

MACROMOLECULAR CHEMISTRY
AND POLYMERIC MATERIALS

**Nanocomposites Based on Polyimide Thermoplastics
and Magnesium Silicate Nanoparticles
with Montmorillonite Structure**

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Abstract—Nanocomposites based on a thermoplastic polyimide, poly{1,3-bis(3',4'-dicarboxyphenoxy)benzene [4,4'-bis(4"-N-phenoxy)diphenyl sulfone]imide}, and synthetic magnesium silicate nanoparticles with montmorillonite structure were prepared from melts. Efficient modification of the surface of the initial nanoparticles with (aminoethylaminomethyl)phenethyltrimethoxysilane was performed.

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At present one of the most efficient approaches to the development of new polymeric materials is the preparation of hybrid nanocomposites of polymers with inorganic nanoparticles, i.e., with inorganic particles of size no more than 100 nm. It should be noted that the polymeric materials formed on both molecular and supramolecular levels from organic (polymer) and inorganic (nanoparticles) components are absolutely new polymeric systems and not a simple “sum” of these components. This fact is confirmed in a series of experimental studies [1, 2]. It is known [3–8] that lamellar silicates, when added as fillers, strongly enhance characteristics of the resulting polymeric materials, e.g., they improve the strength, crack resistance, softening point, and heat resistance of polymers and decrease their coefficient of linear thermal expansion, gas permeability, etc.

Polyimides (PIs) are highly thermally stable polymers widely used in various branches of industry, such as electrical engineering and electronics. Polymer–inorganic nanocomposites based on PI thermoplastics and natural lamellar silicate montmorillonite were prepared and studied in [9–12]. For example, PI nanocomposites prepared from natural montmorillonite modified with various organic compounds [11, 12] exhibit elevated barrier and mechanical properties as compared to unfilled PIs. At the same time, composites with natural montmorillonite filler have certain drawbacks associated with heterogeneity of the chemical, phase, and disperse composition of

the filler [13–15]. The use of synthetic nanoparticles eliminates these drawbacks.

Lamellar silicates are capable of isomorphic substitution of atoms in their structure, allowing direct synthesis of nanoparticles of given composition. The choice of the composition and size of nanoparticles is dictated by the destination of the resulting composites. Thus, synthetic nanoparticles with given characteristics provide preparation of polymeric composites with required properties.

In this study we prepared nanocomposites based on polyimide thermoplastics and synthetic magnesium silicate montmorillonite (MMT-Mg) synthesized under the hydrothermal conditions [13] and examined the mechanical characteristics of these materials.

EXPERIMENTAL

Synthetic magnesium silicate montmorillonite was used as a filler to prepare composites based on polyimide matrices. Montmorillonite was prepared under the hydrothermal conditions given elsewhere [13]. The size of the resulting particles was about 50 nm, and the composition of the resulting magnesium silicate montmorillonite (analog of natural saponite) was $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$.

The hydrophobicity and affinity for polymeric materials of the MMT-Mg nanoparticles were improved by modification of their surface with (aminoethyl-

aminomethyl)phenethyltrimethoxysilane (hereinafter, silane). A weighed portion (1 g) of MMT-Mg nanoparticles was preliminarily dispersed in ethanol (50 ml) using an ultrasonic bath (20 kHz) for 1 h. Then, the resulting dispersion was mixed with silane (0.2 ml) and ultrasonic treatment was performed for an additional 10 min. The resulting dispersion in the ethanolic solution of silane was centrifuged, the precipitate was additionally washed with ethanol for 30 min to remove excess silane not consumed in the reaction with MMT-Mg nanoparticles, and the mixture was centrifuged. The resulting MMT-Mg nanoparticles treated with silane were dried to remove ethanol in a vacuum at 60°C for 5 h.

The efficiency of the nanoparticle surface treatment with silane was monitored by X-ray diffraction (XRD) analysis on a MiroMax007 device (Rigaku Denki Co. Ltd, Japan). The increase in the distance between the

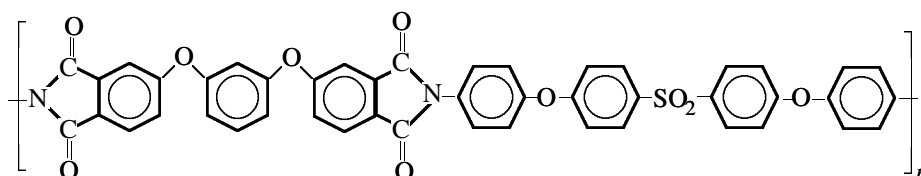
silica layers in MMT-Mg after its treatment with silane was determined from the shift of the (001) reflection toward smaller angles θ , and the corresponding interlayer spacing d was calculated using the Bragg equation:

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

where $\lambda = 1.54 \text{ \AA}$ (wavelength of $\text{CuK}\alpha$ radiation).

The thermogravimetric analysis (TGA) of the MMT-Mg samples before and after treatment with silane was performed on a Perkin-Elmer 7 device under nitrogen atmosphere; the sample weight was 5–10 mg, and the heating rate, 10 deg min^{-1} .

As a polymeric matrix we used, poly{1,3-bis(3',4'-dicarboxyphenoxy)benzene [4,4'-bis(4''-N-phenoxy)-diphenyl sulfone]imide} (PI P-SOD) [13] of the following structure:



The P-SOD + 10 wt % MMT-Mg/silane mixture was prepared on a Haake Minilab microblender, which allows combining a small amount (5 g) of the molten polymer with MMT-Mg/silane powder (0.5 g). Blending was performed at 340°C for 20 min at a screw rotation rate of 100 rpm.

The block samples for mechanical tests were prepared from both unfilled of PI P-SOD and P-SOD + 10 wt % MMT-Mg/silane composite using a microinjector (DACA Instruments); the melt temperature was 360°C, the mold temperature, 90°C, and injection pressure, 100 atm.

The mechanical properties (bending strength σ , bending elastic modulus E , and ultimate bending strain ϵ) of block samples P-SOD polyimide and nanocomposites based on it were determined on a 1958U-10-1 tensile-testing machine (Russia). For mechanical tests, the samples of polyimide and composite were prepared as $1 \times 5 \times 20$ mm plates. The bending properties were studied at room temperature under the mode of active loading at a rate of $10^{-3} \text{ m min}^{-1}$. The shear Young's modulus G' of the block samples was determined with an MK-002 torsional balance wheel (Institute of Macromolecular Compounds) in the mode of

freely damping torsional oscillations (oscillation frequency ~ 0.5 Hz) at room temperature.

Modification of the surface of lamellar silicates is an important stage of the preparation of nanocomposites based on them. Treatment of silicates with organic compounds makes their surface more hydrophobic, improves the compatibility of nanoparticles with the polymer, and increases the interlayer spacing to simplify exfoliation of the silicate filler in the polymer matrix [1, 2]. Since the main process occurring at interaction of the polymers with lamellar silicates is the exchange adsorption, the behavior of the exchanging cations (Na^+ , K^+ , Ca^{2+}) localized between the silica layers is of particular importance. High cation-exchange capacities determine the simplicity and completeness of modification of the clay materials. In turn, the cation-exchange capacity is determined by the composition and structure of the lamellar material. Isomorphic substitution of aluminum atoms for silicon and of magnesium, iron, and some other elements for aluminum in tetrahedral and octahedral positions of the structure provides formation of the surface negative charge and improves the cation-exchange capacity of the lamellar silicate.

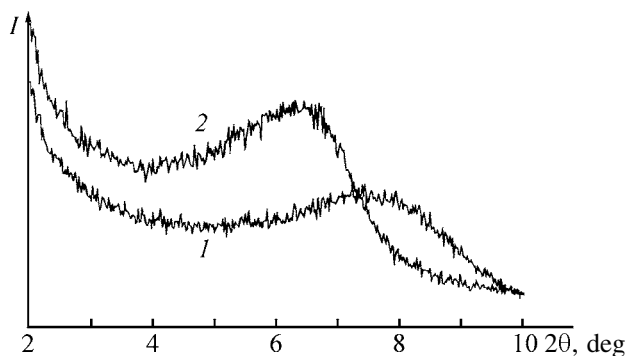


Fig. 1. XRD patterns of (1) initial MMT-Mg and (2) MMT-Mg modified with silane. (I) Intensity and (2θ) Bragg angle.

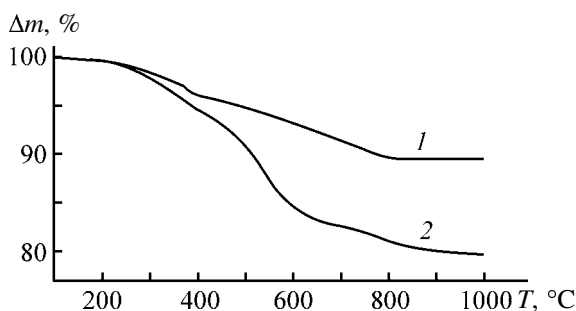


Fig. 2. TGA curves of (1) initial MMT-Mg and (2) MMT-Mg modified with silane. (Δm) Weight loss and (T) temperature.

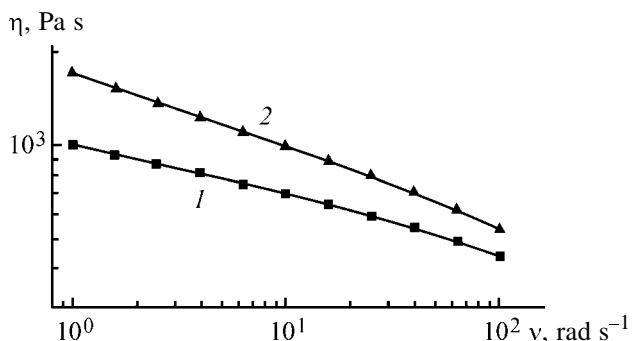


Fig. 3. Viscosity η of melts: (1) PI P-SOD and (2) nanocomposite PI P-SOD + 10 wt % MMT-Mg/silane as a function of frequency ν ; temperature 360°C, deformation amplitude 1%.

In the absence of isomorphic substitution, as in the case of MMT-Mg studied in this work, the crystallochemical charge of the particle surface should be neutral and the cation-exchange capacity should be close to zero. From this viewpoint, the composition of montmorillonite is not optimal. At the same time, synthetic montmorillonite exhibits adsorption capacity allowing efficient modification of its surface with organic compounds. This is due to the fact that the surface of lamellar silicates, along with exchanging cations, contains wide assortment of active adsorption

centers of various nature [16, 17]. Along with exchanging cations and coordination-unsaturated magnesium and aluminum ions, they can include single and geminal OH groups at the silicon atoms at the edges of tetrahedral and octahedral layers, uncompensated bonds at the crack surfaces, etc. [17].

The XRD patterns of the initial MMT-Mg and of MMT-Mg treated with silane are shown in Fig. 1. As seen, the reflection at $2\theta = 7.55^\circ$ (d_{001} 11.7 Å) characterizing the basal distance between the silicon-oxygen layers in the initial montmorillonite shifts toward smaller angles after treatment with silane. The reflection at $2\theta = 6.31^\circ$ corresponds to an increase in the interlayer spacing to 13.8 Å. Thus, treatment of the initial sample with silane increases the interlayer spacing, which confirms formation of a hybrid organic-inorganic material.

As seen from the TGA data (Fig. 2), the MMT-Mg samples treated with silane exhibit relatively high heat resistance; intensive weight loss is observed in the 230–250°C range, which allows their use for modification of heat-resistant polyimide matrices. It should be noted that low stability of aliphatic amines often used in modification of the lamellar silicate surface [3–8] is the main drawback hindering their use for preparing nanocomposites based on polyimides.

Compounding of silane-MMT-Mg nanoparticles modified with PI P-SOD in a microblender only insignificantly increases the polyimide viscosity at 360°C (Fig. 3). For example, filling of PI P-SOD with MMT-Mg/silane (10 wt %) increases the viscosity of the polyimide matrix by a factor of 1.5, which allows preparation of high-quality nanocomposite samples using the DACA microinjector without increasing temperature of the melt or press mold. Small increase in the melt viscosity can be probably explained by a small size (50 nm) of the MMT-Mg nanoparticles. In contrast, coarser natural montmorillonite with the particle size more than 100 nm, when added to the polymeric matrix, strongly increases the viscosity of the polymer melt [4, 5]. Increased viscosity of the resulting composites complicates their molding.

The mechanical characteristics of samples of polyimide thermoplastics and nanocomposites based on P-SOD and filled with MMT-Mg nanoparticles modified with silane are listed in the table. Addition of MMT-Mg/silane (10 wt %) into the PI P-SOD matrix increases the bending strength σ_f of the composite from 170 to 195 MPa and, especially, its bending elastic modulus E_f and shear elastic modulus G' from 2.3 to 3.2 GPa and from 1.3 to 1.8 GPa, respectively. This increase in the strength and hardness of the poly-

Mechanical properties of polyimide thermoplastics and nanocomposites prepared from PI P-SOD and nanoparticles of synthetic MMT-Mg modified with silane*

Sample	σ_f , MPa	E_f , GPa	ε_f , %	G' , GPa
ULTEM-1000	180±3	2.7	>10	1.4
P-SOD	170±4	2.3	>10	1.3
P-SOD + 10wt % MMT-Mg/silane	195±7	3.2	5	1.8

* (ε_f) Bending strength, (E_f) bending elastic modulus, (χ_f) ultimate bending strain, (G') shear elastic modulus.

imide composite confirms the reinforcing effect of MMT-Mg nanoparticles owing to anisotropic plate-like shape of the nanoparticles and their strong binding with the P-SOD matrix. For comparison, the properties of thermoplastic ULTEM-1000 polyamide (GE, the United States), whose test samples were prepared by a similar procedure using a DACA microinjector, are also listed in the table. As seen, the strength and elastic characteristics of commercial ULTEM-1000 composite are slightly higher than those of PI P-SOD thermoplastics, but they are lower than those of P-SOD + 10 wt % MMT-Mg/silane nanocomposite. Slight decrease in the ultimate bending strain ε_f of the nanocomposite is probably due to insufficiently uniform distribution of the MMT-Mg nanoparticles in the PI P-SOD matrix and formation of submicron particle aggregates, which can initiate formation of critical microcracks in the composite bulk.

CONCLUSIONS

(1) The surface of magnesium silicate nanoparticles with montmorillonite structure was modified using (aminoethylaminomethyl)phenethyltrimethoxysilane. As a result, the basal spacing between the silicon-oxygen layers increased from 11.7 to 13.8 Å, which confirms the efficiency of the surface modification.

(2) Nanocomposites based on thermoplastic polyimide poly{1,3-bis(3',4-dicarboxyphenoxy)benzene [4,4'bis(4''-N-phenoxy)diphenyl sulfone]imide} and magnesium silicate nanoparticles modified with silane were prepared.

(3) Filling of the polyimide matrix with magnesium silicate nanoparticles modified with silane (10 wt %) increases the nanocomposite strength by 15% and its bending elastic modulus and shear elastic modulus by a factor of 1.4.

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