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A study on the heat of fusion of β-polypropylene

J.X. Li[1a], W.L. Cheung[a,]*, Demin Jia[b]

[a]Department of Mechanical Engineering, The University of Hong Kong, Pokfulam Road, Hong Kong
[b]Department of Polymer Materials Science and Engineering, South China University of Technology, Guangzhou 510641, People's Republic of China

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Abstract

Isotactic polypropylene (iPP) resin was doped with 1% of pimelic acid/calcium stearate (composition ratio = 1/1.5). It was crystallized in a two-step isothermal process, first at 130°C and then at 95°C, and finally cooled at a rate of 0.5°C min^{-1} to room temperature. The specimens were basically free of α-crystals and could be considered as pure β-PP. The crystallinity of the specimens was determined on the basis of their density. The heat of fusion of the β-crystal was found to be 168.5 J g^{-1}. In comparison, the heat of fusion of the α-crystal in the undoped resin was slightly higher at 177.0 J g^{-1}.

Keywords: Pure β-PP; Crystallization; Heat of fusion

1. Introduction

Padden and Keith [1] first noted that the formation of β-PP was favoured by rapidly quenching the polyropylene (PP) melt to below 128°C. Later, Turner-Jones et al. [2] reported that samples containing predominantly β-phase could be produced by rapidly quenching the melt of a special PP type in a mixture of water and glycerine at 100–120°C. Since then a number of methods, such as doping the resin with certain heterogeneous nucleating agents [3–11], directional crystallization in a temperature-gradient field [12,13] and shear-induced crystallization [14,15], have been found to be effective in promoting the formation of β-PP. Although pure β-PP was observed in the crystallizing polymer between the upper and lower critical temperatures [16,17], some α-crystals would form due to conversion of the growth pattern from β to α when the sample was cooled below the lower critical temperature [16,18]. So far, we are not aware of any report on the presence of pure β-PP at room temperature.

In theory, if the crystallizable material is exhausted before reaching the lower critical temperature, the β-to-α growth conversion can be avoided and pure β-PP be obtained even when the sample is subsequently cooled down to room temperature. It was shown earlier [19] that the doped iPP resin has a lower critical temperature of about 85°C, which is significantly lower than 105°C as reported by Lotz et al. [18]. This will provide a wider temperature range for β-growth and is favourable for depletion of the crystallizable material, thus restraining the formation of the α-phase in the subsequent cooling to room temperature. In this study, a stepwise crystallization process between the upper and lower critical temperatures has been adopted in an attempt to prepare pure β-PP. The heat of fusion of the β-phase has been determined and compared with that of the α-phase.

2. Experimental

2.1. Preparation of pure β-PP

The isotactic polypropylene (iPP) resin used was Himont 6501 in powder form. The resin was first screened with a 60 mesh sieve to eliminate the large particles so that it can be mixed well with the nucleating agent. It was doped with 1% of pimelic acid/calcium stearate (composition ratio = 1/1.5). The doping process has been reported earlier [19]. Two crystallization methods were used to prepare the pure β-PP samples: crystallization in a differential scanning calorimeter (d.s.c.) and compression moulding.

In the d.s.c. crystallization method, a DuPont 910 differential scanning calorimeter was used. About 10 mg of the

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* Corresponding author.

[1] Present address: Department of Chemical Engineering, Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong.

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doped resin was heated in nitrogen to 200°C and kept for 2 min to eliminate all α-phase entities in the melt. It was cooled quickly down to 130°C and allowed to crystallize isothermally for 30 min. Then it was cooled at 3°C min^{-1} to 95°C and kept for 10 min for the second-step isothermal crystallization. Finally it was cooled extremely slowly at 0.5°C min^{-1} to room temperature in order to deplete the remaining crystallizable material before reaching the lower critical temperature, i.e., 85°C.

In the compression moulding, the doped resin was placed in a stainless steel mould and melted in a press at 200°C for 5 min. It was moulded into a 1 mm thick plate and then moved quickly to another press at 130°C. It was allowed to crystallize isothermally at 130°C for 25 min, then the temperature setting of the press was adjusted to 100°C and the sample was allowed to crystallize further for 15 min before the heater was turned off. The sample was cooled down to room temperature in the press under pressure. Similarly, iPP samples containing pure α-phase were prepared; in this case, the resin was not doped.

2.2. Measurement of density

The densities of the polymer samples were measured with a density bottle and propyl alcohol solution. Propyl alcohol was mixed with distilled water to form an aqueous solution less dense than the specimen to be measured. Once the two liquids were mixed the temperature of the solution would rise owing to the heat of mixing. The warm solution was degassed in a vacuum and left at ambient temperature for more than 12 h. For density measurement, three polymer specimens were placed into a 100 ml graduated cylinder and the solution was poured gently into the cylinder. After the solution had become still and the specimens sunk to the bottom of the cylinder, a few drops of distilled water were added and mixed to increase the density of the solution. The position of the specimens was observed after 30 min. If they still remained on the bottom, another three drops of distilled water were added. This procedure was repeated until the specimens became suspended in the solution column for at least 2 h. The temperature of the solution was measured and the specific gravity of the solution was determined by use of the density bottle. The density of the solution was calculated by multiplying the measured specific gravity by the density of distilled water at the same temperature and the result was taken as the density of the polymer sample.

2.3. Determination of crystallinity based on density

The specific volume, υ, of a semicrystalline polymer is related to its degree of crystallinity, ϕ, as follows:

$$\upsilon = \phi \upsilon_c + (1 - \phi)\upsilon_a \tag{1}$$

where υ_c and υ_a are the specific volumes of the crystalline and amorphous phases, respectively. Therefore,

$$\phi = \rho_c(\rho - \rho_a)/\rho(\rho_c - \rho_a) \tag{2}$$

where ρ is the density of the polymer sample, and ρ_c and ρ_a are the densities of the crystalline and amorphous phases, respectively. For the iPP resin, ρ_a was chosen as 0.854 g cm^{-3} while $\rho_c = 0.949$ g cm^{-3} and 0.939 g cm^{-3} for the α-phase and β-phase, respectively, based on a close match of the melting temperatures of the respective crystalline phases with those in the literature [20].

2.4. Calculation of heat of fusion

The heat of fusion, $\Delta H°$, of a particular crystalline polymer phase was calculated as

$$\Delta H° = \Delta H/\phi \tag{3}$$

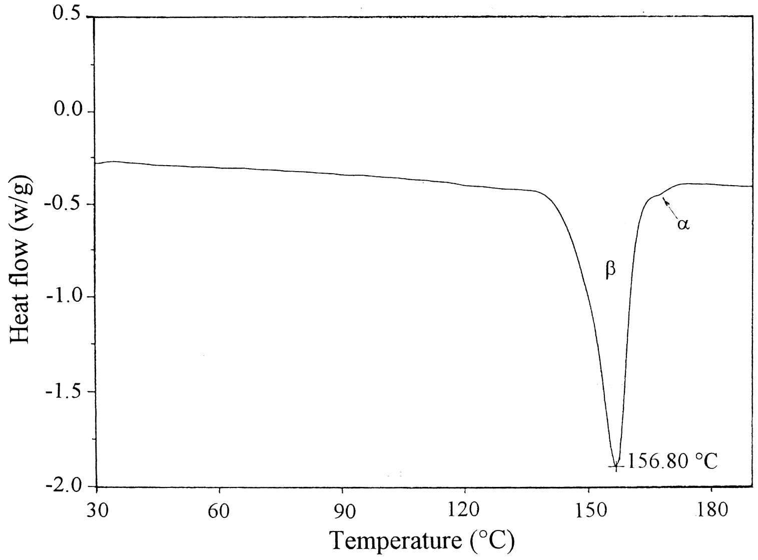

Fig. 1. A typical d.s.c. thermogram of the doped iPP sample, isothermally crystallized at 130°C for 30 min, then at 95°C for 10 min and finally cooled at 0.5°C min^{-1} to room temperature. Scan rate 10°C min^{-1}, nitrogen gas flow 20 ml min^{-1}.

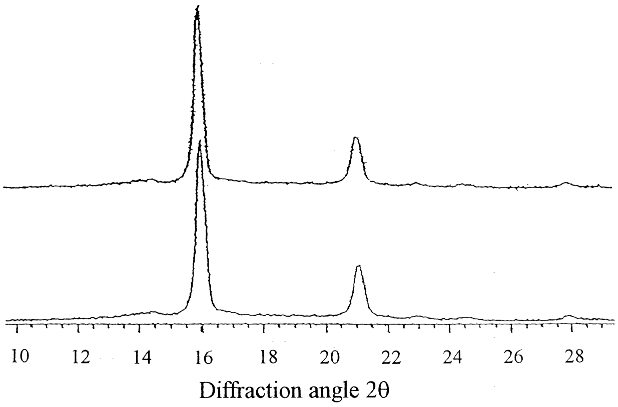

Fig. 2. Cu K_α X-ray diffraction curves of the doped iPP sample, compression-moulded at 130°C for 25 min, then at 100°C for 15 min and finally cooled in the press to room temperature. The curves were obtained for two mutually perpendicular surfaces of the sample.

where ΔH is the heat of fusion of the polymer sample (containing a mixture of crystalline and amorphous phases) measured by d.s.c. at a scan rate of 10°C min^{-1} and ϕ is the degree of crystallinity determined based on density.

3. Results and discussion

Fig. 1 shows the typical fusion behaviour of the doped iPP samples crystallized in the d.s.c. The thermogram exhibits a large β-fusion peak and a very small trace of α-fusion peak, indicating that the sample contained almost pure β-phase PP crystals. Actually, the remaining amount of crystallizable material was extremely small after the second isothermal step at 95°C. It was further depleted in the subsequent slow cooling process before reaching the lower critical temperature (85°C). Consequently, the amount of crystallizable material became negligible for α-growth below the lower critical temperature and the sample could practically be considered as pure β-PP. Fig. 2 shows the typical wide-angle X-ray scattering (WAXS) pattern of the compression-moulded samples. There were two peaks at diffraction angle $2\theta = 16.0°$ and 21.1° which corresponded to the primary reflection of the (3 0 0) and (3 0 1) planes of β-phase PP crystals, respectively. No reflection due to α-PP crystals, i.e., $2\theta = 14.1°$, 16.9° and 18.8°, could be identified. This clearly demonstrated that the compression-moulded samples were generally free of α-PP.

The successful preparation of iPP samples containing extremely high purity hexagonal (β) crystals can be attributed to the following factors. (1) The nucleating agent system produces fine precipitates of calcium pimelate which disperses evenly in the iPP resin to promote the formation of the β-phase crystals [11]. (2) The doped resin has a low β-to-α growth conversion temperature of about 85°C which provides a wider temperature range for β-growth before the start of α-growth [19]. (3) The special moulding or crystallization procedure minimizes the length of time above the upper critical temperature by transferring the sample from 200°C to 130°C rapidly so as to avoid nucleation of α-PP. On the other hand, the slow cooling process after the second isothermal step provides enough time to deplete the crystallizable material before reaching the lower critical temperature, and hence the α-growth is suppressed.

However, it should be pointed out that the samples produced in the d.s.c. were full of bubbles owing to the lack of pressure during the crystallization process. The following procedures were adopted to prepare bubble-free pure β-PP samples for density measurement. Small specimens were cut from the compression-moulded plate and fitted into the d.s.c. sample pans. They were melted and recrystallized in the d.s.c. as described above. Although the compression-moulded samples were generally free of the α-crystals, specimens taken from different parts of the moulding were found to vary slightly. The recrystallization process was performed to ensure uniformity of the pure β-PP samples.

Table 1 summarizes the results for density, crystallinity and heat of fusion of the samples. The heat of fusion of the α-phase was found to be 177.0 J g^{-1}, comparable to values reported in the literature [20]. In comparison, the heat of fusion of the β-phase was 168.5 J g^{-1}, which is slightly lower than that of the α-phase. The result was reasonable and consistent with the fact that the β-crystal has a slightly higher packing energy than the α-crystal [21]. Furthermore, the lower melting temperature of β-PP, its thermal instability and tendency to transform to the α-phase are also signs to indicate that β-PP should have a lower heat of fusion.

Table 1
Crystallinity and heat of fusion of α- and β-PP

Sample	Set no.	Density, ρ (g cm^{-3})	Crystallinity, ϕ (%)	Heat of fusion, ΔH (J g^{-1})	Heat of fusion, $\Delta H°$ (J g^{-1})
α-PP	1	0.911	62.5	111	177.6
	2	0.912	63.5	112	176.4
β-PP	1	0.904	61.0	102	166.9
	2	0.905	61.8	106	170.1

Note: each set contained three specimens. ΔH is the heat of fusion of the polymer sample which contained a mixture of the crystalline and amorphous phases and $\Delta H°$ is the heat of fusion the crystalline phase concerned.

4. Summary

Isotactic polypropylene samples containing pure β-phase crystals were prepared from resin doped with pimelic acid/calcium stearate in a stepwise crystallization process which aimed to suppress the α-growth. The heat of fusion of the β-crystal was found to be 168.5 J g^{-1} while that of the α-crystal was slightly higher at 177.0 J g^{-1}.

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