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MACROMOLECULAR COMPOUNDS AND POLYMERIC MATERIALS

Technology of Liquid-Phase Compounding of Ultra-High-Molecular-Weight Polyethylene with Nanoparticles of Inorganic Compounds under the Action of Ultrasonic Vibrations

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Abstract—A novel technology for preparing nanocomposites on the basis of ultra-high-molecular-mass polyethylene and nanoparticles of inorganic compounds (SiO_2, Al_2O_3, ZrO_2, AlN, Si_3N_4) was developed and tested. The technology consists in liquid-phase compounding of nanocomposite components under the continuous action of ultrasonic vibrations. The developed technology ensures dispersion of nanopaticle agglomerates in a liquid medium, efficient mixing of components of the powder blend, and uniform distribution of nanoparticles in the polymer matrix. The nanocomposites obtained exhibit increased levels of strength and elasticity.

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As novel nanocomposite materials find more and more extensive use in all branches of the economy (machine building, medicine, electronics, means of communications, nuclear power and aerospace engineering), the development of novel technologies for their production becomes a topical problem. Nanocomposites based on ultra-high-molecular-mass polyethylene (UHMWPE) occupy a particular place among structural and functional materials owing to such unique characteristics as low friction coefficient and high levels of strength and resistance to aggressive media and to wear.

A specific feature of processing UHMWPE and composites based on it is that the polymer matrix cannot be brought into the viscous-flow state because of high molecular weight, which complicates the use of traditional methods of polymer processing (extrusion, pressure casting, etc.). Another problem making it necessary to look for additional processing methods is weak interaction at the polymer–filler interface due to essential differences in the surface properties of inorganic nanoparticles (NPs) and polyethylene. It is known that NPs tend to form agglomerates, which leads to a decrease in their structure-making activity and to weakening of electrostatic intermolecular interactions of the system components [1, 2].

Numerous approaches and procedures were suggested in different time periods to solve such problems. Some of them have found wide use, namely: (a) functionalization of the surface of the components with surfactants or by chemical modification to improve their compatibility with each other and prevent the particle agglomeration [3–5]; (2) additional process steps of mixing, disintegration, homogenization, etc. [6]; (3) preparation of a polymeric nanocomposite by in-situ polymerization [7].

The NP dispersion using ultrasound differs from the above methods essentially. The mechanism of material dispersion in an ultrasonic field is primarily associated with the development of ultrasonic cavitation [8]. Collapse of cavitation voids in a liquid gives rise to a compression wave whose maximal amplitude can reach several thousands of atmospheres [9, 10]. Because a compression wave is always followed by a rarefaction wave, tensile stresses act on particle agglomerates in a liquid, causing their disintegration. Compounding of a polymer with a nanosized filler is mainly performed in a polymer melt, e.g., in preparation of composites based on epoxy resins [11–13], polytetrafluoroethylene [14], and polypropylene [15]. This method, however, has not found use in the technology for processing of other polymers, including UHMWPE, as ultrasonic action is inefficient in this case because of high viscosity of the polymer melt, leading to attenuation of ultrasonic vibrations in such media [16]. To overcome the limitation, the use of a liquid phase as ultrasound conductor was suggested with the aim of obtaining a colloidal system consisting of a liquid dispersion medium, UHMWPE, and NPs.

This study was aimed at developing the technology for efficient compounding of UHMWPE and NPs with their uniform distribution on the UHMWPE surface and at preparing nanocomposites based on UHMWPE and NPs.

EXPERIMENTAL

As a polymer matrix we used UHMWPE of Celanese GUR 4022 grade (China) with the molecular mass of 5.0×10^6, bulk density of 0.4 g cm^{-3}, and mean particle diameter of 150–200 μm.

As fillers for UHMWPE we used NPs of crystalline (Al_2O_3, AlN, ZrO_2, CuO) and X-ray amorphous (SiO_2, Si_3N_4) structures (Emfutur Technologies, Spain).

As a dispersion medium we used 99.5% ethanol prepared from rectified ethanol by refluxing over CaO for 6 h, followed by distillation.

To evaluate the size of NP agglomerates in the colloidal system before and after ultrasonic treatment, we used a Zetasizer Nano ZS high-performance two-angle particle and molecule size analyzer (Malvern, the United Kingdom).

The sample morphology was studied with a JSM-7800F high-resolution scanning electron microscope (SEM) (JEOL, Japan) in the secondary electron mode at an accelerating voltage of 1–2 kV. The device was equipped with an X-MAX 20 energy-dispersive X-ray (EDX) spectrometer (Oxford, the United Kingdom), which was used for determining the chemical composition. Atomic-force microscopic (AFM) studies were performed with an NTegra Prima device (NT-MDT, Russia) in the tapping mode using NSG10/Au high-resolution silicon cantilevers (NT-MDT) with a curvature radius of 10 nm on the scanning area of 5.0 × 5.0 μm.

Polymer nanocomposites were prepared by hot pressing with premolding at 4 MPa and pressing at 10 MPa and 175–180°C for 20 min. The filler concentrations were varied in the range 0.1–2.0 wt %. The components were compounded using a combination of a Laborette 17 ultrasonic bath (Fritsch, Germany; output power 240 W, vibration frequency 35 kHz) with a Heidolph Hei-VAP Advantage rotary vacuum evaporator (Germany) equipped with a Rotavac Valve Control vacuum pump ensuring the pressure in the system of down to 7×10^{-4} MPa. The working volume of the ultrasonic bath (4 L) allows replacement of the heating bath of the evaporator (4.5 L).

The ultimate tensile strength and relative elongation at break were determined in accordance with GOST (State Standard) 11262–80 (ASTM D638M) with an Autograph AGS-J testing machine (Shimadzu, Japan) at room temperature.

The suggested technology (Fig. 1) consists in compounding of the components in the liquid phase under the action of ultrasonic vibrations. It includes several steps: (1) disintegration of aggregates of inorganic oxide and nitride NPs, (2) preparation of a suspension of UHMWPE with NPs, and (3) vacuum distillation of the liquid medium.

All the processes occur under the continuous action of ultrasonic waves, which play the following roles in different steps of the process. In the first step, they disperse NP agglomerates; in the second step, they favor uniform distribution of NPs in the bulk of the polymer; and in the third step, they intensify the distillation and prevent the subsequent agglomeration.

Ethanol was chosen as a liquid medium for dispersing and compounding the components, because it meets the following important process requirements.

(1) Ethanol exhibits good cavitation properties, ensuring efficient dispersion of NP agglomerates.

In liquid media, the ultrasonic vibration energy partially transforms into heat owing to various dissipation processes. The main causes of sound attenuation are internal friction, thermal conductivity of the medium,

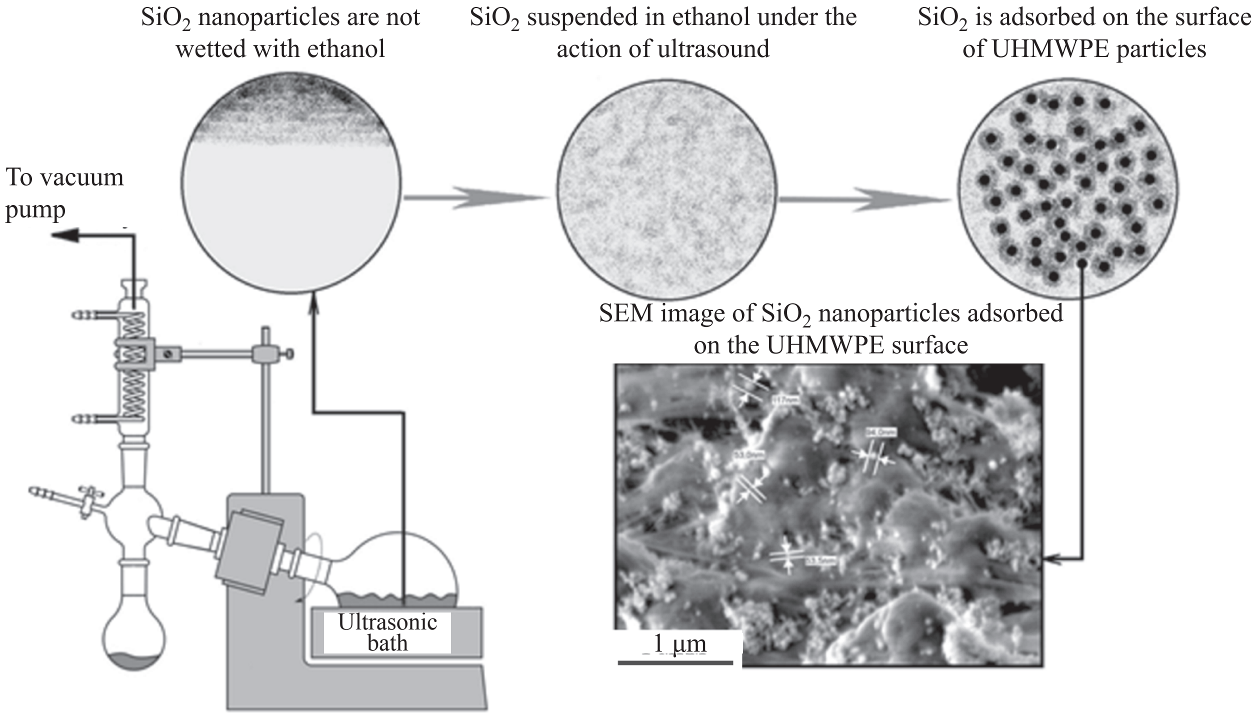

Fig. 1. Principal scheme of the developed technology.

and various relaxation processes [17]. To evaluate the ultrasonic dispersion efficiency, we used the attenuation coefficient calculated for various media using the Stokes–Kirchhoff formula

$$\alpha = \frac{C^2}{2\rho c^3}\left[\frac{4}{3}\eta + \varsigma + \chi\left(\frac{1}{C_V} - \frac{1}{C_P}\right)\right], \qquad (1)$$

where ρ is the density of the medium; c, speed of sound in the medium; $\omega = 2\pi f$, circular frequency of the sound wave; f, ultrasound frequency; η and ς, coefficients of shear and volume viscosity; χ, thermal conductivity coefficient; and C_P and C_V, heat capacities of the medium at constant pressure and constant volume, respectively.

At low frequencies, when the values of η, ς, and χ are independent of frequency, the sound attenuation is often characterized by the quantity α/f^2, ratio of the attenuation coefficient to the ultrasound frequency squared. In this case, this parameter is independent of the frequency and characterizes the properties of the medium. With this parameter, Eq. (1) has the form

$$\frac{\alpha}{f^2} = \frac{2\pi^2}{\rho c^3}\left[\frac{4}{3}\eta + \varsigma + \chi\left(\frac{1}{C_V} - \frac{1}{C_P}\right)\right]. \qquad (2)$$

The ultrasound attenuation parameters (Table 1) calculated from the experimental data for various liquid media in which polyethylene is insoluble allow a conclusion that the attenuation ability of ethanol is low.

(2) Ethanol does not react with the components of the colloidal system. However, ethanol, in contrast to water, wets both NPs and the polymer. A hypothesis was put forward that the adsorption layer of ethanol molecules on the NP surface plays an important role in ensuring the adhesion interaction of the NPs with the UHMWPE surface, as illustrated in Fig. 2.

Table 1. Experimental parameters of ultrasound attenuation in liquids at 20°C

Liquid	$\alpha/f^2 \times 10^{15}$, m^{-1} s^2
Water	23
Ethanol	55
Carbon tetrachloride	500
Nitrobenzene	80
Cyclohexane	77

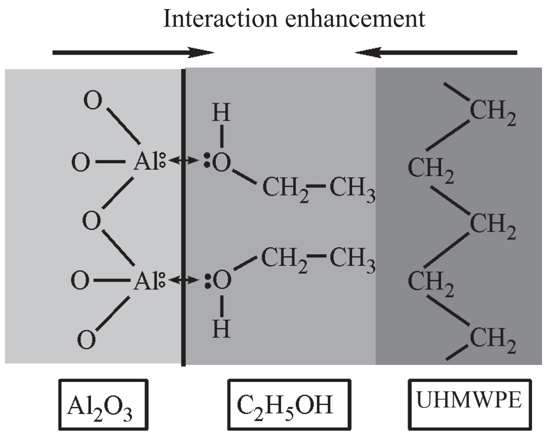

Fig. 2. Intermolecular interaction pattern in the Al_2O_3–C_2H_5OH–UHMWPE system.

According to published data [18, 19], adsorption of molecules of hydrocarbon hydroxy derivatives on the NP surface occurs specifically and is caused by interaction of the oxygen atom of the ethanol OH-group with Lewis acid sites of the NPs. In the adsorption layer of ethanol molecules, the hydrocarbon radicals are oriented apart from the NP surface and favor the retention of NP on the UHMWPE surface owing to the solubilization of the C_2H_5 group in the UHMWPE surface layer.

(3) Owing to relatively low boiling point and high volatility, ethanol can be readily removed from the mixture. In addition, ethanol, compared to other substances (e.g., acetone), is less toxic and less harmful for the environment.

Step I: ultrasonic dispersion of NP aggregates. NPs are dispersed in ethanol placed in the cavitation field of ultrasonic vibrations. This field prevents formation of NP agglomerates in the near zone and their adhesion to reactor walls, whereas mechanical stirring prevents formation of heterogeneities in the remote zone.

To obtain NPs with the smallest size, it is necessary to choose the optimum time of ultrasonic treatment. To this end, we determined with a particle size analyzer the size of NP agglomerates dispersed in ethanol by sampling at definite time intervals.

We analyzed how the size of dispersed phase (ZrO_2) particles depends on the ultrasonic treatment time and revealed an optimum, 3–4 min. As the ultrasonic treatment time is increased further, the NPs undergo reverse agglomeration caused by an increase in the temperature of the medium due to ultrasound absorption. Thus, each series of tests was preceded by disintegration of NP agglomerates for 3 min.

Step II: addition of polymer particles to a suspension of NPs in ethanol. After preparing a uniform suspension of NPs in alcohol, under the conditions of ultrasonic treatment, we introduced reactor UHMWPE powder with continuous mechanical stirring by rotation of the autoclave with the suspension at a rate of up to 280 rpm. The NP concentrations in the powder mixture were 0.05, 0.10, 0.5, and 2.0 wt %. The polymer addition to the NP suspension under the simultaneous action of intense cavitation ultrasonic field and continuous mechanical stirring of the mixture components ensures uniform distribution of the polymer particles and NPs in the volume of the dispersion medium.

Step III: removal of the dispersion medium. To find the conditions for distilling ethanol off, we performed calculations using the integral form of the Clausius–Clapeyron equation assuming that the molar heat of vaporization of the liquid, $\Delta H^0_{\mathrm{vap}}(C_2H_5OH)$ = 42 320 kJ mol^{-1} in this case, is independent of temperature and pressure:

$$\ln\,(p/p_0) = \frac{\Delta H_{\mathrm{vap}}(1 - TT_0)}{RT_0}. \qquad (3)$$

The calculations show that the pressure favoring the shift of the equilibrium toward gaseous ethanol at 330–340 K is less than 40 kPa. Thus, ethanol was distilled off from the mixture at a pressure of 700 Pa and a temperature of 330–340 K under the continuous action of ultrasound and stirring.

As the liquid medium is removed, the NPs remain adsorbed on the surface of UHMWPE particles owing to adhesion interaction. The ultrasonic treatment combined with continuous mechanical stirring ensures uniform distribution and deposition of NPs on the UHMWPE surface.

The efficiency of the dispersion and adsorption of NPs on the UHMWPE surface was evaluated from the SEM images. Figure 3 confirms the suggested theoretical model of ultrasonic dispersion. As can be seen, without acoustical treatment the NPs form agglomerates, whereas compounding by the suggested technology ensures uniform distribution of NPs on the surface of UHMWPE granules.

Strain and strength tests of the materials. Ultrasonic vibrations cause structural rearrangement of polymer chains [20] and changes in the thermomechanical properties [21], which influences the mechanical

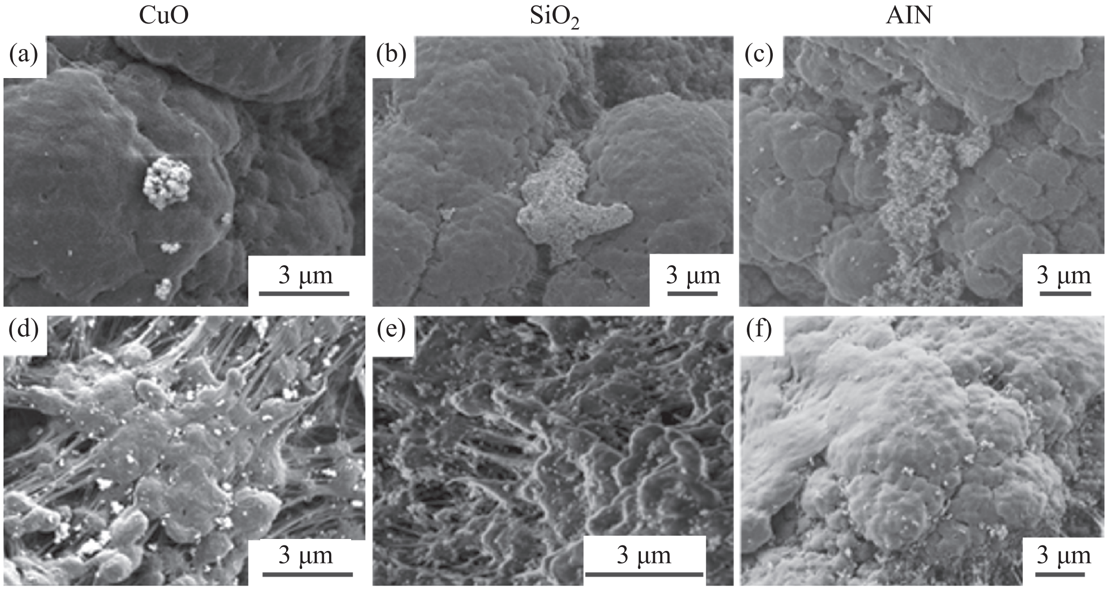

Fig. 3. Examination of the UHMWPE surface and of NPs adsorbed on it (a–c) before and (d–f) after ultrasonic treatment.

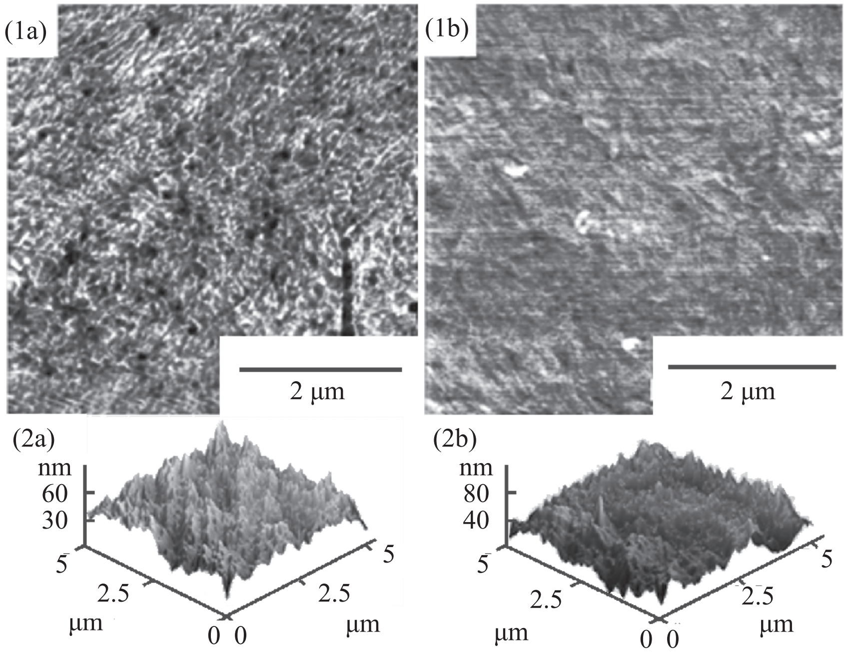

Fig. 4. (1) Phase contrast and (2) topographic AFM images of the (a) initial UHMWPE and (b) UHMWPE ultrasonically treated for 60 min. Examination area 5 × 5 μm.

characteristics of the polymer material. To reveal the effect of ultrasonic treatment on the initial polymer, we performed experiments on ultrasonic treatment of the initial UHMWPE for 10, 20, 40, 60, and 80 min, followed by strain and strength tests (Table 2).

Considerable enhancement of the strength and a decrease in the relative elongation at break after the ultrasonic treatment can be attributed to changes in the structural organization of UHMWPE. To study the supramolecular structure of UHMWPE modified by ultrasonic treatment, we examined its samples with an atomic-force microscope (Fig. 4).

It is known [22, 23] that the phase pattern reflects local differences in mechanical properties (adhesion,

Table 2. Physicomechanical characteristics of UHMWPE before and after ultrasonic treatment[a]

Sample	τ, min	σ_t, MPa	ε, %	ρ, g cm^{-3}
UHMWPE	0	33–36	300–320	0.930
Ultrasonically treated UHMWPE	40	34–37	245–260	0.992
	60	40–42	275–290	0.997
	80	38–41	260–280	0,942

[a] (τ) Ultrasonic treatment time, (σ_t) ultimate tensile strength, (ε) relative elongation at break, and (ρ) density.

elasticity, viscosity). In many cases, especially in studying polymer material, this mode of taking patterns appears to be more informative. For example, lamellar crystalline structure of UHMWPE can be clearly seen in image *1a* of Fig. 4. Ultrasonic vibrations cause densification of the lamellar structure of UHMWPE (image *1b* in Fig. 4) and smoothening of the UHMWPE surface relief (image *2b*), which is also consistent with the results of sample density measurements (Table 2).

Crystallization from the melt leads to predominant formation of the spherulite supramolecular structure in the UHMWPE–NP system. This structure was analyzed in detail in our previous papers [24, 25].

One of the most obvious criteria of the efficiency of the chosen compounding method is the uniformity of the distribution of filler NPs in the bulk of the polymer, determined by surface mapping of the UHMWPE/Al_2O_3 nanocomposite with respect to the aluminum content using EDS spectroscopy (Fig. 5).

Application of the traditional compounding method with a blade mixer to the UHMWPE–NP system leads to less efficient compounding, as the filler NPs are present in the polymer matrix as agglomerates (Fig. 5a). Such areas of filler agglomeration, as shown previously [24], act as stress concentrators deteriorating the physicomechanical characteristics of the material. The deformation, crack propagation, and pore growth under the action of mechanical stresses occur at such structural defects. On the other hand, ultrasonic treatment (Fig. 5b) ensures uniform distribution of filler NPs in the bulk of the polymer.

We have performed tests (Fig. 6) to confirm the hypothesis that compounding of UHMWPE with NPs using the suggested technology will lead to considerable improvement of the strain and strength characteristics.

As can be seen, the strain and strength characteristics of all the samples are considerably improved already at small degrees of filling (0.1–0.5 wt %) and become somewhat worse as the NP content is increased further. Such dependences of the properties on the nanofiller content are typical of polymers with nanosized fillers [26]. This pattern is primarily associated with high

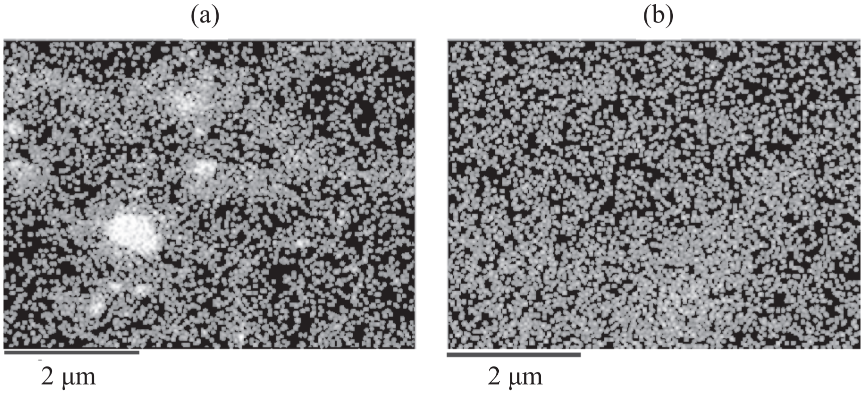

Fig. 5. Aluminum distribution in the bulk of UHMWPE + 0.5% Al_2O_3 polymer nanocomposite. (a) Blade mixing in ethanol and (b) compounding with ultrasonic treatment.

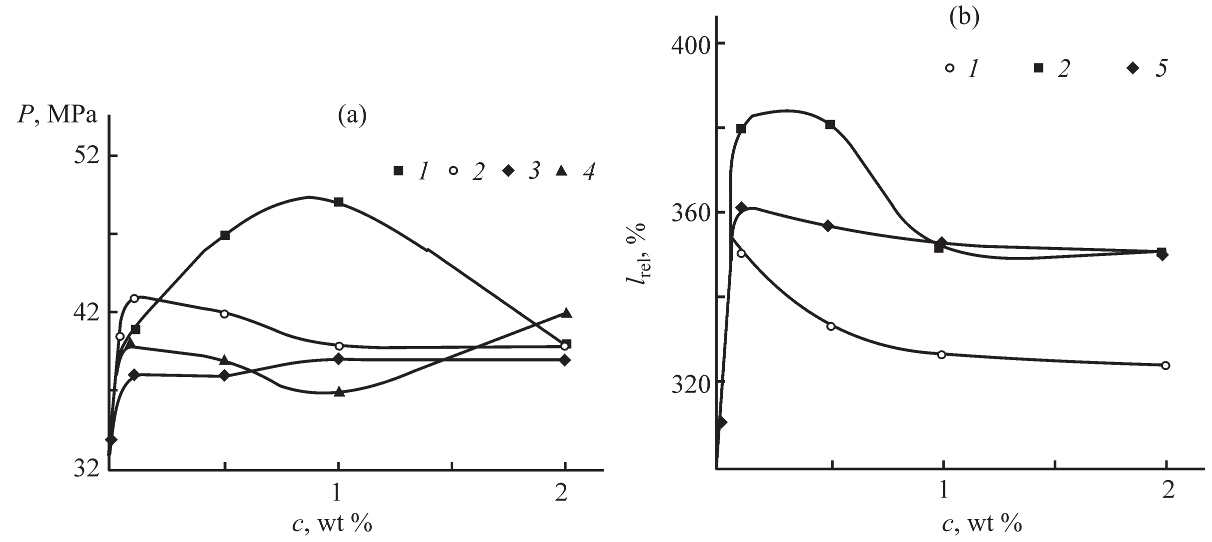

Fig. 6. (a) Tensile strength P and (b) relative elongation at break l_{rel} as functions of the NP content c. (*1*) UHMWPE + Al_2O_3, (*2*) UHMWPE + Si_3N_4, (*3*) UHMWPE + ZrO_2, (*4*) UHMWPE + AlN, and (*5*) UHMWPE + SiO_2.

specific surface area of the filler and hence with the large fraction of the interfacial layer, reaching the critical level already at low NP content. Further increase in the interfacial layer fraction leads only to an increase in the rigidity but not to enhancement of the strength. In this case, overstresses and defective areas arise, the viscosity of the system increases, and the mobility of UHMWPE macromolecules becomes restricted, which complicates the relaxation processes and prevents the deformation development [27].

Another possible cause of deterioration of the strain and strength characteristics is agglomeration of filler nanoparticles with an increase in its content. Negative effect of NP agglomeration processes on the properties of polymer nanocomposites was proved in [28–30].

CONCLUSIONS

The tendency of nanoparticles to aggregation and formation of agglomerates and high viscosity of ultra-high-molecular-weight polyethylene melt are serious problems complicating production of polymer nanocomposites. A liquid-phase compounding procedure ensuring uniform distribution of nanoparticles in the polymer matrix without altering the composition and structure of the components was developed. It consists in continuous action of ultrasound in the course of stirring in ethanol. The nanocomposites prepared using the developed process exhibit enhanced levels of strength and elasticity due to uniform distribution of nanoparticles in the bulk of ultra-high-molecular-mass polyethylene.

The main distinctive feature of the developed process is low, compared to mechanochemical methods, probability of contamination of the compound with foreign impurities and biological objects in the step of compounding of ultra-high-molecular-mass polyethylene and nanoparticles. This advantage is significant for the development of materials for medicine, e.g., prostheses and implants. The developed process can be used for preparing polymer composite materials with wide application spectrum.

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