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Relaxation Properties and Structures of Polymer Nanocomposites Based on Modified Organoclays

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Abstract—Nanocomposite materials composed of HDPE and new guanidine-containing organoclays have been investigated. The basic changes in the relaxation properties of HDPE after the addition of guanidine-containing organoclays that vary in composition and content have been found. It has been shown that, depending on their structures and affinities for the polymer, guanidine-containing modifiers of montmorillonite have different effects on the structure and relaxation properties of the polymer.

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INTRODUCTION

The extension of the variety of polymer materials through modification of their properties is an urgent problem of materials science and technology. It is widely known that the presence of a nanofiller in the polymer matrix of a composite material makes it possible to change its physical and mechanical properties. Thus, the urgency to develop and investigate new nanocomposites is beyond question [1–3].

The addition of layered silicates (organoclays) as fillers leads to improvement in the mechanical properties of materials, even at low contents (up to 5 wt %) of filler in the polymer matrix [4].

The development of nanocomposites based on polyolefins and layered silicates will make it possible to extend their application area as structured materials with improved mechanical characteristics (rigidity, strength, deformation thermal stability, heat resistance) and to reduce their cost owing to the use of domestic organoclays.

Guanidine-containing compounds were chosen as nanofiller modifiers owing to the following considerations. First, the presence of quaternary ammonium cations in guanidine offers the possibility of ion exchange with the interlayer inorganic cations of montmorillonite (organoclay). Second, the active functional groups of guanidine-containing salts of the vinyl series improves adhesion to montmorillonite, a phenomenon that is necessary for the formation of organophilic layers that provide the thermodynamic compatibility of clay with nonpolar polyolefin macromolecules. Moreover, as is known, guanidine $(H_2N)_2C{=}NH$ and its derivatives are ecologically safe compounds and have wide applications in the production of materials with biological activity, heat resistance, and fire resistance. A selection of the characteristics of the mentioned organic modifiers is given in Table 1.

EXPERIMENTAL

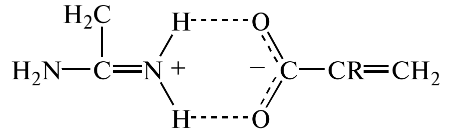
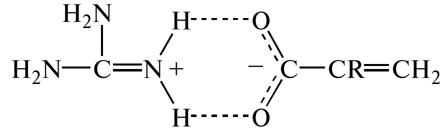
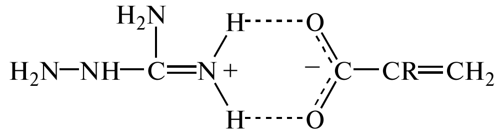
Nanocomposites were obtained via melt mixing of HDPE 2NT 22-12 and organoclays of different compositions (Table 1) in amounts of 3–7% of the mass of PE. The mixing was performed with a double-screw extruder at 190°C.

As fillers, natural Ca^{2+}-montmorillonite (Gerpegezh deposit, Kabardino-Balkaria, Russia) with particles 1–5 nm thick and 100–200 nm long and a cation exchange capacity of 95 mg-eq/100 g clay and activated Na^+-montmorillonite (Na^+-**MMT**) prepared from Ca^{2+}-montmorillonite were used. The presence of Ca^{2+} cations was monitored according to the absorption bands due to calcite in the IR spectra. Guanidine acrylate and methacrylate synthesized through a procedure described in [5] were used as organic modifiers of montmorillonite.

Organically modified montmorillonite was obtained as follows: To an aqueous suspension of natural MMT, a guanidine-containing salt (10% of the mass of MMT) was added, and the system was stirred for 2 h. The resulting organoclay was filtered, washed with distilled water via repeated decantation, and dried at room temperature.

The efficiency of the treatment of montmorillonite with guanidine acrylate (GA) and guanidine methacrylate (GMA) was monitored according to the data of X-ray diffraction analysis on a DRON-6 automated

Table 1. Structures and characteristics of organic modifiers of MMT

Organic modifier	MM	T_m, °C	Structure
Guanidine acrylate	130	175–176	 where R=H
Guanidine methacrylate	145	161–163	 where R=CH_3
Aminoguanidine methacrylate	160	171–173	 where R=CH_3

diffractometer (36 kV, 20 mA, λCuK_α, a graphite monochromator with a secondary beam, Bragg–Brentano recording in the angular range 2θ = 2°–30° with a step of 0.05°, a scanning rate of 1 deg/min). The increase in the basal distance between aluminosilicate layers of MMT after treatment with guanidine-containing salts was determined from the shift of the (001) reflection to smaller θ angles. After the incorporation of a guanidine-containing salt into MMT, the X-ray pattern of MMT demonstrates a shift from 2θ = 7.5° for the pristine MMT to 2θ = 4.9°, a result that is indicative of the modification of MMT.

The relaxation properties of nanocomposites were studied via dynamic mechanical analysis (DMA) in the mode of bending resonance vibrations [6]. The structures and properties of nanocomposites were studied with the use of DSC on a PerkinElmer DSC4000 calorimeter (United States) with automated changing of samples and scanning electron microscopy on a Jeol JSM-7500 F high-resolution scanning electron microscope (Japan) with an autoemission cathode. The microscopic examination was performed in the mode of low-energy secondary electrons because this mode provided the highest resolution. (At primary beam energies of 1 and 5 keV, the resolution was as high as 1.5 and 1 nm, respectively.) The structural studies were additionally performed via transmission electron microscopy on a Hitachi H-800 transmission electron microscope (Japan).

RESULTS AND DISCUSSION

Figures 1 and 2 show the dependences of the dynamic moduli of HDPE–organoclay nanocomposites on temperature and the contents of organoclays of various compositions. As can be seen from Fig. 2, the moduli of nanocomposites exceed the modulus of the unfilled PE matrix in almost all cases. The maximum values of the dynamic modulus are observed in the presence of guanidine acrylate as modifier. The addition of the compatibilizer compline, which is PE modified with maleic anhydride CO/LL 05 (Auserpolimeru SRL, a density of 0.920 g/cm^3, MFI = 0.8 g/10 min (190°C, 16 kg)), to a sample with the threshold content of filler (corresponding to a significant decrease of the mechanical characteristics of the composite) is of interest for further investigation. In this case, the decrease in properties is observed at a filling degree above 7%, a phenomenon that is related to the transition from the exfoliated structure to the intercalated structure. Moreover, at a higher degree of filling, aggregates form, a result that was corroborated by the scanning-electron-microscopy data. The dependence of the jump of the dynamic modulus on the compline content, the change in modulus after the addition of compline to samples with modifier contents different from the threshold values, and the qualitative estimation of this effect remain unclear. Our assumption is related to the intercalated and exfoliated structures, i.e., silicate plates. If compline interacts with an exfoliated plate (at the threshold concentration), the dynamic modulus increases, and if it interacts with an intercalated region, the dynamic modulus decreases. In our case, no pronounced jump in the dynamic modulus is observed, and the tensile strength and elongation at break decrease insignificantly.

The difference in the effects of MMT modified with GA and GMA on the PE properties may be explained by the higher affinity of the ethylene fragments of GA for the PE macromolecule and a stronger adhesion interaction between them. The above assumption is additionally confirmed by the absence

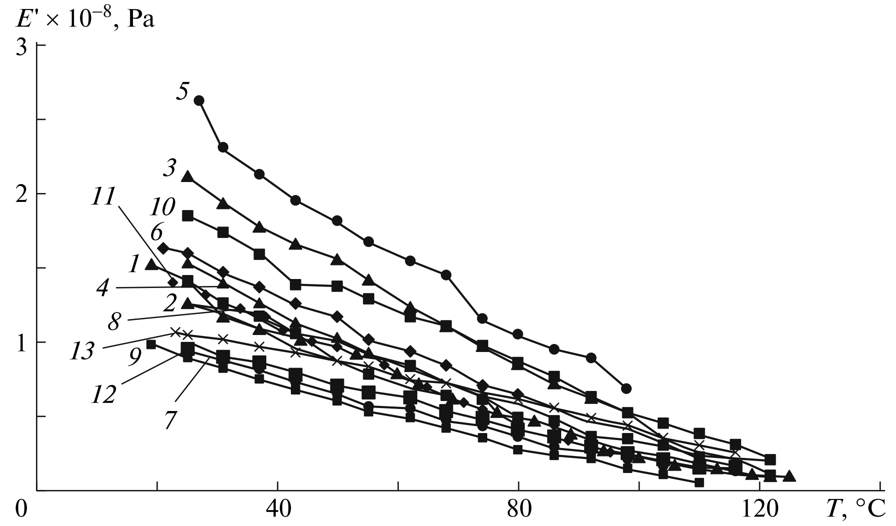


Fig. 1. Temperature dependences of dynamic moduli of (*1–12*) HDPE nanocomposites and (*13*) pure HDPE: (*1–4*) MMT–GMA, (*5–8*) MMT–GA, and (*9–12*) MMT–AGMA as fillers. The filler contents are (*1*, *5*, *9*) 3, (*2*, *6*, *10*) 5, and (*3*, *4*, *7*, *8*, *11*, *12*) 7%; (*3*, *8*, *12*) composites with compline.

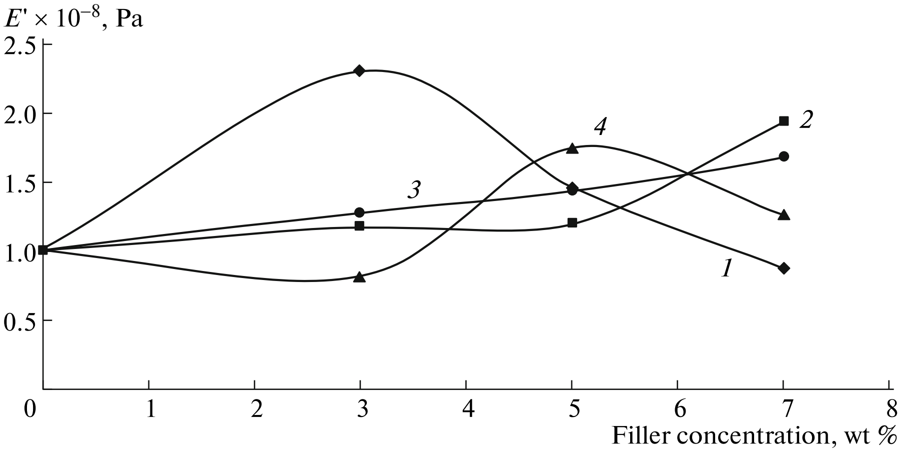


Fig. 2. Dynamic moduli of nanocomposites vs. contents of the organoclays (*1*) MMT–GA, (*2*) MMT–GMA, (*3*) MMT–melanin, and (*4*) MMT–AGMA; $T = 20$ °C.

of a substantial change in the elastic moduli of nanocomposites during the use of guanidine-containing salts with an inorganic anion (guanidine carbonate and aminoguanidine) for MMT modification.

As is shown in Figs. 1 and 2, the dependences of the elastic characteristics on the compositions and contents of organoclays in HDPE are the extremum type. For example, after the addition of 3 wt % organoclay containing 10% GA to HDPE, the dynamic modulus increases significantly, and with a further increase in the filler content, the modulus decreases.

At the same content (3 wt %) of MMT modified with GMA, a marked gain in the elastic modulus is not observed. The improvement in the characteristics of a composite with an organoclay filler modified with GMA was obtained at a 7% content of filler.

It is evident that the threshold concentration, which allows the distribution of modified layered silicate at the nanoscale in the polymer of a given chemical structure, depends on the type of organic modifier.

As is known, the separation of MMT crystallites into elementary crystallite packets and into monolayers is accompanied by an increasing degree of anisodiametry, a circumstance that provides higher mechanical characteristics than those of the material containing clay crystallites in the polymer matrix. The deterioration of the composite properties with an increase in the organoclay content may be related to a nonuniform distribution of nanofiller in the polymer matrix. This supposition is confirmed by an increased background of mechanical losses and an increased intensity of the maxima of relaxation transitions (Figs. 3, 4) in nanocomposites in comparison to the values for the initial polymers.

Studying the relaxation spectra of three series of composite samples with GA, GMA, and aminoguanidine methacrylate (AGMA) yielded the following results.

For HDPE + MMT–GA samples, the addition of 3% organoclay (MMT + 10% GA) results in a decrease in mechanical losses throughout the temperature range (Fig. 3a, curves *1*, *5*). The intensity of the relaxation process drops sharply: Only one "great" maximum at 62°C is observed. The incorporation of 5% organoclay is accompanied by a sharp increase in the intensity of the maxima of mechanical losses in the region up to 86°C followed by an abrupt drop of intensity. After the addition of 7% organoclay, the intensity of losses increases also. The introduction of 7% organoclay and 10% compline results in an additional maximum, which apparently is related to the formation of an interfacial layer based on compline [7, 8].

Note that, at temperatures above 96°C, the sample with compline softens and loses its form. Thus, for this sample, the maximum operating temperature was no higher than 96°C, whereas other samples can be studied even at 125°C.

HDPE with the MMT–GMA nanofiller behaves as follows (Fig. 3b). The addition of 3% organoclay decreases the mechanical losses throughout the temperature range, and the intensity of relaxation transitions diminishes also. For samples with 5% organoclay, the intensity of relaxation transitions grows and they are shifted to higher temperatures. After the addition of 7% organoclay, increases in intensity of α-, α'-, and λ-relaxation transitions, along with their shifts to higher temperatures, are observed. The addition of 10% compline to the nanocomposite results in a shift of the relaxation spectrum along the temperature scale and a significant drop in intensity relative to that of the sample without compline. On the basis of the classification of relaxation transitions [7, 9], it may be suggested that the α process is due to the unfreezing of the segment mobility in the amorphous zones of HDPE. We relate the α'-relaxation transition to the occurrence of molecular mobility in the polymer-matrix regions at the interface with the nanofiller; this transition appears owing to the interaction of the surface of the nanofiller with the polymer matrix and to the limited set of polymer chain conformations in the vicinity of the solid surface. The high-temperature λ transition supposedly may be related to relaxation transitions in the ordered microzones at the interface between the amorphous and crystalline phases of HDPE and to the onset of melting of crystalline regions.

For composites based on HDPE and MMT modified with AGMA, the loss tangent changes with temperature as follows.

After the addition of 3% MMT + 10% AGMA, the losses do not diminish throughout the temperature range; i.e., the decrease in intensity of the relaxation process (Fig. 4), as for the case of MMT modified with GMA and GA at the same low filler concentration, is not observed. At a filler concentration of 3%, the intensity is even greater than that at a higher concentration and in the presence of compline. Moreover, the maxima are shifted to low temperatures.

At a filler content as high as 5%, the maxima remain at practically the same temperatures as those for unfilled HDPE.

At a filler content of 7%, the maxima of mechanical losses are shifted to higher temperatures, while their intensities increase.

The incorporation of compline into a sample with 7% filler results in a shift of $\tan\delta$ maxima to higher temperatures. In this case, their intensities increase and an additional maximum appears. Note that the basic maximum that was thought to be located in the region of 125–140°C was not fixed, because of the temperature instability of the sample with compline.

A selection of the physical and mechanical characteristics of the studied samples is given in Table 2.

The intensity of $\tan\delta$ (T) for the nanocomposite at a low concentration of nanofiller (3%) decreases relative to that of the pristine HDPE, a result that suggests a denser packing of polymer chains and a uniform distribution of the nanofiller throughout the polymer matrix. The samples with 5 and 7% organoclay are less uniform, a circumstance that is confirmed by the presence of two or more mechanical-loss peaks at 80–120°C and by enhanced intensity of relaxation transitions. The comparison of the viscoelastic properties of nanocomposites with GMA (HDPE + MMT–GMA) showed that the maximum elasticity is typical for composites with 5 and 7% organoclay (Fig. 1, curves *6*, *7*) [2].

For a sample with MMT–GMA (Fig. 3b, curve *4*), as for the series with MMT–GA, an additional relaxation process (at 92°C) is observed. Supposedly, it is related to the incorporation of compline into the matrix and to the formation of an additional interfacial layer. A number of inflections of the loss-tangent curves for nanocomposites and the initial polymer in the range from room temperature to 50°C probably is related to the presence of moisture in samples. The verification of this assumption calls for further investigation.

A comparison of the speed of sound in the pristine polymer and in the nanocomposites (Fig. 5) showed that the speed of sound passes through the maximum as the nanofiller content increases.

It is of interest that, for the above samples, no sharp drops in the elastic modulus and speed of sound that

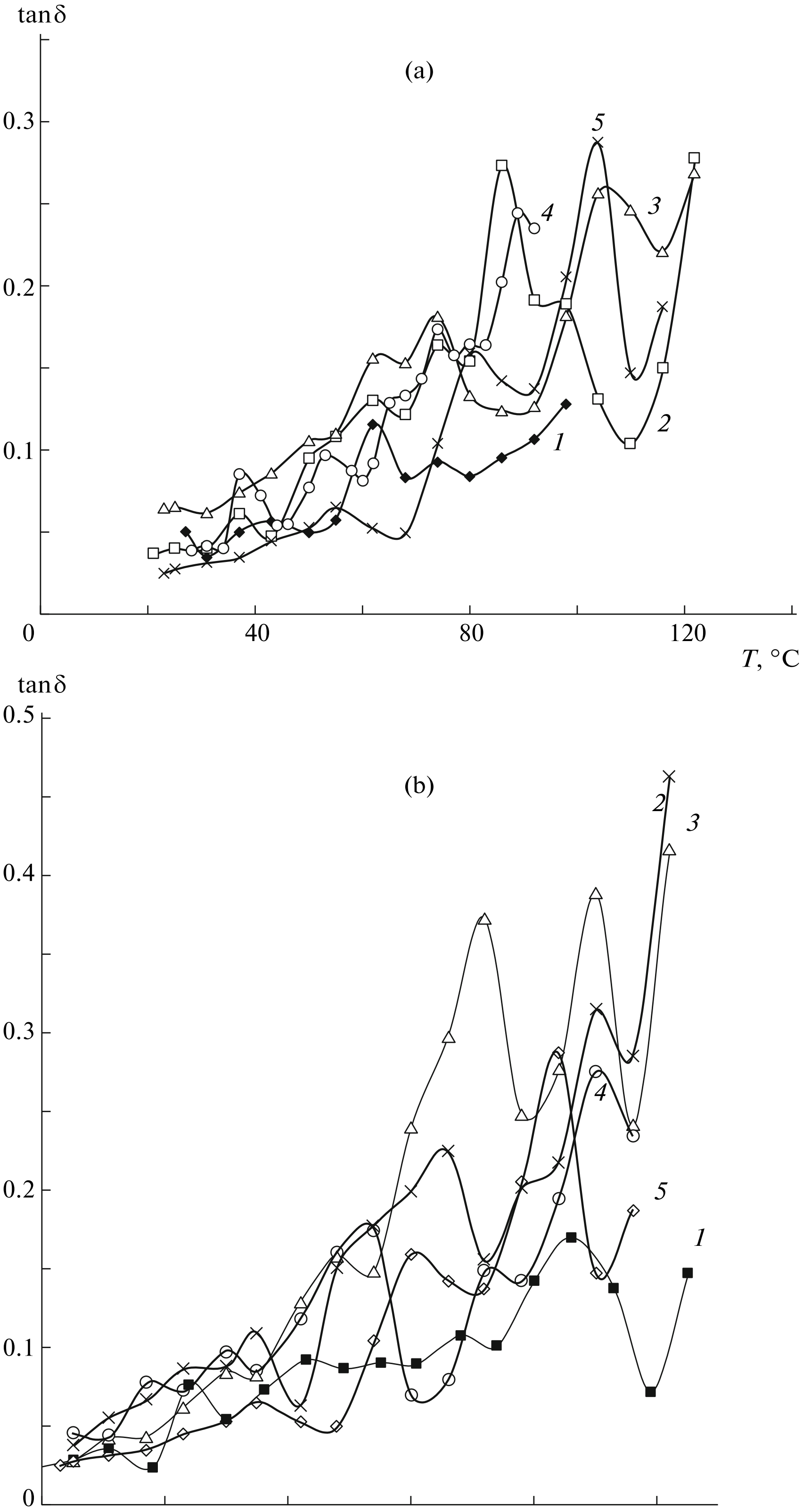


Fig. 3. Temperature dependences of tanδ for (*1*–*4*) HDPE–organoclay nanocomposites and (*5*) pure HDPE. The organoclay contents are (*1*) 3, (*2*) 5, and (*3*, *4*) 7%; (*4*) the composite with 10% compline; (a) MMT–GA and (b) MMT–GMA.

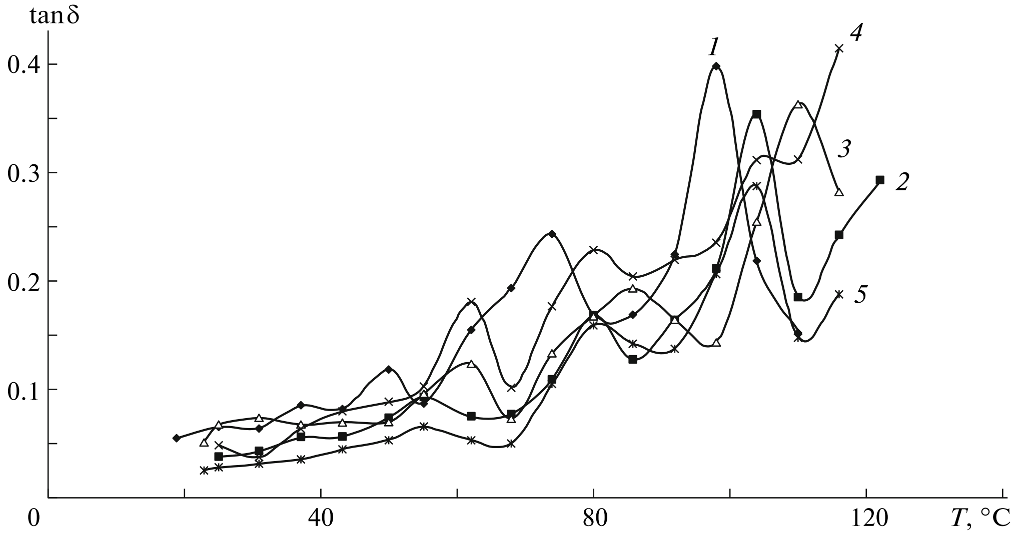


Fig. 4. Temperature dependences of tanδ for HDPE nanocomposites with (*1–4*) the organoclay MMT–AGMA and (*5*) pure HDPE. The organoclay contents are (*1*) 3, (*2*) 5, and (*3*, *4*) 7%; (*4*) the composite with 10% compline.

are characteristic of the transition from one physical state to another (from the viscoelastic state to the viscous-flow state) are observed, unlike in the case of macrocomposites during transitions from the glassy state to the rubberlike state and viscous-flow state [7, 9, 10].

The presence of several relaxation transitions in nanocomposites suggests that there are several regions characterized by the effective mobility of segments located in these regions. The differences in mass and structure of the segments are responsible for the multiplicity of the basic relaxation transition. The multiplicity, in turn, is indicative of the quasi-multistructural model of the amorphous phase (especially in samples with high MMT contents).

The shift of tanδ maxima for nanocomposites to higher temperatures and some increase in the loss tangents with variations in the filler concentrations are explained by change in the interaction between components. It is not clear exactly what kind of interaction affects the degree of interdiffusion of components. The question of the qualitative and quantitative estimation of the mechanical-loss background and its physical interpretation is still open.

The results of studying the relaxation properties showed that the organic modifier makes a significant contribution to the change in the relaxation and structural properties of polymer nanocomposites.

According to the data of X-ray diffraction analysis, the incorporation of GA salt into the interlayer tunnels of MMT is accompanied by a shift of the peak in the X-ray pattern to small angles.

The X-ray pattern for the pristine MMT displays a characteristic peak in the region of $2\theta = 7.5°$ (Fig. 6, curve *1*). The incorporation of GA salt into the interlayer tunnels of MMT results in a shift of the this peak to the small-angle region of $2\theta = 4.5°$ (curve *2*). After the addition of the same organoclay in an amount of 3 wt %, the peak due to the organoclay is absent, a result that is indicative of the formation of an exfoli-

Table 2. Physical and mechanical characteristics of HDPE/MMT–M(GMA) nanocomposite

Filler content, wt %	Density, kg/m^3	Transition temperature, °C			Dynamic modulus E', GPa		Speed of sound, m/s	
		α_1'	α_1	α_2	at 25°C	at 116°C	at 25°C	at 116°C
3	919.7	50	74	98	0.89	0.04	987	243
5	933.4	55	80	104	1.86	0.32	1411	583
7	915.4	62	86	110	1.40	0.14	1236	410
7 (composite with compline)	953.5	62	80	–	1.09	0.15	1026	394

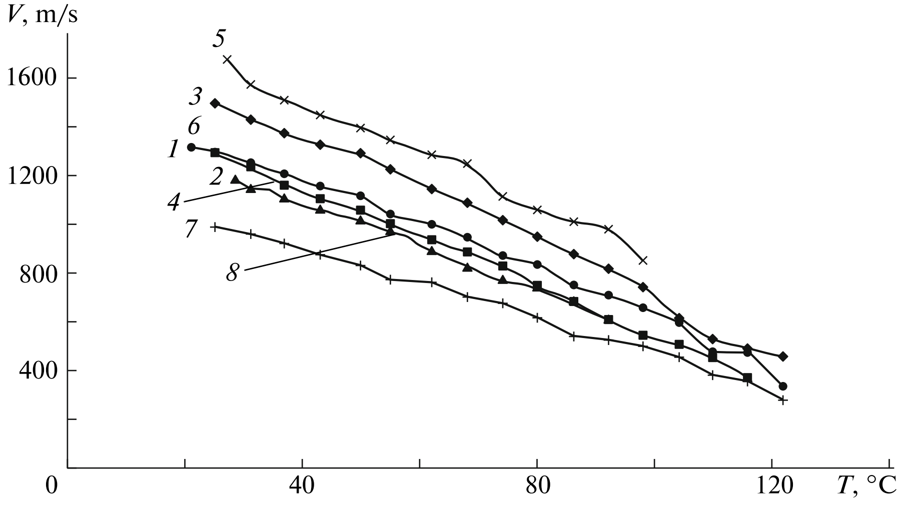


Fig. 5. Temperature dependences of the speed of sound for HDPE nanocomposites with the organoclays (*1–4*) MMT–GMA and (*5–8*) MMT–GA. The filler contents are (*1*, *5*) 3, (*2*, *6*) 5, and (*3*, *4*, *7*, *8*) 7%; (*4*, *8*) the composite with compline.

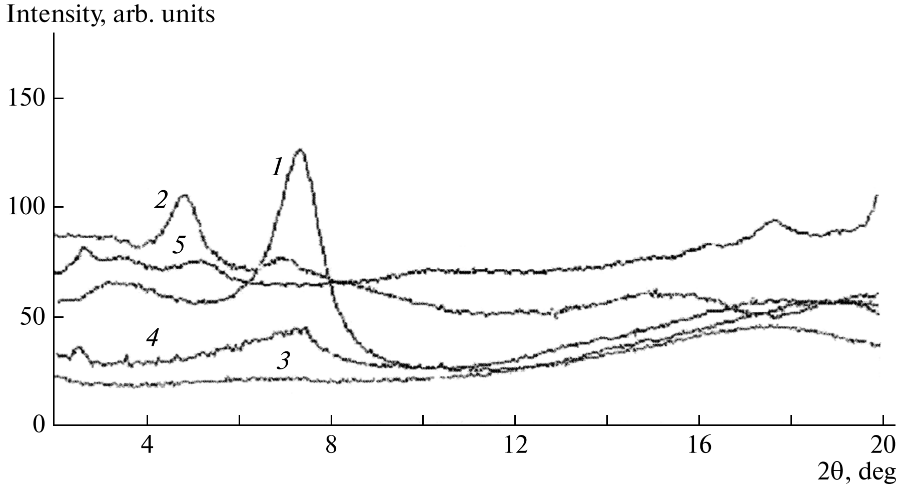


Fig. 6. X-ray patterns for (*1*) MMT, (*2*) MMT modified with GA, (*3*) initial HDPE, and (*4*, *5*) HDPE–MMT–GA composites. The MMT–GA contents in the composites are (*4*) 3 and (*5*) 7%.

ated nanocomposite. At higher degrees of HDPE filling (7 wt %), a weak peak at $2\theta = 2.5°$ appears, a phenomenon that implies the formation of a mixed structure containing both intercalated and exfoliated silicate plates (curve *5*). This statement is corroborated by the microscopic examination and may be indicative of the threshold concentration of the filler, above which complex aggregated structures form [11].

The study of the surfaces of composites based on MMT and its modified forms via X-ray diffraction analysis in the contact mode of scanning showed the morphological changes due to modification with organics.

The effect of the properties of composites with MMT modified with guanidine acrylate and methacrylate derivatives was studied via DSC. From the DSC thermograms, the temperatures and enthalpies of melting for composites of different compositions were determined, and the obtained values were recalculated for pure HDPE (Fig. 7, Table 3).

The results suggest that both pure PE and all of the filled samples have practically the same melting temperature (125–126°C) and practically the same crystallization temperature (115–117°C), even at high filler concentrations.

The drop in the melting enthalpies of nanocomposites suggests that, in the material bulk, the internal mechanical stress increases and the degree of crystallinity decreases.

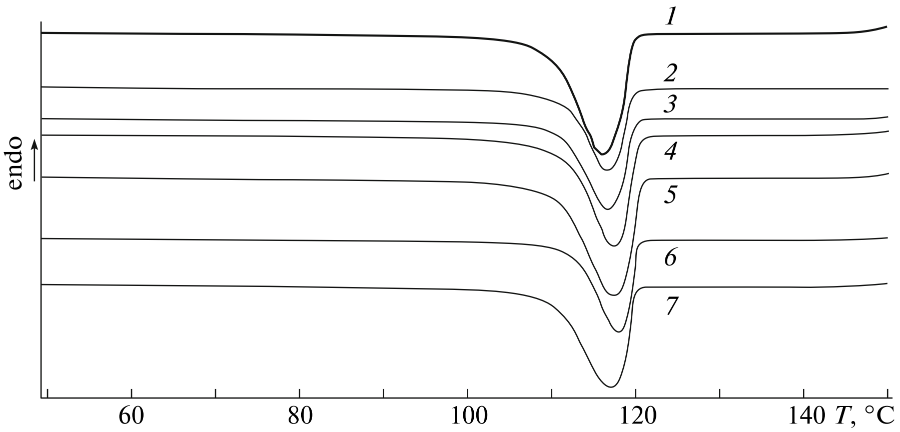


Fig. 7. DSC curves for (*1*) initial HDPE, (*2*, *4*, *6*) MMT–GA composites, and (*3*, *5*, *7*) MMT–GMA composites. The filler contents are (*2*, *3*) 3, (*4*, *5*) 5, and (*6*, *7*) 7%; (*6*, *7*) the composites with compline.

As is known [12], the higher the number of PE chains intercalating into an organoclay (the larger the distance between the packets), the more significant the drop in the melting enthalpy of the polymer. In our case, the most significant drop in melting enthalpy is observed in nanocomposites with MMT modified with GA, a result that indirectly corroborates the assumption on the higher affinity of ethylene fragments of GA for PE macromolecules. The stress–strain characteristics of the nanocomposites with MMT modified with GA improve as well, a result that confirms the stronger adhesion interaction between PE and the above organoclays.

It may be suggested that the decrease in melting enthalpy of nanocomposites is a result of the loss of the crystallization capacity by the fraction of PE matrix intercalated in the interlayer space of clay.

As can be seen from Table 3, the minimum melting enthalpy is characteristic of samples with compline. This circumstance suggests the positive effect of compline on the compatibility between PE and organoclay.

In addition, the results of X-ray diffraction analysis were confirmed by the data of transmission electron microscopy (TEM) and scanning electron microscopy (SEM). Figures 8 and 9 present microscopic images of nanocomposite based on MMT modified with GA.

The dark lines in the TEM images correspond to nanolayers of the silicate filler distributed in HDPE (Fig. 8).

The TEM data confirm our assumption about the existence of the threshold concentration, at which an organomodified layered silicate is capable of distribution in the polymer matrix on the nanoscale and the formation of a nanocomposite with an exfoliated structure. Above this threshold, a complex structure with intercalated layers and organoclay nanoparticle aggregates may form (Fig. 9).

Table 3. DSC data for PE–organoclay nanocomposites

Sample	Filler content, %	T_{initial}, °C	T_{m}, °C	T_{final}, °C	ΔH, J/g	T_{cr}, °C	Degree of crystallinity, %
Extruded PE	0	126.0	133.4	137.6	161.1	115.7	54.5
PE–MMT–GMA (composite with compline)	7	125.3	132.8	137.4	112.4	117.6	38.13
PE–MMT–GA (composite with compline)	7	125.7	131.8	135.0	102.5	116.6	30.8
PE–MMT–GMA	5	125.6	133.2	137.5	154.4	116.9	52.3
PE–MMT–GA	5	125.3	132.6	136.6	133.2	117.1	51.9
PE–MMT–GMA	3	125.4	132.3	136.2	125.0	116.3	43.3
PE–MMT–GA	3	126.1	133.0	136.8	118.1	116.3	38.03

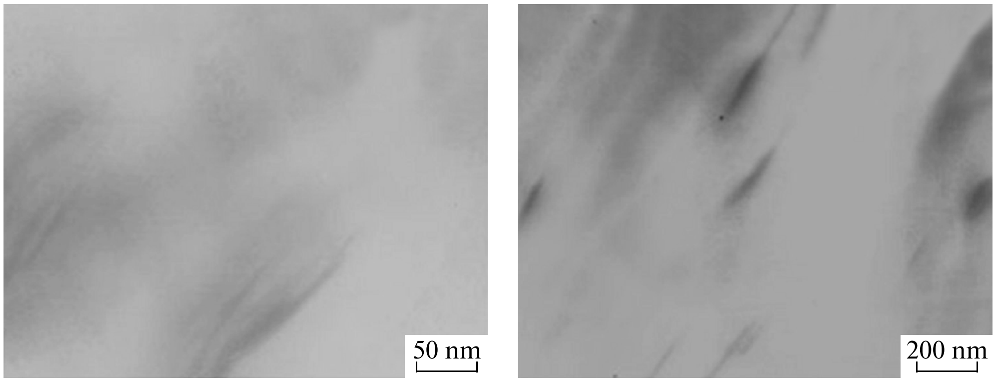


Fig. 8. TEM images of HDPE + the 5% MMT–GA nanocomposite at different magnifications.

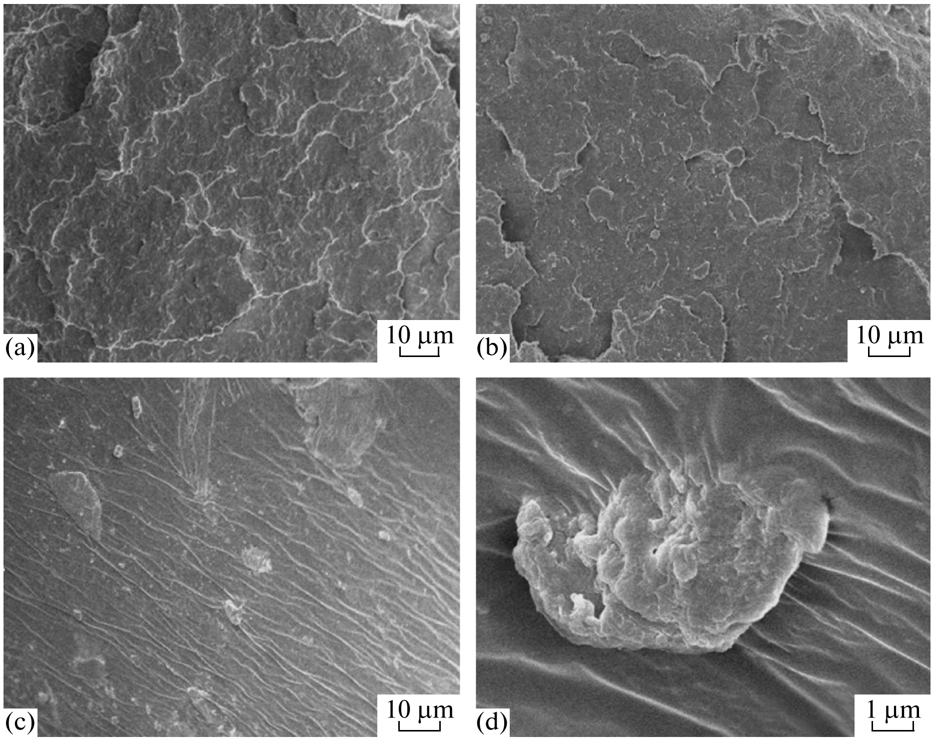


Fig. 9. SEM images of nanocomposites: (a) HDPE, (b) HDPE + 3% MMT–GA, (c) HDPE + 7% MMT–GA, and (d) an aggregation of MMT–GA nanoparticles; ×1000 magnification.

CONCLUSIONS

On the basis of montmorillonite from a Russian deposit and guanidine-containing modifiers, new organoclays have been developed. Nanocomposites of HDPE and the aforementioned clays have been studied.

It has been found that, in the nanocomposites, multiple (three or more) relaxation transitions related to matrix heterogeneity and the formation of interfacial layers occur. It has been shown that the developed guanidine-containing organoclays are functional fillers for PE that result in improved mechanical and engineering properties of composites. The results open up possibilities for the production of polymer nanocomposites based on domestic organoclays that are competitive in terms of quality and cost with foreign analogs.

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