

## Obtaining Nanoporous Inorganic Sheets

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**Abstract**—An original technique to obtain porous sheets from various inorganic substances (silicon dioxide, hydroxyapatite, and silver) using polymer matrices whose high-disperse structure is formed by the crazing mechanism has been described. The structure of a porous sheet and its characteristics can vary in wide ranges (the diameter of pores can vary from several nanometers to several micrometers) and depend on the matrix morphology of the initial polymer, its strain degree, and the amount of the inorganic component and the method of its introduction. The conditions needed to form a sheet are formulated: the degree of the polymer film strain should be no less than 50% and the filler content should be no less than 10 vol %.

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### INTRODUCTION

Porous materials based on various compounds of inorganic nature (metals, oxides, and salts) find wide applications as filters, catalyst carriers in hydrogen energetics, matrices for synthesis, etc. [1–3]. The properties of such materials are determined by their chemical composition, thermal and chemical stability, pore sizes, morphology, the character of their distribution, and their specific surface.

Several main methods used to obtain porous inorganic materials are described in the literature: baking under pressure [4–6], chemical [7] or electrochemical [8] etching, matrix synthesis with the subsequent removal of the matrix [9–11], sol-gel technology [12, 13], and foam casting [14]. All these methods have their own advantages, e.g., simplicity, as in the case of baking, or the production of ordered pores of a small diameter by electrochemical etching or sol-gel formation in the presence of polymer micellar and colloid systems. However, the methods listed are used for a concrete class of chemical substances and the possibilities for controlling the morphology of a resulting porous system are limited.

In this work we propose an original method to obtain porous sheets from inorganic substances. Porous polymer films are used as matrices, and their high-disperse structure is formed according to the crazing mechanism [15, 16]. Crazing is a fundamental property of the strain of amorphous vitreous and partially crystalline polymers by their strain in adsorption-active media (AAMs) and makes it possible to create porous structures of a nanometer dispersity level with an average pore diameter of 5–20 nm. Universal methods for obtaining various composites with a high level of mutual dispersity of the matrix and filler are developed on its basis [17]. In this case a strong

control of the morphology of composites is possible because the formation of the second component phase takes place only in crazed polymers. When the matrix is removed by dissolution or burning, an introduced inorganic substance forms a solid residual, in certain cases, in the form of a porous sheet [18, 19].

This work is aimed at creating porous inorganic sheets of various natures from metals, oxides, and salts with the use of porous polymer matrices obtained by the crazing mechanism.

### OBJECTS AND METHODS OF STUDIES

To obtain porous polymer matrices, we used industrial isotropic films of isotactical polypropylene (PP) ( $M_w = 3 \times 10^5$ , thickness 140  $\mu\text{m}$ , degree of crystallinity 54%,  $T_{\text{melt}} = 165^\circ\text{C}$ ) and extruded films of polyethylene of high density (PEHD) ( $M_w = 2 \times 10^5$ , thickness 75  $\mu\text{m}$ , degree of crystallinity 60%,  $T_{\text{melt}} = 130^\circ\text{C}$ ). Both an initial film of PP (IPP) and one annealed at  $140^\circ\text{C}$  for 3 h (APP) were used. In the latter case, the degree of crystallinity increased to 65%.

A porous structure of polymers was formed according to the crazing mechanism. For this purpose, initial polymers were uniaxially deformed in various liquid media (isopropyl alcohol, heptane, superbranched polyethoxysiloxane<sup>1</sup> (PEOS) [20]) to strain degrees of 70 and 200% with a rate of 5 mm/min at a temperature of 20–25°C. The obtained matrices were character-

<sup>1</sup> Superbranched polyethoxysiloxane ( $M_w = 3 \times 10^4$ , density 1.17 g/cm<sup>3</sup>, viscosity 18.8 spz, efficient diameter of molecules 2–5 nm) was synthesized at the Enikolopov Institute of Synthetic Polymer Materials, Russian Academy of Sciences, under the guidance of A.M. Muzafarov.

Main types of composites used to obtain porous sheets

Sample	Polymer matrix		Type of reaction {reagents}	Time of reaction, h	Content of filler, mass %*
	Degree of strain, %	Porosity, vol %			
IPP-SiO <sub>2</sub>	70	35	hydrolytic condensation {PEOS/H <sub>2</sub> O(HCl)}	24	23
APP-SiO <sub>2</sub>	200	54		“	32
PEHD-SiO <sub>2</sub>	“	41		“	30
PEHD-Ag	“	50	reduction {AgNO <sub>3</sub> /NaBH <sub>4</sub> } {H <sub>2</sub> [PtCl <sub>6</sub> ]/N <sub>2</sub> H <sub>4</sub> }	72	63
PEHD-Pt	“	50		24	34
IPP-HAP	70	28	exchange	72	15
APP-HAP	200	45	{Ca(NO <sub>3</sub> ) <sub>2</sub> /(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub> }	72	15

ized by the value of efficient bulk porosity according to the method described in [21].

The porous structure of the matrix was filled with a substance or precursor from which a sheet was further obtained. The formation of a substance proceeded according to its synthesis directly in the volume of polymer pores. Detailed synthesis techniques are described in works devoted to the production of polymer composites containing silicon dioxide [22], silver and platinum [23], and hydroxyapatite (HAP) [24]. All chemical reactions were carried out at 20–25°C. The content of a filler was controlled by the concentration of initial reagents and reaction duration. The main samples from which porous sheets were obtained are listed in the table. The formation of sheets was carried out by heating the described composites in air atmosphere from 25 to 700°C with a rate of 20°C/min.

The characteristics of a porous structure of sheets were determined from isotherms of the low-temperature adsorption–desorption of nitrogen. The isotherms were measured on an ASAP 2010 (Micromeritics) automatic sorptometer.

Structural–morphological investigations were carried out using scanning electron microscopy methods on a JEOL JSM-6390LA microscope (cleavages were prepared by the method of fragile destruction in liquid nitrogen and deposited with gold) and transmission electron microscopy on a LEO 912 AB OMEGA microscope (ultrathin cuts were made according to the method of ultramicrotoming with a diamond knife).

## RESULTS AND DISCUSSION

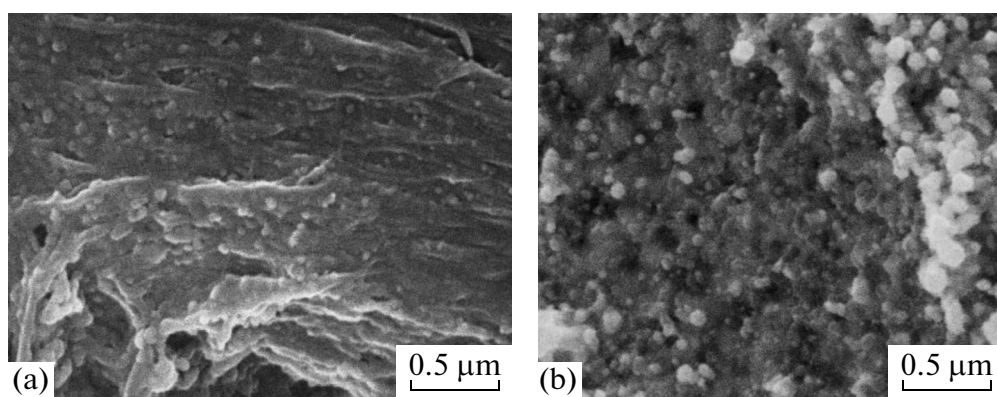
### *Method of Obtaining Porous Sheets*

The use of porous materials from synthetic and natural polymers, e.g., polyurethane, polycarbonate, cellulose, or carbon, as the base for the production of porous inorganic systems is a well-known approach [6, 10]. In this case, the matrix is impregnated with a highlyconcentrated solution or suspension of the necessary substance or its precursor with a subsequent conversion and then the basis is removed, for example,

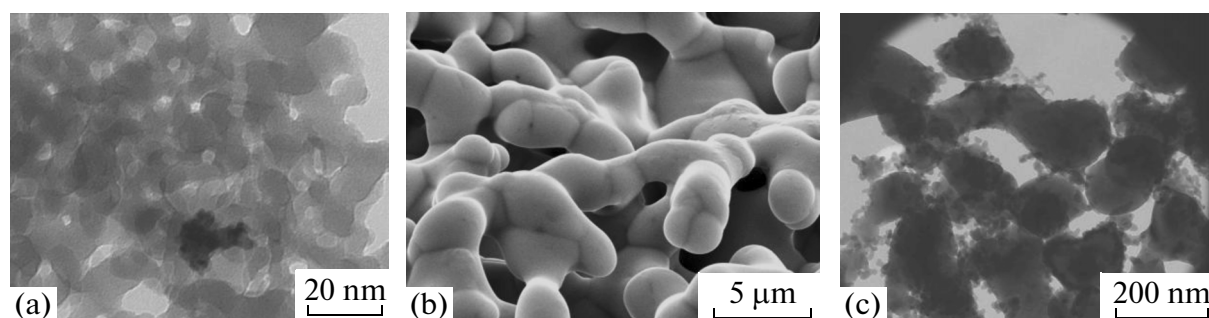
by pyrolysis. As a rule, such a method is used to obtain macroporous materials with a pore diameter greater than 1 μm. However, a similar method was used in [25] to obtain silicon dioxide with a pores diameter of 5–20 nm. In this case, the synthesis of SiO<sub>2</sub> was carried out directly in the volume of matrix pores from polypropylene according to the sol-gel mechanism in the presence of Pluronic.

The essence of the method proposed in this work consists of the use of porous matrices obtained by the oriented stretching of polymer films in liquid AAM according to the crazing method to synthesize inorganic compounds. The resulting pores serve as microreactors to obtain a filler in situ. Figure 1a shows a microphotograph of the composite cleavage region based on PEHD (the strain degree is 200%) and Pt, where it is seen that, in the process of chemical reduction by hydrazine, the filler is formed in the polymer volume in the form of closely located spherical particles 30–50 nm in diameter.

When the polymer matrix is removed due to the composite being heated in an oxidizing medium, a porous sheet remains which consists of filler particles (Fig. 1b). In this case, it should be noted that contact between the particles may arise both at the stage of the second component formation, since a porous system formed by the crazing mechanism is mutually penetrating one, and in the process of thermal treatment. Figure 2 shows possible ways for the formation of bonds between particles of a filler of a different nature synthesized in polymer pores. For example, in the case of silicon dioxide, the connection between the particles probably arises due to the interaction between surface functional hydroxyl groups and the formation of covalent bonds; therefore, no clear boundaries between the particles are seen in the photograph (Fig. 2a), unlike sheets from silver or platinum, when contact between the particles is formed by baking. The boundaries at which particles were joined are clearly seen in Fig. 2b. The formation of a porous sheet from HAP proceeds in an unusual way: contact between coarse particles is achieved with the help of smaller ones (Fig. 2c).



**Fig. 1.** SEM microphotographs (a) of a fragile cleavage of an initial PEHD-Pt composite and (b) of a porous Pt sheet obtained on its basis.



**Fig. 2.** (a, b) TEM and (c) SEM microphotographs of fragments of porous sheets from (a) SiO<sub>2</sub>, (b) Ag, and (c) HAP.

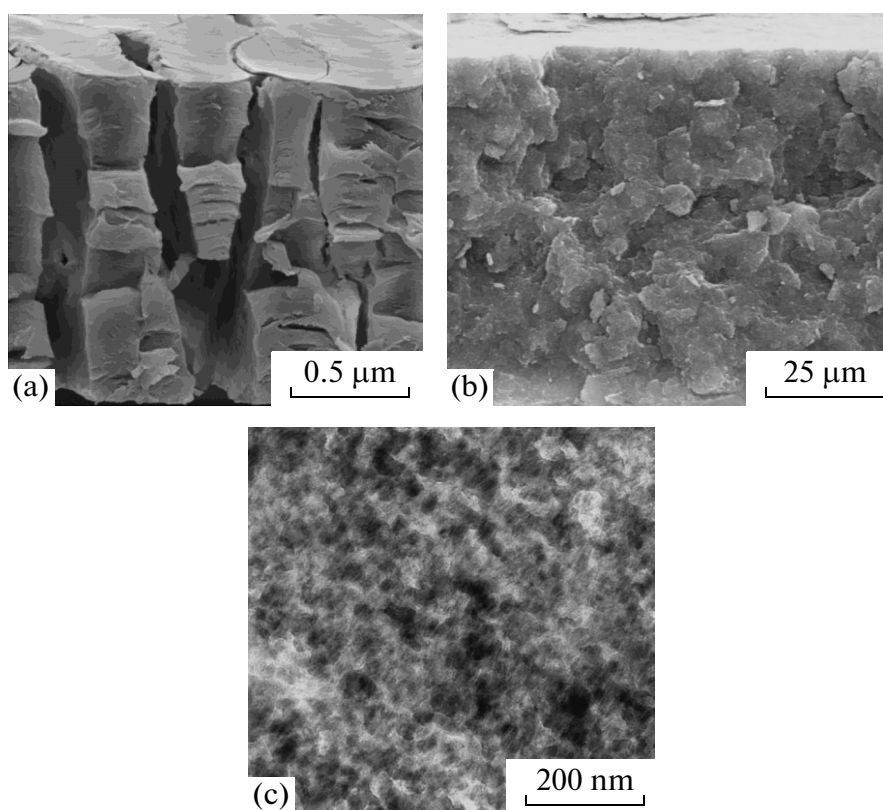
Let us further consider the abilities of the proposed method on the example of producing porous systems of three types: oxides (silicon dioxide), metals (silver and platinum), and salts (HAP). In this case, to form a phase of the filler, we used three different types of chemical reactions: hydrolytic condensation, chemical reduction, and exchange. Most attention will be focused on defining the conditions needed for sheet formation and the parameters determining the porous structure morphology and characteristics.

#### *Structure of Polymer Matrix*

There are two types of porous structures obtained by the crazing mechanism: the classical one, when the pores emerge and develop in local regions called crazes, and the delocalized one, when the formation of pores proceeds uniformly enough within the whole polymer volume [26]. Since the synthesis of an inorganic component proceeds only in the pores, then by varying the structure of an initial polymer matrix we can vary the sheet morphology. Actually, as is seen from Fig. 3, the structure of the sheets from SiO<sub>2</sub> obtained on the basis of IPP (a), whose strain proceeds according to a classical crazing, and of that based on APP (b), which is deformed according to the mechanism of delocalized crazing, are different.

It is evident that the sizes of pores will be determined by the sizes of polymer regions in the initial composite, which represent either long enough non-deformed regions or thin fibrilles of a diameter of about 10 nm. In the case of a classical crazing, the sizes of unit-block nondeformed polymer regions, which separate crazes, amount to several microns, while by a delocalized mechanism they are crystallites of several tens of nanometers. Figure 3c shows a microphotograph of a finer structure of a porous sheet, which is formed after burning out of fibrilles, and is typical for crazed regions in IPP and over the whole volume in APP matrices. It should be noted that the mechanical strength of the sheets obtained by the use of classical crazing is substantially lower than that obtained by the use of a delocalized mechanism. In addition, to form a long sheet using a matrix with a classical crazed structure, it is necessary for the filler particles to be formed not only in the polymer bulk, but also at the composite surfaces in the form of a layer.

Another important property of polymer matrices which has a bearing on the formation of a porous sheet is the degree of strain. It is known that the formation of classical crazes starts in the region of the forced elasticity limit; then they grow through the polymer film cross section and spread. When a certain degree of strain is reached and the crazes become too wide (on



**Fig. 3.** (a, b) SEM and (c) TEM microphotographs (a, b) of a fragile cleavage and (c) ultrathin section of SiO<sub>2</sub> sheets obtained after burning matrices on the basis of (a) IPP and (b, c) APP.

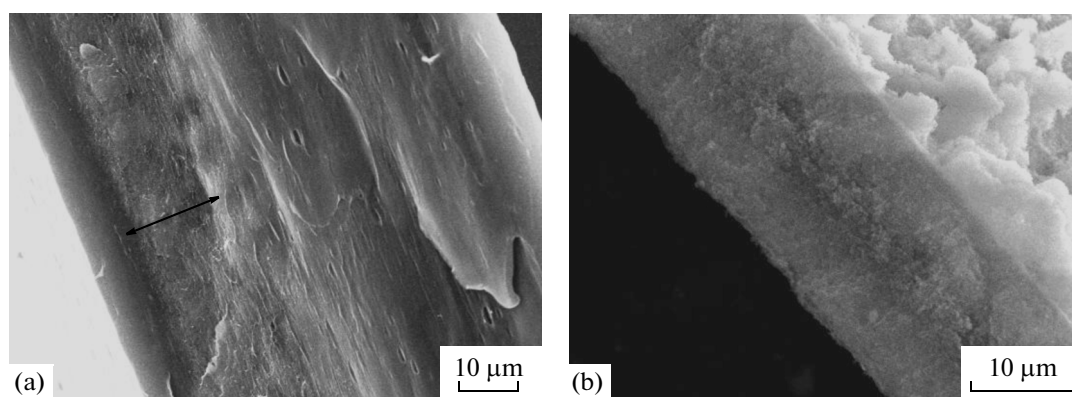
the order of 10 μm), a substantial reconstruction of the porous structure starts, which is accompanied by a merge of crazes and a transfer of the whole polymer bulk into an oriented state. Thus, to form a porous sheet with the morphology shown in Fig. 3a, it is necessary to have crazes which are well formed and grown through the matrix cross section. It was found that, beginning with  $\epsilon = 50\%$ , it is possible to obtain solid sheets. As the degree of the matrix strain increases, which is accompanied by an increase in the craze width and the amount of the introduced second component, the strength of a sheet is increased. When a film is stretched to high  $\epsilon$  close to a natural polymer stretching in the neck, the sheet morphology radically changes and it becomes similar to that which is obtained by the use of matrices with a delocalized crazed structure shown in Fig. 3b.

Despite the fact that the development of crazes proceeds uniformly enough over the whole polymer bulk by the localized mechanism, the formation of a continuous phase of the second component is possible also only in matrices with a degree of strain of no greater than 50%. This is associated with the fact that the emergence of crazes takes place not simultaneously over the whole bulk, but it starts in certain local strain zones gradually occupying the rest of the polymer volume. It is necessary to achieve the forma-

tion of a mutually penetrating structure when individual crazes form through channels of penetration both along and across the matrix. The best results, when the formation of a fast enough porous sheet was observed, were obtained by the use of matrices with  $\epsilon > 100\%$ . It should be noted that the application of polymers with a porous structure formed by the mechanism of delocalized crazing does not require the formation of filler layers at the matrix surfaces.

#### *Introduction and Concentration of the Second Component*

There are two main methods for filling the porous structure of the matrix obtained by the crazing mechanism [17]: direct and indirect. In the case of the direct method, the second component is introduced during the uniaxial strain of a polymer in a melt or in a solution of the needed substance simultaneously with the formation of a porous structure. However, this method is applicable only for low-melting organic compounds (e.g., hydrocarbons) or substances well-soluble in organic solvents (e.g., alcohols), which are traditional AAMs. Since inorganic compounds (oxides, metals, and salts) are usually insoluble or weakly soluble in organic solvents, it is impossible to introduce a sufficient amount of the second component into the matrix



**Fig. 4.** SEM microphotographs of fragile cleavages (a) of an APP-HAP composite and (b) of a sheet of HAP obtained from it. The arrow indicates the width of the region in a polymer matrix filled with HAP.

with the help of the direct method. It is noteworthy that the use of highly concentrated suspensions for the filling of a crazed structure, like in the case of the traditional matrix method described in [6, 10], is impossible due to the nanodimensional diameter of pores. Therefore, indirect methods of filling are usually used when the filler is synthesized directly in the polymer pores. In this case, the reagents (precursors) can be introduced via crazing or according to the method of counterflow diffusion.

In our work, composites containing silicon dioxide were obtained by a sol-gel technology when a liquid precursor PEOS or its alcoholic solutions were introduced at the stage of an oriented drawing of the polymer with its subsequent conversion into  $\text{SiO}_2$  by the mechanism of a hydrolytic condensation in the presence of an acid or base. In this case, the formation of the filler in crazes proceeds homogeneously enough. The morphology and characteristics of a porous sheet depend on the polymer matrix structure (Fig. 3), which is formed in the process of crazing, and on the concentration of a precursor in AAMs. The thickness of a sheet is 10–15% smaller than for an initial composite due to the reaction of condensation between surface hydroxyl groups of synthesized  $\text{SiO}_2$  particles in the process of polymer burning.

Metals and hydroxyapatites were synthesized in pores using the technique of counterflow diffusion, when a porous polymer matrix is preliminarily obtained by crazing in traditional AAMs, and then it is used as a separating membrane between reagent solutions in a dialyze cell. In this case, the formation of the second component proceeds in a certain reaction region of a polymer, whose width and location are determined by the relations between the reagent diffusion and chemical reaction rates, as well as by the process duration [27]. Figure 4a shows a microphotograph of the composite APP–HAP cleavage, from which we can see that the width of the reaction region corresponding to the thickness of the second component layer in the polymer amounts in a given case to

about 20  $\mu\text{m}$ . The thickness of a porous sheet remaining after the removal of the matrix will be equal to the thickness of this layer, which is clearly seen from Fig. 4b. Thus, by varying the size of the reaction region, we can control the thickness of the sheet to be obtained.

It should be noted that the basic condition for the formation of a solid sheet with perfect mechanical properties by the matrix technique is the provision of the filler phase continuity in an initial composite. It was established experimentally that the sheets from  $\text{SiO}_2$  start forming at a content of silicon dioxide in the composite of 15–20 mass % (7–9 vol %). In the region of these concentrations, discrete nanoparticles of the second component join into a continuous phase. Using the data of the table, we calculated a bulk content of the filler in various composites taking into account its distribution in the matrix bulk; i.e., in the case of silicon dioxide, the calculation was carried out for the whole polymer bulk, while for metals and HAP it was carried out for the bulk of the second component layer. It was found that the minimal concentration of an inorganic component in the filled samples under study was, for  $\text{SiO}_2$ , 13 vol %; for Ag it was 7 vol %; and for HAP it was 15 vol %. A decrease in the concentration of an inorganic component will give rise to a substantial deterioration in the sheet mechanical properties, and below a certain critical concentration it will not be formed at all.

#### *Characteristics of Porous Sheets*

Porous systems are characterized by the volume value of pores, the specific surface, the average diameter of pores, and their size distribution. In the porous sheets under consideration, the volume of pores is determined by the volume of a burned polymer phase, while the diameter is determined by the size of nondeformed polymer regions and fibrilles. The efficient bulk porosity of the matrices obtained by the crazing mechanism depends on the conditions of stretching (rate, activity of AAMs, and temperature) and the

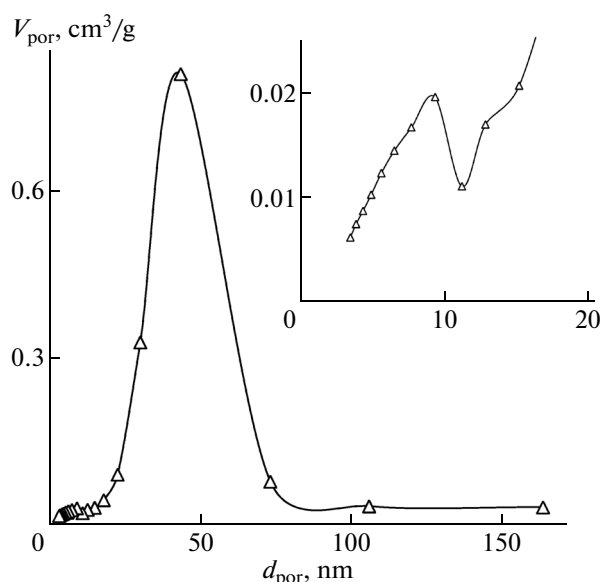


Fig. 5. Dependence of the diameter of pores in a sheet from  $\text{SiO}_2$  obtained with the use of the crazing mechanism. Insert shows a scaled initial segment of the curve.

nature, structure and thickness of the initial polymer film and its degree of strain. The maximum volume of pores, which arises in the process of crazing, amounts to 60–70 vol %. This is the volume that can be filled with the second component. Thus, on the other hand, the minimal volume of pores in a porous sheet consisting of the filler after burning the matrix will amount to only 30–40 vol %. The maximum volume of pores will be achieved in systems with a minimal amount of the second component (about 10 vol %), and its theoretical value may achieve 90 vol %.

It can be clearly seen from Figs. 2 and 3 that the method under consideration allows us to vary the sizes of pores in a wide range, from several nanometers to several micrometers, which depends on the polymer phase dispersity in an initial composite. In addition, we may expect a bimodal and rather wide size distribution of pores, because the matrix consists of non-strained regions of sizes from several tens of nanometers (e.g., the size of crystalline regions) to several micrometers and of thin fibrilles with a diameter of 10 nm.

The characteristics of the systems under study will be considered in more detail using the example of a sheet from silicon dioxide obtained from a composite on the basis of a partially crystalline film of APP with a strain degree of 200% containing 40 mass %  $\text{SiO}_2$ . The density of the sheet was about  $0.7 \text{ g/cm}^3$ . The main parameters of a porous structure were obtained from low-temperature sorption curves of nitrogen, which represent a classical S-shaped form. Figure 5 shows the size distribution of pores in a sheet. It can be seen that it is really rather wide (the sizes of pores vary from 5 to 80 nm) and is bimodal. The average diame-

ters of the pores are 9 nm, which corresponds to the size of fibrilles, and 43 nm, which probably corresponds to the size of nonstrained crystalline regions of a polymer remaining after crazing. The specific surface of pores turned out to be rather high and amounted to  $305 \text{ m}^2/\text{g}$ . The volume of pores in a sheet turned out to be unexpectedly big,  $1.5 \text{ cm}^3/\text{g}$ , which is usually 2–3 times smaller in porous systems at such a pore size.

Thus, the technique for obtaining porous inorganic sheets with the use of the crazing mechanism for polymers in a liquid media proposed in this work is rather universal and makes it possible to create porous systems, including those with nanometric levels of pore sizes from various substances of inorganic natures (metals, oxides, salts). The morphology and parameters of a porous structure of such sheets are easily controllable at the stage of acquisition and are variable in a wide range on account of their subsequent application, e.g., as filters, catalyst systems, or porous carriers.

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