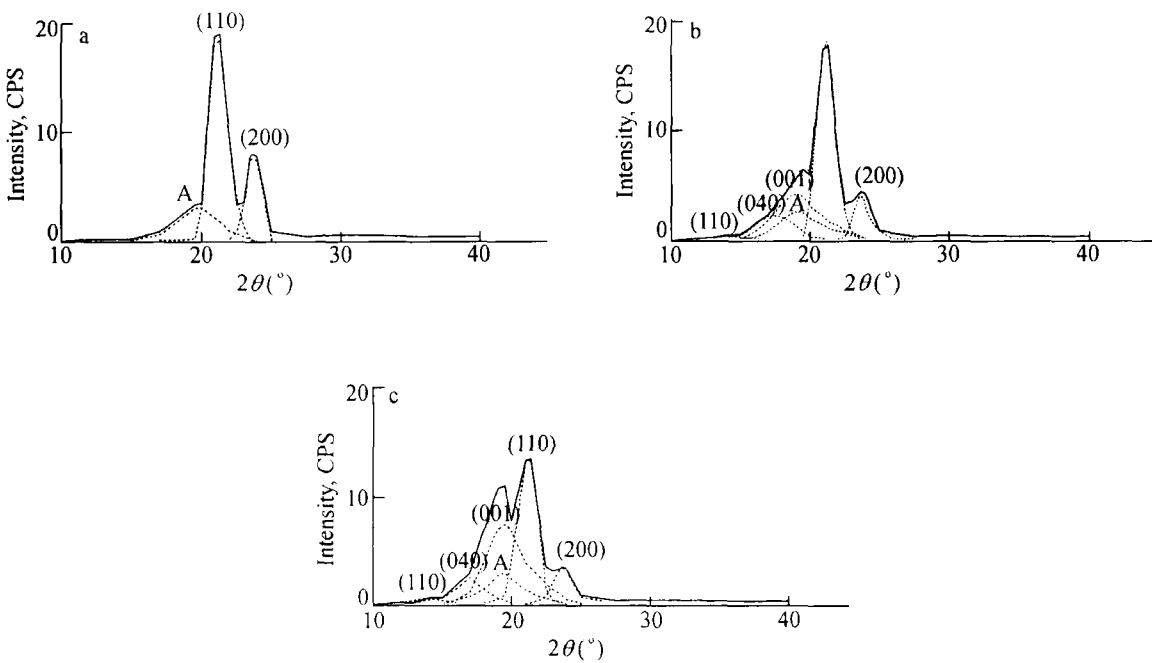


Fig. 1 X-ray diffraction curves of milled and unmilled HDPE
a) Unmilled HDPE
b) HDPE milled 4 times
c) HDPE milled 15 times
A: amorphous halo

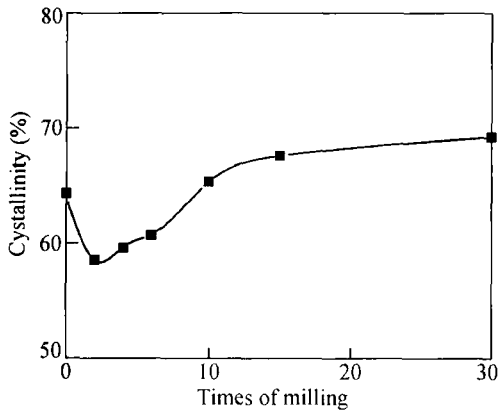


Fig. 2 Crystallinity (X_c) of milled and unmilled HDPE measured by X-ray diffraction method

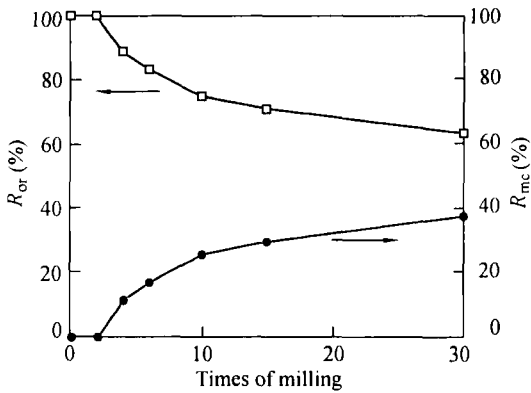


Fig. 3 Proportion of orthorhombic (R_{or}) and monoclinic (R_{mc}) phases in milled and unmilled HDPE

Crystallinity may be calculated after peak separation (by Gauss function, as shown in Fig. 1) by using the following equation:

$$X_c = I_c / (I_c + KI_a) \times 100\% \tag{1}$$

where X_c is the crystallinity, I_c and I_a are the peak intensities for crystalline and amorphous peaks respectively, K is a constant (0.75 for PE). The calculated results were plotted in Fig. 2. Crystallinity initially decreased with increasing times of milling, then followed by gradual increases. This is in good agreement with the DSC analysis results.

Similarly, the proportions of monoclinic (R_{mc}) and orthorhombic (R_{or}) phases in the crystal part of milled and unmilled HDPE were calculated and plotted in Fig. 3. With increasing times of milling, the proportion of monoclinic phase increased markedly while the proportion of orthorhombic phase decreased greatly. After milling 15 times, the proportion of monoclinic phase increased from 0% to about 40% while the proportion of orthorhombic phase decreased from 100% to about 40%. The trend in the change of the total crystallinity must be a result of the combination of the above effects.

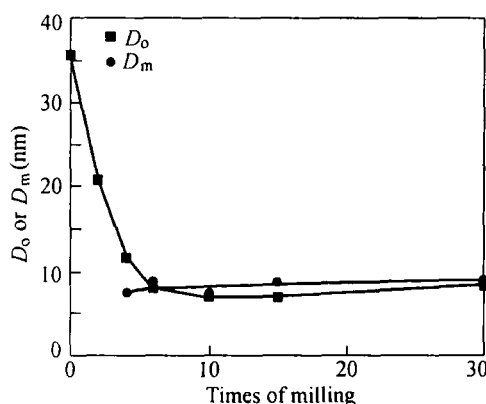


Fig. 4 Sizes of orthorhombic crystallites (D_o) and monoclinic crystallites (D_m) in milled and unmilled HDPE

Crystallite size may be calculated from the Sherrer equation:

$$D = 0.89 \lambda / \beta \cos \theta \quad (2)$$

where D is the crystallite size, $\lambda = 0.154$ nm, β is the width of diffraction peak at half peak height. The size of orthorhombic crystallites (D_o) and monoclinic micro-crystals (D_m) were then calculated and plotted in Fig. 4. Crystallite size of the orthorhombic form decreased rapidly with increasing times of milling and remained almost constant after milling 6 times. Monoclinic crystal phase appeared after four cycles of milling and its crystallite size was almost constant.

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