STRUCTURE,
PROPERTIES

Crazing of Polymers in the Presence of Hyperbranched Poly(ethoxysiloxane)[1]

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Abstract—The crazing of various polymers (PET, isotactic PP, and HDPE) in the presence of branched poly(ethoxysiloxane) and its low-molecular-mass analog—tetraethoxysilane—has been studied. The hyperbranched poly(ethoxysiloxane) is shown to be an effective adsorptionally active medium for crazing of various solid polymers and development of nanoporous structures with a volume porosity of up to 60%. Depending on the nature of polymers, two mechanisms of crazing (either classical or delocalized crazing) can take place. The reactions of hydrolysis (basic and acidic) within the pores leading to formation of solid silica have been performed. Electron microscopic observations provide evidence that the transformation of a viscous adsorptionally active liquid into a solid compound directly within the volume of a polymer matrix leads to the stabilization of a highly dispersed polymer structure that arises in the course of crazing.

INTRODUCTION

Crazing is known to be the process of polymer self-dispersion under the joint action of mechanical stress and adsorptionally active liquid environment (AALE) [1]. In this case, the formed structure represents a system of interpenetrating pores and fibrils whose diameters are ~10 nm. Hence, this approach allows achievement of the nanometric level of polymer dispersion. At the present time, the process of solvent crazing has been well studied and the parameters of the formed porous structure have been characterized for various solid amorphous and semicrystalline polymers stretched in the presence of AALEs of different chemical structures (alcohols, hydrocarbons, and amines) [2]. Therefore, the crazing of polymers in the presence of liquid environments can be treated as a universal means suitable for modification of various polymers.

An important feature of solvent crazing is an effective filling of the formed microvoids inside the structure of a growing craze by the surrounding liquid environment. This filling of the nanoporous structure with a low-molecular-mass component implies that this component is also dispersed to colloid dimensions. As a result, the mutual dispersion and uniform blending of a polymer and an incompatible low-molecular-mass or high-molecular-mass component may be achieved.

Nanoscale pores can be used as microreactors for different chemical reactions (reduction and exchange) and in situ synthesis of nanophases of a required level of dispersion and desired morphology [3–5]. This approach for the preparation of nanocomposites with predicted properties makes it possible to solve several fundamental problems: nanoscale blending of thermodynamically incompatible components and stabilization of nanophases due to the limiting factor of walls.

The use of chemical compounds with functional groups as a second component offers wide opportunities for the chemical modification of porous polymer materials. In our opinion, liquid components that serve as crazing-promoting agents and precursors for the preparation of compounds with desired physicochemical properties are of utmost interest. In this study, hyperbranched poly(ethoxysiloxane) (PEOS) was used as the second component [6, 7]. Owing to a practically spherical shape of macromolecules, even high-molecular-mass hyperbranched PEOS (its M_w is several tens of thousands) is a liquid with a relatively low viscosity. The hyperbranched PEOS involves reactive ethoxy groups that can be easily replaced with any other functional groups via chemical reactions carried out within the volume of nanopores of the polymer matrix. On the other hand, ethoxy groups are characterized by polymer

affinity and this behavior provides adsorptionally active properties of the hyperbranched PEOS.

Hence, the goal of this study is to investigate the specific features of solvent crazing in different amorphous (PET) and semicrystalline polymers (isotactic PP and HDPE) in the presence of the high-molecular-mass hyperbranched PEOS and its low-molecular-mass analog—tetraethoxysilane (TEOS), which has a similar chemical composition but quite a different viscosity.

EXPERIMENTAL

As polymers, the commercial films of isotactic PP ($M_w = 3 \times 10^5$, and the film thickness was 140 µm), HDPE ($M_w = 2 \times 10^5$, and the film thickness was 75 µm), and an amorphous PET ($M_w = 3 \times 10^4$, and the film thickness was 100 µm) were used. The uniaxial tensile drawing of the polymer films was performed in the presence of TEOS (the density was 0.9334 g/cm^3) and the hyperbranched PEOS ($M_w = 3 \times 10^4$, the density was 1.17 g/cm^3, and the effective molecular dimensions were 2–5 nm) under tensile strains varying from 50 to 400%; the strain rate was 10–500%/min.

The dynamic viscosity of liquids was measured via rotary viscometry on a RheoStress-600 rheometer with a cone–plane working unit (the cone angle was 2°, and $d = 35$ mm). Viscosity was estimated from the shear stress versus shear rate plots. For both TEOS and hyperbranched PEOS, the above dependences were approximated by a straight line. The slope of this line corresponded to the viscosity of a given liquid. The experimental errors were 5 and 1% for TEOS and hyperbranched PEOS, respectively.

Stress–strain tests were performed in the mode of uniaxial tensile drawing. Polymer samples were stretched in air and liquid environments with the aid of an Instron-4301 universal tensile machine at 20–25°C; the strain rate was varied from 10 to 500%/min. The test samples were cut from the initial films as dumbbell-shaped specimens with a gage length of 10 mm and a width of 4.3 mm.

The effective volume porosity W (vol %) of solvent-crazed polymers was measured during tensile drawing in the presence of liquid environments as an increase in the volume of the test samples in accordance with [8].

The content of the loaded hyperbranched PEOS and the degree of its hydrolysis were estimated by two methods: (i) gravimetrically through measurements of changes in the weight of the initial polymer film after introduction of the hyperbranched PEOS and subsequent hydrolysis and (ii) from analysis of a solid residue after burning of the polymer matrix via heating in air from 25 to 800°C (at a heating rate of 10 K/min) on a Mettler TG-50 instrument. The composition of the solid residue was studied by elemental analysis.

The chemical composition of the samples was studied by IR spectroscopy in the transmission mode with the aid of a Specord M-80 instrument; the wavelength was varied from 400 to 4000 cm^{-1}. The IR bands were identified with the use of standard tables.

Structural and morphological studies were performed by the methods of electron microscopy. The samples were prepared as ultrathin sections with the use of a diamond-tipped knife according to the standard procedure of ultrathin section cutting; the samples were examined on a LEO 912 AB OMEGA transmission electron microscope. SEM studies were performed on a Hitachi S-520 scanning electron microscope; the test samples were prepared by the method of brittle fracturing in liquid nitrogen; the fractured samples were decorated with gold.

RESULTS AND DISCUSSION

Stress–Strain Behavior of Polymers in Hyperbranched PEOS and TEOS

As is known [2], the uniaxial tensile drawing of a polymer film in a liquid environment proceeds via the mechanism of solvent crazing, wherein this liquid shows adsorptionally active properties with respect to this polymer. In this case, practically no swelling of the polymer in the selected liquid takes place. but this liquid effectively wets the polymer and reduces its interfacial surface energy. The liquid PEOSs used in this study are interesting fillers: on the one hand, they are characterized by a low viscosity and, on the other hand, they are known to be polyfunctional compounds. In other words, polymer-analogous reactions and formation of new compounds are possible. Silicon-containing alkoxy derivatives (the hyperbranched PEOS and TEOS) contain ethoxy groups and can show adsorptionally active properties toward the selected polymers. The viscosities of the above liquids differ by more than 25 times: the dynamic viscosity of TEOS is 0.7 cP, whereas the viscosity of the hyperbranched PEOS is 18.8 cP (at 25°C).

As was found, all polymers (PP, HDPE, and PET) practically do not swell in the hyperbranched PEOS and TEOS. The degree of swelling at the test temperature (20–25°C) is below 1 wt % for PP and PET and 2.0–3.5 wt % for HDPE. With an increase in temperature to 60°C, the degree of swelling increases to 3.0–4.5 wt %.

The tensile tests at a given strain rate were performed for the samples in air and liquid environments. As air is not an AALE for all the polymers under study, we compared the stress–strain curves for the polymers stretched in air and in the presence of the hyperbranched PEOS. Figure 1 shows the stress–strain curves for the initial PP film (the isotactic PP without annealing) during its stretching in air and ethoxysiloxanes. Similar curves were obtained for all other polymers.

For all the test polymers, the tensile drawing in the presence of liquid environments is accompanied by a

σ, MPa
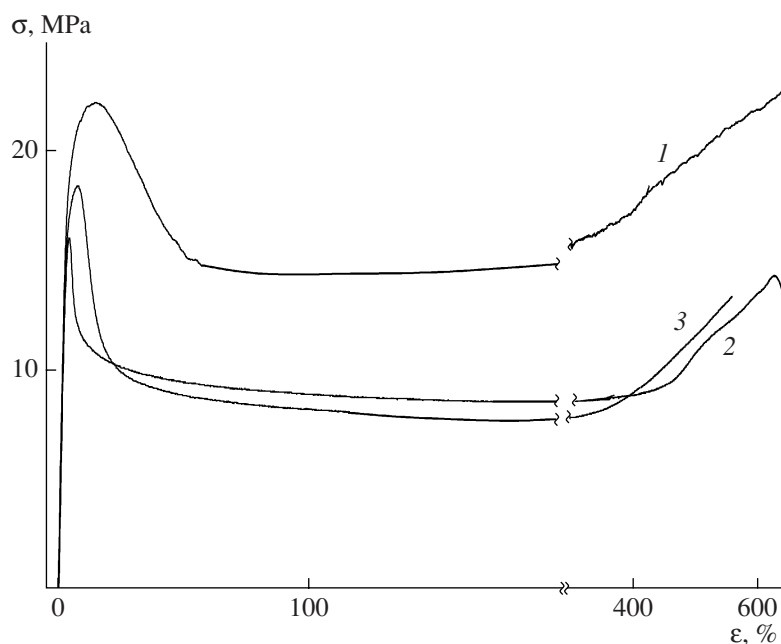
Fig. 1. Stress–strain curves of the isotactic PP recorded in (*1*) air, (*2*) TEOS, and (*3*) hyperbranched PEOS. The strain rate was 10%/min.

marked decrease in both the yield stress and the post-yield stress. In TEOS, the above parameters decrease by 20–50% relative to the corresponding values in air; in the presence of a more viscous liquid, such as the hyperbranched PEOS, this decrease amounts to 15–20%. The above observations indicate that both TEOS and the hyperbranched PEOS are able to reduce the interfacial surface energy of polymers and serve as efficient AALEs.

Table 1 lists the yield stress σ_y for the polymers during their stretching in air and in the presence of TEOS and the hyperbranched PEOS at different strain rates.

For all polymers, a difference between the values of the yield stress in air and liquid environments decreases with an increase in the strain rate. The effect of the strain rate is the most pronounced for PP and HDPE; namely, at a strain rate of 500%/min, the corresponding stress–strain curves recorded in air, TEOS, and hyper-

Table 1. Yield stress σ_y for PET, isotactic PP, and HDPE during their stretching in air and in the presence of TEOS and hyperbranched PEOS

| Polymer	Environment	σ_y (MPa) at different strain rates (%/min)		
		10	100	500
PET	Air	52.3	60.8	64.0
	TEOS	25.2	34.7	36.6
	Hyperbranched PEOS	40.3	54.0	53.3
Isotactic PP (without annealing)	Air	22.2	25.0	26.8
	TEOS	16.1	21.8	24.2
	Hyperbranched PEOS	18.3	22.1	23.7
Annealed PP	Air	35.3	39.1	34.6
	TEOS	24.8	30.0	33.5
	Hyperbranched PEOS	29.6	33.1	34.0
HDPE	Air	20.2	23.4	26.6
	TEOS	19.7	24.8	25.6
	Hyperbranched PEOS	19.0	25.9	28.0
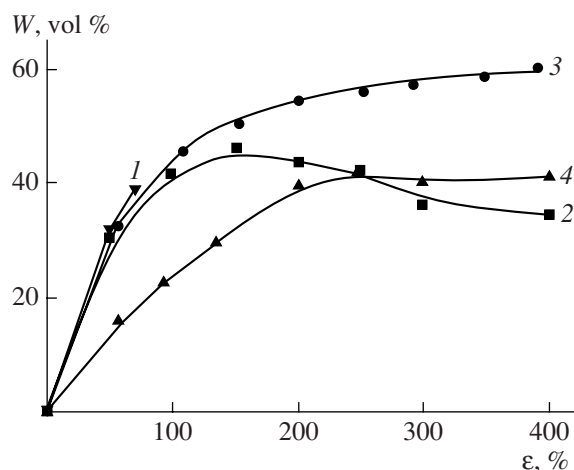
Fig. 2. Effective volume porosity of solvent-crazed films based on (*1*) PET, (*2*) isotactic PP, (*3*) annealed PP, and (*4*) HDPE vs. the tensile strain of the samples prepared via stretching in the presence of (*1–3*) hyperbranched PEOS and (*4*) TEOS. The strain rate was 10%/min.

branched PEOS appear to be practically the same. Therefore, one can conclude that crazing is suppressed, since under these conditions the rate of liquid flow to a growing crack tip is lower than the overall crack growth rate in the polymer samples [9].

Therefore, the liquid hyperbranched PEOS with given characteristics (the dimensions of particles are 3–5 nm, and the viscosity is 18 cP) can serve as a crazing-promoting agent and can provide the development of a porous structure in polymers.

As the hyperbranched PEOS was used as a crazing-promoting liquid for the first time, a question arises as to what amount of this component can be introduced into the polymer matrix and how this parameter is affected by the polymer nature and its structure. In this case, volume porosity and pore dimensions are the key characteristics of porous systems.

In this study, we measured the effective porosity of polymer films during tensile drawing in TEOS and the hyperbranched PEOS as a function of tensile strain (Fig. 2). These relationships are very important since changes in the volume porosity with varying tensile strains can provide important information concerning the mechanism of crazing. As is seen, the initial isotactic PP film (without annealing) is characterized by a nonmonotonic dependence $W(\varepsilon)$ with a maximum; at 150–200%, the porosity achieves its maximum value equal to 45–50 vol % (Fig. 2, curve *2*). This profile of the $W(\varepsilon)$ plot is typical of polymers, when their tensile drawing in the presence of AALEs proceeds via the mechanism of classical solvent crazing [2]. For the annealed PP and HDPE, porosity constantly increases up to breaking strains. This behavior is typical of polymers during their deformation via the mechanism of
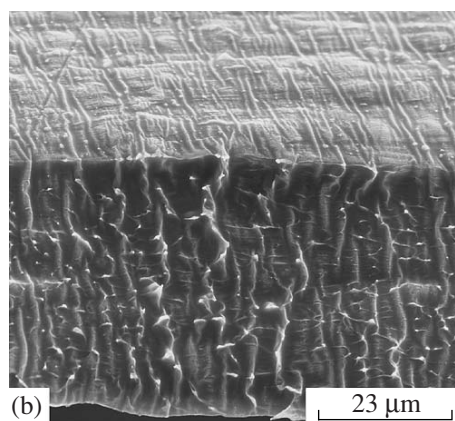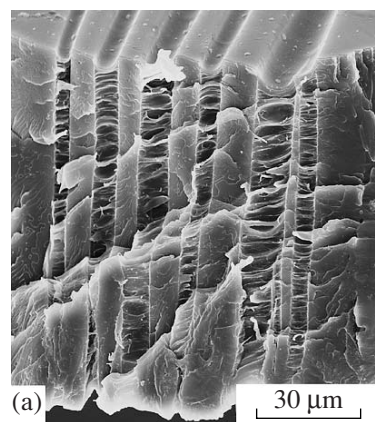
Fig. 3. SEM images of fracture surfaces for the solvent-crazed films based on (a) the solvent-crazed PET stretched by 70% in TEOS and (b) HDPE stretched by 200% in the hyperbranched PEOS.

delocalized solvent crazing [2]. The amount of involved liquid in the porous polymer matrix is 40–60 vol % (Fig. 2, curves, *3*, *4*). It should be mentioned that the volume porosity of the annealed PP film after its tensile drawing in the hyperbranched PEOS is higher by a factor of 1.5 than that in isopropanol. This fact indicates that the hyperbranched PEOS is an effective crazing agent.

Indeed, microscopic studies confirm that the tensile drawing of the films based on the initial isotactic PP and PET (Fig. 3a) in TEOS and the hyperbranched PEOS proceeds via the development of classical crazes: the corresponding microscopic images clearly show alternating regions of the crazed and bulk polymer.

For the solvent-crazed samples based on the annealed PP and HDPE, their fracture surfaces (Fig. 3b) do not show any well-defined regions of crazed and bulk polymer. This pattern is typical of delocalized solvent crazing.

Note that, for the tensile drawing of the HDPE film in the presence of the hyperbranched PEOS, the dependence of porosity shows a well-pronounced maximum that is equal to 25 vol % at a tensile strain of 150%.

Table 2. Characteristics of the composites based on the annealed PP and the hyperbranched PEOS before and after hydrolysis

Conditions of hydrolysis	Volume content of hyperbranched PEOS, vol %	Weight content of hyperbranched PEOS, wt %		Residue after annealing, wt %
		before hydrolysis	after hydrolysis	
Acidic	50	58	50	41
Basic	50	58	49	38

However, microscopic observations demonstrate that the deformation of HDPE proceeds via the mechanism of delocalized solvent crazing. This behavior in the presence of AALE is typical of HDPE: earlier, similar dependences of porosity with maxima were obtained for tensile drawing in isopropanol [10].

Hence, TEOS and the hyperbranched PEOS are good adsorptionally active environments (similar to the well-known aliphatic alcohols) and the tensile drawing of semicrystalline (PP and HDPE) and amorphous (PET) solid polymers in the presence of the above liquid environments proceeds via the mechanism of solvent crazing. The maximum filling of pores is achieved for the films of the annealed PP for which this parameter is as high as 60 vol %. Depending on the nature and supramolecular structure of polymers, one can observe both basic mechanisms of solvent crazing: namely, classical and delocalized solvent crazing.

Hydrolysis of Hyperbranched PEOS within Pores of the Polymer Matrix

In this study, compounds introduced into a porous polymer matrix were involved in polymer-analogous reactions. Let us remember that the above functional liquids contain reactive ethoxy groups that can be easily transformed into solid crosslinked silica gels via hydrolytic polycondensation. This chemical process was used in this study.

The films filled with the hyperbranched PEOS and TEOS under isometric conditions and at room temperatures were exposed to vapors of 10% aqueous solutions of hydrochloric acid or ammonia. In this case, the reaction proceeded directly within the pores of the polymer matrix. The hydrolysis of the hyperbranched PEOS and TEOS in the polymer matrix was monitored with IR spectroscopy. The recorded IR spectra show well-pronounced IR bands at 800 and 1050–1200 cm^{-1}. These bands correspond to vibrations of a Si–O bond. This fact indicates the presence of ethoxysiloxanes within the volume of the polymer sample. After hydrolysis, the 960-cm^{-1} band corresponding to vibrations of Si–OC$_2$H$_5$ groups disappears, but the bands at 900–950 cm^{-1} (the vibrations of Si–OH groups) and 1630 and 3350 cm^{-1} emerge (deformation and stretching vibrations of OH groups, respectively). This fact indicates that ethoxy groups are transformed into hydroxyl groups via hydrolysis and poly(silicic acid) is formed.

Table 2 summarizes the data concerning the content of the hyperbranched PEOS involved in the matrix based on the annealed PP after tensile drawing and hydrolysis. The data on the volume and weight contents of the hyperbranched PEOS in the polymer matrix lend support for the conclusion that this compound fills the pores arising during tensile drawing via crazing. According to the mechanism advanced in [6] for the hydrolysis of the hyperbranched PEOS, the degree of hydrolysis can be calculated from thermogravimetric measurements. This value achieves 100%, and the reactions of intramolecular and intermolecular condensation of hydroxyl groups can take place.

Silica gel formed during hydrolysis is a solid substance that can suppress the occurrence of shrinkage in the crazed polymers. Therefore, when the solvent-crazed samples were unloaded, their geometric dimensions were preserved. Let us note that the shrinkage of the samples before hydrolysis can achieve 80–90%. Figure 4a shows the SEM image of the fracture surface of the silica-containing PP sample.

Stabilization of a Highly Porous Structure of Solvent-Crazed Polymers

A highly dispersed structure in polymers is known to be very unstable, and the removal of the AALE from the pores leads to marked structural changes. This process is accompanied by a decrease in the pore volume down to a complete collapse of the porous structure. This property of solvent-crazed matrices presents serious difficulties for visualization of their structure and morphology via direct microscopic methods. The above highly dispersed structure of solvent-crazed polymers can be stabilized when a volatile AALE, in which the tensile drawing is performed, is replaced with some other nonvolatile compound, for example, sulfur [11]. However, this approach does not make it possible to avoid certain structural rearrangements in the polymer that are related to changes in the surface activity of the compound involved in pores. Another approach to stabilization concerns changes in the aggregative state of the AALE within the volume of pores, for example, through crystallization of low-melting compounds, whose melting temperature is lower than the glass transition temperature (or the melting temperature) of polymers. This approach has been applied in [12] where melts of some low-molecular-mass organic compounds (*n*-octadecane, heneicosane,
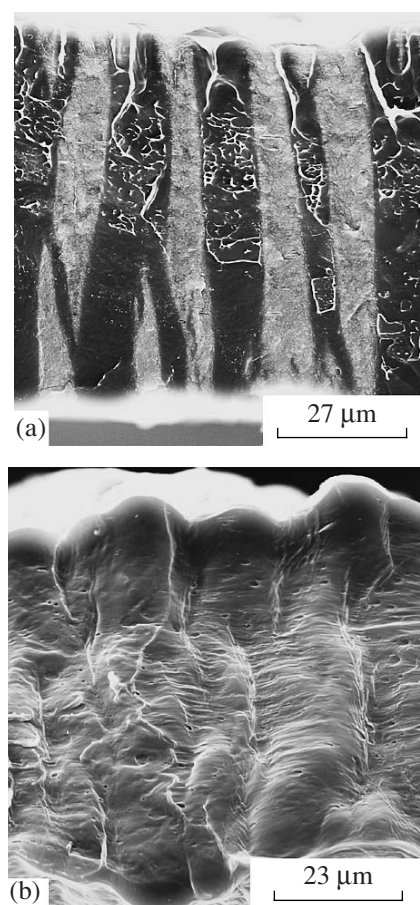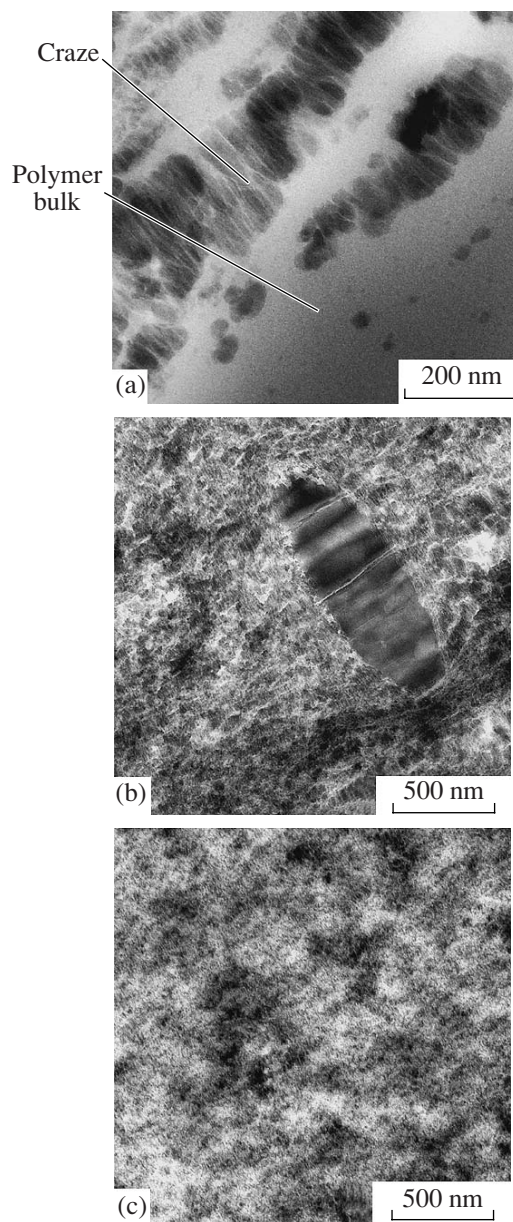
Fig. 4. SEM images of fracture surfaces for the isotactic PP after stretching in hyperbranched PEOS and hydrolysis in NH$_3$ vapor (a) before and (b) after treatment with HF solution.

Fig. 5. TEM images of ultrathin sections of solvent-crazed films based on (a, b) isotactic and (c) annealed PP after stretching in hyperbranched PEOS and hydrolysis in HCl vapor.

cetyl alcohol, and tridecanoic acid) were used as AALEs.

In this study, an alternative approach for the stabilization of a highly dispersed structure of solvent-crazed polymers has been proposed. This approach implies changes in the aggregative state of the hyperbranched PEOS within the volume of pores via the hydrolytic polycondensation of reactive ethoxy groups that can be easily transformed into solid crosslinked silica gels. This chemical process was used herein for stabilization of the solvent-crazed structure of the polymer matrix.

To verify the assumption concerning the stabilizing role of the formed silica gel in pores, the following experiment was conducted. The test samples after hydrolysis were treated with a solution of hydrofluoric acid. Figure 4 shows the SEM images of the fracture surface of silicate PP sample before and after treatment. As is seen, owing to interaction with HF and silica gel, the solid phase is fully removed from the crazes of the polymer matrix. As expected, this effect leads to the collapse of the porous structure (Fig. 4b).

Therefore, the solid phase of poly(silicic acid) formed within the craze pores actually limits the mobility of thin polymer fibrils and probably makes it possible to preserve a high level of the polymer dispersion. This assumption was confirmed via direct TEM observations: in this case, the hyperbranched PEOS was used as an AALE. Figure 5 displays the TEM images of the ultrathin sections of solvent-crazed films after hydrolysis of the initial PP sample and the annealed PP sample.

Indeed, the corresponding TEM images clearly show a highly dispersed polymer structure that is com-

posed of thin (5 nm) oriented polymer fibrils (white regions); between fibrils, one can observe solid filler particles (dark regions). Both scanning and transmission electron microscopy methods show that, in the case of the classical solvent crazing, the highly dispersed polymer structure and the particles of poly(silicic acid) being formed are localized only in crazes; in the case of the delocalized solvent crazing, they are distributed throughout the whole volume of the polymer sample. In other words, after hydrolysis, the initial morphology of solvent-crazed samples is preserved. Furthermore, in the case of the classical solvent crazing, crazes are seen to involve oval inclusions of the bulk polymer with dimensions of no more than 0.5–2.0 μm (Fig. 5b). The above inclusions are probably formed owing to the incomplete coalescence of neighboring crazes at the stage of craze widening.

The transformation of a low-volatile adsorptionally active liquid into a solid compound directly within the volume of the polymer matrix actually facilitates stabilization of the highly dispersed polymer structure formed in the course of crazing. This approach to fixation of a fine craze structure and the use of the high-resolution transmission electron method for studying thin sections make it possible to visualize the highly dispersed structure of solvent-crazed polymers.

In the case of a highly volatile and mobile TEOS, the yield of silica gel in hydrolysis is rather low and the shrinkage of solvent-crazed polymer is suppressed owing to formation of a silica gel layer on the film surface. Within the volume of the polymer matrix, the removal of AALE from the porous structure is accompanied by marked structural changes that entail the collapse of the highly dispersed polymer structure.

Therefore, the hyperbranched poly(ethoxysiloxane) is an effective adsorptionally active medium providing crazing in various solid polymers and leading to development of a nanoporous structure with a volume porosity of up to 60%.

The proposed approaches can be used to prepare hybrid nanomaterials with predicted physicochemical characteristics on the basis of commercial polymers and functional dendrite macromolecules.

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