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Influence of SiO_2 Nanoaddition on the Self-Organization via UV-Polymerization of Acrylate Nanocomposites

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In our research, we investigate a method of nanocomposite preparation based on self-organization processes due to the formation of a thick polymerizable shell around each nanoparticle and allowing one to get a uniform optical quasihomogeneous material.

In the present work, we will study changes of the optical and structural properties of polymer nanocomposites. An UV-curable active matrix was polymerized on the surface of SiO_2 nanoparticles. The set of structural modifications of polymeric nanocomposites were observed by using ASM, SEM, light scattering, and water sorption and by measuring the Brinell hardness. Hypotheses concerning the participation of nanoparticles in the photopolymerization are discussed.

Keywords Filled polymer; nanocomposite structure; nanocrystal; nanoparticle; refractive index; UV-curable nanocomposite

Introduction

In recent years, the introduction of metal nanoparticles and their oxides into a polymer matrix is the intensively developed branch of physics and chemistry of the nano-sized state. The structural organization of such nanocomposites is a serious problem. Without solving it, is difficult to determine and to optimize the field of their practical use. The need to improve the stability of nanocomposites and to control the reversible transitions in such systems attracts a lot of attention aimed at the search of ways to control their morphology, structural organization, and architecture [1]. The investigations of self-regulating systems, in which the synthesis of a polymer matrix and the growth of nanoparticles take place simultaneously, can be the best way to solve the problem of nanocomposite stabilization and its structural organization.

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In other words, the challenging problem is to develop methods for creating nanocomposites with architecture "microcapsulated nanoparticles in a polymer shell" formed *in situ*. This is done by generating a polymerized matrix of cluster dispersions, thereby by limiting the growth of nanoparticles. Ways to do this can be very different: the polymerization of vinyl monomers at the intense mechanical dispersion of metals (initiator is an as-formed metal surface), the introduction of organometallic compounds to the polymerizing system, which are decomposed at temperatures close to the temperature of polymerization, γ-coirradiation of a precursor and a monomer at room temperature, polymerization of metal-containing monomers, *etc*. [1–3].

In spite of the diversity of researches, there are no data on the optical nanomaterials, in which a high concentration of nanoparticles is combined with good optical properties.

The difficulty of this task consists in that a high concentration of structuring additives is accompanied, as usual, by a significant light scattering on them or by fluctuations of their concentration.

This work is a continuation of our research in the field of the nanostructuring of polymers for optical purposes [4,5]. We have made optically transparent nanocomposites obtained by the synthesis of a polymer matrix in the presence of nanoparticles which strongly affect the morphology of a material.

The aim of the work is to study the structural changes of polymeric UV-curable nanocomposites as the main causes that determine their properties such as mechanical, sorption, and optical ones.

It has been found that SiO_2 nanoparticles are actively involved in the process of UV-curing. The introduction of SiO_2 nanoparticles to a polymerizable composition leads to the formation of a transparent low-scattering nanocomposite with good characteristics.

Experimental

We used monomers 2-Carboxyethyl acrylate (2Carb, Aldrich No. 552348) and Bisphenol A glycerolate (BisA, Aldrich No. 41,116-7). As a structuring nanomodificator, we used aerosil nanoparticles 14 nm in size (SiO_2, Aldrich No. 066K0110).

Polymer films (thickness of 100 and 12 microns) were obtained from the previously prepared monomer solution with implanted nanoparticles. Solution was placed between two polyester films to exclude inhibitory effects of oxygen and was UV-cured. All experiments were accomplished at room temperature in air without a special inert atmosphere (argon). The UV curing was made with a mercury lamp (100 W) with maximum emission at a mercury line of 365 nm.

The transmission spectra of the films were measured on a spectrophotometer Perkin-Elmer 555 UV-Vis. For the IR spectra, we used a Fourier IR spectrometer FSM 1201 of the "Monitoring" Company. Samples for studies were prepared by pressing pellets with KBr.

The refractive index was measured on an Abbe refractometer in accordance with the recommendations of the European standard ASTM D542.

In this paper, we study the sorption of water vapor by the gravimetric method. Hardness is measured by the Brinell-hardness method with a Bulat-T1 device. Light scattering is measured by the photometric sphere method in accordance with the recommendations of the European standard ASTM D1003. The investigation of the surface profile of samples was conducted in the contact mode on an atomic-force microscope Ntegra.

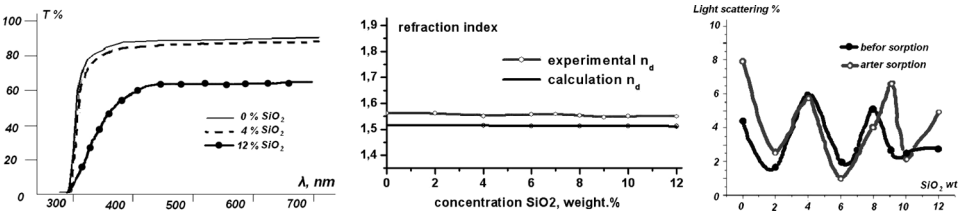

Figure 1. Transmission (left), refractive index (center), and light scattering before (– – –) and after (—) the water sorption (right) of the BisA/2Carb = 30/70 composition vs. the SiO_2 concentration (0, 4, and 12 wt.%).

Results and Discussion

With the introduction of SiO_2 into the monomer composition BisA/2Carb (30/70), the viscosity of solutions increases with a concentration starting from 7 wt.% up to concentrations of 10 wt.% and higher.

The compatibility of SiO_2 nanoparticles with BisA/2Carb monomer mixture to form a transparent film with UV-polymerization is observed up to 12 wt.%. Above 12 wt.%, the addition of SiO_2 particles to the monomer mixture resulted in turbid films. The system becomes heterogeneous.

The films are transparent in the visible and UV spectral regions (Fig. 1). A significant decrease in the optical transmission is observed at high concentrations of aerosil (more than 8 wt.%).

The calculated and experimental values of the refractive index of nanocompositions are shown in Figure 1. In the theoretical calculation of the refractive index, we used the effective medium model of Maxwell–Garnett [6]:

$$\frac{\varepsilon_{eff} - \varepsilon_2}{\varepsilon_{eff} + 2\varepsilon_2} = f_1 \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + 2\varepsilon_2}.$$

Here, ε_1 – permittivity of the medium, ε_2 – permittivity of inclusions, ε_{eff} – permittivity of the composite medium, $f_1 = (1/V)\,\Sigma_i V_i$ – volumetric filling factor, V_i – volume of the i-th particle, and V – volume of the composite environment.

This model is applicable in the case where the volume filling factor $f_1 \leq 1/3$, i.e., the fraction of inclusions is small. The experimentally obtained refractive index of the film samples are greater than theoretically calculated. The refractive index of the composition with the maximum SiO_2 concentration (12 wt.%) is reduced by 0.02 as compared with polymer without aerosil.

Figure 1 presents the light scattering by a polymer composition vs. the concentration of SiO_2 nanoparticles before and after the water sorption.

As shown in Figure 1, the data spread of the light scattering is observed prior to a SiO_2 concentration of 9 wt.%. We think that if the concentration is less than 9 wt.% (deficiency of aerosil), the nanostructured polymer composite is heterogeneous. It is revealed in nonmonotonic changes of the light scattering intensity.

When the concentration of aerosil is more than 9 wt.%, the light scattering is independent of the concentration of additives. The aerosil amount is sufficient for the distribution to be uniform in volume, and the homogeneous polymer composite

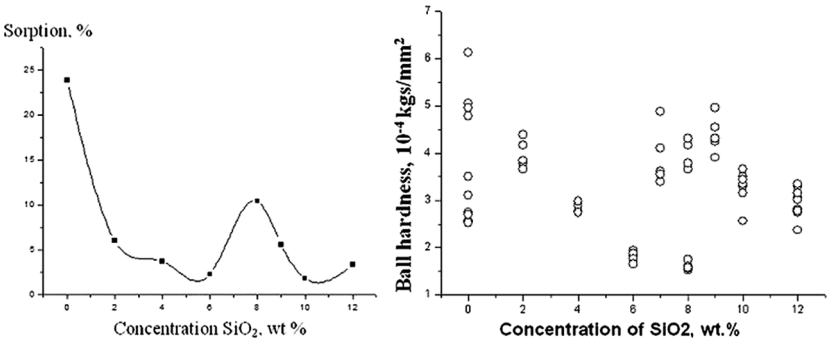

Figure 2. Water sorption (left) and the hardness (right) of BisA/2Carb = 30/70 composites vs. the SiO_2 concentration.

is formed. In this structure, the light scattering decreases approximately twice as compared with that of pure polymer.

After the tests for water sorption, the light scattering dependence of samples is conserved. For all compositions, except for pure composite and the composite with the addition of 12 wt.% SiO_2, the scattering is qualitatively unchanged, but its value increases twice. This phenomenon is explained by the possible water plasticizing effects [7,8].

The water-sorption experiments were conducted to study changes in the internal volume of the polymer as a result of its SiO_2 nanomodification (Fig. 2).

For pure polymer, the value of sorption is 23%. With the introduction of aerosil, the sorption decreases monotonically. The sorption reach 2.5% at 12 wt.% SiO_2 concentration. The water sorption of the nanocomposite is reduced by about one order as compared with the unmodified polymer. The existence of an extremum (at 8 wt.% SiO_2) may be due to the singularity of the formation of an internal structure of the polymer during the polymerization at a high viscosity of the monomer composition.

The hardness investigations of films are an effective way to study the aerosil influence on the nanocomposite structure (Fig. 2).

After the introduction of 2 wt.% SiO_2, the hardness of films increases sharply as compared with that of the unmodified polymer. In the concentration range 2–8 wt.% SiO_2, the composite hardness decreases, i.e., the polymer structure is loosening. At the further increase of the concentration of aerosil, the hardness begins to increase and becomes comparable with that of pure polymer at the maximum aerosil concentration of 12 wt.%.

Changes of the polymer nanocomposite properties (water sorption, light scattering, and hardness) confirm that nanoadditions influence the structure of a formed polymer due to possible interactions of aerosil with active groups of the polymer [9].

The researches of the surface relief and the rigidity of nanocomposites made by atomic force microscopy support the above assumptions (Fig. 3).

As is seen, there are the substantial changes in the composition structure as compared with the original one due to the introduction of 4 wt.% of SiO_2 nanoparticles. The formation of separate polymer regions with structured SiO_2 is clearly observed. The grain structure is observed to be uniform throughout the material

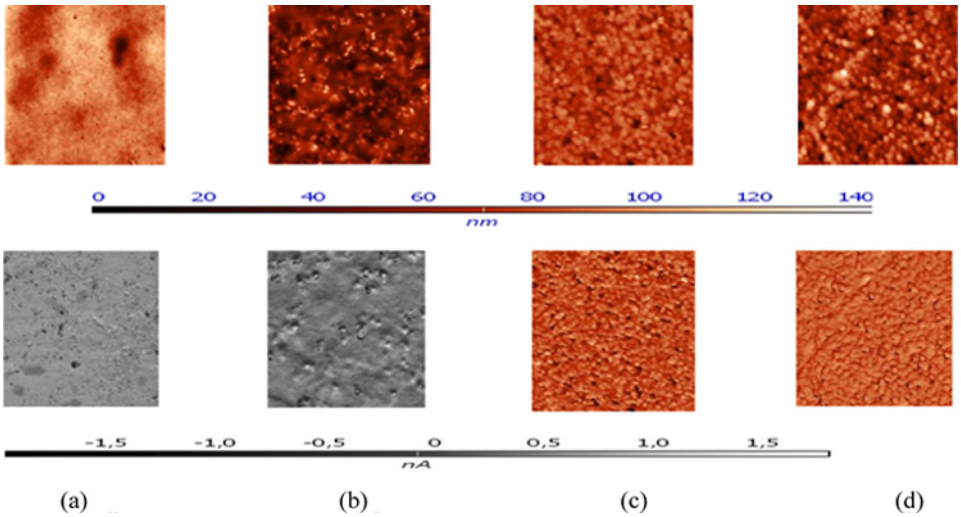

Figure 3. Relief (top) and the rigidity of surface (bottom) polymer films at the introduction of 0 (a), 4 (b), 8 (c), and 12 wt.% (d) of aerosil nanoparticles by the AFM. The size of photos is 5×5 mμ.

when the SiO_2 concentration reaches 12 wt.%. Apparently, the formation of this structure is due to the ability of nanoparticles to create weak bonds with the active groups of monomer molecules and to serve centers of polymerization.

Figure 6 shows that, at low concentrations of nanoparticles, two phases (pure polymer and a structured nanocomposition) are observed.

At the concentrations of aerosil of more than 8 wt.%, the free polymer phase disappears, and the whole available polymer forms spheres on nanoparticles.

The FTIR spectra of nanocompositions confirm the ability of aerosil nanoparticles to form bonds with the active groups of monomer molecules and to serve centers of polymerization, as shown in Figure 4. The peaks around 471 and 1107 cm^{-1} were indicated as the stretching vibrations of Si–O–Si bounds on SiO_2 surfaces [10]. The disappearance of these strong SiO_2 bands and an appearance new band 730 cm^{-1} may be the evidence of the polymerization on the nanoparticles surface.

Thus, the aerosil nanoparticles act as centers of formation of a new polymer phase – a nanocomposite with other properties than those of pure polymer.

At low nanoparticles concentrations the modified polymer areas are not numerous, and composites heterogeneous affects on their properties. With increase in the aerosil concentration, the size and the number of hybrid fields are grown and completely different structure are formed.

The appearance of submicron spheres around each nanoparticle is the reason of formation of quasihomogeneous materials and light scattering is insignificant. Indeed, submicron spheres formed around each nanoparticle (see Fig. 3) have almost identical diameters, which can be explained by their identical growth rates.

As a result, all spherical nanoparticles combine into a self-organized quasilattice. Eventually, these processes lead to a uniform nanoparticle distribution and formation of a homogeneous optical environment.

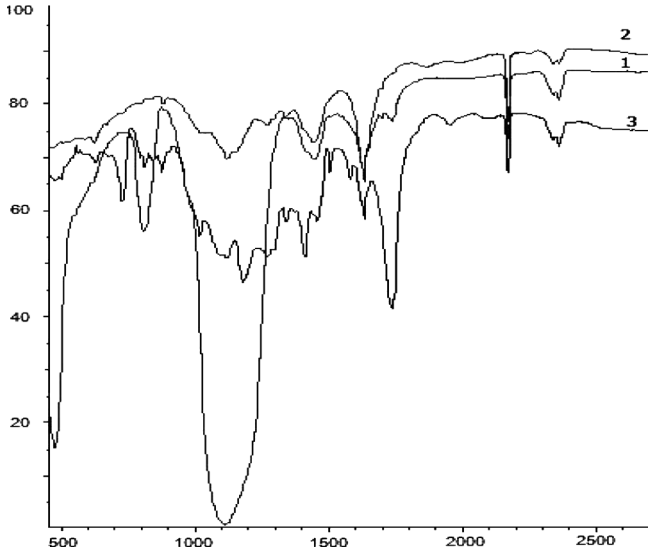

Figure 4. FTIR spectra: pure polymer 2Carb (1), SiO_2 (2), and composition 2Carb + 8 wt.% SiO_2 (3).

Conclusions

We have studied the sorption of water vapor, Brinell hardness, optical transmission, refractive index, and light scattering of film polymer SiO_2-nanocomposites.

Composites are transparent in the visible spectrum at high concentrations of SiO_2 nanoparticles (12 wt.%). At the introduction of 12 wt.% SiO_2, the refractive index of the composite decreases to 0.02, the sorption decreases by one order and hardness does not exceed the hardness of pure polymer, and the light scattering is not increased as well.

Nonmonotonic changes in the properties, the AFM data, and the IR spectra demonstrate the ability of nanoparticles to be centers of polymerization and to form a granular structure of the nanocomposite.

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