Nanocomposites Based on Polyethylene and Modified Silica Phase

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Abstract—Polymer nanocomposites based on solvent-crazed porous matrices of polyethylene of high density and modified phases of silica with a second component homogeneously distributed over the volume of the polymer have been obtained. It is shown that the content of the silica phase can be varied within wide limits; the maximum degree of filling amounted to about 50 wt %. The thermal stability of nanocomposites is studied. It is found that it depends on the content of solid filler and chemical composition of silica phases. When the content of the second component exceeds 20 wt %, the retention of the sample's geometric shape at temperatures above the melting temperature of the polymer matrix is observed, which indicates the appearance of a framework structure of silica. The sorption properties of the composites and porous phase of silica, which is formed after removing the polymer matrix, have been studied. It is found that the composites practically do not absorb nitrogen under the conditions of low-temperature sorption. The specific surface area of porous silicon residuals amounted to 70–130 m^2/g.

INTRODUCTION

Composition materials based on polymers find ever wider application compared to homopolymers. New functional properties of the composites are achieved by introducing the particles of inorganic origin and obtaining hybrid materials [1, 2]. One of the most widely used fillers for industrial polymers is silicon dioxide, because it substantially improves their mechanical barrier and for its other properties [3, 4]. Such polymer–silica systems appeared to be interesting as sensor materials on pairs of polar liquids [5] and as the basis for the preparation of mesaporous plates from silica [6] and a proton exchange membrane for the fuel element [7, 8].

The phenomenon of crazing of polymers in liquid media [9, 10], as a result of which a nanoporous structure with controllable sizes of pores is formed in a polymer matrix, was used to obtain polymer composition materials with a high level of mutual dispersity of the components [11–13]. By applying such an approach, silica-containing polymer nanocomposites based on polymer matrices of various origins were obtained earlier [14–16]. In this case, it was found that silica particles in a polymer matrix form a continuous phase and fill almost all the pores, which makes the system inaccessible for a further modification.

This work is aimed at preparing nanocomposites based on a matrix of a polyethylene of high density whose porosity is formed according to the mechanism of delocalized crazing and modified forms of silica as a filler, as well as studying the influence of the concentration and chemical composition of an inorganic phase on the thermal and sorption properties of such composition materials. As the precursors of the silica phase, organic silicon compounds of various chemical compositions were used, namely, hyperbranched polyethoxysiloxane and polymethylsilsesquioxane and siloxitriisopropoxititanium derivatives, which makes it possible to vary the density and functionality of the silica phase formed as a result of a hydrolytic condensation of the initial precursor compounds in the volume of pores of the polymer matrix.

OBJECTS AND METHODS OF STUDIES

As a polymer matrix, in this work we used an industrial extruded film of polyethylene of high density (PEHD) (M_w = 200 kDa, degree of crystallinity 70%, T_{melt} = 130°C, thickness 75 μm). Samples of rectangular shape with a length of 50 mm and width of 100 mm were cut from this film. Hyperbranched polyethoxysiloxane (HPEOS) 17] (M_w = 30 kDa, the density is 1.17 g/cm^3, the efficient diameter of molecules is 2–5 nm), hyperbranched polymethylsilsesquioxane
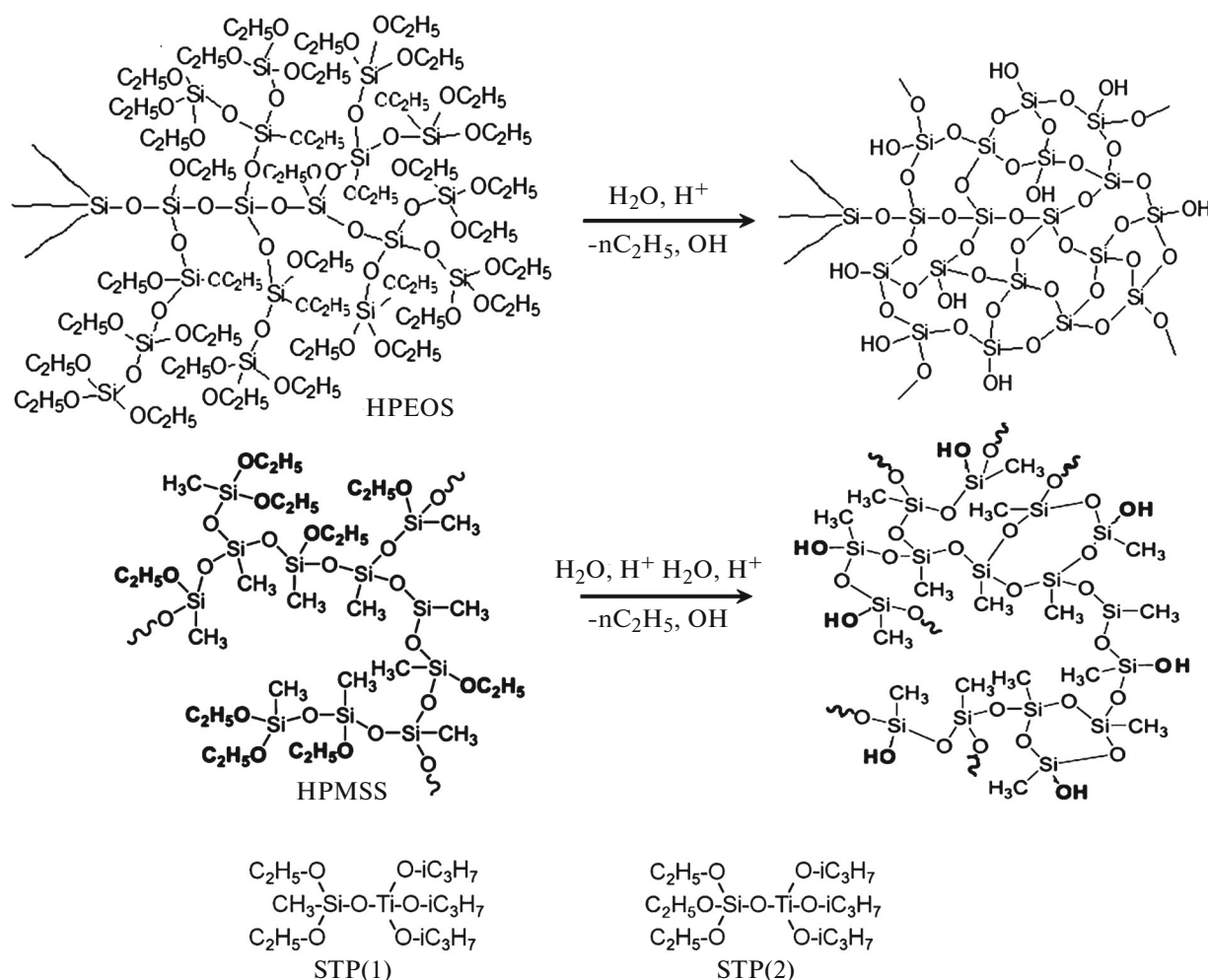
Fig. 1. Chemical formulas of the precursors of a silica phase used in the work and schemes of hydrolytic condensation reactions of HPEOS and HPMSS.

(HPMSS) (M_w=0.5 − 1 kDa), methyldiethoxisiloxit-riisopropoxititanium STP(1) (50% solution in toluene), and triethoxisiloxitriisopropoxititanium STP(2) (55% solution in toluene) were used as the precursors, whose chemical formulas are presented in Fig. 1. The precursors were synthesized in the Laboratory of Synthesis of Elementoorganic Polymers at the Enikolopov Institute of Synthetic Polymer Materials, Russian Academy of Sciences (ISPM RAS).

A porous polymer matrix was obtained by a uniaxial deformation of the initial PEHD film along the direction of extrusion in the medium of n-heptane (reagent grade) or isopropanol (reagent grade) to a deformation degree of 200% with a rate of 50%/min at a temperature of 20−25°C. Under these conditions, as was established earlier in [18], the deformation of PEHD is being developed according to the mechanism of delocalized crazing. After stretching, the films were fixed on the perimeter by metal frames—

clampers. The value of the efficient bulk porosity, which is determined as the ratio of the polymer volume increment to its volume after deformation, amounted to 35−50 vol %. The liquid medium (heptane or isopropanol) was removed from the pores by blowing the deformed films with air flow for 30 min.

In order to obtain the composites, dry porous matrices of PEHD were impregnated with precursors for a day and subjected to a hydrolysis over the vapors of 10% aqueous solution of HCl for two days. The schemes of the possible reactions of hydrolytic condensation of HPEOS and HPMSS and the products of reactions are presented in Fig. 1. The samples were rinsed by distilled water and dried at room temperature to a constant mass.

The amount of introduced filler was determined by a dry residual after burning of the polymer matrix under the conditions of heating of the samples in an open porcelain crucible by a temperature variation
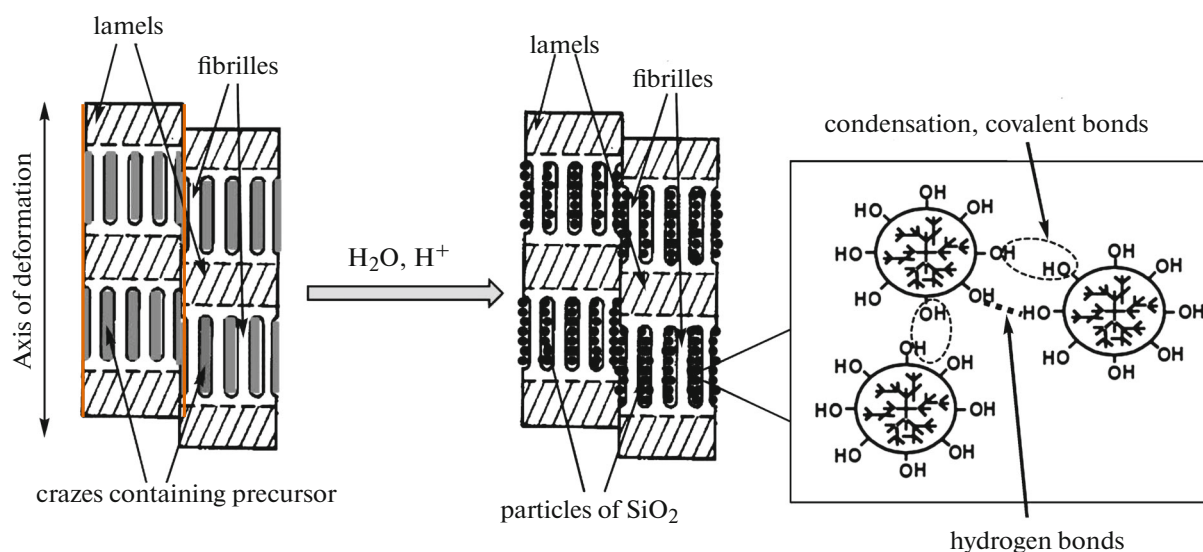
Fig. 2. Scheme of the formation of a silica phase with a framework structure inside a porous polymer matrix.

from 25 to 700°C with a rate of 20°C/min on a Mettler-TG50 device. Simultaneously, the curves of the dependence of mass losses by the samples on the temperature growth were obtained, which characterize the process of thermal-oxidative destruction of nanocomposites. From the curves of TGA, the temperature of mass loss start T_{st} and a temperature of 50% mass loss by the samples ($T_{1/2}$) were determined.

The determination of the characteristics of the porous structure for the composites and silica residuals after burning of the polymer matrix was carried out by calculating the isotherms of low-temperature nitrogen adsorption−desorption. The survey of the isotherms was carried out on an ASAP 2010 automatic sorbtometer (Micromeritics). The calculation of the isotherms was carried out with the use of the device's standard software.

The sorption properties with respect to liquids were determined by the mass increment of the composites after their impregnation with orthophosphoric acid (reagent grade) or the precursors for a week. The weighing of the samples was carried out on an electronic balance AND ER- 182A with an accuracy reaching 0.001 g.

The structural−morphological studies of the samples were carried out by scanning electron microscopy (SEM) on a JEOL JSM-6390LA microscope at the Nanochemistry and Chemistry of Atmosphere Scientific-Research Center for Collective Use. The cleavages were prepared according to the method of brittle destruction in liquid nitrogen; then they were fixed with the help of a viscous carbon strip to a special table and sputtered with gold. The maps of element distribution in the samples were built by energy-dispersion X-ray spectroscopy using an attachment to a JEOL EX-54175JMH electron microscope.

A change in the geometric shape of the composites in the process of heating was studied in this work. For this purpose, round samples with a diameter of 1 cm were cut, and changes in the ratio d_{per}/d_{par} were studied, i.e., the diameter perpendicular with respect to the direction of the initial deformation (d_{per}) to the diameter in parallel to it (d_{par}). The linear dimensions and their changes were determined at temperatures of 25, 50, 80, 110, 130, and 160°C. The heating and thermostatical control of the samples at each temperature was carried out for 30 min.

RESULTS AND DISCUSSION

In this work, the nanocomposition materials were obtained on basis of the PEHD matrices, whose porous structure was formed according to the mechanism of delocalized crazing when the arisen pores are localized in the interlammilar regions and are rather homogeneously distributed over the whole matrix bulk [10, 18]. As AAM media, heptane and isopropyl alcohol were used for which the maximum porosity by deformation of 200% amounted to about 40 vol %. After the introduction of a liquid precursor in pores of a polymer matrix by impregnation, it can be modified in a chemical way directly in the volume of the pore. The reaction of hydrolytic condensation in the presence of an acidic catalyst leads to the conversion of precursor compounds into a silica solid phase [19, 20]. Figure 1 presents general schemes of hydrolytic condensation reactions for HPEOS and HPMSS, leading to the formation of silica-phase particles of various chemical compositions. Depending on the precursor used, the functionality and hydrophobicity of the silicas is different. When the content of a solid filler is above 20 wt %, a three-dimensional (framework) structure of silica is formed that significantly changes

Table 1. Characteristics of silica-containing composites on the basis of PEHD

Precursor	Content of silica, wt %	Shrinkage, %	Sorption of liquids at 295K, wt %		Sorption of nitrogen at 77K	
			H_3PO_4	precursor	V_{por}, cm^3/g	S_{por}, m^2/g
HPEOS	22	6	7	9	−	−
	33	13	5	8	3×10^{-3}	2.2
HPMSS	29	5	1−2	2	−	−
	42	6	3−4	6	0	−
STP (1)	21	10	8	12	−	−
	24	16	2−3	11	7×10^{-4}	1.0

the properties of the initial polymer. The general scheme of the formation of a framework structure is shown in Fig. 2.

Following the described method, we have obtained composites based on PEHD and HPEOS, HPMSS of silicon–titanium precursors. As a result of hydrolytic condensation in the composites based on HPEOS, a three-dimensional structure is obtained with a common formula $\{SiO_2\}$, HPMSS − $\{CH_3SiO_{1.5}\}$, STP(1) − $\{CH_3SiO_{1.5}–TiO_2\}$, STP(2) − $\{SiO_2–TiO_2\}$. Table 1 presents the main characteristics of the composites. The content of the second component was varied within rather wide limits, from 18 to 42 wt % in a calculation on a dry residual after burning of the polymer matrix. When the samples were removed from the clampers, they practically did not change their linear dimensions, which can be a verification of the formation of solid three-dimensional framework from silica in the bulk of a porous polymer matrix in the reaction process of hydrolytic condensation. It should be noted that usually the value of a relative shrinkage of an empty PEHD film, which is deformed according to the crazing mechanism, amounts to 70–80%.

The electron microscopic study of the structure of the obtained composites has shown that silica is really distributed over the whole volume of the polymer matrix. Figure 3 presents typical images of the brittle cleavage of such materials and the maps showing the distribution of chemical elements of the main components for the phases of the nanocomposites (carbon for a polymer matrix and silicon for a silica phase), which are usually obtained independently from the chemical nature of the initial precursor. This indicates
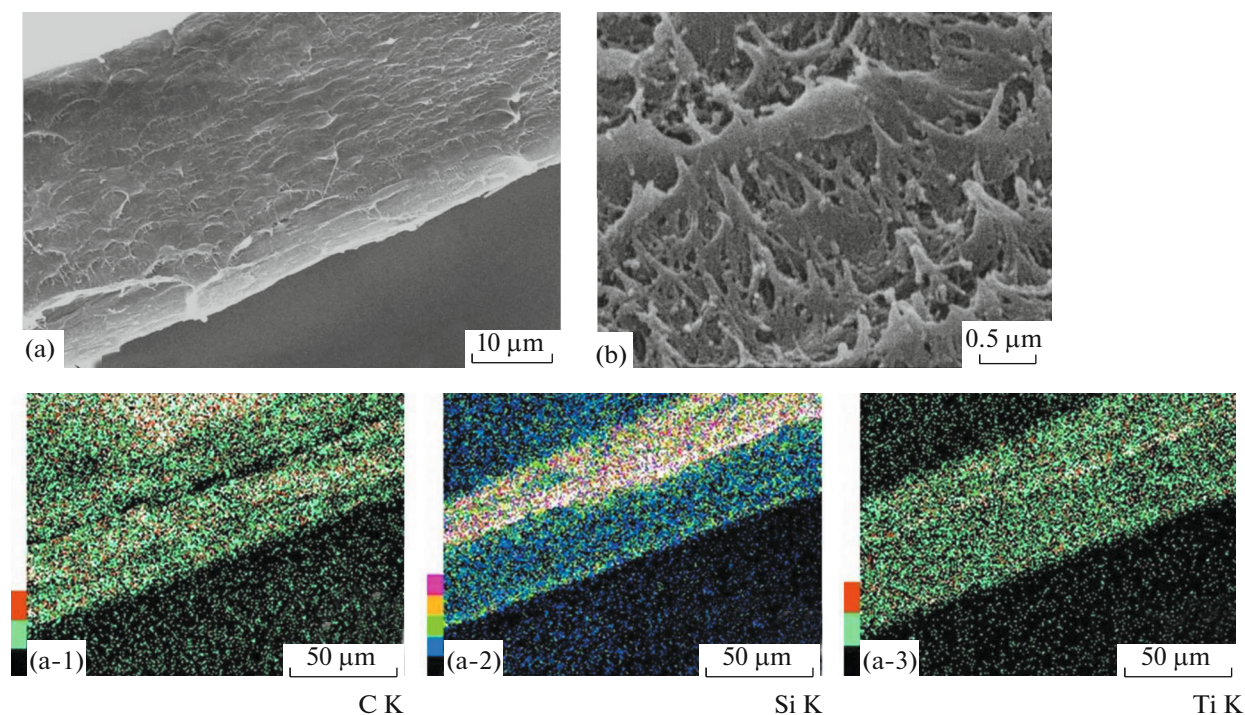

Fig. 3. (a, b) SEM-microphotographs of a brittle cleavage of a composite based on PEHD and STP(1); maps of the distribution of atoms (a-1) C, (a-2) Si, and (a-3) Ti. Microphotograph (b) is a magnified image of a region of the microphotograph (a).
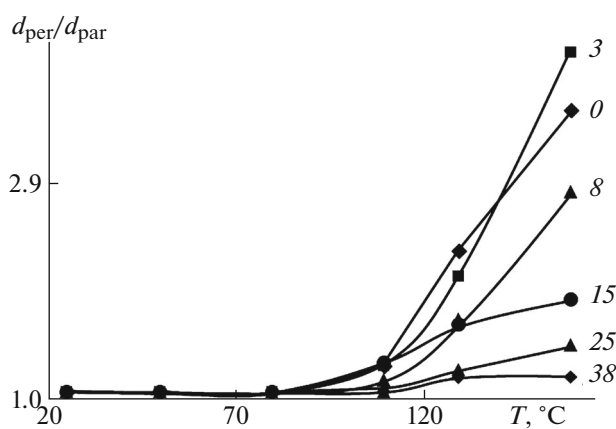
d_{per}/d_{par}

Fig. 4. Change in the shape of composites obtained on basis of HPEOS by heating in dependence on the concentration of the filler. Mass content of the filler in the composite in a recalculation on SiO_2 is indicated near the curve.

that the morphology of samples and the character of the distribution of the second component in the polymer matrix bulk are determined by the structure of a porous matrix, which depends on the mechanism of crazing.

One important characteristic of the polymer–silica composites is their ability to sorb various substances in liquid or gaseous states and from solutions. It can be seen from the data of Table 1 that the best sorption properties with respect to hydrophilic liquid media (orthophosphoric acid) are possessed by the composites based on HPEOS. The samples based on HPMSS sorb worse, which can be associated both with the presence of a hydrophobic methyl group in the precursor and, hence, in the formed silica phase and with the lower content of hydroxyl groups. However, it should be noted that the amount of the sorbed liquid medium is small and does not exceed 9 wt % for orthophosphoric acid and 12 wt % for the precursors.

For an additional characteristic of the sorption properties of the obtained composites, the samples were impregnated with solutions of three various dies: sudan in heptane, eosin in water, and rhodamine C in ethanol. In an aqueous solution of a dye, the samples were colorated rather badly aside from a composite based on HPEOS. However, from ethanol and heptane solutions of dies, the coloration of the composites was much more intense than for the initial porous polymer film. In this case, a the samples obtained using HPMSS had less intense coloration, while those based on HPEOS had the most intense coloration. Thus, the combination of a hydrophilic silica phase and hydrophobic polymer matrix imparts diphilic properties to a composite, which is manifested in its ability to sorb substances of various origins. In this case, a variation in the chemical composition of the initial precursors makes it possible to obtain in the PEHD matrix of various modified forms of silica and, respectively, to change the ratio between hydrophilic and hydrophobic properties of the composites.

However, unexpected results were obtained by studying the composites by low-temperature nitrogen sorption. This study was carried out for samples with approximately the same content of a filler (about 50 wt %), but differing in the chemical composition of the silica phase. It was found that such composites, regardless of the chemical composition of the second component and the structure of the three-dimensional framework, practically do not sorb nitrogen. This indicates that, after carrying out the reaction of hydrolytic condensation, the available volume of pores is practically filled by a filler and the composites possess rather low sorption properties.

We may suggest that the observed substantial differences in the character of sorption for liquid media, solutions of dies, and nitrogen by the obtained composition materials are associated with the differences in the mechanisms of the corresponding processes. For a porous polyethylene matrix, the sorbing ability is determined by the presence of available pores. For example, according to the data of low-temperature sorption of nitrogen, a porous thermally fixed PEHD matrix obtained according to the mechanism of delocalized crazing has a volume of pores of 0.22 cm^3/g and the average diameter of pores amounts to about 30 nm. The introduction of a hydrophilic filler into a hydrophobic matrix sharply changes the mechanism of adsorption. In this case, the chemical processes between the filler and the absorbed substance begin to play a substantial role, which is proven by the above-mentioned data on the sorption of dies. In particular, the coloration of the composites with silica is more intense than for the initial porous matrix of polyethylene. To all appearances, in the case of a low-temperature sorption of nitrogen, mainly the process of physical adsorption of gas takes place at available interfaces between the silica particles and the polymer matrix and in the pores up to its condensation. The absorption of liquid media is rather accompanied by the destruction of hydrogen- and, in the case of phosphoric acid, possibly ether bonds between the particles of the filler, which are formed in the process of the formation of a framework structure (Fig. 2). This probably results in the loosing of the phase of the second component and the increase in the sorbing ability of the composite. In the case of coloration of the samples with a solution of sudan in *n*-heptane, the additional possibility exists of increasing the dye concentration in the bulk of the composite due to swelling of the PEHD matrix in a given solvent. The very process of the formation of a silica phase by hydrolytic condensation is accompanied by a small shrinkage of the fibrillar matrix structure, which additionally results in a decrease in the composite porosity by 5–7 vol %. The use of liquids such as heptane and alcohol as solvents for dies, which are AAMs for PEHD in the process of impregnation, can lead to a peptization of the structure of the fibrillar polymer, which collapsed in the process of the formation of silica phase, which also facilitates an increase in the sorption capacity of the nanocomposites.
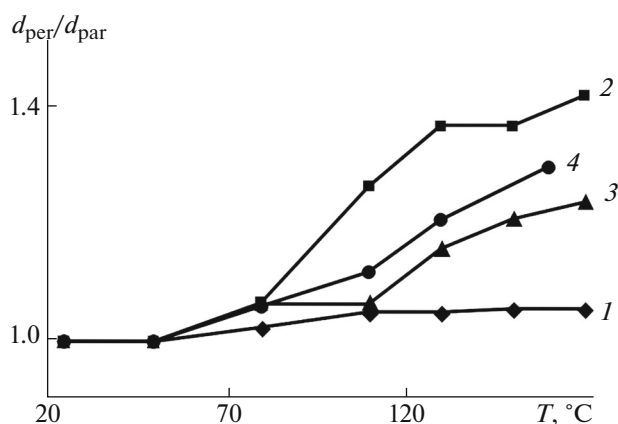
Fig. 5. Change in the shape of composites obtained on basis of (*1*) HPEOS, (*2*) HPMSS, (*3*) STP(1), and (*4*) STP(2) by heating. Mass content of the filler in all the samples amounted to 25−35 wt %.

Let us consider the effect of the concentration and chemical composition of the precursor and, hence, the silica phase obtained from them on the thermal properties of the composites. For this purpose, we annealed standard samples at various temperatures up to the temperatures above that of melting of a polymer matrix (130°C) and observed a change in their geometric shape in the process of heating. Figure 4 presents the dependences of a change in the ratio d_{per}/d_{par} for the initial sample of a round shape on the temperature of heating for the composites based on HPEOS depending on the silica content. By relatively low con-

centrations, the filler does not form a continuous phase in the matrix, and the geometry of samples strongly changes at high temperatures. When a concentration of 20 wt % and above is achieved, the amount of filler is sufficient for the formation of a continuous framework from silica, which preserves the sample shape above the temperature of melting of a polymer matrix.

Figure 5 shows the dependences of a change in the ratio d_{per}/d_{par} on the temperature of heating for the composites containing a modified silica phase of various chemical composition (the content of the filler is 25−35 wt %). The synthesis of the solid phase of the second component in the PEHD matrix makes it possible to keep the geometric dimensions of the samples at temperatures above that of melting of a polymer. The composites based on HPEOS keep the shape best of all. As follows from Fig. 4, the content of the filler in this study exceeds the percolation threshold of creation of a framework-structure. A rigid framework from silica keeps the sample shape well, and its geometry in fact is not changed even at 160°C. The shape is kept worst of all by composites based on HPMSS, which may be associated with the condensation processes in the silica phase and its densification at an elevated temperature.

Figure 6 shows SEM-microphotographs of the surfaces of the composites after heating of the samples in air to 160°C. It can be seen that the polymer redistributes in the silica framework, moving from the bulk to the surface. The most intense processes of redistribution proceed in a composite based on HPEOS, which
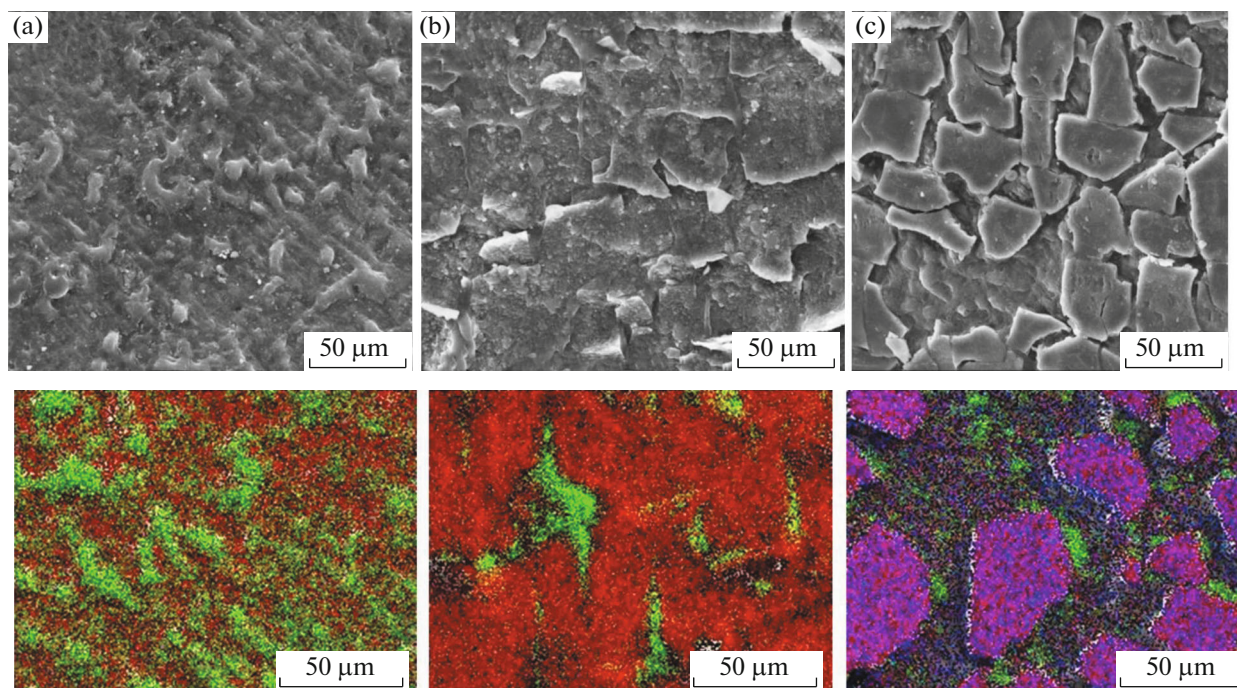

Fig. 6. SEM-microphotographs of the surfaces of the composites (above) and maps of the distribution (below) of carbon atoms (green), silicon (red), and titanium (blue) after heating to 160°C. The composites are obtained on basis of the precursors (a) HPEOS, (b) HPMSS, and (c) STP(1).
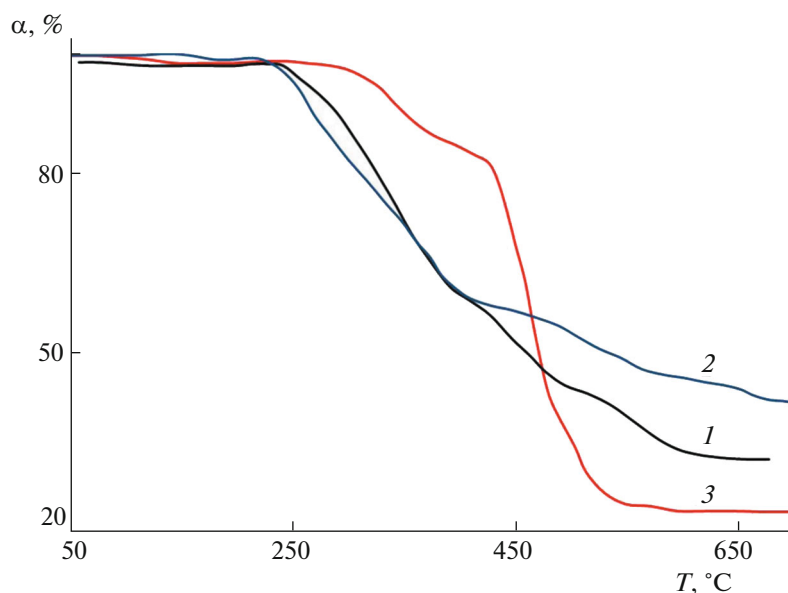
Fig. 7. Curves of the dependence of mass loss on the temperature (curves of TGA) for the composites obtained on basis of (*1*) HPEOS, (*2*) HPMSS, and (*3*) STP(1).

may be associated with the greatest inconsistency between polymer and inorganic phases. In the case of HPMSS and STP(1), the consistency of the components is better due to the presence of a methyl group in the chemical structure of silica.

Heating of polyolefins in air atmosphere usually leads to a start of intense oxidative processes, which results in their destruction. In this work the processes of the thermal-oxidative destruction of the silica-containing composites of various chemical composition were studied. Figure 7 presents the curves of mass loss for the composites based on HPEOS, HPMSS, and STP(1); Table 2 presents the main parameters characterizing the process of thermal-oxidative destruction. A mass loss for pure PEHD matrix starts at 270°C. Introducing a silica phase practically does not change

Table 2. Characteristic parameters of the process of thermal-oxidative destruction for silica-containing composites based on PEHD.

Filler	Content of the filler, wt %	T_{st}, °C	$T_{1/2}$, °C
—	0	270	400
SiO_2	22	250	440
	33	270	440
$(CH_3)SiO_{1.5}$	29	230	440
	42	220	410
$(CH_3)Si_{1.5}–TiO_2$	15	300	430
	24	330	450
	33	350	460
$SiO_2–TiO_2$	16	310	400
	21	340	450

the temperature of the mass loss start, while introducing $CH_3SiO_{1.5}$ even decreases it somewhat. The introduction of a silica–titanium phase significantly increases the temperature of mass loss start (by 30–80°C), and the higher the concentration of the filler is, the more substantial the shift in temperature towards a higher temperature region is. Such a stabilizing action may be associated both with the structure of titanium atoms, which have vacant d-orbitals and are able to disactivate the radicals formed in the process of oxidation, and with an organic shell, which remains in the composites after the hydrolysis of STP. An analogous influence of titanium dioxide phase on the processes of thermal-oxidative destruction of an isotactic polypropylene was observed earlier in [21].

By studying the thermal-oxidative properties of the composites, it was found that, after burning out the polymer matrix, porous residuals of silica phase remain. The residuals of the composites obtained on basis of HPEOS and STP form plates that, in regards to their shape and external view, correspond to the initial samples of the composites. After burning out PEHD from the composites based on HPMSS, no integral residual is formed and it decomposes into separate fragments. This can indicate the lower stability of the grid of the silica phase in such composites due to the lower functionality of a silicon atom in the initial precursor (in HPMSS the index of branching is 3; in HPEOS it is 4).

The porous structure of the residuals was characterized by the low-temperature sorption of nitrogen. Table 3 presents the characteristics of a porous structure of inorganic residuals calculated from the curves of sorption–desorption. It was found out that silica–titanium residuals possess the greatest volume and specific surface area of pores of all the samples stud-

Table 3. Characteristics of the structure of porous silica phase calculated from curves of sorption–desorption of nitrogen.

Sample	V_{por}, cm³/g	S_{por}, m²/g	d_{por}, nm
SiO_2	0.484	104	27
SiO_2 (50%)–$SiO_{1.5}$	0.318	104	14
SiO_2 (20%)–$SiO_{1.5}$	0.219	71	14
SiO_2 (10%)–$SiO_{1.5}$	0.207	60	16
SiO_2 (5%)–$SiO_{1.5}$	0.184	75	12
$SiO_{1.5}$	0.21	72	14
$SiO_{1.5}$–TiO_2	0.511	129	23
SiO_2–TiO_2	0.627	109	25

ied; their value achieves 0.5–0.6 cm³/g and 110–130 m²/g, respectively.

An interesting fact was observed by studying the porous residuals obtained from the composites based on a mixture of the precursors HPEOS/HPMSS of various compositions. It was found that, when the content of HPEOS in the mixture is from 5 to 20 vol %, the parameters of the porous residuals are analogous to those formed from the composites based on SPMSS. From the composite, where the content of SPEOS amounted to 50 vol %, the residual was obtained in which the volume of pores and their specific surface were the same as from the composite based on HPEOS, and the size of pores was two times smaller, i.e., like from the composite based on HPMSS. This fact opens up the possibility of controlling the architecture of porous silica by varying the combinations of the precursors of various chemical compositions.

Thus, the studies carried out have shown that, on basis of one porous PEHD matrix obtained by the mechanism of delocalized crazing and modified forms of silica precursors, it is possible to obtain both nanocomposites with various thermal and sorption properties and porous plates from silica with a variable specific surface of 70–130 m²/g and an average diameter of pores of about 15–30 nm.

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