Hybrid Nanocomposites Based on Guanidine Methacrylate Monomer and Polymer and Layered Aluminosilicates: Synthesis, Structure, and Properties

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Abstract—Hybrid nanostructures (organomodified montmorillonite) have been synthesized on the basis of activated Na^+-montmorillonite and new water-soluble ionogenic Na^+-montmorillonite monomers containing quaternary ammonium guanidine cations. The structure and properties of poly(guanidine methacrylate) nanocomposites have been studied. It has been shown that these compounds efficiently adsorb heavy metals and exhibit a prolonged biocide effect due to the presence of quaternary ammonium guanidine cations.

Interesting directions in the design of promising nanocomposite materials (nanocomposites) have emerged in recent years. As is known, the composition of a matrix and a filler and their mutual orientation, ratio, and structure determine the desired combination of performance, engineering, and other specific characteristics of nanocomposites, in which the synergistic effect of valuable properties of parent inorganic and organic components as a rule makes itself evident.

The objects of research in this study are nanocomposite materials (nanocomposites) that have been prepared for the first time from the activated Na^+ form of layered natural aluminosilicates (montmorillonite) and new biocide water-soluble ionogenic guanidine methacrylate monomers and polymers containing quaternary ammonium cations.

This study concerns the synthesis of organomodified montmorillonite containing quaternary ammonium guanidine cations and nanocomposites formed on their basis that efficiently adsorb heavy metals and exhibit a prolonged biocide effect.

EXPERIMENTAL

Parent Components

Activated Na^+-montmorillonite (Na^+-MMT) was prepared from the natural clay of the Gerpegezh Deposit (Kabardino-Balkaria) as described in [1]; the cation capacity was 95 mg-equiv/100 g clay. The presence of Ca^{2+} cations was checked from IR maxima typical of calcite. Guanidine methacrylate (GMA) was synthesized in accordance with [2]; $T_m = 161–163°C$. Chemically pure vacuum-dried ammonium persulfate (APS) was used as an initiator of radical polymerization.

Synthesis of New Hybrid Nanostructures and Nanocomposites

The calculated amounts of GMA and APS were added to an aqueous suspension containing Na^+-MMT (50 g) and distilled water (200 ml), and the suspension was prepared by mixing of Na^+-MMT with a magnetic stirrer for 2 h. Stirring was continued for another 4 h until a homogeneous mass was obtained. Then, the suspension was poured into ampoules with joints, and each ampoule was purged with nitrogen to remove air. After polymerization was performed at 60°C for 8 h, the ampoules were broken and the as-prepared samples were rinsed with distilled water and allowed to stand for a day in a closed vessel in an excess amount of distilled water. The samples of hybrid nanostructures were removed and vacuum dried to a constant weight at 40°C over P_2O_5. The dry residue was ground.

The structure and purity of parent compounds and final products were estimated by elemental analysis, ^1H NMR spectroscopy on a Bruker MLS-300 spectrometer (300 MHz), and IR spectroscopy on a Specord M-82 spectrophotometer. Samples for IR studies were prepared as KBr pellets or Vaseline oil suspensions

X-ray diffraction data were collected at room temperature on a DRON-6 automated diffractometer (36 kV, 20 mA, CuK_α radiation, a graphite monochromator on the secondary beam, Bragg–Brentano

geometry in the range of angles $2\theta = 1° - 35°$, a step of $0.05°$, and a scan rate of 1 K/min).

The specific surface area of nanomposites and their particle size distribution were studied on a MicroSizer 201 laser particle analyzer (an ultrasound of 200 W, a dispersion time of 60 s, and a transmission coefficient of 79).

Heavy metals in water samples before and after purification with composites were determined on an MGA-915 atomic-absorption spectrometer. The content of metals was estimated from the integral analytical signal and calculated from the preconstructed calibration plot.

RESULTS AND DISCISSION

It is known that the preparation of organomodified nanostructures based on natural montmorillonite clays and organic monomers and polymers involves difficulties related to their incompatibility [3]. This drawback can be eliminated via selection of parent organic and inorganic components that contain functional groups capable of additional modification. The preliminary synthesis of the activated Na^+-MMT and cationotropic organomodifiers (vinyl monomer–quaternary imino derivative salt of GMA and the related polymer) allowed us to solve this problem.

As applied to the natural clay and its activated Na^+ form of montmorillonite, it should be taken into account that their surfaces possess different adsorption characteristics, which define the final design of the nanocomposite: outer basal surfaces limiting the dimensions of nanoparticles and inner basal surfaces determining intercalation and other processes which can be described in terms of approaches adopted in the chemistry of intracrystalline structures (guest–host systems).

The interaction of $Si-O^-$ and $Si-OH$ groups of the basal surfaces of MMT with monomer or polymer zwitterion pairs of GMA yields organomodified nanostructures stabilized by hydrogen bonds and ionic bonds. In this study, the hydrophobization of basal surfaces of Na^+-MMT via displacement of Na^+ from exchange positions was first performed with the use of not only the vinyl monomer containing the cationotropic quaternary imino derivative salt of GMA but also the related polymer (PGMA) prepared in situ.
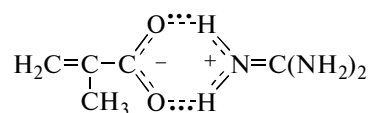
The guanidine-containing monomer was polymerized in situ in the presence of APS. The optimal conditions of polymerization were as follows: a temperature of 60°C, 1% APS based on the monomer weight, and a time of 60 min. This study was mostly devoted to hybrid nanocomposites in which the layered aluminosilicate MMT served as a matrix and which differed in the degree of filling with Na^+-MMT–GMA and Na^+-MMT–PGMA.

The combination of hydrophobization, polymerization, and formation of nanosized particles signifi-
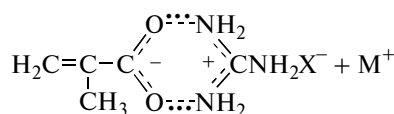
cantly simplifies the technique of preparing organic–inorganic nanostructures, facilitates the homogeneous dispersion of the inorganic component, decreases the time of the process, and ensures a good yield of the target nanocomposite.

The chemical structure of model compounds (zwitterionic delocalized resonance structures of GMA and PGMA) and the presence of similar structures in nanocomposites prepared on its basis and Na^+-MMT were studied by IR and ^1H NMR spectroscopy and X-ray diffraction.

It is known that the carboxyl group of a weak (methacrylic) acid readily protonates the nitrogen atom of the azomethine group of guanidine and leads to formation of true quaternary imino derivatives of the salt [4]. In this case, the following zwitterionic delocalized resonance structures can presumably form.

$$H_2C=C-C \underset{O\cdots H}{\overset{O\cdots H}{\langle}} {}^- \quad {}^+N=C(NH_2)_2$$
$$CH_3$$

First type of binding

$$H_2C=C-C \underset{O\cdots NH_2}{\overset{O\cdots NH_2}{\langle}} {}^- \quad {}^+CNH_2X^- + M^+$$
$$CH_3$$

Second type of binding

In our case, the first type of binding of the carboxylate anion is the most probable and is typical for true quaternary imino derivatives of weak acids. The second type of binding of the carboxylate anion most probably should be expected for N,N-dialkylimino derivatives of quaternary ammonium cations of guanidine [5] and quaternary ammonium cations of the imino group of guanidine in the presence of halides MX (i.e., if there are anions that compete with carboxylate anions for stabilization of quaternary ammonium cations of the imino group but do not form true guanidine resonance structures).

It should be expected that such monomer/polymer guanidine zwitterion delocalized resonance structures can interact with $Si-O^-$ and $Si-OH$ groups of basal surfaces of natural clays. The above interactions and bonds in the zwitterions can fail and recover readily (sometimes other structures arise) under the effect of various factors, such as the pH of the medium, temperature, and nature of solvent, as well as owing to interaction with competing exchange cations or the membrane surface of a bacterial cell.

The effect of the solvent nature can be exemplified by the failure of the delocalized resonance structure of the monomer zwitterion based on GMA under the action of DMSO-d_6. It is well known that DMSO (an aprotic dipolar solvent) practically does not solvate anions, whereas cations are well solvated by this solvent [6]. Thus, it begins to compete with the carboxylate anions of methacrylic acid for stabilization of qua-

Table 1. ^{1}H NMR characteristics of methacrylate derivatives in DMSO-d$_6$

| Experi-ment	Compound	Chemical shift, δ (ppm) of protons					Carboxylate anion
		CH$_3$	H$_a$	H$_b$	NH	COOH	
1	MAA	1.83	5.56	5.96	—	12.31	
2	Na$^+$-MA	1.73	5.04	5.54	—	—	
3	GMA	1.76	5.04	5.59	7.79	—	
4	GMA*	2.05	5.50	5.82	—	—	

* In D$_2$O.

ternary ammonium cations of the imino group of guanidine.

A comparison of the ^{1}H NMR spectra of methacrylic acid and its salts—sodium (MA-Na$^+$) and quaternary imino derivatives of GMA in DMSO-d$_6$—shows (Table 1) that the values of δ (H$_c$, H$_a$, CH$_3$) for the carboxylate anion (experiments 2, 3) are similar. In addition, the absence of the signal due to the proton of the carboxyl group in solution (experiment 3) (δ = 12.31 ppm) and the presence of the signal due to protons (δ = 7.79 ppm) that is typical for imino derivatives of quaternary ammonium cations suggest the decomposition of zwitter structures into cation and anion. Therefore, as expected, an increase in delocalization of the negative charge over bonds of the carboxylate anion of methacrylic acid is observed along with a marked enhancement of nucleophilicity. This fact is confirmed by a smaller strong-field shift of signals due to vinyl protons of GMA measured in D$_2$O relative to DMSO-d$_6$ (Table 1).

Along with the ^{1}H NMR spectroscopy, the structure of Na$^+$-MMT, GMA, PGMA, and the related nanostructures (Na$^+$-MMT−GMA and Na$^+$-MMT−PGMA) was studied by IR spectroscopy (Figs. 1, 2),

The IR spectrum of Na$^+$-MMT (Fig. 2, spectrum *1*) shows typical absorption bands at 3635 and 3400 cm^{-1} due to free and associated forms of Si−OH, a band at 1635 cm^{-1} due to bending vibrations of adsorbed H$_2$O molecules, bands at 1453 and 1374 cm^{-1} due to CO$_3^{2-}$, and a broad clearly defined band at 970−1100 cm^{-1} corresponding to silanol groups Si−OH and fragments Si−O−Si.

The IR spectrum of GMA (Fig. 1, spectrum *2*) shows two broad well-defined bands at 3385 and 3100 cm^{-1}, which are attributed to the stretching vibrations of NH bonds of the guanidine cation. Absorption bands at 1680 and 1656 cm^{-1} correspond to the stretching vibrations of −N=C< groups and bending vibrations of NH$_2$ groups. The ionized coordination bonded carboxyl manifests itself in the spec-
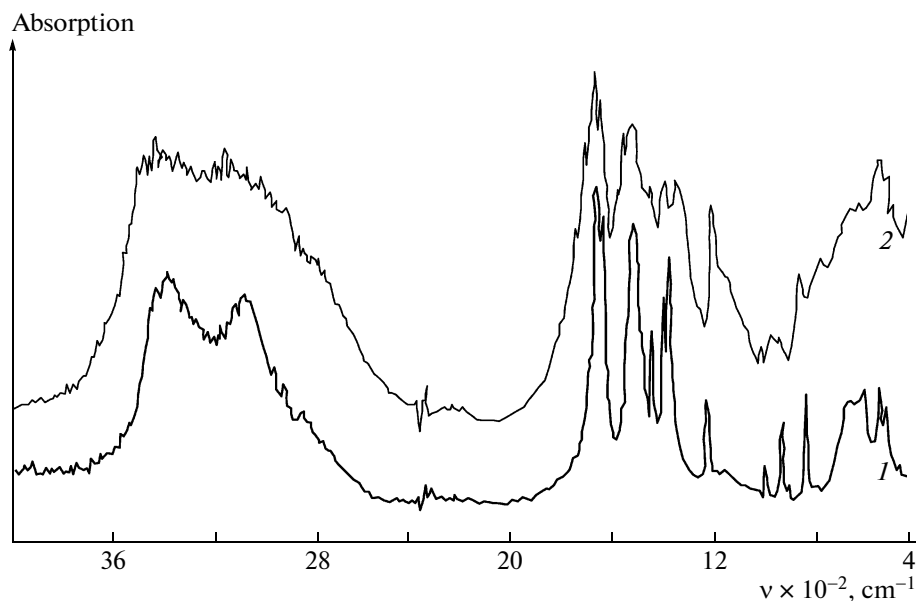
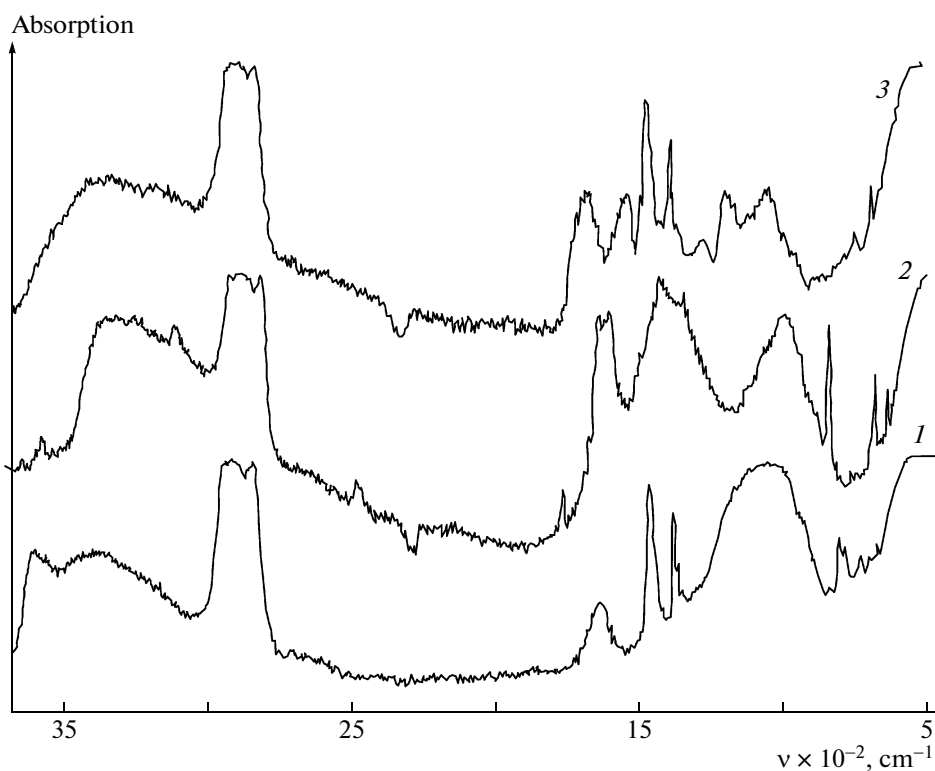**Fig. 1.** IR spectra of (*1*) GMA and (*2*) PGMA taken in KBr pellets.

Absorption

Fig. 2. IR spectra of (*1*) Na$^+$-MMT, (*2*) Na$^+$-MMT−GMA, and (*3*) Na$^+$-MMT−PGMA (50 : 50) taken in vaseline oil.

trum as a typical intense absorption band at 1528 cm^{-1}, which is typical for the delocalized zwitterion, whereas the absorption band corresponding to the less delocalized COO$^-$-group of sodium methacrylate is observed at 1540−1560 cm^{-1}.

The qualitative coincidence of absorption bands for both the guanidine fragment (3450−3100 cm^{-1} for −NH$_2$ and 1660−1680 cm^{-1} for >C=N−) and the delocalized zwitterion (1560−1520 cm^{-1}) in the spectra of GMA and PGMA (Fig. 1) indicates that origins of ionic binding in zwitterionic delocalized resonance structures have very much in common.

The most important band is the absorption band at 860 cm^{-1}, which is typical of out-of-plane bending vibrations in fragment CH$_2$=C< in GMA (a vinyl monomer containing the cationotropic quaternary salt of guanidine methacrylate) and in the nanostructure (Na$^+$-MMT−GMA) [7]. Since other absorption bands at 3000−3080 and 1640−1660 cm^{-1}, which are characteristic of double bond CH$_2$=, are superimposed by a strong absorption in these regions due to the guanidine fragment, the above-mentioned band at 860 cm^{-1} is the single spectral test for disappearance of double bonds both for the synthesis of PGMA and the polymerization of GMA in situ in nanostructures. The absence of this band in the case of Na$^+$-MMT and nanocomposite Na$^+$-MMT−PGMA attests to the absence of double bonds in them. At the same time,

formation of Na$^+$-MMT−GMA is characterized not only by the appearance of this absorption band at 860 cm^{-1} but also by an increase in the width of characteristic absorption bands of the clay in the vicinity of 1450−1680 cm^{-1}. This tendency is apparently associated with the formation of relatively strong coordination bands of GMA with active functional centers of the basal surfaces of montmorillonite, Si−O$^-$ and Si−OH (Fig. 2, spectrum 2).

In the case of the Na$^+$-MMT−PGMA sample, the interaction of zwitterion pairs of PGMA with Si−O$^-$ and Si−OH groups of the mineral substrate is accompanied by the formation of systems stabilized by hydrogen and ionic bonds. The pattern of the IR spectrum (characteristic absorption bands at 1100−1750 cm^{-1}, Fig. 2, spectrum *3*) becomes intermediate between those of the carboxylate anion and the carboxyl group [8, 9]. Note that the broad absorption band at 3400 cm^{-1} corresponds to the stretching vibrations, while the band at 1640 cm^{-1} is due to the bending vibrations of adsorbed water molecules in the interlayer space of Na$^+$-MMT. The IR spectra of Na$^+$-MMT−GMA and Na$^+$-MMT−PGMA samples containing small amounts of GMA and PGMA display these absorption bands. This fact indicates that GMA and PGMA molecules taken at the above-mentioned ratios inserted into the interlayer spacing but incompletely displaced water occurring there.

To verify where the organomodification of Na$^+$-MMT by zwitterionic delocalized resonance structures of GMA and PGMA occurred and where similar structures occur in GMA- and PGMA-based nanocomposites, X-ray diffraction analysis of the samples was performed (Fig. 3). Since the basal reflection in the Na$^+$-MMT and GMA- and PGMA-based nanocomposites may shift in a wide range, diffractograms were measured in the range of angles $2\theta = 2°-40°$.

The diffractogram of Na$^+$-MMT (Fig. 3, curve *1*) shows the typical peak at $2\theta = 7.53°$ ($d = 1.1$ nm), which conforms to Bragg's period of arrangement of heterogeneous regions and corresponds to a distance between basal surfaces of the clay. The displacement of exchange sodium cations (Na$^+$) in interlayer galleries by cationotropic quaternary imino derivatives of the GMA salt simultaneously causes hydrophobization (organomodification) of basal surfaces of montmorillonite and brings about a shift in the peak to the small-angle region $2\theta = 3.3°$, thus indicating an increase in the interplanar distance in the GMA nanocomposite to 2.6 nm (Fig. 3, curve *2*).

The free-radical polymerization of the GMA monomer in situ allowed the synthesis of nanocomposites with a degree of filling of Na$^+$-MMT : PGMA = 80 : 20 and 50 : 50 (weight/weight). A shift in the peak to the small-angle region $2\theta = 5.0°$ ($d = 1.76$ nm) relative to Na$^+$-MMT with a degree of filling equal to 20 wt % PGMA (Fig. 3, curve *3*) indicates formation of the intercalated nanostructure. The absence of the peak at a degree of filling of 50 wt % PGMA (Fig. 3, curve *4*) provides evidence for segregation and exfoliation of elementary stacks, as is the case at $d > 8-10$ nm [10].

Note that, when the amount of the initiator is above 1% based on the monomer weight, the amount of the organomodified MMT and hence of the PGMA nanocomposite is decreased. Probably, this circumstance is related to a higher ability of NH$_4^+$ groups of APS in comparison to that of zwitterionic delocalized resonance structures of true quaternary salts of methacrylic acid to displace Na$^+$ cations from exchange positions of the basal surfaces of Na$^+$-MMT. Inorganic cationotropic and anisotropic constituents (NH$_4$)$_2$S$_2$O$_8$ are more philic to Si–O$^-$ and Si–OH groups of interlayer galleries.

An analysis of the specific surface area of nanocomposites and their particle size distribution for samples of varying composition showed that there is no simple relationship between theses parameters. As an illustration, let us present the data for the Na$^+$-MMT–PGMA (50 : 50) composite: $S_{sp} = 9.62$ cm^2/g. It is clear that the composite materials possess a high specific surface area. This is evidence in favor of our assumption that they can be used as sorbents.

Ion-exchange and sorption purification of water is one of the most important application areas of nano-
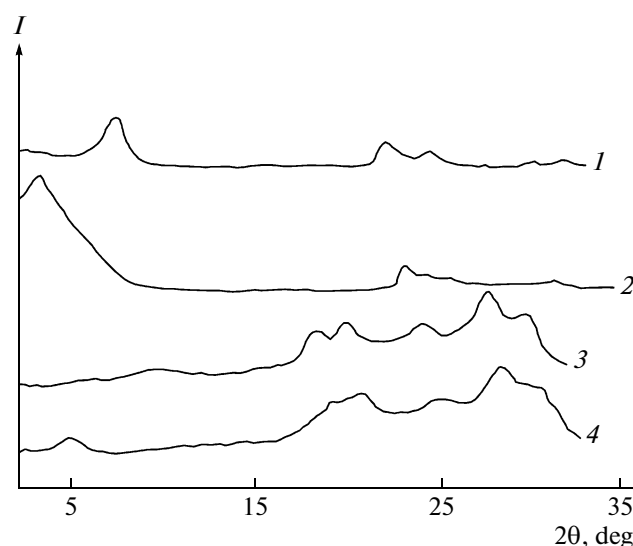

Fig. 3. Diffractograms of (*1*) Na$^+$-MMT, (*2*) Na$^+$-MMT–GMA, and (*3–4*) Na$^+$-MMT–PGMA at compositions of (*3*) 80 : 20 and (*4*) 50 : 50.

composite materials. The extraction of heavy metals from sewage and natural water by the composite materials under study was investigated with the use of model solutions. The relevant data are summarized in Table 2.

The preliminary testing of the bactericidal activity of the nanocomposite materials, which was performed jointly with the Bacteriology Laboratory of the State Health and Disease-Control Agency of Kabardino-Balkaria, showed that these materials are very active and show biocidal activity with respect to some microbiological pollutants of water, in particular, intestinal bacteria. It is pertinent to note that the parent monomers and corresponding polymers are inactive with respect to the intestinal bacillus. It seems that montmorillonite contributes to the biocidal effect.

Table 2. Sorption activity of polymer composite Na$^+$-MMT–PGMA (50 : 50) with respect to heavy-metal ions

Cation	Concentration of metal, mg/l		Degree of sorption, %
	before purification	after purification	
Cu^{2+}	0.1	0.0257	74.2
Pb^{2+}	0.01	0.0020	79.4
Cd^{2+}	0.01	0.0016	83.2
Zn^{2+}	0.01	0.0015	84.4
Co^{2+}	0.01	0.0021	78.6
Cr^{6+}	0.01	0.0022	77.8
Mo^{6+}	0.001	0.0001	87.5
W^{6+}	0.001	0.0001	86.9

Thus, owing to the combination of high biocide activity and an enhanced ability to bind heavy metals, new nanocomposites can be recommended as efficient sorbets for purification and disinfection of water.

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