

# Preparation of Nanoporous Polyolefin Films in Supercritical Carbon Dioxide

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**Abstract**—The peculiarities of uniaxial deformation of semicrystalline polyolefins were studied using high-density polyethylene and isotactic polypropylene as an example in carbon dioxide at 35–75°C and pressures of 0.1–30 MPa. A nanoporous structure (with pore diameters of 3–7 nm) started to form in polymer films by the delocalized crazing mechanism at 4–5 MPa and higher. The increment of the pore volume depends on the parameters (pressure, temperature, and density) of the medium and on the deformation of the polymer, reaching 30–70%. The pore formation by the crazing mechanism was most effective when CO<sub>2</sub> was in the supercritical state at a nearly critical temperature (35°C) and its density approached the density of a liquid.

**Keywords:** crazing, supercritical carbon dioxide, nanoporous structure, polyethylene, polypropylene

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## INTRODUCTION

Polyolefins (predominantly, polyethylene (PE) and polypropylene (PP)) are thermoplastic materials produced on a large scale. They have found use in various fields due to a combination of high elasticity modulus, water resistance, chemical inertness, and easy processing. Porous materials based on PE and PP are used as insulation, membrane, and medical materials.

There are many methods for preparing porous PE and PP [1] with pores with different diameters: powder sintering or fiber fusion (nonwoven fabrics) [2], foaming [3], track etching [4], and extension [5]. The materials obtained by fusion generally have micron pores with very wide pore distribution. Other methods of those mentioned above afford pores with smaller diameters. Foaming is a universal method for obtaining a porous structure in polymers. The foaming agents are porophores [6, 7]—the substances that form pores as a result of chemical decomposition, liberating gaseous products from the polymer matrix, or in a physical process, e.g., evaporation of a liquid.

Recently, polymer foaming in supercritical (SC) carbon dioxide was widely developed [8–11] due to great interest in so-called “green” technologies and high solubility of SC-CO<sub>2</sub> in almost all polymers. The parameters of a porous structure (e.g., the pore diameter and the number of pores per unit volume) can be changed within reasonably wide limits by varying the temperature, saturation pressure, and decompression rate and also by using various cosolvents [8, 9]. How-

ever, foaming of highly crystalline polymers of the type of isotactic PP should be conducted under strictly controlled conditions at a definite temperature (around the melting point) [9–11].

Another widely used method for creating a porous structure is uniaxial stretching; it requires the use of films with a specific highly crystalline ordered structure of “rigid elastic” type [12]. Crazing in liquid adsorption active media is a more universal procedure for creating a nanoporous structure in various amorphous glassy and semicrystalline polymer films and fibers. Crazing is one of the mechanisms of plastic deformation of polymers that occurs during the concurrent action of uniaxial extension and medium [13–15]. As a result, the polymer acquires a specific orientated fibrillar porous structure with nanometer dispersity. As is known, some liquid media capable of decreasing the surface energy of the polymer (e.g., alcohols, hydrocarbons, amines, etc.) facilitate the formation of a structure of this kind [15]. However, their use is limited because of their toxicity and fire and explosion hazard.

In this study, the ability of carbon dioxide in the supercritical state to combine the properties of a liquid (solubility) and gas (low surface tension and the absence of capillary effects) was used to perform environmentally safety crazing. Earlier, it was shown [16–18] that this process can occur for semicrystalline high-density polyethylene (HDPE) and isotactic PP films. The uniaxial deformation of these polymers in SC-CO<sub>2</sub> at a pressure of 10 MPa and a temperature of 35°C occurs uniformly, without neck formation and is

accompanied by active pore formation. The formation of a porous structure of this kind was attributed to the formation of a system of crazes localized mainly in the interlamellar regions (this process is called delocalized crazing according to the mechanism). This method allowed to obtain membranes with parameters close to those generally characteristic for polyolefins deformed by the crazing mechanism in liquid media. The volume porosity was 30–40% and the mean effective pore diameter was 3–9 nm depending on the degree of deformation. The use of small-angle X-ray scattering allowed us to establish that the mean diameter of fibrils that connect the craze walls changed but slightly as the degree of deformation increased and was ~10 nm.

The goal of the present study was to develop the new approach to the creation of porosity in crystalline polyolefins suggested earlier; to investigate the effect of the conditions of uniaxial extension (pressure, temperature, and porosity of SC-CO<sub>2</sub>, and the degree of deformation of the polymer) on the parameters of the porous structure and its evolution in high-density polyethylene and isotactic polypropylene films.

The goal of this study was to determine the conditions of the formation of a porous structure and establish the dependence of the activity of an SC medium as a crazing agent on its physicochemical parameters.

## EXPERIMENTAL

As objects for our study, we used industrial isotactic polypropylene ( $M_w = 3 \times 10^5$ , thickness 120–140  $\mu\text{m}$ ) and high-density polyethylene ( $M_w = 2 \times 10^5$ , thickness 75  $\mu\text{m}$ , melting temperature 130°C, 70% crystallinity) films obtained by extrusion molding from a melt. The starting PP films were preliminarily annealed at 140°C for 3 h. After annealing, the films had a melting point of 165°C and crystallinity 65%. For studies, the starting films were prepared as standard samples of dumbbell-shaped specimens with the working area of 6  $\times$  20 mm.

The uniaxial deformation of the polymer films was performed in a high-pressure stretching device developed at the Institute of Organoelement Compounds in collaboration with the Department of Chemistry, Moscow State University. A scheme of the unit and its description are given in [18]. The high-pressure cell was thermostatted for 30 min at the temperature of experiment before each experiment with a new sample. Then it was filled with CO<sub>2</sub> (reagent grade), the pressure in it was set at a definite level, and it was thermostatted for another 10 min. The working temperature was varied from 35 to 75°C; the CO<sub>2</sub> pressure, from 0.1 to 30 MPa. The sample was then extended to the required degree of deformation 50–400%. The extension rate was 25%/min. CO<sub>2</sub> was removed from the polymers by releasing it out of the device through a valve in the cell and subsequently keeping the samples at atmospheric pressure for 48 h.

The effective volume porosity ( $W$ ) and the increment of the sample volume due to pore formation ( $\Delta V/V_0$ ) in the polymer samples were evaluated under the isometric conditions from the change in their geometrical parameters after the deformation in CO<sub>2</sub>:

$$W = 100\%(V - V_0)/V,$$

$$\Delta V/V_0 = (V - V_0)/V_0,$$

where  $V_0$  is the initial volume of the polymer, and  $V$  is its final volume.

The measurements were conducted at atmospheric pressure after extracting the films from the cell in which polymer extension was performed; the samples remained in the strained state in the stretching device. The film thickness was measured with a U3B-2 optimeter to an accuracy of 0.001 mm; the linear dimensions were determined on a projector (magnification  $\times 8$ ) to an accuracy of 0.01 mm.

The reversibility of polymer deformation in CO<sub>2</sub> was evaluated from the relative shrinking in the longitudinal direction. For this purpose, the starting sample was deformed in CO<sub>2</sub> under definite conditions until the required degree of deformation was achieved and then unloaded by means of the reverse run of the stretching device. Then the polymer film was extracted from the cell, released from the clamps, and allowed to relax in a free state under normal pressure for 2 days. The shrinking was determined as the ratio of the reversible deformation (the difference between the length of the extended sample and that of the sample after shrinking) to the preliminary deformation of the sample (the difference between the length of the extended sample and its initial length).

The morphology of the samples was studied by scanning electron microscopy (SEM) on a Hitachi S-520 instrument. A chip of the deformed polymer film cooled to the liquid nitrogen temperature was preliminarily prepared, fixed on a special observation table, and coated with gold by sputtering.

## RESULTS AND DISCUSSION

As is known [19], the dissolving (or swelling) ability of supercritical carbon dioxide depends on its density, which is unambiguously determined by the pressure and temperature. Figure 1 presents a set of curves that reflect the pressure dependence of the density of SC-CO<sub>2</sub> at three different temperatures above the critical point (31.8°C). It can be seen that all the curves are S-like and that the gas density starts to sharply increase in the region of the critical pressure (7.4 MPa). As the temperature increases, the density increases less abruptly, the change becoming more diffuse. The strongest temperature dependence of the density of SC-CO<sub>2</sub> is observed at a pressure of 10 MPa: at 35°C the gas density is three times higher than that at 75°C. At higher pressures (20–30 MPa) and pressures below the critical difference, the CO<sub>2</sub> densities are less significant.

Characteristics of the porous structure of PP and HDPE uniaxially deformed in supercritical CO<sub>2</sub> at a pressure of 10 MPa and a temperature of 35°C

Degree of deformation, %	Volume porosity, vol %	Pore diameter <sup>1</sup> , nm	Diameter of fibrils <sup>2</sup> , nm	Specific surface of fibrils <sup>2</sup> , m <sup>2</sup> /cm <sup>3</sup>
PP				
50	20	4	10	60
100	29	5	10	100
150	31	6	10	120
HDPE				
100	27	3	—	—
130	29	3	10	—
200	32	7	—	—

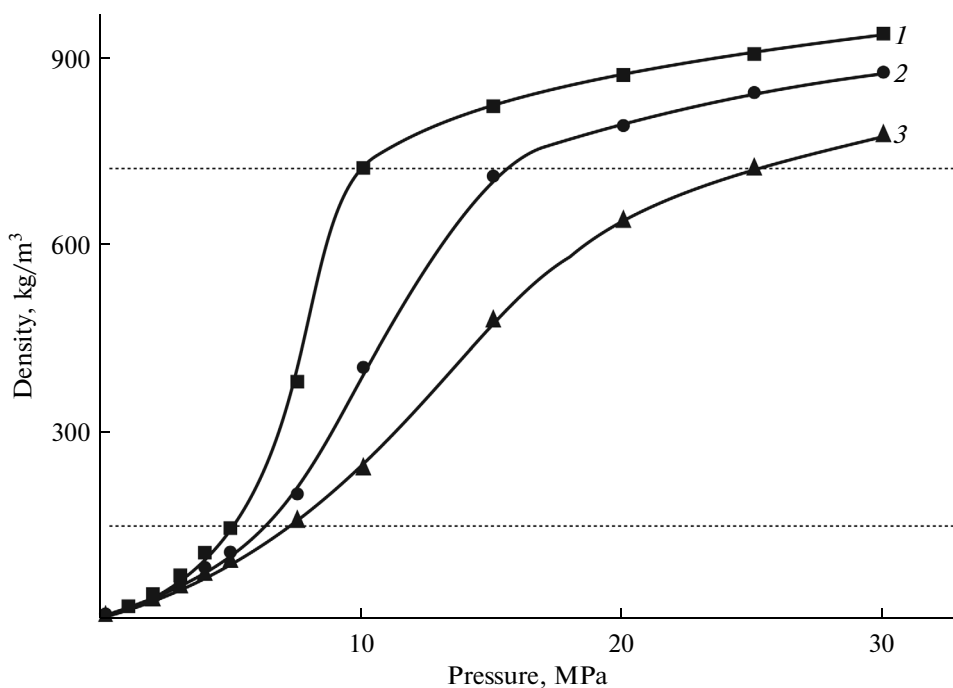
<sup>1</sup> Determined by the liquid permeability method.

<sup>2</sup> Determined by the small-angle X-ray scattering method.

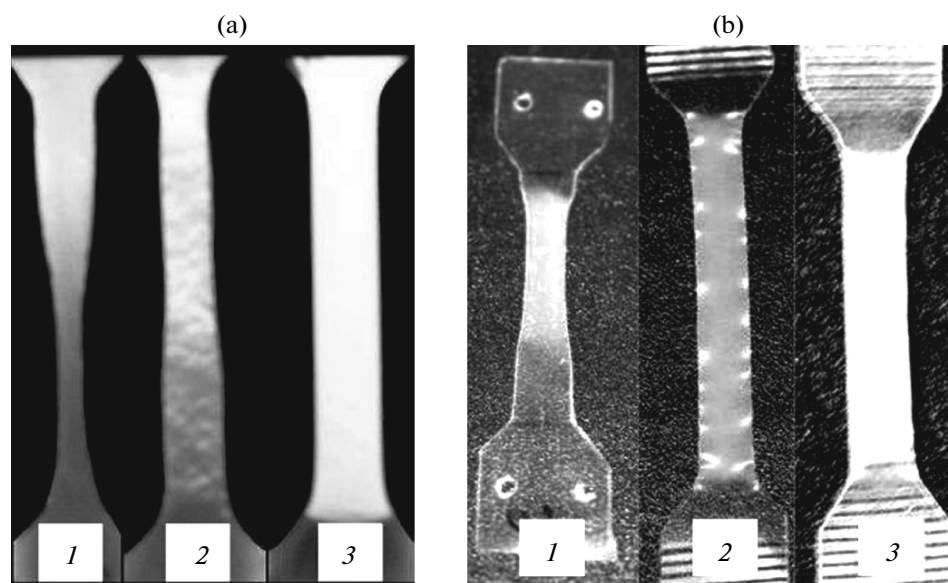
Figure 2 shows the photographs of the isotactic PP and HDPE samples deformed in CO<sub>2</sub> at 35°C and different pressures. At 0.1 MPa, the polymers are deformed via the formation of a neck (the region of drastic narrowing in the samples), like in air at atmospheric pressure. Starting from 4–5 MPa, the shape of the extended films changes, the deformation being quite uniform along the whole length of the working part; the samples start to opalesce, becoming milk-white at higher pressures. Their volume increases considerably compared with that of the nondeformed starting films. This may be indicative of the formation

of a porous structure. The volume porosity  $W$  of the polymer films increases with the degree of deformation, reaching 40 vol % (the fraction per pore volume in the deformed sample).

As is known, SC-CO<sub>2</sub> is an effective foaming agent, which gives porous polymers with cellular-type pores [20]. According to SEM studies, however, the porous films obtained by uniaxial extension have no structure of this kind; the micrographs of the cleavage of 100% deformed HDPE in SC-CO<sub>2</sub> do not show cellular pores (Fig. 3). Similar images were observed earlier for porous HDPE films obtained by uniaxial extension



**Fig. 1.** Theoretical pressure dependence of the density of carbon dioxide at (1) 35, (2) 50, and (3) 75°C. The calculated data were obtained with NIST software (National Institute of Standards and Technology, Gaithersburg, MD).



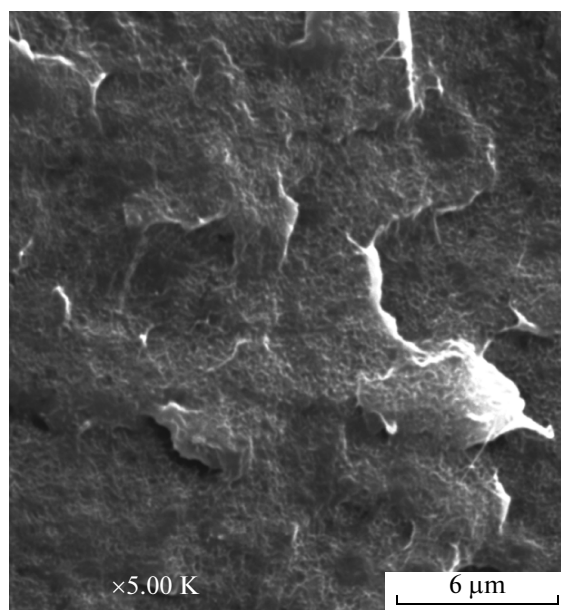
**Fig. 2.** Photographs of (a) HDPE and (b) PP samples after their 100% deformation in  $\text{CO}_2$  at a temperature of  $35^\circ\text{C}$  and pressures of (1) 0.1, (2) 5, and (3) 10 MPa.

according to the delocalized crazing mechanism in liquid adsorption-active media [21, 22]. A porous structure of this type forms as a result of the simultaneous and reasonably regular separation of lamels lying mainly perpendicularly to the direction of extension so that the crazes themselves, which are fractures filled with highly disperse fibrillized material, are localized in the interlamellar regions of the crystalline polymer. In this case, the pores are the space between

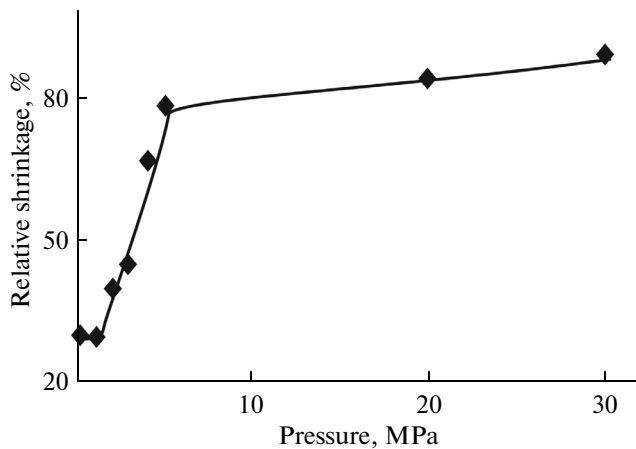
the separated fibrils and the nondeformed regions of the polymer.

Another peculiarity of the samples deformed in  $\text{CO}_2$  at  $35^\circ\text{C}$  above 4–5 MPa lies in the fact that after the external strain was removed, they are characterized by high shrinkages in the longitudinal direction that coincides with the extension axis. Figure 4 presents the dependence of the relative shrinkage on the gas pressure for isotactic PP preliminarily extended to 150% in  $\text{CO}_2$ . This degree of deformation was not chosen randomly. It is quite far from the yield point ( $\sim 30\%$  for isotactic PP); therefore, active plastic deformations (neck and shear deformations, or crazes) occur in this region. However, it is quite moderate in the case of crazing for the contribution of the shear deformation to the total deformation to be minimum. According to Fig. 4, below 1 MPa the shrinkage is independent of pressure and is only 30%, which coincides with its value in the experiment in air at atmospheric pressure. At elevated pressure, the contribution of the reversible deformation increases considerably and at 5 MPa the shrinkage reaches 80%. Further increase in the pressure and the transition into the SC- $\text{CO}_2$  region do not affect the reversible deformation so greatly. For example, at 30 MPa the sample shrinkage increases by only 10% and is  $\sim 90\%$ . Note that reversible deformations as large as this for semicrystalline solid polymers are characteristic only after their deformation by the crazing mechanism [15].

Thus, pore formation in the films of semicrystalline polyolefins during their uniaxial deformation in carbon dioxide occurs by the delocalized crazing mechanism. This process starts already in the precritical range of  $\text{CO}_2$  pressures despite the rather low gas density (140–150  $\text{kg}/\text{m}^3$ , Fig. 1). This may be due to the



**Fig. 3.** Micrograph of cleavage of HDPE deformed in  $\text{CO}_2$  at  $35^\circ\text{C}$  and 10 MPa. 100% deformation.



**Fig. 4.** Dependence of the relative shrinkage of PP samples preliminarily deformed to 150% at 35°C in CO<sub>2</sub> at different pressures.

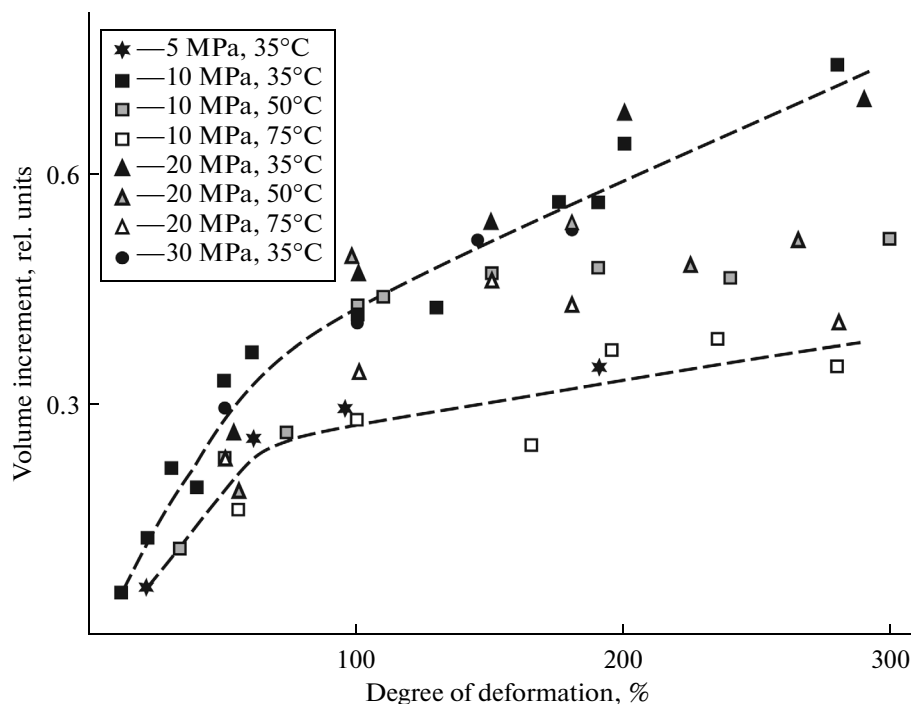
fact that carbon dioxide shows considerable fluctuations of density in the pressure range 5–12 MPa [23].

The effect of CO<sub>2</sub> pressure and temperature in the SC region on the parameters of the porous structure of semicrystalline olefins in the course of extension is considered below on isotactic PP as an example. Figure 5 shows the dependence of the increase in the volume of the polymer film samples due to pore formation on the degree of deformation under various experimental conditions. It can well be seen that all the points lie in a definite region limited by two

curves. The upper curve lies at the values obtained at 35°C and 10–30 MPa when the CO<sub>2</sub> density was high, 720–900 kg/m<sup>3</sup>. The lower curve presents the data for the samples obtained at 35°C and 5 MPa and 75°C and 10 MPa; the gas density in this case was four to six times lower, only 150–220 kg/m<sup>3</sup>. The pore volume in the polymer film increases with the degree of deformation; the maximum increment of volume was ~75% at high gas density and 35–40% at low gas density. Note that an increase in temperature even at high pressure leads to lower porosity at more than 100% deformation (for example, at 50°C, 20 MPa, and ~800 kg/m<sup>3</sup> compared with the data obtained at 35°C). This may be due to the fact that, at high degrees of deformation at elevated temperatures, the contribution of crazing that occurs with pore formation increases and accordingly the percent of shear deformation, which does not lead to an increase in porosity, increases.

Thus, the activity of carbon dioxide as a crazing medium is primarily affected by its density and temperature. Pore formation by the crazing mechanism in polymers in CO<sub>2</sub> is most effective when CO<sub>2</sub> is in the supercritical state at a nearly critical temperature (35°C) and when its density approximates the liquid density. Variation of the gas pressure from 10 to 30 MPa does not significantly affect the film porosity. An increase in the temperature negatively affects the formation of the pore structure, suppressing craze formation.

The porous structure obtained during the uniaxial deformation of polymers in CO<sub>2</sub> by the delocalized



**Fig. 5.** Dependence of the volume increment of PP samples during uniaxial deformation in CO<sub>2</sub> at different pressures and temperatures.

crazing mechanism was studied and its parameters determined by small-angle X-ray scattering and liquid permeability methods under the ethanol pressure. A detailed description of the experimental and calculation procedures was given in [17, 18]. Some results of these studies are summarized in the table. It can be seen that the porous structure is highly disperse and has a highly developed specific surface (up to  $120 \text{ m}^2/\text{cm}^3$ ). The obtained samples can be attributed to nanoporous membranes, whose pore diameter slightly increases with the degree of deformation (3–7 nm).

It is important to note that in contrast to foamed materials, the polymers deformed by the delocalized crazing mechanism in SC-CO<sub>2</sub> have an open-pore interpenetrating structure. For example, they quickly (within a few seconds) get colored by the alcohol solution of the dye rhodamine C throughout the whole volume.

## CONCLUSIONS

A new mechanism of formation of a nanoporous structure in semicrystalline polymers in supercritical carbon dioxide, which differs from the foaming mechanism, was considered. This is the delocalized crazing process, which was earlier found and investigated in studies on uniaxial deformation of polymers in liquid adsorption-active media. In contrast to foaming, which is generally conducted at elevated temperatures close to the vitrification or melting point of a polymer and at rather high pressures, pore formation by the crazing mechanism is most active near the critical point. As a result of crazing, a system of interpenetrating open pores with diameters of several nanometers are formed in semicrystalline polyolefins. Porous membranes of this kind can be of interest as a basis for creating the functional materials with regulated properties.

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