

Shear-induced Crystallization in Phase-separated Blends of Isotactic Polypropylene with Ethylene-Propylene-Diene Terpolymer^{*}

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Abstract The compatibility between isotactic polypropylene (*i*PP) and ethylene-propylene-diene terpolymer (EPDM) in the blends was studied. SAXS analysis indicates that *i*PP and EPDM phases in the binary blend are incompatible. Isothermal crystallization behaviors of *i*PP in phase-separated *i*PP/EPDM were studied by *in situ* POM equipped with a Linkam shear hot stage. It was found that typical spherulites of *i*PP were formed both in neat *i*PP and in *i*PP/EPDM blends. The radial growth rate (dR/dt) of spherulites of *i*PP in the blend was not influenced by EPDM phases. Further investigations on isothermal crystallization of *i*PP in *i*PP/EPDM after shear with a fixed shear time showed that the crystallization rate of *i*PP in the blends increased with increasing shear rates, whereas, the crystallization rate was much lower than that of neat *i*PP. WAXD results showed that β -crystal *i*PP was formed in neat *i*PP as well as in *i*PP/EPDM blends after shearing and the percentage of β -crystal bore a relationship to the applied shear rate. The presence of EPDM resulted in lower percentage of β -crystal in the blends than that in neat *i*PP under the same constant shear conditions. SAXS experiments revealed that shear flow could induce formation of oriented lamellae in *i*PP and *i*PP in the blends, and the presence of EPDM led to a reduced fraction of oriented lamellae.

Keywords: Shear-induced crystallization; Polypropylene; EPDM; Blends; β -Crystal.

INTRODUCTION

Most of the widely used thermoplastic materials show remarkable limitations in their applications when toughness and high impact resistance are required^[1, 2]. Blending (or alloying) plastics with a rubber may be a solution of such questions. And it is well known that the studies on the blends (or alloys) of the polymers have a long history, which involves the phase structure and morphology, phase dispersion, interaction between phases and the compatibility of the blends^[1–16].

The performance and properties of polymer blends are closely related to the morphology and structure in the blends. Meanwhile, the final properties of the blends (or alloys) also bear a relationship to crystalline state when the crystalline phase exists in the blends or alloys. In addition, the formation and evolution of the phase structure and morphology bear a relationship to the condition of formation when the chemical structures of polymers are confirmed. In other words, the different structures and the final properties of materials under different external fields can be obtained. In the polymer processing methods, such as extrusion, injection molding, fiber spinning and blowing film etc., the molten polymer is exposed to varying levels of flow fields^[17–22].

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In recent ten years, the study on the shear induced crystallization behavior of crystalline polymers is a matter of great concern, including the crystallization behavior of polymer blends. The crystallization behavior of *i*PP in the binary blends can be strongly depended on both the components of blends and shear field. For both effects, there is a correlation study separately (see references [23–32] and [33–42]). It is well known that the compatibility between phases in the blends could affect the phase structures^[43–45] as well as the behavior of crystalline phase in the blends^[30].

The blends of ethylene-propylene-diene terpolymer (EPDM) with isotactic polypropylene (*i*PP) have been studied and applied in many fields. Blending of EPDM with *i*PP can improve the impact resistance of *i*PP and can obtain thermoplastic elastomer (TPE) through dynamic vulcanization. Also the study on the crystallization behaviors and structure of *i*PP in *i*PP/EPDM blends is important.

In this paper, the compatibility between *i*PP and EPDM phases in *i*PP/EPDM blends was discussed by small angle X-ray scattering (SAXS). The crystallization behaviors and kinetics of *i*PP in neat *i*PP and the blends under shear field were studied by polarizing optical microscopy (POM). Shear-induced formation of β -crystal *i*PP and the lamellae orientation of *i*PP in neat *i*PP and *i*PP/EPDM blends were investigated.

EXPERIMENTAL

Materials

Polypropylene (isotactic polypropylene (*i*PP), T1701) is a commercial polymer with $M_w = 3 \times 10^5$ g/mol, $M_n = 7.4 \times 10^4$ g/mol, $\rho = 0.9$ g/cm³, $T_m = 167$ °C and melt flow rate (MFR) = 1.2 g/10 min. The particle size is about 4 mm, and it is from the Beijing Yanshan Petrochemical Co. Ltd (China).

Ethylene-propylene-diene terpolymer (EPDM, J-4045) is a commercial material from Jilin Petrochemical Co. Ltd, China with 52.0 wt% ethylene, 40.3 wt% propylene and 7.7 wt% ENB, Mooney viscosity is 45 (ML1 + 4(100 °C) = 45).

Preparation of Blends

Binary blends of *i*PP/EPDM were made by melt-mixing the polymers in a rotating rheological mixer (XSS-30 mixer, China) at a temperature of 185 °C and a rotation speed of 32 r/min for 10 min. The compositions of the binary blends of *i*PP/EPDM were 100/0, 95/5, 90/10, 80/20, and 60/40 by wt%.

Specimen Preparation

The premixed materials were compression-molded to get slabs of 1 mm thick, and films of about 20 μ m in the thickness were hot press molded at 200 °C with a residence time of 5 min under the pressure of 20 MPa. The slabs of 1 mm in thickness were used in scanning electron microscopy, wide angle X-ray diffraction (WAXD) and small angle X-ray scattering (SAXS). A thick film of about 20 μ m in the thickness was used in the polarizing optical microscope (POM) observations.

Experimental Procedures

A Linkam CSS-450 temperature-control shear stage (Linkam Scientific Instruments, Ltd, United Kingdom) coupled to an optical polarizing microscope (POM) with video camera, as Olympus BX51 model, was employed to control thermal and shear conditions for preparing samples (for SAXS and WAXD tests) and the observation of the crystallization process in quiescent condition or under shear. For POM tests, the thin film samples were used and the gap was set to 20 μ m. To prepare samples for SAXS and WAXD tests, 1 mm slabs samples reshaped into discs of adequate size were used and a fixed gap of 500 μ m was used in the experiments. The thermal history and shear conditions in this experiment could be illustrated by Fig. 1. The sample was heated to 200 °C and held for 5 min to remove the thermal history and then the melt was cooled down to the crystallization temperature (135 °C) at -30 K/min. Upon reaching the crystallization temperature, a steady shear was applied with shear rates from 1 s⁻¹ to 8 s⁻¹ and a fixed shear time of 5 s (shear strain from 500% to 4000%) and then the sample was isothermally crystallized for enough time at the same temperature and images as well as the intensity were recorded in the same time for thin film samples. When the procedure was finished, the samples for SAXS and WAXD tests were meticulously collected and stored in the freezer before tests.

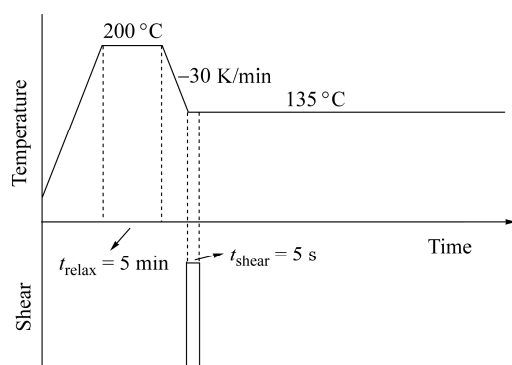


Fig. 1 Schematic diagram of the temperature and shear conditions of experiments

Characterization

SEM analysis

The pre-blended samples were put into liquid nitrogen, taking out samples after 30 min, which were broken cryogenically and the fracture surfaces were etched by xylene at room temperature for 15 s. The surfaces of etched samples were washed with distilled water and then dried in vacuum overnight. The clean surfaces of the samples were sputter coated with gold before taking the SEM micrographs. Analysis of the morphology of the samples was performed using a Hitachi SU1510 scanning electron microscope (Hitachi High-Technologies Corp., Japan) with 10 kV accelerating voltage and object distance of about 10 mm.

X-ray analysis

Small angle X-ray scattering (SAXS) measurements were carried at beamline 16B1 at Shanghai Synchrotron Radiation Facility (SSRF, Shanghai, China). The incident X-ray wavelength was 0.124 nm. The SAXS data were collected by a 2D detector Mar-CCD 165 with sample-to-detector distance of 2100 mm.

The wide angle X-ray diffraction (WAXD) measurements were performed with a Bruker D8 Advance diffractometer ($2\theta = 6^\circ$ to 32° , 40 kV and 40 mA with $\text{CuK}\alpha$ radiation $\lambda = 0.154$ nm, and a linear position-sensitive detector).

RESULTS AND DISCUSSION

Phase Morphology and Compatibility of Phases

The SEM images of neat *i*PP and *i*PP/EPDM blends are shown in Fig. 2, indicating that two phases are separated in the blends.

According to Porod's Law^[46, 47], the intensity in the tail of a diffraction curve from a two-phase structure with sharp phase boundaries is given by

$$\lim_{q \rightarrow \infty} I(q) = C / q^4 \quad (1)$$

where $I(q)$ is the intensity of scattering, q the scattering vector and C a constant. Here, it is assumed that the interface layer (compatible domain) exists. After correction of Ruland, Porod's law is given by

$$\lim_{q \rightarrow \infty} q^4 I(q) = kp \exp(-4\pi^2 \sigma_b^2 q^2) \quad (2)$$

where σ_b is interface layer thickness. When $\sigma_b \ll 1$, and $q \rightarrow \infty$

$$q^4 I(q) \approx kp(1 - 4\pi^2 \sigma_b^2 q^2) \quad (3)$$

A plot of $\ln(q^4 I(q))$ versus q^2 was used and its results were recorded^[48] (Fig. 3). When q increases, the tail of the curve increases (positive deviation, see curve 1 in Fig. 3), showing the deviation caused by the thermal density fluctuations. The tail of the curve leads to flat to show $\sigma_b = 0$ (see curve 2 in Fig. 3) when q increases.

The tail of the curve decreases (negative deviation, see curve 3 in Fig. 3) when q increases, indicating the interface layer is existence, and the interface layer thickness (σ_b) could be calculated by the slope of the curve's tail.

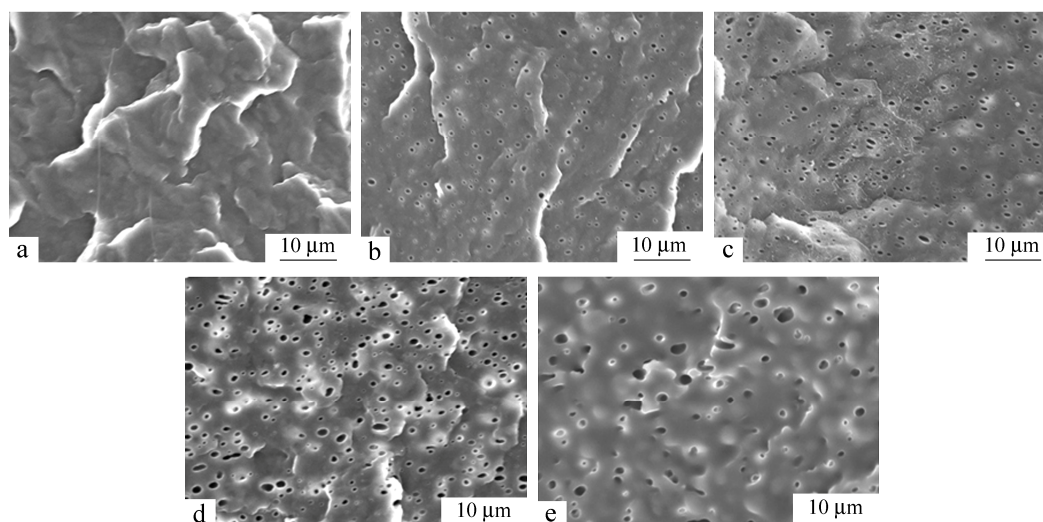


Fig. 2 SEM images of cryogenic brittle fractures of *i*PP (a) and *i*PP/EPDM blends: (b) 95/5, (c) 90/10, (d) 80/20 and (e) 60/40 by wt%

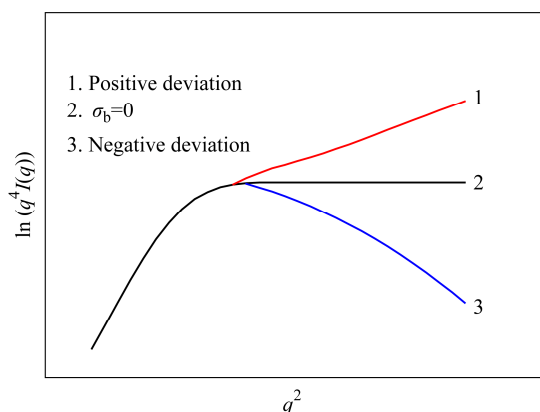


Fig. 3 Sketch of Porod's law

As shown in Fig. 4(b), $\ln(q^4 I(q))$ versus q^2 plots of *i*PP/EPDM blends display positive deviation in the tail region, indicating the interface layer is not existence. So blends of *i*PP/EPDM are incompatible in the composition range studied. The result is consistent with the reported literature^[49, 50].

Crystallization Behavior and Kinetics under Shear Flow

The POM images of *i*PP/EPDM blends at crystalline temperature of 135 °C are shown in Fig. 5. The crystalline morphology of neat *i*PP and *i*PP in the blends is the typical spherulite. And the morphology of spherulites of *i*PP in the blends is unchanged with the content of EPDM in the blends as compared with neat *i*PP.

The radial growth rate (dR/dt) of *i*PP spherulite in the blends is not influenced by EPDM phases as compared with neat *i*PP (see Fig. 6a), and the radial growth rate of spherulite for *i*PP in the blends increasing with crystalline temperature is the same as that of neat *i*PP (see Fig. 6b). Thereby, these results exhibit that EPDM phase in the blends did not affect the crystallization kinetics of *i*PP spherulite in the blends.

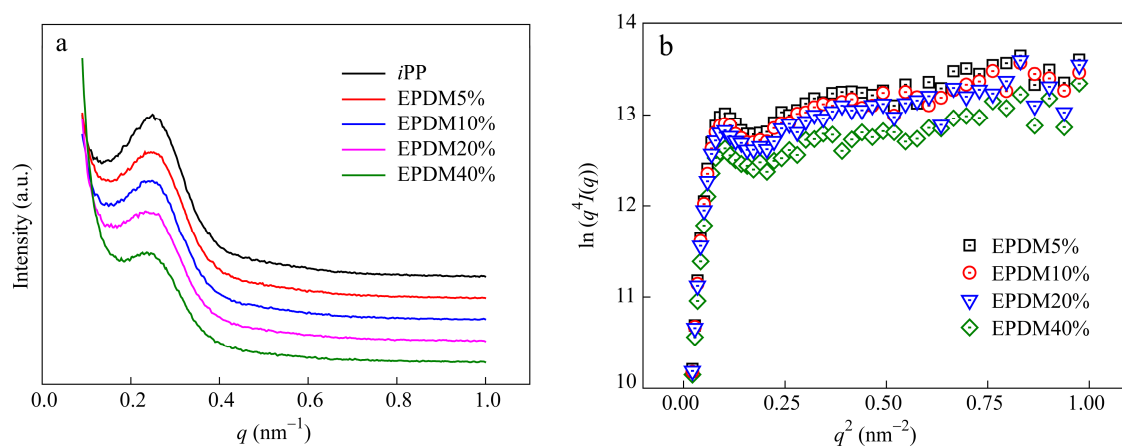


Fig. 4 (a) 1D-SAXS patterns ($I(q)$ - q) of *i*PP/EPDM blends and (b) the corresponding plot of $\ln(q^4 I(q))$ versus q^2

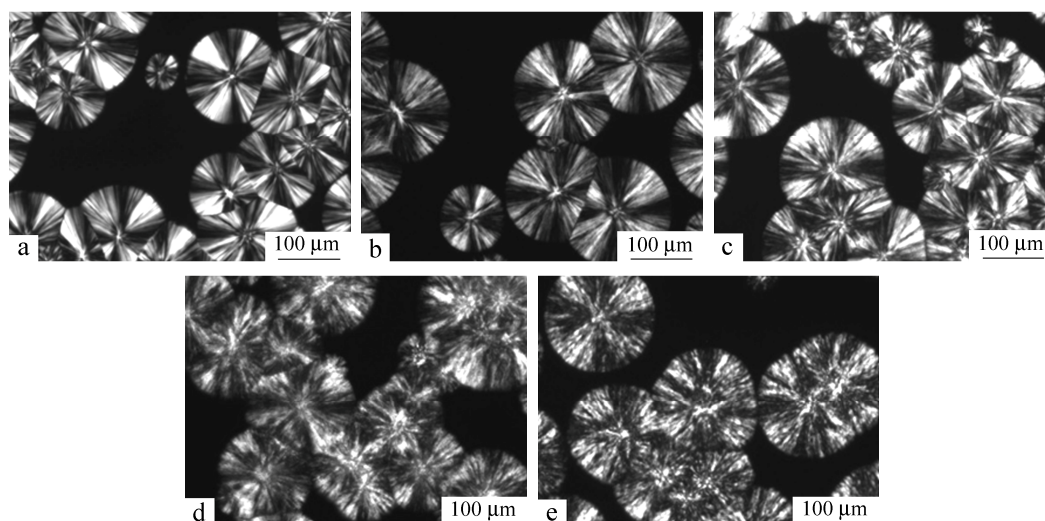


Fig. 5 POM images of *i*PP (a) and *i*PP/EPDM blends: (b) 95/5, (c) 90/10, (d) 80/20 and (e) 60/40 by wt% crystallized at 135 °C for 30 min

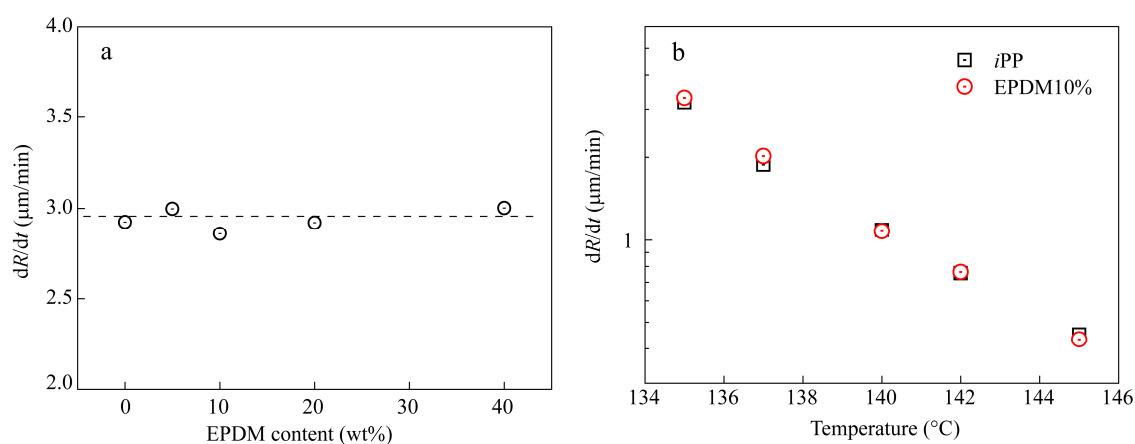


Fig. 6 Spherulite radial growth rate (dR/dt) of *i*PP and *i*PP/EPDM blends as a function of (a) compositions and (b) crystallization temperatures

Figure 7 shows isothermal crystallization curves in quiescence condition and under shear for neat *i*PP and *i*PP in the blends by depolarization method according to reference^[51]. The half time of crystallization ($t_{1/2}$) is defined as the time when the half of the max of intensity was reached.

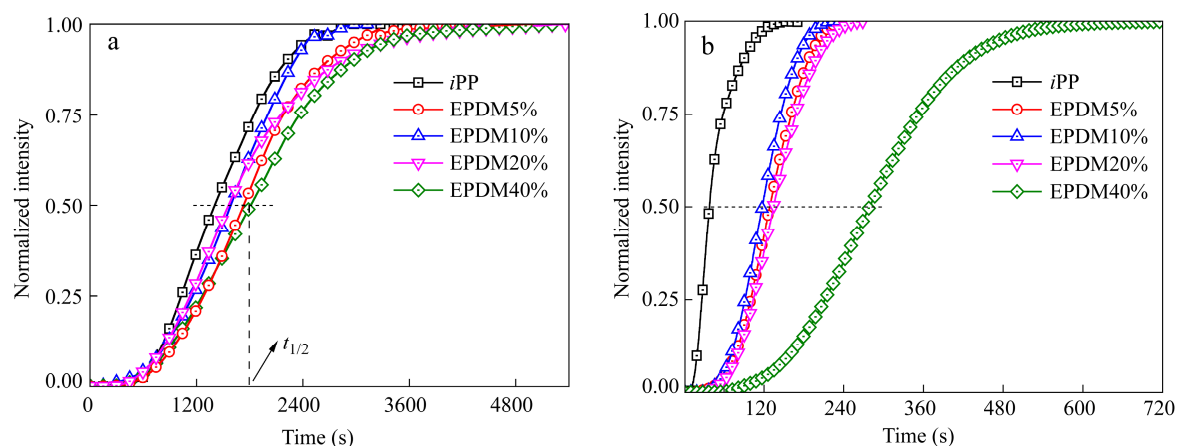


Fig. 7 Crystallization curves of *i*PP and *i*PP/EPDM blends: (a) in quiescence and (b) under shear

The crystallization rate, G , is equal to $1/t_{1/2}$ of *i*PP and *i*PP in the blends (see Fig. 8). The isothermal crystallization rate (in quiescence) G_q of *i*PP in the blends with different contents of EPDM is almost the same as compared with that of *i*PP. The isothermal crystallization rate under shear flow, G_s of *i*PP in the blends are greater than G_q . But G_s values of *i*PP in the blends under shear flow are less than that of neat *i*PP. These results could be explained by the existence of asynchronous shear strain of *i*PP and EPDM in the blends. EPDM is an elastomer with elastic deformation being much greater than that of neat *i*PP when the molten blends were subjected to shear force. Meanwhile, the slippage at interface between *i*PP and EPDM phases in the blends should occur because *i*PP/EPDM blends are incompatible systems bearing weak adhesion at the interphases of the blends. In the case, the shear force would be consumed partly by friction happened in the interphases and the shear strain could not be transmitted efficiently through the sea-island (EPDM in *i*PP) blends system. In another way, from the viewpoint of energy, the dissipation of energy caused by the deformation of dispersed EPDM phases in the blends would weaken the overall shear force which otherwise should do more work on the orientation of *i*PP molecular chains. Obviously, the shear strains of *i*PP domains in the blends under the same shear flow were less than that of neat *i*PP, which led to a smaller G_s of *i*PP in the blends and corresponding differences of crystalline structure between blends and neat *i*PP could be perceived.

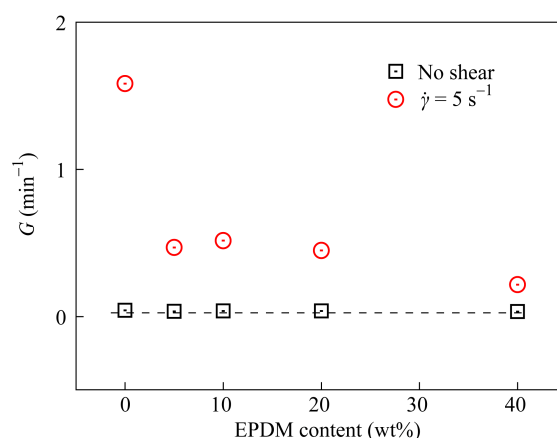


Fig. 8 The relation of crystallization rates (G) of *i*PP and *i*PP/EPDM blends with compositions in quiescent condition and under shear

Shear-induced β -Crystal

The one-dimensional WAXD patterns of the final crystallized samples under quiescence and shear flow are shown in Fig. 9. Figure 9 (a) shows one-dimensional WAXD patterns of neat *i*PP under shear flow, indicating the shear induced β -crystal of *i*PP and the peak area of β -crystal bear a relationship to shear rate. The shear induced β -crystal in *i*PP has been studied^[52–54]. The concern here is β -crystal in *i*PP/EPDM blends.

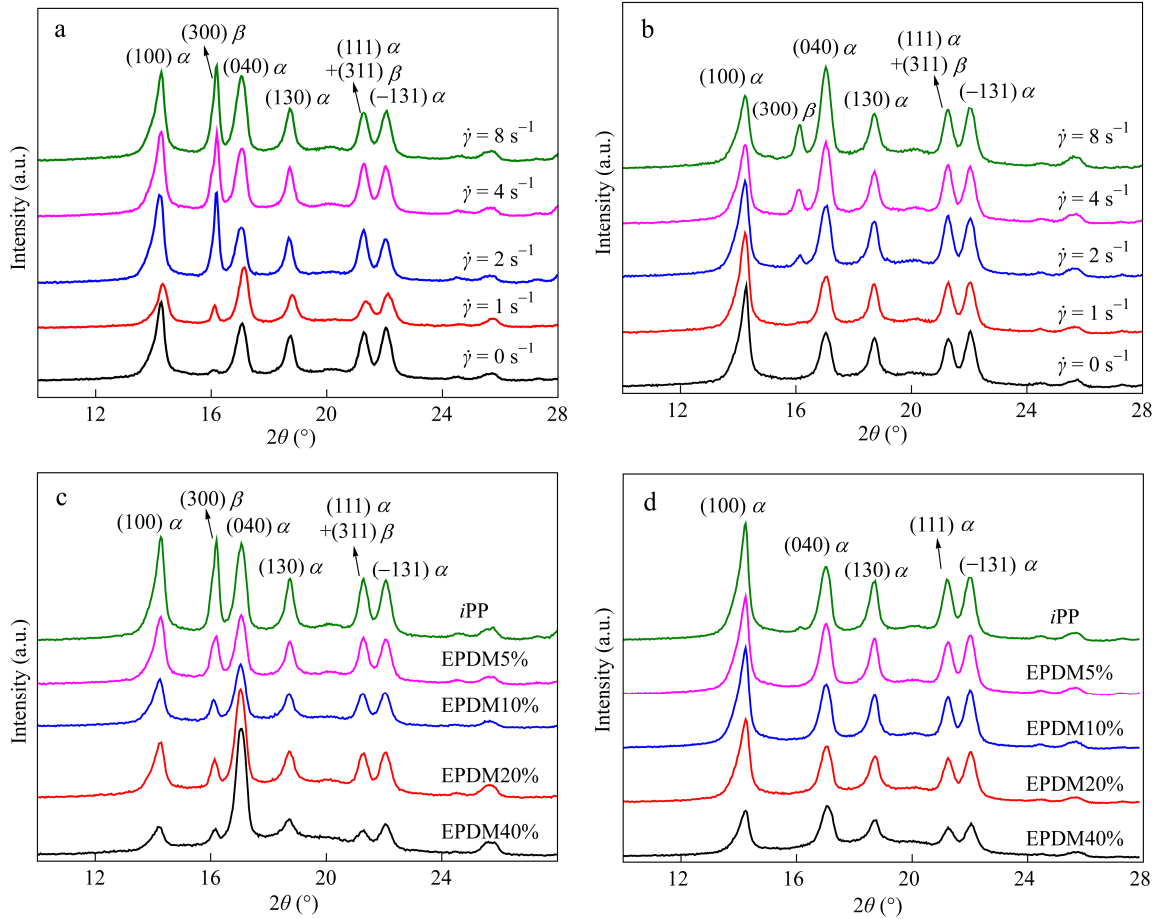


Fig. 9 1D-WAXD patterns of *i*PP and *i*PP/EPDM blends under quiescence and shear flow: (a) *i*PP, (b) *i*PP/EPDM10%, (c) blends at shear rate of 8 s^{-1} and (d) blends in quiescence

Figure 9(b) shows one-dimensional WAXD patterns of *i*PP in the blend of *i*PP/EPDM10% under different shear rates, the peak area of β -crystal increases with increase in shear rate in the blends. One-dimensional WAXD patterns of *i*PP/EPDM blends of different compositions at the same shear condition (Fig. 9c) indicate that the peak area of β -crystal decreases with increase in the content of EPDM. But there is no β -crystal in *i*PP/EPDM blends at quiescent condition (Fig. 9d), showing β -crystal is only induced by shear flow.

The percentage of β -crystal in *i*PP can be calculated by Turner-Jonese equation^[55], as following

$$K_{\beta} = \frac{A_{\beta}}{A_{\beta} + A_{\alpha}} = \frac{A_{300}}{A_{300} + (A_{110} + A_{040} + A_{130})} \quad (1)$$

where A_{300} , A_{110} , A_{040} , and A_{130} are the areas of $\beta(300)$, $\alpha(110)$, $\alpha(040)$, and $\alpha(130)$ reflection peaks, respectively, from WAXD pattern data.

K_β of neat iPP and iPP in the blends is calculated from WAXD pattern data and is shown in Fig. 10. K_β of β -crystal of iPP increases quickly from 0 to 0.2, and then flats when the shear rate is greater than 2 s^{-1} (see Fig. 10). K_β of iPP in the blends increases from 0 to 4 s^{-1} of shear rate and when shear rate is greater than 4 s^{-1} , K_β of iPP in the blends flats also. The values of K_β of iPP in the blends are less than K_β of neat iPP. The variation of K_β with the compositions is shown in Fig. 10(b), indicating that K_β decreases with increase in the content of EPDM in the blends. This result consists with the existence of asynchronous shear strain of iPP and EPDM in the blends. Namely, the reduced shear strain of iPP domains caused by EPDM would be responsible for the decrease in formation of β -crystal.

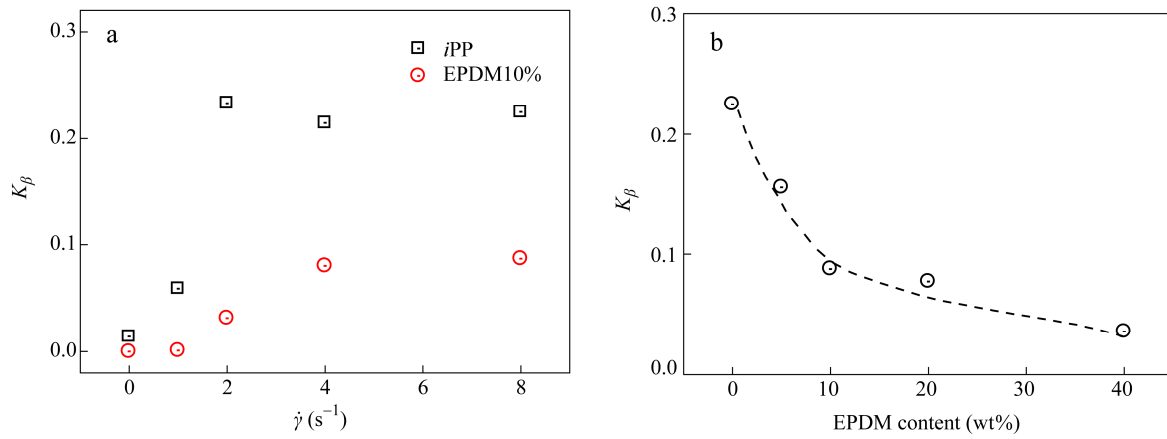


Fig. 10 The relative contents of β -crystal (K_β) in iPP and iPP/EPDM blends with (a) different shear rates and (b) compositions

Shear-induced Lamellae Orientation

Figure 11 shows 2D-SAXS patterns of iPP and iPP/EPDM10% blend under quiescent and shear field, indicating that the another effect of shear field on polymer crystallization is to induce the growth of lamellar crystals with preferring orientation. Both the intensities of 2D-SAXS patterns of pure iPP and the blends appear to be nonuniformly distributed under shear, but that of the blend seems to be weak.

Quantitatively, lamellae orientation was calculated from the azimuthal profiles of 2D-SAXS patterns using the Hermans orientation function^[56], which is defined as follows:

$$f_H = (3 \cos^2 \phi - 1) / 2 \quad (2)$$

where ϕ is an angle between a direction of interest (*e.g.*, *c*-axis of lamellae) and a reference axis (*e.g.*, flow direction), and orientation parameter $\langle \cos^2 \phi \rangle$ is defined as:

$$\cos^2 \phi = \frac{\int_0^{\pi/2} I(\phi) \sin \phi \cos^2 \phi d\phi}{\int_0^{\pi/2} I(\phi) \sin \phi d\phi} \quad (3)$$

where $I(\phi)$ is the scattering intensity at ϕ , being the azimuthal angle in the scattering pattern.

The Hermans orientation function is commonly used to estimate the degree of molecular orientation in the analysis of wide-angle X-ray scattering (WAXS). It is also useful to calculate the degree of lamellar orientation in the analysis of SAXS^[57]. The data analysis in the performed conditions gives the values of Hermans orientation function (f_H), *i.e.* $f_H = -0.5$, when scattered intensity is concentrated in the equator (*i.e.*, perpendicular to flow direction in 2D-SAXS patterns), $f_H = 1$, when scattered intensity is concentrated in the meridian (*i.e.*, parallel to flow direction in 2D-SAXS patterns), and $f_H = 0$, when scattered intensity is diffused (isotropic in nature) and spreads across the pattern.

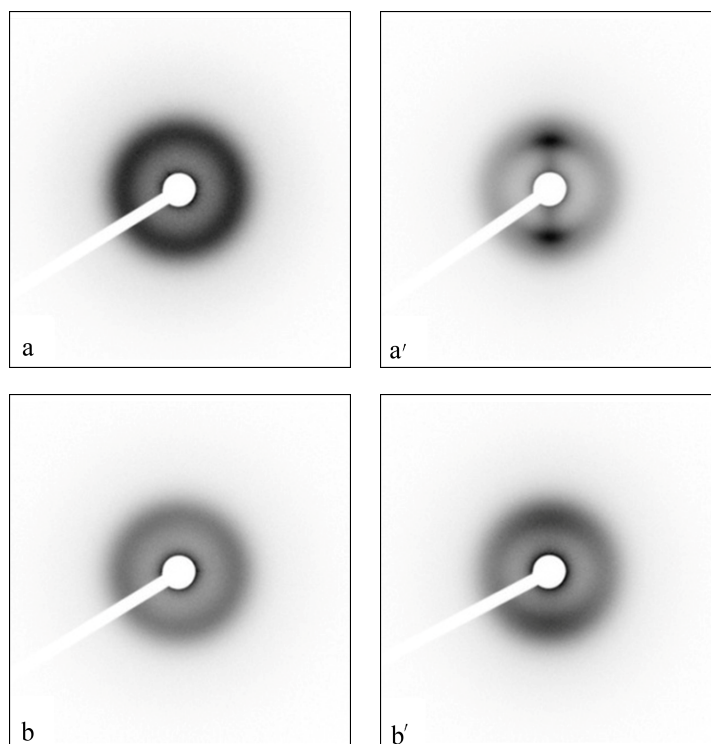


Fig. 11 Selected typical 2D-SAXS image patterns of *i*PP (a, a') and *i*PP/EPDM10% blend (b, b') in quiescence (a, b) and under shear (a', b') with shear rate of 4 s^{-1}

Figure 12 shows a representative 2D-SAXS pattern demonstrating the range of the azimuthal angle. The azimuthal profiles of neat *i*PP and *i*PP/EPDM10% blends are shown in Figs. 13(a) and 13(b). The Hermans orientation function, f_H of lamellae orientation for neat *i*PP and *i*PP in the blends can be calculated by using Eqs. (2), (3) and azimuthal profiles (see Fig. 13), and the results are shown in Fig. 14.

The Hermans function f_H of lamellae orientation for neat *i*PP and *i*PP in *i*PP/EPDM10% blends under shear field increases with increase in the shear rate. But f_H for *i*PP in *i*PP/EPDM10% blends is less than that of neat *i*PP (see Fig. 14). This varying pattern of f_H for neat *i*PP and *i*PP in the blends with shear rate is the same as that of the crystallization rate and we could consider the existence of EPDM in the blends hinders the formation of lamellae orientation of *i*PP crystals.

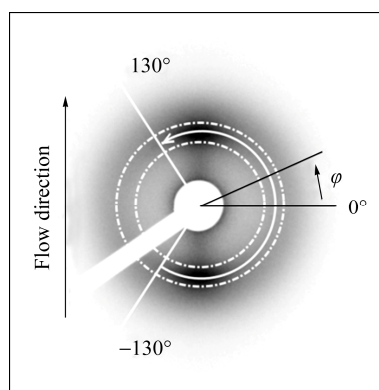


Fig. 12 A marked 2D-SAXS pattern demonstrating the range of the azimuthal angle for circle integration to obtain azimuthal profile ($I(\varphi)-\varphi$)

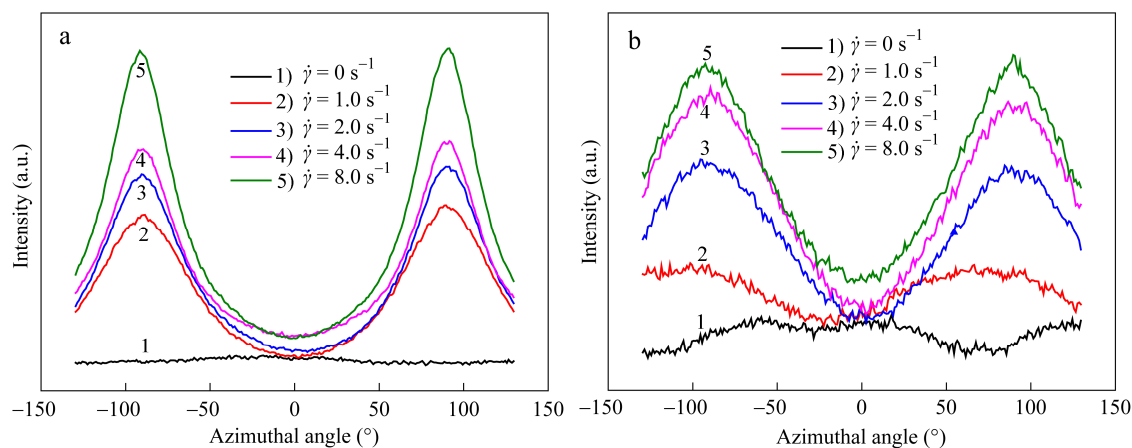


Fig. 13 Azimuthal profiles of SAXS patterns in (a) *i*PP and (b) *i*PP/EPDM10% under different shear rates

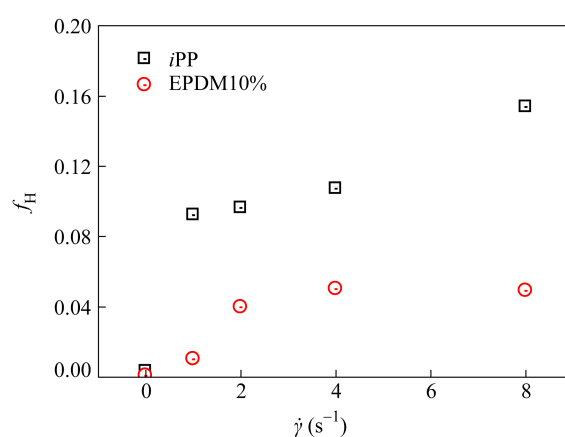


Fig. 14 The relation of Hermans function with shear rate for *i*PP and *i*PP/EPDM10% blend

Figure 15(a) shows azimuthal profiles of *i*PP/EPDM blends under shear field. Figure 15(b) indicates the relation of f_H with the compositions of EPDM in the blends, showing f_H is quickly decreased by the emergence of EPDM in the blends. The variation of f_H of *i*PP in the blends with increase in the content of EPDM is less.

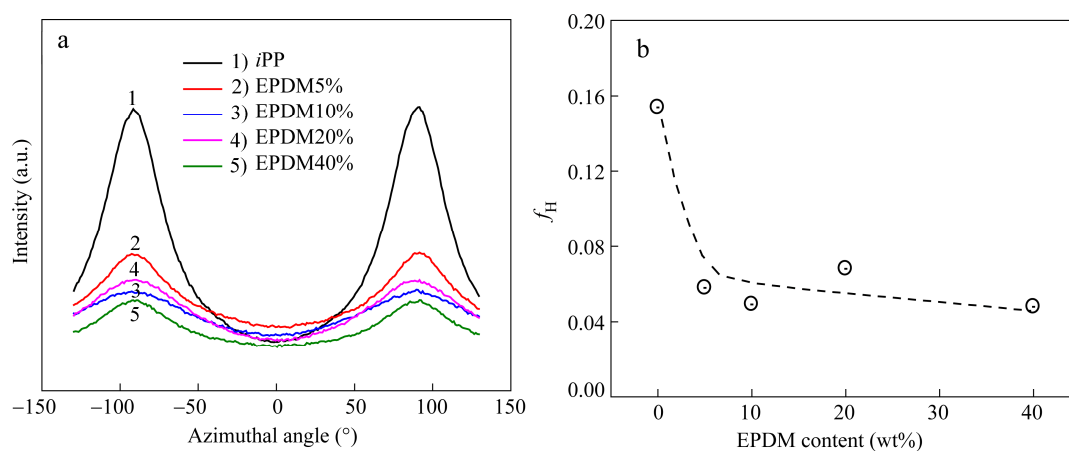


Fig. 15 (a) The azimuthal profiles of SAXS patterns and (b) Hermans function of *i*PP/EPDM blends with different compositions at shear rate 8 s^{-1}

CONCLUSIONS

Combined with SAXS analysis and SEM results, it has been shown that the *i*PP/EPDM blends studied here are incompatible systems with phase separation. In quiescent crystallization conditions, the existence of EPDM phase basically showed no influence on the crystalline structure and crystallization kinetics of *i*PP phase in the blends, whereas, the EPDM rubber phase would display non-ignorable role when the blends were subjected to shear flow.

In shear-induced crystallization conditions, the blends show different characteristics compared with pure *i*PP. The effects of shear flow such as crystallization acceleration, formation of *i*PP β -crystal and lamellae orientation would appear in both of neat *i*PP and the blends system. However, the existence of EPDM phase would markedly weaken those effects, namely, in the same shear conditions the blends systems would show lower crystallization rate, smaller amount of *i*PP β -crystal and lower ratio of lamellae orientation compared with neat *i*PP. This phenomenon could be explained by the asynchronous shear strain of *i*PP and EPDM in the blends and the energy dissipation introduced by EPDM phase.

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