

First Direct Microscopic Study of the Crazed Polymer Structure Stabilized by a Liquid Medium

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Crazing is one of the fundamental types of inelastic deformation of polymers. A characteristic feature of this type of deformation is the development of nano-sized porosity in polymer. Morphologically, the porosity of this sort develops by the nucleation and growth of special zones of plastically deformed polymer. These zones, called crazes, have fibrillar porous structure formed by oriented polymer fibrils 5–20 nm in diameter, separated by microvoids of approximately the same size.

The fibrillar porous structure was detected by direct microscopic study of deformed thin films with a transmission electron microscope [1] and also by small-angle x-ray scattering [2]. Crazing usually accompanies forced elastic deformation of degradation of polymer [3]. There is a simple and very efficient method for polymer deformation only by a crazing mechanism. For this purpose, polymer deformation should be performed in adsorption-active liquid media. This process was described in detail in the literature [4], and here we only note that the structure of crazes emerging in adsorption-active liquid media is very labile and unstable; therefore, the removal of the adsorption-active liquid medium from the bulk of crazes is accompanied by profound structural rearrangements. In this context, the native structure forming directly after deformation, when the polymer still contains the stabilizing adsorption-active liquid medium, is distinguished from the structure after drying and shrinkage of deformed polymer.

The necessity of removing adsorption-active liquid media from the bulk of crazes does not allow one to investigate the native structure by electron microscopy because this method requires the placement of a specimen in a vacuum. Therefore, information on the native structure of crazes has been obtained by small-angle x-ray scattering and investigation of liquid permeability under pressure gradient [5, 6]. However, for interpretation of experimental data, these methods

require the use of model concepts, which makes the obtained results ambiguous.

Importantly, there is one more type of crazing, which typically occurs in deformation of crystalline polymers in adsorption-active liquid media—delocalized crazing [7]. In this case, no individual crazes are observed and the porosity develops simultaneously and uniformly throughout the bulk of the polymer being deformed. Although this type of crazing has been comprehensively studied, data on the morphology of the emerging porosity are completely unavailable. This is, first of all, because the removal of the adsorption-active liquid media from the bulk of the pores is followed by the complete collapse (healing) of the porous structure.

In this work, we proposed to use atomic-force microscopy for investigating the native structure of high-density polyethylene deformed by the delocalized-crazing mechanism. The advantage of atomic-force microscopy is that this method enables one to perform measurements directly in liquid media [8] and obtain images of the surface with a resolution on the order of 1–10 nm.

For our studies, we chose high-density polyethylene films 25 μm thick produced by melt extrusion with subsequent blow molding. The high-density polyethylene crystallinity determined by differential scanning calorimetry was 60%. The films were deformed by 200% in aqueous ethanol (1 : 7 molar ratio) at a rate of 5 mm/min. The working part of the specimens was 40 \times 20 mm in width and length, respectively. The structure of the deformed high-density polyethylene after removal of the medium under isometric conditions and shrinkage was investigated with a Hitachi S-520 scanning electron microscope. The test specimens were cleaved in liquid nitrogen along the tensile axis, and gold was deposited on them by ion plasma spraying.

Figure 1 presents the scanning electron microscopy image of the structure of high-density polyethylene deformed by the delocalized-crazing mechanism. In the image, extended oriented polymer layers are seen, but individual structural elements fail to be observed.

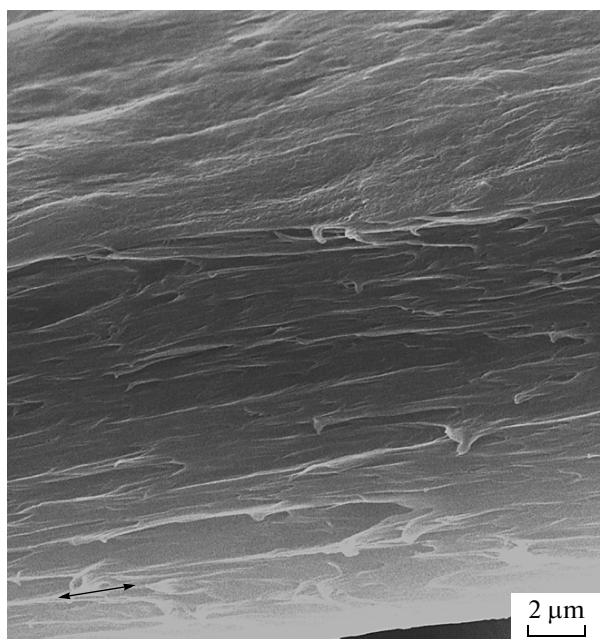


Fig. 1. Scanning electron microscopy image of a cleaved specimen of high-density polyethylene deformed by 200% in aqueous ethanol. The arrow indicates the tensile axis direction.

It is even impossible to confidently state that such a material is porous. Thus, electron microscopic studies of high-density polyethylene that was deformed in an adsorption-active liquid medium and dried under isometric conditions give no indication of fine nanoporous structure and do not allow us to construct a structural model of polymer deformed by the delocalized-crazing mechanism.

The native structure of the deformed high-density polyethylene in an adsorption-active liquid medium was investigated with a Solver BIO Olympus atomic-force microscope (ZAO Nanotekhnologiya MDT). The measurements were performed as follows. After deformation according to the above procedure, a high-density polyethylene sample without removing from the clamps of a tensile-testing machine was fastened to a circular frame in the presence of an adsorption-active liquid medium to prevent the polymer shrinkage and the collapse of the fibrillar porous structure and preserve the native structure. The frame was placed in a Petri dish filled with the adsorption-active liquid medium, and scanning in contact mode was performed using PNP-DB cantilevers (Nanosensors). The obtained images were processed by the FemtoScan Online program.

Figure 2 presents the atomic-force microscopy image of the surface of the high-density polyethylene film deformed by the delocalized-crazing mechanism. The main structural elements of high-density polyethylene obtained by melt extrusion are known [9] to be crystalline lamellas separated by amorphous interlayers. It was assumed [10] that high-density polyethylene deformation in liquid media mainly occurs in amorphous regions simultaneously throughout the bulk of the polymer. The atomic-force microscopy image for the first time visualized the native structure

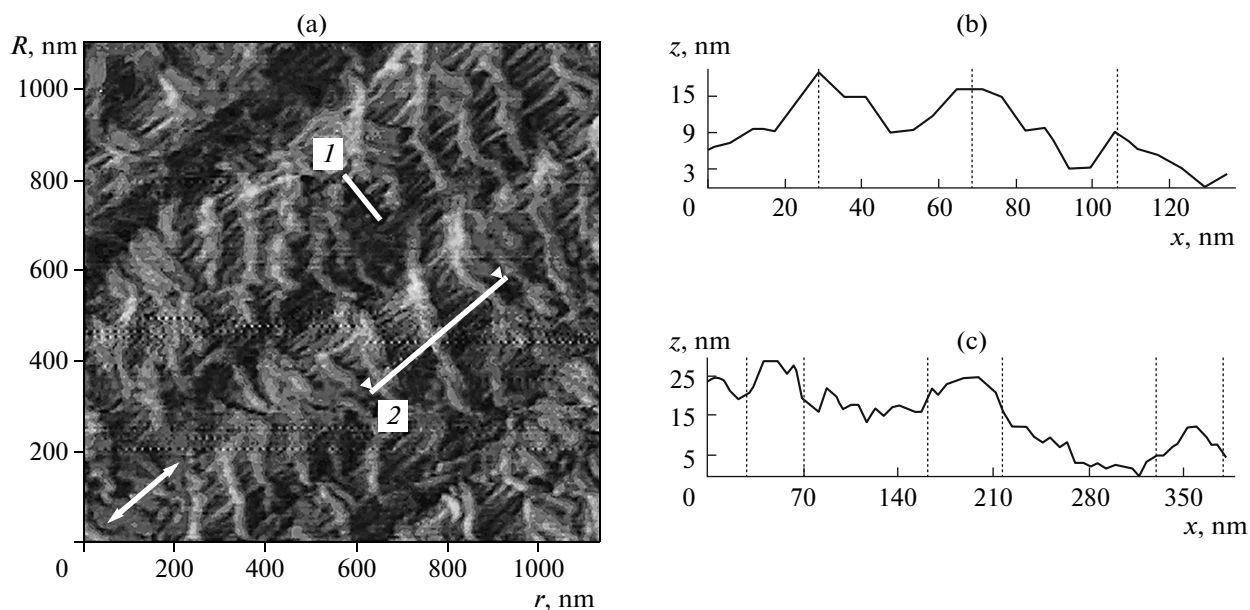


Fig. 2. Atomic-force microscopy image of the surface of a high-density polyethylene film stretched by 200% in aqueous ethanol: (a) the surface image processed using a side illumination filter with the tensile axis direction indicated by the arrow and the profiles of sections along lines (b) 1 and (c) 2 in image a. In profile b, vertical lines show the tops of fibrils, and in profile c, pairs of vertical lines are the boundaries of lamellas oriented perpendicular to the tensile axis direction.

of high-density polyethylene deformed by the delocalized-crazing mechanism.

On the surface of the deformed high-density polyethylene, lamellas oriented mostly perpendicular to the tensile axis are clearly seen. The lamella thickness determined from the section profiles (Fig. 2c) is ~50 nm. Between the lamellas, fibrils oriented strictly along the tensile axis are observed. The fibril length, or the distance between the neighboring lamellas, ranges from 50 to 150 nm. The image presents well voids between fibrils. The distance between the neighboring tops of fibrils is the sum of the diameters of fibrils and voids between them and is ~30–40 nm (Fig. 2b). This distance is independent of the radius of curvature of the cantilever and is measured with an accuracy of ~5 nm. Unfortunately, from this image, it is impossible to absolutely reliably determine the size of voids between individual fibrils, which is assumed to be the pore diameter in model concepts. It can only be noted that this size is no less than 15–20 nm.

Thus, by atomic-force microscopy, we for the first time characterized the native structure of polymer deformed in an adsorption-active liquid medium by the delocalized-crazing mechanism. One can consider that we confirmed the assumption [7, 10] that the deformation of crystalline polymers in adsorption-active liquid media occurs mainly in amorphous regions between lamellas with the transition of polymer to the fibrillized state and the formation of voids between fibrils.

The data on the native structure of high-density polyethylene deformed in an adsorption-active liquid medium enable us to describe common features and differences in structure of polymers deformed by the classical- and delocalized-crazing mechanism. In both cases, polymer passes to the oriented fibrillized state. Classical crazes nucleate on surface asperities (defects) of the structure; therefore, the number of crazes is known [11] to be dependent on the load and the nature of the medium. The nucleation of crazes in

crystalline polymers is determined by their lamellar structure; therefore, the forming fibrillar porous structure is delocalized throughout the bulk of the polymer.

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