Catalytic Activation of Layered Silicates for the Synthesis of Nanocomposite Materials Based on Ultra-High Molecular Weight Polyethylene

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Abstract—The effects of the structure of organomodified montmorillonite and the conditions of its catalytic activation by titanium and vanadium chlorides on the synthesis of nanocomposite materials based on ultra-high molecular weight polyethylene with an exfoliated structure by an in situ polymerization method were studied. It was shown that, with the use of organomodified montmorillonite with the interplanar spacing $d_{001} = 1.6–1.8$ nm, in which the alkyl radicals of a modifier are arranged in parallel to the basal silicate surfaces, the catalyst is adsorbed only on the external surface of particle, and it does not penetrate into the interlayer space (in this case, the exfoliation of a filler does not occur). With the use of montmorillonite samples with $d_{001} > 2$ nm with the packing of a modifier as paraffin-like mono- or bilayers, the catalyst is predominantly intercalated into the interlayer space of the layer silicate. As a result, in the course of polymerization, polyethylene is formed in the interlayer space of particles to facilitate the exfoliation of the filler in separate nanolayers. Conditions for the supporting of a catalyst onto organomodified montmorillonite, which prevent the transfer of the catalyst into solvent and the formation of a free polymer on the synthesis of nanocomposites under the conditions of suspension polymerization in *n*-heptane, were determined. The intercalation of a catalyst into the interlayer space of the particles of layered silicates and the exfoliation of filler particles in the course of the synthesis of composites were confirmed by X-ray diffraction analysis.

Keywords: in situ polymerization, catalyst intercalation, montmorillonite, ultra-high molecular weight polyethylene

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INTRODUCTION

The development of polymer nanocomposites based on layered silicates and a wide range of polymers is the subject matter of intensive current studies because these materials often exhibit unique combinations of properties: improved barrier properties, lowered combustibility, improved mechanical characteristics, and increased thermal stability at a nanofiller content in the material as low as a few percent. Several methods are used for the development of these materials: the in situ polymerization of a monomer in the interlayer space, the incorporation of macromolecules from a polymer solution, and the intercalation of a polymer into interlayer spaces upon the mixing of components in a melt [1–3]. The polymerization method of filler introduction into polyolefins (polymerization filling technology, in situ polymerization) was fist proposed by D'yachkovskii and Novokshonova [4, 5] and Howard [6]. According to

the polymerization method, the composite material is obtained by the polymerization of a monomer on the surface of a filler, activated by a preliminarily supported catalyst, and a matrix polymer is formed in the course of the synthesis as a coating with adjustable thickness on the filler particles. The polymerization technique proposed ensures the uniform distribution of filler particles in a polymer matrix, in particular, in ultra-high molecular weight polyethylene (UHMWPE), which is necessary for reaching a maximally possible level of the mechanical and functional properties of the resulting composites even at high and superhigh filler content (to 80–90 vol %). The method was successfully applied to the development of a number of composite materials based on polyolefins (polyethylene (PE), UHMWPE, and polypropylene (PP)) and dispersed functional fillers [7].

In recent years, many studies on the synthesis of nanocomposite materials based on PE and PP and various nanosized fillers (primarily, layered silicates and carbon nanofillers of different types) have been carried out by the polymerization filling method. Different types of catalysts—the Ziegler–Natta systems, metallocenes, and post-metallocenes—are used for the catalytic activation of nanofillers [8–24]. With the use of layered silicates as fillers, the main goal is to reach the exfoliation of the initial filler particles in separate nanolayers in the course of the synthesis under the action of a polymer, which is formed in the interlayer space. For this purpose, it is necessary to intercalate a catalyst into the interlayer space of a layered silicate [8].

As a rule, montmorillonite, a layered silicate of natural origin, which is capable of exfoliation into separate layers with a thickness of ~1 nm, is used as a filler for the preparation of polymer nanocomposites. In this case, montmorillonite is modified by the replacement of interlayer metal cations by the organic derivatives of ammonium cations with long hydrocarbon radicals of a C_{14}–C_{18} fraction. This organomodification imparts organophilicity to montmorillonite, leads to an increase in the interlayer space, and weakens interlayer interactions; this makes it possible to intercalate different nonpolar compounds (solvents, polymers, and catalysts) into the interlayer space.

Thus, the organomodification of layered silicates is an important factor mainly responsible for the possibility of catalyst intercalation into the interlayer space of montmorillonite; this modification controls the structure and properties of polymer nanocomposite materials with layered silicates. However, although different organomodified silicates were used in works on the synthesis of nanocomposites based on polyolefins, a comparative study of the effect of organomodification (the type and quantity of a modifier) on the processes of catalyst intercalation into the interlayer space and on the structure of the resulting composites was not performed. Furthermore, only in some works, attention was focused on a study of the main stage of the synthesis, which is responsible for the production of nanocomposites with an exfoliated structure—the stage of catalyst intercalation into the interlayer space of a layered silicate. Bergman et al. [9] used X-ray diffraction (XRD) analysis for this purpose to detect the intercalation of the Brookhart palladium catalyst into organomodified montmorillonite based on an increase in interplanar spacing from 1.99 to 2.76 nm. Polymerization on the intercalated catalyst led to a further increase in the interlayer spacing and a gradual disappearance of the interlayer reflection as a result of silicate exfoliation under the action of the polymer formed. Leone et al. [10] studied changes in the crystal structure of organomodified montmorillonite upon treatment with methylaluminoxane (MAO), which is a cocatalyst for metallocene catalysts. They found that MAO interacts with montmorillonite and replaces a large proportion of the modifier in the interlayer space. Previously, we studied the adsorption of Ziegler-type catalyst components, $AlMe_3$ and then VCl_4, on unmodified monocationic Na^+-montmorillonite and organomodified montmorillonite of two types [3, 8]. We found that, with the use of montmorillonite modified with dialkyldimethylammonium chloride (DADMAC, $R = C_{14}$–C_{18}), the adsorbed catalyst amount was greater by almost an order of magnitude than that on montmorillonite particles of other types. The catalyst intercalation was also confirmed by XRD. As a consequence, nanocomposites with an exfoliated structure were synthesized on montmorillonite of this type.

The aim of this work was to synthesize a series of organomodified filler samples based on layered silicates with different cation-exchange capacities with the use of various substituted ammonium cations and to study their structures and the effects of the structure of organomodified montmorillonite and the conditions of the immobilization of an organometallic catalyst based on titanium and vanadium chlorides on the synthesis of nanocomposites with an exfoliated structure on the basis of UHMWPE and montmorillonite in the slurry polymerization mode.

EXPERIMENTAL

Materials

Vanadium tetrachloride VCl_4 and titanium tetrachloride $TiCl_4$ were used as catalysts for the activation of montmorillonite, and $Al(i\text{-}Bu)_3$ (Aldrich) was used as a cocatalyst. The solvent n-heptane (Aldrich) was kept over molecular sieves and distilled from sodium wire in an atmosphere of argon before use. Ethylene was of polymerization-grade purity.

Montmorillonite from two deposits was used as a filler: bentonite from the Dash-Salakhlinskoe deposit (OOO NPK Bentonit, Azerbaijan) with a cation-exchange capacity (CEC) of 79 mequiv/100 g (D-S) and Na^+-Cloisite montmorillonite (Southern Clay Products, the United States) with CEC of 95 mequiv/100 g (CNa). The above layered silicates were treated with a solution of hydrochloric acid in order to change the specific surface area and cation-exchange capacity. The acid treatment was carried out for 3 h by boiling a weighed portion of layered silicate in a 1 M solution of HCl. The activated bentonite was separated by the partial decantation of a sediment with the subsequent centrifugation (5000 rpm, 5 min). For the removal of excess acid, the sediment was washed three times with distilled water followed by precipitation to a value of pH ~ 4.5. The CECs of the samples of Dash-Salakhninske bentonite (D-S/HCl) and Southern Clay Products montmorillonite (CNa/HCl) thus activated were 23 and 44 mequiv/100 g, respectively.

Organomodification of Layered Silicates

The original and acid-activated layered silicates were modified by the substitution of interlayer cations by organic cations (cationic surfactants). A weighed sample was preliminarily dispersed in distilled water for several hours in order to obtain a 2% dispersion. Simultaneously, a 1.5% solution of a modifier was prepared by the dissolution of a weighed portion of a cationic surfactant in heated 5% ethanol. The amount of the cationic surfactant was taken equivalent to the cation-exchange capacity of the layered silicate sample. In the process of synthesis, a solution of the cationic surfactant was gradually added to a dispersion of montmorillonite with the subsequent stirring for 5 h on a magnetic stirrer (400 rpm); thereafter, the system was equilibrated for 7 days with stirring at regular intervals. The organomodified montmorillonite was

separated by centrifugation (5000 rpm, 2 min) with the subsequent washing with distilled water and then 95% ethanol for the removal of physically adsorbed cationic surfactant. The precipitate was dried in air to constant weight and ground in a mortar.

Dimethyldioctadecylammonium bromide (DODAB, Acros Organics), cetyltrimethylammonium chloride (CTAC, Aldrich), a mixed modifier of dialkyldimethylammonium chloride $(CH_3)_2R_2N^+Cl^-$, where R is the mixture of alkyl radicals of a $C_{14}-C_{18}$ fraction (DADMAC, NIIPAV, Russia), alkylbenzyldimethylammonium chloride (ABDMAC, Akzo Nobel), and a modifier based on sunflower oil derivatives—acylamidopropyltrimethylammonium chloride (AATMAC, NIIPAV), where acyl is the residue of sunflower oil acids with the structural formula
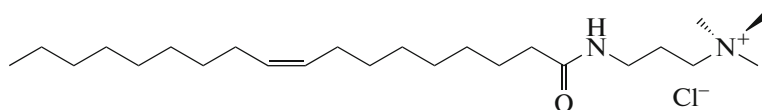
were used as modifiers in this study.

Samples with different organic modifier concentrations were obtained with the use of DODAB; for this purpose, cationic surfactants were taken in amounts equal to or smaller than the equivalent CEC of layered silicate. Commercially produced Cloisite 20A modified montmorillonite (C20A—DADMAC modifier with the alkyl radicals of tallow fats) (Southern Clay Products) was also used as a filler. According to the manufacturer, the amount of the modifier used corresponded to the CEC of the initial montmorillonite (Na$^+$-Cloisite).

Study of the Adsorption of Catalysts

The adsorption of catalyst components on different fillers was investigated using a high-vacuum glass adsorption system like a McBain balance at room temperature (23 ± 1°C). A weighed portion of a filler was placed in a cup for adsorption measurements, which was hung on a quartz spring; thereafter, the system was evacuated to a pressure of 10^{-3} Torr. Before conducting the measurements, a carrier (filler) was heated to 250 or 110°C in the case of unmodified or organomodified samples, respectively. After the cooling of the carrier, the height of the quartz spring was measured by a cathetometer to within ±0.005 mm. Then, adsorbate vapor was supplied to the measuring system, which was equilibrated for ~30 min, and the pressure and the elongation of the quartz spring were measured. For structure analysis, the filler samples with supported catalysts were placed in special capillaries for XRD analysis, which were sealed.

Synthesis of Nanocomposites

The synthesis of nanocomposites based on PE and montmorillonite was performed by two methods under the conditions of gas-phase and suspension polymerization. In both cases, the filler was evacuated for 0.5 h at 100°C for the synthesis of nanocomposites; thereafter, a catalyst (TiCl$_4$ or VCl$_4$) was deposited from a vapor phase. In the course of gas-phase polymerization, the cocatalyst Al(i-Bu)$_3$ was also deposited from a vapor phase. The gas-phase polymerization of ethylene was performed on a McBain balance in a glass reactor at room temperature (23 ± 1°C) and a monomer pressure of 0.1 atm.

The suspension polymerization of ethylene was conducted on a high-pressure installation in a metallic reactor with a volume of 0.2 L. The filler with a supported catalyst was transferred into the reactor in a flow of argon; the reactor was evacuated and thermostatically controlled. Then, a mixture of 100 mL of *n*-heptane with a calculated amount of the cocatalyst Al(i-Bu)$_3$ was added to the reactor (a molar ratio between Al(i-Bu)$_3$ and a transition metal compound was 5 : 1). Ethylene was polymerized at a constant monomer pressure (1 atm) in the reactor with intense stirring (3000 rpm) at a temperature of 40°C. The course of polymerization and the consumption of ethylene were monitored by measuring pressure changes in the graduated cylinder. The polymerization was stopped upon reaching a specified mass of polyethylene.

The polymer product obtained was washed with ethanol and dried in a vacuum at 60°C to constant mass.

Composition and structure of the samples of organomineral fillers and the structure of PE composites synthesized with them

Sample	Montmorillonite	Modifier	Modifier content, wt %	d_{001}, nm	T_m, °C	Composite structure (montmorillonite exfoliation)
CNa	CNa	–	0	1.17	–	–
C20A	CNa	DADMAC	36	2.42	53	+
CNa/DODAB-100*	CNa	DODAB	37	3.81	54	+
CNa/DODAB-70*	CNa	DODAB	27	3.77	51	+
CNa/DODAB-50*	CNa	DODAB	23	3.65, 2.62	48	+
D-S/DODAB-100*	D-S	DODAB	36	3.81	55	+
D-S/DODAB-70*	D-S	DODAB	24	3.46	50	+
D-S/DADMAC	D-S	DADMAC	23	2.67	51	+
D-S/ABDMAB	D-S	ABDMAB	23	3.64	55	+
CNa/HCl/DADMAC	CNa/HCl	DADMAC	26	1.76	No peak	–
D-S/HCl/DADMAC	D-S/HCl	DADMAC	22	1.65	No peak	–
CNa/CTAC	CNa	CTAC	25	1.79	No peak	–
CNa/AATMAC	CNa	AATMAC	36	1.79	No peak	–

* The numbers 50, 70, and 100 indicate the amounts of modifier (in percent of the aluminosilicate CEC) used in the synthesis of the organomineral fillers.

The filler content of the composites was calculated as a ratio of the filler mass to the mass of the synthesized composite.

Characterization of Filler and Polymer Composite Samples

The small-angle X-ray scattering curves of the test samples were measured using an S3-Micropix small- and wide-angle X-ray scattering system (Hecus X-ray Systems, Austria; CuK_α radiation, $\lambda = 1.542$ Å) with the a Pilatus 100K detector (Dectris Ltd., Switzerland). High voltage across the Genix-tube source (Xenocs, France) and current intensity were 50 kV and 1 mA, respectively. The Fox 3D X-ray optics was used for the formation of an X-ray beam, the slit diameters in Kratky collimator were 0.1 and 0.2 mm, respectively. The range of measured diffraction angles was from 0.2 to 7.8 deg. For avoiding the scattering of X-rays in air, the unit of X-ray mirrors and a camera were arranged in a vacuum system (residual pressure, $\sim(2-3) \times 10^{-2}$ Torr). The counting time was varied in a range of 600—5000 s.

The interplanar spacing d was calculated from the Wolf—Bragg formula

$$d = \lambda/2\sin\theta,$$

where λ is the wavelength of X-radiation, and θ is half the scattering angle corresponding to the intensity maximum.

Differential scanning calorimetry (DSC) was carried out on a DSC Netzsch 204 F1 instrument (Netzsch, Germany). The samples were heated from −10 to 160°C and cooled to 20°C at a rate of 10°C/min.

Thermogravimetric analysis was performed on a Netzsch TG 209 F1 instrument (Netzsch) at a heating rate of 20°C/min in air. The organic modifier content of organomodified fillers was calculated from the weight loss in a temperature range of 150—600°C.

The average molecular weight of a polymer matrix of composites was determined by viscometry at 135°C in decalin. M_η was calculated from the formula $[\eta] = 4.6 \times 10^4 M_\eta^{0.73}$ [25].

RESULTS AND DISCUSSION

Based on the four types of layered silicates with considerably different cation-exchange capacities, we synthesized organomodified fillers containing different types of organic cations and different concentrations of organic modifiers. The table summarizes the compositions of the organomodified fillers and their interplanar spacing determined by XRD analysis. The replacement of interlayer Na$^+$ cations by bulky organic cations leads to an increase in the interlayer spacing in the layered silicates.

The results of the structural study of the organomodified fillers show that, with the use of layered silicates with a high CEC (samples based on D-S and CNa bentonites) with the application of DODAB,
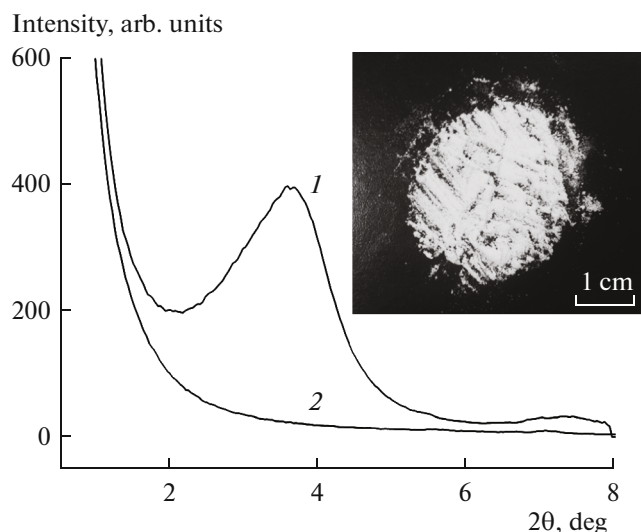
Intensity, arb. units

Fig. 1. Diffraction patterns of (*1*) organomodified montmorillonite C20A and (*2*) PE/15% C20A composite synthesized by gas-phase polymerization. Inset: photograph of the synthesized composite powder.
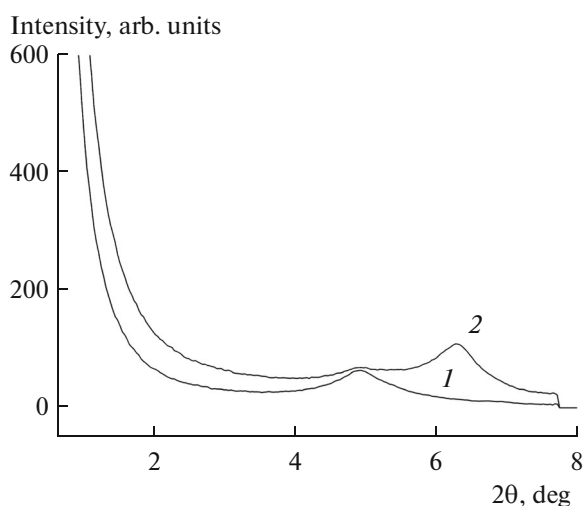
Intensity, arb. units

Fig. 2. Diffraction patterns of (*1*) organomodified montmorillonite CNa/HCl/DADMAC and (*2*) PE/15% (CNa/HCl/DADMAC) composite synthesized by gasphase polymerization.

DADMAC, and ABDMAB modifiers, the interlayer spacing d_{001} considerably increased after the modification. This increase can be correlated with the specific types of the packing of hydrocarbon radicals in the interlayer space in the form of mono- ($d_{001} = 2-3$ nm) and bilayers ($d_{001} > 3$ nm) with inclined and vertical chain orientations [26]. In this type of packing, the modifier forms a defect crystal structure in the interlayer space with an intrinsic melting point of the organic layer at 40–60°C. Variation in the modifier (DODAB) content over a wide range (27–36 wt %) does not lead to a sub-

stantial change in the interlayer spacings in the samples (the samples of CNa/DODAB-100, CNa/DODAB-70, D-S/DODAB-100, and D-S/DODAB-70, see the table), and the formation of structures with different interlayer spacings, which correspond to mono- and bimolecular adsorption layers, was observed with a further decrease in the adsorbed amount (the sample of CNa/DODAB-50, see the table). At the same time, the use of acid-activated layered silicates with CECs of 23 and 44 mequiv/100 g (D-S/HCl and CNa/HCl, respectively) with the DODAB, DADMAC, and ABDMAB modifiers or CNa and D-S silicates with the CTAC and AATMAC modifiers leads to the formation of organosilicates with interplanar spacing of 1.6–1.8 nm, which corresponds to the inclined horizontal arrangement of alkyl radicals in the space between the basal surfaces of single silicate plates. In this packing of radicals, the modifier does not form its own crystal structure, and a melting peak is missing in the DSC profiles of the samples.

All of the prepared samples of organomodified layer silicates were used as fillers for the synthesis of nanocomposites based on UHMWPE. The catalyst components VCl_4 and $Al(i\text{-Bu})_3$ were consecutively supported to the appropriate fillers under identical conditions, and the gas-phase polymerization of ethylene was performed. The synthesized composites with a filler content of 15–20 wt % were investigated by X-ray diffraction. The absence of an interlayer reflection, which is characteristic of the initial layer silicates, in the diffraction patterns of the samples of corresponding polymer composites means that the exfoliation of filler particles to individual nanolayers occurs in the course of synthesis. The study showed that the exfoliation of a filler occurs with the use of organomodified silicates in which the radicals of a modifier form paraffin-type mono- and bilayers ($d_{001} > 2$ nm, a melting peak is present in the thermoanalytical curves) (Fig. 1). In the table, such fillers are marked by the + sign. With the use of fillers in which the organic radicals of a modifier are arranged horizontally with respect to the silicate layers ($d_{001} = 1.6-1.8$ nm, no melting peak is observed in the thermoanalytical curves), the exfoliation of a filler in the course of the synthesis of composites does not occur, and the interlayer reflection of layered silicate is retained in the diffraction patterns of these composites (Fig. 2). In the table, these fillers are designated by the − sign.

The results of the study of catalyst adsorption on montmorillonite of different types allowed us to explain the effect of the packing of an organic modifier in the interlayer space of montmorillonite particles on the possibility of their exfoliation. Figure 3 shows the adsorption isotherms of $TiCl_4$ on the following three types of montmorillonites: CNa sodium montmorillonite ($d_{001} = 1.17$ nm, $S_{sp} = 26$ m^2/g) and the organomodified samples of CNa/HCl/DADMAC ($d_{001} =$

1.76 nm, S_{sp} = 16 m^2/g) and C20A (d_{001} = 2.42 nm, S_{sp} = 9.5 m^2/g). The initial segment (at the relative pressures P/P_s lower than 0.3) of the isotherm of TiCl$_4$ adsorption on CNa sodium montmorillonite (Fig. 3, curve *1*) corresponds to the process of chemisorption as a result of the interaction of titanium chloride with reactive surface hydroxyl groups with the formation of surface titanium oxychlorides. A further increase in the vapor pressure of TiCl$_4$ leads to its physical adsorption. In this case, the pressure dependence of the value of adsorption is nearly linear. The adsorption isotherm of TiCl$_4$ on the organomodified montmorillonite CNa/HCl/DADMAC with an interlayer spacing of 1.76 nm has a similar shape (Fig. 3, curve *2*). A significant change in character of adsorption and the amount of adsorbed catalyst was observed with the use of organomodified montmorillonite C20A with an interlayer spacing of 2.42 nm (Fig. 3, curve *3*). In this case, a considerable catalyst amount was adsorbed even at the P/P_s ratio close to zero. Obviously, the sorption of TiCl$_4$ in the interlayer space of montmorillonite occurs in this section. A further increase in the vapor pressure of the catalyst leads to its adsorption on the external surface of particles.

The residual amounts of sorbed TiCl$_4$ after the evacuation of samples for 2 h at a pressure of 10^{-3} Torr were 0.11, 0.13, and 0.72 mmol/g for the samples of CNa, CNa/HCl/DADMAC, and C20A, respectively. Upon the heating of the sample of C20A to 160°C, the additional desorption of titanium tetrachloride, which was physically sorbed in the interlayer space, in an amount of 0.46 mmol/g occurred. The residue, which corresponds to the chemisorbed catalyst, was 0.26 mmol/g.

Thus, the experimental study showed a fundamental difference in the nature of catalyst adsorption on structurally different layered silicates of different types, which are characterized by different packing of alkyl radicals in the interlayer space and, as a result, by different interlayer spacings. With the use of organomodified montmorillonite with an interlayer spacing of 1.6−1.8 nm, in which the alkyl radicals of a modifier are arranged in parallel to the basal surfaces of the silicate, the catalyst is adsorbed only on the external surface of particles, and it does not penetrate into the interlayer space. In this case, a polymer is also formed only on the external surface of the particles, and the exfoliation of a filler does not occur. With the use of organomodified montmorillonite samples (d_{001} > 2 nm) with the packing of a modifier as paraffin-like mono- or bilayers, the catalyst is predominantly intercalated into the interlayer space of layered silicate. As a result, in the course of polymerization, polyethylene is formed in the interlayer space of particles to facilitate the exfoliation of the filler to separate nanolayers.

The structure of C20A montmorillonite catalytically activated by titanium and vanadium chlorides was investigated by X-ray diffraction. It was found that
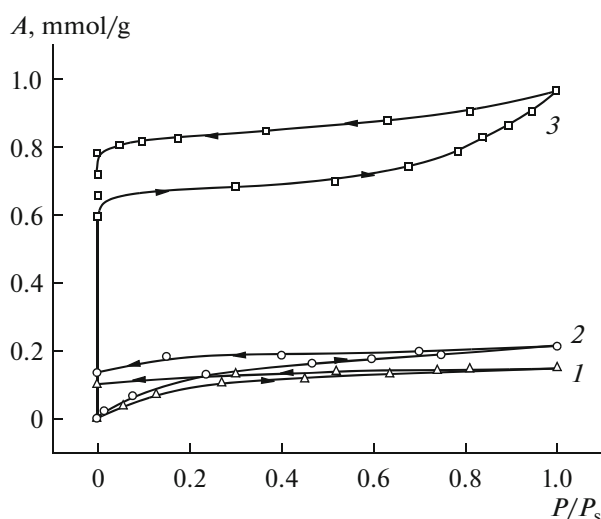

Fig. 3. Adsorption isotherms of TiCl$_4$ on (*1*) unmodified CNa and organomodified (*2*) CNa/HCl/DADMAC and (*3*) C20A montmorillonites.

the adsorption of TiCl$_4$ and VCl$_4$ leads to an increase in the interplanar spacing of the initial montmorillonite, as evidenced by a shift of the interlayer reflection of montmorillonite toward smaller angles (Figs. 4 and 5, curves *2*). An increase in the interplanar spacing was 4 Å in the case of VCl$_4$ or more than 5 Å for TiCl$_4$. The experimental results are direct evidence for the intercalation of catalysts into the interlayer space of organomodified montmorillonite. On the gas-phase polymerization of ethylene on the intercalated catalysts, polyethylene is formed directly in the interlayer space of montmorillonite to split the initial filler particles into separate nanolayers; this leads to the disappearance of an interlayer reflection from the diffraction patterns and the formation of nanocomposites with an exfoliated structure (Figs. 4 and 5, curves *3*).

In the suspension polymerization of ethylene on the obtained C20A/VCl$_4$−Al(i-Bu)$_3$ system in n-heptane as a solvent (in contrast to a gas-phase polymerization process), the formation of free filamentous-ultra-high molecular weight polyethylene (not bound to the surface) was observed. Obviously, this is due to the transfer of the physically sorbed portion of VCl$_4$, which is not removed on evacuation without heating, from the interlayer space into the solvent. In this case, the exfoliation of montmorillonite does almost not occur, as evidenced by an interlayer reflection in the diffraction pattern of the composite (Fig. 6). The heating of the C20A/VCl$_4$ supported catalyst at 160°C leads to the desorption of physically sorbed VCl$_4$ and also facilitates the additional reduction of V^{4+} to V^{3+}. Thus, according to polarographic data, the V^{4+} and V^{3+} contents before heating were 2.6 × 10^{-5} and 2.1 × 10^{-5} mol, respectively. After heating, the fraction of V^{3+} increased and the V^{4+} and V^{3+} contents were 2.0 × 10^{-5}

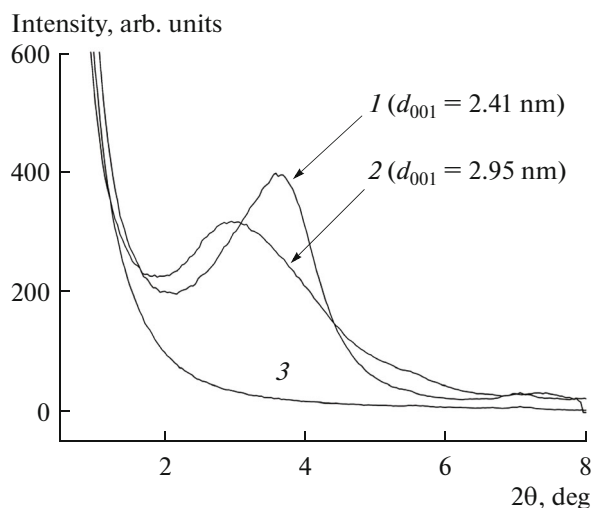Intensity, arb. units

Fig. 4. Diffraction patterns of the following samples: (*1*) C20A montmorillonite, (*2*) C20A activated by $TiCl_4$, and (*3*) PE/15% C20A nanocomposite prepared by the gas-phase polymerization of ethylene in the presence of $Al(i\text{-}Bu)_3$.
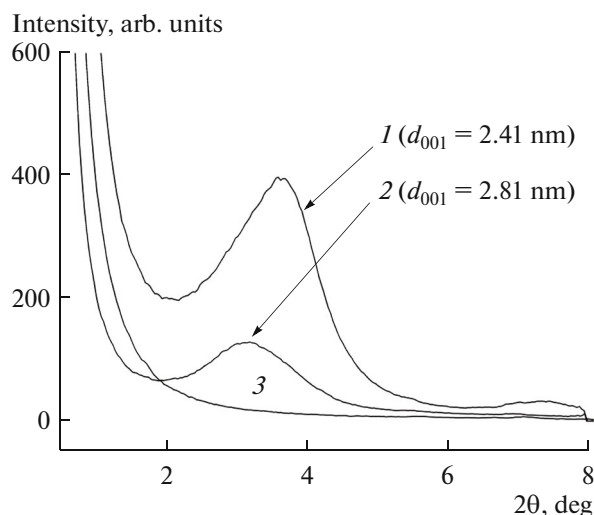
Intensity, arb. units

Fig. 5. Diffraction patterns of the following samples: (*1*) C20A montmorillonite, (*2*) C20A activated by VCl_4, and (*3*) PE/15% C20A nanocomposite prepared by the gas-phase polymerization of ethylene in the presence of $Al(i\text{-}Bu)_3$.
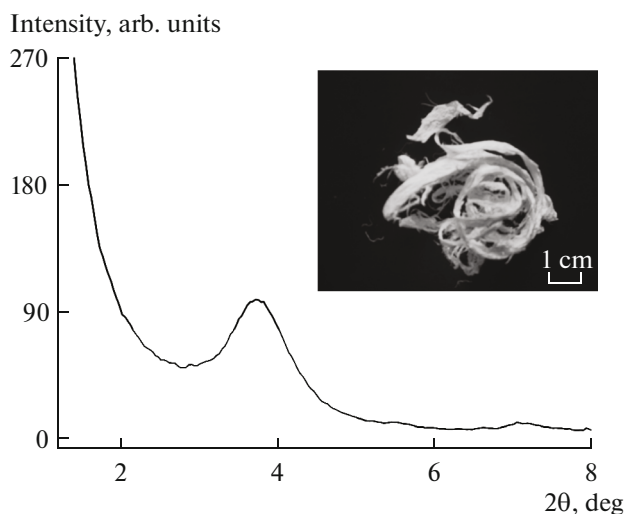
Intensity, arb. units

Fig. 6. Photograph and diffraction pattern of the composite based on PE and montmorillonite synthesized by suspension polymerization in *n*-heptane on the C20A/VCl_4 catalyst. Cocatalyst: $Al(i\text{-}Bu)_3$.
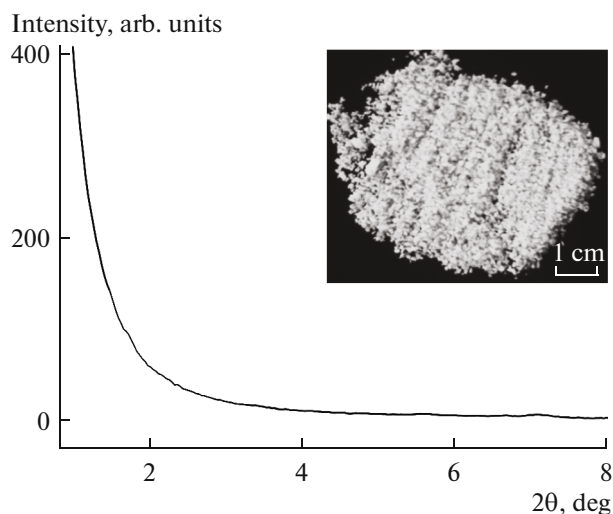
Intensity, arb. units

Fig. 7. Photograph and the diffraction pattern of the composite based on PE and montmorillonite synthesized by suspension polymerization in *n*-heptane on the C20A/VCl_4 catalyst additionally heated at 160°C. Cocatalyst: $Al(i\text{-}Bu)_3$.

and 2.7×10^{-5} mol, respectively. In this case, free polymer is not formed in the polymerization, and the product is powdered material. Note that, in contrast to the gas-phase method of the synthesis, when composite particles with an average size smaller than 100 μm are formed (Fig. 1), larger particles of size 0.2–1.0 mm are formed as a result of suspension polymerization; these particles are the aggregates of weakly bound primary composite particles. The synthesized nanocomposite has an exfoliated structure, as evidenced by the

absence of an interlayer reflection of montmorillonite in the diffraction pattern (Fig. 7).

The kinetic curves of the suspension polymerization of ethylene on C20A/VCl_4 without additional heating and on C20A/VCl_4 heated at 160°C are also considerably different (Fig. 8). In the former case, an increase in the rate of polymerization was observed at the initial stage; this was related to the transfer of physically sorbed VCl_4 into solution; thereafter, a sharp decrease in the catalytic activity occurred due to the
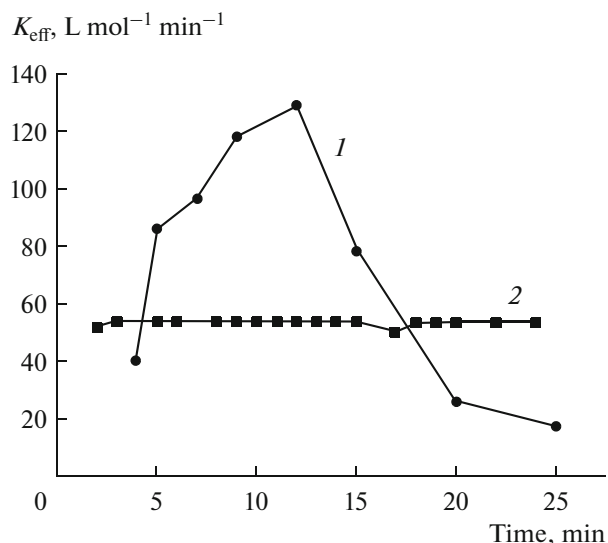
K_{eff}, L mol^{-1} min^{-1}

Fig. 8. Kinetics of the polymerization of ethylene in *n*-heptane on the following catalysts: (*1*) C20A/VCl$_4$ and (*2*) C20A/VCl$_4$ additionally heated at 160°C. Cocatalyst: Al(*i*-Bu)$_3$.

deactivation of vanadium tetrachloride as a result of interaction with an organoaluminum compound (Fig. 8, curve *1*). In the latter case, the polymerization occurred on the catalytic complexes of V^{4+} and V^{3+} immobilized in the interlayer space, and it was a steady-state process in time (Fig. 8, curve *2*).

Analogous results were obtained with the use of TiCl$_4$ as a catalyst. The average molecular weight of the polymer matrix of the synthesized composites was $(2-2.5) \times 10^6$ g/mol; that is, this was ultra-high molecular weight polyethylene.

CONCLUSIONS

As a result of the study of the effects of the structure of organomodified montmorillonite and the conditions of its catalytic activation by titanium and vanadium chlorides on the synthesis of nanocomposite materials based on ultra-high molecular weight polyethylene with an exfoliated structure by the in situ polymerization method, we found that catalyst intercalation into the interlayer space of layered silicate is achieved using organomodified montmorillonite samples ($d_{001} > 2$ nm) as a filler with the packing of a modifier as paraffin-like mono- or bilayers. As a result, in the course of polymerization, polyethylene is formed in the interlayer space of particles to facilitate the exfoliation of the filler to separate nanolayers. We determined conditions for the supporting of catalysts onto organomodified montmorillonite, which prevent the transfer of the catalyst into the solvent and the formation of free polymer in the synthesis of nanocomposites under the conditions of suspension polymerization in *n*-heptane.

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