====================== **EXPERIMENT** ======================

Specific Features of the Formation of the Silicon Dioxide Phase in Porous Poly(propylene) Prepared through the Crazing Mechanism

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Abstract—A new technique is described for preparing poly(propylene)–silica nanocomposites with the use of crazing of polymers in reactive liquid media that exhibit an adsorption capacity with respect to the polymer and contain functional groups able to enter into different chemical reactions, in particular, hydrolytic condensation. The advantage of this technique over conventional mixing is that the components can be mutually dispersed at the nanolevel without using additional modifying additives. The hydrolytic condensation of tetraethoxysilane and hyperbranched poly(ethoxysiloxane) in the presence of acid or base catalysts with the formation of a silica gel in a crazed polymer matrix is investigated. It is established that the morphology of the prepared composites is determined by the structure of the crazed polymer matrix, the nature of the precursor, and the hydrolytic poly-condensation conditions. Composites are prepared in which the silica phase is located either inside the poly(propylene) matrix (in the form of a continuous phase or discrete particles) or on the surface of the polymer. Porous silicon plates are produced through heat treatment of the poly(propylene)–silicate nanocomposites at a temperature of 700°C.

INTRODUCTION

Polymer–silica composites combine the properties of a polymer matrix and a silica filler and exhibit unique mechanical, thermal, barrier, and other characteristics. There exist several techniques for preparing these composites. According to one of these techniques, particles of silicon dioxide [1, 2] or natural layered silicates are introduced into a melt or a solution of the polymer. Since silicate particles are hydrophilic in nature, it is relatively easy to prepare mixtures with hydrophilic polymers, for example, poly(ethylene oxide). In order to produce composites based on hydrophobic polymers, it is necessary to perform an additional modification of the silicate filler and the polymer matrix [2, 4].

Another technique used for preparing polymer–silica composites consists in polymerizing a monomer in the presence of stabilized silicon dioxide sols [5, 6] or between layers of natural silicate [7, 8]. This technique is more laborious. Actually, since the polarity of monomers is higher than the polarity of the resulting polymers, as a rule, it is easy to achieve a good compatibility between the monomer and silicate. However, polymerization is accompanied by phase separation and, consequently, the silicate phase is nonuniformly distributed in the polymer matrix.

Furthermore, polymer–silica composites can also be produced through the hydrolysis of alkoxysilanes [9–11] in the presence of polymers. For this purpose, it is common practice to use polymer surfactants and hydrophilic polymers of the poly(ethylene oxide) and poly(acrylic acid) type.

In this paper, we propose a new approach to the preparation of polymer–silica composites with the use of crazing of polymers in liquid media [12, 13]. During crazing, a reactive liquid medium penetrates into the bulk of the polymer. This leads to the dispersion of the polymer and the formation of a system of nanopores. The use of the proposed technique makes it possible to uniformly fill the polymer with the second component and to effectively disperse the polymer to a nanolevel [14]. In our work, crazing was used as an efficient tool for transferring a precursor compound to the poly(propylene) matrix with the subsequent hydrolysis in the nanopore volume. Moreover, the proposed approach makes it possible to avoid the aggregation of particles during hydrolysis and to retain the high mutual dispersion of the polymer matrix and silica.

Main characteristics of the studied samples based on poly(propylene) (the hydrolysis time is 48 h)

Preparation conditions	W_n, vol %		w_f, wt %	Residue after TGA, wt %
	before hydrolysis	after hydrolysis		
Unannealed poly(propylene)				
Tetraethoxysilane HCl	35	31	29	23
Tetraethoxysilane NH₃	35	31	14	9
Poly(ethoxysilane) HCl	35	33	25	23
Poly(ethoxysilane) NH₃	35	30	–	27
Annealed poly(propylene)				
Tetraethoxysilane HCl	45	37	33	26
Tetraethoxysilane NH₃	45	25	20	15
Poly(ethoxysilane) HCl	45	30	45	32
Poly(ethoxysilane) NH₃	45	38	42	33

In this work, we investigated how the conditions used for the hydrolytic polycondensation of hyperbranched poly(ethoxysiloxane) (PEOS) and its low-molecular analog, i.e., tetraethoxysilane (TEOS), in porous crazed poly(propylene) matrices affect the formation of the silica gel phase and the morphology of polymer–silica composites.

OBJECTS AND METHODS OF INVESTIGATION

In the experiments, we used initial commercial films of isotropic isotactic poly(propylene) ($M_w = 3 \times 10^5$, $h = 140$ µm) and films annealed at a temperature of 140°C for 24 h. Tetraethoxysilane (density, 0.9334 g/cm³) and hyperbranched poly(ethoxysiloxane) ($M_w = 3 \times 10^4$; density, 1.17 g/cm³; effective diameter of molecules, 2–5 nm) were used as liquid media providing the performance of the crazing and subsequent chemical transformations. Poly(ethoxysiloxane) was synthesized according to the original procedure described in [15, 16].

Tetraethoxysilane and poly(ethoxysiloxane) were introduced into the poly(propylene) matrix through the uniaxial drawing of the polymer to 70 and 200% at a rate of 10%/min in the medium of the liquid precursor. The effective volume porosity W_p (vol %) of the polymers upon drawing was determined from the increment of the volume of the reference sample in the course of deformation.

The hydrolytic polycondensation of TEOS and PEOS was performed in vapors of a 10% aqueous solution of hydrochloric acid or ammonia directly in the poly(propylene) matrix at a temperature of 20–25°C under isometric conditions. The reaction time varied from 1 to 72 h. In order to remove volatile products (HCl, NH₃), the samples were held in air at a temperature of 20–25°C for three days.

The content of the introduced filler (w_f, wt %) was determined by two methods: (1) the gravimetric method from a change in the weight of the initial poly(propylene) film after the introduction of the precursor and its hydrolysis and (2) from the dry residue after burning of the polymer matrix under heating from 25 to 700°C at a rate of 10 K/min on a Mettler-TG50 thermobalance in an air atmosphere. The residue composition was determined using the elemental analysis.

The chemical composition of the surface and bulk of the samples was determined using IR spectroscopy in the multiple attenuated total reflection and transmission modes on a Specord M80 spectrophotometer. The measurements were carried out in the frequency range 400–4000 cm⁻¹. The bands were assigned with the use of standard reference tables.

The porous structure of the samples was characterized using the low-temperature nitrogen adsorption–desorption technique. The isotherms were measured on a Micromeritics ASAP 2010 automated sorptometer. The isotherms were calculated with the conventional software package of the instrument.

The structural–morphological investigations were performed using electron microscopy. For this purpose, ultrathin sections of the samples were prepared with the use of an ultramicrotome diamond knife. The examination of the ultrathin sections was performed with a LEO 912 AB OMEGA transmission electron microscope. The cleavages of the films were prepared according to the technique of brittle fracture in liquid nitrogen. Gold was evaporated onto the cleavages, which were analyzed using a Hitachi S-520 scanning electron microscope.

RESULTS AND DISCUSSION

Hydrolytic Polycondensation of PEOS and TEOS in the Poly(propylene) Matrix

In our previous study [17], we thoroughly analyzed the conditions used for the formation of the crazed structure of different polymers in the TEOS and PEOS

media. It was demonstrated that, depending on the structure, poly(propylene) can undergo a deformation by means of different mechanisms: unannealed poly(propylene) films are deformed according to the classical crazing mechanism, whereas annealed poly(propylene) films are deformed by the delocalized crazing mechanism. For unannealed poly(propylene) films, the maximum degree of filling of the film with ethyl silicate is 45–50 vol % at a strain of 150–200%. For annealed poly(propylene) films, the effective porosity increases continuously with an increase in strain up to fracture. The maximum degree of filling is 60 vol %.

According to the analysis of the results obtained, the objects of further investigations were chosen to be unannealed poly(propylene) films with a strain of 70%, which corresponds to the structure of well-developed crazes. In this case, the porosity of the films is approximately 35 vol %. Moreover, we studied the annealed poly(propylene) films with a strain of 200%, which corresponds to a developed porous structure with degrees of filling of 45 and 53 vol % for PEOS and TEOS, respectively.

The poly(propylene) films with the chosen precursor were held in vapors of HCl or NH_3 aqueous solutions. It is known from the data available in the literature [18] that, under these conditions, PEOS liquids undergo hydrolytic polycondensation. The hydrolytic polycondensation of TEOS in water–alcohol solutions has been investigated the most extensively. The use of an acid catalyst leads to a good activation of both the hydrolysis and condensation processes. In this case, terminal groups of the formed polymer and monomers interact the most actively. Consequently, a system of entangled, weakly branched, rarely cross-linked polysiloxane macromolecules, as a rule, is formed under the above conditions.

The rate of hydrolysis of TEOS in the presence of NH_3 is considerably lower. This reaction results in the formation of individual clusters 5–10 nm in diameter, which are strongly branched polysiloxane macromolecules. Subsequently, they form larger particles a few hundred nanometers in diameter [19].

The hydrolytic polycondensation of PEOS in water–alcohol solutions is characterized by specific features. In the presence of an acid catalyst, the hydrolysis of ethoxy groups is predominantly accompanied by the occurrence of intramolecular condensation processes, which lead to the formation of individual silica sol particles coinciding in size with the initial PEOS macromolecules [16]. Similarly to TEOS, the hydrolysis of PEOS in the presence of NH_3 proceeds at lower rates. In this case, condensation occurs predominantly by the intermolecular mechanism with the formation of a dense network over the entire volume.

Thus, analysis of the data available in the literature on the reactions of the hydrolytic condensation of liquid hyperbranched PEOS and its low-molecular homologue TEOS has demonstrated that the polymer nature of the reagent affects the final structure of the hydrolysis products.

In our work, the precursors under investigation were introduced into the porous polymer matrix. The matrix was kept in a strained state in order to avoid the collapse of the porous structure. The catalysts of the hydrolysis from the gas phase penetrated into the porous polymer matrix. It was necessary to reveal whether the hydrolysis of ethoxy groups proceeds in this complex system, to qualitatively evaluate the hydrolysis rate, and to characterize the final hydrolysis product.

The IR spectra of the initial and filled annealed poly(propylene) films before and after hydrolysis are shown in Fig. 1. The strong bands observed in the ranges of 800 and 1050–1200 cm^{-1} are associated with the vibrations of the Si–O bonds. This indicates the presence of the precursor in the polymer matrix. After hydrolysis, there arise bands at frequencies of 1630 and 3350 cm^{-1} attributed to the bending and stretching vibrations of the –OH groups, respectively. This suggests hydrolysis of the ethoxy groups of the precursors. It should be noted that the intensity of the bands attributed to the vibrations of the hydroxyl groups is considerably higher in the case where PEOS is used as a precursor. This circumstance is associated with the specific features of its chemical structure, which brings about a decrease in the probability of intermolecular condensation due to the steric hindrances as compared to TEOS.

We compared the intensity ratios of the bands at frequencies of 1380 cm^{-1} (which is assigned to the bending vibrations of the –CH_3 groups in poly(propylene)) and 1640 cm^{-1} (which corresponds to the bending vibrations of the –OH groups in the silicate filler) in the IR spectra recorded in the transmission and multiple attenuated total reflection modes (characterizing the volume and surface structures, respectively). It was revealed that the content of hydroxyl groups in the surface layer of the poly(propylene)–silica composites prepared by the hydrolysis of PEOS is substantially lower than that in the bulk. In this case, the intensities of the bands associated with the –CH_3 and Si–O groups at the surface and in the bulk are almost identical. After hydrolysis of TEOS in the poly(propylene) matrix, the intensity of the bands associated with the –OH groups is lower than that for the samples based on PEOS and the number of these groups at the surface is equal to that in the bulk of the material. Most likely, the use of TEOS leads to the formation of a silica gel layer on the polymer surface because the intensity of the band attributed to the –CH_3 groups for the surface is considerably lower than that for the bulk of the composite, whereas the intensities of the band corresponding to the Si–O groups are identical.

The hydrolytic condensation under the action of acids and alkalis was studied in more detail for the annealed poly(propylene) film strained to 200% in the PEOS medium. This system was chosen for two reasons. Since the crazing of the annealed poly(propylene)
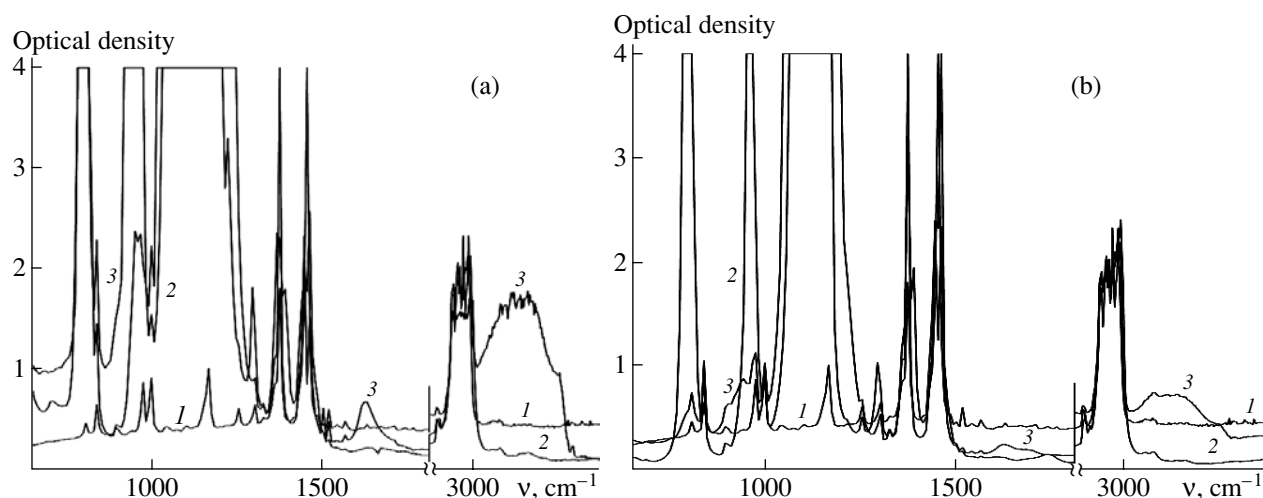
Fig. 1. IR transmission spectra of (*1*) the initial annealed poly(propylene) sample and (*2, 3*) the poly(propylene) sample containing the precursor (*2*) before acid hydrolysis and (*3*) after acid hydrolysis. Precursors: (a) poly(ethoxysiloxane) and (b) tetraethoxysilane. The hydrolysis time is 48 h.
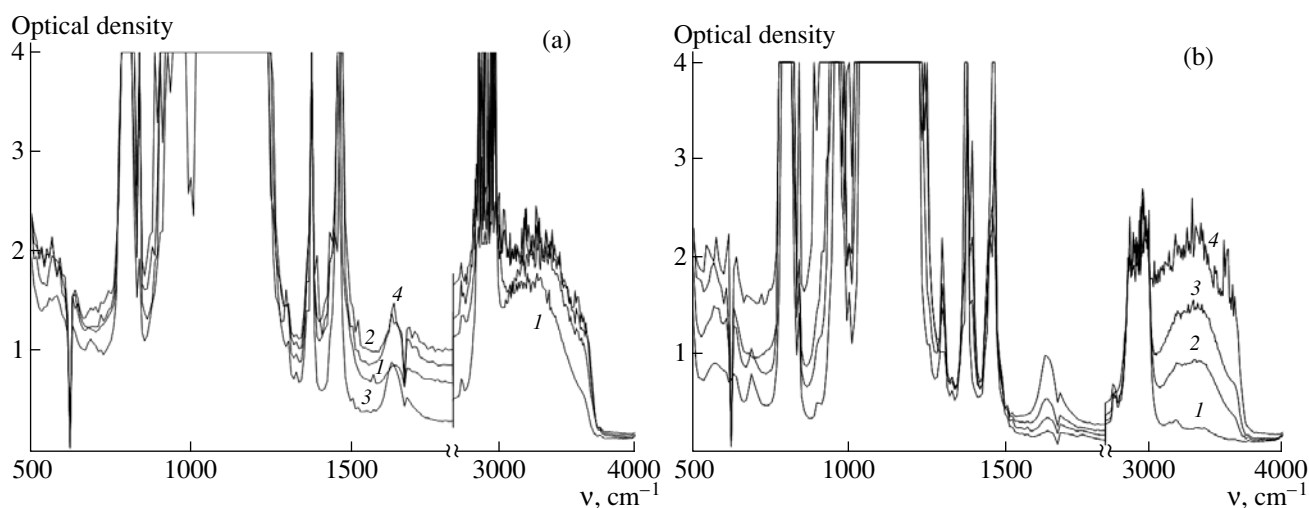
Fig. 2. IR transmission spectra of the annealed poly(propylene)–poly(ethoxysiloxane) samples after treatment in (a) ammonia and (b) hydrochloric acid vapors for different times: (*1*) 30 min, (*2*) 1.0 h, (*3*) 3.5 h, and (*4*) 22.0 h.

in PEOS occurs according to the delocalized mechanism, the polymer is filled with PEOS over the entire volume with the formation of a homogeneous structure. Furthermore, since PEOS is a nonvolatile liquid, its hydrolysis proceeds predominantly in the bulk of the polymer matrix. The IR spectra of the samples subjected to hydrolysis for different times are shown in Fig. 2. The kinetics of the process was judged from the change in the optical densities of the bands at 1640 and 1380 cm^{-1}.

It was found that the hydrolytic condensation in the polymer film in the presence of NH$_3$ proceeds rather rapidly and is completed in 1 h. This can be judged from the coincidence of the IR spectra measured after hydrolysis of the samples for 1.0, 3.5, and 22.0 h (Fig. 2a).

The hydrolytic condensation of PEOS in HCl vapors occurs differently as compared to that in NH$_3$ vapors. The OH groups are formed gradually with an increase in the reaction time (Fig. 2b). The band attributed to the vibrations of the OH groups is not observed in the IR spectrum measured within 30 min after the onset of the process. Then, the intensity of the absorption band corresponding to the OH groups increases with time. The hydrolysis in the presence of the acid catalyst is completed in 22 h. For this sample, the relative optical density of the band at 1640 cm^{-1} is maximum and coincides with that for the base hydrolysis.

The hydrolytic condensation, as a rule, is accompanied by the formation of three-dimensional cross-linked structures, which can stabilize the fibrillar porous structure of the polymer matrix. This should manifest itself in a change in the linear size of the poly-

mer composite film. The linear shrinkage can be used as an additional proof of the occurrence of the condensation reactions with the formation of silica. We determined the linear sizes of the polymer film (shrinkage) for different times of the hydrolysis.

It was revealed that, after hydrolysis for 30 min in the presence of the base catalyst, the shrinkage of the film is 12% and a small amount of liquid material is released on the polymer surface. This can be both the initial precursor and products of the incomplete hydrolysis of PEOS. The linear shrinkage of the samples after hydrolysis for 1–22 h amounts to 6–8%. The absence of release of a particular material in this case indicates that the solid phase is formed inside the polymer matrix.

During acid hydrolysis, the shrinkage gradually decreases with time. The shrinkages of the sample after hydrolyses for 30 min and 4 h are 30 and 18%, respectively. It should be noted that a considerable amount of liquid material is released on the polymer surface upon shrinkage. However, the obtained values of the shrinkage are substantially lower than those observed before hydrolysis, when they can be as high as 80%.

The rate of the base hydrolysis of PEOS in pores of the polymer matrix is considerably higher than that of the acid hydrolysis. The hydrolysis is accompanied by the heterofunctional condensation of ethoxy and hydroxyl groups. The kinetics of the process differs drastically from the kinetics of the hydrolysis in the medium of the common solvent in which the rate of the base hydrolysis is lower than that of the acid hydrolysis [20]. This is indirect evidence that the solvent has a substantial effect on the character of the processes.

The revealed effect can be associated with the specific features in the occurrence of the reactions between immiscible reagents. Since PEOS and TEOS are virtually insoluble in water, the reaction at early stages most likely proceeds at the water–precursor interface. Ethanol is a hydrolysis product. Therefore, the process is accelerated with time and all of the reagent is gradually involved in the reaction. It is known that the hydrolysis rate of ethyl silicate liquids depends substantially on the pH value of the medium [20]. The minimum rate is observed under neutral conditions. A decrease or an increase in the pH value results in a considerable increase in the process rate. It should be noted that, even in the absence of a common solvent, Jones and Fischbach [21] observed a substantial acceleration of the TEOS hydrolysis in the presence of an acid. Since the pH value of the medium in our experiment depends on the amount of the catalyst, the revealed differences are most likely associated with the fact that the concentration of the base catalyst is considerably higher than the concentration of the acid catalyst. Indeed, the partial pressure of NH_3 over a 10% aqueous solution is 10.744 kPa, whereas the partial pressure of HCl under the same conditions is only 0.527 Pa [22]. Furthermore, it should be remembered that the diffusion characteristics of the catalysts in the solution and the porous polymer matrix can differ substantially.

Investigation of the structure of the prepared composite is the subject of a separate study. As is known, the polymerization of monomers immobilized in porous polymers leads to the formation of a composite material in which both polymers form interpenetrating networks [23]. It is interesting to determine the structure of the second component (the silica gel) formed as a result of the hydrolytic polycondensation of PEOS and TEOS.

In order to solve this problem, the polymer matrix of the nanocomposite sample was burned in an air atmosphere under heating to a temperature of 700°C. It turned out that this heat treatment resulted in the formation of a white incombustible residue in the form of a plate with the shape determined by the shape of the treated sample of the initial film. This suggests that a continuous silica phase is formed in the polymer matrix due to the occurrence of intermolecular condensation processes. According to the elemental analysis, the chemical composition of the residue corresponds to SiO_2. After hydrolysis for 22 h, the SiO_2 content in the films is 34–36 wt % (29 wt % after hydrolysis for 30 min).

The main characteristics of the prepared films of the composites based on poly(propylene) and silica gel are listed in the table. It should be noted that the porosity of the polymer during hydrolysis somewhat decreases as a result of lateral contraction due to the considerable decrease in the volume of the filler upon transformation from the liquid state into the solid state and the appearance of unfilled space in the polymer matrix. In the case of TEOS, the free volume can also arise as a result of high volatility of the liquid medium, because hydrolysis in the porous solid in reagent vapors is a slow process.

The density of the silica phase in the polymer matrix was calculated from the data presented in the table. It was found that this density is only 0.7–1.5 g/cm^3, even though the density of the amorphous silicon dioxide prepared under standard conditions is higher by a factor of 1.5–3.0 and reaches 2.3 g/cm^3. This can be associated with the specific features of the structure of similar polymer–silica composites. Examination with the use of low-temperature nitrogen sorption revealed that the specific surface area of the poly(propylene)–silica composite is small and only 1.5 m^2/g; in this case, the contribution of pores less than 2 nm in diameter amounts to 1.1 m^2/g. This means that the composite is a dense material almost without through pores. The low density of the filler is possibly associated with the formation of difficultly accessible closed pores in the silica gel formed in the pores.
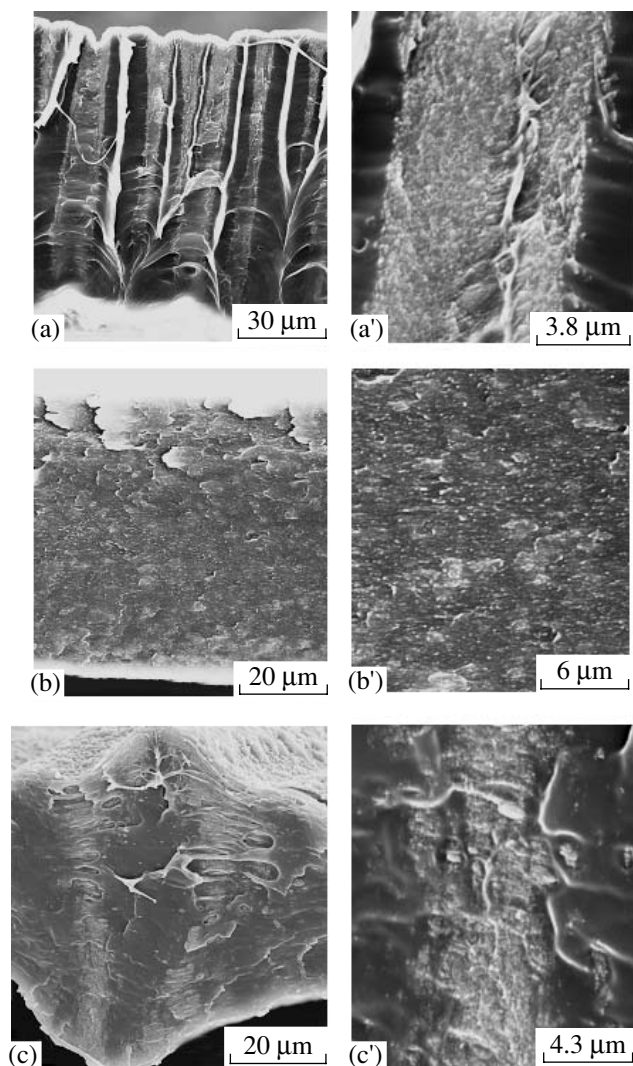
Fig. 3. Micrographs of brittle cleavages of the samples based on (a, c) unannealed and (b) annealed poly(propylene) containing (a, b) poly(ethoxysiloxane) and (c) tetraethoxysilane. Preparation conditions: acid hydrolysis.

Structural–Morphological Investigations of Polymer–Silica Composites

The structural–morphological investigations of the prepared films were performed using electron microscopy.

Since the precursor introduced into the polymer matrix through the crazing mechanism can be located only in crazes, it is natural to expect that the silica gel formed in the course of hydrolysis should also be located only in crazes without penetrating into the block polymer. Actually, the formation of a band structure in which the regions containing the silicate filler alternate with regions of the undeformed block polymer is characteristic of the composites based on the unannealed poly(propylene) (Fig. 3a). However, a structure homogenous over the entire volume is typical of com-
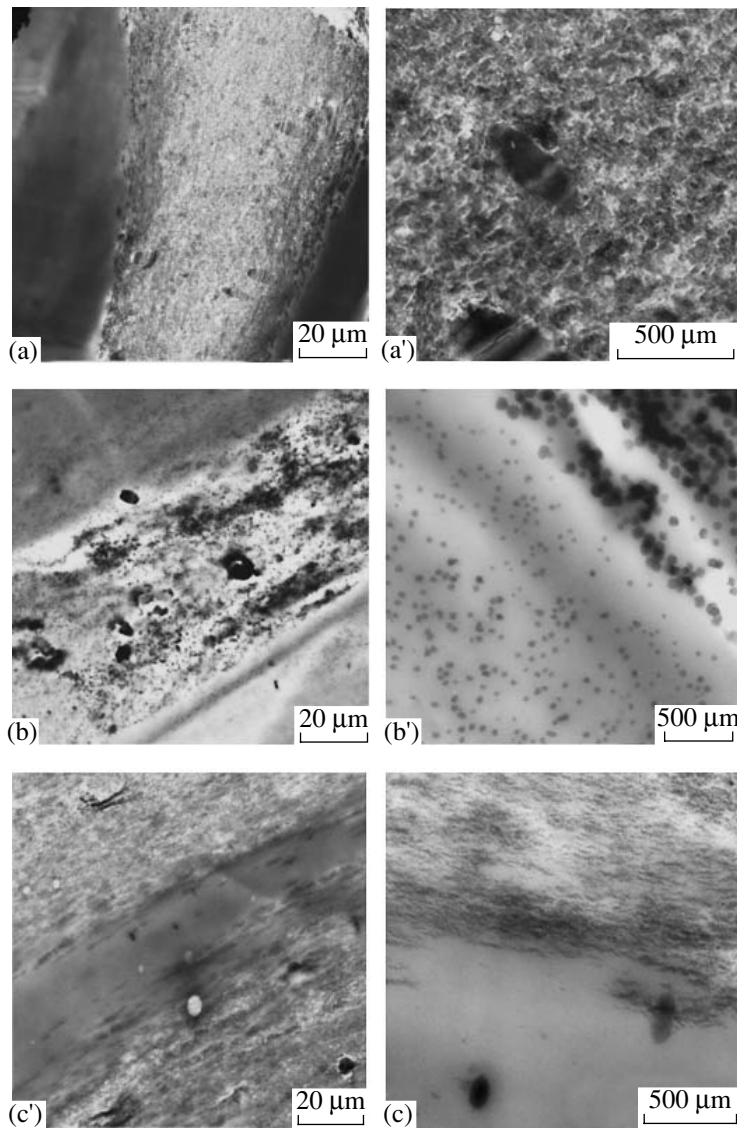
posites based on the annealed poly(propylene) (Fig. 3b). Therefore, the structure of the composite material prepared is determined by the structure of the polymer matrix formed at the crazing stage.

The use of the volatile mobile TEOS as the precursor leads to the formation of composites in which a considerable amount of the silica phase is located on the surface of the polymer film. This is confirmed by the IR spectroscopic data. The removal of the adsorption-active medium from the bulk of the polymer results in the structural transformations accompanied by the collapse of the highly dispersed structure (Fig. 3c).

The dispersion of the silica gel phase is determined by the nature of the precursor and hydrolytic condensation conditions. Since the pores of the crazed polymer are interpenetrating, we can assume that, in this case, a continuous silicate phase is formed in the polymer and the structure of this composite is represented by two mutually penetrating networks of the polymer phase (consisting of oriented polymer fibrils 6–8 nm in diameter) and the silicate phase (Fig. 4a). This can explain why the silica phase after burning of the polymer matrix from the composite remains in the form of a plate.

In the case where TEOS serves as the precursor, the silica phase is predominantly formed on the polymer surface, whereas individual particles with sizes determined by the hydrolytic polycondensation conditions are formed in the bulk. For example, the silica gel in the presence of the base catalyst is formed in the form of spherical particles, which are characterized by a bimodal size distribution and have diameters of ~50 and ~100 nm (Fig. 4b). In this case, it can be seen at large magnifications that these particles are aggregates of smaller sized particles. The obtained result is in good agreement with the data available in the literature [19]. The inhomogeneity of particles can be associated with the nonuniform distribution of the catalyst over the polymer matrix. Smaller sized particles with diameters of no more than 10 nm are formed in the case of the acid catalyst (Fig. 4c). These differences additionally illustrate the high sensitivity of the parameters of the silicate products to a variation in the hydrolytic condensation conditions [18]. However, it is more important that, upon changing over to the PEOS high-molecular precursor, the hydrolytic condensation under both acid and base conditions leads to virtually identical results irrespective of the catalyst type.

Figure 5a shows the micrograph of the brittle cleavage of the silica plate produced after burning of poly(propylene) in which the porous structure was formed through the classical crazing mechanism. This image is actually a replica of the initial composite (Fig. 3a). It should also be noted that the SiO_2 plates have a high porosity. In particular, the plate formed after burning of poly(propylene) with a delocalized crazed structure (Fig. 5b) has a specific surface area of 175–310 m^2/g and a mean pore diameter of 40 nm [24].

Fig. 4. Micrographs of ultrathin sections of the polymer–silicate composites based on the unannealed poly(propylene) prepared through (a, c) acid hydrolysis and (b) base hydrolysis. Precursors: (a) poly(ethoxysiloxane) and (b, c) tetraethoxysilane.
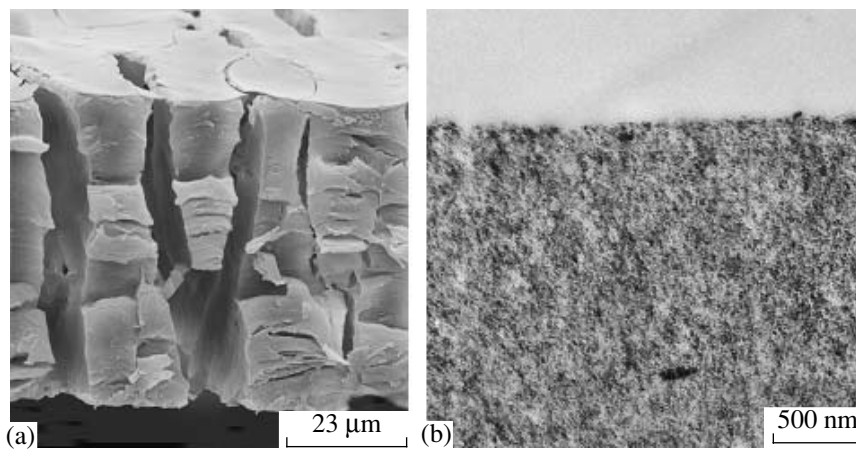
Fig. 5. Micrographs of (a) the brittle cleavage and (b) the ultrathin section of the SiO_2 plate prepared after burning of (a) unannealed poly(propylene) and (b) annealed poly(propylene).

CONCLUSIONS

Thus, it has been demonstrated that polymer–silica composites with different structures in which the silica phase is located either at the surface of the polymer or in the bulk of the polymer matrix can be prepared by varying the structure of the porous polymer matrix, the precursor nature, and the hydrolytic condensation conditions.

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