

Polypropylene/Silicate Composites on the Basis of Crazed Polymer and Hyperbranched Polyethoxysiloxane

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Received June 21, 2007; Revised Manuscript Received September 21, 2007

ABSTRACT: Hyperbranched polyethoxysiloxane (HPEOS) is suggested as an adsorption-active medium in the crazing of commercial polypropylene film and as a precursor of silica. As a result of delocalized crazing of polypropylene, the nanoporous materials characterized by the effective volume porosity to 60 vol % are received. The reaction of HPEOS hydrolysis into pores of a polymer at the presence of acidic and basic catalysts is studied. Obtained silica phase is shown to stabilize the nanoporous structure of crazed polypropylene. The morphology of polymer/silicate composite is fully determined by the structure of crazed polymer matrices, and it is a system of organic/inorganic interpenetrative nets. Because of this structure, the tensile modulus of the composite material exceeds the modulus of the initial polymer by 50–100%.

Introduction

The study of properties of polymer/silicate systems is of great interest and is developing in two main directions. The first is connected with the development of nanocomposite polymer/silicate materials on the basis of industrial important polymers and natural layered silicate.¹ Such materials possess unique mechanical, thermal, and barrier properties. The main methods of composite synthesis are the introduction of layered silicate particles into a melt or solution of a polymer and the polymerization of monomer between layers of silicate. These approaches usually require additional modification of the silicate filler and polymer matrix.

The other direction of investigation of the polymer/silicate systems is related to a search of effective and economical methods of synthesis of highly porous systems on the basis of silica, which is typically used as sorption, selective, sensory, catalytic materials. In these works polymer is used as a template and structuring matrix for silicate phase obtained by hydrolysis of alkoxy silanes.^{6–8} Polymer must form the definite regular structures in solution of silica precursor and specifically interact with the obtained silica.

In this paper we suggest another method for the preparation of polymer/silicate systems using the phenomenon of crazing of polymers in a liquid medium.^{9,10} In the process of crazing active liquid medium penetrates into the volume of a polymer which leads to its dispersion and to formation of nanoporous system. This method allows a polymer to be filled uniformly with the second component and disperse filler effectively to the nanometrical level.¹¹ In the paper crazing was used as a delivery method of the compound precursor into a polymer matrix with its following hydrolysis in nanopores' volume. This approach opens up the possibility to prevent aggregation of particles in the process of hydrolysis and preserve high mutual dispersion of polymer matrix and silicate filler. Dendritic

hyperbranched polyethoxysiloxane^{12,13} was used as a compound precursor. This substance is a low-viscosity liquid in contrast to linear polymer analogue, which is an important condition of solvent-crazing development. Moreover, hyperbranched polyethoxysiloxane is not volatile if it is compared with low-molecular-weight alkoxy silanes so it can be stored in the volume of a polymer over a long period of time.

Experimental Section

In this paper we use commercial films of isotropic isotactic polypropylene, PP ($M_w = 3 \times 10^5$, $h = 140 \mu\text{m}$), annealed at 140 °C. Hyperbranched polyethoxysiloxane (HPEOS), synthesized by this method,¹² was used as filler. HPEOS is colorless oily liquid with density 1.17 g/m³ and $M_w = 3 \times 10^4$; the diameter of its globular macromolecules is 2–5 nm.

The dynamic viscosity of HPEOS was determined by the method of rotational viscosimetry on a rheometer (RheoStress-600, Germany). The obtained dependence of shear stress vs shear rate was approximated by a straight line. The tangent of angle, which corresponds to dynamical viscosity of HPEOS, was 18.8 ± 0.2 cP.

HPEOS was introduced into the PP matrix by uniaxial stretching of the polymer in HPEOS medium to 200% at speed of 10%/min. Then films were annealed in HPEOS medium at 75 °C for 3 h under isometric conditions to stabilize porous structure. Acidic (in steam of 10% water solution of hydrochloric acid) and basic (in steam of 10% water solution of ammonia) hydrolyses of HPEOS were carried out in the PP matrix at 20–25 °C. Volatile products of the reaction and excess of HCl and NH₃ were removed after hydrolysis by enduring specimens in the air at 20–25 °C for 3 days.

The value of effective volume porosity (W , vol %) of PP in stretching in HPEOS medium was measured by a standard procedure, i.e., by increase of volume of polymer during the deformation process. The volume of a polymer film before and after stretching was determined from its geometrical dimensions, which were measured by an optimizer (U3B-2).

The amount of the introduced filler was determined by two methods: (1) using a gravimetric procedure, i.e., by the change of mass of the initial PP film after loading HPEOS and its hydrolysis, and (2) using a thermogravimetric procedure where a polymeric matrix is burned out while heating in the air from 25 to 800 °C at

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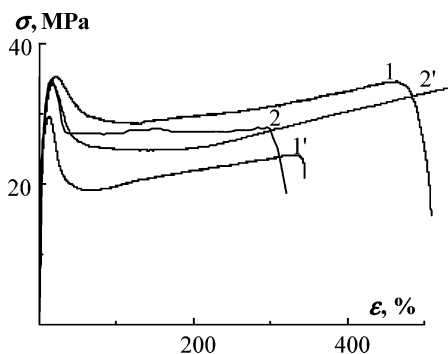


Figure 1. Stress–strain curves for PP obtained at the uniaxial strain at (1, 2) the air and in (1', 2') HPEOS. Extension rates were (1, 1') 10%/min and (2, 2') 500%/min.

a rate of 10 °C/min by a Mettler-TG50. The composition of the residue was identified by elemental analysis.

Chemical composition of surface and specimens' volume were determined by infrared spectroscopy under attenuated total reflection (ATR) and transmission by a Specord M80; shooting was realized in the interval of 400–4000 cm^{-1} .

The process of deformation of PP in HPEOS and mechanical properties of polymer/silicate composites were analyzed by an Instron-4301. Standard specimens with working part of 10 mm length and 4.3 mm width were cut out. Measurements were carried out at different rates of deformation from 10 to 500%/min at 20–25 °C.

Structural morphological analysis of specimens was carried out by SEM with a microscope Hitachi S-520 (splits were prepared using the procedure of brittle fracture in liquid nitrogen and decoration with gold) and by TEM with a microscope LEO 912 AB OMEGA (ultrafine cuts were prepared by the method of an ultramicrotome with a diamond knife).

Results and Discussion

Stretching of PP in HPEOS. Previous studies¹⁰ showed that uniaxial stretching of annealed PP in alcohols proceeded via the mechanism of delocalized crazing and led to the formation of 6 nm pores. The used HPEOS molecules are spherical particles 2–5 nm in diameter with composition of $[\text{Si}(\text{OC}_2\text{H}_5)_2-\text{O}-]$. It was found that PP does not swell in HPEOS at 20–25 °C, and the swelling rating is 4.5 vol % at 75 °C. We suggest that, owing to ethoxy groups, HPEOS will be adsorption active medium for PP. Stress–strain curves were obtained in the air and in HPEOS medium to verify that suggestion (Figure 1).

The yield point and the stationary evolution of tension of the polymer reduce by 15–20% in HPEOS at relatively low rates of extension (10–100%/min). Curve 1' at the yield point becomes more abrupt. These facts prove that HPEOS effectively reduces interfacial energy of a polymer, and stretching of PP in HPEOS proceeds via the crazing mechanism. At higher rate (500%/min) curves of stretching of PP in the air and in HPEOS (curves 2 and 2') are identified. Crazing is suppressed because the liquid flow rate to the top of growing craze is smaller than the deformation spread rate into a polymer under these conditions.

The main characteristics of the porous polymers are effective volume porosity, pore dimensions, and pore size distribution. In Figure 2 (curve 1), we show the dependence of effective volume porosity of polypropylene vs tensile strain (ϵ) in HPEOS. At the initial tensile strain (under 100%) the observations showed a fast increase of the specimen volume, and effective volume porosity comes up to 45 vol % as well. Further increment of porosity rate decreases, and maximum porosity is achieved near the break point with the value of 60 vol %. The

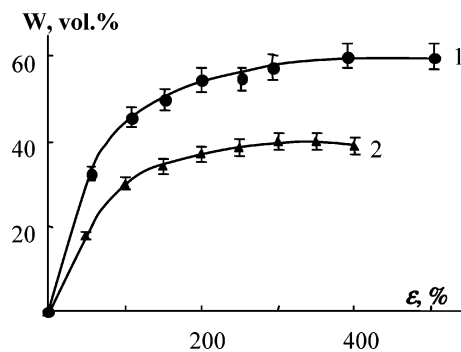


Figure 2. Curves of effective volume porosity vs tensile strain for PP in (1) HPEOS and (2) isopropanol.

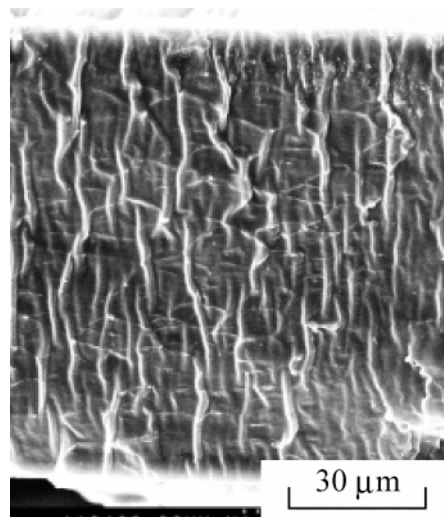


Figure 3. SEM micrograph of the brittle split of PP film filled HPEOS.

same monotonous dependence of $W(\epsilon)$ corresponds to delocalized mechanism of crazing. The curve obtained on stretching of PP in isopropanol by the mechanism of delocalized crazing is shown in Figure 2 (curve 2) for comparison. The volume porosity of PP in HPEOS is stressed to be 1.5 times higher than the one in isopropanol.

The morphology of PP stretched in HPEOS was analyzed by SEM. The micrograph of a brittle split of the specimen is shown in Figure 3. The structure of the classical crazed polymer was not detected on the micrograph. One can see the image without neatly parted areas of crazes and bulk polymer, which is typical for the delocalized crazed polymer.

Thus, HPEOS is a really adsorption active liquid relative to PP and uniaxial stretching of a polymer in similar medium proceeds via the mechanism of delocalized crazing.

Hydrolysis of HPEOS in a PP Matrix. As was shown, a PP matrix can be easily filled with HPEOS using crazing. Further features of HPEOS hydrolysis in pores of the PP matrix will be studied. Characteristics of specimens obtained are shown in Table 1. Comparison of volume and mass content of HPEOS in polymer matrix confirms that it completely fills pores formed in stretching.

IR spectra of the initial and filled PP films before and after hydrolysis are shown in Figure 4a. The appearance of very strong bands at areas of 800 and 1050–1200 cm^{-1} on curve 2 refers to vibrations of the Si–O bond. This fact confirms that HPEOS is really into the PP matrix. After the hydrolysis, bands at 1630 and 3350 cm^{-1} related to deformation and stretching vibrations of –OH appear on curve 3. Because IR spectra are poorly resolved in the area from 800 to 1300 cm^{-1} , we have received the comparison IR spectrum of the sample after

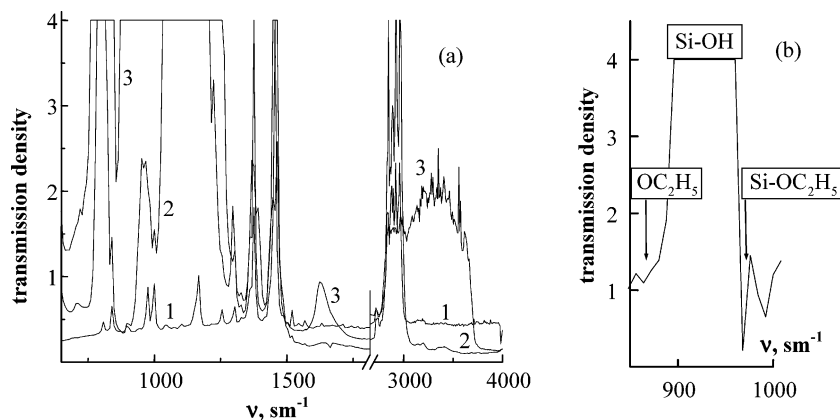


Figure 4. (a) IR spectra of (1) initial PP film and PP filled by HPEOS (2) before and after basic hydrolysis (3). (b) IR spectrum of the PP/silicate composite obtained relatively PP film contained HPEOS before hydrolysis.

Scheme 1

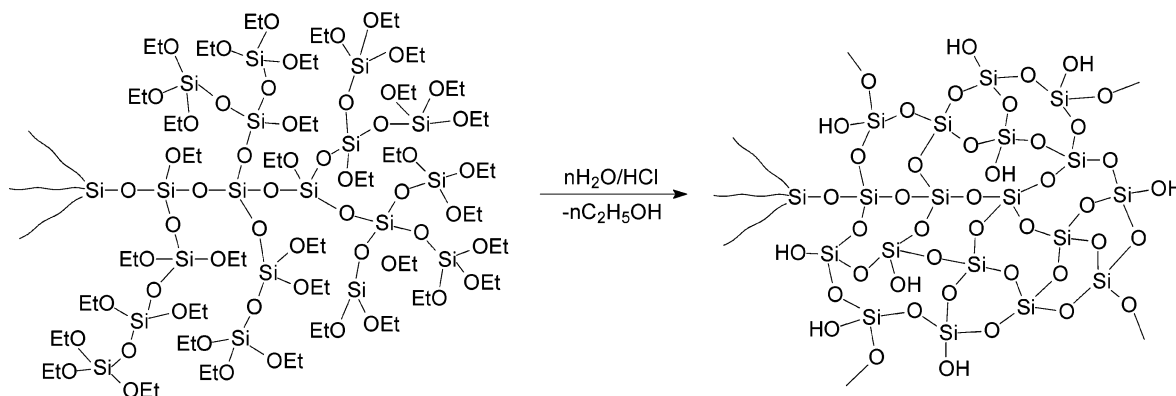


Table 1. Characteristics of PP/HPEOS Composites before and after Hydrolysis

hydrolysis of HPEOS, condition	vol content vol %	weight content of HPEOS, wt %		residue after annealing, wt %
		before hydrolysis	after hydrolysis	
HCl, 48 h	50	58	50	41
NH ₃ , 48 h	50	58	49	38

hydrolysis relative to the sample containing initial HPEOS (Figure 4b). One can see that bands at 870 cm^{-1} (vibration of $-\text{OC}_2\text{H}_5$) and 960 cm^{-1} (vibration of $\text{Si}-\text{OC}_2\text{H}_5$) are absent, and the band at $900\text{--}950\text{ cm}^{-1}$ (vibration of $\text{Si}-\text{OH}$) appears. Obtained IR data point out the proceeding of ethoxy group hydrolysis of HPEOS to hydroxyl groups. The ratio of the intensity of deformation vibrations of the $-\text{CH}_3$ band (1380 cm^{-1}) to the intensity of deformation vibrations of the $-\text{OH}$ band (1640 cm^{-1}) on ATR spectra is 4–5 times higher than on transmission spectra. This fact points out that concentration of $-\text{OH}$ groups on the composite surface is appreciably less than in the composite volume.

In the literature¹³ scheme of HPEOS hydrolysis was presented. Acid hydrolysis of HPEOS by HCl leads to the transformation of free ethoxy groups to hydroxyl groups with the following inner cyclization and silica solid formation according to Scheme 1. During basic hydrolysis by NH_3 formed hydroxyl groups undergo an intermolecular condensation reaction, resulting in gel formation.

We suppose that HPEOS hydrolysis into pores is a result of the continuous silicate phase formation throughout volume of the polymer matrix irrespective of reaction conditions. For example, dry residues obtained from all specimens via annealing in the air at $550\text{--}800\text{ }^\circ\text{C}$ were white sheets with thickness about $50\text{ }\mu\text{m}$, and their contents were near 40%. Elemental analysis

of these residues showed us that their composition corresponded to pure SiO_2 .

There is another fact pointing out the formation of cross-linked structure of filler. It turned out that PP film stretched to 200% in HPEOS without temperature treatment and hydrolyzed under isometric conditions does not practically shrink, but before the hydrolysis the PP film filled by HPEOS shrinks more than 80% after unloading. Thus, processes of polycondensation are likely to proceed during HPEOS hydrolysis.

Structure and Morphology of PP/Silicate Composites. In the previous section the silica solid phase was supposed to save high-dispersed structure of a crazed polymer and prevents its collapse. PP/silicate composites obtained are transparent films. Composites' morphology was investigated by methods of electronic microscopy. SEM micrographs of brittle splits of PP/HPEOS after acid and basic hydrolysis are shown in Figure 5. One can see that specimens have close-grained structure, and spherical particles of 100 nm diameter are located in all cross sections of a split.

Individual particles of a silicate phase are not observed in the micrograph (in Figure 6) obtained by TEM. It can be the evidence of continuity of silicate phase in the volume of a polymer matrix that agrees with pores of a crazed polymer being interpenetrative. The presence of very dark and very bright parts on the photo is connected with inhomogeneity of silicate phase density in different parts of a polymer matrix.

Moreover, superfine threads of $6\text{--}8\text{ nm}$ diameter oriented along the direction of polymer strain are distinctly discovered in the TEM micrograph (Figure 6). Apparently, they are polymer fibrils which are formed in crazing of PP. So a highly dispersed system is really developed in delocalized crazing of PP in HPEOS medium. The solid phase of silica formed in hydrolysis

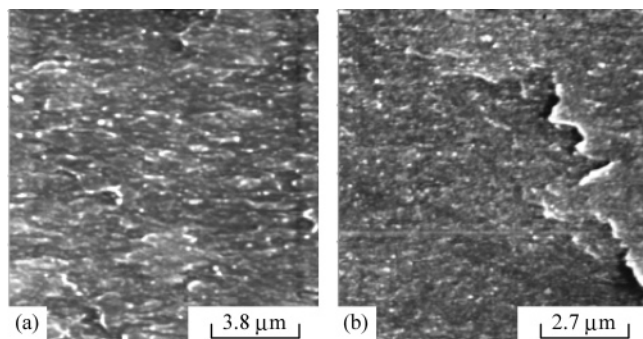


Figure 5. SEM micrographs of brittle splits of PP/HPEOS specimens after (a) acid and (b) basic hydrolyses.

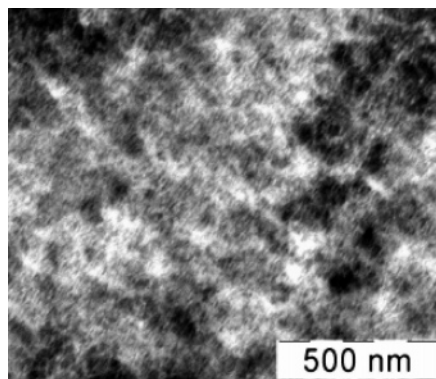


Figure 6. TEM micrograph of ultrafine cut of PP/HPEOS specimen after acid hydrolysis.

prevents the collapse of the fine fibrillar porous system of a polymer. For the first time this method permits us to visualize the polymer nanostructure produced via the delocalized crazing mechanism.

Thus, we suggest that the structure of obtained composite is a system of two interpenetrative nets: polymer (organic net) and silica (inorganic net). These PP/silicate composites can be expected to possess unusual mechanical properties.

Mechanical Properties of PP/Silicate Composites. Stress-strain curves of porous crazed PP films deformed previously in isopropanol to 200% are presented in Figure 7 (curves 1). Mechanical anisotropy is observed for crazed PP films depending on directions of previous deformation of the polymer in crazing process and stress-strain test. Tension in the film quickly increases with stretching in the direction paralleled to previous one (Figure 7a, curve 1); the sample destruction takes place at tensile strain of 50–100%. Stretching the crazed film in the direction perpendicular to previous one passes through yield point, and the break point is about 750% (Figure 7b, curve 1). PP containing HPEOS is deformed without yield point and is characterized by a considerable decrease of a magnitude of tension and tensile modulus. The influence of HPEOS to polymer is analogous to the effect of plasticizer; nevertheless, PP does not swell into HPEOS.

After the hydrolysis PP/HPEOS samples become brittle; their destruction occurs relatively easily in the direction perpendicular to previous deformation. In the parallel direction we observed a detachment of the work part of a sample along the previous deformation direction. The break point on the stress-strain curves of PP/silicate composites is marked in Figure 7a by the arrow. Taking into account that the composite structure consists of two interpenetrative nets of polymer and silica, shrinkage of a polymer and reorientation of PP macromolecules in stretching are impossible owing to rigid fixation of the PP frame by silica solid phase located in interfibrillar areas.

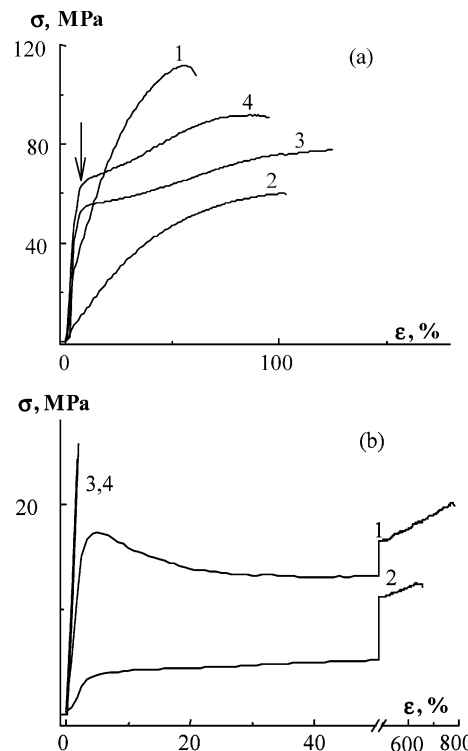


Figure 7. Stress-strain curves of PP previously deformed to 200%: (1) nonfilled film, (2) PP/HPEOS and PP/HPEOS after (3) acid and (4) basic hydrolyses. Test was conducted in (a) parallel and (b) perpendicular directions relative to previous stretching at the rate of 100%/min.

Table 2. Mechanical Properties of the Initial and Filled PP Films^a

sample	E , MPa	σ_{\max} , MPa	ϵ_{break} , %
	par/per	par/per	par/per
PP initial	890/950	39/35	420/440
PP porous	1130/660	112/17	55/750
PP/HPEOS	140/100	49/4	100/650
PP/HPEOS, HCl	1720/1200	86/25,5	40/2
PP/HPEOS, NH ₃	2050/1100	73/24	40/2

^a Stress-strain test was conducted in parallel (par) and perpendicular (per) directions relative to previous stretching at a rate of 100%/min.

In Table 2, tensile modulus (E), loads about yield point (σ_{\max}), and breaking strains (ϵ_{break}) of the initial and filled PP films are presented. The data of Table 2 show the anisotropy of mechanical parameters of samples. In the direction paralleled by the previous deformation the tensile modulus and breaking strain are 1.5–2.0 and 3–10 times, respectively, higher than in the perpendicular direction. It was stressed that the tensile modulus of PP/silicate composite is 1.5–1.8 times higher than the tensile modulus of oriented nonfilled PP films irrespective of the direction of the mechanical test. In spite of the composite material is characterized by the low value of breaking strain, it keeps some flexibility.

Conclusion

In the work the original method of preparation of the film polypropylene/silicate nanocomposite used a well-known process of polymer crazing in liquid media is described. The advantage of this approach in comparison with the traditional blending is receiving of highly dispersed mixture of a polymer and silica without using modifying additives, which usually decrease mechanical properties of composite materials. The structure of the obtained composites is fully determined by the structure of crazed polymer matrices, and it is a system of two

interpenetrative nets. This structure permits us to considerably increase tensile modulus of material, namely, the tensile modulus of PP/silicate composites exceeds modulus of the initial polymer by 50–100%.

The developed approach can be used for the preparation of nanocomposites based on other industrially important polymers such as polyethylene, poly(ethylene terephthalate), poly(vinyl chloride), and acrylates.

Acknowledgment. This work has been financially supported by the Russian Foundation for Basic Research (projects 05-03-32482 and 06-03-32906) and by the Grant of the President of the Russian Federation (project MK-3532.2007.3).

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MA071379D