Effect of elastomer on crystalline transition and deformation behavior of isotactic polypropylene

Guoming Liu, Xiuxin Zhang, Yufeng Liu, Xiuhong Li, Hongyu Chen, Kim Walton, Gary Marchand, Dujin Wang

A R T I C L E   I N F O

Article history:
Received 24 July 2012
Received in revised form 30 October 2012
Accepted 8 January 2013
Available online 12 January 2013

Keywords:
Isotactic polypropylene
Deformation
Crystal transition

A B S T R A C T

The structural evolution during uniaxial tensile deformation of isotactic polypropylene (iPP) and its blend with olefin block copolymer (OBC) was comparatively investigated by in-situ synchrotron X-ray scattering. Small angle X-ray scattering showed that cavitation in iPP/OBC blend took place at a smaller strain than in neat iPP. The reorientation of the cavities in iPP/OBC blend occurred at a lower strain than that in iPP as well. Wide angle X-ray scattering was applied to study the crystal-mesophase transition and the orientation process. Compared to the sharp transition in neat iPP, the mesophase formation and orientation in iPP/OBC blend proceeded gradually. The mesophase content and degree of orientation of iPP matrix in iPP/OBC blend were much lower than that in neat iPP within the investigated strain range. By the combination of scattering results and morphological observations, a deformation mechanism based on strain distribution and fracture mechanics was proposed.

1. Introduction

With hierarchical structures in various length scales, semicrystalline polymers usually show a complex plastic deformation behavior. Among the various deformation modes, tensile process is the most frequently investigated. Morphologically speaking, the isotropic polycrystalline lamellar structure gradually transforms into fibrillar structure with chain axis preferentially aligned parallel to the drawing direction during tensile deformation. As one of the most abundantly used polymers with chemical inertness, processing ease and good mechanical properties, the tensile deformation of iPP has been extensively studied.

One feature of iPP during stretching is cavitation [1–4]. The formation and growth of cavities are the main reasons for the volume change during tensile drawing. Cavitation occurs in the isotropic phase, and it depends on the intrinsic properties of materials and the testing conditions. General ideas of the evolution of shape and orientation of the cavities have been well established [3,5]. The onset of cavitation generally occurs around the macroscopic yield point. At the very beginning, the cavities are ellipsoidal, oriented perpendicular to the tensile direction. Then, the cavity volume increases significantly during necking. Finally, the cavities are elongated and oriented along the tensile direction. Cavitation is strongly influenced by molecular parameters, strain rate, temperature and additives [3,5,6]. Rozanski et al. [5] observed that iPP after purification using extraction of supercritical CO2 or a mixture of nonsolvents exhibited surprisingly more intense cavitation than pristine iPP, which they concluded that the initiation of cavitation in iPP had a homogeneous nature.

Another structural feature during tensile deformation of iPP is the formation of mesomorphic phase (mesophase). Mesophase was firstly obtained through fast quenching of iPP melt [7]. Recent study showed mesophase could form even at temperatures below the glass transition temperature [8]. The mesophase can be identified by the appearance of two broad peaks in the wide angle X-ray powder diffraction pattern (or a 6-point feature in the fiber diffraction pattern). Similar to the monoclinic crystal phase, the mesophase exhibits a 31 helical chain conformation [9,10]. When annealed at temperatures above 60 °C, the mesophase in iPP can transform into the monoclinic a-form [11–13]. Stretching induced a crystal–mesophase transition in iPP has been studied extensively. It was founded that stretching iPP with β crystal at room temperature
yielded mesophase as well [14]. Formation of mesophase was also observed in blends of iPP and propylene based ethylene–propylene copolymer during stretching [15]. Ran et al. believed that the formation of the mesophase followed by the destruction of the lamellar crystalline phase probably by pulling chains out from crystals [16]. Li and coworkers estimated that the free energy of the stretching-induced mesophase was about 2.5 J/cm³ lower than that of α crystal at room temperature, and the energy barrier for the formation of critical nucleus during the α crystal-mesophase transition was about 71 kgT [17].

It is well known that rubber or elastomer toughening of iPP is an effective approach for achieving higher toughness [18–20]. The well-accepted mechanism for the toughening effect is the change of the stress state around a rubber particle through cavitation. However, to our best knowledge, a systematic comparative study, concerning both the cavitation and crystal-mesophase transition of iPP and iPP/elastomer blend, has not been reported yet. In the present study, we chose an olefin block copolymer (OBC, Dow INFUSE™) as the toughening elastomer, and the tensile process of iPP and iPP/OBC blend was investigated by in-situ small-angle and wide angle X-ray scattering (SAXS/WAXS). The objective is to uncover the role of elastomer on the cavitation and mesophase formation of iPP.

2. Experimental

Isotactic polypropylene with MFR = 35 g/min at 230 °C/2.16 kg and a multi-block OBC, together with the sample information, were provided by the Dow Chemical Company. The molecular information of the OBC is shown in Table 1. The iPP/OBC blend (70/30 w/w) was prepared using a co-rotating twin screw extruder (ZSK-25, D = 25 and L/D = 48) operated at 200 °C and a screw rotation speed of 500 rpm. Separate computer-controlled, loss-in-weight feeders were used to feed the two pelletized ingredients. An antioxidant (Irganox™ B225) was added to the blend with a weight fraction of 0.2% to avoid degradation during processing. Plaques were prepared by compression molding at 200 °C. Mini tensile bars about 1 mm thick were cut from the plaques.

In-situ X-ray measurements were carried out at the beamline BL16B1 in the Shanghai Synchrotron Radiation Facility (SSRF). The wavelength of the radiation source was λ = 1.24 Å. The mini tensile bars were stretched stepwise at a crosshead speed of 1.20 mm/min on a Linkam TST 350 hotstage and scattering patterns were collected during the stretching intervals. Engineering stress was defined conventionally as force per initial cross-sectional area. Scattering patterns were collected by a MAR CCD (MAR-USA) detector with a resolution of 2048 × 2048 pixels and pixel size of 79 × 79 μm². Image acquisition time was 60 s. The sample to detector distance was 1969 mm for SAXS and 186 mm for WAXS. All the X-ray images were corrected for background scattering, air scattering and beam fluctuations.

A JSM-6700F JEOL scanning electron microscope (SEM), operated at 5 kV, was utilized to examine the morphology of the iPP and iPP/OBC blend. The specimens were frozen in liquid nitrogen for several minutes, and then cut by a sharp blade quickly to obtain the fracture surface. The iPP/OBC blend was etched with xylene at 80 °C to remove the OBC phase from the iPP matrix.

3. Results and discussion

3.1. Stress–strain curves of iPP and iPP/OBC blend

The engineering stress–strain curves obtained from tensile tests are plotted in Fig. 1. iPP displays sharp yielding, whereas yielding is diffuse in iPP/OBC blend, which agrees well with previous reports [21–24]. The overall stress of iPP/OBC blend is lower than that of neat iPP. A maximal engineering strain of 300% was measured, which is well beyond the yield of iPP. The periodic drops of force in the stress–strain curves are caused by the stress relaxation during data collection. According to our previous study [25], this blend displayed a phase separated morphology with OBC distributed in iPP matrix as micrometer scale domains.

3.2. In-situ small angle X-ray scattering (SAXS)

Fig. 2 presents the selected SAXS patterns of neat iPP and iPP/OBC blend. In the unstretched state, both iPP and iPP/OBC blend show relatively weak scattering. It is worth noting that the unstretched SAXS patterns for iPP and iPP/OBC blend exhibit long period reflection peak, which is not visible in Fig. 2 because of the displaying contrast. At stain = 20%, a sudden increase of scattering intensity can be observed in neat iPP. The scattering intensity on the meridian is much stronger than that on the equator, indicating that the cavities are elliptical with the major axis perpendicular to the drawn direction. With strain increasing, the scattering intensity increases in neat iPP. When strain = 53%, the intensity on the equator becomes comparable with that on the meridian. With increasing strain, the scattering intensity on the equator increases, while the intensity on the meridian comparatively decreases. At strain = 233%, the SAXS pattern of neat iPP becomes streak-like, suggesting that the cavities are reoriented and elongated with major axis aligned along the drawn direction. The general feature of cavitation in neat iPP with increasing strain is in accordance with the previous reports [3,5]. With respect to iPP/OBC blend, the SAXS

| Table 1 |
| Sample code | Density (g/cm³) | Mw (kg/mol) | Mn (kg/mol) | Octene content in soft segment (mol%) | Octene content in hard segment (mol%) | Zn content (ppm) | Hard segment (wt%) | Xc, α* (wt%) |
| OBC | 0.867 | 76 | 180 | 22.6 | 1.13 | 177 | 16 | 10 |

*(a) Determined by 13C NMR.
(b) Determined by enthalpy of fusion.*
patterns show similar general feature during deformation with several remarkable differences. The first difference is that iPP/OBC blend show higher scattering intensity than neat iPP in the unstretched state. This can be interpreted by the unneglectable scattering of OBC, as expatiated in our previous study [25,26]. Second, the strain for onset cavitation in iPP/OBC blend is lower than that in neat iPP, confirming that elastomer can indeed promote the cavitation of iPP. Third, the strain for cavities to undergo “reorientation” in iPP/OBC blend is around 20%, much smaller than that in neat iPP (around 53%).

The scattering patterns in Fig. 2 can be analyzed in a more quantitative manner. The parameter “eccentricity” was introduced to describe the anisotropy of a SAXS pattern [3], which can be determined by finding points with the same intensity (e.g., half of the maximum) in a pattern and determining lengths of sectors of straight lines between the center of symmetry and points of equal intensity. The lengths of sectors measured in the drawing direction and transverse directions were used for the determination of eccentricity. For elliptical shape, the eccentricity is defined by the equation $e = (a^2 - b^2)^{0.5}/a$, where $a$ is the longer and $b$ is the shorter semiaxis of the ellipse. The values of eccentricity are presented in Fig. 3. Initially, the eccentricity is around 0.15 for both neat iPP and iPP/OBC blend. With increasing strain, the eccentricity sharply increases to 0.9 at a strain of 20%, and then decreases to 0.35 at a strain of 53% for neat iPP. With further increasing strain, the eccentricity increases again to 0.9 for iPP. The second increase of eccentricity indicates transformation of the shape of cavities from perpendicular to the drawing direction to along the drawing direction. For iPP/OBC blend, the value of the first maximum is around 0.5, much lower than that of neat iPP. Furthermore, the strain for the minimum of eccentricity in iPP/OBC blend is 20%, much lower than that in neat iPP (strain = 53%). The final value of eccentricity for iPP/OBC blend is similar with that for neat iPP. The above results indicate quantitatively that the cavities in iPP/OBC blend are less elongated initially and easily to reorient.

3.3. In-situ wide angle X-ray scattering (WAXS)

Fig. 4 shows the selected WAXS patterns of neat iPP and iPP/OBC blend during tensile deformation. The 2D scattering patterns have been averaged over 360° to obtain 1D intensity profiles, as shown in Fig. 5. The peaks at Brag angle 11.4°, 13.6°, 15.0°, 17.1° and 17.6° can be assigned to be the reflections of (110), (040), (130), (111) and (041)/(131) of iPP monoclinic α modification, respectively. The WAXS patterns of unstretched neat iPP and iPP/OBC blend exhibit isotropic reflection rings, indicating that the initial samples are isotropic. Upon deformation, the WAXS patterns of neat iPP gradually become anisotropic. The (110), (040) and (130) reflections intensify on the equator, whereas the (111) and (041)/(131) reflections gradually become into off-meridian arcs. At strain = 93%, clear six-point pattern, typical for mesophase, can be seen for neat iPP. For iPP/OBC blend, the WAXS patterns are nearly isotropic until...

---

**Fig. 2.** Selected SAXS patterns of iPP and iPP/OBC blend at various strains. The drawing direction is vertical.

**Fig. 3.** Eccentricity of scattering patterns as a function of engineering strain for iPP and iPP/OBC blend.

**Fig. 4.** In-situ wide angle X-ray scattering (WAXS)
strain reaches 67%. However, the degree of anisotropy is much lower than that for neat iPP at similar strain. At strain = 233%, only weak anisotropy can be seen in the WAXS pattern of iPP/OBC blend.

The structural evolution during tensile deformation can be further analyzed by 1D intensity profiles presented in Fig. 5. With increasing strain, the reflections in neat iPP become wider, which can be interpreted as the breaking of crystal blocks. At strain = 233%, the WAXS pattern of neat iPP exhibits two broad halos with d spacing of 0.59 nm and 0.41 nm, respectively, which is in accordance with the mesophase [27]. For iPP/OBC blend, however, reflections of α phase are still strong, though their fraction is decreased compared with the initial value. It must be noted that the (111) and (041)/(131) reflections are two distinguishable peaks in 1D intensity profile of undeformed neat iPP. However, they seem to be indistinguishable in undeformed iPP/OBC blend, which might be caused by the scattering of OBC. Fig. 6 presents the scattering profiles of neat iPP and neat OBC calibrated by radiation flux, exposure time and sample thickness. The (110) peak of orthorhombic OBC locates exactly right at the middle of (111) and (041)/(131) reflections. The convolution of these three peaks results in the broad “single-peak-like” appearance in iPP/OBC blend. As shown in Fig. 6, the scattering of OBC is relatively weak compared to iPP.

Apparently, the fractions of different phases are different between neat iPP and iPP/OBC blend, as well as the degree of orientation. Because of the severe convolution of several peaks of different phases, estimation using ordinary peak fitting method would cause unacceptably large uncertainties. To characterize the overall orientation, we adopted a data treatment method (“halo method”) firstly proposed by Hsiao et al. [28] The two-dimensional WAXS pattern of stretched samples after being corrected for the background and air scattering can be separated into two fractions: the isotropic and anisotropic parts. An azimuthal scan is firstly drawn along the angular axes (2θ), starting from the center of the WAXS pattern. At each angular pixel position, a minimum intensity value is obtained from the azimuthal scan, which eventually yields the isotropic part. The anisotropic part is obtained by subtracting

![Fig. 4. Selected WAXS patterns of neat iPP and iPP/OBC blend during tensile deformation. The drawing direction is vertical.](image)

![Fig. 5. Selected 1-D intensity profiles of iPP/OBC blend at different strains.](image)
the isotropic part from the WAXS pattern. As shown in Fig. 7, the isotropic part mainly contains the amorphous phase and unoriented monoclinic crystalline phase, whereas the anisotropic part is constituted by mesophase and oriented monoclinic crystalline phase. We assume that the stretched sample has a cylindrical symmetry around the stretching axis, where the 2-D WAXS patterns can be used to calculate the fraction of each phase. For neat iPP, the 1-D profile with a 2θ range of 8°–22° of the isotropic part was fitted by six Gaussian type peaks: one amorphous peak, five monoclinic α peaks, respectively. The anisotropic part was fitted by seven Gaussian type peaks: two mesophase peaks and five monoclinic α crystal peaks. The center positions of amorphous peak, monoclinic α peaks and mesophase peaks were fixed according to literature during parameter optimization. For iPP/OBC blend, because the crystallinity of OBC is around 10%, we used an extra Gaussian peak to represent the scattering of OBC in the deconvolution of isotropic part. It should be aware that the ignorance of OBC crystalline reflections may cause minor error to the estimated phase fractions. Nevertheless, the result is satisfactory under this approximation condition.

Fig. 8 shows the fractions of different phases of neat iPP and iPP/OBC blend during deformation. For neat iPP, up to strain = 25%, the fractions of amorphous phase, crystalline phase and mesophase keep invariant. Upon strain further increasing, the faction of monoclinic α phase exhibits a sharp transition, decreasing from ~65% to ~30%. Meanwhile, the fraction of mesophase increases from 0 to ~60%, and the fraction of amorphous phase decreases from ~35% to ~15%. This observation is similar to that reported by Zuo et al. [29]. For iPP/OBC blend, however, the fraction variation of different phases in iPP/OBC blend is less obvious compared to that in neat iPP. The fraction of amorphous phase nearly keeps constant during deformation. At strain of 233%, the residual monoclinic α phase is still higher than 45%. The above results suggest that the crystal-mesophase transition is much slower in iPP/OBC blend than that in neat iPP during uniaxial tensile deformation.

It is obvious that the degree of anisotropy is different between neat iPP and iPP/OBC blend. A widely used method characterizing orientation is the Hermans orientation factor [30]:

\[ f = \frac{3\langle \cos^2 \phi \rangle - 1}{2} \]

where \( \phi \) is the angle between the chain axis and the reference axis (stretching axis). \( \langle \cos^2 \phi \rangle \) is defined as:

![Corrected pattern](image1)

**Fig. 6.** Scattering curves of undeformed neat iPP and neat OBC.

![Isotropic part and anisotropic part](image2)

**Fig. 7.** An example showing the separation of a WAXS pattern into the isotropic and anisotropic parts.

![Fraction of different phases in neat iPP and iPP/OBC blend](image3)

**Fig. 8.** Fractions of different phases in neat iPP and iPP/OBC blend during tensile deformation.
where $I(\varphi)$ is the scattering intensity along the angle $\varphi$. The range of Hermans orientation factor is in the range of $-0.5$ to $1$. When $f = -0.5$, it is recognized that all the chains align perpendicular to the reference axis. When $f = 1$, all the chains are perfectly parallel to the reference axis. This method is versatile to characterize the uniaxially orientated materials. However, because the basis of Hermans orientation factor is the azimuthal distribution of intensity, the prerequisite for applying this method is well-separated Bragg reflections. In the present case, the reflections of monoclinic $\alpha$ phase are strongly convoluted with the reflections of mesophase. Particularly, the population of different phases varies during deformation. To apply Hermans method, complicated 3D peak fitting is needed.

Since we are only interested in the overall orientation of the stretched samples, the fractions of isotropic and anisotropic parts are calculated and presented in Fig. 9. It is observed that the neat iPP and iPP/OBC blend have a similar initial isotropic part fraction of $80\% - 90\%$, which may be due to some orientation resulting from compression molding. With increasing strain, the fraction of isotropic part in neat iPP has a sudden drop. The anisotropic part has a peak accordingly. This comes from the change of relative fractions of the oriented and unoriented monoclinic crystalline phase. The sudden increase of anisotropy is attributed to the unit cell parameter change. At small strains, the crystal deforms under stress, which leads to a shape change of the reflections from circular to elliptical. With increasing strain, the crystal starts to slip and the stress applied on the crystal can be mostly relaxed. Thus the fraction of isotropic part increases. It can be seen that this phenomenon in iPP/OBC blend is less obvious than that in neat iPP, indicating that the stress applied on the monoclinic crystal is either relatively small or easier to relax. With further increasing strain, the isotropic part of neat iPP decreases monotonically to a plateau of around $20\%$ at strain $= 100\%$. Accordingly, the anisotropic part in neat iPP increases with increasing strain, and reaches a plateau around $80\%$ at strain $= 100\%$. For iPP/OBC blend, the isotropic fraction decreases slowly from $90\%$ to $65\%$ within the investigated strain range till strain $= 233\%$. The transition-like feature at low strain for neat iPP is in accordance with the known deformation mechanism: shortly after the yield region, a lamellar–fibrillar transition takes place for semi-crystalline polymers, producing a highly oriented structure $[31,32]$. The deformation process of iPP/OBC blend is somewhat astonishing. Instead of a sharp transition, a continuous decrease of the isotropic fraction in iPP/OBC blend indicates a clearly different behavior from neat iPP.

3.4. Morphological observation

To further understand the deformation process, the cryo-fractured surfaces of neat iPP and iPP/OBC blend were observed...
by SEM, as shown in Fig. 10. At strain = 300%, the fracture surface of neat iPP is quite flat under low magnification (Fig. 10A). Under higher magnification, it can be observed that the surface of neat iPP is constituted by microfibrils with diameter of 50–70 nm (Fig. 10B). Highly elongated cavities along the stretching direction are seen in between the microfibrils (Fig. 10C). This is in line with the SAXS and WAXS observations: elongated cavities are responsible for the SAXS streak and the highly oriented microfibrils contain multiple oriented phases including monoclinic phase and mesophase. For iPP/OBC blend, in order to get better resolution of the iPP matrix, the OBC phase was etched prior to observation. As seen in Fig. 10D, the fracture surface is filled with holes at micrometer length scale. The majority region of iPP matrix is quite smooth under higher magnification (Fig. 10E), which is obvious different from the morphology of iPP in Fig. 10B. In most regions, no fibrillar structure can be seen. Microfibrils and nanoscale cavities can only be observed in certain local regions (Fig. 10F). The scattering pattern for iPP/OBC blend correlates with the real space structure as follows. The possible interface voids between iPP and OBC phase resulting from debonding, together with the cavities in between the microfibrils, contribute to the SAXS streak. The localized microfibrils are responsible for the anisotropic part in the WAXS patterns of drawn iPP and iPP/OBC blend.

3.5. Effect of OBC on the deformation of iPP matrix

Now it is interesting to consider the role of OBC on the deformation process of iPP/OBC blend. OBC promotes the occurrence of cavitation in the blend, probably because of the OBC domains leads to less-uniform stress distribution which is prone to cavitate at stress concentration regions. The promotion of voiding is a well-accepted ability of rubber particles [20], which is believed to be a requirement for effective toughening, because it can relax the triaxial stress that favors brittle fracture [33,34]. The strain for “reorientation” of cavities in the blend is slightly lower than that in neat iPP. This higher “mobility” might be related to the softness of OBC phase. Because of the less-uniform stress distribution in the blend, the local strain is less-uniform during stretching. iPP matrix in iPP/OBC blend has smaller local strain than that in neat iPP with the same engineering strain. Therefore, on the engineering strain basis, OBC remarkably “slows down” the orientation process of iPP and the crystal-mesophase transition. Fig. 11 is a schematic illustrating the structure variation of iPP/OBC blend during stretching. OBC particles cavitate under triaxial stress (Fig. 11B). Upon further deformation, the matrix ligaments between horizontally adjacent OBC particles are prone to yield because of the cross-section reduction and stress concentration at the equator of the OBC domains. The local strain of the “OBC rich” regions increases during stretching. However, other regions (the iPP rich region) would have small local strain compared with the apparent engineering strain, as shown in Fig. 11C. Because of the existence of regions with low local strain, the overall degree of anisotropy and the mesophase content in iPP/OBC blend are reduced. Slight Positional adjustments of iPP rich regions could be possibly achieved by slippage with each other or rotation because of the soft OBC phase in between.

It should be noted that the cavities in Fig. 11 are not those manifested in SAXS. Generally, the initial cavity nuclei are in the length scale of 10 nm, which can be detected by conventional SAXS [4,35]. In rubber toughening systems, the cavities grow up to the length scale of rubber particle size, i.e., micrometers, which could be observed directly by optical microscope [36,37]. The well developed cavities in iPP/OBC blend are obviously beyond the detection range of conventional SAXS setups. In our case, the SAXS results merely reflect those cavities like in Fig. 10C and F.

4. Conclusions

Toughening of isotactic polypropylene (iPP) by elastomer has been a long studied topic. Promotion of cavitation has been recognized as a requirement for achieving high toughness. The present study comparatively examined the uniaxial deformation process of neat iPP and its blend with olefin block copolymer (OBC) by in-situ synchrotron X-ray scattering. The promotion of cavitation by adding elastomer was confirmed by the following observation: the onset of cavitation in iPP/OBC blend takes place at relatively lower strain, and reorientation of cavities in iPP/OBC blend is easier to occur than that in neat iPP. The crystal-mesophase transition and orientation both manifest themselves as sharp transitions. In contrast, in iPP/OBC blend, the mesophase formation and orientation proceed gradually. Within the investigated strain range, the overall degree of orientation and mesophase fraction of iPP matrix in iPP/OBC blend are much lower than those in neat iPP. By morphological observations, less-uniform distribution of local strain is identified in iPP/OBC blend. OBC domains in the matrix result in less-uniformed stress distribution, which is derived to account for the promoted cavitation and uneven local strain distribution. The non-uniform local strain distribution, coupled with the softness of OBC phase, contributes to the slower orientation and crystal-mesophase formation in iPP/OBC blend.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (21074141, 50903089). Dujin Wang acknowledges the China National Funds for Distinguished Young Scientists.
The authors acknowledge the Dow Chemical Company for partial financial support.

References