The effect of comonomer content on structure and property relationship of propylene-1-octene copolymer during uniaxial stretching

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ABSTRACT

The structure and property relationships of propylene-1-octene random copolymer having different octene comonomer concentrations were investigated. In specific, the crystal structure evolution in these copolymers during uniaxial stretching at 60 °C was characterized by in-situ synchrotron wide-angle X-ray diffraction (WAXD) and small-angle X-ray scattering (SAXS) techniques. With high octene content, the copolymer behaved like an elastomer with small elastic modulus and yield stress, low crystallinity and low crystal orientation under stretching. Furthermore, step-cycle tensile test showed that the copolymer with high octene content had a high recovery ratio. With low octene content, the copolymer behaved like a plastomer with large elastic modulus and yield stress, high crystallinity and high crystal orientation under stretching. From 2D SAXS results, it was found that in low octene content sample, lamellar fragmentation occurred resulting in a significant decrease in lamellar lateral size. In contrast, in high octene content sample, stress might be mainly concentrated on the amorphous matrix, leading to an inter-lamellar slip and a small decrease in lamellar lateral size. Schematic structural changes of propylene-1-octene copolymer under tensile deformation were illustrated to explain the different elasticity behavior in these copolymers.

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1. Introduction

Polypropylene (PP) is one of the most important polymers in chemical industry due to the low cost and broad applications. It has excellent chemical resistance, good mechanical properties and relatively easy processibility. Polypropylene chains also have excellent ability to crystallize and can form different crystal structures. However, the different crystal structure has different effect on final properties, which are also related to processing conditions. Although polypropylene has widespread usages, it still has limitations for certain applications, such as weak impact strength at low temperatures and poor elastic performance. Recent years, scientists are interested in synthesizing new polypropylene-based materials with modified structure and improved properties to overcome these limitations.

Thermoplastic elastomers (TPE) are a new kind of materials that have gained significant interest in the community as they contain both thermoplastic and elastomeric characteristics. These materials possess improved elastic properties over conventional plastic materials and better processibility than traditional rubber products. There are several pathways to produce new TPE materials. One is through the processing route by mechanical mixing of conventional plastic materials (such as PP) with elastomers, such as ethylene–propylene rubber (EPR) [1–3], ethylene–propylene–diene rubber (EPDM) [4–6] and ethylene–octene copolymer (EOC) [7–10]. Another route is by polymerization, such as copolymerization of polyolefin containing different comonomer type and content, to produce new propylene- or ethylene-based materials. The development of metallocene catalysts has greatly facilitated this method, where incorporation of varying comonomers can be controlled in a random or blocky fashion [11,12]. For example, the propylene-based random copolymer family, containing hexene, butylene, ethylene and octene comonomer units have recently been synthesized [13–23]. With certain copolymer compositions the materials exhibited

both plastic and elastic characteristics having good mechanical strength as well as decent elasticity. The versatile tuning conditions during synthesis clearly provide a new pathway to tailor the final properties. As the propylene segment is the only crystallizable component, the type and content of different comonomer greatly influence the crystalline morphology and thermodynamic properties. Furthermore, the interactions among different segments also lead to phase separation which yields hierarchical structures at different length scales [9,24].

The purpose of the present study is to further understand the relationships between comonomer composition, structure and mechanism property of polyolefin random copolymers. To be specific, propylene-octene (PP−O) random copolymers with different octane contents (mole fraction of 5%, 8% and 10%) were chosen as a model copolymer system to investigate the influence of comonomer on the structural change of propylene during tensile deformation and its relationship with the mechanical performance. In-situ wide-angle X-ray diffraction (WAXD) and small-angle X-ray scattering (SAXS) techniques were used to monitor the structural changes during deformation. The scattering and diffraction results provided useful structural information at different length scales from crystal unit cell to lamella.

2. Experiment

2.1. Materials and preparation

The propylene−octene (PP−O) random copolymer samples were obtained from ExxonMobil Chemical Company. They were synthesized using a solution polymerization method based on the metallocene catalyst. Three different copolymer samples having octene comonomer mole percentages of 5%, 8% and 10% (i.e., weight percentages of 12%, 19% and 23%) were prepared. The weight-average molecular weights of these three copolymers were 114,710 g/mol, 131,500 g/mol and 104,800 g/mol, respectively. They were denoted as PP−O-5, PP−O-8 and PP−O-10 in this paper hereafter.

2.2. Simultaneous X-ray and deformation measurements

Tensile deformation measurements were performed on a modified Instron 4442 tensile apparatus, which allowed the film sample to be uniaxially and symmetrically stretched. The symmetrical deformation ensured the focused X-ray beam always illuminated on the same position of the sample during stretching. The peak melting temperatures of PP−O-5 and PP−O-8 determined by differential scanning calorimetry (DSC) were 96.3 °C and 83.6 °C. For PP−O-10, the melting peak became broad, in the range of 65 °C−75 °C. So in the tensile experiment, 60 °C was chosen as the experimental temperature, since under this condition polymer chains have relatively high mobility in the copolymer and could make it easy to observe the different deformation behavior and larger difference on the lamella structures in these samples from X-ray scattering patterns during the stretching process.

Dumbbell-shaped tensile specimens were prepared by compression molding the samples at 180 °C. All specimens were stored at room temperature for around 1 week before the tensile test in order to minimize any possible aging effects on the sample. The initial length of the specimen between the Instron clamps was 30 mm, having width and thickness of 4 mm and 1 mm, respectively. A constant crosshead speed, 6 mm/min, was applied to the specimen throughout the deformation study. The maximum strain was around 7 due to the limitation of the tensile apparatus. The step-cycle tensile test was also carried out at the chosen experiment temperature (i.e., 60 °C). This test combined the stepwise stretching and loading−unloading cycles to evaluate the elastic recoverability of the specimen. In specific, the specimen was extended step-by-step to the desired strains of 50%, 100%, 200% and 300%, respectively. When the deformation reached the desired strain, the crosshead reversed back at the same crosshead speed until zero stress was detected. The extension was then applied again to reach the next target strain, whereby the process would repeat itself until the completion of the final cycle. The recovery ratio was calculated as $1-(\varepsilon_r/\varepsilon_0)$, where ε_r represents the residual strain and ε_0 represents the target strain. The stress and strain reported in this study were engineering stress and engineering strain measured directly from the Instron machine.

In-situ wide-angle X-ray diffraction (WAXD) and small-angle X-ray scattering (SAXS) measurements during tensile deformation were performed at the X27C Beamline in the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (BNL). The wavelength of the synchrotron radiation was 1.371 Å. To monitor the structural changes, a charged coupled device (CCD, MAR-USA) detector was used to collect 2D scattering/diffraction patterns in real time. The CCD detector had a resolution of 1024×1024 pixels and each pixel size was 158.44 μm. The typical image acquisition time was 30 s for each frame. The sample-to-detector distance was 1910 mm for the SAXS setup (calibrated with Silver Behenate) and 121.1 mm for the WAXD setup (calibrated with Al_2O_3). All X-ray images were corrected for background scattering, air scattering and synchrotron beam fluctuations.

2.3. X-ray data analysis

Quantitative analysis was applied on all 2D WAXD patterns, which were also compensated for Fraser correction due to the distortion from the flat-detector [25]. The stretched samples were assumed to possess fiber symmetry, i.e., with cylindrical symmetry along the machine direction. This was proven to be a good approximation in this kind of single axis deformation system. WAXD patterns were integrated along the scattering vector and scattered intensity, where the integrated intensity could be expressed as $I(s) = 2\pi \int_{0°}^{180°} I(s,\varphi)s^2\sin\varphi\mathrm{d}\varphi$, where φ is the polar angle. In this integration, the Lorentz correction factor (s^2) was used to obtain the mass distribution of the system. The integrated intensity profile was then de-convoluted into different crystal reflection peaks and an amorphous background using the peak fitting method. The crystallinity was determined from the ratio of the integrated area under all crystalline components to the total integrated area.

Typical SAXS image exhibited a broad meridional 2-bar pattern superimposed with an equatorial streak during stretching. The image indicated the lamellar structure under deformation, where the lamellar long period, lamellar thickness, orientation and lateral size could be estimated. Lamellar long period was obtained by the maximum scattering position in the Lorentz-corrected integrated 1D SAXS profile. Lamellar thickness, lateral size and orientation were obtained by a semi-quantitative fit of the 2D SAXS pattern, which are described below. For the stretched system, fiber symmetry was assumed in the SAXS/WAXD pattern, which was verified in our earlier studies [26−29]. This assumption greatly simplified the theoretical approach for the analysis of 2D scattering/diffraction images. The 2D WAXD analysis has been demonstrated earlier [26−29] and will not be repeated here. The 2D SAXS analysis for the system with preferred orientation is adopted in our group recently [30] and the principle will be briefly described as follows. Fig. 1 illustrates the spherical trigonometric relationship of the scattering system with preferred orientation in the reciprocal space [26,31]. In this case, the scattered intensity $J(s,\varphi)$ can be expressed as [26,31,32]: