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Investigation on double yielding behavior under tensile loading in isotactic polypropylene

Tong Wu [1], Ya Cao [1], Feng Yang *, Ming Xiang [1]

State Key Laboratory of Polymer Materials Engineering, Polymer Research Institute of Sichuan University, Chengdu 610065, People's Republic of China

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ABSTRACT

In this article, a peculiar phenomenon of double yielding was first discovered in isotactic polypropylene (iPP) under tensile loading. The results of differential scanning calorimetry (DSC), wide-angle X-ray diffraction (WAXD) and polarized light microscopy (PLM) show that all the three samples, which were subjected to different crystallization procedures, only form α-crystals that are composed of radial lamellae and tangential lamellae. These α-PP samples display different double yield behaviors under tensile loading. PP-quenched sample exhibits double yield points when stretched at low cross-head speed (CHS), while one single yield point appears accompanied with a marked shear band when stretched at high CHS. However, in the case of PP-annealed, only one yield point appears at low CHS accompanied with the formation of a large number of crazes in the necked region, meanwhile, a second yield point gradually develops with increasing CHS. Furthermore, as for PP-isotherm, only one yield point is observed with homogenous deformation and concomitant whitening along the whole sample at any CHS. Based on the characterization of crystalline structure changes after yielding, we propose two plastic processes that contribute cooperatively in the yield process of α-PP, namely the inter-spherulitic deformation and intra-spherulitic deformation. The inter-spherulitic deformation which is prone to be initiated in the sample of strong spherulites is predominant in the first yield process, while the intra-spherulitic deformation enters into action after the appearance of the second yield point in the case of weak spherulites. Moreover, due to the polydispersity of lamellae thickness, the two deformation processes are co-existed and operate competitively in double yielding of α-PP.

1. Introduction

The plastic deformation of semi-crystalline polymers has been the subject of numerous investigations for the last forty years. Many authors have devoted to clarify the mechanism of deformation of semi-crystalline polymers at small strains that it usually proceeds via a yield phenomenon which is associated with a morphological change of the material from a spherulitic structure into a fibrillar one, during this process, the lamellae have been reported to separate, tilt, untwist, and to undergo inter-lamellar slip [1–9]. Semi-crystalline polymers were traditionally regarded as materials which show upon extension only one yield point on the nominal stress–strain curve [1,3–5]. However, in recent years, several studies dealing with polyethylene (PE) have disclosed a singularity in the shape of the stress–strain curves about yield point [2,10–17]. This peculiar feature that consists of a hump in the vicinity of the upper yield point, raised no comment until Mandelkern [18] reported well-resolved double yield points for low crystallinity ethylene copolymers and branched PE under tensile testing. He ascribed the occurrence of double yield points to the great lamellae thickness distribution of PE specimens. Furthermore, some authors also reported double yielding phenomena in polyamide (PA) [19] and poly(tetramethylene terephthalate) (PTMT) [20].

Young [5] and Argon [6] assumed two main processes of plasticity associated in double yield behavior, namely a fine slip relevant to a homogeneous shear of the crystal blocks and a coarse slip involving fragmentation of the crystalline lamellae into blocks. Seguela and co-workers [7,11,14] reported analogous findings form tensile testing of PE and related copolymers and showed that the double yield points are due to the homogeneous shear of the crystal blocks (ductile process) and the slip of crystalline blocks past each other (brittle process). Furthermore, based on a comprehensive study on the structural changes during the yield process of PE with different branch contents, Brooks and co-workers [10,13]

* Corresponding author. Tel.: +86 28 85403118; fax: +86 28 85402465.
E-mail addresses: wutong19851128@163.com (T. Wu), caoya@scu.edu.cn (Y. Cao), yangfengscu@126.com, jiankang@scu.edu.cn (F. Yang), teylor112@163.com (M. Xiang).
[1] Tel.: +86 28 85403118; fax: +86 28 85402465.

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constructed a deformation model that can successfully explain the phenomenology of the double yielding with a clear picture of the morphological changes involved. They declared that the first yield point represents the onset of a recoverable reorientation process of the lamellae within the spherulites in which the orientation can almost recover upon unloading after 3–9 days depending on the density of the sample. The second yield point which related to the destruction of lamellae by *c* axis shear is the onset of necking and is the beginning of the spherulitic to fibrillar morphological transformation.

In our study, we discovered the phenomenon of double yielding in isotactic polypropylene (iPP) under tensile loading, which has never been reported before. It is well established that iPP is a typical polymorphic material with several crystal modifications, of which the α-phase is the most common crystalline form found in normal processing methods [9,21–25]. Unlike other semi-crystalline polymers whose lamellae always grow radially, the lamellae of α-PP can grow in two directions, radially (R-lamellae) and tangentially (T-lamellae). The presence of T-lamellae improves the strength of spherulites by acting like "knots" and providing anchor spots when the spherulites deform [9,21–30]. This unique cross-hatched pattern of spherulites might provide peculiar mechanical properties for α-PP. Lin et al. [26,27] have created microporous membranes by stretching annealed iPP. They claimed that the microporous structure was generated by the combination of intra-spherulitic and inter-spherulitic deformations. Nevertheless, there is no further explanation and explicit relationship between the crystalline structure and plastic deformation of α-PP.

The uniaxial tensile testing as a function of strain rate was conducted to investigate the double yielding behavior of α-PP with different crystalline structure. The motivation of this study is to provide deeper understandings of relationship between spherulitic structure and plastic deformation of α-PP during yielding.

2. Experimental details

2.1. Materials and sample preparation

A commercially available iPP, model T38F, with a melt flow rate (MFR) of 2.9 g/10 min (230 °C, 2.16 kg), $M_w = 3.8 \times 10^5$ g/mol and $M_w/M_n = 4.7$, was purchased from Petroleum Chemical Incorporation (Lanzhou, China). 500 μm thick sheets were produced by pellets molding in a pressure of 5 MPa at 200 °C. After melting, the sheet was quickly put into ice water which was approximate 0 °C to obtain the sample "PP-quenched". To modify the crystalline structure, sample designated hereafter as "PP-annealed" was heated from the quenched state to the temperature of 140 °C in the oven and was held for 2 h, after that, turned off the oven and the sample slowly cooled down at about 1 °C/min. Furthermore, after melting at 200 °C for 10 min, the sample called "PP-isotherm" was then placed between another two metal plates at 130 °C and held for 2 h before turning off the heater, which allowed the temperature to gradually drop at 2 °C/min.

2.2. Measurements

2.2.1. Tensile testing

Uniaxial tensile experiments were performed in accordance with **ASTM: D882-12** using an MTS Universal tensile testing machine. Samples were cut into a mold $25 \times 10 \times 0.5$ mm^3 from the precursor sheets and then were tested with cross-head speed (CHS) of 1, 5, 10, 50 and 100 mm/min. All tensile measurements were carried out at about 25 °C.

2.2.2. Differential scanning calorimetry (DSC)

All the calorimetric experiments were carried out using a Mettler Toledo DSC1 differential scanning calorimeter (DSC) under nitrogen atmosphere (50 mL/min). Calibration for the temperature scale was performed using indium as a standard to ensure reliability of the data obtained. 5 mg round samples were punched out the sheets and heated from 25 °C to 190 °C at a rate of 10 °C/min. The melting temperature (T_m) of the precursor sheet was determined from the heating curve. The crystallinity (X_{dsc}) of the sample was calculated from enthalpy change values obtained in the heating curve, and by assuming 209 J/g as the heat of fusion of a 100% crystalline sample.

2.2.3. Wide-angle X-ray diffraction (WAXD)

WAXD patterns were recorded with a DX-1000 diffractometer. The wavelength of Cu Kα was $\lambda = 0.154$ nm and the spectra were recorded in the 2θ range of 5–35°, a scanning rate of 2°/min, and a scanning step of 0.02°. The overall crystallinity, X_{XRD}, was calculated according to the following equation [31,32]:

$$X_{XRD} = \frac{\sum A_{cryst}}{\sum A_{cryst} + \sum A_{amorp}} \quad (1)$$

where A_{cryst} and A_{amorp} are the fitted areas of crystal and amorphous region, respectively.

2.2.4. Polarized light microscopy (PLM)

The samples were cut directly from the molded precursor sheets and were analyzed using a Leica DMIP polarized light microscopy, and the morphological photographs of crystallization were recorded with the aid of a digital camera.

2.2.5. Scanning electron microscopy (SEM)

The SEM experiments were performed using a Hitachi S3400tED X SEM instrument to inspect the cryofractured surface of α-PP etched by a mixed acid solution [33]. The samples were gold-coated and observed under an acceleration voltage of 20 kV.

3. Results and discussion

3.1. Characterization of crystalline structure

The WAXD spectra of the three iPP samples subjected to different crystallization procedures, namely PP-quenched, PP-annealed and PP-isotherm, are shown in Fig. 1a. It can be clearly seen that all the three samples exhibit four typical diffraction peaks of α-crystal, namely α_1 (110), α_2 (040), α_3 (130) and α_4 (111), (041) and (131), indicating that only α-crystals form in these processing methods [21,22,26,27,32,34,35]. On the other hand, the melting curves of the three precursor sheets shown in Fig. 1b vary considerably: sample of PP-quenched has a low T_m but wide melting peak, whereas the PP-isotherm displays a high T_m but narrow melting peak. In addition, the morphological characteristics of the three PP samples listed in Table 1 further reveal that the PP-quenched has the lowest crystallinity, while the crystallinity of PP-annealed and PP-isotherm, which are obtained from WAXD and DSC testing, increase about 10%. It is also worth mentioning that there is no significant shift in the main melting peak of PP-annealed compared with PP-quenched, however, a shoulder is observed in both the thermograms of PP-annealed and PP-isotherm. Alamo et al. [36] and Wu et al. [28] suggested that this low temperature discontinuity is due to the melting of the T-lamellae. Moreover, the full width of the melting peak at half maximum (*FWHM*) of the three samples decline in the sequence of PP-quenched (9.1 °C), PP-annealed (6.8 °C)