

Crazing of Polymers in a Supercritical Carbon Dioxide Fluid

E. S. Trofimchuk, A. V. Efimov, L. N. Nikitin, N. I. Nikonorova, A. A. Dolgova,
L. M. Yarysheva, O. V. Arzhakova, Corresponding Member of the RAS A. L. Volynskii,
Academician N. F. Bakeev, and Academician A. R. Khokhlov

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Deformation of amorphous and partially crystalline solid polymers in liquid adsorption-active media occurs by a crazing mechanism [1]. Crazing gives rise to fine fibrillar-porous oriented structure with an average diameter of pores and fibrils of about 10 nm.

In this work, supercritical carbon dioxide (CO₂) is proposed to be used as an adsorption-active media. Supercritical media combine the properties of liquids (dissolving power) and gases (high diffusion coefficient, low surface tension). In addition, their physicochemical properties can be smoothly varied over wide ranges while varying temperature and pressure [2, 3].

Some polymers were subjected to orientation stretching in a supercritical CO₂ fluid to form high-modulus fibers (poly(ethylene terephthalate), polyamides, ultra high molecular weight polyethylene) [5, 6] and porous films (polycarbonate) [7]. Supercritical CO₂ in these cases was found to have a plasticizing effect. The main difference of the approach proposed in this work from those described before consists in the use of the adsorption properties of supercritical CO₂ for producing porous polymers by the crazing mechanism.

Note that the removal of the liquid adsorption-active media from the pore space under the action of capillary phenomena is accompanied by significant structural rearrangements, which lead to a considerable decrease in the porosity down to zero value. The porous structure of polymer can be preserved while drying only by applying special procedures, e.g., replacement of the liquid medium, freeze drying [4], or annealing under isometric conditions. One can

believe that using supercritical media will solve this problem.

Thus, in this work, we study specific features of uniaxial deformation of various isotropic nonoriented crystalline and amorphous polymer films in a supercritical CO₂ fluid and determine the formation conditions and parameters of the nanoporous structure by the crazing mechanism.

Here, we will show for the first time that uniaxial polymer deformation in a supercritical CO₂ fluid can occur by a delocalized crazing mechanism, which allows one to obtain open-pore polymer membranes with nanosized pores.

The objects of investigation were commercial non-oriented films of isotactic polypropylene (PP, $M_w = 3 \times 10^5$, thickness 140 μm), amorphous poly(ethylene terephthalate) (PETP, $M_w = 3 \times 10^4$, thickness 100 μm), poly(vinyl chloride) (PVC, $M_w = 1.5 \times 10^5$, thickness 80 μm), and extruded high-density polyethylene (HDPE, $M_w = 2 \times 10^5$, thickness 75 μm). Preliminarily, the PETP films were crystallized at 150°C for 1 h (the degree of crystallinity was 39%) and the PP films were annealed at 140°C for 3 h.

The polymer films were subjected to uniaxial deformation on a high-pressure stretching machine of original design,¹ which was thermostated for 30 min at 35°C and a CO₂ pressure of 10 MPa. The specimens were stretched at a rate of 5% per minute. Supercritical CO₂ was completely removed from the polymer space by simply reducing the pressure in the setup below the critical value (7.38 MPa at 31.1°C).

The bulk porosity was determined as the ratio of the volume increment (calculated by the changes in the geometric sizes) of the specimens while stretching in

Moscow State University, Moscow, 119991 Russia
Nesmeyanov Institute of Organometallic Compounds,
Russian Academy of Sciences, ul. Vavilova 28, Moscow,
119991 Russia

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supercritical CO₂ to the final volume. The average pore size was found by the method of liquid permeability under pressure [8] in an FMO-2 ultrafiltration cell under conditions preventing shrinkage of the specimens. The permeating liquid was ethanol, which was passed through a specimen at a pressure of 0.2 MPa.

The structure of porous specimens was studied by small-angle X-ray scattering on a URS-60 setup (pin-hole collimation, CuK_α radiation, $\lambda = 1.54 \text{ \AA}$) and on a KRM-1 small-angle X-ray camera (slit collimation).

Commercial films of various amorphous and crystalline polymers were subjected to uniaxial deformation in a supercritical CO₂ fluid. The deformation of the amorphous PETP and PVC films in supercritical CO₂ was not accompanied by the formation of classical crazes. The deformed films had very low porosity and were ethanol-impermeable. However, it is known that these polymers below the glass transition temperature in conventional liquid adsorption-active media, e.g., alcohols, are deformed by the classical crazing mechanism. The absence of crazes in the deformation of amorphous PETP and PVC in the supercritical CO₂ fluid can probably be explained by the plasticizing effect of the low-molecular-weight component on these polymers.

While stretching the film of partially crystalline PETP in the supercritical CO₂ fluid, a system of short branching cracks formed. However, on the chips of the specimens, there were neither crazes, nor pores. Perhaps, crazes nucleated on the surface of the PETP film but ceased to grow because of the plasticizing action of supercritical CO₂. Note that keeping the partially crystalline PETP film in the supercritical CO₂ fluid was accompanied by a noticeable (by 10%) increase in its degree of crystallinity.

At the same time, the deformation of the partially crystalline polymers, PP and HDPE, in supercritical CO₂ was uniform, without necking, and was accompanied by intense pore formation. In this case, the working parts of the specimens become white, whereas films stretched in air with necking remained semi-transparent. Figure 1 presents the bulk porosity of the PP and HDPE specimens versus their strain in supercritical CO₂. It is seen that the porosity of the specimens rapidly increases to $\varepsilon = 150\%$ and then remains virtually constant to 300%. The maximal porosities for the annealed PP and HDPE were about 40 and 35 vol %, respectively.

Important data on the microporous structure forming while stretching in supercritical CO₂ were obtained by analyzing the permeability of the deformed specimens and performing dye staining experiments. The specimens were detected to be stainable by alcohol solutions of organic dyes. This may indicate that they contain sufficiently many open

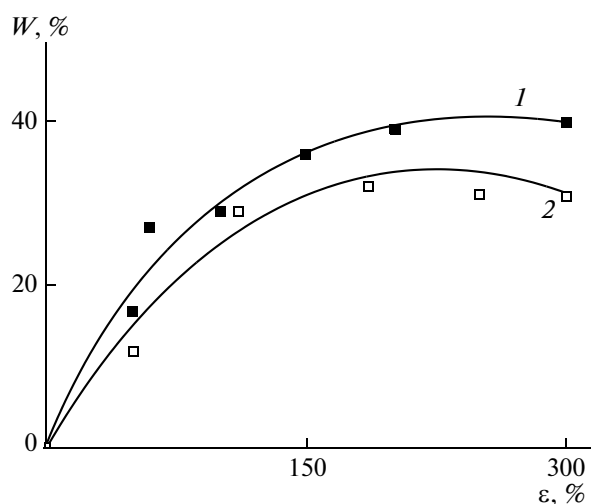


Fig. 1. Effective bulk porosity of (1) annealed PP and (2) HDPE specimens versus their strain in supercritical CO₂.

through pores. The ethanol permeability through the PP and HDPE films stretched in supercritical CO₂ was measured, and the effective cross-sectional sizes of through pores were calculated by Poiseuille's law [8]. Figure 2 shows that the pore size d in the HDPE film within the strain range 80–150% increases from 5.5 to 7.5 nm. With a further increase in the polymer strain in supercritical CO₂, the pore diameter changes insignificantly (from 7.5 to 9 nm). In the PP specimens at the same strains, the pore diameter was 4–8 nm.

It is known from published data that the formation of pores of a size on the order of tens of angstroms is a characteristic feature of deformation of partially crystalline polymers to form crazes. According to small-angle X-ray scattering data, the cross-sectional size of pores between fibrils in crazes forming in deformation of partially crystalline polymers (HDPE, PP) in liquid media is 5–25 nm [9].

The totality of the data obtained suggests that the deformation of PP and HDPE in contact with supercritical CO₂ occurs by a crazing mechanism. Note that the forming porous structure fails to be visualized by microscopic methods. In this case, the so-called delocalized crazing is likely to take place, which is the formation of a system of interconnecting small pores localized within interlamellar regions of partially crystalline polymers. This type of crazing is mainly observed in deformation of partially crystalline polymers (in particular, PP and HDPE) in active liquid media capable of causing limited swelling of the polymers [10].

The structure of the specimens crazed in the supercritical CO₂ fluid (by the example of the annealed PP) was studied by small-angle X-ray scattering. The initial isotropic PP specimen is characterized by an

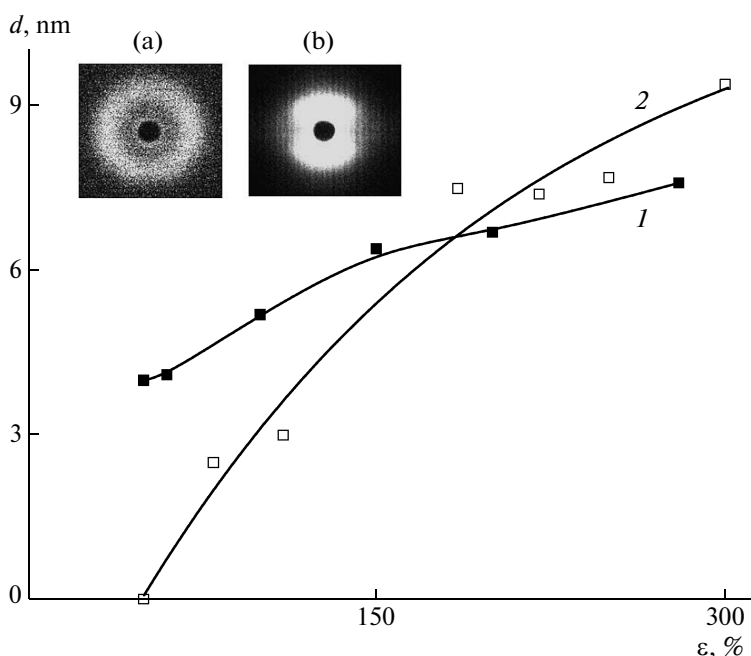


Fig. 2. Average pore diameter d of (1) annealed PP and (2) HDPE specimens versus their strain in supercritical CO_2 and small-angle X-ray scattering patterns of annealed PP (a) without deformation and (b) deformed by 100%.

annular reflection with virtually uniform darkening along a circle corresponding to the long period 240 Å (Fig. 2). Crazeing causes an abrupt (by several orders of magnitude) increase in the small-angle X-ray scattering intensity in comparison with the initial undeformed polymer. The small-angle X-ray scattering pattern of the PP specimen stretched in supercritical CO_2 by 100% exhibits two types of scattering: more intense fanlike diffuse meridional scattering and less intense equatorial scattering extended in the stretching direction (Fig. 2). It was assumed that the meridional scattering is by X-ray diffraction from a system of small pores whose long axes are mostly perpendicular to the stretching direction. The equatorial scattering is from spatially separated fibrils aligned with the stretching direction that connect the walls of crazes. Similar small-angle X-ray scattering patterns were previously recorded for PP films deformed by the delocalized crazeing mechanism [9].

In this work, the equatorial distributions of small-angle X-ray scattering intensity measured in absolute units were used for determining the specific internal surface area of fibrils connecting the walls of crazes by the Porod method modified for oriented systems [11]. The fibril diameter was found by the Guinier method. It was established that the diameter of polymer fibrils in the strain range from 50 to 200% varies insignificantly and is 11–12 nm and the specific surface area of fibrils in this case increases from 70 to 130 m^2/g . The data presented show that the crazes forming in defor-

mation of polymers in the supercritical fluid have fine structure and highly developed surface.

A characteristic feature of crazed materials is the lability of their structure. Specimens of glassy and crystalline polymers the deformation of which is by a crazeing mechanism are largely capable of restoring their sizes after unloading, which is because of collapse of crazes [12]. For example, the relative longitudinal shrinkage of HDPE and PP specimens after stretching in liquid adsorption-active media by hundreds of percent reaches 80–95% of prestrain. At the same time, forced elastic strains of partially crystalline polymers, occurring without violating the continuity of the material, are largely irreversible. For example, the shrinkage of HDPE and annealed PP specimens stretched in air with necking to a relative strain of 100–200% did not exceed 30–40%. After stretching the PP and HDPE films in the supercritical CO_2 fluid by 50–200%, their shrinkage while rapidly unloading was 95–85 and 85–75% of a given strain, respectively. These data confirm the above conclusion of crazeing while stretching partially crystalline polymers in a supercritical CO_2 fluid.

Thus, in this work, we have shown for the first time that uniaxial deformation of polymers in a supercritical CO_2 fluid can occur by a crazeing mechanism and may give rise to a nanosized open-pore fibrillar structure. Since supercritical carbon dioxide is an environmentally clean and fire- and explosion-safe fluid, it is highly promising as a crazeing medium in comparison with conventional liquid adsorption-active media.

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REFERENCES

1. Volynskii, A.L. and Bakeev, N.F., *Solvent Crazing of Polymers*, Amsterdam: Elsevier, 1995.
2. Haytt, J.A., *J. Org. Chem.*, 1984, vol. 49, pp. 5097–5101.
3. McHugh, M.A. and Krukoni, V.J., *Supercritical Fluid Extraction: Principles and Practice*, Stoneham: Butterworth-Heinemann, 1993.
4. Sinevich, E.A., Prazdnichnyi, A.M., and Bakeev, N.F., *Vysokomol. Soedin., Ser. A.*, 1995, vol. 37, no. 9, p. 1521–1528.
5. Hobbs, T. and Lesser, A.J., *J. Polym. Sci., Part B: Polym. Phys.*, 1999, vol. 37, pp. 1881–1891.
6. Garcia-Leiner, M., Song, J., and Lesser, A.J., *J. Polym. Sci., Part B: Polym. Phys.*, 2003, vol. 41, pp. 1375–1383.
7. Hu, X. and Lesser, A.J., *J. Cell. Plastics*, 2006, vol. 42, pp. 517–527.
8. Arzhakova, O.V., Yarysheva, L.M., Gal'perina, N.B., Volynskii, A.L., and Bakeev, N.F., *Vysokomol. Soedin., Ser. B.*, 1989, vol. 31, no. 12, p. 887–889.
9. Efimov, A.V., Lapshin, V.P., Kozlov, P.V., and Bakeev, N.F., *Vysokomol. Soedin., Ser. A.*, 1981, vol. 23, no. 4, p. 882–886.
10. Efimov, A.V., Bondarev, V.P., Kozlov, P.V., and Bakeev, N.F., *Vysokomol. Soedin., Ser. A.*, 1982, vol. 24, no. 8, p. 1690–1695.
11. Efimov, A.V., Bulaev, V.M., Ozerin, A.N., Rebrov, A.V., Godovskii, Yu.K., and Bakeev, N.F., *Vysokomol. Soedin., Ser. A.*, 1986, vol. 28, no. 8, p. 1750–1956.
12. Volynskii, A.L. and Bakeev, N.F., *Strukturnaya samorganizatsiya amorfnykh polimerov* (Structural Self-Organization of Amorphous Polymers), Moscow: Fizmatlit, 2005.