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Structure evolution of polyethylene-plasticizer film at industrially relevant conditions studied by in-situ X-ray scattering: The role of crystal stress

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ABSTRACT

Structure evolution of slightly oriented high density polyethylene (HDPE)-plasticizer film is recorded with small- and wide- angle X-ray scattering (SAXS/WAXS) during stretching. The HDPE has number average molecular weight (M_n) of 300 kg/mol and polydispersity index (M_w/M_n) of 20, respectively. The plasticizer is mixture of aliphatic hydrocarbon with chain length of 11–13 carbon atoms. Experiments are carried out at industrially relevant conditions, with film thickness of 650 μm, plasticizer content of 56%, strain rate of 0.5 s^{-1} and stretch temperature from 80 °C to 100 °C, respectively. An interesting evolution of SAXS patterns from anisotropic ring, four-point, six-point, and two-lobule is observed. From WAXS data, a monotonous increasing after the first decline of crystallinity is obtained, by which melting-recrystallization is validated to occur during stretching. With peak shift of WAXS pattern at different azimuthal angle (Φ), triaxial local stresses exerted on lamellae oriented along different directions are acquired. As consequence, stress exerted along and that perpendicular to chain direction are revealed to induce melting of lamellae at azimuthal angle from 0° to 60° and that from 60° to 90°, respectively. Due to the heterogeneous stress distribution of the system, the appearance of four-point SAXS pattern stems from the sequential melting of lamellae at different azimuthal angles. Through thermodynamic analysis, the physical essence of stress induced melting of lamellae is validated to be elastic energy driven crystal to amorphous phase transition.

1. Introduction

Oriented films like biaxially oriented polypropylene (BOPP) and polyethylene (BOPE) films are highlighted with great mechanical and thermal performance, which have been widely used in packaging, electric industry, etc. [1,2]. Comparing to tensile deformation in common mechanical test, stretch in oriented film manufacture has its own special characteristics. (i) Strain rate is generally high in the order of 1–100 s^{-1}, which is beneficial for inducing oriented structures, raising productivity and enhancing end-use properties. (ii) The stretch temperature is either slightly higher than glass transition temperature T_g or close to melting temperature T_m. (iii) Additives like plasticizers are introduced for either enhancing chain mobility or generating micropores. For example, paraffin oils are commonly employed during producing PE microporous membranes, which are washed out after stretching in machine and transverse directions (MD and TD). Due to these special features, it was relatively challenge to carry out in-situ study on the structural evolution relevant to oriented film processing, as the strain rate required sets a basic level on the time resolution of in-situ structural detecting techniques.

For decades great efforts with in-situ techniques like small- and wide-angle X-ray scattering (SAXS and WAXS) have been devoted on structure-mechanical property of semi-crystalline polymers during tensile deformation, which may be borrowed for understanding film processing, as both share the similarity of stretch-induced transformation from isotropic to oriented structures. Two-dimensional (2D) SAXS measurements usually show stretch-induced evolution from anisotropic ring to four-point to two-lobule scattering patterns during tensile deformation of semi-crystalline polymers [3–10], indicating that the transformation from isotropically oriented lamellae stacks to highly oriented fibrillar crystals, which is strongly affected by the dynamics of chains and crystal [11–14]. As the indicator of the transition structure, the four-point scattering pattern is critical in unveiling the structural transformation mechanism, which has attracted great attention. Two different scenarios have been proposed to account the four-point pattern in SAXS, namely, (i) the destruction of lamellae in meridian first

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and slightly later in the equator while reserving the diagonal lamellae [7,9,10,15]; (ii) the formation of the chevron-like arrangement of lamellae via crystallographic slip [4,16]. These models are widely accepted at temperature far below melting point, while stretch around melting temperature in film processing may follow different mechanism for isotropic-oriented structural transformation, where chain mobility is greatly enhanced and melting-recrystallization may occur, especially with the presence of plasticizer [17,18]. Indeed, the one-way destructive approaches like lamellar fragmenting or crystallographic slip is certainly unfavorable for steady industrial film production, while a destruction-reconstruction process like melting-recrystallization is more favorable [19–21].

Oriented film processing is a stretch-induced structural transformation, which is strongly depended on stress level as well as distribution. As the precursor film generally composes of randomly oriented lamellae and tensile force is commonly imposed uniaxially or biaxially, the stress on lamellae varies with their relative orientations as referring to the tensile axis. The heterogeneous stress distribution may affect the way as well as the sequence of structural transformations for crystals initially oriented in different azimuthal angles. The variation of onset strains for fragmentation with azimuthal angle is qualitatively attributed to stress distribution in early reports [22–24]. Based on shift of crystalline diffraction peaks in tensile deformation, triaxial local stress exerted on lamellae at different azimuthal angles can be obtained, which permits to correlate local stress with structural transformation quantitatively [25–30].

Chain mobility is improved by adding plasticizer, therefore, plastic deformation in terms of crystallographic slippage or melting recrystallization can be greatly enhanced with the presence of plasticizer. Over decades, the influence of plasticizer on the deformation mechanisms of semicrystalline polymers has been extensively studied. Plasticization effect of short chains of ionic liquid on UHMWPE chains is studied by Hsiao, which is observed to facilitate the tilting of lamellae and increase the degree of orientation at high temperature [31,32]. Low molecular weight oligomers can be employed to avoid cavitation and necking during processing [6,33,34]. Moreover, soft segments are introduced in semicrystalline polymers for plasticization by copolymerization, which facilitates the formation of fibrillar crystal [35–39]. In this study, hydrocarbon solvents are employed as plasticizer during preparation of precursor films. This new type of plasticizer can volatilize completely after MD and TD stretches and is recycled as fuel for the product line, saving cost as well as avoiding environmental pollution [40,41].

In this work, time resolved synchrotron radiation SAXS and WAXS are employed to obtain quantified structural parameters of HDPE-plasticizer film during uniaxial roll extension at temperatures of 80 °C–100 °C. Orientation evolution of lamellae from SAXS patterns and crystallinity variation from WAXS is established, which proves the mechanism of melting recrystallization is dominating during stretching process. During stretch induced melting process, the appearance of four-point SAXS patterns stems from the sequential melting of lamellae at different azimuthal angles, which is caused by the heterogeneous stress field. Borrowing the scenario of virtual melting from non-polymeric material [42–45], the physical essence of stretch induced melting process is quantitatively explained.

2. Experimental

2.1. Materials

The HDPE material used in this work is provided by LyondellBasell Industries, Netherlands, which has number average molecular weight (M_n) of 300 kg/mol, and the melt flow index is 0.075 g/10 min (190 °C, 2.16 kg load). Mixture of aliphatic hydrocarbon with chain length of 11–13 carbon atoms are used as plasticizer, which is provided by Qibao petrochemical company, China.

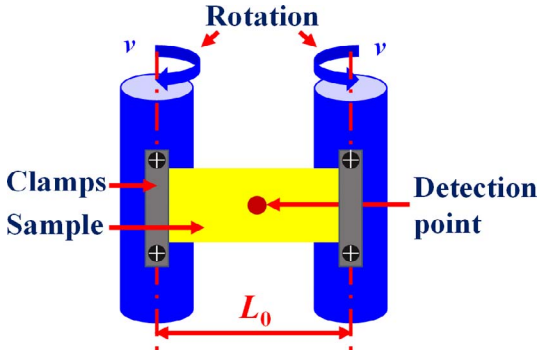

Fig. 1. Schematic illustration of the extension part of the homemade film stretching device.

A system containing twin-screw extrusion and film casting machine is used for preparation of the precursor film with thickness of 650 μm in this study. The blend melt is extruded on the surface of a chill roll with temperature of 45 °C. With differential scanning calorimetry (DSC, Q200, TA instruments), at rate of 10 °C/min, the melting temperature (T_m) and the crystallization temperature (T_c) of the precursor film are measured to be 122.3 °C and 108.2 °C, respectively.

2.2. Stretching device

The experiments are conducted with homemade film stretching device, and the schematic illustration of the stretching part is given in Fig. 1, where L_0 is the distance between axes center of two drums and v the linear velocity of each drum. The design of the stretching part of apparatus is similar to Sentmanat extensional rheometer, where the ends of sample is fixed to the rotation drums by clamps and the sample length being stretched keeps constant as the axes center distance of the two drums. Through which Hencky strain deformation is applied to the sample, also called as logarithmic strain [46–48]. Assuming the linear velocity of each drum during stretching is v, the Hencky strain can be defined as $\varepsilon = 2vt/L_0$, correspondingly, Hencky strain rate is $\dot{\varepsilon} = 2v/L_0$. Stretching is conducted at temperatures of 80, 90, 100 °C, respectively. The strain rate is set as $0.5\,s^{-1}$ according to the industrial stretching condition [2].

2.3. Characterization

The experiments are carried out in BL19U2 in Shanghai Synchrotron Radiation Facility (SSRF). The X-ray wave length is 0.103 nm and a Pilatus 1 M detector (with 1043 × 981 pixels, pixel size of 172 μm) is employed to collect the time-resolved two dimensional (2D) scattering patterns separately for SAXS and WAXS measurements. The patterns are acquired at a rate of 100 ms/frame. The sample to detector distance are calibrated to be 5800 mm for SAXS and 202 mm for WAXS with beef tendon and MnO_2, respectively. The scattering patterns are analyzed with Fit2D software from European synchrotron radiation facility, with which background scattering is corrected by subtracting contribution from air and sample holder.

The 2D SAXS patterns are integrated by integration in the detector plane to get the one dimensional (1D) scattering intensity (I) distribution as a function of the module of the scattering vector $q = 4\pi\sin\theta/\lambda$, with 2θ being the scattering angle, and λ the X-ray wavelength [49–51]. Through scattering peak position of lamellar crystals, long period of lamella is acquired with Bragg's equation ($L = 2\pi/q_{max}$).

Through multiple Gaussian peak fit of the 1D integrated WAXS curves also by integration in the detector plane, crystallinity (χ_C) of the system is obtained. The calculation procedure is listed in Eq. (1), with I_{hkl} the area of ($h\,k\,l$) diffraction peaks and I_{amor} the area of the amorphous diffraction peak.