Polymer Testing 36 (2014) 110–118

Contents lists available at ScienceDirect

Polymer Testing

journal homepage: www.elsevier.com/locate/polytest

Material characterisation

Constrained and free uniaxial stretching induced crystallization of polyethylene film: A comparative study

Lingpu Meng, Jiali Xu, Xiaowei Chen, Nan Tian, Yuanfei Lin, Kunpeng Cui, Jing Li, Liangbin Li*

National Synchrotron Radiation Lab and College of Nuclear Science and Technology, CAS Key Laboratory of Soft Matter Chemistry, University of Science and Technology of China, Hefei, China

ARTICLE INFO

Article history:
Received 26 February 2014
Accepted 5 April 2014

Keywords:
Polymer film stretching processing
Stretching induced crystallization
In situ measurements
X-ray scattering

ABSTRACT

Constrained and free uniaxial stretching induced crystallization of high density polyethylene (HDPE) film were studied with in situ synchrotron radiation small and wide-angle X-ray scattering (SR-SAXS, SR-WAXS). According to the initial structure after stretching, as well as the structural evolution, three characteristic regions can be defined in strain space for both stretching modes, while the strain boundaries between different regions are different for the two stretching modes. Region I is located at low strain levels where completely twisted lamellae are induced. Region II is in an intermediate strain level, which induces the formation of partially twisted lamellae with relatively large lateral size (defined as quasi-micro-fibrils). Region III with large strain produces flat lamellae with small lateral dimensions (micro-fibrils). During the crystallization process, a new type of lamellar stack with smaller long period forms in regions II and III while no new types of lamellae appear in region I for both stretching modes. Along the strain space, the scenario of constrained stretching delays the transition from region I to region II, as well from region II to region III. Also, the draw ratio windows of region I and region II are enlarged by constrained stretching, which is more favorable for film processing.

1. Introduction

Due to the long-chain nature of semicrystalline polymers such as polyethylene and polypropylene, stretching is an effective method to obtain films with excellent mechanical, optical and thermal properties [1]. These end-use properties are essentially controlled by stretching-induced crystallization of the polymer, which is affected by the stretching mode and processing conditions, such as temperature, stretching rate and draw ratio [2]. The basic processing unit of film production is to stretch film in one direction while the constraint is imposed perpendicular to the stretching direction to prevent the film width from shrinking, which is generally termed constrained uniaxial stretching or uniaxial constant width (UCW) [3]. For example, for the current production of biaxially oriented films, sequential biaxial stretching is the most widely used mode, where films are stretched in machine and transverse direction (MD and TD) sequentially.

Although stretching films enjoys great success, studies of constrained uniaxial stretching induced crystallization of polymer films remain scanty [4–8]. Generally, influences of the stretching field on chain orientation and polymer crystallization have been investigated by free uniaxial stretching or uniaxial free width (UFW) [3,9–14], where the film width is free of constraint. Studies show that stretching affects crystallization of the polymer through inducing orientation and stretching of the chains, whose effects

* Corresponding author. Tel./fax: +86 551 63602081.
E-mail address: lbli@ustc.edu.cn (L. Li).

http://dx.doi.org/10.1016/j.polymertesting.2014.04.002
0142-9418/

show up in different ways, such as accelerating crystallization kinetics [12], modifying crystalline morphology from spherulite to shish-kebab structure [15], and inducing new crystal forms. Consequently, the final performance of the resulting film depends strongly on the stretching field during processing. Stretching induced crystallization is considered to be a promising approach to tune the properties of polymer films.

The differences between UCW and UFW stretching modes are that, during UCW stretching, the sides of the film are constrained in order to keep the sample from shrinking. Thus, in UCW stretched films, chains are no longer primarily oriented in the MD but tend towards the TD. The orientation type is similar to biaxial orientation [8]. Few studies have been carried out to compare the difference of UCW and UFW from the aspects of film structure and properties. It has been shown by X-ray and birefringence that UCW stretching does not provide completely cylindrical symmetry around the stretching direction, as encountered in the case of UFW [8]. In another work, the four-point SAXS patterns observed in UFW films were smeared in UCW films due to the orientation tendency towards TD [3]. As for the mechanical properties, stress-strain behavior of films by both stretching modes has been investigated; UCW shows higher elongation along the transverse and diagonal directions than UFW stretching [8].

Polyethylenes are the most widely used resins in the film industry [16,17]. In oriented PE samples, the phenomenon of lamellar twisting has been extensively investigated [18–20]. According to the level of applied stress in flow, the lamellae can be parallel with molecular orientation parallel to the stretch direction or twist, leading to rotations of crystallographic *a*-axis and *c*-axis around the *b*-axis in real space [19]. Generally, weak flow produces completely twisted lamellae, resulting in off-axis (110) and meridional (200) reflections. This structure is also termed the 'Keller/Machin I' mode or '*a*-axis orientation' [21]. In contrast, strong flow often produces lamellae in the 'Keller/Machin II' mode (or the '*c*-axis orientation'), in which the lamellae are flat and the corresponding *c*-axis remains parallel to the flow direction. The characteristic feature of this orientation is the appearance of equatorial (110) and (200) reflections. As for the intermediate mode, partially twisted lamellae can be generated, resulting in off-axis (200) and (110) reflections [18].

In this study, a combination of a homemade tensile tester and in situ synchrotron radiation X-ray scattering has been used to investigate the effect of draw ratios (DR) on the structural development of HDPE film. SAXS and WAXS measurements were employed to track the crystallization process of HDPE films under UCW and UFW stretching. The influence of draw ratio on the film morphology evolution was investigated. Also, the influences of two stretching modes on the film structure were studied.

2. Experimental section

2.1. Sample preparation

The high density polyethylene (HDPE) granules used in this study were supplied by Sinopec Qilu Co. Ltd. It has M_n and M_w of 42 and 823 kg/mol, respectively. The granules were first molded to 1 mm thick plates by compression molding at 180 °C, and then cooled down to room temperature. The plates were annealed under vacuum at 90 °C for 24 h to eliminate residual stress. Then, the plates were radiated by a ^{60}Co γ-ray radiation source (located in USTC, Hefei, China) at room temperature without oxygen. The dose rate was 35 Gy/min and the total absorbed dose was 15 kGy. The trapped free radicals were eliminated through annealing at 90 °C for 24 h under vacuum. Slightly irradiated samples were used so that the molten samples could support the externally imposed stress [22]. HDPE thin plates for stretching tests were cut into rectangular shapes with length, width and thickness of 20, 30, and 1 mm, respectively.

2.2. Homemade uniaxial tensile apparatus

A schematic picture of the homemade uniaxial tensile apparatus is shown in Fig. 1(a). Stretch is carried out

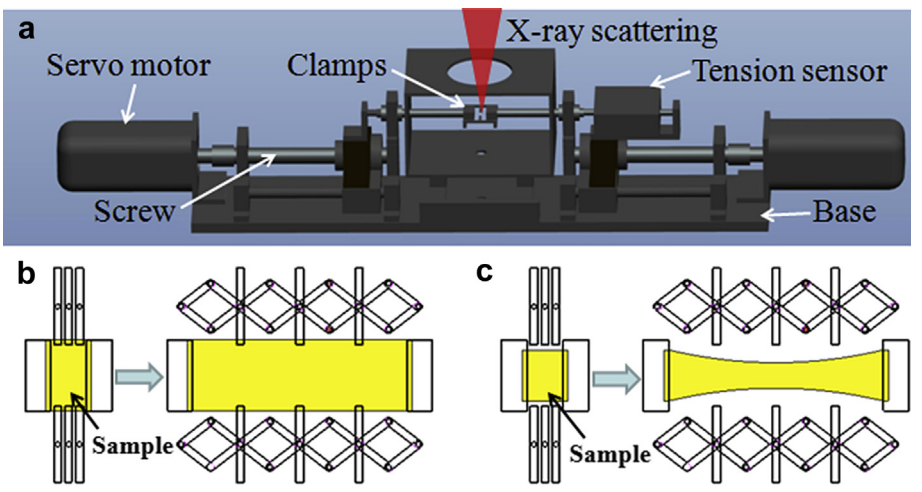

Fig. 1. (a) Three-dimensional view of homemade uniaxial tensile apparatus. Schematic of the constrained (b) and free (c) uniaxial stretching process, respectively.