

Poly(ethylene terephthalate) Deformation in a Supercritical Xenon Medium

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Crazing in liquid adsorption-active media is a fundamental mechanism of inelastic deformation of amorphous glassy and partially crystalline polymers [1]. This process gives rise to an interpenetrating fibrillar-porous structure consisting of oriented fibrils several nanometers in diameter, which connect the walls of crazes and are separated by voids of the same size. Specific features of such a structure are high lability and ability to undergo considerable rearrangements accompanied by reduction of porosity and dispersity, e.g., on removal of the adsorption-active medium from the pore space [1, 2]. These processes are explained to be due to the action of capillary forces and the tendency of a high-dispersion system to minimize the surface energy.

To reduce the capillary effects, crazed films of poly(ethylene terephthalate) (PETP) and polycarbonate were dried by freeze drying, by which the liquid in the craze space was initially frozen and then removed by sublimation [2]. This method preserves a 1.5–3 times larger surface area and smaller fibril diameter in the porous specimens than the drying via evaporation of the liquid adsorption-active medium.

Another way to avoid the effect of capillary forces is to use a supercritical medium (unlikeable dense gas) as a crazing agent [3]. The uniaxial deformation of various polymers in a supercritical CO₂ medium was studied [4, 5]. The stretching of partially crystalline polymers (high-density polyethylene and isotactic polypropylene) in supercritical CO₂ was shown to occur by a delocalized crazing mechanism. This gives rise to a system of small crazes several tens of nanometers in size that are localized primarily within interlamellar regions of crystalline polymer.

However, the deformation of the glassy polymers PETP and poly(vinyl chloride) was not accompanied by crazing. This is likely to be related to the high gas

solubility in PETP and poly(vinyl chloride) and the strong plasticizing effect of the gas on these polymers [4].

In this work, the adsorption-active medium was supercritical xenon, the critical parameters of which are $T_{cr} = 16.6^\circ\text{C}$, $P_{cr} = 5.9\text{ MPa}$, and $\rho_{cr} = 1.155\text{ g/cm}^3$ [6]. Under the experimental conditions in supercritical xenon (at 23°C and 6.8 MPa), the degree of crystallinity of PETP remained unchanged, which may suggest the absence of significant polymer swelling.

The purpose of this work was to study the uniaxial deformation of amorphous PETP films in supercritical xenon, determine the deformation mechanism, and investigate the forming polymer structure.

Here, we showed for the first time that the stretching of amorphous PETP films in the supercritical xenon medium occurs by a classical crazing mechanism. After the removal of the supercritical medium from the craze space, the high-dispersion porous structure, permeable for low-molecular-weight liquids, with fibrils and pores about 10 nm in diameter is preserved.

The objects of investigation were commercial random films of amorphous PETP ($M_w = 3 \times 10^4$, thickness 100 μm). Standard dumbbell specimens of the polymer films with $6 \times 20\text{-mm}$ gage sections were subjected to uniaxial deformation on the previously described [4] high-pressure stretching machine of original design at room temperature ($22\text{--}24^\circ\text{C}$) and a pure xenon pressure of $6.8\text{--}7.3\text{ MPa}$ at a rate of 5% per minute. Supercritical xenon was completely removed from the polymer space by reducing the pressure in the setup below the critical value.

The structure of the deformed specimens was studied by small-angle X-ray scattering on a Nanostar (Bruker AXS) setup (two-dimensional coordinate detector, $\text{CuK}\alpha$ radiation, pinhole collimation system for the primary beam tailoring, angular resolution $7'$).

The morphological studies were performed with a Carl Zeiss (Jena, Germany) polarizing optical microscope and a JEOL JSM-6390LA scanning electron microscope (cleaved specimens were made by brittle

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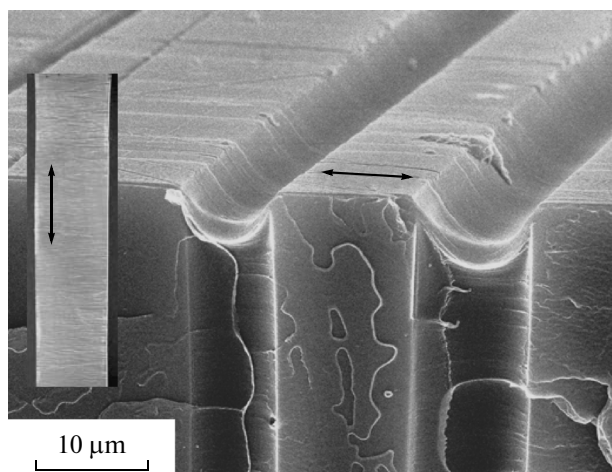


Fig. 1. Scanning electron microscope images of the initial (inset) and cleaved surfaces of an amorphous PETP specimen subjected to uniaxial deformation by 30% in the direction indicated by the arrow in a supercritical xenon medium.

fracture in liquid nitrogen with subsequent gold sputtering).

The uniaxial deformation of amorphous PETP in the supercritical xenon medium occurred without necking, and the development of high polymer strains is mainly due to the growth of crazes.

Figure 1 presents the micrographs of the initial (inset) and cleaved surfaces of an amorphous PETP specimen subjected to uniaxial deformation by 30% in supercritical xenon. On the surface of the deformed specimen, there are milk-white cracks, which are perpendicular to the stretching direction and extend throughout the cross section of the specimen. The material between the cracks is virtually undeformed; there is no transverse contraction. Within the crazes, a quite dense striped structure is seen. Similar behavior was previously observed for polymers deformed by the classical crazing mechanism [1].

The detailed structural studies of the PETP films deformed in supercritical xenon were performed by small-angle X-ray scattering. The crazing causes an abrupt (by several orders of magnitude) increase in the small-angle X-ray scattering intensity in comparison with that for the initial undeformed polymer. Figure 2 shows a typical small-angle X-ray scattering pattern of an amorphous PETP specimen stretched in supercritical xenon. The scattering pattern is seen to consist of two perpendicular reflections and is similar to the well-known pattern of scattering by specimens of glassy polymers containing classical crazes [7, 8]. There are intense meridional scattering extended in the stretching direction and anisotropic scattering extended perpendicular to the equator with an interference maximum.

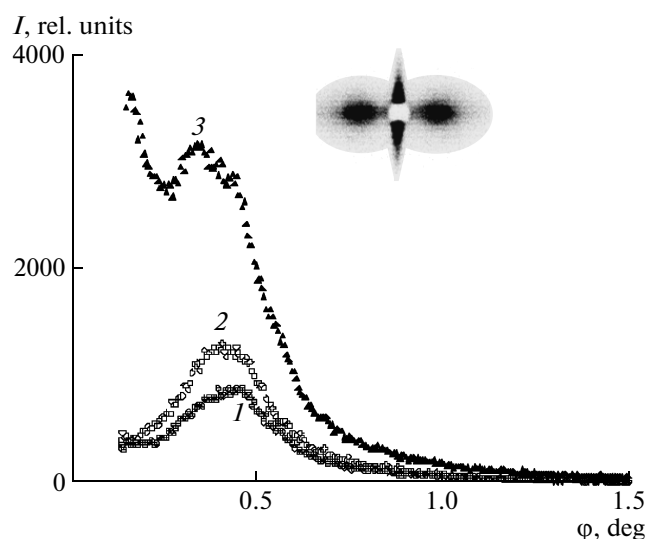


Fig. 2. Equatorial distribution of the small-angle X-ray scattering intensity for an amorphous PETP specimen stretched in supercritical xenon at 20°C and 7 MPa by (1) 6, (2) 30, and (3) 65%. In the inset is the small-angle X-ray scattering pattern of crazed PETP.

It is believed that the meridional (anomalous) scattering is by the X-ray diffraction from the craze walls perpendicular to the stretching direction [8]. The equatorial scattering is by the X-ray diffraction from spatially separated fibrils aligned with the stretching direction that fill the crazes and are perpendicular to the plane of crazes [7, 8].

Figure 2 presents the small-angle X-ray scattering intensity distribution curves recorded in the equatorial direction for amorphous PETP specimens deformed in supercritical xenon. The curves have an interference maximum with the corresponding major period 19–24 nm. This major period value in this case characterizes the distance between the centers of fibrils. The presence of a maximum in a scattering curve indicates a regular arrangement of individual fibrils with respect to one another.

The diameter of fibrils connecting the walls of crazes was found by the Porod method modified for oriented systems [7, 8]. By measuring the absolute values of the scattering intensity, the pore volume and specific surface area of fibrils in PETP crazed in xenon were determined [9]. The cross-sectional size a of pores between fibrils filling the crazes was calculated as the difference of the interfibrillar distance L and the fibril diameter d : $a = L - d$. The table presents the calculated parameters of the porous structure of crazes.

The table shows that the porosity and specific surface area of fibrils increase with increasing strain of amorphous PETP in the supercritical medium. At the same time, the fibril diameter and the interfibrillar distance (major period) change insignificantly. Probably, in this case, as in stretching of glassy polymers in liquid media, the crazing occurs by a surface stretching

Table 1. Characteristics of PETP films after uniaxial deformation in a supercritical xenon medium

Strain, %	Porosity, vol %	Interfibrillar distance	Fibril diameter	Pore diameter	Specific surface area, m ² /cm ³
		nm			
6	8	19.5	8	11.5	14
30	12.5	21.0	8	13	21
65	37	24.0	10	14	50

mechanism, i.e., is accompanied by a continuous increase in the fraction of the material that passes to the oriented state within the crazes. The fibril diameter and the interfibrillar distance remain nearly unchanged.

Note that the stretching of amorphous PETP in supercritical xenon produces a system of crazes with approximately the same parameters (fibril diameter and cross-sectional size of pores between fibrils are ~10 nm) as the stretching of this polymer to form crazes in liquid media [10, 11].

At the same time, comparison of the structures of crazes forming in the amorphous PETP stretching in supercritical media and supercritical xenon shows the following. It is known that the removal of the liquid medium from the space of crazes (by drying) leads to a radical collapse of their fibrillar structure [1, 2]. For example, according to the small-angle X-ray scattering data, isometric drying caused aggregation of fibrils to form large strands more than 50–70 nm in diameter under the action of capillary forces. This was accompanied by an abrupt decrease in the specific surface area of the crazed specimens. The drying disturbed the regular arrangement of fibrils in crazes (the maximum in the $I-\varphi$ curves vanished, and the curves were smooth and abruptly decrease, with the maximal intensity being reached at the smallest scattering angles) [2]. Moreover, the action of capillary forces during isometric drying gave rise to compacted surface layers in crazes, which sharply decreased the (gas and liquid) permeability of the porous structure of crazes [1].

The use of supercritical media as adsorption-active media at temperatures above the critical temperature eliminates the action of capillary forces. Indeed, as the above data show, the high-dispersion structure of crazes with characteristic sizes of fibrils and pores (~10 nm) and regular arrangement of fibrils is preserved after the removal of the medium (xenon) from the craze space.

Furthermore, it turned out that the amorphous PETP specimens stretched in xenon are stained for several second with an alcohol solution of the organic dye rhodamine C. This means that “dry” crazes obtained in a supercritical medium remain permeable for low-molecular-weight liquids (in this case, for ethanol).

Thus, in this work, we showed that the crazes forming by PETP deformation in supercritical xenon have a high-dispersion structure with parameters similar to

those for crazes produced in liquid media. The removal of the supercritical medium from the crazes is accompanied by less significant structural rearrangements than those after the removal of liquids.

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