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Modification of Polymers by Nanodispersed Ceramic Particles

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Abstract

Research results of the effect of nanodispersed ceramic powders on properties of nanocomposites based on high pressure polyethylene are given. It has been shown that the addition of the nanodispersed modifiers SiC, TiO_2 leads to grinding up polyethylene grains up to the sizes of less than 0.1 μm. Herewith, an increase of the density and fastness to rubbing of polyethylene is observed, as well as the decrease in gas permeability (in 1.5 times) and water vapour permeability (in 1.7 times).

Key words: polymeric nanocomposites, nanodispersed ceramic powders, modifying, strengthening, near-surface phase, X-ray phase analysis, crystallinity

INTRODUCTION

To widen the range of properties of plastic masses the method of filling them with inorganic materials have long been used [1]. One of the promising methods of modifying polymers is the use of mechanically activated ceramic powders.

Highlight the main factors that contribute to structuring the activity of nanodispersed powders (NDP), for establishing regularities directed modifying materials.

The presence of the dispersed phase in the volume of the polymer creates the conditions for its hardening having influence on the dynamics of dislocations. In this case, such a material can be considered as a dispersedly-reinforced composite. Consider the mechanism of hardening of composites reinforced with dispersed particles. Under the influence of the applied voltage, the sources of dislocations form dislocation loops, surrounding particles. The number of loops of dislocations (n) depends on the distance between particles:

$$n = l_p\sigma/G_m|b^{\rightarrow}| \quad (1)$$

where l_p is distance between particles; σ is applied voltage; G_m is shear modulus of the matrix material; $b^{\rightarrow}$ is Burgers vector of a dislocation. The shear stress acting on the particle is determined as

$$\tau = l_p\sigma^2/G_m|b^{\rightarrow}| \quad (2)$$

and the yield stress of the material reinforced by particles (σ_s) as

$$\sigma_s = (G_pG_m|b^{\rightarrow}|/l_pC)^{0.5} \quad (3)$$

where G_p is shear modulus of the particle material; C is constant characterising the material type [2].

Thus, when modifying by disperse particles strengthening the composite can be achieved that is the yield stress increase. Herewith, the shear modulus of the particle material (G_p) should exceed by value the shear modulus of the matrix (G_m), otherwise, strengthening will not occur. If the particle is not wetted by the material, then the bubble with the shear modulus, equal to zero, will be located between the material and the particle. According to the equation (3), the yield stress is equal to zero in this case and the material is softened. Hence, for strengthening materials by dispersed particles it is necessary for the particles to be moistened by the material [3]. Otherwise, they will act as defects of the structure worsening the properties of the material.

Two models defining the efficiency of wetting NDP are known. The first one is related to the decrease of the surface tension at the boundary of the seed–melt interface under the action of curvature (nanoparticle size) [4]. The second model is based on lowering the surface tension on the border of the seed–melt interface under the action of the electric field [5].

Causes of the field could be so called electrocontact interaction, as well as various defects of the structure of mechanochemically treated powders: charges at the surface of particles, through nanopores that serve as elevated channel of conductivity, ion radicals, *etc.* The basis is the model of W. Tiller, in which features of the electric field associated with the properties of the particles are analyzed. He estimated the electrostatic contribution for the parameter of wetting of the substrate by the melt. At the close contact of two media, a potential difference, equal to the difference of the Fermi levels arises. As a result, two layers of electric charges of the opposite sign, located on opposite sides of the phase boundary are formed. Thus, the interface turns out to be accommodated at some efficient capacitor. The specific energy of this capacitor was considered by W. Tiller as a negative contribution to the surface tension.

For the wettability of particles introduced into the material, their surface can also be covered with substances, compatible with the material itself.

From the stated above, it follows that ultradispersed particles introduced into the material for its modification should be very small or charged or their surface should be covered with substances, compatible with the material itself.

The authors of [6] defined a minimum particle size of ultradispersed powders (UDP) that ensure the possibility of their wetting by any material. They established that in the case when the particle surface energy is equal to its heat of melting, the minimum particle size is 1 nm. But particles of such sizes in the isolated state cannot be solid and in contact with any material they are wetted by it, and the energy of this interaction exceeds the energy of chemical bonds. Thus, this mechanism can be implemented provided that the particle size of UDP is in the range of 1–3 nm.

The average size of particles, for example, carborundum (SiC) after the mechanochemical treatment is about 50 nm; however, the modification result herewith is not worse. This is due to the fact that at the mechanochemical treatment of carborundum, cleavage of chemical bonds occurs and in the volume of its particles the charge is accumulated. According to the theory by W. Tiller, these charged particles are wetted well by polymers forming a new near-surface phase of a polarized polymer.

In case when the mechanochemical treatment does not allow stabilizing charges in the particles volume (for example, at the treatment of calcium carbonate), their surface should be covered with a substance, compatible with the material, into which they are introduced. Thus, at the joint mechanochemical treatment of calcium carbonate with a polymer it is possible to completely coat the surface of calcium carbonate particles. Then, these particles covered with the polymer can be used for modifying the polymer.

The calculation according to formula (3) becomes incorrect for alloys with a small size of particles. In this case, the shear stress acting on dispersible particles of the spherical shape of the diameter (d) is determined by the ratio, $\tau = 2nG_m|\vec{b}|/d$ and the yield stress of the alloy is inversely proportional to the particle size:

$$\sigma_s = 2G_m|\vec{b}|/d \qquad (4)$$

Here, particles hinder the motion of dislocations; *i. e.* the dislocation loop is great, in comparison with the distance between particles.

Therefore, the yield strength of dispersedly hardened alloys containing large particles (sizes of particles are more than 0.1 μm) depends on both the matrix strength and particles substance. And at small sizes of particles, the alloy strength is directly proportional to the shear modulus of the matrix and inversely proportional to the particles size (particles sizes are

0.001–0.03 μm) and does not depend on particles material.

For the first time, polymeric nanocomposites (PNC) based on montmorillonite layered silicate and nylon-6 were obtained in the early 1990ies by Japanese researchers [7, 8]. The modulus of elasticity and strength of developed PNC exceeded analogous characteristics of starting nylon-6 in 1.7 and 1.4 times, respectively. Such a significant improvement in mechanical properties was accompanied by the decrease of thermal expansion coefficient in 1.5 times and the increase of softening temperature from 65 to 152 °C. Herewith, the content of montmorillonite amounted to only 4.7 mass %. The resulting material is much lighter, compared to traditionally used composites with an analogous complex of mechanical and thermophysical characteristics, in which the content of the inorganic component lies usually in the range of 20–30 mass %. These authors found that the introduction of clay minerals into a polymer leads to a significant decrease of the diffusion coefficient of various gases in the polymer matrix [9].

The shear modulus of polymers is always smaller than shear modulus of ceramics, which ensures the increase of the yield strength when modifying polymers by particles of ceramics. However, from formula (3) it follows that the yield strength can be increased by reducing the distance between by particles of ceramics. This is achieved by the increase of the number of ceramic particles (*i.e.* number of ceramics) or decrease of particles sizes at the same mass of ceramics. Since the number of particles from the same volume increases in 1000 times, then, when decreasing the size of particles in 10 times the distance between particles also decreases in 1000 times. At the present time, masterbatches with the size of ceramic particles of the order of 1 μm are used, the transition into the nanoarea (sizes of particles are less than 0.1 μm) should lead to the increase of the yield strength of the composite at a considerably lower concentration of ceramic particles.

The mechanochemical way of the preparation of masterbatches is most suitable for these purposes, as allows simultaneously obtaining nanodispersed ceramic powders, cladding them for the increase of the wettability and as a result of dispergating, increasing the wettability due to the appearance of charges on particles [10].

The goal of the present work is the investigation of the effect of nanodispersed ceramic powders on properties of nanocomposites made based on of polyethylene of high pressure.

EXPERIMENTAL

The following materials were used in the work: 1) high pressure polyethylenes of the brands PEVD 15803-020 and LLDPE 6101 RQ (PEVD and PE, correspondingly); 2) carborundum SiC with the specific surface of 6–7 m^2/g and size of particles of 2000–100 nm obtained by the mechanochemical treatment (MT) in centrifugal planetary mills (sample M2–SiC: treatment time in AGO-3 is 1 min; sample M3-SiC: treatment time in AGO-3 is 5 min); 3) titanium oxide R-FC5 for plastics with the size of particles of 0.18 μm, S_{sp} = 6.84 m^2/g; 4) SiO_2 Rosil-175, TU 2168-038-00204872–2001, S_{sp} = 155 m^2/g; 5) $CaCO_3$ of the brand RM-1T, S_{sp} = 441 m^2/g; 6) Na-montmorillonite (bentonite), State Standard GOST 28177–89, of the brand P1T1, S_{sp} = 17.36 m^2/g.

Powders of polymers were mixed with powders of modifiers, and then samples of modified polyethylene were made from this mass by the method of hot pressing and extrusion.

RESULTS AND DISCUSSION

Data on the effect of additives on the indicator of abrasion of the compositions PEVD (GOST 11012–69) are given in Table 1. It can be seen that the increase of the amount of the introduced modifier leads to the monotonic increase of the wear resistance.

As follows from the data of the electron microscopic study of samples of starting (unmodified) polyethylene PE obtained by extrusion (Fig. 1, *a*) the grain size is of the order of 0.3 μm. Thermal pressing of starting (unmodified) polyethylene (see Fig. 1, *b*) leads to the increase of the grain size by almost an order of magnitude. Thermal pressing after modifying by ceramic nanopowders 5 and 50 % TiO_2 (see Fig. 1, *c*, *d*) is accompanied by grain PE grinding to the size at the level of 0.1 μm.

TABLE 1

Effect of modifiers on the indicator of abrasion of compositions PEVD

Samples	Density, g/cm^3	Indicator of abrasion, mm^3/m
PEVD (initial)	0.9164	1.12
PEVD + 1 % M2	0.926	0.85
PEVD + 4 % M2	0.939	0.84
PEVD + 7 % M2	0.964	0.78
PEVD + 10 % M2	0.985	0.72
PEVD + 15 % M2	1.017	0.55
PEVD + 20 % M2	1.064	0.45
PEVD + 1 % M3	0.924	1.37
PEVD + 4 % M3	0.935	1.18
PEVD + 7 % M3	0.966	0.98
PEVD + 10 % M3	0.987	0.80
PEVD + 15 % M3	1.019	0.62
PEVD + 20 % M3	1.065	0.59

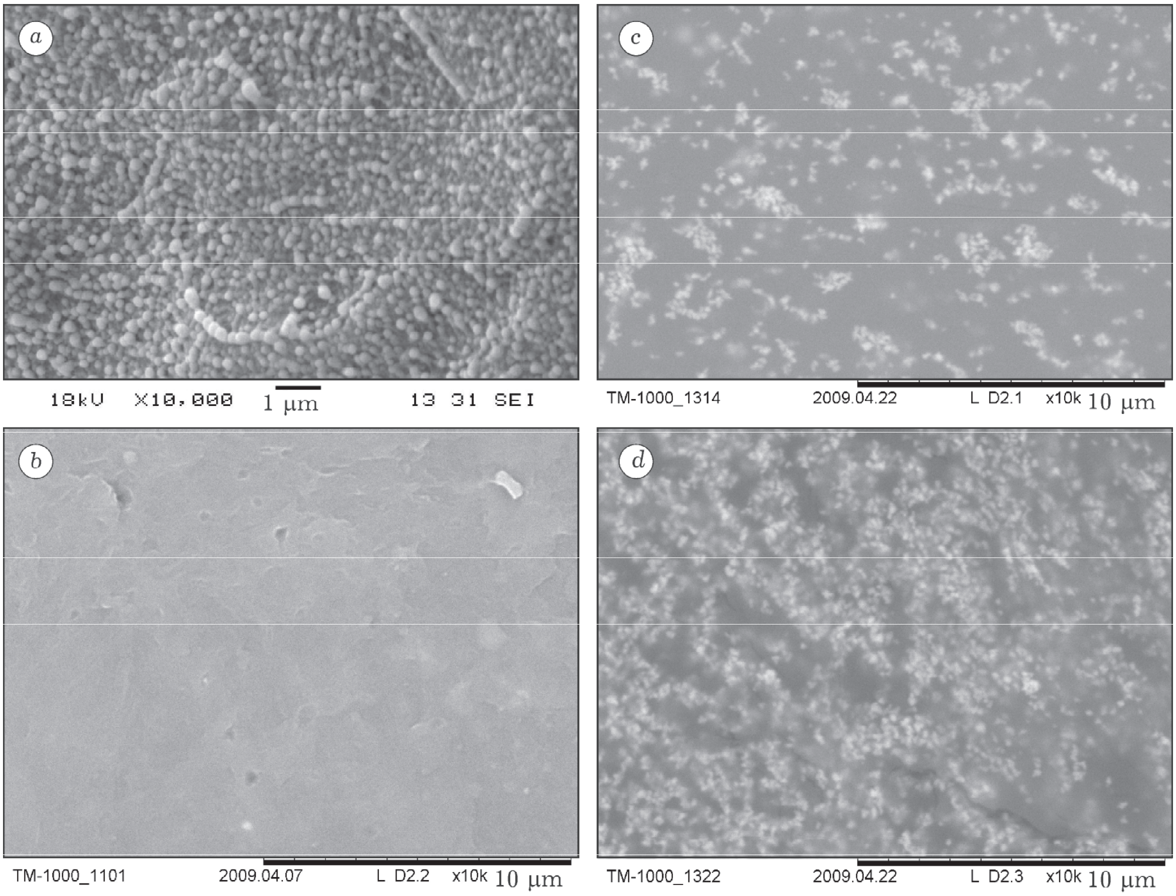

Fig. 1. Electron microscopic images of brand PE polyethylene samples: *a* – initial (unmodified) obtained by extrusion; *b*–*d* – obtained by thermal pressing (*b* – initial; *c*, *d* – after modifying by ceramic nanopowders of 5 and 50 % TiO_2, respectively).

TABLE 2

Density of modified samples of polyethylene PE (density of the initial sample is 0.863 g/cm^3)

Modifiers		Treatment time	Density, g/cm^3
Composition	Amount, %	in AGO-3, s	
TiO_2	25	20	1.05
TiO_2	5	20	0.966
TiO_2	1	20	0.937
TiO_2	0.01	20	0.927
SiO_2	10	20	0.980
SiO_2	5	20	0.952
SiO_2	1	20	0.956
SiO_2	0.01	20	0.929
$CaCO_3$	5	20	0.957
Na-montmorillonite (bentonite)	5	20	0.950

Grinding grain of the polymer can explain the increase of its wear resistance. Herewith, the oxygen permeability of polyethylene decreases in 1.5 times, and vapour permeability – in 1.7 times. The increase in the density of the polymer at introducing in it additives of ceramic nanoparticles even in hundredths of percent (Table 2) is apparently associated with grain grinding.

From the data of the X-ray phase analysis (XPA), it follows (Fig. 2) that the introduction of ceramic nanopowders into the polymer PE leads to the decrease of its crystallinity. If the nanopowder is mixed homogeneously with the polymer, then even hundredths of a percent of the nanopowder is enough for the product to lose the crystalline structure.

The crystallinity change of the polymer when introducing in it ceramic particles is associated with the appearance of the near-surface phase around particles (Fig. 3). The appearance of a new phase is clearly evidenced by data of DTA for polyethylene PEVD (Fig. 4). It can be seen that the thermal effect at the temperature of 140 °C (see Fig. 4, *a*) is observed for the initial sample PEVD. The decomposition of PEVD starts at 460 °C. After the introduction into PEVD of ultrafine powders of inor-

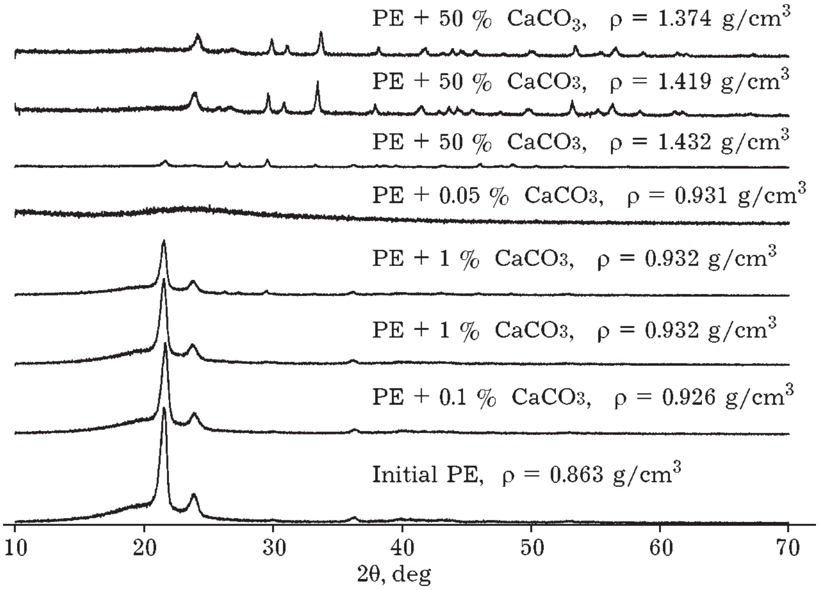

Fig. 2. X-ray patterns of the initial and modified samples of polyethylene PE.

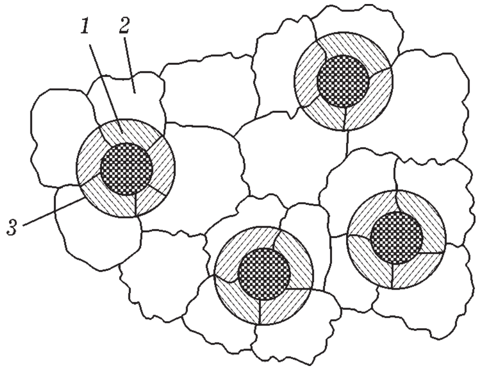

Fig. 3. Scheme of the formation of the polymer structure when its filling by modifying ceramic particles: *1* – modifier particle; *2* – polymer particle; *3* – surface layer of the polymer on the boundary with a modifying particle.

ganic modifiers (7 % SiC) an additional thermal effect at 400 °C (see Fig. 4, *b*) is observed what and proves the appearance of a new amorphous phase with an elevated thermal stability.

CONCLUSION

Thus, modifying polyethylene by nanoparticles leads to grinding the grain of the polymer, as in case of the modifying metals by nanoparticles. It has been discovered that when modifying polyethylene by nanoparticles a new near-surface phase of the polymer is formed and its crystalline structure is destroyed. When modifying polyethylene by silicon carbide (treatment time in AGO-3 is 3 min) in the amount of 1–20 %, the wear resistance of polyethylene increases in 1.3–2.5 times, and at the modification by silicon carbide in the amount of 7–20 % (treatment time in AGO-3 is 5 min) the wear-resistance increases in 1.14–1.9 times. The

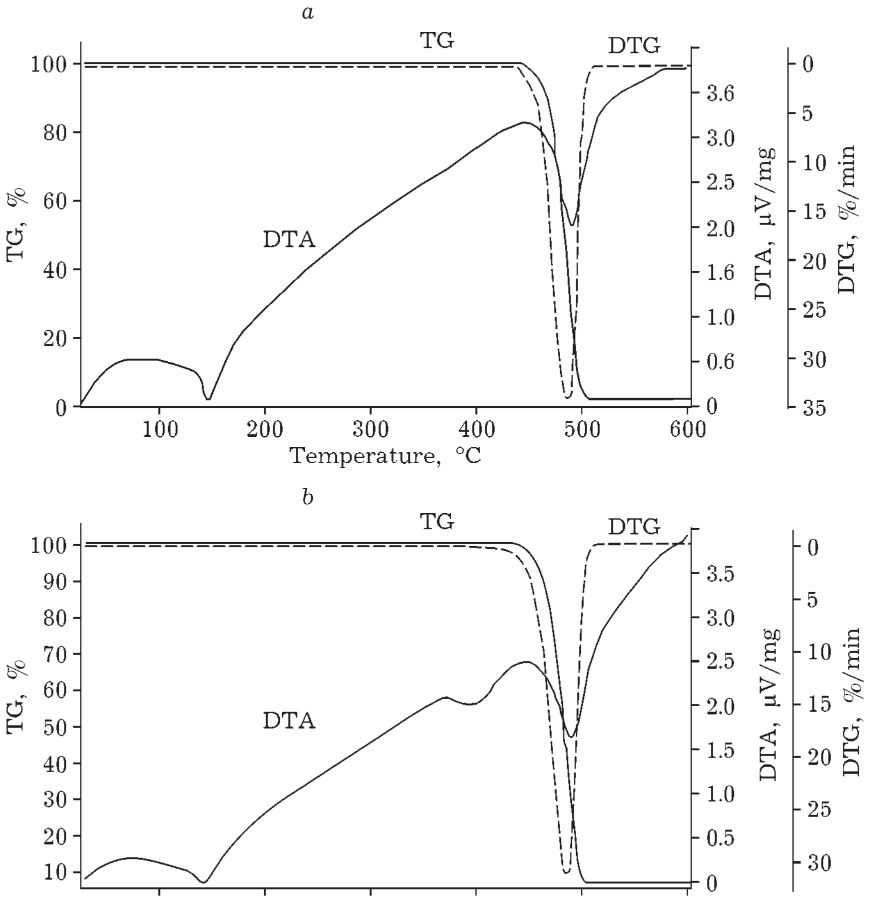

Fig. 4. DTA of polyethylene samples PEVD: *a* – initial, *b* – modified (7 % SiC).

oxygen permeability decreases in 1.5 times, vapour permeability – in 1.7 times for polyethylene with the addition of TiO_2 in the amount of 5–50 %. Improving barrier properties of polymers (of gas permeability) is particularly important in relation to packaging materials.

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