

MICROSTRUCTURE EVOLUTION OF ISOTACTIC POLYPROPYLENE DURING ANNEALING: EFFECT OF POLY(ETHYLENE OXIDE)*

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Abstract The microstructure evolution of isotactic polypropylene (*i*PP) during annealing is reported. A few amount of poly(ethylene oxide) (PEO) which exhibits much lower melt temperature compared with *i*PP was introduced into *i*PP in this work. The crystalline structure of *i*PP was detected using differential scanning calorimetry (DSC) and wide-angle X-ray diffraction (WAXD), and the relaxation of *i*PP was characterized using dynamic mechanical analysis (DMA). The variation of PEO morphology was investigated by scanning electron microscopy (SEM). The results show that the crystallization, including the primary crystallization and second crystallization during annealing, as well as the relaxation of *i*PP matrix is promoted with the presence of PEO.

Keywords: *i*PP; PEO; Annealing; Crystalline structure; Relaxation.

INTRODUCTION

As one of the typical semicrystalline polymers, isotactic polypropylene (*i*PP) exhibits rather complicated crystallization behavior. The most interesting is the complicated crystalline structures of *i*PP which can be achieved at different crystallization conditions, such as the smectic mesophase (a intermediate state between ordered and amorphous phase, and usually presents in the quenched specimens), the monoclinic α -phase (a thermodynamically stable phase and predominating under normal processing conditions), the trigonal β -phase (a thermodynamically metastable phase and sporadically observed in commercial grades of *i*PP products at higher undercooling) and the orthorhombic γ -phase (a thermodynamically metastable phase and is only obtained when crystallization of *i*PP occurs at elevated pressure). Even for the same crystalline structure, the crystalline morphology may be different due to the variation of crystallization condition. For example, β -phase *i*PP exhibits well developed β -spherulites at the critical content of β -phase nucleating agent whereas bundle-like morphology without distinctly developed spherulites at the supercritical content^[1–4]. The presence of other polymer which exhibits lower melt temperature (T_m) compared with *i*PP also influences the crystallization of *i*PP due to the local solution effect of the polymer^[5–8]. On the other hand, the crystallization of *i*PP is relatively difficult during the normal processing conditions, and the degree of crystallinity (X_c (%)) of *i*PP is relatively low compared with that of polyethylene. Thus, increasing the X_c (%) of *i*PP to achieve the comprehensive physical properties as expected has been the main subject of many researches.

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As is well known to all that a simple annealing process is favorable to the improvement of the physical properties of polymer articles through eliminating the residual stress induced during the processing and perfecting the crystalline structures. Usual annealing improves the crystal structure without changing the macroscopic morphological organization such as spherulites^[9]. Zia reported that annealing only permitted a precise adjustment of the size and the thermodynamic stability of the *i*PP crystals, without affecting the external habit of the crystals and their organization in higher order structures^[10]. More precisely, annealing induces the increase of lamellar thickness and the X_c (%) of *i*PP^[11–17]. The former phenomenon is mainly related to the chain segments sliding diffusion or the chain mobility in the amorphous region of *i*PP during annealing process, and the macroscopic response is the enhancement of the T_m ^[11–13]. The latter one is believed to be the result of second crystallization of amorphous region, the transformation of the mesophase to the crystalline phase and the lamellar thickening^[12, 14–16]. A low-temperature endothermic peak before the main endothermic peak (T_m), which depends mainly on the annealing temperature and annealing duration, is usually observed for the annealed *i*PP^[17, 18].

In this work, a few amount of poly(ethylene oxide) (PEO, 5 wt%), which exhibits much lower T_m (65°C) compared with *i*PP, was added into *i*PP, and the injection molded bars were annealed at different conditions. The selection of PEO as a minor phase for *i*PP is mainly attributed to the following consideration. PEO is immiscible with *i*PP, thus, it is expected to know whether the crystalline structure evolution of *i*PP during the annealing process can be influenced dramatically by the immiscible component or not. On the other hand, since the variation of microstructure during annealing is mainly related to the amorphous region away or nearby the lamellae, the presence of PEO, which locates in the amorphous region possibly between spherulites and/or inside spherulites between lamellar stacks, affects the chain segment mobility of *i*PP if the annealing temperature (T_a) is higher than the T_m of PEO. In this condition, PEO is in the molten state and it possibly exhibits a positive effect for *i*PP chain segment mobility to a certain extent, although it is immiscible with *i*PP. Thus, the main attention of this work is focused on the evolution of microstructure in immiscible *i*PP/PEO during annealing, including the crystalline structure and relaxation of *i*PP and the phase morphology of PEO. The macroscopic mechanical responses will be systematically investigated in other work.

EXPERIMENTAL

Materials

All the materials used in this study are commercially available. *i*PP (F401) with a melt flow rate (MFR) of 2.5 g/10min (230°C/2.16 kg) and a density of 0.91 g/cm³ was obtained from Lanzhou Petrochemical Co, Ltd., Lanzhou, China. PEO with a molecular weight of 2.86×10^5 was purchased from Shanghai Liansheng Chemical Co., Ltd., China.

Sample Preparation

Before melt blending, both *i*PP and PEO were dried in an oven at 40°C for 2 h. *i*PP/PEO blend with only 5 wt% PEO was prepared through using a twin-screw extruder (SHJ-20, China) at the screw speed of 200 r/min and the temperatures of 150–210°C from hopper to die. After making droplets, the pellets were dried in an oven at 40°C for 2 h, and then were injection-molded and the standard specimens were prepared using an injection-molding machine (K-TEC40, Germany) with the melt temperatures of 190–215°C from hopper to nozzle and mould temperature of 25°C. To make a comparison, pure *i*PP injection molded specimens were prepared through the same procedure used for preparing the *i*PP/PEO blend.

Some specimens were annealed for 12 h in a fan-assisted oven at different temperatures ($T_a = 50$ –160°C) and others were annealed at 100°C for different durations ($T_a = 12, 24, 48$ and 96 h). After being annealed, the specimens were cooled in the ambient air and then conditioned at 23°C and 50% relative humidity for 48 h before testing.

Polarized Optical Microscopy (POM)

The crystallization morphologies of pure *i*PP and *i*PP/PEO blends were characterized through polarized optical

microscope (POM, XPN203E, China). First, a sample of about 5 mg was heated to 200°C and pressed to obtain a slice with a thickness of about 20 μm . The slice was maintained at 200°C for 5 min to eliminate the thermal and mechanical prehistory. Secondly, the slice was transferred to a hot-stage with a setting temperature of 130°C and maintained at this temperature for 2 h. The crystallization morphologies were recorded *via* a digital camera.

Differential Scanning Calorimetry (DSC)

The crystallization and melting behaviors of the samples were carried out on a Netzsch STA 449C Jupiter (Germany) in nitrogen atmosphere. For the unannealed specimens, sample of about 8 mg was heated from 0°C to 200°C at a heating rate of 10 K/min, and maintained at 200°C for 5 min to eliminate any thermal history, then the sample was cooled down to 0°C at a cooling rate of 5 K/min. For the annealed specimens, the sample was heated directly from 0°C to 200°C at a heating rate of 10 K/min. The values of X_c (%) of PEO and *i*PP were calculated according to the following relationship:

$$X_c (\%) = \frac{\Delta H_m}{\Delta H_m^0 \times \phi} \times 100\% \quad (1)$$

where ΔH_m is the DSC measured value of fusion enthalpy obtained during the heating process, ΔH_m^0 is the fusion enthalpy of the completely crystalline polymer, and ϕ is the weight fraction of each component in the sample. Here, the values of ΔH_m^0 for *i*PP and PEO are selected as 207 J/g^[19] and 203 J/g^[20], respectively.

Wide Angle X-ray Diffraction (WAXD)

The crystalline structures of *i*PP matrix were investigated using wide angle X-ray diffraction (WAXD, Panalytical X'pert PRO diffractometer with Ni-filtered Cu K α radiation at 40 kV and 40 mA). The angular range used was from 5° to 35° (2 θ). The relative β -phase fraction (K_β (%)) was calculated from WAXD diffractograms according to the following relation^[21]:

$$K_\beta (\%) = H_{300}^\beta / (H_{110}^\alpha + H_{040}^\alpha + H_{130}^\alpha + H_{300}^\beta) \times 100\% \quad (2)$$

where H_{110}^α , H_{040}^α and H_{130}^α are the intensities of the (110), (040) and (130) reflections of the α -phase, respectively, and H_{300}^β is the intensity of (300) reflection of β -phase.

Scanning Electron Microscopy (SEM)

The morphology of PEO before and after being annealed was characterized by using a Fei Quanta 200 environmental scanning electron microscope (ESEM, USA) with an accelerating voltage of 20 kV. Before SEM measurements, the cryogenically fractured surface prepared in liquid nitrogen was first etched by toluene at 60°C for 3 h to remove PEO from the *i*PP matrix, and then the etched surface was carefully washed with fresh water. The SEM photographs were analyzed using an image analyzer to calculate the diameter of dispersed phase domains. A minimum number of 600 dispersed particles were considered. The weight average PEO particle diameter ($\bar{d}_w$) was calculated using the following equation:

$$\bar{d}_w = \sum n_i d_i^2 / \sum n_i d_i \quad (3)$$

where n_i is the number of particles with diameter d_i .

Dynamic Mechanical Analysis (DMA)

Dynamic mechanical analysis (DMA) testing was carried out using a DMA Q800 analyzer (USA). The single cantilever mode was selected, and the measurement was carried out on a rectangular cross-sectional bar of 50 mm $\times$ 10 mm $\times$ 4 mm (length $\times$ wide $\times$ thickness) from -40°C to 160°C at a heating rate of 3 K/min and a frequency of 1 Hz. Three samples were tested repeatedly for each composition and the typical curve was reported.

RESULTS AND DISCUSSION

Crystallization and Melting Behavior of *i*PP/PEO Blend

Figure 1 shows the crystallization and melting behaviors of *i*PP/PEO blend. To make a comparison, the results of pure *i*PP were detected too. As one can see that the presence of a few amount of PEO promotes the nonisothermal crystallization of *i*PP matrix to a certain extent. The crystallization temperature (T_c) is increased from 113.2°C of pure *i*PP to 118.5°C of the blend, and the start temperature for crystallization (T_{onset}) is increased too. Furthermore, the exothermic peak of the blend seems sharper than that of the pure *i*PP, indicating the increase of the crystallization rate in the blend. The similar results have been reported for the *i*PP/polydimethylsiloxane (PDMS) blends and the reason is attributed to the enhanced mobility of *i*PP chain segments accompanied with the decreasing viscosity of the sample^[22]. In this work, when the crystallization of *i*PP occurs, PEO is in the molten state, which is believed to be favorable for the chain segments sliding of *i*PP, leading to the acceleration of *i*PP crystallization process. In Fig. 1(b), the endothermic peak observed at relatively lower temperature (51.9°C) is attributed to the fusion of PEO during DSC heating process. One can see that the T_m of PEO in immiscible *i*PP/PEO blend is much lower than that obtained from pure PEO (65°C) possibly due to the following mechanisms. One is the confined crystallization behavior of PEO occurring between spherulites and/or inside spherulites between lamellar stacks of *i*PP matrix. As shown in Fig. 1(a), the T_c of *i*PP matrix is much higher than the T_m of PEO, thus the crystallization of PEO is greatly influenced by the adjacent *i*PP spherulites or lamellar stacks. Such confined crystallization behavior of PEO has been reported elsewhere^[23, 24]. And the other one is that during the sample preparation, the relatively high melt temperatures induce the degradation of PEO, which affects the crystallization kinetics of PEO to a large extent. Further work needs to be done to understand the crystallization behavior of PEO in *i*PP/PEO blends. For *i*PP, although the X_c (%) of matrix maintains invariant, the blend exhibits higher T_m (169.1°C) compared with the pure *i*PP possibly due to the crystallization of *i*PP matrix in the blend occurring at relatively lower supercooling, leading to a larger average lamellar thickness.

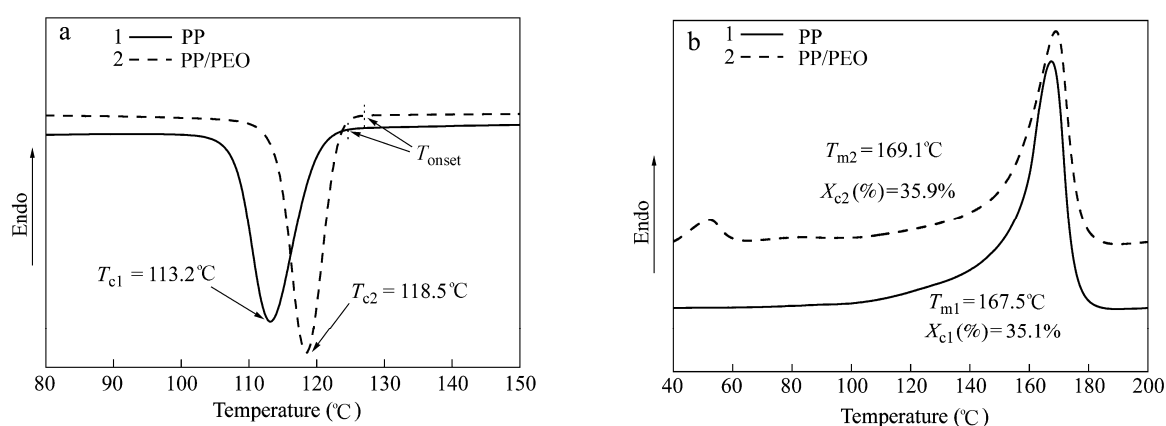


Fig. 1 DSC cooling (a) and heating (b) curves of *i*PP and *i*PP/PEO blend

Figure 2 shows the isothermal crystallization morphologies of pure *i*PP and *i*PP/PEO blend obtained at temperature of 130°C. It can be seen that the blend exhibits decreased nucleation density and largely increased average diameters of spherulites compared with the pure *i*PP. It should be noticed that the isothermal crystallization temperature is much higher than the T_m (65°C) of pure PEO, thus PEO is in the molten state during the crystallization process of *i*PP. Although PEO is immiscible with *i*PP, it most likely exhibits a positive role in decreasing the local concentration of tie molecules of matrix and promoting the chain segments sliding diffusion, leading to a larger spherulites growth rate.

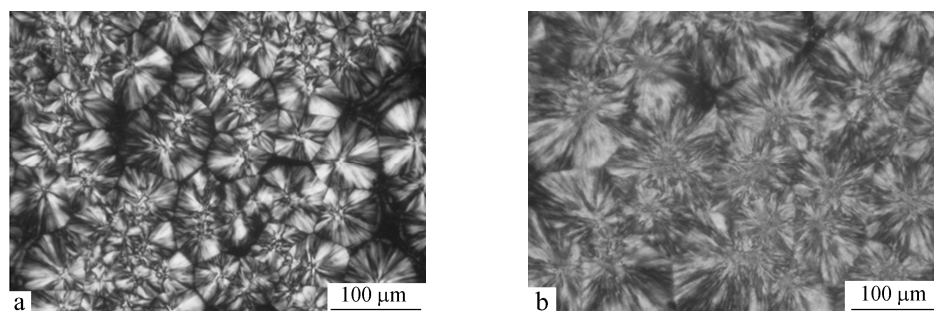


Fig. 2 POM images showing the isothermal crystallization morphologies of (a) *i*PP and (b) *i*PP/PEO blend

Microstructure Change during Annealing

Effect of annealing temperature

The crystalline structure evolution of *i*PP/PEO during annealing process was investigated using DSC and WAXD measurements, and the results are shown in Figs. 3–5. For PEO, both the T_m and X_c (%) are greatly dependent upon the T_a . At relatively low T_a ($\leq 130^\circ\text{C}$), the T_m increases slightly with the increase of T_a whereas X_c (%) maintains nearly invariant. However, at higher T_a ($\geq 140^\circ\text{C}$), both T_m and X_c (%) decreases dramatically. The thermostability of PEO was evaluated through TGA and the result showed that the mass loss of PEO at 160°C was up to 1.5% (not shown here) when the sample was heated from 0°C to 550°C at the heating rate of 10 K/min, indicating the occurring of PEO degradation at this temperature. In this work, the specimen was annealed for 12 h. Thus, the degradation of PEO at relatively higher temperature is inevitable, which is believed to be the main reason for the decrease of T_m and X_c (%) of PEO during the annealing process. Furthermore, it should be noticed that the X_c (%) of PEO in immiscible *i*PP/PEO blend is much lower than that obtained from pure PEO (87.7%), further indicating the confined crystallization of PEO in this work.

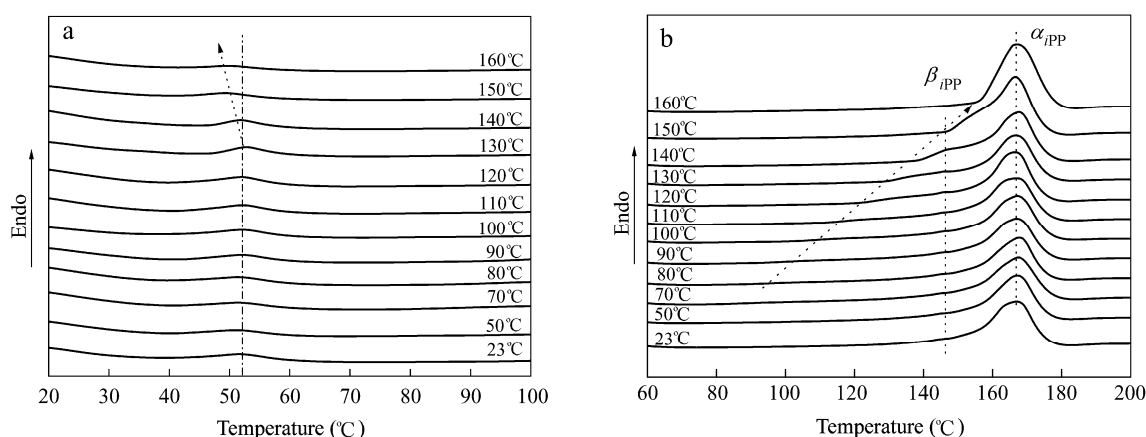


Fig. 3 DSC heating curves showing the melting behavior of PEO (a) and *i*PP matrix (b) in *i*PP/PEO blend after being annealed at different temperatures as indicated

For *i*PP matrix, it can be seen that, besides the main endothermic peak at about 167°C attributed to the fusion of α -*i*PP, a very weak endothermic peak at about 145°C can be differentiated. According to the WAXD measurements as shown in Fig. 5, it is believed that the weak endothermic peak is ascribed to the fusion of small amount of β -*i*PP formed during the injection molding process. After being annealed, a shoulder in the thermogram (premelting endothermic peak) before the main fusion peak of α -*i*PP and the onset temperature of the shoulder increases gradually with the increase of T_a (shown by the arrow), indicating the formation of newly thin and imperfect lamella during the annealing process. The similar results have been reported

elsewhere^[4, 12, 13, 17, 18]. Interestingly, the T_m of α -*i*PP maintains nearly invariant at all T_a in this work, even if the T_a is very close to the T_m of α -*i*PP. In our previous work^[4], when T_a is increased up to 160°C, a significant increase of T_m from 167.3°C to 173.2°C is observed for annealed pure *i*PP attributing to the apparent lamellar thickening during the annealing process^[11, 25]. Thus, it can be deduced that the presence of PEO molten particles possibly prevents the lamellar thickening of *i*PP matrix. More interestingly, the X_c (%) of *i*PP matrix increases gradually with the increase of T_a , especially at relatively higher T_a (> 150°C). Considering the influence of T_a on T_m of matrix, it also can be deduced that the role of PEO is promoting the formation of newly thin and imperfect lamella rather than promoting the further thickening of existed lamella.

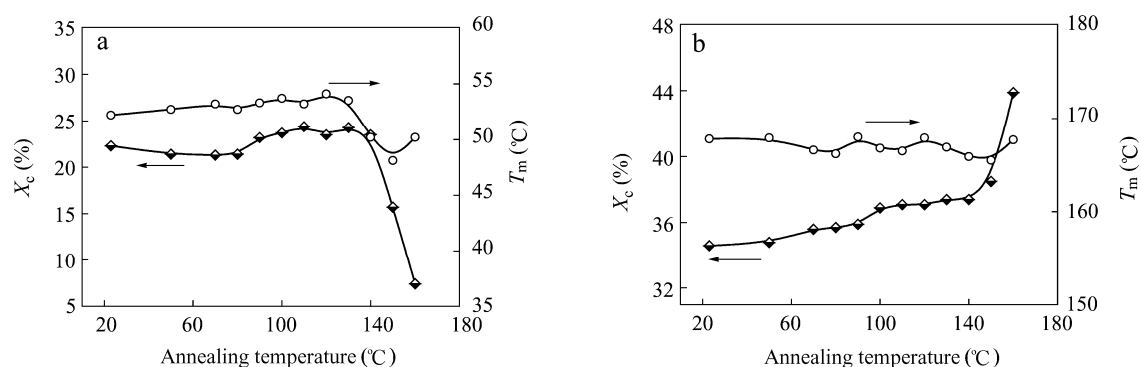


Fig. 4 Variation of melt temperature and the degree of crystallinity of PEO (a) and *i*PP matrix (b) as the function of annealing temperature

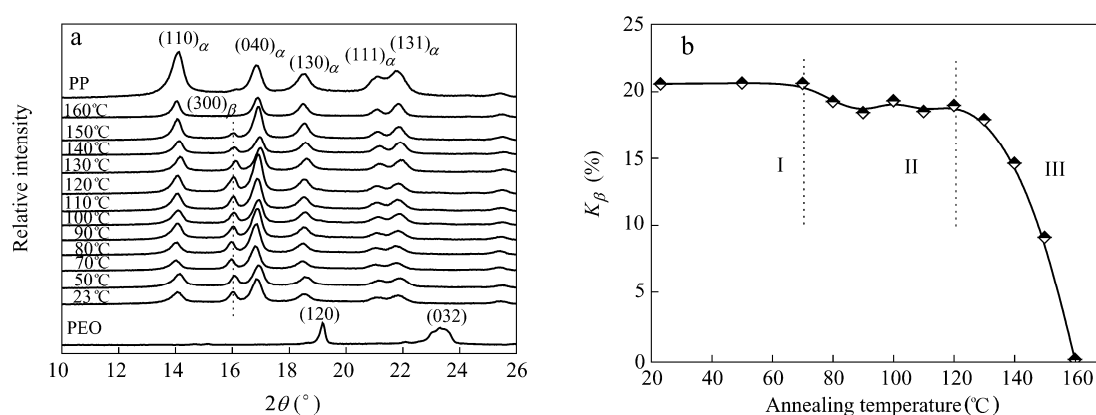


Fig. 5 (a) WAXD profiles of unannealed and annealed *i*PP/PEO blends obtained at different temperatures as indicated; (b) The variation of K_β (%) of β -*i*PP in *i*PP/PEO during the annealing process

Figure 5 shows the variation of crystalline structure of *i*PP matrix during annealing. To make a comparison, the WAXD profiles of pure PEO and *i*PP are shown, too. It can be seen that the characteristic diffraction peaks of PEO in the blend can not be differentiated most likely due to that the content of PEO crystalline structure in the sample is too low to be detected. For *i*PP matrix, the typical diffraction peaks at $2\theta = 14.1^\circ$, 16.8° , 18.5° , 21.1° , and 21.8° , are attributed to the reflections of (110), (040), (130), (111) and (131) crystal planes of α -*i*PP, respectively. Furthermore, a weak diffraction peak at $2\theta = 16.0^\circ$ corresponding to the reflection of (300) crystal plane of β -*i*PP can be observed, indicating the formation of small amount of β -*i*PP during the injection molding process. This agrees well with the observation obtained from DSC measurements. The variation of K_β (%) of β -*i*PP during the annealing process was calculated, and the results are shown in Fig. 5(b). At relatively low T_a (< 70°C), K_β (%) maintains invariant with T_a . At T_a of 80–130°C, although the diffraction of β -*i*PP seems

stronger as shown in Fig. 5(a), indicating the increase of β -iPP amount in the sample, some newly thin and imperfect lamellae of α -iPP form simultaneously during the annealing, as a consequence, the relative fraction of β -iPP calculated according to the methodology of Turner Jones^[21] decreases slightly. At relatively higher T_a ($> 140^\circ\text{C}$), the diffraction peak of β -iPP weakens gradually until it disappears completely and only the diffractions of α -iPP can be observed at T_a of 160°C due to that β -iPP is a metastable phase and it tends to transform into thermodynamically α -iPP during the thermal treatment.

Effect of annealing duration

The effects of annealing duration (t_a) on crystalline structures of PEO and iPP matrix in the blend were investigated simply using DSC measurements, and the results are shown in Fig. 6. It can be seen that long annealing duration is favorable to the enhancement of T_m and X_c (%) of PEO possibly due to the decreased confined crystallization of PEO after being annealed for long duration. This will be further explained by the variation of PEO morphology as proved in the next part. For iPP matrix, the low-temperature shoulder shifts to higher temperatures gradually with the increase of t_a , indicating the formation of thicker and more perfect lamella during annealing process. Furthermore, although the position of main fusion peak maintains invariant, the X_c (%) of iPP matrix increases apparently at relatively longer t_a (96 h), further suggesting the improvement of crystalline structure.

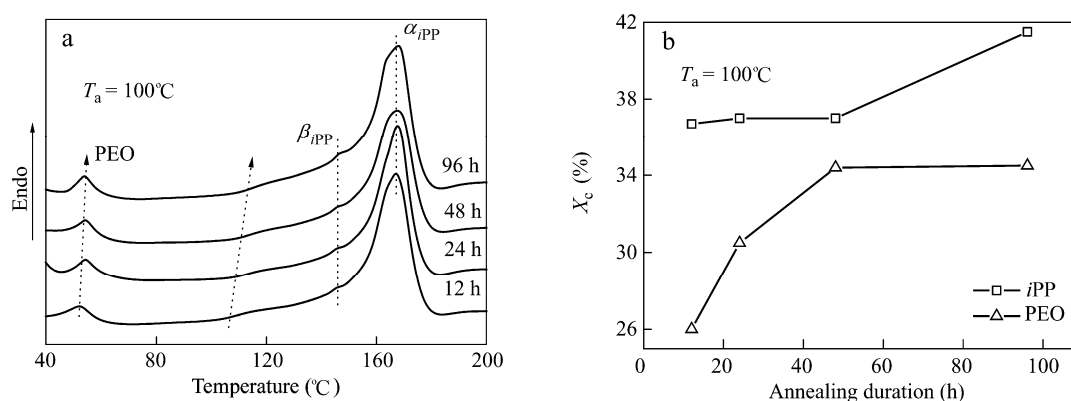


Fig. 6 (a) DSC heating curves showing the melting behavior of PEO and iPP matrix in iPP/PEO blends after being annealed at 100°C for different durations as indicated in the graph and (b) the variation of the degree of crystallinity of PEO and iPP matrix as the function of annealing duration

Effect of Annealing on Relaxation of iPP Matrix

With the presence of newly formed thin and imperfect lamella in the amorphous region of iPP matrix during the annealing process, the chain segment mobility in this region is confined more seriously, leading to the change of the relaxation. As shown in Fig. 7, the mechanical loss factor ($\tan\delta$) curve exhibits two maxima. The maximum at low temperature (13 – 22°C) is related to β -relaxation, accounted for the glass transition of the unrestricted amorphous iPP, while the peak at the higher temperature (70 – 110°C) is related to α_c -relaxation, accounted for the relaxation of restricted iPP amorphous chain segments in the crystalline phase (defects), also known as rigid amorphous molecules^[26, 27]. Herein, glass transition temperatures (T_g) were obtained by the maximum of the loss factor ($\tan\delta_{\max}$) or β -relaxation peak. It can be seen that the T_g of iPP decreases with the increase of T_a , indicating the enhanced chain segment mobility of iPP in the amorphous region. Similar results have been reported elsewhere and the reason for the decreased T_g was attributed to the increase of free volume and/or the decrease of concentration of tie molecules in the amorphous region most likely due to the second crystallization process relating to the change of some chain segments from amorphous state to crystalline state during the annealing process^[28, 29]. However, it should be noticed that the T_g values (13.5 – 19.2°C) obtained in this work is smaller than those reported (18 – 24°C) in previous work when the T_a is the same completely^[30]. This further indicates that the presence of PEO molten particles induces a positive role to a certain extent for the chain

segment mobility of *i*PP matrix during DMA measurements. Furthermore, the magnitude of β -relaxation which is determined by the area under the β -relaxation peak is higher than that of the unannealed sample. It is known to all that the magnitude of β -relaxation is representative of the total energy dissipated because of viscoelastic relaxation of *i*PP matrix. This means at least that, after being annealed, the fracture resistance and damping capacity can be improved simultaneously^[31, 32]. Further investigation on the effect of annealing on fracture resistance of *i*PP/PEO blends will be carried out in other work. Finally, due to the perfection of the whole crystalline structure of *i*PP during the annealing possibly induced by newly formed thin lamella and/or the transition of mesophase to stable phase occurring near the surface of primarily formed lamella, leading to the increase of rigid amorphous molecule^[12], a significant increased temperature corresponding to α_c -relaxation peak is observed as expected.

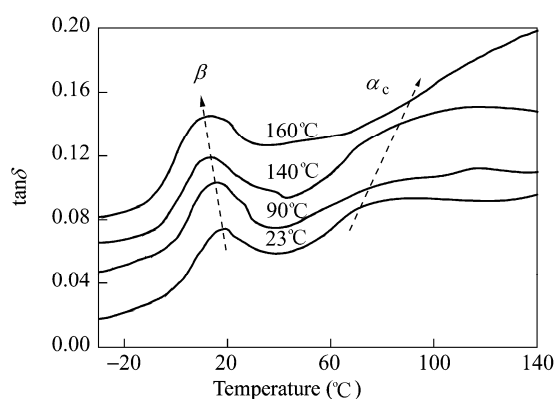


Fig. 7 Mechanical loss factor ($\tan\delta$) of *i*PP matrix obtained before and after being annealed at different annealing temperatures as indicated in the graph

Phase Morphology Change of PEO

Although the most of T_a applied in this work are higher than the T_m of pure PEO and the crystallization of PEO is confined by adjacent *i*PP spherulites or the *i*PP lamellar stacks, the DSC measurements show the slightly increased T_m of PEO in the blends, indicating the increase of average lamellar thickness to a certain extent. In other words, the degree of confinement for the crystallization of PEO seems weaker at relatively higher T_a or longer t_a . To prove this, the phase morphology of PEO in the blends before and after annealing at different T_a was characterized using SEM (Fig. 8) and the average particle diameters (Fig. 9) of PEO were calculated too. As shown in Fig. 8, the dark holes represent the PEO particles, which were removed from the matrix by toluene. Although annealing does not influence the shape of PEO particles apparently and all the PEO particles are spherical, the average particle diameters of PEO tend to increase after being annealed. This means that the degree of phase separation of the sample increases further during the annealing. In other words, the increased PEO particles endow the enough space for the growth of PEO lamella, namely, the confined effect of *i*PP spherulites or lamella stacks on the crystallization of PEO becomes weaker. Similar results have been reported on the relationship between crystallization and dispersed particle diameters in immiscible PP-MA/PA12 blend^[33]. In that work, the size of PA12 particles increased and more perfect crystallization of PA12 was observed simultaneously when the sample was annealed. Work needs to be done to further understand the confined crystallization of PEO particles with different diameters in immiscible *i*PP/PEO blends.

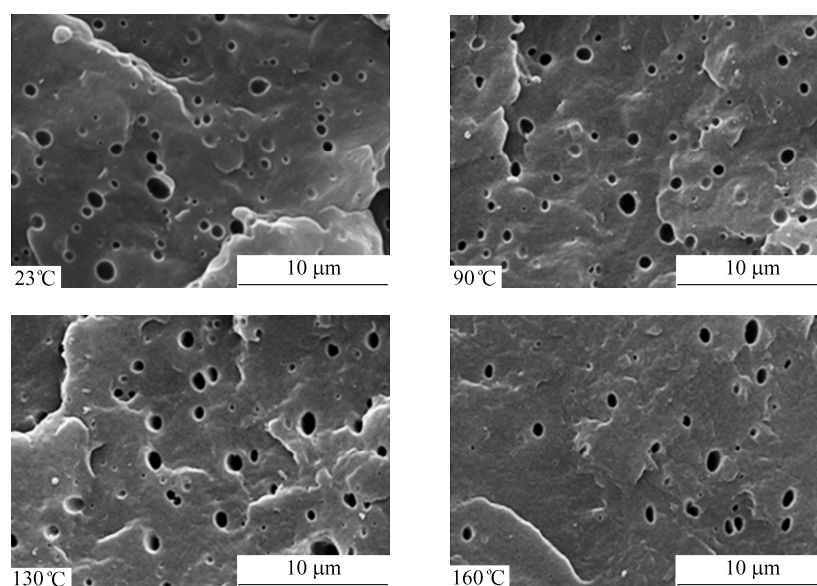


Fig. 8 SEM images showing the phase morphologies of PEO particles obtained before and after annealing at different temperatures as indicated in the images

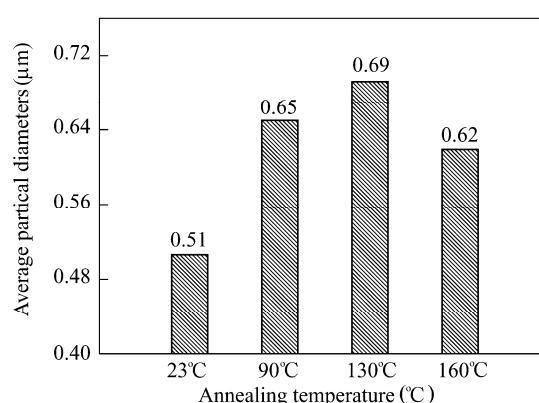


Fig. 9 Variation of average particle diameters of PEO versus annealing temperatures

CONCLUSIONS

In summary, the evolution of crystalline structure as well as the relaxation of *i*PP blends with a few amount of PEO during the annealing process has been investigated. The results show that the presence of PEO promotes the crystallization of *i*PP matrix. With the increase of T_a , the X_c (%) of *i*PP matrix increases gradually whereas the T_m maintains invariant, indicating that the lamellar thickening of *i*PP matrix is prevented with the presence of PEO during annealing, even if the T_a is increased up to 160°C. Further results show that longer t_a is favorable to the improvement of crystalline structure of material. DMA results show that PEO promotes the chain slide diffusion and the relaxation of *i*PP matrix. Slightly increased average diameters of PEO particles have been observed after the sample is annealed, which is thought to be favorable to the improvement of crystalline structure of PEO at relatively lower T_a due to the decreased confining effect originated from adjacent *i*PP spherulites or lamellar stacks on crystallization of PEO.

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