

BRIEF
COMMUNICATIONS

Preparing Film Composites Based on Crazed Polymers and Silica Sol Nanoparticles

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Abstract—Films of polymer/silica nanocomposites based on isotactic polypropylene and high density polyethylene are prepared via solvent-crazing in the tetrahydrofurane solution of molecular silica sol. This method allows us to disperse SiO₂ particles with a diameter of 5–15 nm in a volume of polymer matrices homogeneously and at the nanometer level. The possibility of producing a fragmented riffled silica coating onto polymer surfaces is presented.

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INTRODUCTION

In recent years the requirements for the existent large-tonnage industrial polymers have increased and the problems of improving their mechanical, thermal, tribological, and other properties have become topical. Composite materials with filler, which impart a particular functionality to the composite (for example, incombustibility, sensory, catalytic properties) are more often obtained. However, because of the thermodynamic incompatibility of most industrial polymers and fillers of inorganic nature, preparing their fine-grained mixture turns out to be a difficult problem.

The existent methods of introducing silica nanoparticles into a polymer matrix require either the prior preparation of the components of mixing via chemical modification, a change in the traditional synthetic scheme, or special equipment [1–8].

In this work a new approach for preparing polymer/silica nanocompositions which allows us to avoid the above-listed problems is suggested. To introduce fine-grained particles of SiO₂ into the polymer matrix, the crazing phenomenon of the polymers is suggested. It is known [9] that, during crazing, an active aqueous medium penetrates the polymer bulk, forming nanopores of a specific structure. If a substance is dissolved in the aqueous medium, it will be dispersed by the matrix bulk and, after the aqueous medium removal, it will remain “sealed” in it. This approach was previously used for the formation of the silica phase in the industrial films of different polymers [10–12]. Via crazing a reactive liquid precursor (tetraethoxysilane, hyperbranched polyethoxysilane [13]) was introduced, which was then subjected to hydrolytic polycondensation immediately in the polymer pores. But it

is difficult to control the dispersion of the formed silica phase by this method, because the size of the formed particles of the new phase heavily depends on the hydrolysis conditions. In this work we suggest using a solution of molecular silica sol in organic solvents (for example, tetrahydrofurane, esters, etc.) with controllable particle sizes as the adsorption-active medium [14]. Such an approach excludes the stage of catalytic hydrolysis, and the dispersion of SiO₂ particles is determined by their size in the initial solution.

The purpose of this work is to study the uniaxial deformation process of isotactic PP and HDPE in tetrahydrofurane that contains nanoparticles of silica sol and to investigate the composition and morphology of the obtained polymer/silica nanocomposites.

EXPERIMENTAL

In this work 140- μ m-thick ($M_w = 300000$) industrial films of isotactic isotropic polypropylene PP and 75- μ m-thick ($M_w = 200000$) high-density polyethylene HDPE were used. The PP films were previously annealed at 140°C for 3 h.

The process of uniaxially deforming the polymers was carried out in tetrahydrofurane (THF) of the khch brand containing 3.5 wt % of silica sol (the particle diameter according to light scattering data was 5–15 nm) up to 200% with 6% per min rate. The silica sol solution was delivered either during uniaxial deformation of the polymer in an aqueous medium bulk or via solution watering on both surfaces of the polymer film during tension in hand clamps. For THF removal and to prevent polymer shrinkage, the samples were subjected to isometric conditions at 100°C for 1h after tension.

Characteristics of PP and HDPE uniaxially deformed in THF solutions of silica sol

Polymer/tension method	Medium	W_n , vol %		w_f , wt %
		before drying	after drying	
PP/bulk	THF	32	0	0
PP/bulk	THF/silica sol	35	25	9
PP/watering	"	40	40	12(5)
HDPE/bulk	THF	43	0	0
HDPE/bulk	THF/silica sol	31	26	1
HDPE/watering	"	33	33	13.5(1.6)

* Data after treating the samples with a solution of hydrofluoric acid for 15 s are presented in the brackets.

The value of the effective bulk porosity (W_n , vol %) of the polymers during tension was determined by the increment of the standard sample bulk during deformation. The amount of the introduced filler (w_f , wt %) was determined by the solid residual after the combustion of the polymer matrix under conditions of heating in air atmosphere from 25 to 700°C at a rate of 20K/min on a Mettler-TG50 device.

A structural-morphological investigation was carried out by the electron microscopy method. For this, ultrathin sections of the samples were prepared according to the ultramicrotoming technique with a diamond knife; their examination (scanning) was carried out on an LEO 912 AB OMEGA transmission electron microscope. According to the brittle failure technique in liquid nitrogen, film cleavages were obtained which were sprayed with gold and analyzed on a Hitachi S-520 scanning electron microscope.

RESULTS AND DISCUSSION

The chemical nature of silica sol is nanogel; it is obtained with the intramolecular polycyclization of hyperbranched polyethoxysilane by reaction [14]. The solutions of molecular silica sols with concentrations of 2–10 wt % in THF are usually stable during long-term storage.

The peculiarities of the uniaxial tension of the polymers in the solution of silica sol in THF (concentration of 3.5%) were investigated. It was determined that THF is an adsorption-active medium (AAM) in regards to PP and HDPE, and their deformation in the THF medium leads to the formation of porous structure by the delocalized crazing mechanism. Some characteristics of the polymers after their deformation are presented in the table. From the presented data it can be seen that the bulk porosity of the polymer films in pure THF before drying is 30–40 vol %, which is in agreement with the values obtained previously with aliphatic alcohols [9]. This points to the fact that THF exhibits similar adsorption properties and decreases the surface energy of the polymers during crazing. Figure 1 presents microphotographs of HDPE films after

tension in THF. On the cleavage it was actually seen to be rather uniform, without the zone alternation of the plastic deformation (crazes) or block polymer structure characteristic of delocalized crazing.

Using the molecular solution of silica sol in THF as the AAM practically does not influence the amount of porosity of the polymers. However, the formation of the solid phase of silica during solvent removal has a stabilizing influence on the porous crazing structure during anneal. It is necessary to note that using the watering method allows one to completely retain the geometrical dimensions of the samples after annealing, which is apparently connected with formation of the silica layer on the surface of the samples. Figure 2 shows microphotographs of cleavages (a, b) of HDPE

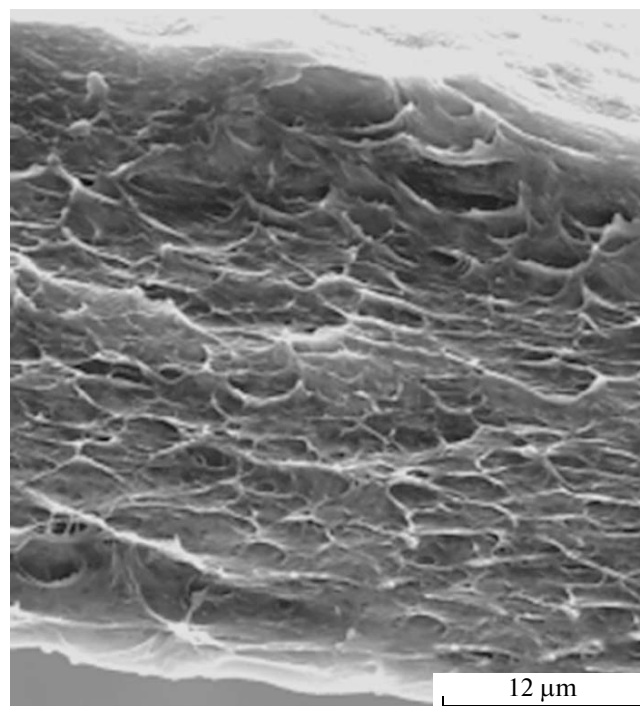


Fig. 1. Microphotographs of cleavage of HDPE deformed in THF at 200%.

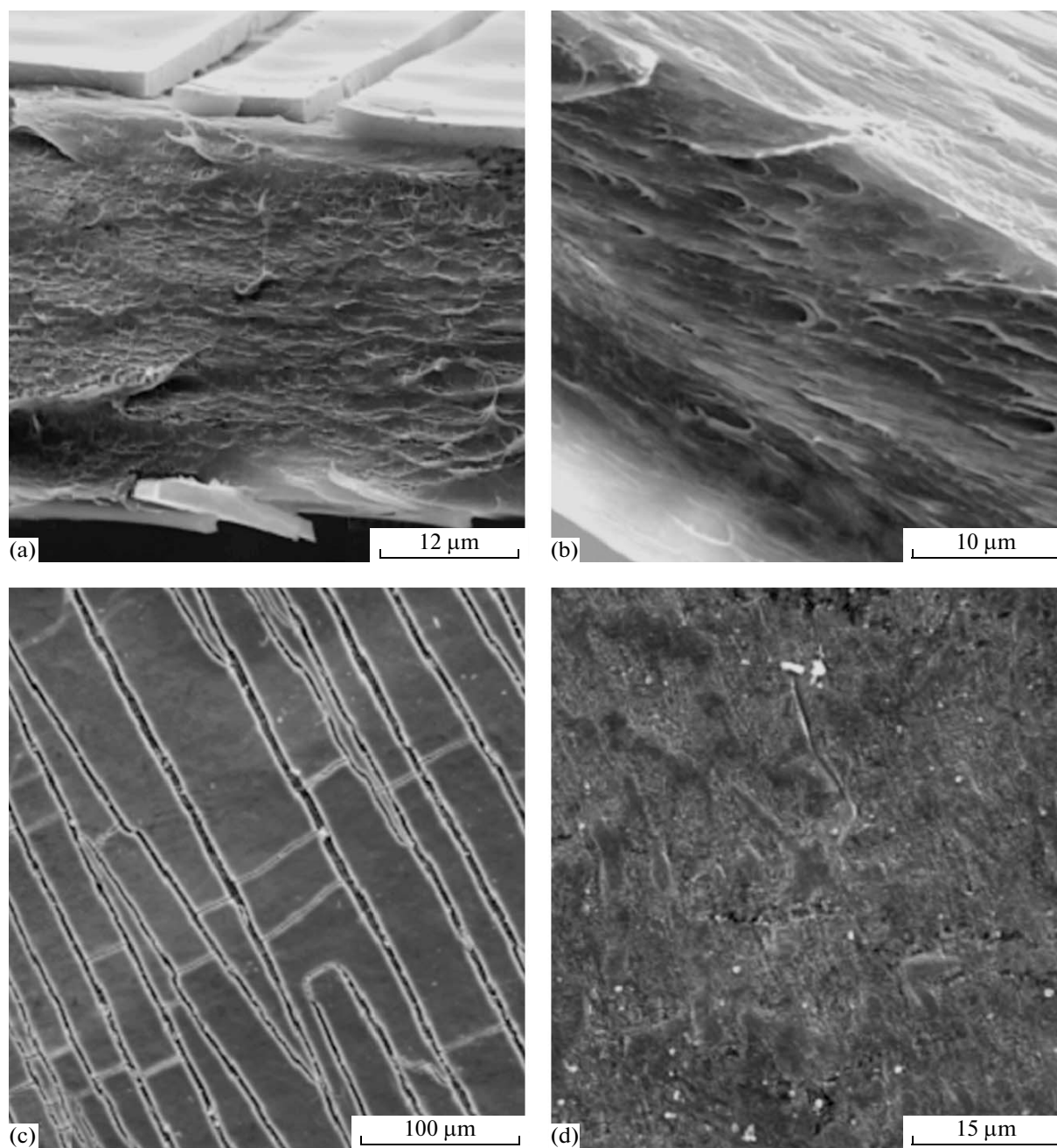


Fig. 2. Microphotographs (a, b) of cleavages and (c, d) surface of silica-containing HDPE, obtained (a, c, d) with watering method on the surface and (b) bulk drawing. Photo (d) presents surface after treatment with hydrofluoric acid.

that are filled with SiO_2 and obtained by two different methods. It can be seen (Figs. 2a, 2c) that when the watering method was used on the polymer surface, it actually formed a 1–2- μm -layer; when drawing in the bulk of silica sol solution, the formation of a surface layer was not observed (Fig. 2b). Let us note that a thick surface layer of silica has good adhesion with the polymer surface and does not delaminate even at significant loads. Besides, this layer is fragmented perpendicularly to polymer drawing and is compressed in a parallel direction (Fig. 2c). The formation of this layer

probably occurs during polymer drawing as a result of the rather fast evaporation of solvent. The thin layer fragments and compresses formed the same way as thin hard coating on a compliant substrate. This phenomenon was previously studied in detail on the polymer-thin metallic coating systems [15]. The following new portion of silica sol apparently settles on the formed fragments, and the thickness of the surface layer increases and does not break the relief. According to the table, the amount of the introduced silica during drawing depends on the polymer nature. This

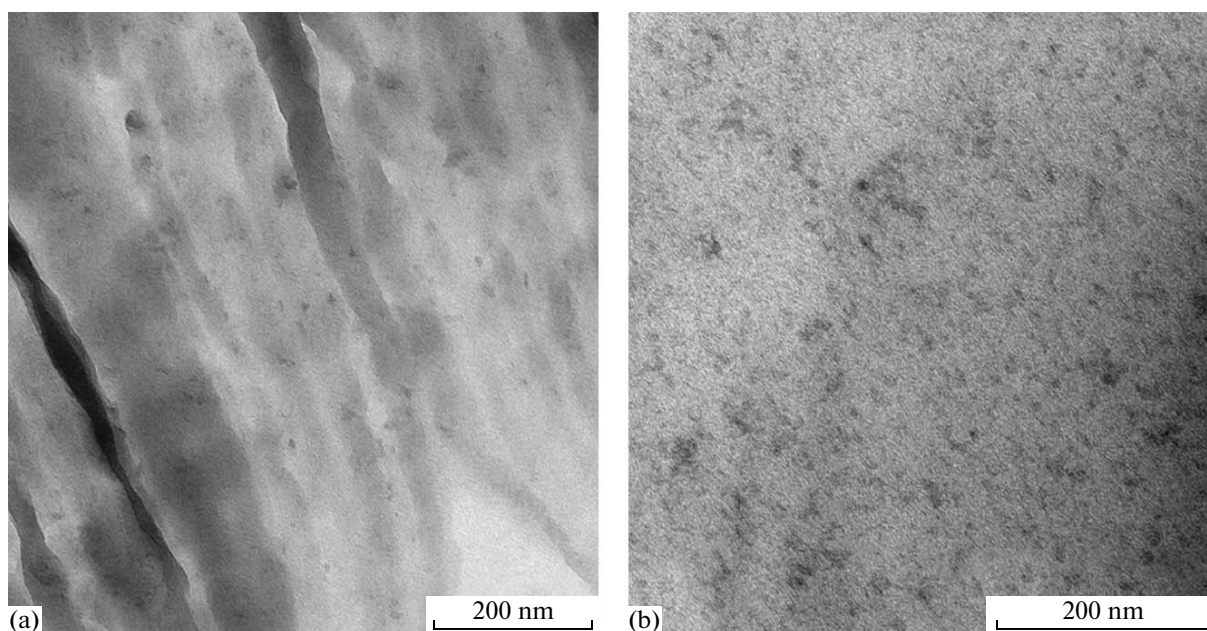


Fig. 3. Microphotographs of ultrathin sections of polymersilica composites based on (a) HDPE and (b) PP containing 1 and 9 wt % SiO_2 , correspondingly.

may be connected with the difference in the diameter and geometry of the pores of initial matrix. During the watering method, the amount of silica is localized on the surface of the samples. It is necessary to note that, after dissolving the surface layer with hydrofluoric acid (Fig. 2d), the remaining amount of silica corresponds to the data obtained with tension in bulk.

High-resolution transmission electron microscopy was used for a detailed investigation of the composite structure. Figure 3 shows the microphotographs of ultrathin sections of the composites. It was determined that the whole bulk of polymer matrices is uniformly filled with SiO_2 nanoparticles with diameters of 5–15 nm, which corresponds with the sizes of the initial particles of silica sol in solution.

Thus, by the direct introduction of the silica sol solution into polymer films using crazing process, polymer/silica nanocomposites were obtained. Depending on the method used for preparation, it is possible to achieve polymer/silica nanocomposites with different architectures: silica is uniformly distributed inside the polymer matrix or a complicated “sandwich” is formed (with the surface layer of silica). These aspects of morphologically describing nanocomposites appear to be important for use as sensors and catalysts. Also, new possibilities of the surface modification of the composites at the expense of the functional groups of silica are revealed.

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REFERENCES

1. E. Kontou and M. Niaounakis, “Thermo-Mechanical Properties of LLDPE/ SiO_2 Nanocomposites,” *Polymer* **47** (4), 1267–1280 (2006).
2. T. H. Zhou, W. H. Ruan, Yu. L. Wang, Yu. L. Mai, M. Zh. Rong, and M. Q. Zhang, “Performance Improvement of Nano-silica/Polypropylene Composites through In-Situ Graft Modification of Nanoparticles during Melt Compounding,” *ee-Polym.*, No. 058 (2007).
3. Yi. Liu and M. Kontopoulou, “The Structure and Physical Properties of Polypropylene and Thermoplastic Olefin Nanocomposites Containing Nanosilica,” *Polymer* **47** (22), 7731–7739 (2006).
4. M. J. Percy, J. I. Amalvy, D. P. Randall, and S. P. Armes, “Synthesis of Vinyl Polymer–Silica Colloidal Nanocomposites Prepared Using Commercial Alcoholic Silica Sols,” *Langmuir* **20** (6), 2184–2190 (2004).
5. R. Palkovits, H. Althues, A. Ruplecker, B. Tesche, A. Dreier, U. Holle, G. Fink, C. H. Cheng, D. F. Shantz, and S. Kaskel, “Polymerization of w/o Microemulsions for the Preparation of Transparent SiO_2 /PMMA Nanocomposites,” *Langmuir* **21** (13), 6048–6053 (2005).
6. Q. Dou, X. Zhu, K. Peter, D. E. Demco, M. Möller, and C. Melian, “Preparation of Polypropylene/Silica Composites by In-Situ Sol–Gel Processing Using Hyperbranched Polyethoxysiloxane,” *J. Sol–Gel Sci. Technol.* **48** (1), 51–60 (2008).
7. S. Grund, P. Kempe, G. Baumann, A. Seifert, and S. Spange, “Nanocomposites Prepared by Twin Poly-

- merization of a Single-Source Monomer,” *Angew. Chem., Int. Ed.* **46** (4), 628–632 (2007).
8. Y. Pihosh, H. Biederman, D. Slavínská, J. Kousal, A. Choukourov, M. Trchova, A. Mackova, and A. Boldyreva, “Composite SiO_x/Hydrocarbon Plasma Polymer Films Prepared by RF Magnetron Sputtering of SiO₂ and Polyethylene or Polypropylene,” *Vacuum* **81** (1), 32–37 (2006).
 9. N. F. Bakeev and A. L. Volynskii, *Solvent Crazeing of Polymers* (Elsevier, Amsterdam, 1995).
 10. E. S. Trofimchuk, N. I. Nikonorova, E. A. Nesterova, A. S. Eliseev, E. V. Semenova, I. B. Meshkov, V. V. Kazakova, A. M. Muzafarov, A. L. Volynskii, and N. F. Bakeev, “Crazing of Polymers in the Presence of Hyperbranched Poly(ethoxysiloxane),” *Vysokomol. Soedin., Ser. A* **49** (10), 1801–1810 (2007) [*Polym. Sci., Ser. A* **49** (10), 1107–1113 (2007)].
 11. E. S. Trofimchuk, E. A. Nesterova, I. B. Meshkov, N. I. Nikonorova, A. M. Muzafarov, and N. F. Bakeev, “Polypropylene/Silicate Composites on the Basis of Crazed Polymer and Hyperbranched Polyethoxysiloxane,” *Macromolecules* **40** (25), 9111–9115 (2007).
 12. E. S. Trofimchuk, N. I. Nikonorova, E. V. Semenova, E. A. Nesterova, A. M. Muzafarov, I. B. Meshkov, V. V. Kazakova, A. L. Volynskii, and N. F. Bakeev, “Specific Features of the Formation of the Silicon Dioxide Phase in Porous Poly(propylene) Prepared through the Crazing Mechanism,” *Russ. Nanotekhnol.* **3** (3–4), 132–140 (2008) [*Nanotechnol. Russ.* **3** (3–4), 201–208 (2008)].
 13. V. V. Kazakova, V. D. Myakushev, T. V. Strelkova, and A. M. Muzafarov, “Hyperbranched Poly(ethoxysiloxanes): Synthesis and Properties,” *Vysokomol. Soedin., Ser. A* **41** (3), 423–431 (1999) [*Polym. Sci., Ser. A* **41** (3), 283–290 (1999)].
 14. A. M. Muzafarov, V. V. Kazakova, V. D. Myakushev, A. N. Ozerin, and L. A. Ozerina, “Molecular Silica-sols—A New Form of Silica and the Technique for Their Preparation,” RF Patent No. 2 140 393 (1998).
 15. A. L. Volynskii and N. F. Bakeev, *Structural Self-Organization of Amorphous Polymers* (Fizmatlit, Moscow, 2005), pp. 26–56 [in Russian].