The structure and properties of composites based on polypropylene and modified Na\textsuperscript{+}-montmorillonite

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Summary
Composites based on polypropylene and modified montmorillonite were produced by mixing in a melt on a twin-screw extruder (Jiangsu Xinda Science & Technology, China). The structure of the obtained composites was investigated using X-ray diffraction analysis and scanning electron microscopy. It was shown that, by comparison with unfilled polypropylene, the elastic modulus, impact strength, and flow index of the composites are higher, while the time of combustion and the flame propagation rate are lower.

Introduction
At this time, researchers are showing heightened interest in the production of new polymeric nanocomposite materials with improved physicochemical and physicomechanical properties, based on polymers and layered silicate materials, in particular montmorillonite (MMT). The development of nanocomposites is complicated by poor compatibility of the organic and inorganic components, and also by the need to select the optimum conditions for dispersion of the silicate filler. Earlier, an attempt was made to solve this problem by modifying the clay by introducing surfactants into its structure, in particular quaternary ammonium compounds with different lengths of the \(\text{N, N-}\text{alkyl substituent}\) \([1–4]\). Such organoclays make it possible to break up the agglomerates formed as a result of the adhesion of individual crystallites of the layered silicate. The adsorption of surfactants promotes an increase in the hydrophobicity of the clay, thereby improving the penetration of macromolecules of the polymer into the interplanar spaces. An analysis of published data indicates that, in earlier studies \([5–9]\) devoted to the problem of producing nanocomposites based on different types of polar polymer (polyesters, polyamides, and others) and montmorillonite modified with quaternary ammonium bases, the possibility is observed of producing intercalated and exfoliated structures, while in the case of using polyolefins, successes in producing nanocomposites are more modest \([10, 11]\).

In view of this, the aim of this work was to produce modified montmorillonite of sodium form using \(\text{N, N-}\text{diallylaminoethanoic acid}\) differing structurally from the previously investigated types of quaternary ammonium bases \([12, 13]\), and to investigate the effect of nanoparticles of layered silicates on the properties and structure of polypropylene-based nanocomposites.

Experimental
Investigations were conducted on a polypropylene homopolymer of grade PPG 1035-08 (PPS below), trade name Stavrolene, with a melt flow index (MFI) of 3 g/10 min.

\(\text{N, N-Diallylaminoethanoic acid}\) (DAAEA) was produced by the alkylation of \(\alpha\)-aminoethanoic acid with allyl chloride by a procedure described earlier \([12, 13]\).

The activated Na\textsuperscript{+}-form of montmorillonite (Na\textsuperscript{+}-MMT) was prepared from natural clay of the Gerpegezh field (Kabardino-Balkaria Republic, Russia) by the procedure described earlier \([14]\); the cation exchange capacity of the clay was 95 mg-equ/100 g clay. The presence
of Ca\(^{2+}\) cations was monitored from absorption bands characteristic of calcite in IR spectra.

Modified Na\(^{+}\)-MMT–DAAEA was produced by the adsorption on Na\(^{+}\)-MMT of a 30% aqueous solution of DAAEA.

Composites were produced by adding 3–7 wt% modified organoclay to polymer PPS. Dry mixtures of components were prepared, and then mixing was carried out in a melt on a twin-screw extruder (Jiangsu Xinda Science & Technology, China) with a screw diameter of 20 mm at a temperature of 210–230°C and a screw rotational speed of 120–150 rev/min. The extrudates were then pelletised and used for the manufacture of the corresponding specimens for investigations.

Test specimens were obtained by extrusion moulding on a Politeest machine (Ray-Ran, UK) with a temperature of the injection cylinder of 230–240°C, a mould temperature of 100°C, and a closure pressure of 8 bar.

The physicomechanical tests were conducted by the following procedures: the melt flow index (MFI) according to the GOST 11645-73 standard, the Izod impact strength according to GOST 19109-84, the elastic modulus, tensile strength, and breaking elongation of dumb-bell testpieces according to GOST 11262-80. Tests were conducted on a universal testing machine (Gotech Testing Machine CT-TCS 2000 (West Germany)) at a temperature of 293 K and a strain rate of \(-2 \times 10^{-3}\) s\(^{-1}\). IR spectra of polypropylene mixtures were obtained using a Spectrum Two PerkinElmer FT-IR spectrometer (USA).

Measurements of Shore D microhardness HB were conducted according to GOST 24621-91 on a Hildebrand hardness meter after 1 s (maximum HB value) and 15 s (HB value after stress relaxation) residence time of the specimen under load. At least five microhardness measurements were conducted at different points of the surface of the specimen at a distance of at least 6 mm from the point of the previous measurement. The arithmetic mean of at least five measurements was adopted as the test result. Specimens for measuring HB had a cylindrical shape with a diameter of 40 mm and a height of 5 mm.

IR spectra were recorded on a Specord M-82 spectrophotometer in the region 4000–400 cm\(^{-1}\). A finely ground polymer specimen was mixed with KBr powder and pressed under high pressure into thin transparent discs. The thickness of the pressed disc was 1 mm, its diameter 12 mm, and its transmission 95%. In all cases the samples weighed the same and made it possible to compare the results of spectral investigations (and also recorded on a PerkinElmer Spectrum Two in the region 4000–400 cm\(^{-1}\)).

The structure of the obtained composites was investigated by methods of X-ray diffraction (XRD) analysis on a D2 Phaser compact powder diffractometer and scanning electron microscopy (SEM) on a Vega 3 Tescan microscope (Czech Republic) with an X-ray detector for microanalysis (Oxford Instruments, UK).

**RESULTS AND DISCUSSION**

Earlier it was established that, for the formation of intercalated and exfoliated structures of organoclay, it is necessary to use a cationic modifier with at least 16–18 CH\(_2\) groups in the main fatty aliphatic chain [3] at an optimum concentration of 25–75 wt% of the cation exchange capacity (CEC) of the clay. Here, it was possible to achieve a 50% increase in the elastic modulus of the PE, a 20% increase in tensile strength, an increase in the barrier properties of the nanocomposites [11], and a 75% increase in the elastic modulus of the PE [15]. Mikitaev et al. [16, 17], Borisov et al. [18], and Bakhov [19] have noted that the use of a layered filler as a fireproofing agent reduces considerably (by 30–50%) the rate of heat generation during combustion of nanocomposites in relation to an unfilled polyolefin.

The structure of the Na\(^{+}\)-MMT modifier used by us differs from that of the surfactants previously used as clay modifiers.

N,N-Diallylaminoethanoic acid is a monomer, a derivative form of diallylamine, into the molecule of which a carboxylic group has been introduced. On the IR spectrum of Na\(^{+}\)-MMT (Figure 1) there are characteristic absorption bands at 3635 and 3400 cm\(^{-1}\) of the free and associated forms of Si–OH, a band at 1635 cm\(^{-1}\) (deformation vibrations of adsorbed H\(_2\)O molecules), and a broad absorption band in the 970–1100 cm\(^{-1}\) region, relating to Si–O–Si fragments. Absorption bands characteristic of a carbonate group in the 1374–1453 cm\(^{-1}\) region are practically absent.

In the IR spectrum of modified organoclay Na\(^{+}\)-MMT–DAAEA (Figure 2b) there is a certain displacement of the characteristic absorption bands for the free and associated forms of Si–OH (deformation vibrations of adsorbed H\(_2\)O molecules) and the broad absorption band in the region relating to Si–OH groups and Si–O–Si fragments. An intense absorption band appears in the region 1453–1460 cm\(^{-1}\), characteristic of stretching vibrations of NH and the –COO– carboxyl group. The presence of a polar –CH\(_2\)–COO– terminal group in DAAEA promotes penetration into the interlayer space of the layered silicate; it is possible that a carboxylate anion replaced the cation bound to it with an inorganic cation from Na\(^{+}\)-MMT. This is indicated by the practically complete disappearance of the 2630–2640 cm\(^{-1}\) band from the ammonium cation (Figure 2b). The fairly intense absorption band in the 3450 cm\(^{-1}\) region was caused by the presence of residual moisture, OH groups of Na\(^{+}\)-MMT, and OH groups of silicate (3626 cm\(^{-1}\)). From the ratio of the intensities of these bands and of bands in the region of absorption it is possible to assume that...
Figure 1. IR spectrum of Na⁺-MMT

Figure 2. IR spectra of DAAEA (a) and modified organoclay Na⁺-MMT–DAAEA (b)
the charge on the nitrogen atom of DAAEA is partially extinguished by increase in the concentration of the negatively charged hydroxyl OH group that is contained in Na+-MMT, on account of which the organoclay acquires hydrophobic properties. These assumptions were confirmed by XRD methods.

**Figure 3** presents the diffraction pattern of a composite with 5 wt% organoclay.

From **Figure 3a** it can be seen that a composite of PPS with 5 wt% organoclay is characterised by the formation of an intercalated structure $\theta = 18.53^\circ$ ($d_{001} = 4.63$), $\theta = 25.31^\circ$ ($d_{001} = 3.51$), and $\theta = 26.65^\circ$ ($d_{001} = 3.34$).

The XRD results are confirmed by SEM micrographs (**Figure 4**).

Comparing the micrographs (**Figure 4**), it can be noted that the clay particles are homogeneously distributed in the polymer matrix in the form of small tactoids (**Figure 4c**). The distance between the clay layers in the nanocomposite increased by 2.3 Å by comparison with montmorillonite. These data also indicate the formation of an intercalated structure of the composite.

The effectiveness of modification of the composite was assessed from the change in the physicomechanical properties (**Table 1**) and flammability of the composite (**Table 2**).

**Table 1** presents the mechanical characteristics for composites with a different content of organoclay.

When PPS is filled with 3 wt% organoclay, the impact strength increases by 120.89% (unnotched) and by 109.44% (5 mm notch), the elastic modulus in bend increases by 115.75%, and the tensile elastic modulus increases by 113.97%. In the case of the filling of PPS with 5 wt% organoclay there is an increase in the impact strength by 104.67% (unnotched) and by 106.15% (5 mm notch), an increase in the elastic modulus in bend by 151.25%, and an increase in the tensile elastic modulus by 110.43%. In the case of the filling of PPS with 7 wt%
organoclay there is a certain reduction in the mechanical properties – a reduction in impact strength by 84.83% (unnotched) and by 104.19% (5 mm notch), a reduction in the elastic modulus in bend by 149.88%, and a reduction in the tensile elastic modulus by 111.41%. In all cases, the breaking elongation is reduced. The intercalated structure formed in the composite implies a change in the conformation of the molecular chains of polypropylene, which leads to denser packing of the interphase regions by comparison with the bulk polymer matrix. The obtained composites can be used as structural materials; most optimum are additions of 3–5 wt% organoclay in the PPS.

The flammability of the composites was assessed from the parameters of the flame propagation rate $\nu$ and the time of combustion of the specimens (Table 2).

As can be seen from Table 2, when 3–5 wt% of modified Na+-MMT + DAAEA is introduced into PPS, there is a reduction in the flame propagation rate by 74–79%. Slowing down of the rate of combustion of the composite is due to the limitation of diffusion of air oxygen into the material on account of the presence of a barrier layer created by flat MMT particles. The presented data are in agreement with results obtained in earlier studies [20–22].

**CONCLUSIONS**

Thus, the conducted assessments of the mechanical properties and flame resistance of the composites make it possible to conclude that N,N-diallylaminioethanoic acid, the structure of which differs from that of surfactants used previously, works as a modifier. The type of arrangement of the modifier in Na+-MMT promotes the formation of an intercalated structure of composites and ensures an increase in elastic modulus and impact strength and a reduction in flammability.

**REFERENCES**