

MODIFICATION OF SOME SEMICRYSTALLINE POLYMERS BY MEANS OF SUPERCRITICAL CARBON DIOXIDE

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INTRODUCTION

Recently, steadily increase the flow of scientific publications on the study of the behavior of polymers in supercritical (SC) media, and especially in supercritical carbon dioxide (SC-CO₂). This increased attention due to the fact that SC-CO₂ is a solvent or plasticizer for a variety of polymers, while possessing such advantages as compared to traditional solvents, such as low cost, environmental friendliness, non-inflammability, easy to remove from the polymer after the process, and others.

Speed and quantitative characteristics of SC-CO₂ diffusion in polymers can be finely adjusted by varying the pressure and / or temperature in the volume where the process takes place. Very promising is the possibility of the formation of directed polymers in a porous structure by varying the pressure and / or temperature of SC-CO₂ exposure, as well as the speed of decompression. Obtaining materials with a given morphology of the porous structure is extremely important and relevant scientific direction.

Creation and study of materials with a given porous structure is extremely important and topical field of research science and technology of polymers. Now most of the processes of porous structures is associated with significant amounts of toxic chlorine and fluoride of low-boiling solvent. They are very hard to remove from the polymer at the end of the process. Therefore, recently much attention is paid to porous materials with the use of gaseous substances and, in particular, the SC-CO₂ as an active pore-forming environment.

To further develop the theory of pore formation requires a thorough study of all factors affecting the morphology of the porous structure in the polymer after desorption of CO₂ from them. Especially important is the opportunity to influence the crystalline structure of polymers to change their

thermomechanical characteristics of for intensification and optimization of processes for further processing of polymers in SC-CO₂, such as extraction, impregnation, pore formation, lamination, changing the surface properties and morphology of the distribution of free volume for non-porous polymers.

In the description of the morphology of porous structures using various techniques - mercury porosimetry to fill with water at high pressures, the nitrogen adsorption method, scanning and transmission electron microscopy, etc. .However, in some cases there is discrepancy in the values of parameters obtained by different methods. To analyze the factors influencing changes in the morphology of the porous structure as a result of external action is necessary to use a large number of experimental techniques due to limitations as the range of measured characteristics and properties of specific material (hydrophobicity, crystallinity, etc.) and parameters of its interaction with external environment . To account for the influence of environment on the behavior of polymers can be applied to various models and equations of state . There are various theoretical approaches. Among them, the methods of discrete molecular dynamics , thermodynamic approaches, as well as molecular (discrete and continuous) theory. One promising approach to describe the experimental data on the characterization of the morphology of porous structures is the lattice-gas model (LGM), , with which it is possible to calculate the morphology of the porous structure in a wide range of parameters obtained from the set of experimental techniques that can make a complete picture of changes in porous structure of polymers as a result of exposure to supercritical carbon dioxide.

To investigate the possibilities of changing the structure of polymers as a result of the impact of SC-CO₂ and describe the observed effects with the LGM interest semi-crystalline polymers such as UHMW polyethylene (UHMWPE), to study the processes of pore formation which is an important component for supercritical technologies for the production of nanoporous materials for biomedical tribology and in general understanding of the effects on crystalline polymers with supercritical carbon dioxide in terms of obtaining directional gradient porous Organizational Structure.

Another promising recently for studying the effect of SC-CO₂ on the structure of polymers and are highly porous aerogels based on microcrystalline cellulose with a porosity greater than 95% and a density of less than 0.1 g/cm³.

In the case of highly porous and so semi-crystalline polymers is of interest to examine how they influence SC-CO₂ and possibilities of experimental techniques for describing data structures.

RESULTS

Effect of SC-CO₂ in the polymer matrix of polyethylene and aerocellulose.

The main purpose of the experimental work was to obtain new data, which in the future be used to test the theory of modeling the swelling of polymers in supercritical conditions at pressures of 70-250 atmospheres. The samples used ultra-high molecular polyethylene (UHMWPE), which is widely used for medical tribology, and highly porous aerogels based on cellulose. The polymer is partially crystalline UHMWPE with a degree of crystallinity of 40-50%. Therefore, this research is particularly important to predict the behavior of the polymer and the study of changes in its nanoporous structure in the supercritical medium. In the course of the UHMWPE samples were obtained, processed in SK-CCL at different exposure modes - the supercritical pressure of the medium and the speed of decompression, which should affect both the amorphous and a crystalline portion of the polymer. The obtained samples were studied using small-angle X-ray scattering and wide-angle, as well as by adsorption of nitrogen. As a result of the scattering curves were obtained (from the method of X-ray scattering) and adsorption curves (adsorption of nitrogen).

As a highly porous samples using cellulose-based aerogels [Budtova, Aerocellulose: New Highly Porous Cellulose Prepared from Cellulose-NaOH-Aqueous Solutions, Biomacromolecules 2008, 9, 269-277] with the densities of 0.1-0.3 g/cm³ and above an average pore size range of 0.7-1 microns, prepared on the basis of commercial celluloses with degrees of polymerization from 187 to 500 from solutions of cellulose / NaOH / water by multiple-method in the presence of surface-active agents (surfactants), followed by drying in supercritical carbon dioxide at 37 ° C, 8 MPa in a flow mode with flow velocity of the supercritical medium 5 kg / h. To obtain X-ray scattering curves used diffractometer Bruker-AXS SMART 1000 to coordinate (CCD) detector. To obtain sorption isotherms used high-speed analyzer for measurement of gas adsorption specific surface area of the company Nova Quantachrome were used. To study the behavior of polymers in SC-CO₂ using the original setup [Gallyamov et al, Polymer Science, v. 44, № 6, p. 946, 2002]. Carbon dioxide in accordance with GOST 8050-85, had a purity of 99.998% (of BKZ, Linde Gas AGA, Balashikha). According to his passport moisture volume fraction of CO₂ was not more than about 5*10⁻⁶ %. Fig. 1-4 show the experimental data.

Fig. 1 and 2 show the experimental X-ray scattering curves of samples aerocellulose and UHMWPE, respectively.

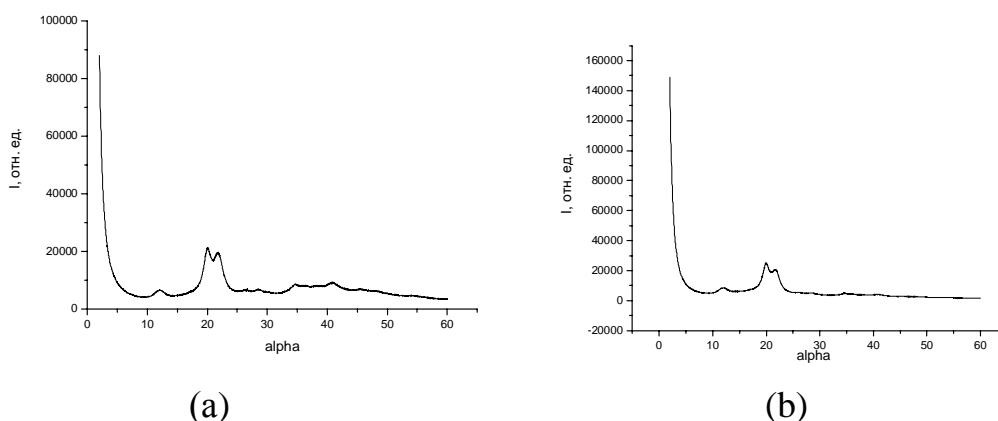


Fig.1. Aerocellulose scattering curves before (a) and after (b) processing in SC-CO₂

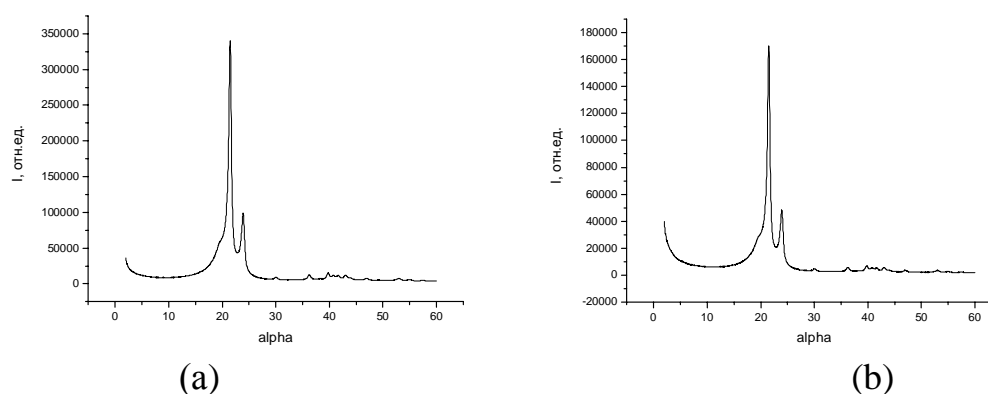


Fig.2. UHMWPE scattering curves before (a) and after (b) processing in SC-CO₂

By analyzing the area under the curve for the corresponding peaks in the scattering curve were determined degree of crystallinity for all samples. It was found that the degree of crystallinity of UHMWPE as a result of treatment in the SF-conditions varies slightly and is in both cases, 53-57%, which may be due to the lack of sorption of carbon dioxide, because known that the polymers are largely exposed to SC-CO₂ modified the degree of swelling is usually more than 10%.

Whereas for an appreciable reduction aerocellulose degree of crystallinity from 27 to 19%, due to the amorphization of the crystal under the influence of SC-CO₂, which can provide a good basis for modifying the data structure of the samples to create different kinds of inhomogeneous structure of the composites. Fig. 3 and 4 shows sorption isotherms for both materials before and after treatment in SK-conditions that were used to analyze the morphology of the porous structure of the adsorption method.

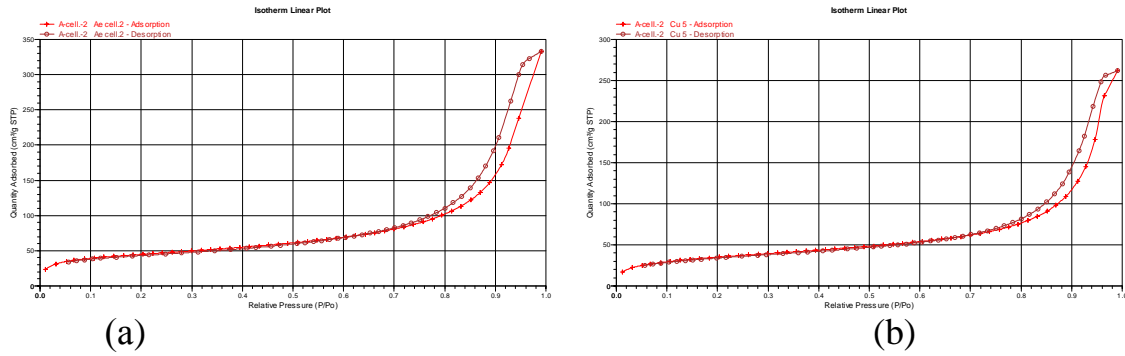


Fig.3. Sorption isotherms aerocellulose before (a) and after (b) processing in SC-CO₂

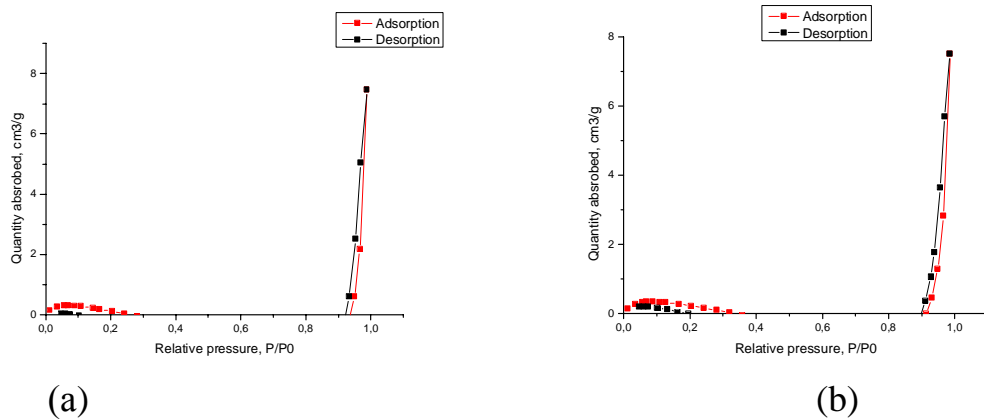


Fig.4. Sorption isotherms of UHMWPE (a) before and after (b) processing in SC-CO₂

The experimental data were interpreted within the frame of the model were obtained pore size distribution before and after treatment in SC-CO₂.

Determination of the size distribution function.

To calculate the local equilibrium distributions of molecular adsorbate lattice gas model is used. Description of the structure of complex cellular systems based on the procedure for the selection of model sites of the porous system with a simple ideal geometry (supermolecular level) and the description of adsorption in the pores of different sizes.

Porous structure will be modeled using a dispersed body parts has a certain characteristic size of $L > \lambda$ where λ - the size of adsorbate molecules. Supermolecular level includes parts of the porous body with a specific geometry of the characteristic size, in this case, the cylinder diameter D . In general, $D < L$, with $D = L$ is time for all the considered area, with $D = 0$ there is no time that captures the presence of dead-end pores, adjacent to this site q .

Supramolecular structure of a given distribution function F_q , characterizing the fraction of sites of type q , and F_{qp} , characterizing the probability of finding near the site of the type q plot of the p ; $\sum_p F_{qp} = F_q$, $1 < q$, $p < Q$, where Q - the number of types examined sections of the porous body. Also, we introduce

a function H_{qp} - conditional probability of finding a plot of the p pores near the site of the pore type q (in some chosen direction) $F_{qp} = F_q H_{qp}$, with $\sum_p H_{qp} = 1$. The function allows H_{qp} relatedness of different types of sites have to supermolecular level. It allows you to weigh the probability of sequences of specific types of pores with pair distribution function, which are known analogues of pair functions at the molecular level, including analogs of the radial pair functions of X-ray analysis.

Within each plot q supramolecular scale of the set of nodes that are available particles of the adsorbate, divide into groups (types of nodes) with the same energy due to the atoms of the solid and given the fact that within each group nodes have the same configuration of neighbors (up to rotation / reflection).

As the basic lattice structure will use the grid with the number of nearest neighbors $z = 6$, as repeatedly pointed out that this structure leads to the best agreement with the critical parameters of bulk fluids. Pore space is divided into elementary volumes (nodes) v_0 , equal to the size of the particle, and of them are groups of nodes with the same adsorption capacity, including, with the same energy of interaction between sorbate-sorbent Q_k , where k varies up to 1 up to t , t - the number of groups of nodes. Fraction of nodes that are in the group k to be denoted by f_k .

In the cylindrical pore ratio of shares of different types of units is determined by the geometrical considerations $\frac{f_k}{f_{k+1}} = \frac{R_p - r(k)}{R_p - r(k+1)}$, where $r(k)$ - the distance from the node type to the to pore surface, and R_p - the radius of the pores. Number of neighbors along the layer is fixed as $z_{qq} = 4$, so that the core of a balanced ratio of $\sum_q z_{pq} = z$ obtain $z_{qq+1} + z_{qq-1} = 2$. Considering the second balanced ratio $f_q + z_{qq+1} = f_{q+1} + z_{q+1q}$ system is deployed.

One of the most important aspects of the theory is the definition of pore size distribution $F(D)$, which characterizes the fraction of pores having a diameter D . The essence of this procedure is to solve the inverse problem of determining the function of the experimental data on the desorption branch of the hysteresis loop, which corresponds to the equilibrium adsorption. It is usually assumed that all pores are isolated, so calculating the adsorption in the pore diameter D , can be varying the weights of individual contributions has a total isotherm, which correlate with experimental isotherm $\theta_{\text{exp}}(p/p_0)$, here p_0 - vapor pressure

$$\theta_{\text{exp}}(p/p_0) = \int_{D_{\text{min}}}^{D_{\text{max}}} F(D) \theta(D|p/p_0) dD, \text{ where } D_{\text{min}} \text{ and } D_{\text{max}} - \text{maximum and}$$

minimum size range of pore diameters considered. Therefore, the type of theoretical isotherms $\theta(D|p/p_0)$ depends obtained distribution function $F(D)$. Such calculations currently being carried out on the basis of the equations of functional density. As a measure of differences between the theoretical curve

is taken from the experimental integral square difference between the two functions. Distribution function is optimized to minimize this measure.

As an illustration of the method we consider the nitrogen adsorption isotherm model aerocellulose. Interaction in the system are described by only three parameters: the size of a cell and two energy interaction parameter adsorbate molecules with each other and with the walls of the pores. As the cell size used the size of the nitrogen molecule $\lambda \approx 0.4$ nm. To determine the interaction parameter of adsorbate molecules with each other were calculated isotherms of nitrogen in the variation of this parameter. When compared with the experimental isotherm was found that the best fit isotherm is reached at a value of interaction parameter nitrogen molecules to each other is 190 cal/mole. This value was used in further calculations. Figure 5 shows the results of the optimization procedure to determine the distribution function of pore size.

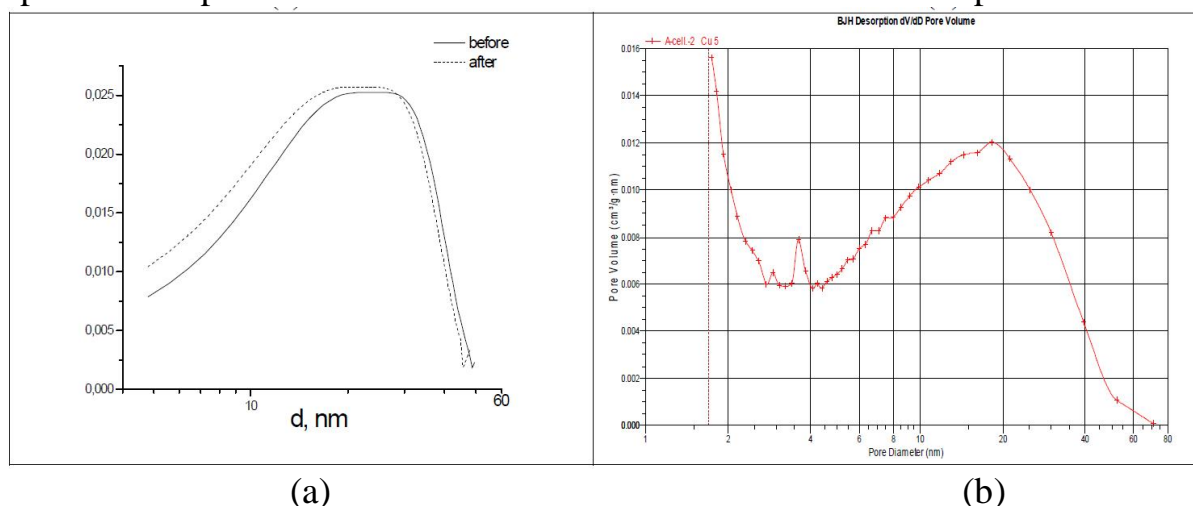


Fig. 5 (a) The theoretical pore size distribution, d - pore diameter in nanometers, (b) a similar distribution obtained by standard methods based on the equations of Kelvin.

The theory of the LGM developed a method for calculating the distribution of pores in the polymer matrices based on the size of the adsorption isotherm of nitrogen. The study sample aerocellulose showed that as a method that uses the theory of the LGM, and the standard technique based on the Kelvin equation lead to different results, both in small and large sizes of the pores. Obviously, the results of standard analysis in the small pores lead to unphysical values of the distribution function, since the curves in Fig. 3b that for sizes less than 4 nm is observed hysteresis loop. It was found that after treatment with SC-CO₂ distribution function of pore size is changing its parameters. Similar results were obtained for the polymeric matrix of polyethylene.

As a result, work was to investigate the influence of supercritical carbon dioxide on the morphology of the porous structure and crystallinity of the samples UHMW polyethylene and aerocellulose. It was found that SC-CO₂

can significantly modify the crystalline part of cellulose and not too much effect on the crystallinity of UHMWPE. At the same time he is able to change the morphology of the porous structure of both samples. The combination of experimental data on electron microscopy and nitrogen adsorption, together with the theoretical method of calculating porosity allowed to fully explore the porous structure of both materials before and after exposure to SC-CO₂ and get the most complete picture regarding the applicability and limitations of each method that may further contribute towards acquiring various kinds of gradient structures and composites of polymers under the influence of supercritical carbon dioxide.

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