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A CORRECTION FUNCTION TO DETERMINE THE β-FUSION HEAT IN A MIXTURE OF α- AND β-PP

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Abstract

Blends of known amounts of α- and β-PP crystals were prepared from pure α- and pure β-PP samples. Their fusion behaviours were studied by differential scanning calorimetry (DSC). The fusion heats of the α- and β-crystals were approximated from the DSC curves and compared with those calculated on the basis of the compositions of the blends. A correction function was found which improved the accuracy of the respective fusion heats significantly from the DSC analysis. The correction function can be used to determine the respective fusion heats of a PP sample which contains an unknown mixture of the α- and β-crystals.

Keywords: α- and β-PP blends, β-fusion heat, DSC analysis

Introduction

In the preparation of β-phase polypropylene (β-PP), the sample normally contains a mixture of the α- and β-phase crystals. Its DSC curve possesses two (or more) fusion peaks as a result of melting of the α- and β-phase crystals [1–3]. The α- and β-fusion peaks are partially overlapped, therefore, it is difficult to determine the respective fusion heats and hence their degrees of crystallinity. In our previous studies [4–5], the respective fusion heats were approximated by drawing a vertical line through the maxima between the two peaks. The area ($\Delta H_{\alpha}^{\mathrm{exp}}$) enclosed by the vertical line, the α-fusion peak and the base line was taken as the fusion heat of the α-phase. Similarly, the area ($\Delta H_{\beta}^{\mathrm{exp}}$) enclosed by the vertical line, the β-fusion peak and the base line was taken as the fusion heat of the β-phase. However, this method tended to underestimate the value of the α-fusion heat as some of the less perfect α-crystals melted before the temperature at which the vertical line was drawn. The error became rather significant when the samples contained more α-PP. So far, we are not aware of any method in the literature which enables us to determine the true values of the fusion heats from the overlapped fusion peaks. As a result, it is

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not possible to determine the exact amount of the α- and β-phase crystals from the DSC analysis. Although there is an alternative method on the basis of WAXS which gives a value to indicate the relative amount of the β-phase [6], it does not provide the true crystallinity or mass percentage of the β-phase in the sample. In an earlier study [7], isotactic polypropylene (iPP) samples of pure β-phase was produced. This enables us to prepare blends of known amounts of the α- and β-crystals. In this study, the fusion behaviours of such blends were studied by DSC. The relationship between area $\Delta H_\beta^{\mathrm{exp}}$ of the overlapped fusion peaks and the calculated value of the β-fusion heat, $\Delta H_\beta^{\mathrm{calc}}$, based on composition was investigated. A correction function was developed to determine the β-fusion heat from the overlapped fusion peaks of an iPP sample which contained a mixture of the α- and β-phase crystals.

Experimental

The iPP resin used was Himont 6501 in powder form. The degrees of crystallinity of the pure α- and pure β-phase samples based on density were 63 and 61.4% respectively and their preparation methods were reported earlier [7]. Blends containing different mass ratios of the α- and β-phase crystals were prepared from small samples cut from the pure α- and pure β-phase mouldings. The fusion heats, $\Delta H_\alpha^{\mathrm{calc}}$ and $\Delta H_\beta^{\mathrm{calc}}$, of the blends were calculated according to the following equation,

$$\Delta H_{\mathrm{i}}^{\mathrm{calc}}=w_{\mathrm{i}}^{\mathrm{c}}\Delta_{\mathrm{c}}^{1}H_{\mathrm{i}} \tag{1}$$

where $\Delta H_{\mathrm{i}}^{\mathrm{calc}}$ is the fusion heat due to the crystalline phase concerned, either α or β, in a unit mass of the blend (containing a mixture of α, β and amorphous phases); $w_{\mathrm{i}}^{\mathrm{c}}$ is the degree of crystallinity of the crystalline phase and $\Delta_{\mathrm{c}}^{1}H_{\mathrm{i}}$ is the specific fusion heat of the 100% crystalline material. The values of $\Delta_{\mathrm{c}}^{1}H_\alpha$ and $\Delta_{\mathrm{c}}^{1}H_\beta$ were taken as 177 and 168.5 J g^{-1} respectively [7]. DSC analyses of the blends were carried out at a scan rate of 10°C min^{-1} in nitrogen.

Results and discussion

Table 1 shows the compositions of a number of α- and β-PP blends used in this study. The α- and β-fusion heats, i.e. $\Delta H_\alpha^{\mathrm{calc}}$ and $\Delta H_\beta^{\mathrm{calc}}$ of the blends were calculated according to Eq. (1) and were listed in Table 2. Figure 1 shows the DSC curves of the blends. Two fusion peaks at about 155 and 168°C were observed, corresponding to the melting of the β- and α-phases respectively. They were partially overlapped, especially for blends with a high α-phase content. In principle, the DSC curves for blends of α- and β-PP may be constructed as the sum of two curves: one for the melting of pure α-PP of a certain crystallinity and the other for the melting of pure β-PP of a certain crystallinity. By varying the α-crystallinity and the β-crystallinity the calculated curve can be made to resemble the experimental curve. Then the crystallinities and the α- and β-fusion heats of the blends can be determined. However, the pure β-PP sample can only be prepared under some stringent thermal conditions and its crystallinity cannot be controlled deliberately to match with those of the blends. Therefore, an indirect approach was adopted to determine the α- and β-fusion heats of the blends. The values of $\Delta H_\alpha^{\mathrm{exp}}$ and $\Delta H_\beta^{\mathrm{exp}}$ were determined from the DSC curves as described above and were also listed in Table 2. It can be seen that when the blend contained a high percentage of the β-phase, this method gave a good approximation of the β-fusion heat. However, when the blend had a high content of the α-phase, it tended to underestimate the α-fusion heat and overestimate the β-fusion heat. A correction factor (C_f) is therefore required in order to obtain a better approximation of the β-fusion heat from the DSC analysis of an unknown α- and β-PP blend.

Table 1 Compositions of the α- and β-PP blends

Sample No.	m_α/	m_β/	m_t/	$m_{\alpha,\mathrm{c}}$/	$m_{\beta,\mathrm{c}}$/	w_α^c/	w_β^c/	w^c/
			mg				%	
1	1.1	6.9	8.0	0.69	4.24	8.6	53.0	61.6
2	1.4	5.8	7.2	0.88	3.56	12.2	49.4	61.6
3	2.2	5.1	7.3	1.38	3.13	18.9	42.9	61.8
4	3.0	4.5	7.5	1.89	2.76	25.2	36.8	62.0
5	3.6	3.9	7.5	2.27	2.39	30.3	31.9	62.2
6	4.1	3.0	7.1	2.58	1.84	36.3	25.9	62.2
7	5.5	2.4	7.9	3.46	1.47	43.8	18.6	62.4
8	5.4	1.7	7.1	3.40	1.04	47.9	14.6	62.5
9	6.1	0.9	7.0	3.84	0.55	54.8	7.9	62.7

m_α, m_β and m_t: masses of pure α-PP (including amorphous material), pure β-PP and total mass of the blends

$m_{\alpha\mathrm{c}}$ and $m_{\beta\mathrm{c}}$: masses of α- and β-phase crystals in the blends

w_α^c, w_β^c and w^c: crystallinity of α-phase, β-phase and overall crystallinity of the blends

Table 2 Comparison between fusion heats calculated on the basis of composition and areas of the fusion peaks divided by a vertical line through the maxima between the peaks

Sample No.	$\Delta H_\alpha^{\mathrm{calc}}$/	$\Delta H_\beta^{\mathrm{calc}}$/	$\Delta H_\alpha^{\mathrm{exp}}$/	$\Delta H_\beta^{\mathrm{exp}}$/	$C_\mathrm{f}=\dfrac{\Delta H_\beta^{\mathrm{calc}}}{\Delta H_\beta^{\mathrm{exp}}}$
		J g^{-1}			
1	15.2	89.3	12.4	89.7	0.996
2	21.6	83.2	16.6	86.0	0.967
3	33.5	72.3	24.0	79.7	0.907
4	44.6	62.0	28.0	75.0	0.827
5	53.6	53.8	35.3	70.6	0.762
6	64.3	43.6	39.0	66.0	0.660
7	77.5	31.3	50.6	55.3	0.566
8	84.8	24.6	50.2	54.0	0.456
9	97.0	13.3	66.9	46.7	0.285

Ideally, the correction factor should yield the calculated β-fusion heat ($\Delta H_\beta^{\mathrm{calc}}$) as follows:

$$\Delta H_\beta^{\mathrm{calc}} = C_\mathrm{f} \Delta H_\beta^{\mathrm{exp}} \tag{2}$$

For a known blend, the value of C_f may be determined easily since the β-fusion heat, $\Delta H_\beta^{\mathrm{calc}}$, can be calculated based on composition which can then be compared with $\Delta H_\beta^{\mathrm{exp}}$ from the DSC curves. To obtain the values of C_f for the whole range of composition from pure α-phase to pure β-phase, however, a lot of experimental work would be required to prepare the blends. In this study, another correction factor (C_f^*) was assumed as follows:

$$C_\mathrm{f}^* = \left[1 - \frac{h_2}{h_1}\right]^n \tag{3}$$

where h_1 and h_2 are the heights from the base line to the β-fusion peak and to the maxima between the α- and β-fusion peaks respectively (Fig. 1) while 'n' is a positive constant to be determined by experiment. The ratio h_2/h_1 depends on the relative amount of β-PP in the sample. From the experimental observations, when the content of β-PP was low, the β-fusion peak would become small and tend to merge with the maxima between the fusion peaks. In this case, the value of h_2/h_1 is near 1 and the correction factor C_f^* tends to zero. On the other hand, when the sample contained a high percentage of β-PP, the β-fusion peak became very distinctive and the maxima tended to move towards the base line, hence, giving a small h_2/h_1 ratio and C_f^* near 1.

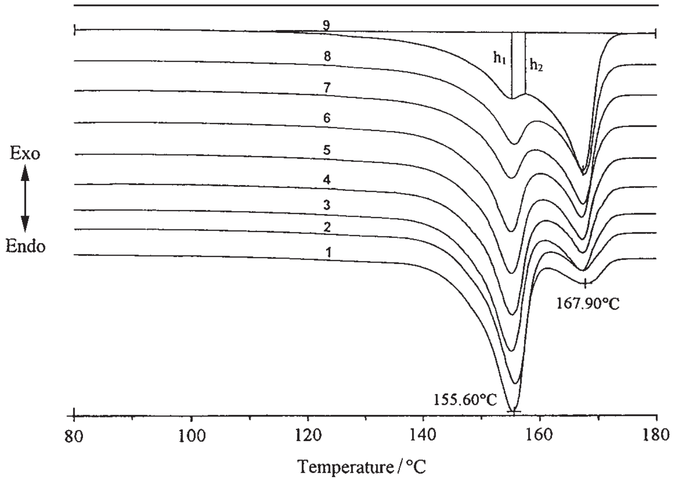

Fig. 1 DSC curves of the α and β blends, compositions are shown in Table 1

The values of h_1 and h_2 for each blend were measured from their curves. Then, C_f^* was calculated according to Eq. (3) for different n values. Table 3 shows the results of C_f^* for a number of n values from 0.4 to 1.0. The results were compared with the values of C_f calculated according to Eq. (2). It can be seen that the lowest root mean square difference between C_f and C_f^* occurred at about n=0.6. Therefore, the correction function can be written as

$$C_f^* = \left[1 - \frac{h_2}{h_1}\right]^{0.6} \tag{4}$$

Table 3 Correction factor C_f^* at different n values

Sample No.	h_1/	h_2/	Correction factor C_f^* at n=				
	mm		0.4	0.5	0.6	0.7	1.0
1	122	7.5	0.975	0.969	0.963	0.957	0.939
2	114	15	0.945	0.932	0.919	0.906	0.868
3	102	20	0.916	0.897	0.877	0.858	0.804
4	133	36	0.881	0.854	0.827	0.802	0.729
5	121	44	0.835	0.798	0.762	0.729	0.636
6	130	57	0.794	0.749	0.707	0.668	0.562
7	102	66	0.659	0.594	0.535	0.482	0.353
8	97	69	0.608	0.537	0.474	0.419	0.289
9	60	55	0.370	0.289	0.225	0.176	0.083
$\frac{[\sum(C_f - C_f^*)^2]^{0.5}}{N^{0.5}}$			0.022	0.006	0.004	0.010	0.058

Figure 2 shows a plot of the non-corrected approximation (ΔH_β^{exp}) and corrected approximation ($C_f^* \Delta H_\beta^{exp}$) of the β-fusion heat *vs.* the calculated β-fusion heat (ΔH_β^{calc}) based on composition. In blends with a high β-PP content, the values of ΔH_β^{exp} were reasonably close to those of ΔH_β^{calc}. However, as the content of β-PP decreased, i.e. more α-PP, ΔH_β^{exp} became increasingly larger than ΔH_β^{calc}. This phenomenon can be explained

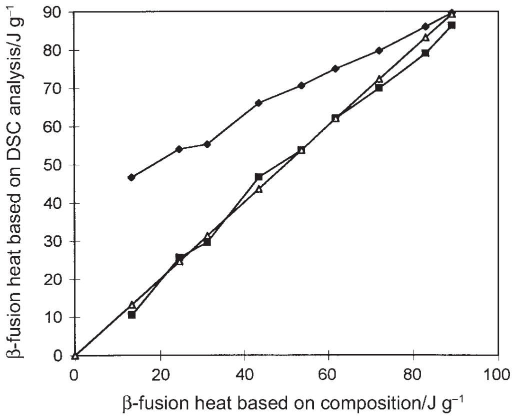

Fig. 2 Plots of β-fusion heat from DSC analysis *vs.* the calculated β-fusion heat based on composition: ◆ – before correction (ΔH_β^{exp}); ■ – after correction ($C_f^* \Delta H_\beta^{exp}$) with n=0.6 and △ – DSC results and the calculated fusion heat are equal

as follows. When more α-PP was present in the blends, a substantial amount of the less perfect α-crystals would melt at temperatures below that of the dividing line drawn between the two peaks. In other words, their fusion heat would fall within the $\Delta H_\beta^{\mathrm{exp}}$ region of the DSC curve. Consequently, this would overestimate the amount of β-PP but underestimate that of α-PP in the sample.

In comparison, the corrected results ($C_\mathrm{f}^* \Delta H_\beta^{\mathrm{exp}}$) gave a good approximation of the true β-fusion heat over the whole range of compositions studied. This suggests that the correction function can be used to determine the β-fusion heat of a mixture of α- and β-PP within the composition range. Nevertheless, it should be pointed out that the value of '*n*' in the correction function may vary if the thermal analysis is carried at a different heating rate. β-PP is known to be thermally unstable and it will transform to α-PP by means of a melting and re-crystallization mechanism during heating [1, 2, 8–10]. During the DSC test, when the sample is heated to a temperature high enough to melt the β-crystals but below the melting temperature of the α-phase, the molten material will re-crystallize into the α-phase. Since re-crystallization is an exothermic process which will affect the shape of the fusion curves. A slow heating rate is more favorable for the re-crystallization to occur. When the DSC analysis was performed at 2.5°C min^{-1}, a distinctive exothermic peak was observed between the α- and β-fusion peaks, namely, the maxima between the α- and β-fusion peaks lay above the base line of the curve [11]. In this study, the DSC analysis was performed at 10°C min^{-1} in which the amount of recrystallization was insignificant and its effect on the fusion curves was minimal.

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