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INFLUENCE OF THE STRUCTURE OF A MODIFIER LAYER ON THE COMPATIBILITY OF POLYMERS WITH A MODIFIED MONTMORILLONITE

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The dependence of the compatibility of a modified montmorillonite with different-polarity polymers on the structure of a modifier layer formed on the montmorillonite surface has been investigated. It is shown that the layers forming an ordered structure in the interplane spaces of the clay do not provide an exfoliation of the silicate plates of the clay or a significant intercalation of polymer chains into the interlayer space of the montmorillonite. An optimum structure of a modifier layer, providing a significant intercalation of polymer chains into the interlayer spaces of the montmorillonite and an exfoliation of the clay in its compounds with a maleinized polypropylene, obtained by mixing in a melt, has been determined.

Systems based on polyolefins and inorganic clay materials capable of swelling (smectites) are promising nanocomposite materials. Na^+-montmorillonite (MMT) is used usually as the filler of these compounds. This montmorillonite possesses a high dispersivity and can, under certain conditions, exfoliate into individual plates of thickness ~1 nm and diameter 20–250 nm [1]. It is precisely this fine-dispersion substance with a clearly defined shape anisotropy that can actively change many properties of polymers. It is used for obtaining intercalated composites (macromolecules penetrate into the space between the filler plates) or exfoliated composites (clay crystals exfoliate into individual plates and distribute uniformly in the polymer matrix). Such composite materials, as a rule, have large values of the modulus of elasticity, strength, thermal stability, and combustion resistance as well as good barrier properties and elastic properties that are retained at high concentration of a filler (as high as 30–35%).

Compatibility of the organic and inorganic components in a montmorillonite and an intercalation of macromolecules to the space between its silicate layers is provided by adsorption of various surface-active substances on the surface of montmorillonite particles [2, 3]. Cationic (alkylammonium) surface-active substances, having a single charged group and volumetric organic "tails," are usually used for this purpose. When a montmorillonite is modified, the polar centers of a surface-active substance are chemically adsorbed on the surface of silicate plates and the chemical component of this substance enters the space between the clay plates. As a result of the sorption of alkylammonium cations and desorption of sodium cations, the interplane distance in the montmorillonite increases, which is favorable for the penetration of polymer molecules to the clay.

It has been shown in [4–6], which are devoted to a theoretical study of the influence of the structure of the layers formed by the molecules of a surface-active substance on the surface of silicate plates on the thermodynamic compatibility of this substance with polymer macromolecules, that this problem is of crucial importance in the development of nanocomposite materials based on polymers with nonpolar chains and layered silicates.

The aim of the present work is to obtain organophilic layers in the interplane space of a montmorillonite with the use of bromide dioctadecyldimethylammonium (BDODA) molecules and to investigate the influence of the structure of organophilic layers on the ability of polyolefins to intercalate to the space between the silicate plates and, in the limit, to exfoliate a montmorillonite in a polymer matrix into individual plates.

To solve the problems set, it is necessary to determine the relation between the amount of a BDODA adsorbed on a montmorillonite, the set of organophilic layers formed in the interplane spaces of the layered silicates, and

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TABLE 1. Interplane Distances (nm) in a Pure Filler and in Its Composites with Oligomers

Composite	MMT	MG1-0.5	MG1-1.0	MG1-2.0
Free of oligomer	1.0	2.1	3.7	4.2
PE	1.0	4.1	4.3	4.3
POE	1.8	3.9	3.9	4.2
POE–PE	1.8	4.2	4.3	6.9
PPMO	2.3	Basal reflections of MMT are absent		4.3

the distance between the silicate plates, on the one hand, and the possibility of intercalation of macromolecules to the interplane spaces of the clay on the other hand.

Experimental. *Materials.* A natural clay montmorillonite with a cationic-exchange capacity of 95 mg-eq/100 g was investigated. The cationic exchange capacity is a characteristic of a clay material that determines the number of exchangeable cations (calculated per 100 g of the clay and expressed in mg-equivalents) capable of substitution for other cations. A 99%-purity BDODA ("Acros Organics") was used as the modifier.

The compatibility of a modified montmorillonite was determined in the process of mixing of it with a polyethylene (PE) with $M_{\mathrm{w}} = 700$ ("Polysciences Inc."), a polyoxyethylene (POE) with $M_{\mathrm{w}} = 40{,}000$ ("Ferak Berlin"), a polyoxyethylene–polyethylene block copolymer with $M_{\mathrm{w}} = 570$, a low-pressure polyethylene (LPPE) with $M_{\mathrm{w}} = 300{,}000$, a maleinized polypropylene oligomer (MPPO) ("Clariant GmbH"), and a Polybond 3002 maleinized polypropylene (MPP) containing 0.2 wt. % of maleic anhydride ("Uniroyal Chemical Crompton").

Investigation methods and preparation of samples. The main investigation methods used in the present work were described in [7–9]. A modified montmorillonite was prepared by the method described in [10]: 1.0 g of the clay was dispersed in 300 ml of distilled water in the process of intensive continuous mixing. The BDODA modifier was dissolved in hot water at 70°C to a concentration of $5\cdot10^{-3}$ mole/liter. A continuously mixed solution (95, 190, and 380 ml) was added to the clay suspensions in portions of 1 ml per minute, with the result that montmorillonite with a sorbed-modifier content of 0.5, 1.0, or 2.0 of the cation-exchange capacity of the clay, called hereafter MG1-05, MG1-1.0, or MG1-2.0, was obtained. The solutions were filtrated and the precipitates formed were washed with distilled water. A fine-dispersion powder of a modified clay was obtained by lyophylic drying.

To investigate the compatibility of the pure and modified montmorillonite with oligomers, we prepared oligomer–clay mixtures in a weight ratio of 1:0.2 at a temperature of 120°C (160°C for the maleinized polypropylene oligomer) on a microscope slide and periodically mixed them for 30 min. Water (1–2 ml) was added to the polyoxyethylene–montmorillonite system to decrease its viscosity. After the mixing, the samples were dried for 1 h in a vacuum cabinet at 100°C. The montmorillonite was mixed with the low-pressure polyethylene and maleinized polypropylene (polymer–clay weight ratio 1:0.05) in a plunger-type mixer at a temperature of 160–180°C for 15 min with addition of an antioxidant (Irganox) in an amount of 0.2% of the polymer mass.

The composites obtained were positioned between aluminum sheets and pressed at a temperature of 180°C for 5 min, with the result that films of thickness ~0.2 mm were obtained. These films were then hardened in cold water for 2 min.

Results and Discussion. *Compatibility of montmorillonite with oligomers.* We investigated the compatibility of the "pure" and modified montmorillonite with oligomers whose melts have a lower viscosity as compared to that of polymers. They were intercalated into the clay for the purpose of decreasing the kinetic factors. The distances between the plates of a montmorillonite before and after its mixing with oligomers were determined by the method of x-ray structural analysis. The corresponding data obtained for oligomer–montmorillonite composites are presented in Fig. 1 and in Table 1.

It has been established that the polar polymers polyoxyethylene, polyoxyethylene–polyethylene, and maleinized polypropylene intercalate to the montmorillonite free of modifier, and the largest degree of intercalation was detected for the maleinized polypropylene oligomer — the increase in the interplane distance reached 1.2 nm (Fig. 1a, curve 4). Molecules of the nonpolar polyethylene did not penetrate into the interplane spaces of the clay.

On the roentgenogram of the MG1-0.5 there are basal reflections corresponding to the interplane distances 1.1 and 2.1 nm (Fig. 1b, curve 1). It was shown in [9] that, because of the cooperative character of the BDODA adsorp-

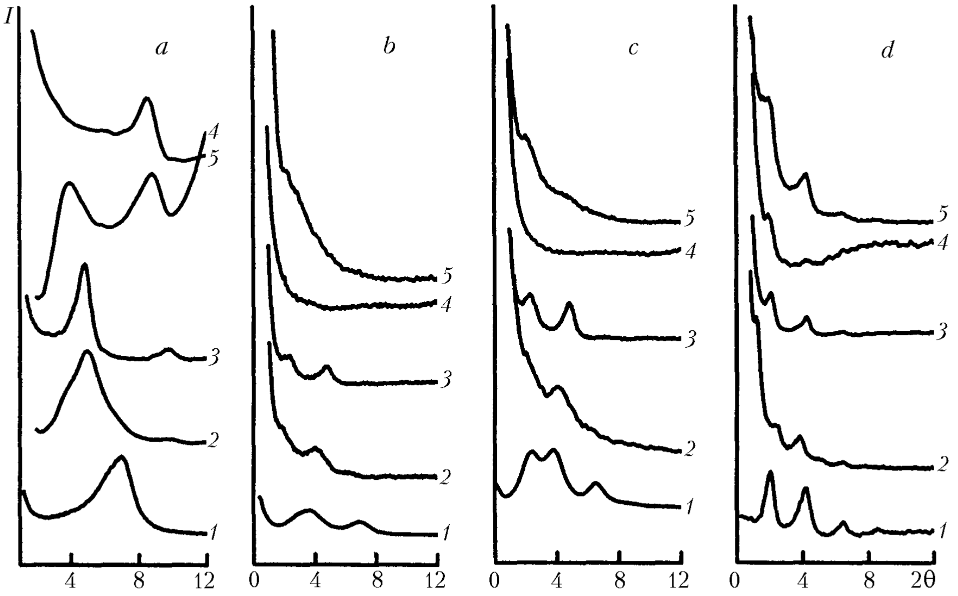

Fig. 1. Roentgenograms of oligomer–clay composites. The fillers in the composites are the pure MMT (a), MG1-0.5 (b), MG1-1.0 (c), and MG1-2.0 (d); the oligomers are a filler (1), POE–PE (2), POE (3), PPMO (4), and PE (5). *I*, rel. units.

tion, a mixed-layer structure is formed at low degrees of filling with the montmorillonite. In this structure, some layers remain nonmodified, and the distance between the silicate plates in the other layers is increased as a result of the intercalation of modifier molecules found in the liquid state.

As a result of the combination of the MG1-0.5 with the polyoxyethylene and polyoxyethylene–polyethylene, the interplane space increased by 1.8 and 2.1 nm respectively (Fig. 1b, curves 2 and 3), and the clay in combination with the maleinized polypropylene oligomer was completely exfoliated — reflections were absent on the roentgenogram in the small-angle region (Fig. 1b, curve 4). An even more interesting effect was observed when the MG1-0.5 was mixed with the polyethylene. In this case, a broad reflection with a maximum corresponding to an interplane distance of 4.1 nm appeared on the roentgenogram (Fig. 1b, curve 5). Thus, all the oligomer substances studied, even the polyethylene with M_W = 700 representing a low-molecular analog of nonpolar polyolefins, intercalate into the montmorillonite with the above-indicated modifier-layer structure. The interplane distance in the MG1-05 mixed with the polyethylene was increased by 1.8 nm.

When the amount of the BDODA sorbed into the montmorillonite was increased to 1.0 of the cation-exchange capacity (Fig. 1c, curve 1), three reflections appeared on the roentgenogram of the sample in the small-angle region; these reflections correspond to the distances between the clay plates equal to 1.2, 2.3, and 3.7 nm. The first reflection characterizes the nonmodified montmorillonite layers, and the second and third reflections characterize adsorbed layers of different structure. In [9], it has been shown that, when the interstack distance reaches 3.7 nm, in the organophilic layers there arises an ordered structure similar to clusters consisting of BDODA molecules, part of which are at the exchange positions and the others of which are combined with the "attached" molecules by the Van der Waals forces.

An increase in the amount of the BDODA sorbed into the montmorillonite to 1.0 of the cation-exchange capacity decreases the ability of the oligomers polyethylene, polyoxyethylene–polyethylene block-copolymer, and polyoxyethylene to intercalate into the clay: they increase the distance between the layers in the MG1-1.0 only by 0.7, 0.5, and 0.2 nm respectively (Fig. 1c, curves 2, 3, and 5). Molecules of the maleinized polypropylene oligomer, as in the case of a low modifier content in the montmorillonite, completely exfoliated the clay layers (Fig. 1c, curve 4).

The saturation of the montmorillonite with a superequivalent amount of the modifier (2.0 of the cation-exchange capacity) leads to the formation of layers with an ordered structure that is more perfect than the structure of the layers in the MG1-1.0. The interplane distance in the MG1-2.0 did not change when it was mixed with the polyethylene, polyoxyethylene, and maleinized polypropylene oligomer (Fig. 1d, curves 3–5). However, we detected a

TABLE 2. Melting Temperature and Heat of Oligomers in Composite with Pure and Modified MMT

Composite	Pure oligomer		MMT		MG1-0.5		MG1-1.0		MG1-2.0	
	T_m, $^\mathrm{o}$C	ΔH_m, J/g	T_m, $^\mathrm{o}$C	ΔH_m, J/g	T_m, $^\mathrm{o}$C	ΔH_m, J/g	T_m, $^\mathrm{o}$C	ΔH_m, J/g	T_m, $^\mathrm{o}$C	ΔH_m, J/g
PE	95	222	96	220	96	180	98	198	96	202
POE	63	152	61	127	58	130	50	36	56	90
POE–PE	83	170	83	154	82	139	83	145	83	160
PPMO	150	49	150	44	149	37	151	43	150	50

marked intercalation of the block-copolymer into the MG1-2.0 — the interplane distance in the clay was increased from 4.2 to ~7.0 nm (Fig. 1d, curve 2).

Thus, oligomer molecules actively penetrate into the interlayer spaces of the montmorillonite when the surface of the silicate plates is partially covered by an organophilic layer (the content of the modifier in the clay should not exceed 0.5 of the cation-exchange capacity). It should be noted that nonpolar-polyethylene molecules penetrate into the MG1-0.5. The significant intercalation of the oligomers can be explained by several factors: 1) a high thermodynamic compatibility of them with the modified surface of the silicate plates; 2) a large interplane distance in the modified clay; 3) the absence of ordering of the modifier molecules in the organophilic layer, which, in this case, does not prevent the penetration of the oligomer molecules into the spaces between the silicate plates of the montmorillonite.

The data on the melting heat and temperature of oligomer–montmorillonite systems, presented in Table 2, supplement the data obtained by the method of x-ray structural analysis. There is little likehood that the oligomer chains intercalated into the interlayer space of the montmorillonite will crystallize; therefore, the melting heat determined by the method of differential scanning calorimetry on an oligomer-mass basis should decrease. It has been established that the melting heat of an oligomer matrix in the composites containing a montmorillonite, e.g., the polyethylene–MG1-0.5 system, is much lower (by approximately 20%) than that of the pure oligomer; in this case, the interplane distance in the filler is markedly increased. The melting heat of the polyethylene in the polyethylene–MG1-1.0 and polyethylene–MG1-2.0 was lower by approximately 10%, while the interplane distance changed insignificantly. Thus, in this case there is a correlation dependence between the melting heat and the relative increases in the distance between the layers of the clay.

The polar oligomer polyoxyethylene, capable of wetting the surface of silicate plates, was intercalated into the pure montmorillonite, with the result that its melting heat decreased by 16%. The modification of the montmorillonite led to an increase in the distance between its layers, which made the penetration of polyoxyethylene molecules into the interlayer space of the clay easier. When passing from the liquid to the cluster structure of a modifier layer, the silicate-plate area open for wetting by the polyoxyethylene increases. This provides an intercalation of a major portion of the oligomer molecules, which is evidenced by the decrease in the melting heat of the polyoxyethylene in the composition with the MG1-1.0 by 76% and the decrease in the melting temperature by 13$^\mathrm{o}$C. A further increase in the content of the modifier in the clay, i.e., in the number of clusters, leads to a decrease in the silicate-plate area that can contact with the polyoxyethylene, which is evidenced by the value of the melting heat of the oligomer in this composite.

The low-molecular polyoxyethylene–polyethylene block-copolymer representing a bifilar compound can wet the surface of silicate plates due to the polyoxyethylene fragment and, at the same time, is thermodynamically compatible with the aliphatic chains of the modifier due to the polyethylene fragment. Therefore, the polyoxyethylene–polyethylene block copolymer can intercalate into both the pure and modified montmorillonite. The ability of the block copolymer in the polyoxyethylene–polyethylene–montmorillonite system to combine with the clay is largely due to the polyoxyethylene (the melting heat decreases by approximately 9%). In the compositions of the block copolymer with the MG1-0.5 and MG1-1.0, the properties of the polyethylene manifest themselves — the melting heat decreases by 18 and 15%, respectively; these changes are close to the changes in the melting heat of the compositions of the polyethylene with modified clays.

In the maleinized polypropylene oligomer–montmorillonite composites, the oligomer molecules penetrating into the clay decrease the melting heat by 10%. The melting heat of the montmorillonite MG1-0.5 was decreased by 24%

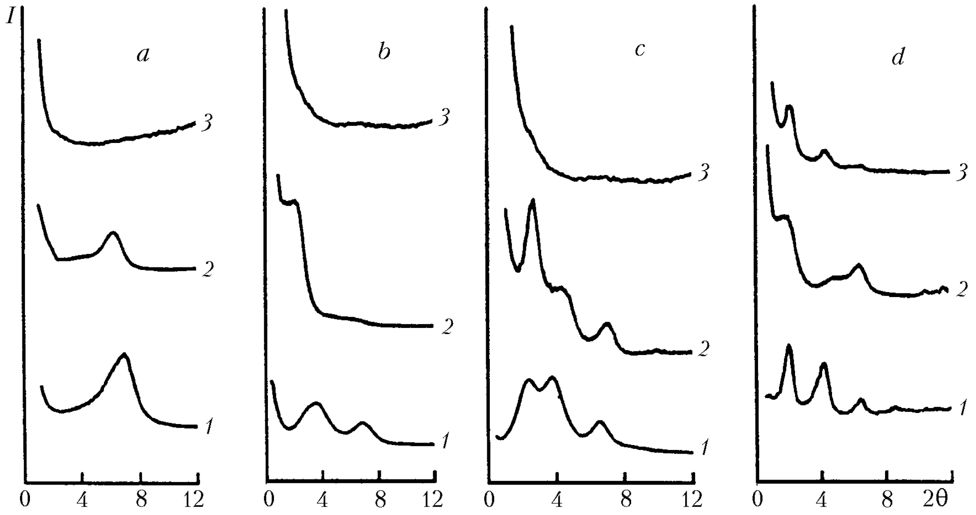

Fig. 2. Roentgenograms of polymer–clay composites. The fillers in the composites are the pure MMT (a), MG1-0.5 (b), MG1-1.0 (c), and MG1-2.0 (d); the polymers are a filler (1), LPPE (2), and MPP (3). *I*, rel. units.

and the melting heat of the montmorillonite MG1-1.0 was decreased by 12%. Because of the perfect ordered structure of a modifier layer in the MG1-2.0, the maleinized polypropylene oligomer cannot intercalate into this clay.

Compatibility of montmorillonite with polymers. Having investigated the ability of various oligomers to intercalate into the modified montmorillonite, we considered the ability of high-molecular substances to intercalate into the interlayer spaces of this clay.

Compositions of a modified montmorillonite (5 wt. %) with a low-pressure polyethylene and a high-molecular maleinized polypropylene, serving as the polymer matrix, were obtained by mixing in a melt. We investigated the properties of composite films obtained by pressing and subsequent hardening of the indicated composites. The interplane distances in the dried montmorillonite and the montmorillonite composites are presented in Fig. 2 and Table 3.

The roentgenograms obtained show that the nonpolar molecules of the low-pressure polyethylene do not penetrate into the interlayer spaces of the montmorillonite, which is evidenced by the positions of the basal reflections in the pure montmorillonite and in the montmorillonite mixed with polymers (Fig. 2a, curves 1 and 2). Molecules of the maleinized polypropylene containing polar maleic groups penetrate into the interplane spaces of the montmorillonite and, in doing so, separate them by a distance at which the order of the silicate plates is disrupted; therefore, basal reflections of the montmorillonite are absent on the roentgenogram (Fig. 2a, curve 3).

When the MG1-0.5 is mixed with the low-pressure polyethylene, the interlayer distance in the filler increases significantly — the montmorillonite plates are pushed apart to a distance of 1.8 nm (Fig. 2b, curves 1 and 2), which is equal to a triple thickness of the polyethylene chains, i.e., low-pressure polyethylene molecules intercalate into the interlayer distances of the montmorillonite. Note that the increase in the interplane distance in the montmorillonite is equal to that in the case of mixing of the MG1-0.5 with the polyethylene oligomer. If the matrix of a composite is the maleinized polypropylene, basal reflections of the clay are absent on the roentgenogram in the small-angle region (Fig. 2b, curve 3), as in the case of mixing of the maleinized polypropylene with the pure montmorillonite, which can be due to the exfoliation of the montmorillonite plates.

Intercalation of the low-pressure polyethylene molecules was absent when the BDODA concentration in the montmorillonite was 0.1 of the cationic-exchange capacity of the clay: the positions of the basal reflections of the MG1-1.0 were retained (Fig. 2c, curves 1 and 2), while the clay exfoliated in the presence of the maleinized polypropylene (Fig. 2c, curve 3). When the montmorillonite was saturated with a superequivalent amount of the BDODA modifier (double excess), as compared to the cationic-exchange capacity, molecules of both polymers did not intercalate into the interplane spaces of the montmorillonite (Fig. 2d, curves 1–3). Thus, the data of x-ray structural analysis of the polymer–montmorillonite composites agree quantitatively and qualitatively with the data on the intercalation of the oligomers. In particular, the conclusion that the low-pressure polyethylene molecules penetrate ac-

TABLE 3. Interplane Distances (nm) in a Pure Filler and in Its Composites with Polymers

Composite	MMT	MG1-0.5	MG1-1.0	MG1-2.0
Free of polymer	1.0	2.1	3.7	4.2
LPPE	1.0	4.1	3.9	4.2
MPP	Basal reflections of MMT are absent			4.2

TABLE 4. Enthalpy of Melting (J/g) of Polymers in Compositions

Composite	Pure polymer	MMT	MG1-0.5	MG1-1.0	MG1-2.0
LPPE	114	114	89	113	115
MPP	81	81	75	82	79

tively into the interlayer spaces of the montmorillonite in the case where the concentration of the modifier in the filler is ~0.5 of the cationic exchange capacity of the clay was supported.

Table 4 presents data on the melting heat of polymer–montmorillonite composites. The enthalpy of melting of the polymer matrix of the composites of the low-pressure polyethylene with the MG1-1.0 and MG1-2.0 is close to the enthalpy of melting of the pure polymer, which supports the conclusion made on the basis of the x-ray structural analysis data. The melting heat of the low-pressure polyethylene–MG1-0.5 system is 22% lower, which is due to the intercalation of a part of the low-pressure polyethylene to the space bounded by the silicate plates, in which the polymer molecules cannot be easily crystallized. The melting heat of the maleinized polypropylene–MG1-0.5 composite is insignificantly lower than the melting heat of the pure polymer, which is evidently explained by the features of its crystallization in the presence of the developed clay surface formed as a result of the exfoliation.

In our opinion, the regularities revealed are of crucial importance for the production of nanocomposites and can be used for obtaining materials on the basis of various nonpolar polymers and layered silicates of the smectite type. It is significant that, as has been shown in the present investigation, the intercalation stage can be attained in the case where the filler has organophilic layers with modifier (BDODA) molecules in the liquid (unordered) state.

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NOTATION

I, intensity, rel. units; H_m, melting heat, J/g; M_w, molecular weight, dimensionless quantity; T_m, melting temperature, ^oC; θ, angle of scattering of x rays, deg. Subscripts: w, weight; m, melting.

REFERENCES

1. R. E. Grim, *Clay Mineralogy*, McGraw-Hill Series in Geology, New York–London–Toronto (1953).
2. M. Alexander and P. Dubois, Polymer-layered silicate nanocomposites: Preparation, properties and uses of a new class of materials, *Mater. Sci. Eng.*, **28**, 1–64 (2000).
3. S. S. Ray and M. Okamoto, Polymer/layered silicate nanocomposites: A review from preparation to processing, *Prog. Polym. Sci.*, **28**, 1539–1634 (2003).
4. R. A. Vaia, R. K. Teukolsky, and E. P. Giannelis, Interlayer structure and molecular environment of alkylammonium layered silicates, *Chem. Mater.*, **6**, 1017–1022 (1994).
5. G. Lagaly, Interaction of alkylamines with different types of layered compounds, *Solid State Ionics*, **22**, 43–47 (1986).
6. E. Hackett, E. Manias, and E. P. Giannelis, Molecular dynamics simulations of organically modified layered silicates, *J. Chem. Phys.*, **108**, 7410–7422 (1998).

7. E. M. Antipov, M. A. Guseva, V. A. Gerasin, Yu. M. Korolev, A. V. Rebrov, H. R. Fischer, and I. V. Razumovskaya, Structure and deformation behavior of nanocomposites based on a low-density polyethylene and modified clays, *Vysokomolek. Soed. A*, **45**, No. 11, 1874–1884 (2003).
8. E. M. Antipov, A. A. Barannikov, V. A. Gerasin, B. F. Shklyaruk, L. A. Tsamalashvili, H. R. Fischer, and I. V. Razumovskaya, Structure and deformation behavior of nanocomposites based on polypropylene and modified clays, *Vysokomolek. Soed. A*, **45**, No. 11, 1885–1899 (2003).
9. V. A. Gerasin, M. A. Guseva, F. N. Bakhov, O. V. Kargina, N. D. Merekalova, Yu. M. Korolev, B. F. Shklyaruk, and E. M. Antipov, Nanocomposites based on layered silicates and polyolefins, in: *Ext. Abstr. of Papers presented at the IIIrd All-Russia Karginsk Conf. "Polymers-2004"* [in Russian], Vol. 62, January 27–February 1, 2004, MGU, Moscow (2004), p. 66.
10. K. H. Wang, M. H. Choi, C. M. Koo, Y. S. Choi, and I. J. Chung, Synthesis and characterization of maleated polyethylene/clay nanocomposites, *Polymer*, **42**, 9819–9826 (2001).