ISSN 1070-4272, Russian Journal of Applied Chemistry, 2009, Vol. 82, No. 3, pp. 483–487. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © I.I. Konstantinov, V.V. Karbushev, A.V. Semakov, V.G. Kulichikhin, 2009, published in Zhurnal Prikladnoi Khimii, 2009, Vol. 82, No. 3, pp. 489–493.

MACROMOLECULAR CHEMISTRY AND POLYMERIC MATERIALS

Combining Carbon and Polymeric Particles in an Inert Fluid as a Promising Approach to Synthesis of Nanocomposites

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Received June 4, 2008

Abstract—Effective method for introduction of dispersed filler particles into a polymeric matrix was developed. The method is based on disaggregation and uniform deposition of the filler onto the surface of polymeric particles in an inert liquid medium under the action of ultrasound. Particles of detonation nanodiamond were used as the filler.

DOI: 10.1134/S1070427209030240

Formation of polymeric composites containing ultradispersed fillers is an intensively developing area of modern material science. Here are meant not only structural composites, for which mechanical properties are the most important, but also functional materials with redused gas-permeability and combustibility and increased heat conductivity and atmosphere resistance. On the whole, of interest are multifunctional construction materials for which introduction of nanofillers improves their basic mechanical characteristics and imparts important service properties [1, 2].

As a rule, the role of modification objects is played by large-tonnage polymers, which additionally stimulates research and development in this area, because introduction of a minor amount of nanoparticles can markedly extend the application areas of the already existing polymers without organization of new chemical industries. At present, the most promising fillers are layered silicates [2–4] and detonation nanodiamonds (DNDs) [5–9]. Aluminosilicate particles are anisometric and have the shape of disks in which elementary layers form galleries characterized by a certain interplanar spacing. DND particles are closer in shape to spheres, their structure is monolithic, and hydroxy, carbonyl, and carboxy functional groups are present on their surface [5–10].

Owing to the high surface energy and presence of active groups, DND particles tend to form agglomerates up to tens of micrometers in size [10]. The existence of such coarse particles in a composite frequently hinders obtaining the desired modification effect, although numerous publications disregard the agglomeration effect and report that polymers are filled with nanoparticles, rather than with the actually introduced microparticles. One of the most important problems in development of polymer/DND composites is to devise a combining method in which nanosize particles are introduced into a polymer and the content of micrometer aggregates is insignificant.

The aim of this study was to develop a new approach to combining polymers with nanodiamonds, based on a specific interaction of two kinds of particles, of DNDs and polymers, in inert liquid media under conditions of an ultrasonic treatment.

EXPERIMENTAL

We used in experiments DNDs of PUOO-SKh 96 brand, manufactured by Elektrokhimpribor combine (Lesnoi, Russia) and having the form of a light gray powder. The powder had the following parameters: mass fraction of DNDs no less than 98%, density 3.3 g cm^{-3}, specific surface area 350 m^2 g^{-1}. The following polymeric matrices were chosen: hydrophilic

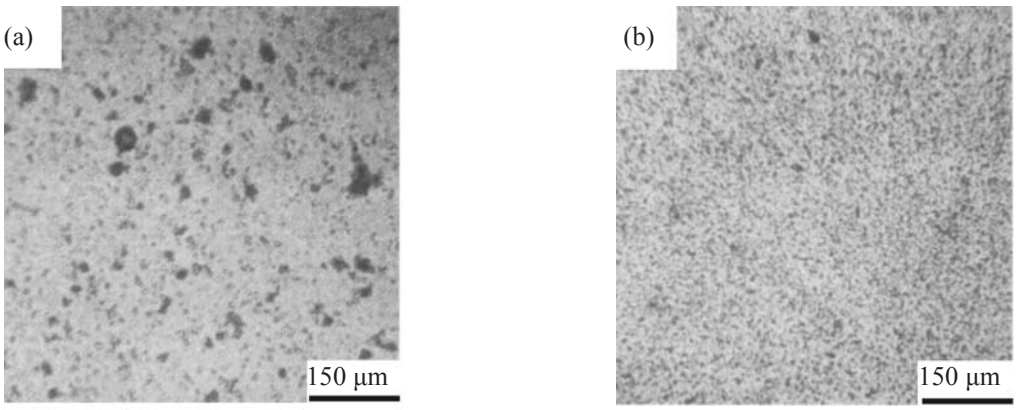

Fig. 1. Micrographs of PSF/DND composites prepared by (a) mixing in a solution of PSF in chloroform and (b) immobilization in the medium of hexane. DND concentration 1 wt %; the same for Fig. 4.

hydroxy propyl cellulose (HPC) with MM = 8×10^4 and average particle size of 300 μm (Klucel EF brand, manufacturer Hercules/Aqualon), thermally stable hydrophobic polysulfone (PSF) with MM = 3 104 and average particle size of 180 μm (PSF-150 brand, NIIPM Open Joint-Stock Company), and amphiphilic copolymer of styrene and acrylonitrile (SAN) with MM = 17.5×10^4 and average particle size of 150 μm (M100 brand, Bayer GmbH). Hydroxy propyl cellulose forms liquid-crystal melts upon melting ($T_m \approx 120$°C), PSF and SAN are amorphous and their melts are isotropic. Thus, the chosen polymeric matrices differ in the hydrophilic-hydrophobic balance and have different phase compositions.

We used two methods for combining a polymer and the filler. The original method consisted in disaggregation and dispersion of the filler in a low-molecular-weight liquid medium inert toward the polymeric matrix, subjected to the action of an ultrasonic field. A polymer powder was added to the resulting suspension without terminating the intermittent sonication. Under these conditions, the so-called heteroadagulation occurred, i.e., nanodiamond particles were deposited (immobilized) onto the surface of coarser polymer particles. As the process was complete, the solid phase was separated by filtration, dried, and used to obtain nanocomposites by extrusion or hot compaction. Because of the lack of analogies, this way to produce nanocomposites was named the "immobilization filling" method.

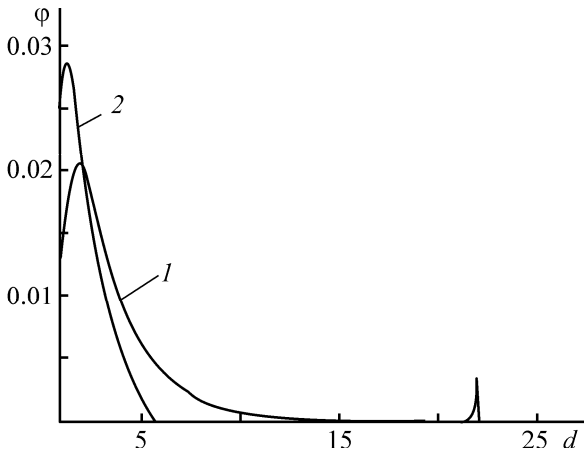

Fig. 2. Particle size distribution of nanodiamond (1 wt %) in polysulfone for various methods used to prepare composites. (φ) Fraction of particles and (*d*) particle diameter); the same for Fig. 5. (*1*) Solution method and (*2*) immobilization filling method.

As an example, we describe stages of the process for synthesis of composites on the basis of SAN matrices. A DND powder was dispersed in hexane in an ultrasonic field (E 15 H ultrasonic disperser of the bath type, power 90 W, frequency 37 kHz) for a certain period of time (minutes). A SAN powder was introduced into the resulting suspension and the combined dispersion was additionally twice treated with ultrasound. In the process, disintegrated DND particles were deposited onto the surface of SAN particles. The multiple short-time sonication was used because a prolonged continuous ultrasonic treatment may cause DND aggregation [11].

The powder obtained was separated from hexane by filtration, dried to constant mass, and used to produce composites by compaction or extrusion. The refractive index of the hexane-filtrate after several cycles (n_D = 1.3779) remained nearly equal to the refractive index of the starting hexane (n_D = 1.3772). Hence follows that, first, the solid phase is separated nearly

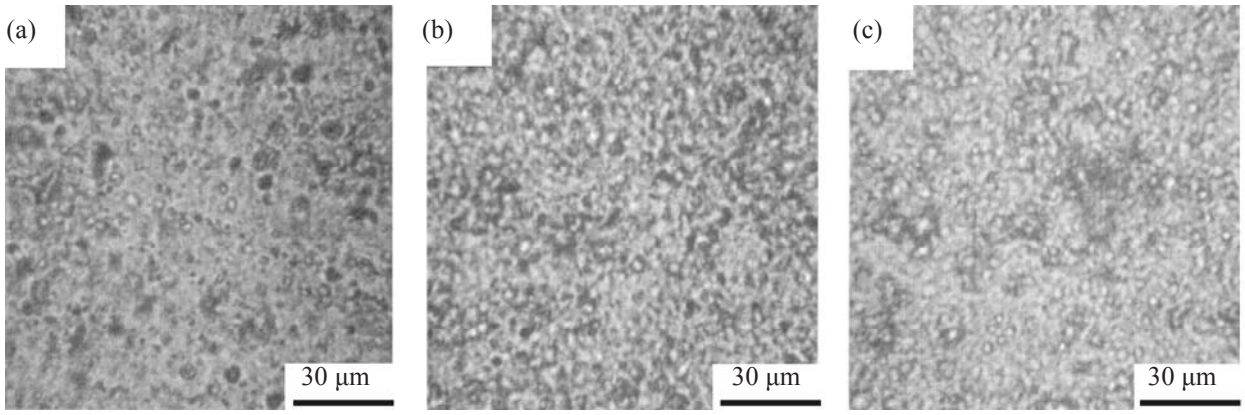

Fig. 3. Micrographs of SAN/DND composites produced by immobilization filling with (a) 0.5, (b) 1, and (c) 2.5 wt % DNDs.

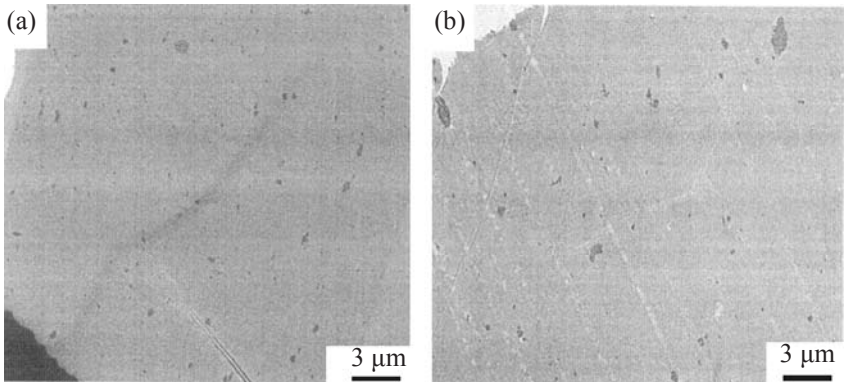

Fig. 4. Micrographs of SAN/DND composites produced by (a) immobilization filling in hexane and (b) mixing in a solution of SAN in chloroform.

completely and, second, there is no need to regenerate hexane for recycling.

We compared the results obtained in measuring the size and distribution uniformity of particles produced by the method described above with the corresponding data for composites formed using polymer solutions. For this purpose, the filler was dispersed in a polymer solution under the action of ultrasound. We used 4% solutions of HPC in distilled water, SAN in acetone, and PSF in chloroform. In this case, composite films were produced by casting, followed by evaporation of the solvent. Composites with DND contents of 0.5, 1.0, 2.5, 5, and 10 wt % were formed by each of the above methods.

The granulometric composition of DND particles in polymeric matrices was determined by optical (MIN-8 microscope with a digital camera) and transmission electron (Zeiss LEO 912AB OMEGA) microscopies. The particle size distribution was found by computer processing of digital photographs. The algorithm for finding the granulometric composition consisted in determining the mass fraction of objects having a given size in the image. In the process, image fragments were "screened" through a sieve with mesh varied from the minimum determined by the instrumental resolving power and noises to the maximum corresponding to the field of vision.

For a granulometric analysis in a wide range of sizes, from 1 nm to 100 μm, the electronic and optical images were combined by a special method using the Photoshop software. The image was prepared for analysis by superposition of electron micrographs on optical micrographs in accordance with the size scale. The whole program complex for image processing was based on the MathLab software package.

Because presence of coarse micrometer aggregates can especially adversely affect the final properties of the composite, particular attention was given to the morphology of mixtures in the optical spectral range. Typical micrographs of the composites at a filler

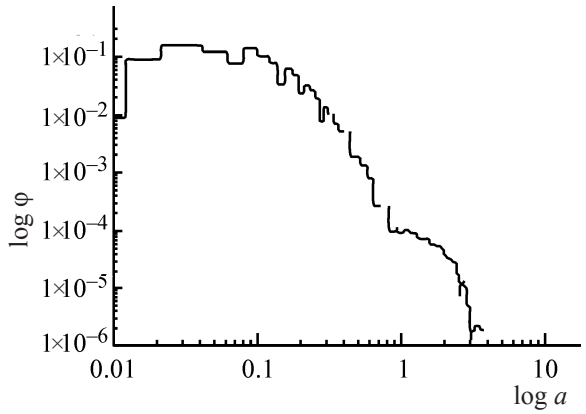

Fig. 5. Complete polydispersity curve of the 1 wt % DND/SAN composite produced by the immobilization filling method (in log–log coordinates).

content of 1 wt %, obtained by different combining techniques, are shown in Fig. 1, and particle size distributions of these composites, in Fig. 2.

It can be seen that the quality of the particle distribution strongly depends on the mixing type. For example, in the "solution" method, the characteristic size of agglomerates markedly, increases compared with the immobilization filling technique. The peak of the distribution function lies at 1.7–2.0 μm in the case of introduction of DND particles into solutions, and at 0.9–1.1 μm for the immobilization filling method. In addition, the distribution curve is broader for the solution method, compared with the immobilization technique, and shows that a considerable fraction of coarse particles is present. The amount of DNDs in agglomerates 4–14 μm in size exceeds 20 μm for the solution method, whereas in the case of the immobilization method, the composites contain no agglomerates coarser than 6 μm, with 90% of particles falling within the range of particle sizes less than 1.5 μm.

Similar results were obtained for SAN/DND and HPC/DND composites.

The effect of the concentration of the filler on its distribution in the SAN matrix in the case of the immobilization filling is illustrated by micrographs presented in Fig. 3. An analysis of the micrographs of the composites demonstrated that, irrespective of the concentration (up to 5 wt %), the maximum size of agglomerates of DND particles remains unchanged (0.9–1.1 μm). For a composite produced by the solution method, the size and number of coarse agglomerates (up to 40–50 μm at a DND content of 2.5 wt %) are proportional to the content of the filler introduced. Qualitatively similar results were obtained for PSF/DND and HPC/DND composites.

The effect of the method used for composite preparation on the filler distribution in the matrix in the submicrometer range, we considered by the example of a mixture composed of SAN and 1 wt % DNDs. Figure 4 shows TEM micrographs of SAN/DND com-posites. It can be seen that the immobilization filling method yields a more uniform filler distribution in the submicrometer size range, too.

A similar procedure for analysis of micrographs was employed for electron micrographs in the range of sizes smaller than 1 μm. A comparison of particle size distributions for particles combined with polymer matrices by the immobilization filling method in the micrometer and submicrometer ranges and an analysis of the electron and optical images made it possible to construct the generalized polydispersity curve for DNDs in SAN (Fig. 5).

The data obtained suggest that the main part of nanodiamond aggregates in polymeric matrices have sizes in the range 20–200 nm, whereas agglomerates with sizes of 500 nm and more constitute less than 1% of the total amount of DNDs. We did not analyze the effect of the intensity of the ultrasonic treatment on the characteristic particle size, although it would be expected that the peak should be shifted along the size scale to the left upon an increase in the ultrasonic field intensity.

Thus, the method of immobilization filling proved to be more efficient as regards obtaining small sizes of uniformly distributed dispersed filler particles in polymeric matrices, compared with the solution method. Presumably, this is due to collisions of polymer and DND particles in the ultrasonic field, disaggregation of both kinds of particles, and immobilization (deposition) of DND particles onto polymeric particles.

The composites produced by the new method contain no coarse (>6 μm) agglomerates, which can eliminate the modifying effect of the dispersed filler, and have a comparatively narrow particle size distribution of the filler in the submicrometer range. The method can be used in practice, the more so as the inert fluid (hexane in our case) can be recycled without additional purification.

CONCLUSIONS

(1) A new method for synthesis of nanocomposite materials, immobilization filling method, is developed. The method yields a uniform particle size distribution of the filler at a high dispersity in the bulk of the polymer.

(2) In composites produced by the immobilization filling method, the main part of nanodiamond aggregates are 20–200 nm in size, with agglomerates larger than 500 nm constituting less that 1% of the total amount of nanodiamonds.

ACKNOWLEDGMENTS

The study was supported by State contracts nos. 02.513.11.3147 and 02.523.11.3003, Russian Foundation for Basic Research (grant nos. 07-03-00998 and 06-03-89403-NVO_a), and International Science & Technology Center (grant no. 3238).

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