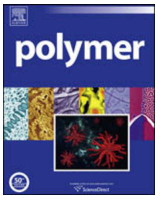
Polymer 50 (2009) 3714–3723

Contents lists available at ScienceDirect

Polymer

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



Plastic deformation of spherulitic semi-crystalline polymers: An *in situ* AFM study of polybutene under tensile drawing

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A R T I C L E I N F O

Article history:
Received 4 June 2009
Accepted 8 June 2009
Available online 16 June 2009

Keywords:
Polybutene
Atomic force microscopy
Spherulites

A B S T R A C T

The plastic deformation of semi-crystalline polybutene (PB) has been studied at the micrometric and nanometric scales by Atomic Force Microscopy (AFM). Owing to a movable tensile drawing stage, capturing images from the same locus of the sample allowed for quasi *in situ* observations of the plastic processes. In the case of PB films having an average spherulite diameter of about 20 μm, the macroscopic deformation was homogeneous over the whole gauge length of the sample, up to rupture. In parallel, the local deformation at the scale of the spherulites was very close to homogeneous and obeyed an affine deformation law over the whole strain range: the shape of the deformed spherulites was kept roughly elliptical up to rupture without clues of fibrillar transformation. The inter-spherulitic boundaries displayed very high cohesion. Fragmentation of the crystalline lamellae proved to be a predominant process, while crystal slip could not be detected at the scale of the AFM resolution, i.e. a few nanometers. Wide-angle and small-angle X-ray scattering yet revealed the occurrence of crystal plastic shear. Similar observations have been made in the case of PB films having an average spherulite diameter of about 5 μm. In the conclusion, a comparison is made with a previous study regarding the deformation mechanisms of a PB sample having 200 μm wide spherulites which displayed brittle behavior.

1. Introduction

In recent years, the demand for predictive approaches of the mechanical behavior of semi-crystalline polymers has aroused increasing efforts for introducing physical concepts in the mechanical modeling (see Ref. [1] and refs cited therein). Benefiting from the drastic increase of computing capacities, this resulted in the development of complex strategies that can yet only account for a limited number of factors of the structural hierarchy of semi-crystalline polymers. Moreover, the deformation processes at the various scale levels of the structure are far for being thoroughly understood, so that numerous assumptions have to be used in the modeling.

Poly(1-butene), otherwise PB, is a kind of "model system" for studying the incidence of the various structural factors on the mechanical behavior, keeping constant the physico-chemistry and the crystallography of the system. Indeed, the morphological habits of PB are strongly sensitive to the crystallization conditions [2]. The spherulite size can be as large as 500 μm down to 3 μm, the crystallinity being in the range 60–40%. The crystal thickness, in the range 20–8 nm, is particularly convenient for performing investigations by Atomic Force Microscopy (AFM). We recently reported [3] the quasi *in situ* AFM study of the plastic deformation mechanisms of PB films having large spherulites of diameter 200 ± 20 μm. Owing to the isothermal crystallization of the films from the melt with a free surface, a good number of adjacent spherulites could grow with their core located right on the free surface of the film. This made it possible capturing the plastic deformation processes at a nanometric scale within the various regions of the spherulites, without any chemical treatment. Under tensile drawing, crazing appeared to be the predominant process of plastic deformation in the equatorial regions, whereas profuse lamella fragmentation developed in the polar regions. Combinations of the two processes occurred in the diagonal regions. The material broke in a relatively brittle manner at a strain of about 15%.

In the present paper, we address the plastic behavior of PB films having small size spherulites, i.e. below 20 μm in diameter. Such films display much greater ductility than the ones of the former study. Besides, considering that the film thickness (about 100 μm) is much greater than the spherulite size, we can easily assume that the AFM surface observations of the deformation processes are representative of the bulk-operating processes that emerge at the sample surface. This point was already argued in the previous work

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doi:10.1016/j.polymer.2009.06.023

[3] from experimental findings that gave evidence of stress triaxiality. We will point out some particular features of the deformation processes that must be ascribed to free surface effects but do not modify the general conclusions.

2. Experimental

The poly(1-butene) material (PB) from Shell has number- and weight-average molar weights $M_n \approx 28$ kDa and $M_w \approx 174$ kDa. The polymer pellets were compression-molded into 100 μm thick sheets between steel plates at 170 °C for 2 min before cooling at about 20°/min. Borrowing from Weynant's isothermal crystallization study [2], two kinds of polymer films were prepared: the initial sheets were melted again at 170 °C on a steel plate with free-upper surface for 5 min, before to be quenched into a water bath at either 25 °C and 0 °C. The films were stored for at least 5 days at room temperature (RT) prior to investigation in order to promote complete structural transformation of the thermodynamically unstable tetragonal crystals grown during the crystallization step into the stable hexagonal crystal form [2,4,5].

After structural stabilization, the average spherulite size determined from AFM experiments (see details below) was 20 ± 5 μm (PB-20) and 5 ± 2 μm (PB-5) for the crystallization at 25 °C and 0 °C, respectively. The peak temperature and crystallinity were determined by Differential Scanning Calorimetry (DSC) using a DSC-7 calorimeter (Perkin–Elmer, Waltham MA, USA) at a heating rate of 10°/min. The crystal weight fraction, X_c, was computed from the melting enthalpy of the samples as compared with the melting enthalpy of perfectly crystalline PB, i.e. $\Delta H_f = 120$ J/g [6].

The glass transition of the amorphous phase not observable from the DSC trace was determined by Dynamic Mechanical Analysis using an RSA3 apparatus (TA Instruments, Wilmington DE, USA) at 1 Hz and a heating rate of 1 °C/min.

Wide-Angle X-ray Scattering (WAXS) and Small-Angle X-ray Scattering (SAXS) experiments have been performed in transmission mode using the Ni-filtered Kα radiation of a 2kW sealed tube (Panalytical, Paris, France). The 2D-patterns were recorded on a CCD camera (Photonic Science, Millham, UK) placed at 50 mm and 800 mm from the sample for WAXS and SAXS, respectively.

Atomic Force Microscopy observations were performed at RT on a Dimension 3100 apparatus (Digital Instruments, Santa Barbara, USA) operated in Tapping mode™. The Nanoworld silicon SPM sensors (type NCL) had a tip radius less than 10 nm, the nominal spring constant and resonance frequency of the cantilever being respectively 48 Nm^{-1} and 190 kHz. The *height* and *error* images were recorded in a so-called light tapping mode using a set-point amplitude ratio $r_{sp} \approx 0.9$–0.95 that prevents indentation in order to optimize the topographic contrast. This point is largely discussed in Ref. [7]. The 512×512 pixels images were recorded by operating the 90×90 mm^2 piezoelectric scanner at a scanning rate of 0.5 Hz. The *error* images, often abusively referred to as *amplitude* images, are displayed to enhance the visibility of the topological features by highlighting the regions of large variations of the AFM cantilever oscillations. The AFM apparatus was equipped with a home-made drawing stage that enabled stepwise deformation of films at constant crosshead speed and holding the sample at chosen constant strains for the duration of the image recording [3]. The initial strain rate was 10^{-3} s^{-1} and the samples were allowed to relax for 10 min before starting image recording for several tens of minutes at practically constant stress. The whole microscope was enclosed in a coffer for preventing vibrations during the image recordings. The macroscopic or engineering tensile strain, $\varepsilon = \Delta L/L_o$, was determined from the displacement of the crosshead ΔL, L_o being the sample gauge length. The local strain, ε_{local}, at the scale of the spherulites was occasionally estimated from the AFM images using the displacement of specific details at the centre of the spherulites and about the inter-spherulitic boundaries. All AFM images are reported with the tensile direction oriented vertical.

Table 1
Structural parameters of the PB films.

Material	Spherulite diameter (μm)	Crystallinity (weight %)	Melting point (°C)	Crystal thickness (nm)
PB-5	5 ± 2	44 ± 1	119.5 ± 0.5	8 ± 2
PB-20	20 ± 5	49 ± 1	120.5 ± 0.5	10 ± 2
PB-200	200 ± 50	55 ± 1	123.5 ± 0.5	15 ± 2

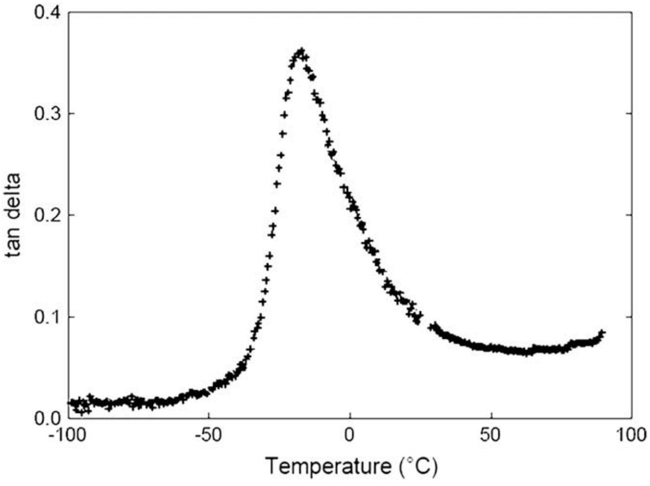

Fig. 1. Loss tangent versus temperature for PB-20.

3. Results

The structural and physical characteristics of the PB-20 and PB-5 films are reported in Table 1. The crystalline lamella thickness was estimated from the long period of the lamellar stacking determined from AFM *height* images and the DSC crystal volume fraction, taking the densities $\rho_c = 0.95$ g/cm^3 and $\rho_a = 0.87$ g/cm^3 for the crystalline and the amorphous phase, respectively [8]. In spite of quite large departure in spherulite diameter, the two kinds of films have very close crystallinity and crystal thickness, and melting point as well.

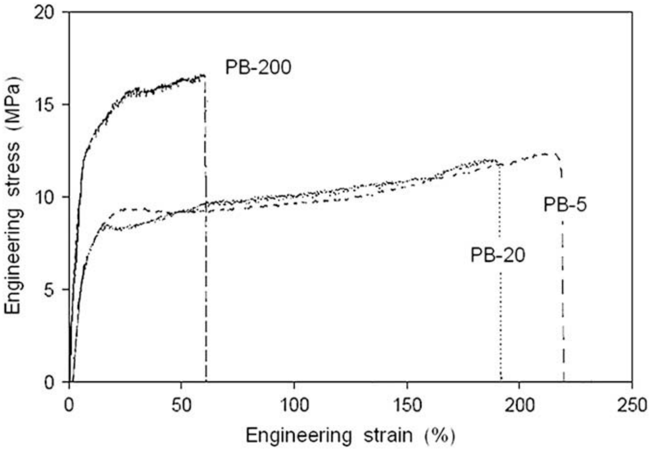

Fig. 2. Engineering stress–strain curves of the PB-20 and PB-5 films at room temperature, for an initial strain rate of 10^{-3} s^{-1} (the data for PB-200 are included for comparison).