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The structural evolution of high-density polyethylene during crazing in liquid medium

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ABSTRACT

Atomic force microscopy (AFM) was employed to study structural transformations occurring in high-density polyethylene (HDPE) during deformation in a liquid medium by crazing mechanism. Processing of the obtained images yielded the parameters of HDPE structure at different tensile strains. It was shown that crazing causes the development of a fibrillar–porous structure in the interlamellar space, the fragmentation of lamellae, and the displacement of lamella fragments relative to each other. Moreover, the deformation is accompanied by the separation of lamellae and the long period increases in the proportion to the tensile strain. The scheme of HDPE deformation upon crazing in liquid medium was constructed based on the AFM images.

1. Introduction

High-density polyethylene (HDPE) is a profoundly investigated semicrystalline polymer, and numerous works [1–10] have been focused on studying the mechanism of its deformation and the evolution of its structure upon stretching in air. At the same time, items made of HDPE are frequently exploited in contact with various liquid and gaseous media. In this situation, physically active media, such as hydrocarbons, oils, alcohols, and surfactants, which do not modify the chemical structure of the polymer, can affect the mechanical properties of polyethylene and decrease its endurance. Since the breakage of a polymer being deformed in a liquid medium is preceded by nucleation of crazes and cracks, the functional properties of polymers are estimated by monitoring their appearance upon the complex action of an ambient liquid and stress [11–16]. In the literature, this phenomenon is referred to as the environmental stress cracking/crazing (ESC), and the main efforts of researchers have been focused on the suppression or deceleration of the craze/crack development.

At the same time, the development of crazes upon polymer deformation in physically active media (wet crazing or solvent crazing) may be a positive factor, because this process is accompanied by the appearance of a finely disperse fibrillar–porous structure with pore and fibril sizes of about 5–20 nm [17–19]. Works [19–21] were the first to determine the conditions under which deformation of amorphous glassy and semicrystalline polymers in liquid media occurs by the crazing mechanism and gives rise to the formation of nanoporous materials with a porosity as high as 40–60%. It is of particular interest that polymer deformation in solutions of various low- and high-molecular-mass compounds is accompanied by their penetration into the nanoporous structure of crazes. Therefore, polymer crazing in liquid media may be considered as a

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method for obtaining nanoporous materials (membranes and sorbents) and as a process for producing nanocomposites and highly disperse polymer–polymer blends [22–28].

Hence, the study of polymer crazing in physically active media is an interesting problem from the viewpoints of both determining the influence of liquid media on the deformation mechanism of polymers and obtaining highly disperse fibrillar–porous structures in them.

Spherulites consist of lamellae, which are oriented in different directions, and form the morphology that prevails in crystalline structures of polymers that are produced by crystallization from melts in the absence of substantial external actions. Being crystallized under the conditions of a tensile stress, a melted polymer may form samples containing anisotropically arranged stacks of lamellae, which are predominantly oriented perpendicularly to an extrusion axis [29–37]. Such anisotropic structures, which are referred to as row-structures, are more convenient for investigating structural rearrangements that accompany the deformation of semicrystalline polymers, because these structures are characterized by a smaller number of possible orientations relative to an applied force. Therefore, the study of their structural transformations upon deformations directed along and normal to the extrusion axis makes it possible to simulate the deformation of the lamellar stacks occurring in the equatorial and meridional regions of the spherulites, respectively.

Fundamental data on the structural evolution of HDPE upon its stretching in air have been obtained by wide- and small-angle X-ray scattering [38,39], differential scanning calorimetry, IR [40] and Raman [41] spectroscopy, as well as atomic force [42,43] and electron microscopy [44–47]. It is obvious that microscopic investigations are of particular interest, because they enable one to directly observe structural transformations that result from polymer deformation.

Polymer deformation by the crazing mechanism in liquid media is accompanied by fibrillization of a polymer material and the development of a porous structure with a large surface area (as large as 100 m^2/g) [17,19]. As a result, the structure of crazed polymers is thermodynamically unstable and substantially changes after stress relaxation or removal of the medium. Therefore, the investigation of the structure of deformed polymers directly in a physically active media and under the conditions preventing them from shrinkage is of especial significance. As has been shown [48], atomic force microscopy (AFM) is very suitable for investigation of polymer deformed by the crazing mechanism, although this method allows one to examine only the surface of a polymer film. Note that the structure of HDPE deformed by the crazing mechanism was investigated by AFM in the same liquid medium in which the deformation had been carried out. Samples deformed to different tensile strains were fastened to a circular frame to prevent them from shrinkage. The samples thus prepared made it possible to observe the structure that directly resulted from the polymer stretching.

The goal of this work is the AFM investigation of the structural evolution of HDPE with an initial row-structure upon stretching in a liquid physically active medium to different tensile strains. The work consists of several sections. The initial HDPE structure is considered in the first section of the work, and the second section is devoted to the features of HDPE deformation in the liquid media and in air. Then, AFM is employed to characterize the structures of HDPE deformed in the liquid medium to different tensile strains.

2. Experimental

2.1. Materials

The objects for the study were HDPE (M_w = 210000 and M_n = 7000 g/mol) films 25 μm thick (Stamylan, DSM) produced by extrusion blow molding. Films with sizes of 40 × 20 mm were deformed upon planar stretching in a water–ethanol solution (1:7, vol/vol) at room temperature and a rate of 5.4 mm/min.

2.2. Methods

2.2.1. Differential scanning calorimetry (DSC) experiments

The experiments were performed using a TA 4000 thermoanalyzer (Metter). The mass of an examined sample was 1.5 mg. Ideal crystal melting heat, which was used to calculate the degree of crystallinity, was 293 J/g. The heating rate was 10 K/min. Lamella thickness was calculated by the following formula:

$$L_c = K_c L_{saxs}(d/d_c), \quad (1)$$

where L_{saxs} is the long period determined by small-angle X-ray scattering (25 nm); d and d_c are the densities of the polymer and its crystalline phase (0.960 and 1.003), respectively; and K_c is the degree of crystallinity (59%) determined from the DSC data.

2.2.2. X-ray diffraction analysis

Small- and wide-angle X-ray scattering measurements were carried out with a Nanostar instrument (Bruker AXS) equipped with a Cu Kα generator of X-rays (λ = 0.154 nm).

2.2.3. Volume strain

Volume strain (W) of the deformed polymer was calculated from changes in the geometric sizes of the films as the ratio of volume increment (ΔV) resulting from film stretching to initial sample volume (V_0), $W = (\Delta V/V_0) \times 100$ (%). The geometric dimensions of the deformed HDPE sample were measured with a projector with a tenfold magnification and an IZV2 optimeter, the measurement error was ±1 μm.

2.2.4. Procedure for investigating the structure of HDPE deformed in the liquid medium

The structure of HDPE was studied in the following way. Initially, a sample was stretched to some tensile strain with a stretching unit operating in the liquid medium. Then, without removing the sample from the liquid medium and the clamps of the stretching unit, it was fastened to a circular frame to fix its sizes throughout the perimeter