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# Crystallization behavior, crystal transformation, and morphology of polypropylene/polybutene-1 blends

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## Abstract

The effects of composition on crystallization behavior, crystal transformation, and morphology of crystalline/crystalline PP/PB-1 blends are complicated. The crystallization rate of PP decreases with increasing PB-1 content in the cooling or isothermal crystallization process. Avrami constants of the PP crystallization are, however, insignificantly dependent on the PB-1 content. The crystallization rate and spherulite size of PB-1 are both enhanced by PP in PB-1-rich blends. As prepared by the solution–precipitation method, pure PB-1 exhibits crystal forms I' (or III) and II, whereas the PB-1 in the blends exhibits only crystal form I'; pure PP and PP in the blends both exhibit only crystal form  $\alpha$ . Crystal transformation from form I' to form II for PB-1 in the blends can occur upon dynamic heating and cooling, but the transformation is retarded with increasing PP content. The crystal form II of PB-1 can be transformed to form I upon aging at room temperature, and this transformation can be facilitated by the PP in PB-1-rich blends. The similar helix conformation, of crystal form  $\alpha$  of PP and of crystal forms I' and I of PB-1, is found to be a driving force in preventing crystal form I' of PB-1 in PB-1 in PB-1 in PB-1 in the blends transformation from form I' and I of PB-1, is found to be a driving force in preventing crystal form I' of PB-1 in PB-1 in PB-1 in PB-1 in the blends transformation form I' of PB-1 in PB-1 in PB-1 in the blends.

Keywords: Polyblends; Morphology; Crystal transformation

## 1. Introduction

The properties of polymer blends, whether amorphous or semicrystalline, depend, in general, on the method of mixing the components and their compatibility (or miscibility) as well as on the components' individual properties. The crystallization characteristics of polyblends in which both components are crystallizable are rather complicated. The constituents can either cocrystallize or form two separate crystalline phases. Moreover, in these semicrystalline polyblends, they can form a single or multiphase amorphous structure depending on the miscibility of the constituents. In the crystallization behavior of some pairs, the crystallinity of the crystallizable component was found to increase upon addition of lower  $T_g$  polymers, such as polycaprolactone (PCL) to polycarbonate (a compatible pair) [1], and ethylene-propylene rubber (EPR) to polypropylene (an incompatible pair) [2,3]. On the contrary, the crystallization rate of a crystallizable polymer was found to be retarded by the addition of higher  $T_{\rm g}$  polymers if these two polymers are compatible and the  $T_{g}$  of their blend is higher than that of this crystallizable polymer [4-9]. The resulting crystallinity of the lower  $T_{g}$  crystallizable component in the blend is equal to or slightly lower than that of its pure state as found in many polyblends, such as polycaprolactone/polyvinyl chloride (PCL/PVC) [10,11], polyvinylidene fluoride/polymethyl methacrylate (PVF2/PMMA) [12,13], polyvinylidene fluoride/polyethyl methacrylate (PVF<sub>2</sub>/PEMA) [14,15], polybutylene terephthalate/polyethylene terephthalate (PBT/PET) [16], PCL/saran [17], polylactones/PVC [18]. Although, in the blend of PVF<sub>2</sub>/ polyvinyl acetate [19],  $PVF_2$  having a lower  $T_g$  develops a slightly higher crystallinity in the blend than in the pure state in a cyclic thermal scan, no explanation was given. When a blend of two crystallizable polymers, having different characteristic crystallization temperatures, is cooled from the melt, each component could act, if miscible, as a polymeric diluent for the other crystallizing polymer. The lower melting polymer crystallizes in the presence of an

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Crystal form		Crystal lattice	Helix conformation	X-ray diffraction angle, $2\theta$ , (°)	Melting points (°C)	Reference
PP	α	Monoclinic	31	14.1/16.9/18.5/21.8	160–176	[37-39]
	β	Hexagonal	3 <sub>1</sub>	16.1/23.1	140-153	[37-39]
PB-1	I	Hexagonal	$3_1$ (twinned)	10.1/17.4/20.5	120-135	[25,41,42]
	$\mathbf{I}'$	Hexagonal	$3_1$ (untwinned)	10.1/17.4/20.5	90-100	[36,40-42]
	II	Tetragonal	113	11.7/16.7/18.2	110-120	[26,40-42]
	III	Orthorhombic	41	12.2/17.2/18.6	90-100	[27,36,41,42]

Crystal lattice, helix conformation, X-ray diffraction angles, and melting points of crystal forms  $\alpha$  and  $\beta$  of PP and of all four crystal forms of PB-1

already crystallized phase, which may act as a nucleating agent for the crystallization.

Polypropylene (PP) and polybutene-1 (PB-1) are both crystallizable polymers. PP has a higher melting temperature than PB-1. Some properties of PP/PB-1 blends have been studied and reported [20–22]. Siegmann [20,21] has studied the mutual influence of these two polymers, regarding their crystallization process from molten blends, their interaction in the amorphous phase, and the resulting tensile mechanical properties. The crystallization was followed by a differential scanning calorimeter (DSC), showing two separate PP and PB-1 crystallization processes that are both affected by the presence of the other component. The crystallization temperature of PP is significantly affected only in PB-1-rich blends whereas that of PB-1 is affected in the whole composition range. The PP crystalline phase, acting as a nucleating agent, increases the PB-1 crystallization temperature whereas the PP amorphous phase, acting as a high viscosity polymeric diluent, reduces the PB-1 crystallization temperature. The interaction between the two polymers in the amorphous phase was studied by applying dynamic mechanical analysis, and a single glass transition was observed, suggesting that the blends were compatible. Lee and Chen [22] have found that, contrary to the cases mentioned previously, PB-1, whose  $T_g$  is lower than that of PP, unexpectedly develops significantly higher crystallinity in the blends than that in the pure state under the same conditions, not only in the cyclic thermal scan but also in isothermal crystallization at temperatures higher than 90°.

PB-1 and PP are both polymorphic crystalline polymers. PB-1 exhibits four crystal modifications including I, II, III, and I' depending on the formation conditions [23,24]. Among these forms, form I crystals, twined hexagonal with a  $3_1$  helix [25], are the most stable and are usually obtained from the transition from the unstable form II, tetragonal with an 11<sub>3</sub> helix [26]. The unstable form II crystals can be obtained by cooling the melted PB-1 and slowly transform into stable form I crystals on aging at room temperature [27-32]. This phase transformation is accelerated by the application of stress or strain on a form II sample [32-35]. Forms III, orthorhombic with a 4<sub>1</sub> helix [27,36], and I', untwined hexagonal with a  $3_1$  helix [36], can be obtained by crystallization of PB-1 solution or polymerization of butene-1. Form I is similar to form I' in morphology and X-ray diffraction patterns, but is different from form I'

in melting temperature [24,25,36]. The melting temperature of crystal form I is in the range 120–135°C whereas form I' is in the range 90–100°C. PP exhibits three crystal forms including  $\alpha$ ,  $\beta$ , and  $\gamma$  [37]. Form  $\alpha$  crystals are the most stable and are mostly obtained by cooling of melted PP. Form  $\beta$  crystals can be obtained by crystallization in the range 100–125°C [37]. Form  $\gamma$  crystals can be obtained by crystallization under high pressures [37]. Lattice types, molecular conformations, X-ray diffraction angles, and melting points of crystal forms  $\alpha$  and  $\beta$  of PP [37–39] and crystal forms I, I', II, and III of PB-1 [24–27,36,40–42] are listed in Table 1.

Since both PB-1 and PP are crystallizable and have polymorphic morphologies, the effects of blend composition on morphologies and crystal transformations of the constituent polymers in the blends are complicated and have not been reported in the literature. In this work, we intend to investigate these complicated crystallization characteristics of PB-1/PP blends prepared by a different method, that is, the solution–precipitation method, using X-ray diffractometry, DSC and polarized optical microscopy (POM).

## 2. Experimental

## 2.1. Sample preparation

Polypropylene [Profax PC366-MFR3,  $M_w = 220,000$ ,  $M_{\rm w}/M_{\rm p} = 7.2$ , melt flow index = 4.3 g/10 min at 230°C with a load 2160 g (ASTM D1238)] used was obtained from Taiwan Polypropylene Co. Polybutene-1 [Duraflex 0200,  $M_{\rm w} = 428,000, M_{\rm w}/M_{\rm n} = 9.5$ , melt flow index = 8.3 g/10 min measured under the same conditions as for the PP] was supplied by Shell Chemical Co. Infrared (IR) spectroscopic identification shows that both polymers are highly isotactic. The PB-1/PP blends were prepared by the solution-precipitation method. With this method, a desired amount of each component was dissolved in xylene at 130°C at a total polymer concentration of about 3% by weight and precipitated by pouring the so-obtained hot and clear solutions into cool methanol. The white precipitates taken from the mixture were dried at room temperature and then dried again under vacuum for more than 3 days at room temperature. The two pure polymers were also prepared by the same method.

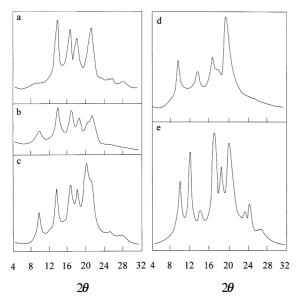


Fig. 1. X-ray diffraction patterns of PB-1/PP blends that are prepared by the solution–precipitation method: (a) PP; (b) 25 PB-1/75 PP; (c) 50 PB-1/50 PP; (d) 75 PB-1/25 PP; (e) PB-1.

## 2.2. Thermal analysis

A differential scanning calorimeter, Perkin-Elmer DSC-IIC, was used for thermal analysis. The temperature reading and the energy involved in DSC thermograms were calibrated with indium (m.p. 156.6°C,  $\Delta H_{\rm f} = 6.8$  cal/g) and tin (m.p. 231.88°C,  $\Delta H_{\rm f} = 14.45 \ cal/g$ ). The weight of the sample was kept at  $5 \pm 0.5$  mg. To control the thermal history, residual crystallites were eliminated by heating all the samples first in the DSC cell under nitrogen atmosphere at 230°C for 10 min. For crystallization during the cooling scan, the blend was cooled to 40°C at a rate of 10°C/min, and this was immediately followed by a heating-up step at a rate of 20°C/min until the blend was completely melted to complete a cooling/heating cycle to study the crystallization and melting behavior of the blends. Some blend samples that had cooled to 40°C were left at room temperature for various durations and this was followed with a heating scan at 20°C/min to obtain their endotherms for studying the effect of blend composition on the crystal transformation rate of PB-1 at room temperature. The percent content of a crystal form in the PB-1 was calculated by dividing the endothermic enthalpy of the corresponding peak by that of all peaks combined for all crystal forms in a DSC thermogram. The fusion heats of crystallites taken for the calculations are 15 cal/g for PB-1 crystal form II, and 20 cal/g for PB-1 crystal forms I' and I. For isothermal crystallization in a temperature range of 125-132.5°C used for determining Avrami constants for PP crystallization, the sample, which was held at 230°C in the DSC cell, was quenched as quickly as possible to a predetermined crystallization temperature. The time required for complete isothermal crystallization of the PP was determined by performing the experiment until

the crystallization exotherm, recorded as a function of time in the DSC thermogram, was completely finished. The percent crystallinity of the PP as a function of isothermal time was determined by the ratio  $A_t/A_{\infty}$ , where  $A_t$  is the area of the exothermic peak integrated from the initial time to time t and  $A_{\infty}$  is the integration area of the whole exothermic peak.

## 2.3. Wide-angle X-ray diffraction

The wide-angle X-ray diffraction patterns for the blend samples were analyzed on a Toshiba GD-2 X-ray diffractometer operating at 40 kV and 35 mA using CuK $\alpha$  radiation with a wavelength of 1.54 angstrom as the X-ray source. Samples were scanned in the 2 $\theta$  range of 4–32°.

#### 2.4. Polarized optical microscopy

Samples were treated under nitrogen in a hot stage to a desired temperature for a certain time and were then transferred to a polarized optical microscope (POM, Carl Zeiss D-07740) to observe their crystal morphologies.

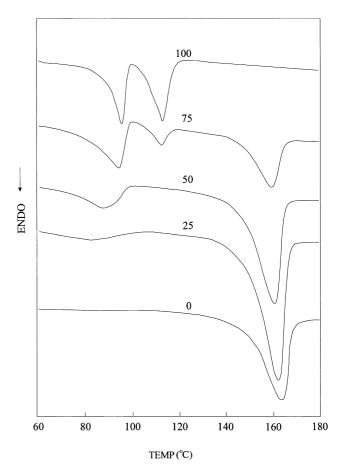


Fig. 2. DSC thermograms of heating scans for PB-1/PP blends that are prepared by the solution–precipitation method. The figures on the curves are PB-1 wt% in blends.

# 3. Results and discussion

## 3.1. Characterization of initial samples

Fig. 1 shows X-ray diffraction patterns for polypropylene, polybutene-1, and their blends with various compositions prepared by the solution-precipitation method. According to the diffraction angles listed in Table 1, Fig. 1a and e demonstrates that the PP precipitate from the xylene solution gives only crystal form  $\alpha$ ; however, the PB-1 precipitate does not clearly show any of the four crystal forms. PB-1 in the precipitates of the binary blends exhibits only crystal form I' or I as demonstrated in Fig. 1b-d from a diffraction peak appearing at angle (2 $\theta$ ) of 10.1° but missing at 11.7 and 12.2°. PP in the precipitates of the blends remains in the crystal form  $\alpha$  because the blends give a peak at around 14° but do not give a peak at around 23°.

Fig. 2 shows DSC endothermic thermograms for the blends' precipitates with a heating rate at 20°C/min under nitrogen. In Fig. 2, the endothermic peak at around 163° is for pure PP or PP in the blends. This indicates that PP, both in the pure state and in the blends, exhibits only crystal form  $\alpha$  because the melting temperature of the form  $\alpha$  crystals is in the range 160–176°C as listed in Table 1. The demonstration from DSC data that PP exhibits only crystal form  $\alpha$  is, thus, consistent with that from X-ray diffraction data as discussed previously. For PB-1, there is a broad peak in

the range 60–100°C when the PB-1 content in the blends is low. This broad peak becomes sharp and shifts to a higher temperature at around 95°C corresponding to crystal form I' as the PB-1 content in the blends increases. Blends with high PB-1 content, e.g. 75 wt%, give an extra peak at around 115°C corresponding to the crystal form II. This extra peak appears to be strong for pure polybutene-1. Comparing the DSC thermograms for pure PB-1 and the blend with 75 wt% PB-1 content, an exothermic peak is found at around 103°C for the blend. This exothermic peak is due to crystallization of the melted form I' crystals during heating to transform to form II crystals as evidenced by an endothermic peak at higher temperature for form II crystals [43]. The transformation from crystal form I' to form II in the heating scan is not found in Fig. 2 for blends with low (50 wt% or less) PB-1 content, suggesting that PP in the blend can suppress the crystal transformation of PB-1 upon heating. In Fig. 2, no sample shows any endotherm in the range 120–135°C, an indication that PB-1 in the pure state or in the blends prepared by the solution-precipitation method does not exhibit crystal form I.

## 3.2. Crystallization temperature and degree of crystallinity

Table 2 lists crystallization peak temperatures obtained from the DSC thermograms of the cooling scans for pure PP and PP in the blends. As can be seen in Table 2, as PB-1

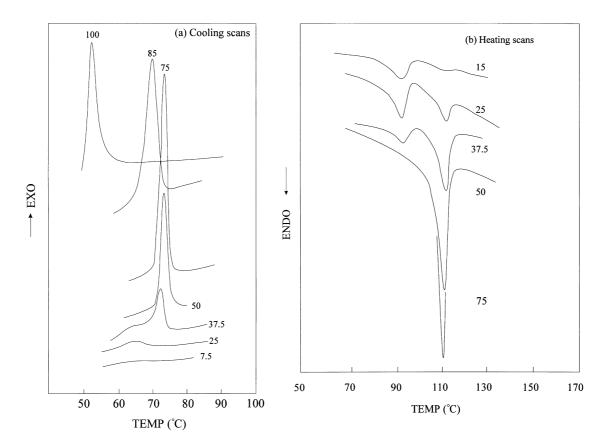


Fig. 3. DSC thermograms of (a) colling scans, and (b) heating scans for the PB-1 in PB-1/PP blends. The figures on the curves are PB-1 wt% in blends.

Table 2 Crystallization peak temperatures, obtained from the DSC thermograms of cooling scans, for the PP in PP/PB-1 blends

PP/PB-1	Crystallization peak temperature of PP (°C)	
100/0	116	
75/25	109	
50/50	107	
25/75	105	
15/85	_	

content increases, the crystallization peak temperature of PP decreases and when the PB-1 content is 85 wt%, PP in the blend does not crystallize. This indicates that the crystallization rate of PP is retarded by the presence of PB-1 in the blends. Fig. 3a and b are the DSC thermograms of cooling scans and heating scans for PB-1 in the blends, respectively. As can be seen in Fig. 3a, the crystallization peak temperature of PB-1 increases from about 53°C for pure PB-1 to 73°C for the blend containing 75 wt% PB-1, and then decreases to 65°C for that containing 25 wt% PB-1. Table 2 and Fig. 3a indicate that during cooling the PP in the blends crystallizes before the PB-1 does and the crystallization peak temperature of pure PB-1 is 20°C lower than that of PB-1 in the blend containing 75 wt% PB-1. This suggests that the PP in the blends acts as a nucleating agent during crystallization of PB-1 and, thus, enhances the crystallization rate of PB-1 [21,44]. Moreover, in Fig. 3a, the blend containing 37.5 wt% PB-1 seems to have two crystallization peaks corresponding to perhaps two crystal forms; the crystallization peak temperature decreases from 73°C for the blend containing 50 wt% PB-1 to 65°C for that containing 25 wt% PB-1. This suggests that two crystal forms of PB-1 form during cooling of blends having low PB-1 content. The formation of two crystal forms of PB-1 in blends containing 37.5 wt% or less PB-1 is demonstrated by immediately heating the blends after cooling as shown in the DSC thermograms of heating scans for PB-1 in Fig. 3b. In Fig. 3b, two PB-1 endothermic peaks are observed for blends having 37.5 wt% or less PB-1 content; the lower temperature peak is predominant as PB-1 content decreases. The peak temperatures of these two PB-1 melting endotherms correspond to the melting points of crystal form II (110–120°C) [24] and I' (90–100°C) [24], respectively. Only one PB-1 endotherm corresponding to crystal form II for PB-1-rich blends having 50 wt% or higher PB-1 content is, however, observed after cyclic heating and cooling scans. The presence of PP in PP-rich blends can, thus, help maintain the crystal form I' for PB-1 upon dynamic heating and cooling, perhaps due to similar helix conformations of the crystal form  $\alpha$  of PP and the form I' of PB-1.

## 3.3. Crystal transformation of PB-1

The crystal form II of PB-1 is easily transformed to form I at room temperature by the presence of PP [45]. The effect

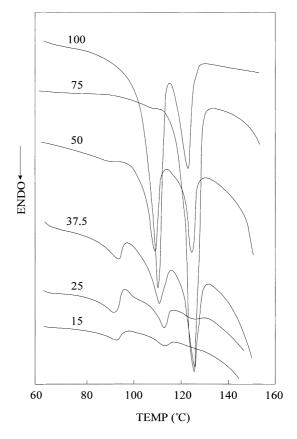


Fig. 4. DSC thermograms of heating scans for PB-1 in the blends that have been cooled from the melts and been left at room temperature for 3 days. The figures on the curves are PB-1 wt% in blends.

of PP content on the transformation rate, however, has not been investigated. In this study, the blend samples were cooled on DSC from the melts to 50°C, followed by removal from the calorimeter and being left at room temperature for various durations. At the end of aging at room temperature, the samples were heated on DSC to observe their melting behavior. Fig. 4 shows DSC thermograms of heating scans for PB-1 in the blends after being aged at room temperature for 3 days. As shown, the transformation for PB-1 from crystal form II to form I is apparent for the blend containing 75 wt% PB-1. The formation of crystal form I' corresponding to the melting endotherm at around 90°C by the presence of PP is also apparent in Fig. 4 for blends containing 37.5 wt% or less PB-1. The observation of crystal form I' for PB-1 in PP-rich blends as shown in Fig. 4 is consistent with that in Fig. 3b. The DSC thermograms of heating scans in Fig. 4 can be used to determine the contents of PB-1 crystal forms II in the blends by integrating the peak areas and calculating the percent content in enthalpy of the corresponding endotherm. Fig. 5 is the plots of the percent contents of the crystal form II in PB-1 as functions of aging time at room temperature. As can be seen, the percent content of crystal form II in PB-1 is 100 wt% for all blend compositions studied except the blend containing 25 wt% PB-1. The transformation rate from crystal form II to form I

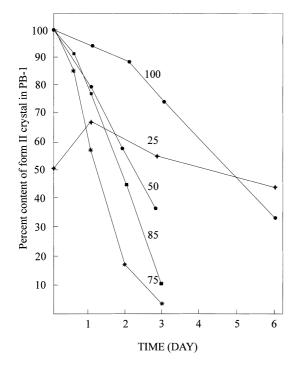


Fig. 5. Percent content of form II crystals in PB-1 as a function of aging time at room temperature. The figures on the curves are PB-1 wt% in blends.

is the greatest for the blend containing 75 wt% PB-1. Due to lower PP content in the sample, pure PB-1 and the blend containing 85 wt% PB-1 give slower transformation rates than does the blend containing 75 wt% PB-1. The blend containing 25 wt% PB-1 shows 50 wt% of crystal form II initially in PB-1 and the transformation from crystal form II to form I for PB-1 at room temperature is insignificantly dependent on time. The blend containing 15 wt% PB-1 shows no formation of crystal form I as shown in Fig. 4 because crystal form I' is predominant in PB-1 and crystal form I' can not directly be transformed to crystal form I. As demonstrated and discussed above, the presence of PP in PP-rich blends can facilitate the formation of crystal form I' in PB-1 whereas the PP in PB-1-rich blends can facilitate the transformation from crystal form II to form I in PB-1. The explanation for the role of PP is the same as that previously described, that is similarity in helix conformation for crystal form  $\alpha$  of PP and forms I' and I of PB-1, all having a 3<sub>1</sub> helix conformation (Table 1).

## 3.4. Avrami constants for crystallization of PP

For isothermal crystallization of the blend in a temperature range of 125 to 132.5°C, an exothermic crystallization peak can be observed for PP on the DSC thermogram as shown in Fig. 6. Since PB-1 is not able to crystallize in this temperature range, the DSC thermograms in Fig. 6 are, thus, used to investigate the effect of PB-1 content in the blend on the crystallization rate of PP in the blend. As can be seen in Fig. 6, the crystallization rate of PP decreases with increasing PB-1 content in the blend because the exothermic

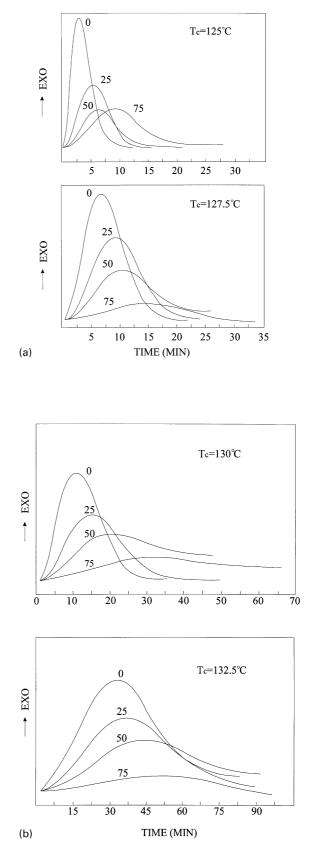


Fig. 6. Exotherms of PB-1/PP blends in isothermal crystallization as a function of time at various temperatures. The figures on the curves are PB-1 wt% in blends.

PB-1 content (wt%)	<i>n</i> value				$\frac{K \text{ value (min^{-n})}}{T_{c, iso} (^{\circ}C)}$			
	T <sub>c, iso</sub> (°C)							
	125	127.5	130	132.5	125	127.5	130	132.5
0	2.5	2.8	2.8	2.8	$3.2 \times 10^{-2}$	$2.6 \times 10^{-3}$	$1.3 \times 10^{-4}$	$3.3 \times 10^{-5}$
25	2.6	2.9	2.7	2.9	$7.8 \times 10^{-3}$	$9.5 \times 10^{-4}$	$1.9 \times 10^{-4}$	$1.8 \times 10^{-5}$
50	2.8	3.1	3.2	2.9	$3.5 \times 10^{-3}$	$5.4 \times 10^{-4}$	$6.3 \times 10^{-5}$	$1.3 \times 10^{-5}$
75	3.1	3.8	3.0	3.0	$7.2 \times 10^{-4}$	$3.0 \times 10^{-5}$	$3.2 \times 10^{-5}$	$6.2 \times 10^{-6}$

Table 3 Avrami constants *n* and *K* for crystallization of PP in PB-1/PP blends crystallized isothermally in the temperature range  $125-132.5^{\circ}$ C

crystallization peak for PP at any temperature studied is complete in a shorter time period for a higher content of PB-1 in the blend. By integrating the peak in Fig. 6, the relations of percent crystallinity of PP and crystallization time can be established. The percent crystallinity at time t,  $X_t$ , is determined by the ratio  $A_t/A_{\infty}$ , where  $A_t$  is the area of the peak integrated from the initial time to time t and  $A_{\infty}$  is the integration area of the whole peak. Substituting the values of  $X_t$  and t into the Avrami equation in the following, the Avrami constants n and K for crystallization of PP can thus be obtained as listed in Table 3.

$$Ln(1-X_t) = -Kt^n$$

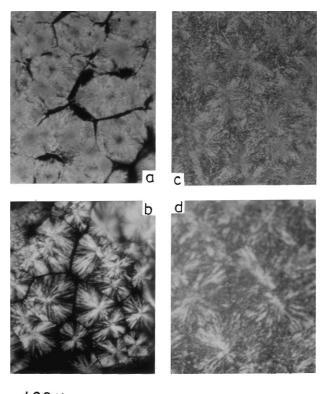
As seen in Table 3, the *n* values are around 3.0 for various PB-1 contents in the blends at all four crystallization temperatures studied, suggesting that the effect of PB-1 content on nucleation and the forms of growth in PP crystallization is insignificant. The *K* values at any crystallization temperature studied appear to decrease as PB-1 content in the blend increases, an indication that the crystallization rate of PP decreases with increasing PB-1 content in the blend.

#### 3.5. Morphological studies

Figs. 7-9 show polarized optical micrographs of PB-1/PP blends that have been isothermally crystallized at 150°C for 7 d, 130°C for 1 h, and 100°C for 16 h, respectively. As PB-1 does not crystallize at 150 and 130°C, the micrographs in Figs. 7 and 8 represent only morphologies of PP. As can be seen in Fig. 7a for pure PP, there are many spherulites impinging on each other. The addition of PB-1 results in decreased spherulite size with less perfection (Fig. 7c), and at higher PB-1 content the spherulites can not be clearly observed (Fig. 7d). As in Fig. 8a for pure PP, some large spherulites are dispersed along with many small spherulites or crystallites. The addition of PB-1 results in decreased spherulite size with much less perfection (Fig. 8b and c), and at higher PB-1 content no spherulites can be observed (Fig. 8d). Figs. 7 and 8 both indicate that spherulite size and perfection of PP crystals decrease with increasing PB-1 content. Compared with Fig. 7, Fig. 8 demonstrates greater PB-1 content effects on decreasing spherulite size and perfection of PP crystals because of the faster crystallization rate of PP at 130°C than that at 150°C. For spherulite growth

of PP at 130°C, the radial diffusion of rejected PB-1 is outstripped by the more rapidly growing PP lamellae, so that PB-1 diffuses aside and is trapped in interlamellar channels and results in much less perfection of PP spherulites in, for example the blend containing 75 wt% PB-1 (Fig. 8d).

At 100°C, both PP and PB-1 can crystallize as can be seen in Fig. 9a and e. Pure PB-1 (Fig. 9e) gives much larger spherulite size than pure PP (Fig. 9a) does because at 100°C PB-1 has a slower crystallization rate than PP. The spherulite size of PB-1 increases with increasing PP content up to 50 wt% in the blend, as seen by comparison of Fig. 9a, b, and c. This is because PP in the blend crystallizes before PB-1 does and the already crystallized PP is dispersed in the crystallizing PB-1 phase in PB-1-rich blends. In other



400 μ

Fig. 7. Polarized optical micrographs of PB-1/PP blends in isothermal crystallization at 150°C for 7 days: (a) PP; (b) 25 PB-1/75 PP; (c) 50 PB-1/50 PP; (d) 75 PB-1/25 PP.

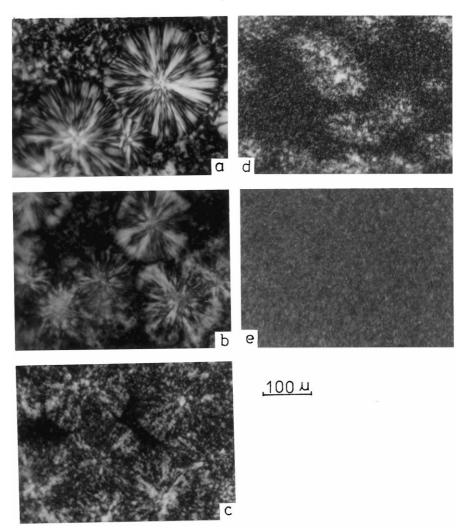


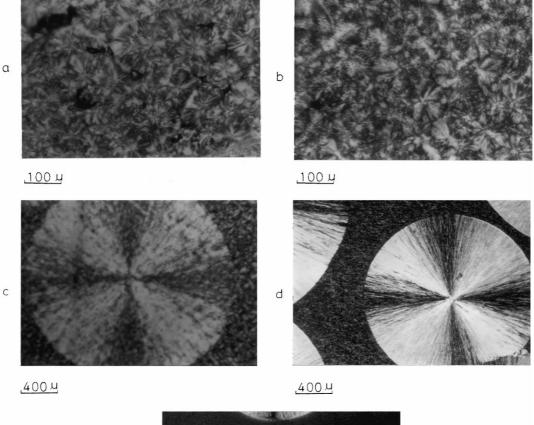
Fig. 8. Polarized optical micrographs of PB-1/PP blends in isothermal crystallization at 130°C for 1 h: (a) PP; (b) 25 PB-1/75 PP; (c) 50 PB-1/50 PP; (d) 75 PB-1/25 PP; (e) PB-1.

words, spherulites of PB-1 grow in a matrix consisting of PP crystals. Consequently, the spherulite size of PB-1 can be enhanced by the presence of PP in the PB-1-rich blend as well, in addition to the finding that the crystallization rate of PB-1 is enhanced by PP as demonstrated by DSC data (Fig. 3a) previously.

# 4. Conclusions

The crystalline/crystalline PP/PB-1 blends, prepared by the solution-precipitation method, are investigated for their crystallization behavior, crystal transformation and morphologies. The crystallization rate of PP is found to decrease with increasing PB-1 content in a cooling or isothermal crystallization process. The effects of PB-1 content on the Avrami constants of PP crystallization, however, are found to be insignificant. The crystallization rate and spherulite size of PB-1 can both be enhanced by the

presence of PP in PB-1-rich blends. As prepared by the solution-precipitation method, pure PB-1 exhibits crystal forms I' (or III) and II, whereas PB-1 in the blends exhibits only crystal form I'; pure PP and PP in the blends exhibit only crystal from  $\alpha$ . The crystal form I' of PB-1 in PB-1-rich blends can be transformed to crystal form II upon heating, but the transformation is retarded with increasing PP content. PB-1 in PP-rich blends exhibits crystal forms I'and II whereas PB-1 in PB-1-rich blends exhibits only crystal form II upon dynamic heating and cooling. The crystal form II of PB-1 can be transformed to form I by aging at room temperature and the transformation can be facilitated by the presence of PP in PB-1-rich blends. Therefore, PP not only helps maintain the crystal form I' for PB-1 in PP-rich blends upon dynamic heating and cooling but also facilitates the transformation from crystal form II to form I for PB-1 in PB-1-rich blends upon aging at room temperature. The similar helix conformation of crystal form  $\alpha$  of PP and forms I' and I of PB-1 results in these findings.



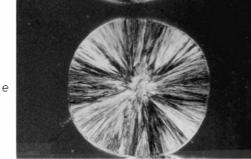




Fig. 9. Polarized optical micrographs of PB-1/PP blends in isothermal crystallization at 100°C for 16 h: (a) PP; (b) 25 PB-1/75 PP; (c) 50 PB-1/50 PP; (d) 75 PB-1/25 PP; (e) PB-1.

## References

- [1] Cruz CA, Paul DR, Barlow JW. J Appl Polym Sci 1979;23:589.
- [2] Karger-Kocsis J, Kallo A, Szaffner A, Bodor G, Senyei Z. Polymer 1979;20:37.
- [3] Martuscelli E, Silvestre C, Abate G. Polymer 1982;23:229.
- [4] Olabisi O, Robeson IM, Shaw MT. Polymer-polymer miscibility. New York: Academic, 1979 (Chap. 6).
- [5] Paul DR, Barlow JW. In: Klempner D, Frisch KC, editors. Polymer alloys. New York: Plenum, 1982. p. 239.
- [6] Wang TT, Nishi T. Macromolecules 1977;10:421.
- [7] Martuscelli E, Pracella M, Yue WP. Polymer 1984;25:1097.
- [8] Ong CJ, Price FP. J Polym Sci, Polym Symp 1978;63:59.
- [9] Berghmans H, Overbergh N. J Polym Sci, Polym Phys Ed 1977;15:1757.

- [10] Robeson LM, Joesten BL. Pap. New York Academy of Sciences, 1975.
- [11] Khambatta FB, Warner F, Russell T, Stein RS. J Polym Sci, Polym Phys Ed 1976;14:1391.
- [12] Morra B, Stein RS. J Polym Sci, Polym Phys Ed 1982;20:2243.
- [13] Nishi T, Wang TT. Macromolecules 1975;8:909.
- [14] Kewi TK, Patterson GD, Wang TT. Macromolecules 1976;9:780.
- [15] Eshuis A, Roerdink E, Challa G. Polymer 1982;23:735.
- [16] Escala A, Stein RS. In: Cooper SL, Estes GM, editors. Multiphase polymers. Advances in Chemistry Series, 176. 1979. p. 455.
- [17] Aubin M, Bedard Y, Morrisette MF, Prud'homme RE. J Polym Sci, Polym Phys Ed 1983;21:233.
- [18] Aubin M, Prud'homme RE. Macromolecules 1980;13:365.
- [19] Bernstein RE, Paul DR, Barlow JW. Polym. Engng Sci 1978;18:683.
- [20] Siegmann A. J Appl Polym Sci 1979;24:2333.

- [21] Siegmann A. J Appl Polym Sci 1982;27:1053.
- [22] Lee MS, Chen SA. J Poly Sci, Part C: Polym Lett 1987;25:37.
- [23] Luciani L, Sepala J, Lofgren B. Prog Polym Sci 1988;13:37.
- [24] Nakamura K, Aoike T, Usaka K, Kanamoto T. Macromolecules 1999;32:4975.
- [25] Natta G, Corradini P, Bassi IW. Nuovo Cimento Suppl 1960;15:52.
- [26] Turner-Jones A. J Polym Sci 1963;B18:455.
- [27] Kopp S, Wittmann JC, Lotz B. Polymer 1994;35:908.
- [28] Hsu CC, Geil PH. J Macromol Sci Phys 1986;B25:433.
- [29] Danusso F, Gianotti G. Makromol Chem 1963;61:139.
- [30] Boor Jr. J, Mitchell JC. J Polym Sci 1963;A1:59.
- [31] Oda T, Maeda M, Hibi S, Watanabe S. Kobunshi Ronbunshu 1974;31:129.
- [32] Asada T, Sasada J, Onogi S. Polym J 1972;3:350.
- [33] Goldback G. Angew Makromol Chem 1973;29/30:213.
- [34] Goldbach G. Angew Makromol Chem 1974;39:175.

- [35] Yang Y, Geil PH. Macromol Chem 1985;186:1961.
- [36] Miller RL, Holland VF. Polym Lett 1964;2:519.
- [37] Turner-Jones A, Aizlewood JM, Beckett DR. Macromol Chem 1964;75:134.
- [38] Trotignon JP, Lebrun JL, Verdu J. Plast, Rubber Compos Process Appl 1982;2:247.
- [39] Lovinger AJ, Chua JO, Gryte CC. J Polym Sci, Polym Phys Ed 1977;15:641.
- [40] Golbach G, Peitscher G. Polym Lett 1968;6:783.
- [41] Danusso F, Gianotti G, Polizzotti G. Makromol Chem 1964;80:13.
- [42] Boor Jr. J, Youngman EA. J Polym Sci, Polym Lett 1964;2:903.
- [43] Ceacintov C, Miles RB, Schuurmans HJL. J Polym Sci: Part A-1 1966;4:431.
- [44] Foglia AJ. Appl Polym Symp 1969;11:1.
- [45] Boor Jr. J, Mitchell JC. J Polym Sci 1962;62:570.