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Mechanical energy and thermal effect controlled micropore nucleation and growth mechanism in oriented high density polyethylene

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ABSTRACT

Aiming to reveal the effects of mechanical energy and thermal effect on micropore nucleation and growth in oriented high density polyethylene (HDPE) film, stress relaxation after cold stretching was imposed at low and elevated temperature with strain holding constant, respectively, and corresponding structure evolution was tracked by *in situ* and *ex situ* small angle X-ray scattering (SAXS). It was found that stress-induced density fluctuation during cold stretching could be completely recovered as soon as the stress was unloaded, which was called as micropore embryo. Mechanical energy release at low temperature can promote micropore nucleation after an induction period. However, the growth of micropore nuclei is inhomogeneous, developing as non-uniform micropores with poor interconnectivity during hot stretching. While during temperature elevation, micropore embryos can be converted into evenly distributed micropores together with formation of fibrils, which can supply growth sites for through pores during hot stretching. Consequently, microporous membranes with narrow micropore size distribution and good permeability could be obtained after the subsequent hot stretching.

1. Introduction

Applications of polyolefin microporous membranes cover a large range, including lithium-ion battery separator [1–3], medical separation [4,5], personal thermal management [6,7], etc., which all put forward strict requirements on the morphology and properties of microporous membranes. For instance, to ensure cycle life, safety, and power density of lithium-ion battery, the polyolefin separator should meet pore size<1 μm, narrow pore size distribution, porosity between 40% and 60%, appropriate Gurley value, etc. [8–10]. In fact, the morphology and performance of final microporous membranes are determined by processing methods as well as the processing conditions [11–13]. Therefore, studies focusing on the relationship of processing-structure-properties and corresponding physical mechanisms provide useful guidance on controlling morphology and performance of the membranes.

By stretching precursor films with row nucleated lamellar structure, microporous membranes with interconnected slit-like pores are prepared, which is called as dry process [1,14]. Generally, precursor film is firstly stretched at low temperature to initiate formation of "micropore nuclei" (called cold stretching) and subsequently stretched at elevated temperature to enlarge the "micropore nuclei" to be micropores (called hot stretching) during this process [15]. Nevertheless, it is still controversial what is the structure initiated by cold stretching. It is widely accepted that cold stretching initiated irreversible pores or cavities [16–19], even the nano-size cavities could survive after three months of recovery at room temperature for PP [20]. On the contrary, Cayrol [21] found voids between stretching lamellae produced at room temperature could be closed when the stress was unloaded. In our previous work [22], in the light of the faint scattering with periodicity in equator of *in situ* SAXS pattern, we suggest density fluctuation between high and low chain density areas rather than micropores generated during cold stretching. Also, with the combination of stretching-strain recovery experiment and SAXS measurements, we found that the sample subjected to cold stretching and immediate recovery almost have the same scattering intensity near beam stop with that of undeformed sample, indicating the cold stretching

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induced formation of reversible "micropore nuclei", which was thus defined as micropore embryo [23]. Nevertheless, how cavities or micropores nucleate and grow from the embryo is still unclear.

Due to the hard elastic property, precursor films have more than 60% elastic recovery after cold stretching without other treatments [24,25]. Thus, the "micropore nuclei" produced during cold stretching can be recovered after stress is unloaded. However, nonlinear time-dependent response of stress is observed after cold stretching, owing to the superposition of elastic, viscous or plastic behaviors [26–28]. When the strain holds constant after cold stretching, the elastic deformation can convert into viscous or plastic deformation with mechanical energy release, which is known as stress relaxation [29–31]. Thus, the elastic behavior can be reduced at the process of stress relaxation. During the microporous membrane preparation, the nucleation and growth of "micropore nuclei" are initiated when holding samples at stretched state at elevated temperature [22,32,33], which is coupling effect of mechanical energy release and thermal effect. Thus, mechanical energy release and thermal effect are prerequisites for preparation of microporous membranes. Understanding the effect of mechanical energy release and thermal effect on micropore nucleation and growth, respectively, is critical for high performance microporous membrane preparation.

The aim of this work is to figure out how irreversible micropore nucleate and grow under the common effect of mechanical energy release and thermal effect, respectively, as well as the corresponding effects on the morphology and properties of final membrane. High density polyethylene (HDPE) film with highly oriented row nucleated lamellae was selected as the research object. The mechanical energy release was performed by strain holding at 25 °C after cold stretching. The thermal effect was performed by elevating temperature to 110 °C. *In situ* and *ex situ* small angle X-ray scattering (SAXS), scanning electron microscope (SEM), and Gurley value measurement were performed for morphology and property characterization. Micropores nucleated and grew non-evenly from micropore embryos during mechanical energy release at low temperature, while homogenously at elevated temperature. Micropore nucleation during mechanical energy release at low temperature deteriorates micropore size distribution and air permeability while temperature elevation could result in narrow micropore size distribution and good permeability of membranes. This work provides useful guidance on morphology and property control during microporous membranes preparation.

2. Experimental section

The HDPE precursor film with highly oriented row nucleated lamellar structure used in this study was supplied by Wuhan Bosheng Technology Company, Ltd. The grade of resin is Novatech HD HB530, which was purchased from Japan Polychem Co. The precursor film was prepared via extruding-casting process, and the thickness of the film is 25 μm. The structural details of the precursor film can be found in our previous work [22,23].

The precursor film was firstly subjected to cold stretching for 30% strain at 25 °C with a speed of 0.2 mm/s along machine direction (MD) using a home-made constrained uniaxial tensile apparatus, which was equipped with a tension sensor to record the force information [34]. Subsequently, the strain was held constant (called strain holding in this work) and stress relaxed with time, which was also the process for mechanical energy release. To achieve different amount of mechanical energy release at low temperature, the strain holding times (t_{sh}) were varied from 0 to 60 min for different samples. To figure out the structure formed during cold stretching and subsequent evolution mechanism after cold stretching, three groups of samples were prepared. The preparation conditions of all the samples are listed in Table 1. LR were the samples subjected to completely strain recovery (the clamps are reversed to the initial position before stretching) after strain holding, recorded as L0R to L60R for t_{sh} from 0 min to 60 min, respectively. LH represented that the samples were heated to 110 °C and kept at 110 °C after strain holding, then cooled to 25 °C and recovered completely. The corresponding samples were recorded as L0H to L60H for t_{sh} from 0 min to 60 min, respectively. The time for heating and keeping at 110 °C is 10 min. During heating and keeping at 110 °C, stress relaxation at elevated temperature was recorded. Through different strain holding time and temperature elevation, the effect of mechanical energy release and thermal effect on the micropore nucleation and growth can be adjusted, respectively. To enlarge micropores formed during strain holding and temperature elevation for morphology and performance measurements, hot stretching was performed. Samples LM were samples subjected to hot stretching for 60% strain at 110 °C and heat setting for 10 min at 120 °C after the 10 min of heating and keeping at 110 °C, recorded as L0M to L60M for t_{sh} from 0 min to 60 min, respectively.

To explore the structure formed during cold stretching, *in situ* SAXS measurements were performed with an in-house small-angle X-ray scattering system with a vertical layout for L0R and L60R samples, respectively. The details of the X-ray scattering measurements have already been described elsewhere [35]. The X-ray wavelength was 0.154 nm and Pilatus 1M detector was employed to collect the 2D SAXS data. The sample-to-detector distance was calibrated to be 3886 mm. To balance the resolution of structure evolution and scattering intensity, a time resolution of 15 s (20 layers of films stacked together) and 30 s (10 layers of films stacked together) for L0R and L60R were employed, respectively. Also, *ex situ* SAXS measurements were performed to characterize structure of all samples, the testing time was 10 min (1 layer, testing position is same with the *in situ* samples). Fit2D software from the European Synchrotron Radiation Facility was used to analyze the data, which were corrected for background scattering through subtracting contributions from the air. As the SAXS patterns of samples LM show a cylindrical symmetry. A projection operation [36] was applied to obtain the integrated intensity on the meridian $I_1(q_3)$ using the expression:$I_1(q_3) = \int_0^\infty I(q_{12}, q_3) q_{12} dq_{12}$, where, q_3 is the project direction that corresponds to meridian, and all the intensities in the q_{12} plane, which has the same q_3 value have been projected onto an array member $I_1(q_3)$. The scattering vector is $q = 4\pi(sin\ \theta)/\lambda$, with 2θ being the scattering angle and λ the X-ray wavelength. The long period in meridional (L_m) was obtained according to ref [22]. The meridional direction is along the MD.

The morphology was characterized by field emission SEM (ΣIGMA, Germany). This microscope provided high resolution of 2.8 nm at a low accelerating voltage of 1 kV. The uniformity of the micropores was analyzed using an image processing software called Image-Pro Plus [26].

The air permeability of microporous membranes was characterized by Gurley Precision Instrument (model No.4110N, USA) according to ASTM D726 [37]. The Gurley value was defined as the time required for 100 cc air passing through a specific area (1.0 square inches) of the membrane under a specific pressure (20 kgf/cm^2 for this instrument). Lower Gurley value corresponds to better air permeability.

3. Results

Fig. 1a shows the evolution of stress during cold stretching and immediate strain recovery (L0R). During cold stretching to 30% strain, elastic deformation, yield, and strain hardening occur successively. As strain recovers to 7.5%, stress decreases to zero. Fig. 1b