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Conversion of growth and recrystallisation of β-phase in doped iPP

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Abstract

Isotactic polypropylene (iPP) was doped with pimelic acid/calcium stearate to promote the formation of the hexagonal (β) crystals during melt crystallisation. The conversion of growth pattern from the β- to the α-phase due to lowering of the crystallisation temperature was studied by a two-step crystallisation process in a DSC. The polymer melt was first allowed to crystallise isothermally at 130°C to produce almost pure β-phase and then the crystallising polymer was cooled to different temperatures between 115 and 25°C for a second-step crystallisation. It was found that the amount of α-phase was negligible after the second-step crystallisation process at 85°C or above. When the second-step crystallisation process was below 85°C, however, the amount of α-PP increased abruptly with a corresponding drop in the β-phase. This indicated that a major conversion of the β-growth to α-growth occurred near 85°C. Recrystallisation of the β-phase during heating was dependent upon the heating rate as well as the crystallisation condition of the samples.

Keywords: β-PP; Growth conversion; Lower critical temperature

1. Introduction

Under normal melt–crystallisation conditions, the β-phase of iPP occurs only sporadically among the predominant α-phase. However, high content of β-phase crystals can be acquired under special conditions, such as quenching the melt to a certain temperature range [1,2], directional crystallisation in a temperature gradient field [3], shear-induced crystallisation [4], or doping the resin with certain heterogeneous nucleating agents [5–11]. Regardless of whether nucleating agents are present or not, high content of β-PP can only be obtained within a limited range of crystallisation temperature and the most favourable temperature for β-growth is near 130°C [12–15]. There are lower and upper temperature limits beyond which the β-growth will convert to α-growth. The lower critical temperature was about 105°C while the upper critical temperature was 140°C [16–18].

In a previous study [19], pimelic acid/calcium stearate was found to be very effective in promoting β-growth in iPP when the doped resin was slowly cooled from the melt in a DSC or crystallised isothermally at 130°C during compression moulding. In this study, the doped resin would be crystallised in a two-step process, first step at 130°C and the second step between 115 and 25°C. The fusion behaviours of the samples would be analysed using a DSC and the amounts of α- and β-PP would be determined from the respective fusion heats. A relationship between the increase in the α-phase and the second-step crystallisation temperature would be established, and used as a guideline for developing a crystallisation procedure to prepare pure β-phase for further studies. Also, some samples would be quenched in air after the first isothermal step and different DSC scan rates would be used to investigate the melting–recrystallisation process.

2. Experimental

2.1. Polymer material and doping process

The isotactic polypropylene (iPP) resin used was Himont 6501 in powder form. It was first screened with a 60-mesh sift to eliminate the big granules so that the nucleating agent can be mixed well with the resin. The β-nucleating agent was prepared by mixing a 1% alcohol solution of pimelic acid with a 2% suspension of calcium stearate in alcohol and the mixture had a pimelic acid/calcium stearate composition ratio of 1/1.5. The resin was added to the mixture and then dried in an oven at 100°C. After drying, the resin contained 1.5% pimelic acid/calcium stearate.

2.2. Crystallisation and DSC analysis

About 10 mg of the doped resin was melted in the DSC at 200°C for 2 min to eliminate any remnant α entities. The

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crystallisation process was in two steps. First, the sample was cooled at 5°C/min to 135°C, followed by 1°C/min to 130°C (T_1) and allowed to crystallise isothermally at T_1 for 30 min. In the second step, the sample was cooled from 130°C at 3°C/min to a lower temperature (T_2) and maintained at this temperature for 10 min for further crystallisation. After the second crystallisation step, the sample was heated directly from T_2 at 10°C/min and its fusion behaviour was studied. Finally, the degrees of crystallinity of α- and β-PP in the sample were determined from the respective fusion peaks of the DSC thermograph according to Eq. (1) below

$$\phi_i = (\Delta H_i / \Delta H_i^{\mathrm{o}}) \times 100\% \qquad (1)$$

ΔH_i is the fusion heat of the crystalline phase concerned, i.e. either α- or β-PP, from the DSC thermograph and ΔH_i^{o} is the standard fusion heat, i.e. fusion heat for 100% crystalline material of that particular crystalline phase. The standard fusion heat of α-PP was taken as 178 J/g and that of β-PP was 170 J/g [20]. The percentage of β-PP, X_β, was calculated according to Eq. (2)

$$X_\beta = [\phi_\beta / (\phi_\alpha + \phi_\beta)] \times 100\% \qquad (2)$$

where ϕ_α and ϕ_β are the degrees of crystallinity of the α- and β-phases, respectively.

3. Results and discussion

Fig. 1 shows a typical DSC thermograph of the doped iPP resin after the first isothermal crystallisation step at 130°C. It exhibits a distinctive β-fusion peak at 156°C and a trace of α-fusion at 167°C. The result suggests that the sample contained almost pure β-phase PP after the isothermal crystallisation process. In order to approximate the fusion heats due to melting of the α- and β-crystals, the temperature range of the α-fusion was assumed to be symmetrical about the melting point of the α-crystals, i.e. 167°C. The fusion process was considered complete at the temperature where the fusion curve first met the baseline, i.e. 168.5°C, and then the starting temperature of the α-fusion was taken as 165.5°C. In fact, some of the α-phase crystals may melt at a temperature below 165.5°C, therefore, the assumption slightly underestimates the value of ΔH_α. The β-fusion heat, ΔH_β, was calculated by subtracting ΔH_α from the overall fusion heat, ΔH, which was integrated between 135 and 180°C. The percentages of the α- and β-phase crystals were calculated to be 0.5 and 99.5%, respectively, according to Eqs. (1) and (2).

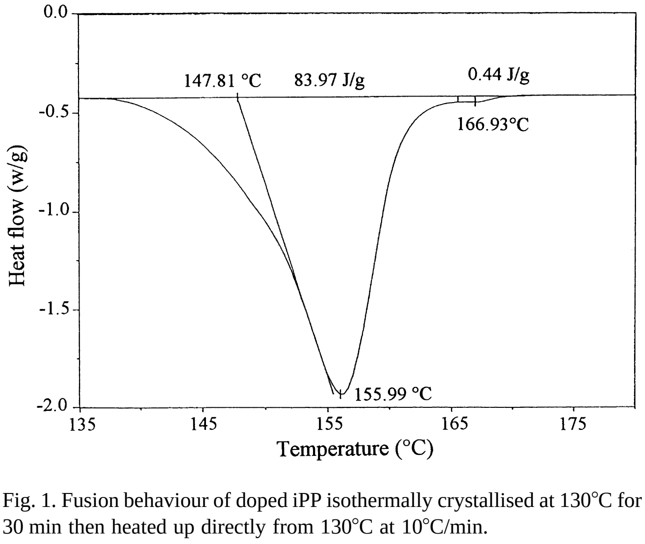

Fig. 1. Fusion behaviour of doped iPP isothermally crystallised at 130°C for 30 min then heated up directly from 130°C at 10°C/min.

The growth of β-PP spherulites during isothermal crystallisation at 130°C was investigated using a polarised light microscope equipped with a hot stage. The spherulites were found to be fully developed, i.e. in contact with each other, after about 10 min. In general, polymer crystallisation can be divided into two stages. The first stage or primary crystallisation is associated with the growth of spherulites at the expense of the melt. The second stage or the so-called secondary crystallisation is associated with material trapped within or between the spherulites. It is a slow and long term process but only involves a small proportion of the total amount of the crystallisable material.

In fact the crystallisation process was not complete after the first isothermal step at 130°C. It would continue when the sample was cooled below 130°C to form either the α- or β-crystals depending on the cooling condition. Fig. 2 gives a comparative view of the fusion behaviours after the second-step crystallisation process at T_2 between 115 and 25°C. The curves can be divided into three groups according to the level of heat flow at the α- and β-fusion peaks. The first group consists of curves (a), (b), (c) and (d) corresponding to samples which have undergone second-step crystallisation at 115, 105, 95 and 85°C, respectively. Despite the differences in T_2, the four α-fusion peaks are extremely close, being practically overlapped on each other. In fact they are similar to the α-fusion peak in Fig. 1. The second

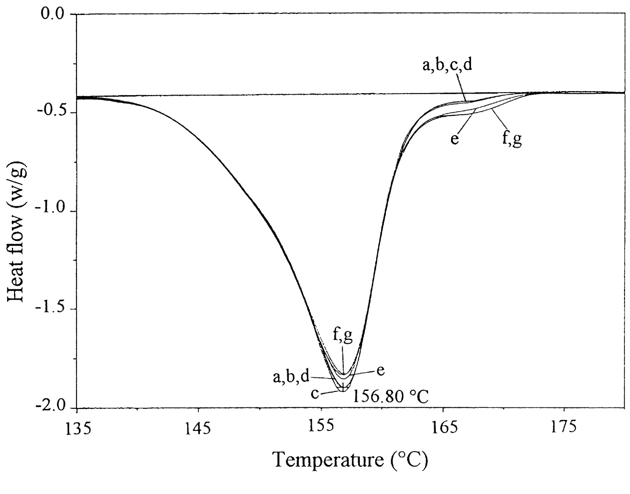

Fig. 2. DSC thermographs of doped iPP after second-step crystallisation at different temperatures, letters a–g indicating results for 115, 105, 95, 85, 75, 60 and 25°C, respectively.

Table 1
Variation of fusion heats with second-step crystallisation temperature

Second-step crystallisation temperature (T_2)	(°C)	130	115	105	95	85	75	60	25
Total specific fusion heat, ΔH	(J/g)	84.4	87.0	86.9	87.0	86.9	87.0	87.2	87.8
$\Delta H^{\mathrm{sec}} - \Delta H^{130}$	(J/g)		2.6	2.5	2.6	2.5	2.6	2.8	3.4
β-fusion heat, ΔH_β	(J/g)	84.0	86.5	86.4	86.6	86.4	85.0	84.6	85.2
$\Delta H_\beta^{\mathrm{sec}} - \Delta H_\beta^{130}$	(J/g)		2.5	2.4	2.6	2.4	1.0	0.6	1.2
α-fusion heat, ΔH_α	(J/g)	0.4	0.5	0.5	0.4	0.5	2.0	2.6	2.6
$\Delta H_\alpha^{\mathrm{sec}} - \Delta H_\alpha^{130}$	(J/g)		0.1	0.1	0	0.1	1.6	2.2	2.2

ΔH^{130}: fusion heat after isothermal crystallisation at 130°C for 30 min.
ΔH^{sec}: fusion heat after second-step crystallisation.

group is represented by curve (e), for $T_2 = 75$°C. Its α-fusion peak is slightly larger than those in curves (a–d), indicating that more α-PP was present in the sample. The third group includes curves (f) and (g), for $T_2 = 60$ and 25°C, respectively. Again they are almost overlapped and at the lowest level of all the α-fusion peaks. It is noted that there is a slight reduction in the β-fusion peak for T_2 below 85°C. This suggests that the amount of β-phase crystals had decreased whilst more α crystals were formed.

The total specific fusion heat (ΔH), α-fusion heat (ΔH_α) and β-fusion heat (ΔH_β) were determined using the same method as for Fig. 1 and listed in Table 1. It can be seen that there was a slight increase in ΔH from 84.4 to about 87 J/g after the second-step crystallisation, representing an increase in the overall crystallinity of the samples. Despite the range of T_2 used in this study, the increase in the total fusion heat ($\Delta H^{\mathrm{sec}} - \Delta H^{130}$) remained generally constant between 2.5 and 2.8 J/g which was equivalent to 3% of the total fusion heat. In other words, the crystallisation process was 97% complete after the first isothermal step at 130°C and the subsequent cooling and second isothermal step at T_2 constituted only 3% of the whole crystallisation process. The value of $\Delta H^{\mathrm{sec}} - \Delta H^{130}$ could be divided into two parts, namely $\Delta H_\alpha^{\mathrm{sec}} - \Delta H_\alpha^{130}$ and $\Delta H_\beta^{\mathrm{sec}} - \Delta H_\beta^{130}$, and Fig. 3 depicts the relationship between them and T_2. It is apparent that the increase in the total specific fusion heat ($\Delta H^{\mathrm{sec}} - \Delta H^{130}$), curve (a), remained generally constant at 2.5–2.8 J/g almost over the whole temperature range, except for 25°C which rendered a slightly higher value of 3.4 J/g. It is worth noting for T_2 above 85°C that the increase in the total specific fusion heat is mainly due to the increase in the β-fusion heat $\Delta H_\beta^{\mathrm{sec}} - \Delta H_\beta^{130}$, curve (b). In other words, the second-step crystallisation within the temperature range from 85 to 130°C mainly produced β-phase crystals and the increase in α-PP was insignificant, curve (c). When T_2 was below 85°C, however, the value of $\Delta H_\alpha^{\mathrm{sec}} - \Delta H_\alpha^{130}$ increased sharply with a corresponding drop in $\Delta H_\beta^{\mathrm{sec}} - \Delta H_\beta^{130}$. It is believed that the major conversion of β-growth to α-growth occurred at about 80°C which corresponds to the onset of homogeneous nucleation of the α-crystals [21,22].

Some samples were quenched in air after the isothermal crystallisation procedure at 130°C and their typical fusion behaviour is shown in Fig. 4. The total fusion heat of the air quenched sample is 87.6 J/g. Compared with Fig. 1, there is an increase of 3.2 J/g which is very similar to that of the sample after the second crystallisation step at $T_2 = 25$°C. In other words, the increase in the overall crystallinity in both

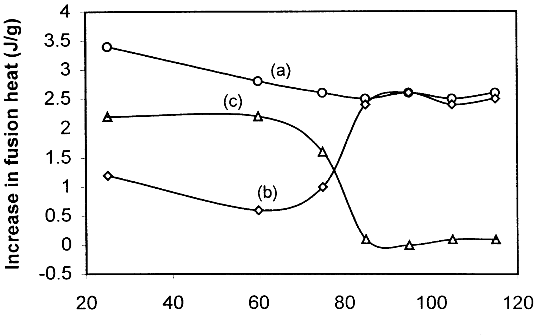

Fig. 3. Increase in various fusion heats due to second-step crystallisation at different temperatures: (a) total specific fusion heat; (b) β-fusion heat; and (c) α-fusion heat.

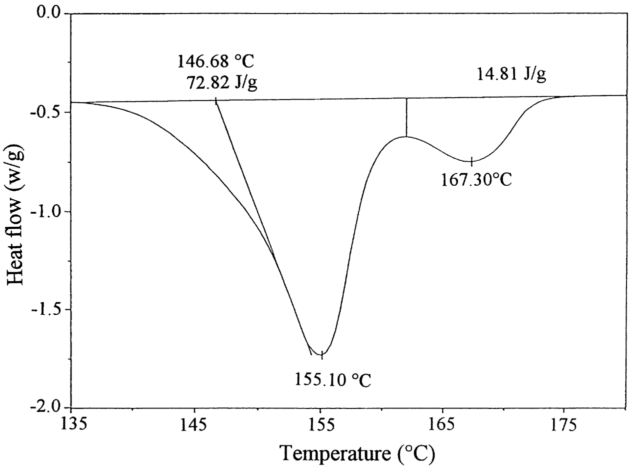

Fig. 4. Fusion behaviour of doped iPP first isothermally crystallised at 130°C for 30 min and then quenched in air.

samples was similar. However, the air quenched sample has a much larger α-fusion peak. The α- and β-fusion heats were approximated to be 14.8 and 72.8 J/g, respectively, by dividing the fusion peaks through the maxima between them. It is surprising to find that the increase in the α-fusion heat well exceeds the increase in the overall fusion heat due to the quenching process. The anomaly can be explained by melting of β spherulites and recrystallisation of the melt into α-phase. The phenomenon was first reported by Padden and Keith [1] and later confirmed by several other authors [12,13,15,23]. Furthermore, Garbarczyk et al. [11] demonstrated, using WAXS with synchrotron radiation, that the β–α recrystallisation was preceded by the transition of the β-phase into a disordered state. Fillon et al. [22] showed that there are two nucleation mechanisms to produce α-phase nuclei for the recrystallisation: (1) secondary crystallisation below the lower critical temperature which yields highly dispersed α-phase overgrowths in β-spherulites and (2) the α-nucleation mechanism takes place in melting β-spherulites as a result of high temperature ($T > 140$°C) β to α transition. The low temperature nucleation mechanism is the more important one. In the air quenched samples, a large number of α-phase overgrowths was present and they acted as nuclei for the β to α recrystallisation during the subsequent heating process, thus giving rise to the large α-fusion peak.

The magnitude of the α-fusion peak was found to increase with decreasing scan rate. At a low scan rate, 2.5°C/min, the DSC thermograph showed a distinctive exothermic region between the β- and α-fusion peaks. Such phenomenon has been reported earlier [12] and attributed to an exotherm associated with the recrystallisation into α-phase of some of the melted polymer. Furthermore, the α-fusion peak shifted up from 167 to 171°C. This can be explained by the fact that the recrystallisation occurred within a relatively high temperature range, and the resulting α-phase crystals would have a higher melting temperature.

After an extensive study on crystallisation and melting of β-PP, Varga et al. [15–17] pointed out that the β to α transition during heating is not a general feature of β-phase PP crystals, but a reflection of the thermal history of the samples. Solid–liquid–solid transformation only occurred in samples which had been cooled below the lower critical temperature and α-phase blocks had formed in the β-spherulites. Heating or annealing pure β-phase iPP samples between the lower and upper critical temperatures only resulted in a structural perfection of the β-lamellae instead of the β–α recrystallisation.

In this study, α-phase was observed in all samples, including those not being cooled below the lower critical temperature, i.e. 105°C. The trace of α-phase in Fig. 1 and in samples (a) and (b) of Fig. 2 was probably a result of heterogeneous nucleation induced by dust and remnant catalysts or of high temperature β to α transition during heating. Although samples (c) and (d), Fig. 2, were cooled below 105°C and α-phase overgrowths were expected to form in β spherulites, their α-fusion heats did not differ significantly from those in samples (a) and (b). The major growth conversion from β to α was detected at T_2 below 85°C which coincided with the onset of homogenous nucleation of the α-crystal [21,22].

References

[1] Padden FJ Jr, Keith HD. J Appl Phys 1959;30:1479.
[2] Turner-Jones A, Aizlewood JM, Beckett DR. Makromol Chem 1964;75:134.
[3] Lovinger AJ, Chua JO, Gryte CC. J Polym Sci 1977;B15:641.
[4] Dragaum H, Muschik HJ. J Polym Sci 1977;B15:1779.
[5] Leugering HJ. Makromol Chem 1967;109:204.
[6] Turner-Jones A, Cobbold AJ. J Polym Sci 1968;6:539.
[7] Jacoby P, Bersted BH, Kissel WJ, Smith CE. J Polym Sci, Polym Phys Ed 1986;24:461.
[8] Binsbergen FL, DeLange BGM. Polymer 1968;9:23.
[9] Garbarczyk J, Paukzta D. Polymer 1981;22:562.
[10] Garbarczyk J, Paukzta D. Colloid & Polym Sci 1985;263:985.
[11] Garbarczyk J, Sterzyski T, Paukzta D. Polym Comm 1989;30:153.
[12] Morrow DR. J Macromol Sci 1969;B3:53.
[13] Shi GY, Huang B, Cao Y. Makromol Chem 1986;187:643.
[14] Rybnikar F. J Macromol Sci, Phys Ed 1991;B30:201.
[15] Varga J, Schulek-Toth F, Ille A. Colloid & Polym Sci 1991;269:655.
[16] Varga J. J Thermal Analysis 1986;31:165.
[17] Varga J. J Thermal Analysis 1989;35:1891.
[18] Lotz B, Fillon B, Therry A, Wittmann JC. Polym Bull 1991;25:101.
[19] Li JX, Cheung WL. J of Vinyl & Additive Technology 1997;3:151.
[20] Li JX, PhD thesis, The University of Hong Kong, 1997.
[21] Burns JR, Turnbull D. J Appl Phys 1966;37:4021.
[22] Fillon B, Thierry A, Wittmann JC, Lotz B. J Polym Sci Polym Phys 1993;31:1407.
[23] Zhou G, He Z, Yu J, Han Z. Makromol Chem 1986;187:633.