

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

Guoming Liu^a, Xiuqin Zhang^{b,*}, Yufeng Liu^a, Xiuhong Li^c, Hongyu Chen^d, Kim Walton^e, Gary Marchand^e, Dujin Wang^{a,*}

^a Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Engineering Plastics, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

^b Beijing Key Laboratory of Clothing Materials R & D and Assessment, School of Materials Science & Engineering, Beijing Institute of Fashion Technology, Beijing 100029, China

^c Shanghai Synchrotron Radiation Facility, Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201204, China

^d The Dow Chemical (China) Company Limited, Shanghai 201203, China

^e The Dow Chemical Company, Freeport, TX 77541, USA

ARTICLE INFO

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

ABSTRACT

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 that in neat iPP. The reorientation of the cavities in iPP/OBC 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.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

With hierarchical structures in various length scales, semi-crystalline 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. The cavitation process 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, by 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 α -form [11–13]. Stretching induced α crystal-mesophase transition in iPP has been studied extensively. It was founded that stretching iPP with β crystal at room temperature

* Corresponding authors.

E-mail addresses: clyzqx@bift.edu.cn (X. Zhang), djwang@iccas.ac.cn (D. Wang).

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/cm^3 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 $71 k_B T$ [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 $\lambda = 1.24 \text{ \AA}$. 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 $79 \times 79 \text{ \mu m}^2$. 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.

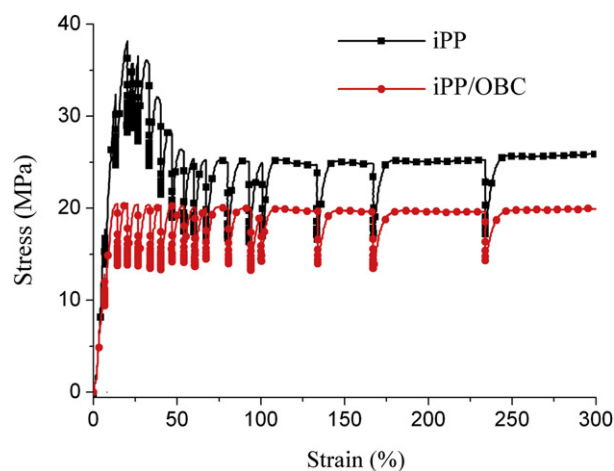


Fig. 1. Engineering stress–strain curves of iPP and iPP/OBC blend.

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 strain = 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
Molecular characteristic of OBC.

Sample code	Density (g/cm ³)	M_n (kg/mol)	M_w (kg/mol)	Octene content in soft segment ^a (mol%)	Octene content in hard segment ^a (mol%)	Zn content (ppm)	Hard segment (wt%)	$X_c, \Delta H^b$ (wt%)
OBC	0.867	76	180	22.6	1.13	177	16	10

^a Determined by ¹³C NMR.

^b Determined by enthalpy of fusion.

Download English Version:

<https://daneshyari.com/en/article/5182875>

Download Persian Version:

<https://daneshyari.com/article/5182875>

[Daneshyari.com](https://daneshyari.com)