Spatial distribution of crystal orientation in neck propagation: An *in-situ* microscopic infrared imaging study on polyethylene

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ABSTRACT

The deformation behaviors of three types of polyethylene (PE) with different molecular weights and short chain branch contents were studied by *in-situ* Fourier transformation infrared microspectroscopic imaging (FTIRI) with a Focal Plane Array (FPA) detector during uniaxial tensile test. The crystal orientation distributions within a $250 \times 250 \ \mu m^2$ region during tensile test were obtained, especially in the front of necking profile. The results show that either increasing the molecular weight or adding the short chain branches could enhance the resistance of crystal to be orientated. With the aid of the Landau–de Gennes theory of nematic–isotropic transition, the spatial distribution of crystal orientation during the steady neck propagation is quantitatively analyzed, coupling with its corresponding mechanical behavior coherently. The theoretical analysis reveals that the constant Φ_0 and the coefficient of the Gaussian term A in the Landau–de Gennes model are valid parameters to evaluate the mechanical property of PE materials, which may be generalized as a new method to quantify the mechanical property of semi-crystalline polymers.

1. Introduction

The relationship between molecular structure and mechanical properties of polymers is a long-standing challenge in polymer physics [1–14], which has been attracting great efforts owing to its fundamental interest and industrial importance. Extensive researches in this field have been done on amorphous polymers [1–7], and a few achievements have been acquired through the study on their deformation behavior. However, it is still formidable to describe the structure–property relationship of semi-crystalline polymers [8–14] due to the complexity of multi-scale structures, including molecular architecture, conformation, and supramolecular organizations like lamellar stacks and spherulite [15,16]. By combining mechanical test with *in-situ* structural characterization, a great progress has been made on phenomenological correlation between structures and mechanical properties recently. However,

there is still short of a coherent theoretical description to couple mechanical properties and structural parameters together.

It has been well reported that tensile properties of semi-crystalline polymers are strongly dependent on their superstructure in which crystalline and amorphous regions coexist [17,18]. The crystalline phase generally offers desirable attributes such as stiffness, strength, chemical resistance, and dimensional stability, while the amorphous phase imparts such characters as toughness and resistance to slow crack growth, where tie-chains and entanglements play important roles. At the molecular level, an effective approach to enhance the concentration of such tie-chains is to decrease the crystallization time [19], increase the molecular weight [13,20–22] or incorporate noncrystallizable entities, such as short chain branches (SCB) from comonomers like 1-butene, 1-hexene and, 1-octene, where SCB are preferentially located on the longest molecular chains [13,23–25].

Yielding and necking are important features of semi-crystalline polymers during tensile deformation, whose molecular mechanisms have been widely studied before, especially on polyolefin. Ericksen [26] found a remarkable analogy between the necking process of a forced elastic bar and phase transition in the Van der

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Waals gas. The equilibrium coexistence of un-necked and necked portions was determined by Maxwell rule devising the graphical method to identify equilibrium. The Ericksen theory was subsequently extended to a linear viscoelastic solid by Bernstein and Zappas [27]. Hutchinson and Neale [28] demonstrated that the tensile necking process can be treated as a first-order phase transition induced by force. G'Sell et al. [29,30] have done lots of work on neck propagation in polyethylene (PE) with *in-situ* photography, and proposed that the transverse compressive stresses associated with the shoulders of the neck could play a significant role in neck propagation. Recently, on the basis of a qualitative model by Gent et al. [31,32], Leonov [33] developed a theory that necking is caused by transferring unfolding chains of crystalline blocks into amorphous network phase. Nitta et al. [34] applied catastrophe theory to the neck-initiation to account for the interlamellar connectivity, where Landau-de Gennes type of free energy expression is suggested to explain the necking. Indeed, necking in semi-crystalline polymer is essentially a deformation-induced crystal orientation process, which shares phenomenological similarity with isotropic–nematic phase transition. And this may be understood with the aid of the Landau-de Gennes model based on spatial and temporal distributions of crystal orientation.

Orientations induced by the tensile deformation as direct indicators can reflect the capabilities of different structures on resisting deformation as well as the stress distributions. With a combination of X-ray scattering (or infrared dichroism) and miniature tensile tester, correlation between crystal orientation and mechanical behavior like yielding or necking has been established [35,36]. However, as crystal orientation distributes heterogeneously during yielding or necking, crystal orientation without spatial resolution may lead to miscorrelation between macroscopic mechanical property and microstructural evolution. Thus, techniques with both tempo and spatial resolutions are necessary to establish direct correlation between structural evolution and mechanical behavior. One of such techniques is Fourier transformation infrared microspectroscopic imaging (FTIRI) with a Focal Plane Array (FPA) detector, which has an advantage to image a wide field with high spatial resolution in relatively short data collection time [37–41]. Combining FTIRI with a tensile device, it is possible to observe the evolution of orientation distribution in a wide region during tensile test in real time.

In this work, *in-situ* FTIRI with a detective area of $250 \times 250\ \mu m^2$ is applied to study the evolution of crystal orientation of PE films with different molecular weights and short chain branch contents during uniaxial tensile test. Emphasis is placed on neck propagation, during which the orientation distribution in a large area is captured to reflect the capability of resisting neck propagation. Results show that either increasing molecular weight or adding short chain branches can increase the content of entanglement and improve the capability of resisting deformation. The Landau-de Gennes model of isotropic–nematic phase transition is employed to analyze neck propagation of different PE materials, which reveals that the constant Φ_0 and the coefficient of the Gaussian term A are valid parameters to evaluate mechanical property of PE materials.

2. Experimental section

2.1. Materials and sample preparation

Three types of PE materials varying with molecular weight and short chain branch are kindly supplied by Beijing Research Institute of Chemical Industry of Sinopec, and their detailed parameters are listed in Table 1.

For preparing PE sample with the same history, PE films with a thickness of about 80 μm obtained by compression molding at 180 °C were heated at 200 °C for 10 min and then isothermal crystallized for 20 min after cooling to 120 °C at a rate of 10 °C/min. The crystallized films were cut into rectangular specimens (20 mm × 3 mm) for uniaxial tensile test.

The crystallized samples are also well characterized. The crystallinities (X_c) and melting temperatures (T_m) were obtained by differential scanning calorimeter (DSC 204 F1 Phoenix); the long period (L), amorphous phase thickness (d_a) and lamellar thickness (d_c) were measured with small-angle X-ray scattering (SAXS) at the beamline BL16B of Shanghai Synchrotron Radiation Facility (SSRF), which have been given in Table 1.

2.2. Tensile test and in-situ FTIRI measurement

A homemade miniature tensile tester combined with FTIRI was employed to carry out the tensile test. The rectangular shaped sample was mounted between two clamps of the miniature tensile tester, which was installed on the sample platform of FTIRI. The schematic drawing of the progress for *in-situ* FTIRI measurement is presented in Fig. 1. A notch was made to ensure that the initial necking occurs in the middle of the sample. Before stretching, the observed area was fixed to the left of the notch presented in Fig. 1a. During stretching, necking occurred in the notch region first and then propagated along with the stretching direction, and, the observed area went through the non-necking area, necking edge and necking area successively during tensile deformation (Fig. 1b and c).

Samples were drawn with a constant tensile speed of 18 μm/min at 25 ± 0.3 °C. Due to low tensile speed, the test could be regarded as a quasi-static process, during which the sampling region of FTIRI was kept relatively static.

In-situ FTIRI measurements were carried out with an IFS66v Fourier transformation infrared (FTIR) spectrometer, an infrared microscope (HYPERION 3000) and a 64 × 64 (4096) mercury cadmium telluride (MCT) FPA detector and a Specac KRS5 polarizer. Each image was measured in transmission mode in 5 min for areas of $250 \times 250\ \mu m^2$, with 4.0 cm^{-1} spectral resolution, 4000–800 cm^{-1} spectral range, and 128 scans. The spectra were evaluated using the Bruker software OPUS 5.5.

The 64 × 64 element FPA detector consists of 4096 individual detector elements, and 4096 FTIR spectra are obtained simultaneously during neck propagation. The intensity distribution images of interested absorption bands are obtained by integrating the heights of the corresponding peaks. The effect of anisotropy on a particular absorption band in the infrared spectrum of polymer is characterized by the dichroic ratio R:

$$R = A_{//}/A_\perp \tag{1}$$

where $A_{//}$ and $A_\perp$ are the integrated absorbance measured with radiations polarized parallel and perpendicular to the tensile direction, respectively.

The orientation function (η) is related to dichroic ratio R by expression:

$$\eta = \left\langle 3\cos^2\theta(t) - 1 \right\rangle \Big/ 2 = (R-1)(R_o+2)/(R+2)(R_o-1) \tag{2}$$

where $\theta(t)$ is the orientation angle of the main chain with respect to the tensile direction and $R_o = 2\cot^2\psi$ is the perfect dichroic ratio of a transition moment making an angle ψ with the direction of molecular main chain axis.

The orientation functions η_a and η_b of crystal axes a and b can be evaluated from the FTIR dichroic ratios R for the 1472 and 1463 cm^{-1} bands (R_{1472} and R_{1463}) [36,39,42–44] by the following relations:

$$\eta_a = (R_{1472} - 1)/(R_{1472} + 2) \tag{3}$$