

Fractionated and Confined Crystallization of Polybutene-1 in Immiscible Polypropylene/Polybutene-1 Blends

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Abstract In this work, the crystallization of immiscible polypropylene (PP)/polybutene-1 (PB) blends, in particular the effect of crystal morphology of PP (HTC, high T_m component) on the subsequent crystallization behavior of PB (LTC, low T_m component) was studied. Herein, we firstly indicated that PP/PB blends were not completely compatible but characterized as the LCST-like phase diagram above the melting temperature of PP. Crystallization of PP at different crystallization temperatures brought about different PP crystal morphologies and PB was segregated and confined at different locations. Much larger-sized domain of PB component appeared in PP spherulites resulting from the effects of non-negligible phase separation and the slower PP crystallization rate as PP crystallized at high temperature. As temperature continued to fall below T_m of PB, the fractionated and confined crystallization of PB occurred in the framework of PP spherulites, reflected by the decreased crystallization temperature (T_c) of PB and the formation of form I' beside form II. Notably, if PP previously crystallized at high T_c , fractionated crystallization of PB became predominant and confined crystallization of PB became weak due to the much wider droplet-size distribution of PB domains.

Keywords Polypropylene; Polybutene; Confined crystallization; Morphology

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INTRODUCTION

Blending of crystalline PP and crystalline PB attracts considerable attentions whatever from the viewpoints of the reduced cost of “plastic gold” PB^[1] or the property improvement of common plastic PP^[2–4]. PP and PB are both deemed as polymorphic polymers when they crystallize from chaos melt, respectively. Diverse crystal superstructure could be obtained from PP/PB blends by mediating the phase transition, phase separation and crystallization behavior of the two components due to the admixing and other crystallization characters. Until present, although much progress has been achieved to understand the phase morphology control and the enhanced mechanical properties of PP/PB blends, some essential problems still exist and need to be solved theoretically and experimentally. For instance, the miscibility between PP and PB does not get consensus owing to the molecular weight dependence and the T_g difference of PP and PB less than 20 °C. Siegmann^[3] firstly claimed that PP/PB blend was a compatible system due to the existence of a single T_g ; the fact, however, that T_g of PP and PB is different by only around 15 °C makes the conclusion of

the compatibility of PP/PB blend to be questionable. Lee^[4] just reported that crystalline/crystalline PP/PB blend possesses compatibility in amorphous regions by the interaction parameter calculated from the changes in melting temperature of the blends. Recently, Ji^[5] inferred that PP/PB blends are immiscible and characterized as the typical UCST phase diagram according to the changes in crystal modifications with temperature and compositions. Despite the controversy on compatibility of PP/PB, the direct and more convincing experiments need to be carried out to identify the phase behavior between PP and PB.

As far as crystallization is concerned for crystalline/crystalline polymer blends, many studies focus on the interrelated crystallization process and the final superstructure through the two step crystallization process. Upon melt cooling the HTC firstly crystallizes as temperature falls below its melting point, simultaneously, the LTC acting as the diluent is rejected and segregated probably at interlamellar, inter-fibrillar or inter-spherulite of HTC crystals. The accurate location of LTC is related to not only the chain diffusion rate of LTC, the crystal growth rate of HTC, but also the dynamic and thermodynamic competition between crystallization and phase separation if the incompatibility of both components is referred to. When temperature continues to fall below the melting point of LTC, LTC starts to crystallize in the confined crystalline spaces of HTC^[6]. Accordingly, there is a strong link between

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the crystallization of LTC and the morphology of pre-existing spherulite of HTC. Han *et al.*^[7] have investigated the crystallization kinetics of poly(ethylene oxide) (PEO) confined in the pre-existing different crystalline morphology of poly(butylene succinate) (PBS). It is found that both the crystal nucleation and growth of PEO were restricted on different length scales within the scaffolds of PBS, and fractionated crystallization of PEO occurred due to the interface assisted nucleation. Qiu *et al.*^[8] have reported that the pre-existing poly(vinylidene fluoride) (PVDF) crystals enhanced the nucleation ability but reduced the crystal growth rates of poly(butylenes succinate-co-butylene adipate) (PBSA). Inoue and coworkers^[9, 10] have studied the crystallization behavior of PEO following the crystallization of PBS at different T_c s, and suggested that the confined crystallization of PEO occurred as the PEO component distributed in the interlamellar regions of PBS. What should be pointed out is that the above cited cases are all the miscible blends. The interrelated crystallization process has also been observed in a large number of immiscible blends^[11–16]. However, when phase separation and crystallization occurred simultaneously, both the segregation of LTC in various crystal space of HTC and crystallization kinetic of both HTC and LTC became complicated and were determined by the competition and interaction between these phase transitions^[17–19].

For PP/PB blends, the addition of PP promoted the crystal-crystal transition of PB from the kinetically favored form II to the thermodynamically favored form I^[20–22], seen as the similar results with small molecules addition^[23]. PB in form I' was observed *via* mediating its thermal history prior to crystallization, following incorporation of PP^[5]. In case of the crystallization of PB confined, not only the changes of polymorphic behaviors but also the variation of mechanical performance occurred, such as the decreased tensile properties and the improved flexural properties^[24]. The complex features of the PP/PB blends, such as the binary crystalline characters, polymorphic behaviors, crystal transition of PB phase and the controversial compatibility between PP and PB, resulted in the complicated crystallization behavior and the final morphology of the blends. In this study, the direct and more convincing phase diagram of PP/PB blends has been provided. The fractionated and confined crystallizations of PB in the multiscale crystal structures of PP phase have been investigated. It is found that the pre-formed PP morphologies have great influence on the fractionated crystallization and confined crystallization of PB phase.

EXPERIMENTAL

Materials

PP used in this work was obtained from Maoming Shihua Co. Ltd., China, with melt flow index of 0.62 g/10min (190 °C, 2.16 kg) and the number-average molecular weight of 71.8×10^4 g/mol. Polybutene-1 pellets with melt flow index of 0.4 g/10min (190 °C, 2.16 kg) and the number-average molecular weight of 73.4×10^4 g/mol were supplied by Dongfang Hongye Chemical Co. Ltd., China.

Sample Preparation

Both PP and PB were dissolved in xylene at 130 °C for 30 min to obtain 10 mg/mL polymer solutions, in which the solid content of PB was ranged from 0 wt% to 100 wt%. Before utilization, PP/PB blends were precipitated from xylene by adding 3 times the amount of ethanol. After filtration, PP/PB blends were dried in a vacuum oven at 45 °C for 48 h. The melting temperatures (T_m) of purified PP and PB were measured to be about 165 and 115 °C, respectively, by differential scanning calorimetry (DSC) at a heating rate of 10 °C/min.

Optical Microscopy

Polarized optical microscopy (POM) and phase contrast optical microscopy (PCOM) images were observed by an Olympus (BX 51-P) optical microscope equipped with an Olympus camera (DP26). The sample temperatures were controlled by a Linkam (LNP95) hot stage. The thickness of sample sandwiched between two glass slides for optical microscopy measurements was about 25 μ m. To obtain the static phase diagram of PP/PB blends, samples were heated above the T_m of PP and then annealed at the selected temperature around 1 h to observe whether the cloud point was presented. In consideration of the high T_m of PP (above 160 °C), as the observed temperature fell below 200 °C, samples were heated to 200 °C and kept for 5 min to assure the crystals of PP melted, and then cooled down to the selected temperature. Herein, the studied temperatures of phase diagram for PP/PB blends ranged from 160 °C to 260 °C with 10 °C of intervals. As approaching the transitional temperature, the interval for observation temperature was reduced to 2 °C for better accuracy. In the two-step crystallization, samples were firstly annealed at 200 °C for 5 min to erase thermal history, then cooled down to T_c of PP (110–140 °C), which was much higher than T_m of PB. After the complete crystallization of PP, samples were further quenched to the T_c of PB with 10 °C/min of cooling rate.

Differential Scanning Calorimetry

After the complete crystallization of PP at different T_c s, the nonisothermal crystallization processes of PB component and the second heating process of PP/PB blends were recorded by a differential scanning calorimeter (DSC 8500 PerkinElmer). The heating rates for all samples were 10 °C/min. The temperature and heat flow were calibrated by pure indium under nitrogen atmosphere before use.

Scanning Electron Microscopy

After the complete crystallization of PP at different T_c s, followed by the nonisothermal crystallization of PB and the etching of PB phase at 50 °C for 1 h, the morphologies of PP/PB blends were observed using a scanning electron microscope (SEM, JSM-7500F). Every sample was coated with platinum.

X-ray Diffraction (XRD)

X-ray diffraction experiments (XRD) were performed on Rigaku Ultima IV with Cu K α ($\lambda = 0.154$ nm) radiation at a generator voltage of 45 kV and a current of 40 mA.

RESULTS AND DISCUSSION

Miscibility of PP and PB and the Temperature Profiles for the Two-step Crystallization of PP/PB Blends

The static phase diagram of PP/PB blends shown in Fig. 1 was determined by optical microscopy. The cloud point finding was based on the appearance of phase-separated structure after samples annealed at the selected temperature for 1 h. Clearly, the phase diagram of PP/PB blends showed LCST-like type, though the lowest critical point was not obtained because of the blending melt entering another liquid-solid phase transition, as the crystallization temperature fell below 160 °C.

Fig. 2 shows the crystallization temperatures of PB after PP components isothermally crystallized at 140 °C in PP/PB blends where the compositions of PP/PB blends were 95/5, 85/15, and 50/50. We found that the lower content of PB in blends was associated with the lower and much wider T_c of PB after the crystallization of PP, signifying the reduced and fractionated crystallization tendency of PB. The much smaller droplets of PB and confined crystallization of PB in the scaffolds of PP crystals are both responsible for PB crystallization at larger super-cooling condition during two-step crystallization. Herein, to simplify the study on confined crystallization of PB, PP/PB blends with a constant ratio of 85/15 were used hereafter. PP as the major components in such blend crystallized first, which made it easy to achieve

the diversity crystalline scaffolds from the immiscible melt by mediating crystallization temperatures. According to the phase diagram of PP/PB blends, PP/PB blends with the higher content of PB easily fall in the unstable phase region. This means that the larger domain of PB tends to form, which automatically causes the reduced confinement of PB crystallization. It is also noted that the crystallization of PP caused the changes of composition in the amorphous components, and accelerated the dynamic of phase separation. Herein, the detailed temperature profiles for the observation of crystallization by two-step crystallization were designed as follows (shown in Fig. 1). Firstly, PP/PB blends at the weight ratio of 85/15 were heated to the chaos melt (200 °C) for 5 min before they cooled down for the complete isothermal crystallization of PP at different T_{cs} . Secondly, the temperatures continued to fall to room temperature at 10 °C/min of cooling rate for nonisothermal crystallization of PB.

Isothermal Crystallization of PP in the PP/PB Blend

Upon PP crystallization at temperatures above T_m of PB, PB was still in the chaos melt state, thus PP/PB blends could be treated as crystalline/amorphous system. At different T_{cs} for PP, the dynamics of PP and PB molecular chains was different, which reflected on the crystalline morphology of PP and the residence of amorphous PB, as shown in Fig. 3. Since amorphous PB in this case was the minor component,

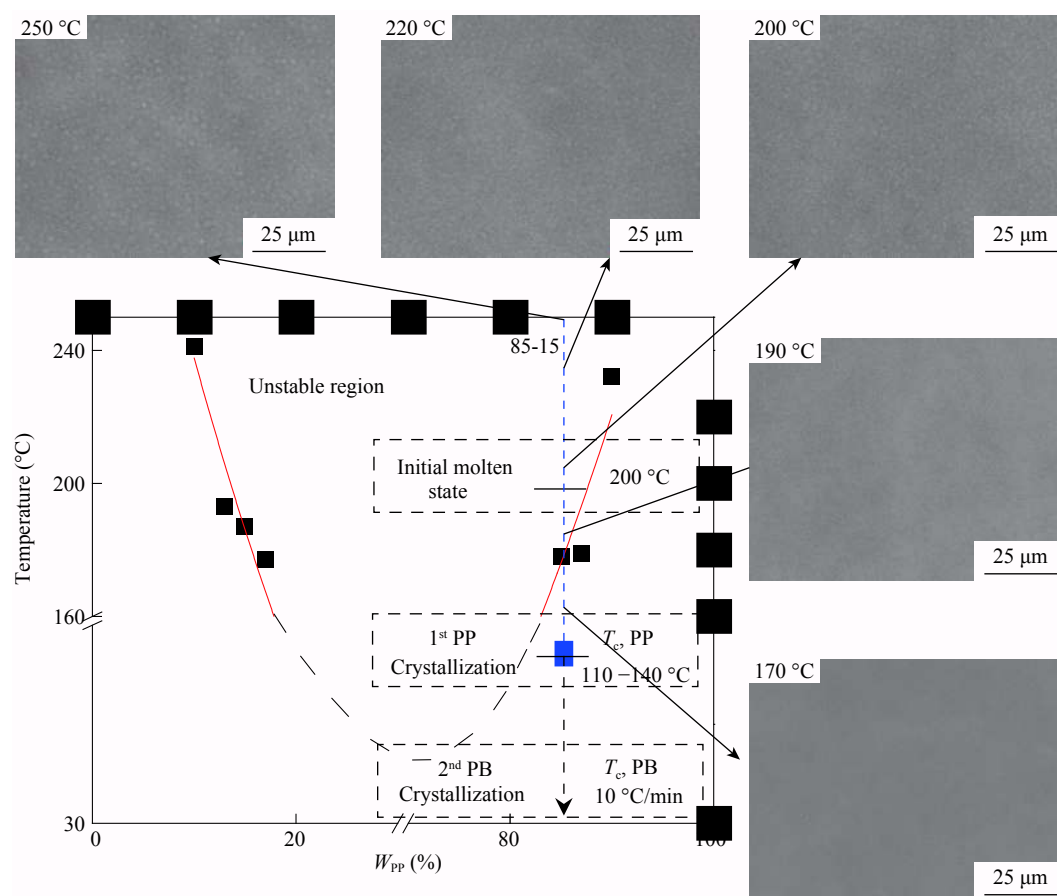


Fig. 1 Phase diagram of PP/PB blends and the adopted two step-crystallization temperature profiles with the phase contrast optical microscopies of PP/PB (85/15, W/W) blends annealed for 1 h at different temperatures

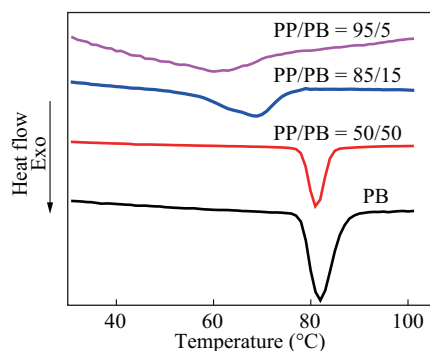


Fig. 2 DSC curves of non-isothermal crystallization of PB after the complete isothermal crystallization of PP at 140 °C for PP/PB blends (The cooling rate was 10 °C/min.)

the large distinct bright spherulites of PP were observed at most T_c . Not surprisingly, the higher the T_c for PP, the larger the spherulite of PP formed, for the slower crystallization rate let PP chains fully and orderly attach to the crystal growth front. When PP crystallized at a relatively lower temperature, the crystallization rate dramatically increased due to the larger supercooling. The result was that the rapid nucleation and solidification allowed the presence of small crystals of PP in the observation windows of POM. PB acting as amorphous diluents at this step was excluded or engulfed by PP spherulites, probably segregated in different regions (interlamellar, interfibrillar or interspherulite).

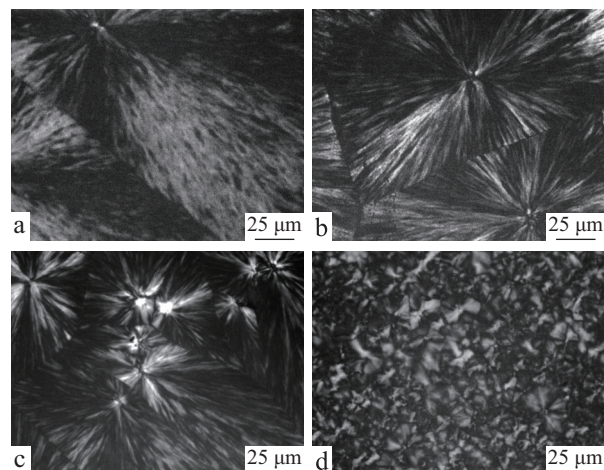


Fig. 3 Polarized light micrographs of PP spherulites after PP/PB (85/15) blends crystallized at different temperatures: (a) 140 °C, (b) 135 °C, (c) 130 °C, and (d) 110 °C, respectively

To make clear the accurate residence of amorphous PB after PP crystallization, the cross-sections of PP/PB samples were observed by SEM (Fig. 4) after the complete crystallization of PP at different T_c s and the etching of PB phase by cyclohexane (50 °C, 1 h) following the non-isothermal crystallization of PB. The holes in the crystalline scaffold of PP revealed the domains of PB component. Clearly, PB was mainly aggregated in the inter-fibrillar

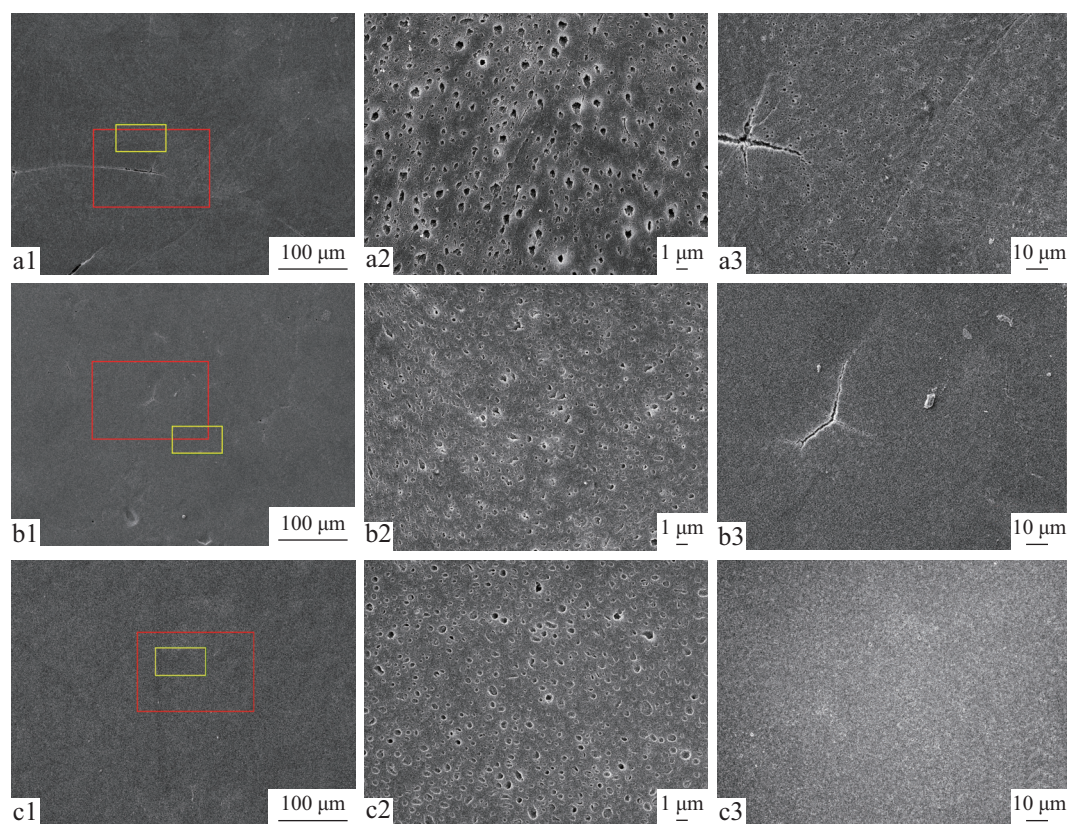


Fig. 4 SEM images of the cross-section of PP/PB samples (85/15, W/W) after PP crystallized at different temperatures: (a) 140 °C, (b) 130 °C, (c) 110 °C (Before observation by SEM, PB was etched by cyclohexane. Images 2 and 3 are zoom-in images of 1, corresponding to the yellow and red rectangular windows, respectively.)

regions (Figs. 4a2, 4b2 and 4c2), and also a few PB domains located at the interspherulite space (Figs. 4a3, 4b3 and 4c3). Interestingly, when PP crystallized at 140 °C, the averaged domain size of PB was larger than that observed as PP crystallized at 130 and 110 °C. As we have known that PP/PB blends were thermodynamically immiscible, when temperature dropped to T_c of PP, phase separation simultaneously occurred in this blends. The higher T_c revealed as the lower supercooling is normally followed by the slower crystallization rate. Resultantly, the prolonged phase separation during PP crystallization enlarged the domain size of PB phase, which could not be excluded from the crystal growth front but *in situ* engulfed by PP spherulites. In addition, the mobility of PB chains was enhanced at the high T_c of PP, and the aggregation of PB to form drops was thus proposed.

Non-isothermal Crystallization of PB after PP Crystallization

Following the crystallization of PP component, PB crystallized subsequently inside the spherulites of PP as temperature fell below T_m of PB. Fig. 5 shows the DSC cooling curves of PP/PB blends at the second crystallization step. As a control, crystallization of neat PB is also displayed here. The crystallization temperature and complete crystallization time of PP are shown in Fig. 5 to identify the previous heat history of the sample. Firstly, the PP/PB blends showed much lower temperature and much wider PB crystallization peaks compared to those of neat PB. Secondly, the double crystallization peaks of PB: T_{c1} (small supercooling) and T_{c2} (large supercooling) were observed if PP crystallized at the high T_c , illustrating the occurrence of fractionated crystallization of PB. The detailed values of crystallization parameters of PB are all summarized in Table 1.

As Table 1 shows, compared to pure PB that crystallized at high T_c 71.8 °C with crystallization enthalpy of -33.4 J/g, PB components in PP/PB blends, however, showed the declined crystallization ability based on the decreased T_c and the reduced enthalpy. As PP crystallized at a relatively high temperature (135–145 °C), the crystallization peak of T_{c1} became much broader, and a weak crystallization peak of T_{c2} was discerned at about 62 °C. It is suggested that the fractionated crystallizations of PB corresponding to different nucleation and growth mechanisms in the pre-existing scaffold of PP spherulites occurred^[25, 26], which are closely related to the T_c of PP and normally observed in immiscible polymer blends. Once PP/PB blends cooled down from 200 °C to higher T_c of PP, phase separation should not be neglected; the competition and interaction between faster phase separation and slower crystallization started

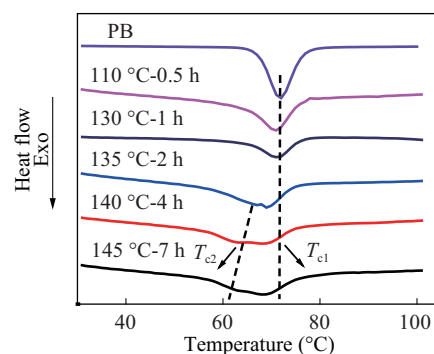


Fig. 5 DSC cooling curves of pure PB and PB in the PP/PB (85/15, W/W) blend after PP crystallized at various T_c s (Cooling rate: 10 °C/min. The notes on curves illustrate the time spent for PP complete crystallization at various T_c s.)

immediately. Therefore, the larger domains of PB existed in PP spherulites before PB crystallization. As a result, it allowed the presence of the fractionated crystallization of PB from PB domains with different sizes^[27]. The larger PB domains accounted for T_{c1} and much smaller PB domains were responsible for T_{c2} . To visualize phase separation exerting influence on the formation of PB domains, PP/PB blends were annealed at 190 °C for different time prior to PP crystallization at 130 °C (Fig. 6). It is verified that though PB was the minor component, the longer phase separation time (Fig. 6c) did yield the larger size distribution of the PB droplets: partial PB droplets were in the range of 50 μ m, while other PB droplets were in the range of several microns.

For the two-step crystallization, the fractionated crystallization of PB occurred in PP spherulites for PP/PB blends. The problem was that since both PB and PP are polymorphism, whether anyone shows any influence on their crystal modification. Fig. 7 shows the DSC behaviors of the PP/PB blends after two-step crystallization. It is seen that all PP/PB blends have the same crystal structure of PP, namely α -form crystal morphology with T_m at 165–175 °C whatever the T_c of PP was. This implied that the existence of PB exerted little effect on the polymorphic behavior of PP. Not surprisingly, the higher the T_c for PP, the higher the crystallinity was observed due to more PP chains have enough time diffusing and orderly aligning as shown in Table 2. It is noted that the melting point of PP crystals revealing the lamellar thickness and chain packing mode in crystal regions was balanced by the crystallization rate and PB drop size. For the polymorphism features of PB, the confinement effect was reflected on the crystal modification. It is found that both crystal forms I' and II of PB appeared in the blend, which was different from neat PB samples;

Table 1 Non-isothermal crystallization parameters of PB in PP/PB (85/15, W/W) blends

Sample (T_c , PP- t)	T_{c1} (°C)	T_{c2} (°C)	$T_{c\text{onset}}$ (°C)	ΔH_c (J/g)	Half peak width T_{c1} (°C)	Half peak width T_{c2} (°C)
PB	71.8	—	76.5	-33.4	5.2	—
110 °C-0.5 h	71.7	—	76.4	-4.8	6.8	—
130 °C-1 h	70.8	—	78.0	-4.5	7.0	—
135 °C-2 h	69.2	66.4	74.6	-4.2	4.7	8.6
140 °C-4 h	69.3	62.3	75.1	-3.6	7.5	8.0
145 °C-7 h	68.7	61.3	75.2	-3.6	17.9	17.9

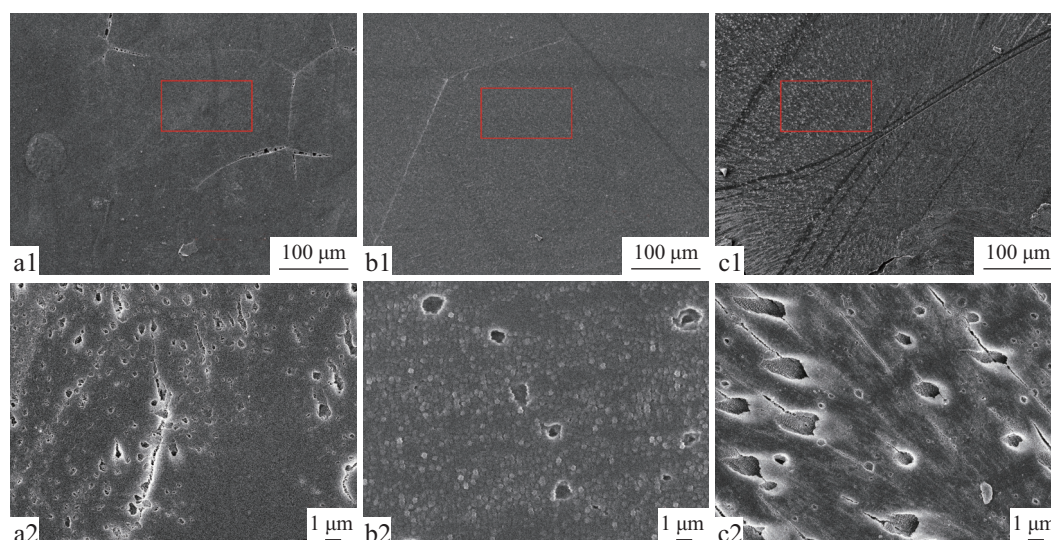


Fig. 6 SEM images of PP/PB (85/15, *W/W*) blends undergoing phase separation at 190 °C for (a) 0.5 h, (b) 1 h, (c) 2 h prior to PP crystallization at 130 °C (PB was etched by cyclohexane (50 °C, 1 h) before observation. Images 2 are the zoom in images of the rectangular window in images 1.)

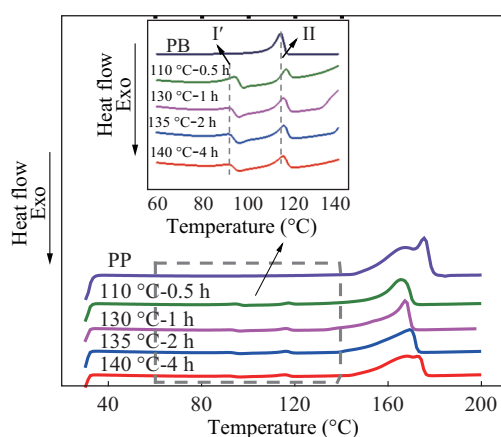


Fig. 7 The DSC heating curves of pure PP, PB and PP/PB (85/15, *W/W*) blend after the crystallization of PP at various T_c and following non-isothermal crystallization of PB (heating rate: 10 °C/min. Notes on curves illustrate the time spent for PP complete crystallization at various T_c .)

normally, kinetically favored form II was yielded as pure PB cooled directly from melt. I' was commonly defined as the thinner lamellae of crystal form I and rarely formed directly from melt cooling of PB. Here, the presence of form I' was totally the reflection of PB confined crystallization. As Table 2

Table 2 Values of peak melt temperatures I', II, and corresponding crystallinity (X_c) of PB and PP during the non-isothermal crystallization of PB in PP/PB (85/15, *W/W*) blends

	PB				PP		
	$T_{mI'}$ (°C)	T_{mII} (°C)	X_c (%)	$\Delta H_{mI'}/$ ΔH_{mII}	T_m (°C)	ΔH_m (J/g)	X_c (%)
PB	—	114.0	53.5	—	—	—	—
PP	—	—	—	—	175.5	106.8	65.5
110 °C-0.5 h	94.9	117.3	35.1	1.5	165.4	71.3	53.9
130 °C-1 h	92.7	116.4	39.5	0.5	167.4	84.1	59.8
135 °C-2 h	92.2	116.3	43.1	0.7	169.5	86.7	61.6
140 °C-4 h	91.5	115.8	41.0	0.4	168.1	87.0	61.9
145 °C-7 h	92.0	115.2	45.0	0.4	166.0	90.3	64.2

shows, when PP crystallized at the lower T_c , the I'/II ratio was relatively high, indicating that the confinement of PB became prominent. Anyway, the higher T_c will definitely lead to the weakness of this confinement due to the aggregation of partial PB droplets from phase separation.

CONCLUSIONS

In this work, we firstly offered the convincing LCST-like phase diagram for PP/PB blends by direct observation using POM. More importantly, the fractionated and confined crystallization of PB as the minor component in blends was investigated by two-step crystallization. Crystallization of PP at different temperatures brought about different PP crystal morphologies, and then PB was confined in different locations. After PP crystallized at various temperatures, confined crystallization of PB occurred in the framework of PP spherulites. It was revealed by the decreased T_c and formation of both forms I' and II for PB components. When PP crystallized at the high temperature, fractionated crystallization of PB became prominent and the confined crystallization of PB became weak due to the much wider droplet-size distribution of PB domains arising from the non-negligible phase separation and slower PP crystallization.

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