

NEW METAL COMPLEXES DERIVED FROM GUANIDINE-CONTAINING DIALDEHYDE CELLULOSE

Z. Yu. Isupova, S. Yu. Khashirova,
A. A. Zhansitov, V. A. Kvashin,
E. V. Khakyasheva, Yu. I. Musaev,
and Yu. A. Malkanduev

UDC 669.017

New metal-polymer complexes of iron-containing composites of dialdehyde cellulose with guanidine acrylate or methacrylate have been developed. The structure and properties of these materials have been established by physicochemical testing. The polymeric iron-containing complexes obtained by radical polymerization (in situ) are formed due to intra- and intermolecular coordination of the metal ions with carboxylate oxygen atoms, and amino group nitrogen atoms of the guanidine fragment as well as hydroxyl groups of dialdehyde cellulose. The complexes obtained by mixing the metal salt with polymers in aqueous solution are formed due to replacement of water molecules in the coordination sphere of the solvated metal ions by hydroxyl groups of dialdehyde cellulose and the reaction of metals with carboxylate ions and guanidine groups of the polymer located on the composite surface. Guanidine-containing cellulose composites were found to be effective matrices for stabilizing the size of the growing particles containing a new metallic phase and to form polymer complexes with a narrow size distribution of both micro- and nanoparticles. These results suggest that the synthesized compounds hold promise for reagent transport when using composites as catalysts for various chemical reactions or for targeted delivery of drugs.

The use of cellulose materials for the preparation of metal-polymer complexes is extremely convenient due to their low cost, availability, biocompatibility, and tendency to undergo biodegradation. However, cellulose, despite its high affinity toward biological materials, does not dissolve in water and biological liquids due to its highly ordered structure and strong intermolecular interactions. Furthermore, cellulose has low reactivity in various reactions including complex formation [1].

The traditional methods for activating cellulose are complex and involve the use of highly toxic intermediates. In previous work [2, 3], we found that guanidine acrylate and methacrylate may activate cellulose derivatives and convert them into water-soluble forms. In the present work, we prepared and studied metal-containing composites derived from polyguanidine acrylates and dialdehyde cellulose.

The synthesis of polymeric metal complexes derived from guanidine-containing cellulose composites was carried out by two methods:

Method 1. Radical polymerization (*in situ*) of dialdehyde cellulose (DAC) previously treated with guanidine acrylate (GA) or guanidine methacrylate (GM) in aqueous solutions of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in the presence of ammonium persulfate as a radical initiator.

Method 2. Saturation of guanidine-containing cellulose composites with ferrous ions by mixing aqueous solutions of the polymers (or composites) and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ at room temperature.

The reaction of the composites with metal ions was studied by spectrophotometry, IR spectroscopy, x-ray phase and x-ray fluorescence analysis, electron microscopy, differential scanning calorimetry, and thermogravimetric analysis.

The IR spectral study of the new polymer complexes showed (Fig. 1) that the introduction of ferrous ions into the composite material derived from dialdehyde cellulose and guanidine acrylate derivatives both in radical polymerization and upon mixing leads to significant change in their IR spectra.

Kh. M. Berbekov Kabardino-Balkaria State University, Nalchik, Russia. E-mail: azamat-z@mail.ru. Translated from *Khimicheskie Volokna*, Vol. 49, No. 6, pp. 92-96, November—December, 2018.

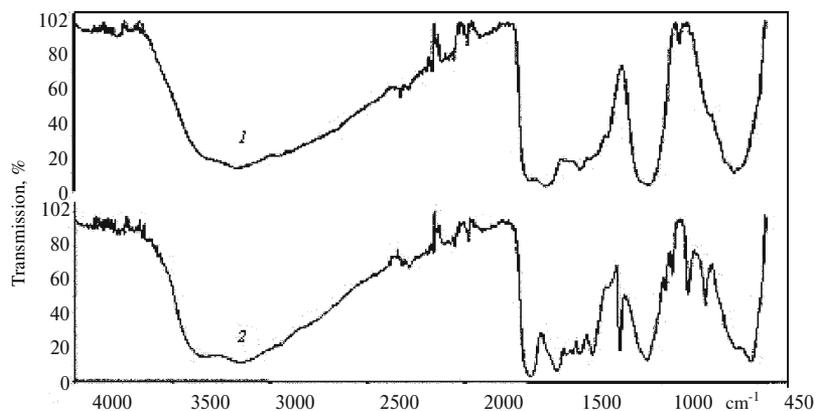


Fig. 1. IR spectra of PAG/DAC (1) and PAG/Fe²⁺/DAC (*in situ*) (2).

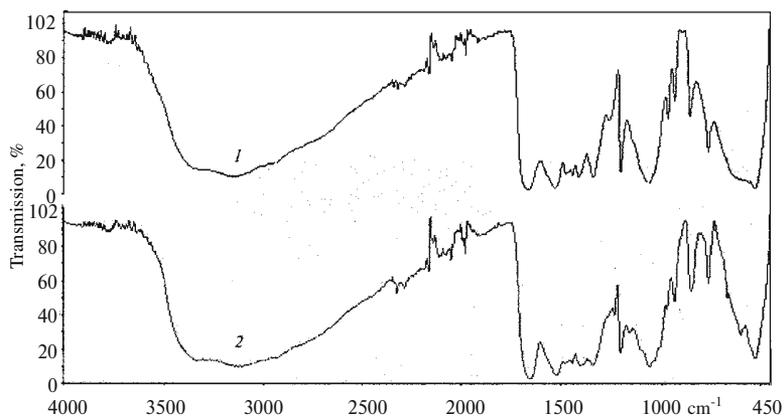


Fig. 2. IR spectra of PMAG/DAC (1) and PMAG/Fe²⁺/DAC (*in situ*) (2).

The IR spectra of the starting DAC/PAG composite and the new compound DAC/PAG/Fe²⁺ show virtually complete redistribution of the absorption bands. The interaction with the guanidine fragment is indicated by the significant broadening of the NH stretching bands of the guanidine cation at 3385 and 3100 cm⁻¹. The increase in intensity and appearance of new absorption bands at 1479, 1444, 1258, 847, and 764 cm⁻¹ indicate that the ferrous ions are found in the structure of the DAC/GA composite due to an interaction with the carboxylate ion oxygen atoms and amino group nitrogen atoms of guanidine acrylate. The IR spectra also demonstrate an interaction with the cellulose fragment of the composite. For example, in the DAC/PAG/Fe²⁺ composite, there is considerable enhancement of the intensity of the peaks at 1100-1160 cm⁻¹, corresponding to dialdehyde cellulose.

The appearance of a narrow peak at 670 cm⁻¹ and several small absorption bands in the low-frequency region in the IR spectrum of DAC/PAG/Fe²⁺ indicate the formation of a new coordination compound. Analogous behavior was also seen for the PMAG/DAC composite with ferrous ions (Fig. 2).

The peaks, which appear in the vicinity of 600 cm⁻¹ in all cases, were assigned to stretching vibrations of the SO₄²⁻ group located in the external coordination sphere of the complex.

Comparative analysis of the IR spectra of the metal-polymer composites obtained by mixing (method 2) shows that, in contrast to the complexes obtained by radical polymerization, there is virtually complete redistribution of the band intensities (Fig. 3).

Thus, the IR spectra of PAG/Fe²⁺/DAC show greater intensity of the peak at 1539 cm⁻¹, the appearance of small peaks at 1480, 1444, and 1403 cm⁻¹, and splitting of the peak at 1055 cm⁻¹ of the starting composite with formation of several bands at 1190-1057 cm⁻¹, corresponding to peaks of adsorbed water. In addition, new peaks appear at 847 and 764 cm⁻¹, which correspond to the M-N bond, while the peak of the starting polymer at 614 cm⁻¹ disappears and peaks for the M-O bond appear at 590-524 cm⁻¹.

Hence, the formation of the composite cellulose-containing polyguanidines with ferrous ions upon mixing (method 2) occurs as the result of replacement of water molecules in the coordination sphere of the solvated metal ion by

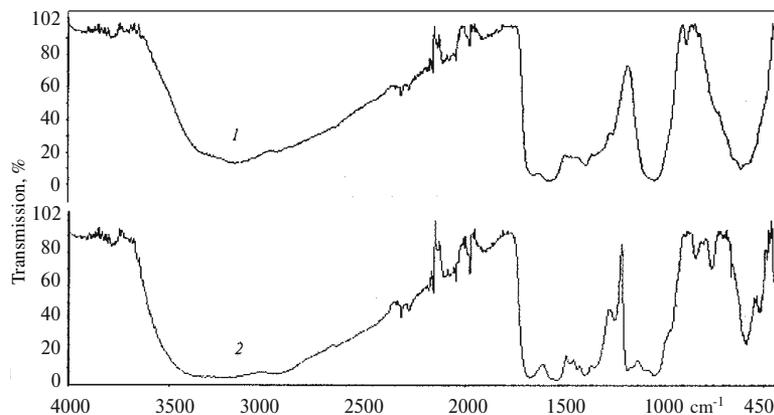


Fig. 3. IR spectra of PAG/DAC (1) and PAG/Fe²⁺/DAC (obtained by mixing) (2).

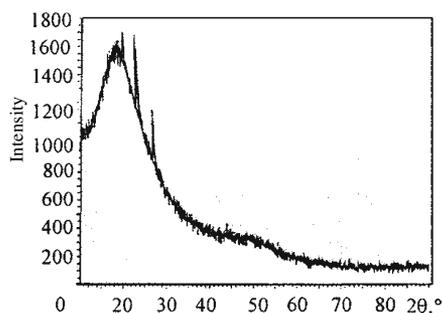


Fig. 4. Diffractogram of the DAC/PAG composite.

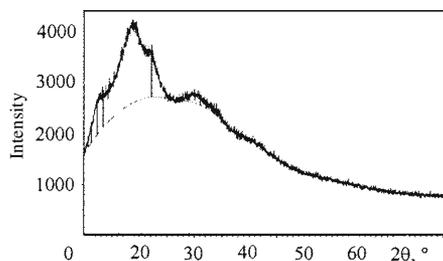


Fig. 5.

Fig. 5. Diffractogram of PAG/Fe²⁺/DAC (*in situ*).

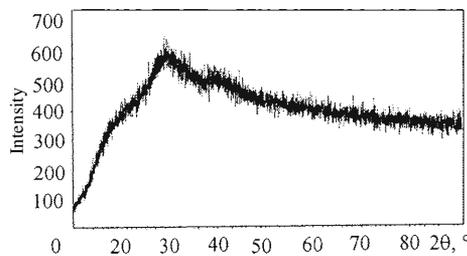


Fig. 6.

Fig. 6. Diffractogram of PAG/Fe²⁺/DAC (prepared by mixing).

OH groups of dialdehyde cellulose and the interaction of ferrous ions with the carboxylate ions and guanidine groups on the composite surface. The hydrated metal ions in solution cannot penetrate into the narrow interfibrillar spaces of dialdehyde cellulose due to their large size. Thus, the adsorption of the metal ions occurs predominantly on the surface of the large pores of the composite material.

The x-ray data show that the starting PAG/DAC composite has predominantly amorphous structure (Fig. 4).

The introduction of metal ions into the PAG/DAC matrix by radical polymerization leads to a change in the supramolecular structure as seen in the diffractogram of the complex given in Fig. 5. The peaks corresponding to the crystalline segments of the composite are smoothed out, indicating enhanced amorphization.

Complete recrystallization is observed when the metal-polymer composite was prepared by the mixing method (Fig. 6).

The observed change in the supramolecular organization of the composite is related to the disappearance of internal strains in cellulose upon the adsorption of water and hydrated metal ions. The water and hydrated metal ions penetrate between the dialdehyde cellulose macromolecules into less ordered regions, displacing them. This leads to rearrangement of the supramolecular structure.

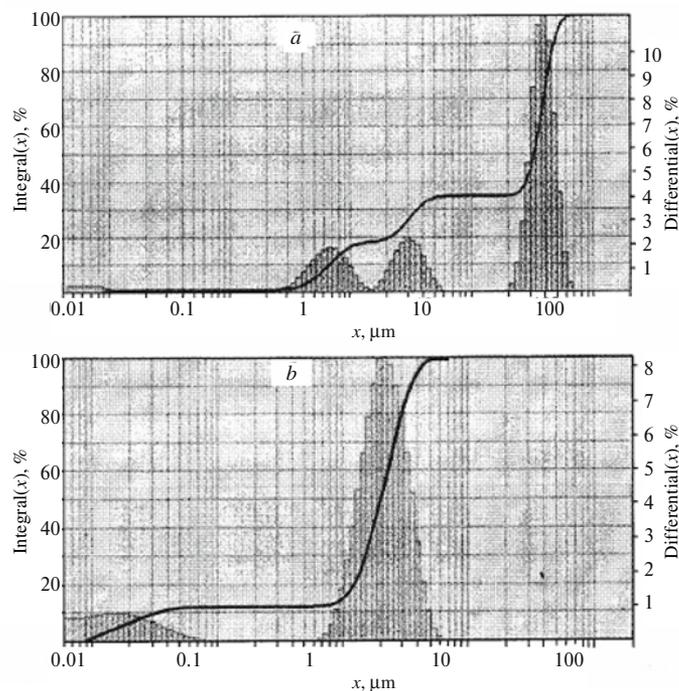


Fig. 7. Size distribution of particles in metal complexes PAG/Fe²⁺/DAC (a) and PMAG/Fe²⁺/DAC (b)

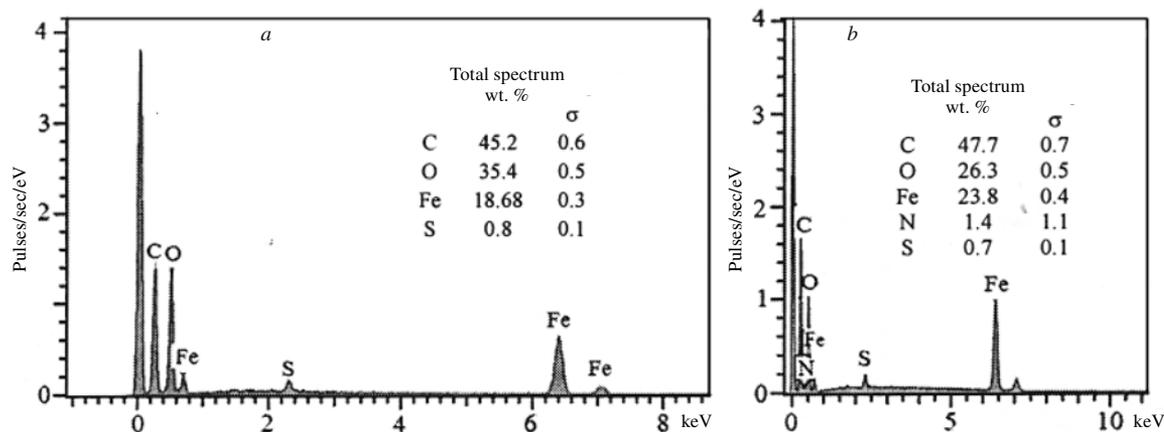


Fig. 8. X-ray microanalysis spectra for PAG/Fe²⁺/DAC (*in situ*) (a) and PAG/Fe²⁺/DAC (mixing) (b).

Electron microscopy and particle size diffraction analysis showed that both nano- and microparticles with diameter ranging from 10 nm to 100 μm are obtained upon the formation of the polymer metal complexes depending on the structure of the polymer macroligand (Fig. 7). The greatest content of the nanoparticle fraction in the complexes is 10%.

Particles with a narrow size distribution were shown to be formed in the composites. This finding indicates that during the radical polymerization the composite macromolecules efficiently stabilize the growing particles containing a new metallic phase while they are still rather small, forming a unique protective shield on their surface.

Litmanovich et al. [4, 5] have discovered pseudo-matrix character in the formation of particles of the new phase in polymer solutions, specifically, cessation of particle growth due to shielding of their surface upon the formation of a thermodynamically-stable macromolecule nanoparticle complex upon reaching a certain particle size.

X-ray microanalysis of segments of the metal complex samples given in Fig. 8 showed that a greater content of the metallic phase is found in the composites obtained by mixing in aqueous solution. We should note that in both cases, the electron microscopy data showed that porosity is greater for the metal composites obtained by the mixing method.

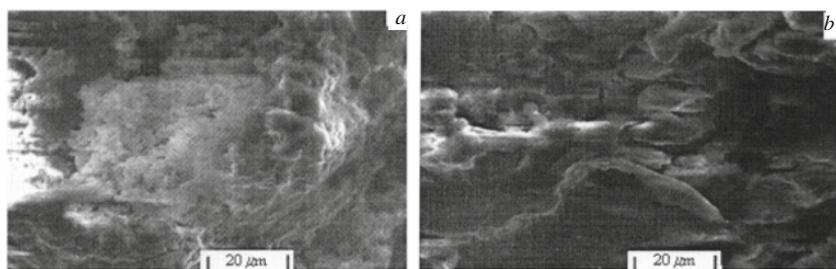


Fig. 9. Microphotographs of PMAG/Fe²⁺/DAC (*in situ*) (a) and PMAG/Fe²⁺/DAC (mixing) (b).

The dialdehyde cellulose metal-polymers have a loose three-dimensional structure. The surface morphology of the polymer composite with metal ions is significantly different from that of the starting composite and has well-developed sponge-like porous structure with many channels (Fig. 9). This may be an important feature providing for reagent transfer when the composites are used as catalysts of various chemical reactions or the controlled delivery of drugs.

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