

## EXFOLIATED CLAY-POLYETHYLENE NANOCOMPOSITES OBTAINED BY *IN SITU* POLYMERIZATION. SYNTHESIS, STRUCTURE, PROPERTIES

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*Intercalation of titanium complexes active in olefin polymerization into interlayer gaps of natural laminated aluminosilicate of Na<sup>+</sup>-montmorillonite modified by dimethyldioctadecylammonium ions has been realized. Using in situ ethylene polymerization on intercalated complexes, polyethylene-modified montmorillonite nanocomposites with an aluminosilicate content from 4 to 43 mass % have been obtained. It has been proved by x-ray structural analysis that at a filler content of up to 24 mass % they represent exfoliated nanocomposite systems. The physicomechanical properties of the obtained materials have been investigated. It has been established that nanocomposites with a filler content of 4–8 mass % have the best complex of properties. Compared to pure (unfilled) polyethylene obtained under the same conditions, they are characterized by a higher value of the elastic modulus with the same level (which is particularly important) of tensile strength and specific elongation at rupture.*

Nanocomposites based on polyolefins (PO) and laminated silicates (LS) are highly promising from the point of view of developing composite materials with improved properties that are unattainable for ordinary polymeric materials. Recent years have seen the growing interest of researchers in the synthesis of such nanocomposites by the *in situ* polymerization method. Compared to the method of mixing in solution or in melt, it has an undoubted advantage, since it permits avoiding problems connected with the incompatibility of hydrophobic POs and hydrophylic LSs preventing penetration of macromolecules of the former into the gaps between the layers of the latter, which is an essential condition for the formation of nanocomposite structures.

To obtain PO-LS nanocomposites by *in situ* polymerization, it is essential that the polymerization process proceeds, at least in part, in the LS interlayer gaps, leading to the formation of intercalated or, in the limiting case, delaminated (exfoliated) systems. Apparently, this is only possible when interlayer gaps contain active centers catalyzing olefin polymerization. In the literature, there are reports on the synthesis of catalytic systems based on zirconium and palladium active complexes intercalated into different LSs and their successful application for synthesizing nanocomplexes based on polyethylene (PE) and polypropylene by *in situ* polymerization of the corresponding olefin monomers [1–5].

In [6], intercalation of titanium tetrachloride into interlayer gaps of natural layered aluminosilicate Na<sup>+</sup>-montmorillonite modified by methylalkylbis(2-hydroxyethyl)ammonium ions was realized. Subsequent treatment with triethylaluminum led to the formation of intercalated titanium-complex active centers. The ethylene polymerization on this catalytic system made it possible to obtain nanocomposites in which the modified clay was completely exfoliated. As the authors see it, the presence in the modifier situated in the interlayer gaps of aluminosilicate of functional (in the given case, hydroxyl) groups able to chemically bind titanium compounds is essential for intercalation of titanium-complex active centers and, consequently, for the formation of nanocomposite system in the subsequent ethylene polymerization.

In the present paper, an attempt has been made to intercalate titanium-complex active centers into the interlayer gaps of Na<sup>+</sup>-montmorillonite modified by dimethyldioctadecylammonium (modified clay-MC) ions and use the catalyst obtained to synthesize PE-MC nanocomposites by *in situ* ethylene polymerization. The substantial difference

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of our approach from that used in [6] lies in the modifier nature. In our case, it does not contain any functional groups and, therefore, is unable to chemically bind titanium compounds.

**Experimental.** MC with a modifier content of 25 mass % was obtained from natural nonmodified  $\text{Na}^+$ -montmorillonite. To this end, adsorption of dimethyldioctadecylammoniumbromide from an aqueous solution onto the surface and into the interplane gaps of natural clay was carried out [7]. Analytically pure toluene was dried over calcinated molecular sieves (4 Å), blown with an inert gas for 1 h, and transferred into a Shlenk vessel equipped with a microvalve. Titanium tetrachloride ( $\text{TiCl}_4$ ) was boiled in a vacuum over copper chips, recondensed into the Shlenk vessel, and diluted with purified toluene to a concentration of 1 mole/liter. We used the available Aldrich Chemical Co. triisobutylaluminum (TIBA) in the form of 1 M solution in toluene. Ethylene with a total content of impurities of < 5 mole fractions obtained from the "Nizhnekamskneftekhim" company was used without additional purification.

Immobilization of  $\text{TiCl}_4$ , formation of active titanium complexes, and ethylene polymerization were carried out sequentially in a metal periodic reactor equipped with a high-speed mixer and a heat-exchange jacket. The MC sample was placed in the reactor and heated in a vacuum at 393 K for 6 h until complete removal of moisture. Then toluene was introduced into the reactor and the dehydrated sample was allowed to swell for 2 h at 353 K. The next step was to add the  $\text{TiCl}_4$  solution in toluene and hold it for 2 h at 353 K. In all cases, such a quantity of the solution was taken that the Ti/MC ratio was 1 mole/1 g. Active titanium complexes were formed due to the interaction with a TIBA solution at a mole ratio of Al/Ti = 1:1. Ethylene polymerization was carried out at a temperature of 313 K and a pressure of 0.3 MPa under induced agitation of the reactive medium. The quantity of reacted ethylene was determined by the pressure drop in the calibrated measuring vessel. On completion of polymerization a diluted solution of HCl in methanol was introduced into the reactor to deactivate the catalyst. The product obtained was filtered off, washed sequentially on the filter with a diluted HCl solution in methanol, aqueous solution of KOH, and distilled water, and vacuum-dried at 373 K.

The structures and physicochemical properties of the PE–MC composites obtained were investigated by methods analogous to those described in detail in [8].

**Results and Discussion.** PE–MC composites with a content of modified aluminosilicate of 4, 8, 15, 24, and 43 mass % have been obtained. In addition, in the same reactor and under the same conditions on the homogeneous  $\text{TiCl}_4$  + TIBA (Al/Ti = 1:1) catalytic system in a toluene medium pure (unfilled) PE has been obtained for use as a comparison system.

The structure of the clayey filler in the composites obtained has been investigated by the X-ray diffraction (XRD) method in large and small diffraction angles with the sample positioned to the primary beam for photography in the "reflection" and "transmission" regimes, respectively.

Figure 1 shows the diffractograms of the obtained composites, pure PE, and completely dehydrated MC taken in the "reflection" regime. The latter (curve 1) shown a clearly defined basal reflex at a diffraction angle of  $2\theta = 3.3^\circ$ , which corresponds to an interlayer spacing of  $d_{001} = 2.7$  nm. The x-ray photographs of the PE–MC composites with an aluminosilicate content of no more than 24 mass % in the region of diffraction angles of  $1^\circ < 2\theta < 4^\circ$  do not show any reflexes. This points to the fact that in these samples the aluminosilicate layers are either widely spaced but preserve the long-range order of arrangement or are completely exfoliated in the polymer matrix.

Figure 2 shows the x-ray photographs taken in the region of small diffraction angles in the "transmission" regime for the PE–MC composites obtained and for pure PE. For samples with a filler content of 15, 8, and 4 mass % no reflexes are observed in the region of diffraction angles  $2\theta < 1^\circ$ . This points to the fact that these systems are nanocomposites with completely exfoliated aluminosilicate layers. The formation of such systems in the process of *in situ* polymerization is possible only in the case where the active centers (complexes) catalyzing the polymerization process are situated in the interlayer gaps of aluminosilicate. Consequently, it may be stated that the approach used by us permits solving the problem of intercalation of active titanium complexes.

The diffractograms of PE–MC composites with a relatively large content of MC (e.g., 24 mass %) show a strongly blurred basal reflex of aluminosilicate localized at a diffraction angle somewhat smaller than that corresponding to the dehydrated MC ( $d_{001} = 2.7$  nm). It is likely to be a set of unresolved reflexes corresponding to a different extent to the sheared clay layers with the preservation of the long-range order in their arrangement. Its small intensity enables us to suppose that nevertheless an appreciable part of the initial clay has undergone exfoliation. At an even larger content of aluminosilicate in the system (e.g., 43 mass %), the basal reflex becomes somewhat more intensive

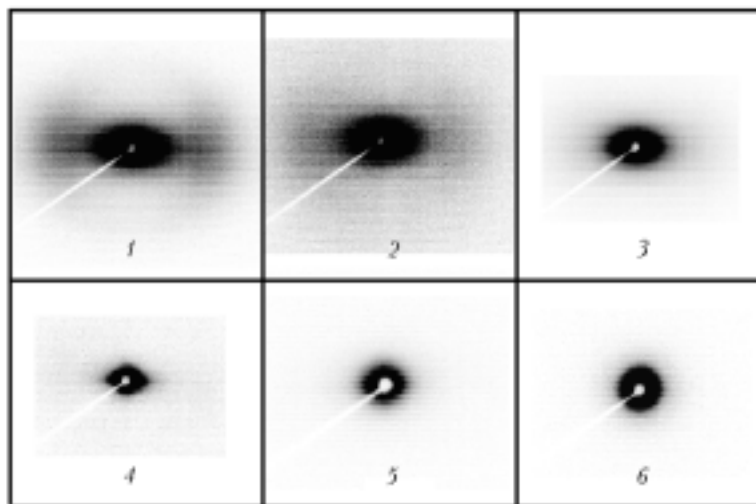
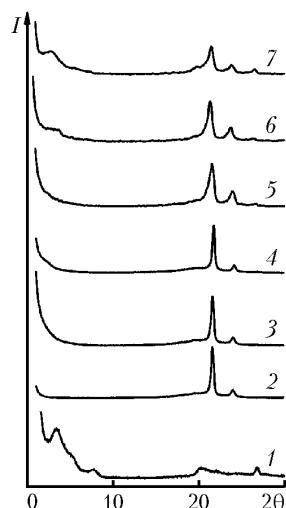


Fig. 1. Diffractograms taken in large diffraction angles in the "reflection" regime of the dehydrated MC (1), pure PE (2), and the PE–MC composite (3–7) obtained by *in situ* ethylene polymerization ( $W = 4$  (3), 8 (4), 15 (5), 24 (6), and 43 (7)).

Fig. 2. X-ray photographs taken in small diffraction angles in the "transmission" regime of pure PE and the PE–MC composites obtained by *in situ* ethylene polymerization:  $W = 43$  (1), 24 (2), 15 (3), 8 (4), 4 (5), and 0 (6).

TABLE 1. Melting Temperature and Enthalpy of Pure PE and PE in the Composites Obtained by *in situ* Polymerization

| $W$ | Nascent           |                          | Upon extrusion    |                          |
|-----|-------------------|--------------------------|-------------------|--------------------------|
|     | $T_{\text{melt}}$ | $\Delta H_{\text{melt}}$ | $T_{\text{melt}}$ | $\Delta H_{\text{melt}}$ |
| 0   | 411               | 158                      | 402               | 118                      |
| 4   | 412               | 154                      | 401               | 118                      |
| 8   | 411               | 176                      | 402               | 127                      |
| 15  | 409               | 197                      | 404               | 137                      |
| 24  | 410               | 215                      | 403               | 121                      |
| 43  | 408               | 193                      | 403               | 125                      |

and is observed at a diffraction angle of  $2\theta = 2.7^\circ$ , corresponding to  $d_{001} = 3.3$  nm. Obviously, in this system the quantity of PE formed in the interlayer gaps of aluminosilicate turns out to be insufficient for attaining exfoliation. This conclusion is confirmed by the analysis of the x-ray photographs of the samples with an aluminosilicate content of 24 and 43 mass % (Fig. 2), in which equatorial reflexes corresponding to the total reflections of ordered silicate layers are observed.

The PE structure formed in the process of *in situ* polymerization has been investigated by the XRD method in the "transmission" regime and by the differential scanning calorimetry (DSC) method. Table 1 gives the values of the melting temperature and enthalpy of pure PE and the PE in the composites for nascent samples and upon extrusion of film from them at 453 K followed by water quenching. The respective thermograms are given in Fig. 3.

It should be noted that the DSC curves of all samples upon heating have one endopeak characteristic of the PE crystal-phase melting. With increasing content of MC in the composite the enthalpy increases and the melting temperature of the polymer somewhat decreases. If we take, as a reference point, the reference value — melting enthalpy of a PE crystal of "infinite dimensions" equal to 295 J/g [9] — then at higher levels of filling the degree of crystallinity of the polymer obtained constitutes  $\sim 70\%$ .

It should also be noted that the DSC curves of both nascent and refined composites show no endoeffects in the 323–343 K range corresponding to the melting of clusters formed under modifier adsorption in the interplane gaps

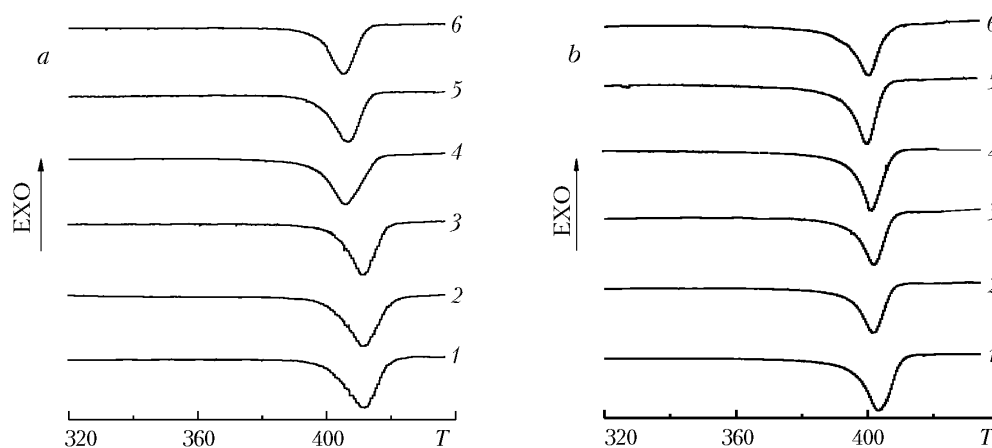


Fig. 3. Thermograms of PE (1) and the PE–MC composites obtained by *in situ* ethylene polymerization (2–6) for nascent (a) and hardened samples (b):  $W = 4$  (2), 8 (3), 15 (4), 24 (5), 43 (6); vertical arrows marked "EXO" show positive directions of the thermal flow (heat release by the sample into the environment).

TABLE 2. Parameters of the Crystal Cell of PE in the Pure Polymer and in the Composites

| Sample | $W$ | Cell parameters, nm |             |             |
|--------|-----|---------------------|-------------|-------------|
|        |     | $a$                 | $b$         | $c$         |
| PE     | 0   | 0.741/0.742         | 0.495/0.496 | 0.255/0.254 |
| PE–MC  | 8   | 0.742/0.743         | 0.495/0.497 | 0.255/0.254 |

Note. The degree of crystallinity of pure PE is 50%, of PE in the composite — 55%; in the numerator — for isotropic samples, in the denominator — for oriented samples.

of clay [7]. This points to the fact that during PE synthesis melting or dissolution of these clusters occurs. It may be suggested that on the surface of exfoliated silicate plates in the composites solutions from aliphatic chains of the modifier and PE macromolecules are formed. As a result of this, it may be expected that a high level of adhesive interaction between the nanodimensional filler and the polymer matrix will be attained, which should affect the mechanical properties of the thus-obtained composites and, primarily, the value of the Young modulus.

Upon extrusion of nascent samples, the melting temperature of PE is practically independent of the filler quantity. The melting enthalpy of the polymer in the MC-containing samples increases with increasing degree of filling.

Table 2 gives the elementary cell parameters and the crystallite sizes in pure PE and composites with modified clay. It is seen that these values are practically equal in both cases. Consequently, MC has no effect on the structure of the crystalline part of PE.

We have investigated the physicomechanical properties of pure PE and the PE–MC composites obtained by *in situ* polymerization (Figs. 4 and 5). Samples with an aluminosilicate content of 4–8 mass % have the best complex of properties. Compared to pure PE, the value of the elasticity modulus increases in this case by a factor of 1.5–1.8 with an insignificant (no more than 5%) decrease in the tensile strength and the same specific elongation at rupture (~520%). The latter fact is of particular importance, since usually upon introduction of any inorganic filler into the polymer a sharp increase in the brittleness of the material is observed.

An increase in the MC content in the composite leads to a further increase in the value of the elasticity modulus, which reaches 1260 MPa at a filler content of 43 mass %, exceeding the analogous value for pure PE (255 MPa) by a factor of five. Unfortunately, this has an adverse effect on the other characteristics of the material, and already at a clay concentration of 15 mass % the specific elongation decreases to 10%. The tensile strength sharply decreases in the range of filler values between 8 and 15 mass % (by 40% compared to pure PE) and remains practically unchanged as the concentration is further increased.

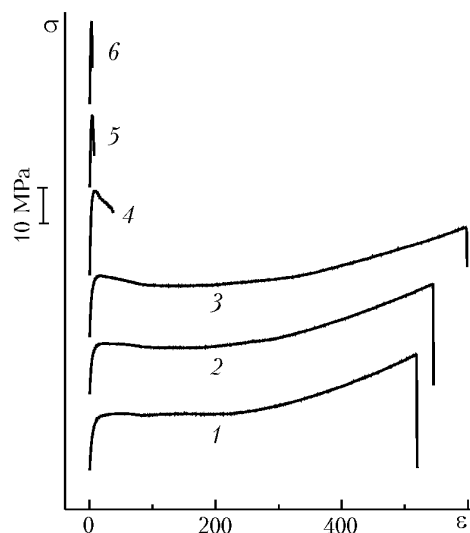


Fig. 4. Deformation curves of the PE–MC composites:  $W = 0$  (1), 4 (2), 8 (3), 15 (4), 24 (5), and 43 (6).

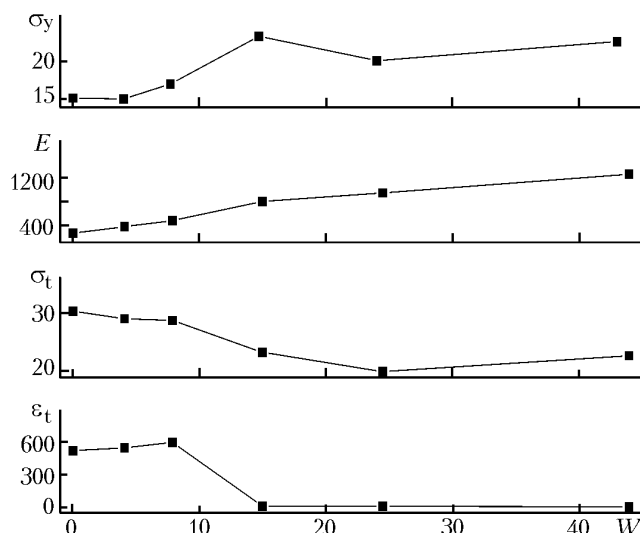


Fig. 5. Physicomechanical properties versus the degree of filling of the PE–MC composites obtained by *in situ* ethylene polymerization.

The investigation of the influence of the filler on the change in the structure of the crystalline part of PE in the process of uniaxial deformation of the nanocomposite has demonstrated (Table 2) that upon failure of the samples the elementary cell parameters and the crystalline sizes are practically the same in both the pure and the filled material. The determination of the thermophysical characteristics of the samples upon rupture has shown that the melting temperature of PE crystallites increases by 4–5 K compared to the isotropic state. The melting enthalpy of pure PE increases by a factor of 1.5. In the composite containing 8 mass % of MC, which practically has the same elongation at rupture as in pure PE, the enthalpy value increases by a factor of 1.1. It is felt that the uniaxial elongation of this sample is due to not only the polymer matrix deformation but also the formation of voids in the oriented material.

The yield point of composites with a filler content of up to 15 mass % slightly exceeds the yield point of pure PE. At high degrees of filling it increases by 30–40%. According to [10], if the yield point of a filled polymeric system is higher than the yield point of the pure polymer, then this points to a strong adhesive matrix–filler interaction, exceeding the cohesive strength of the matrix, which is precisely observed in the nanocomposites obtained by us. This confirms the assumption made by us on the basis of investigating the thermophysical properties of the samples.

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## NOTATION

$a$ ,  $b$ ,  $c$ , PE crystal cell parameters, nm;  $d_{001}$ , interlayer spacing in laminated aluminosilicate, nm;  $E$ , Young modulus, MPa;  $\Delta H_{\text{melt}}$ , melting enthalpy of PE, J/g of polymer;  $I$ , x-ray intensity, rel. units;  $T$ , absolute temperature, K;  $T_{\text{melt}}$ , melting temperature of PE, K;  $W$ , filler (MC) content in the composite, mass %;  $\varepsilon$ , current value of specific tensile elongation of the sample, %;  $\varepsilon_r$ , specific elongation of the sample at rupture, %;  $\sigma$ , current value of tensile stress of the sample, MPa;  $\sigma_r$ , stress at the moment of tensile rupture of the sample, MPa;  $\sigma_y$ , tensile yield point of the sample, MPa (stress value in going from the region of elastic deformation to the region of plastic deformation);  $2\theta$ , diffraction angle of x-rays, deg. Subscripts: melt, melting; t, tensile rupture of the sample; y, yield.

## REFERENCES

1. J. Tudor, L. Willington, D. O'Hare, and B. Royan, Intercalation of catalytically active metalcomplexes in phyllosilicates and their application as propene polymerisation catalysts, *Chem. Commun.*, 2031–2034 (1996).

2. J. Tudor and D. O'Hare, Stereospecific propene polymerisation catalysis using an organometallic modified mesoporous silicate, *Chem. Commun.*, 603–605 (1997).
3. J. Heinemann, P. Reichert, R. Thomann, and R. Mülhaupt, Polyolefin nanocomposites formed by melt compounding and transition metal catalyzed ethylene homo- and copolymerization in the presence of layered silicates, *Macromol. Rapid Commun.*, **20**, No. 8, 423–430 (1999).
4. J. S. Bergman, H. Chen, E. P. Giannelis, M. G. Thomas, and G. W. Coates, Synthesis and characterization of polyolefin–silicate nanocomposites: A catalyst intercalation and *in situ* polymerization approach, *Chem. Commun.*, 2179–2180 (1999).
5. C. Liu, T. Tang, D. Wang, and B. Huang, *In situ* ethylene homopolymerization and copolymerization catalyzed by zirconocene catalysts entrapped inside functionalized montmorillonite, *J. Polym. Sci., Polym. Chem.*, **41**, 2187–2196 (2003).
6. Y. H. Jin, H. J. Park, S. S. Im, S. Y. Kwak, and S. Kwak, Polyethylene/clay nanocomposite by *in situ* exfoliation of montmorillonite during Ziegler-Natta polymerization of ethylene, *Macromol. Rapid Commun.*, **23**, No. 2, 135–140 (2002).
7. 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 III All-Russia Kargin'sk Conf. "Polymers-2004"* [in Russian], Vol. 2, MGU, Moscow (2004), p. 66.
8. 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 polypropylene and modified clays, *Vysokomolek. Soed. A*, **45**, No. 11, 1874–1884 (2003).
9. B. Wunderlich, *Macromolecular Physics*, Vol. 1, Academic Press, New York–London (1973), p. 217.
10. I. L. Dubnikova and V. G. Oshmyan, Influence of the size of inclusions on interphase delamination and yield point of filled plastic polymers, *Vysokomolek. Soed. A*, **40**, No. 9, 1481–1492 (1998).