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MACROMOLECULAR COMPOUNDS AND POLYMERIC MATERIALS

Synthesis and Thermal Solid-Phase Transformations of Cellulose–Iron(II, III) Oxide Composite

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Abstract—Possibility of obtaining cellulose–iron(II, III) oxide composites with various component ratios was studied. The specific magnetization of the material was determined in relation to the mass fraction of the magnetic component in the composite.

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Development and synthesis of polymeric composites with prescribed functional (including magnetic), electrical, and other properties is a topical task for modern materials science. The undiminishing researchers' interest in composite polymeric materials is due to the fact that, in some cases, additives introduced into polymers provide a fundamental change in their properties. Because of the combination of properties of a polymer and filler, the composite as a whole becomes a new material suitable for some practical applications.

It is known that such a natural polymer as cellulose can be used to create salt-containing composites and convert them by pyrolysis into, depending on the medium, metal–carbon materials [1], fibers of refractory oxides [2], and complex oxide compounds [3], which can serve as intermediates for obtaining practically important materials.

In this study, a cellulose composite containing iron(II, III) oxide of the magnetite modification was prepared. Owing to the magnetic properties of the oxide component, the composite may find direct practical application. Some aspects of solid-phase thermal transformations of the cellulose composite in a vacuum and in air were studied.

EXPERIMENTAL

The cellulose composite with inclusion of finely dispersed iron(II, III) particles is prepared by carrying out a number of successive procedures. First, cellulose is impregnated with a solution of iron(II) sulfate and iron(III) chloride salts mixed in a 1 : 2 molar ratio, with the concentrations of the salts equal to 0.75 and 1.5 M, respectively, at a solid–liquid impregnation ratio of 2 ml g^{-1}. Then follows treatment of the salt-containing cellulose with a concentrated sodium hydroxide solution; washing of a sample with distilled water to remove the unchanged alkali, sodium chloride and sulfate formed in the reaction, and excess amount of iron oxide not fixed on the fabric; and drying. The starting cellulose was preliminarily subjected to mercerization with a 17% sodium hydroxide solution at 18°C for 30 min.

The content of iron oxide (Fe_3O_4) in the cellulose composite obtained using the above scheme was found gravimetrically after thorough washing and drying of the samples and on a Netzsch STA 449C combined thermal analyzer (Germany) by thermal gravimetric analysis (TG) from the mass of the residue formed on burning a sample in an oxygen atmosphere. In addition to measuring the mass change on the thermal analyzer, heat effects were determined by differential scanning calorimetry (DSC) on heating the samples in the temperature range from room temperature to 600°C.

The phase composition of the samples was analyzed with a DRON-3.0 X-ray diffractometer with iron-filtered CoK_α radiation (λ = 1.6208 Å). The morphology of the cellulose–Fe_3O_4 composite was analyzed by scanning electron microscopy (LEO-906 E, FRG).

The magnetic properties (specific magnetization) of samples were determined on a Faraday balance. A cotton fabric was chosen as the starting cellulose

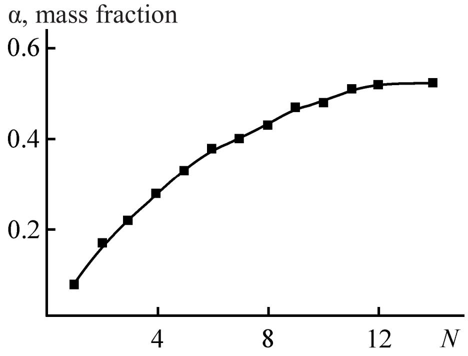

Fig. 1. Fe_3O_4 content α in the iron oxide–cellulose composite vs. the number *N* of sorption–deposition cycles.

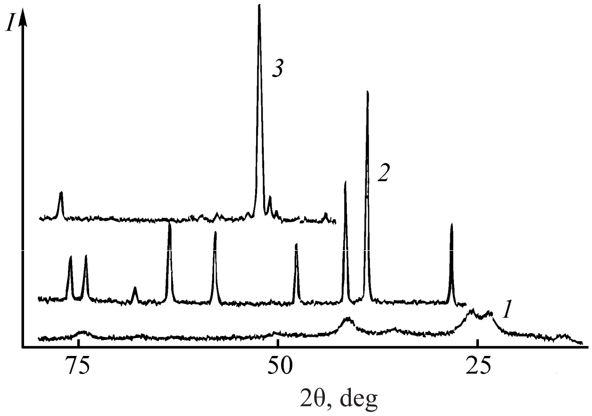

Fig. 2. X-ray diffraction patterns of (*1*) iron oxide–cellulose composite with a Fe_3O_4 mass fraction of 0.27 and of products of its thermal transformations (*2*) in air and (*3*) in a vacuum. (*I*) Signal intensity and (2θ) Bragg angle.

material. Its mercerization with a sodium alkali in the first stage was performed to impart a developed internal sorption surface. It is known that alkaline hydrolysis of a mixture of salts of bi- and trivalent iron with a molar ratio of, respectively, 1 : 2, yields Fe_3O_4 (magnetite) [4]. After impregnation of the cellulose fabric with a stoichiometric mixture of the iron salts and treatment of the iron-containing cellulose with sodium hydroxide, the gain weight due to Fe_3O_4 in a sample is about 80 wt %. However, the X-ray diffraction pattern of the sample contains only reflections at Bragg angles of 14.0°, 23.5°, and 25.3°, which are characteristic of cellulose II and appear upon treatment of natural cellulose (cellulose I) with a concentrated alkali in the first stage [5]. A similar result, lack of an X-ray diffraction evidence of the inorganic phase deposited onto the polymeric matrix, has been observed for cellulose structurally modified with 68% nitric acid and impregnated with an organic salt [3]. This fact is attributed to formation of isolated X-ray amorphous iron oxide particles within the internal system of pores and capillaries and on the fiber surface.

The amount of magnetite capable of being retained in the cellulose matrix without any noticeable washing-out and desorption was raised by performing multiple cycles of impregnation of the cotton fabric with a mixture of salts of bi- and trivalent iron, taken in a prescribed ratio, and an alkaline treatment of the salt-containing cellulose. As the number of these cycles increases, the sorption equilibrium in the system approaches saturation (Fig. 1). In this case, the maximum mass fraction of magnetite in the composite reaches 0.54. In the X-ray diffraction pattern of a sample subjected to three sorption–deposition cycles (Fig. 2, curve *1*), there appear reflections characteristic of magnetite at 2θ = 35.1°, 41.4°, 50.4°, 67.2°, and 74.1°. The average crystal size *L* found by the Scherrer formula [6] is 5.0 nm. As follows from electron micrographs (Fig. 3), magnetite deposited onto cellulose in the initial cycles rather uniformly covers fabric fibers, and only upon the saturation of the surface with magnetite, separate crystals start to be formed. The specific magnetization of the samples grows with the number of sorption–deposition cycles. As seen from the table, it reaches 14.0 A m^2 kg^{-1} at room temperatures in a magnetic field with a strength 3.97×10^5 A m^{-1}.

The cellulose–iron(II, III) composite obtained acquires magnetic properties and retains mechanical properties characteristic of cellulose, primarily elasticity and ability to take on a prescribed shape, which enables its direct use as elastic magnetic shields against electromagnetic radiation [7].

A study of the solid-phase thermal transformations of the cellulose composite in a vacuum and in air revealed a number of specific features of its thermal decomposition, compared with cellulose. The thermal treatment in a vacuum was performed at a residual pressure of 1.3 Pa with the temperature raised at a rate of 10 deg min^{-1}; after the final temperature of annealing was reached, the samples were kept under isothermal conditions for 60 min.

Our experiments showed that annealing of composite samples with varied content of Fe_3O_4 without admission of air up to temperatures of 800°C led to transformation of cellulose fibers to carbon fibers and of Fe_3O_4 particles to Fe particles. As a consequence, the specific magnetization of the samples substantially increased and exceeded by approximately an order of

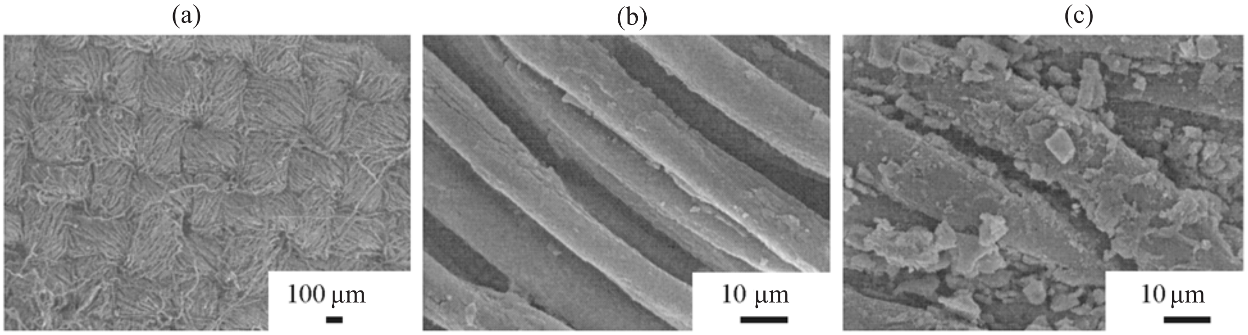

Fig. 3. SEM micrograph of iron oxide–cellulose samples. (a) General view of the composite material; Fe_3O_4 mass fraction in the composite: (b) 0.27 and (c) 0.54.

magnitude the maximum magnetization of the starting cellulose–oxide composite. The specific magnetization of the samples also grows with the number N of sorption–deposition cycles to reach 160.3 A m^2 kg^{-1}.

The formation of the iron phase in the carbon composite matrix is confirmed by the X-ray diffraction pattern of a sample with Fe_3O_4 mass fraction of 0.27, thermally treated in a vacuum (Fig. 2, curve *3*). Figure 2 shows that the X-ray diffraction pattern contains basic α-Fe reflections, with a crystallite size of approximately 30.0 nm. According to a calculation, the content of iron in this sample is 65 wt %. In the cellulose–iron oxide sample with a Fe_3O_4 mass fraction of 0.54, subjected to a similar treatment, the mass fraction of iron reaches 1.0. The sample composed of a purely iron phase retains the structure of the precursor composite and, upon annealing in a vacuum at 1050°C, transforms into a high-strength metallic fabric-grid. In thermal transformations of the oxide–cellulose composite in a vacuum, the iron phase is apparently formed in the same way as it does in thermal treatment of cellulose impregnated with salts of variable-valence inorganic cations, as a result of a chain of transformations: $Fe_3O_4 \rightarrow FeO \rightarrow Fe$ [8]. The procedure described in [8] is intended for synthesis of iron–carbon fibrous materials that contain approximately 10 wt % iron, exhibit important magnetic and catalytic properties, and are pyrophoric.

It should be noted that fully porous metallic fibrous structures can be produced from salt-containing cellulose [9]. However, as noted in [10], their synthesis requires a considerable change in the experimental conditions: in particular, the thermal treatment of salt-containing cellulose should be performed in the medium of ammonia decomposition products at 900–1000°C. As follows from the results obtained, by setting a certain content of Fe_3O_4 in a composite, it is possible to obtain upon its thermal treatment either an iron–carbon composite or a nearly single-phase product that is composed of α-Fe and reproduces the fabric texture of the precursor composite. The specific magnetization of the single-phase product exceeds by an order of magnitude that of the oxide–cellulose precursor composite.

The main aspects of thermal transformations of oxide–cellulose samples in air were found by analysis of their TG and DSC curves. Figure 4a shows TG curves of thermal decomposition of cellulose modified with a 17% sodium hydroxide solution. It can be seen that the thermal degradation of cellulose subjected to an activating treatment with the alkali occurs in two stages. In the first stage of intensive thermal decomposition, which involves with the main loss of mass, the tarry fraction burns out in a narrow temperature range, with the maximum of the exothermic effect at 340°C. The second, low-intensity stage of smoldering of the carbon residue ends at 520°C. The thermal decomposition of the oxide–cellulose composite almost ends at a temperature 200°C lower than that for cellulose. Accord-

Specific magnetization of the iron(II, III) oxide–cellulose composite, σ, and iron–carbon composite, σ', at room temperature at a field strength of 3.97 × 10^5 A m^{-1}

Number N of sorption–deposition cycles	σ	σ'
	A m^2 kg^{-1}	
3	9.6	95.2
8	13.7	116.4
12	14.0	160.3

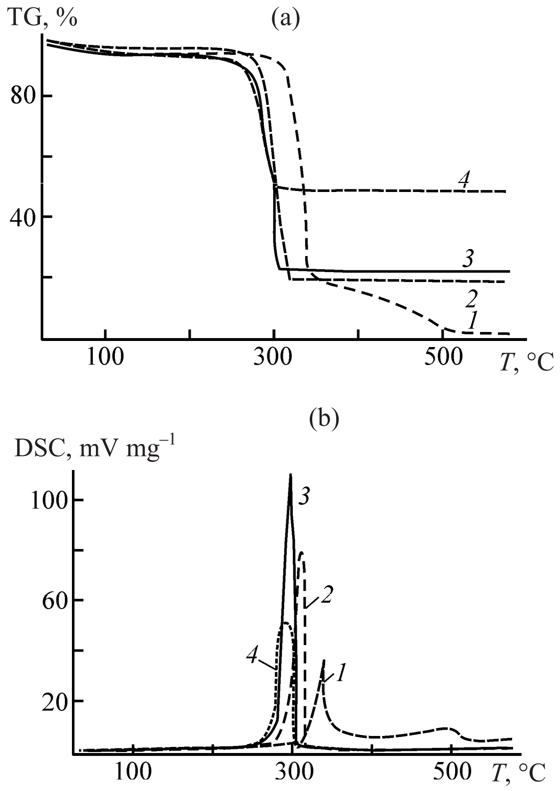

Fig. 4. (a) TG and (b) DSC curves: (*1*) cellulose activated with a 17% aqueous solution of sodium hydroxide and (*2–4*) cellulose–iron oxide composites with Fe_3O_4 mass fraction of 0.21, 0.27, and 0.54, respectively. (*T*) Temperature.

ing to the DSC data in Fig. 4b, the thermal decomposition of the composite occurs with a higher total heat release and the maximum of the exothermic effect lies at 295–313°C depending on the Fe_3O_4 content of a composite, i.e., lower than the low-temperature peak associated with the decomposition of the cellulose matrix (340°C). The second stage of the process, the smoldering of the carbon residue, is not separated by a time–temperature interval from the first stage. Apparently, the intensification of the thermal decomposition of the cellulose matrix in the composite is due not only to the catalytic effect of the filler, but also to the occurrence of the exothermic reaction

$$Fe_3O_4\ (FeO,\ Fe_2O_3) \rightarrow \alpha\text{-}Fe_2O_3.$$

In all probability, the metal phase is not formed in thermal decomposition of the oxide–cellulose composite in air, in contrast to the case of its thermal treatment in a vacuum. This is indicated by the fact that the X-ray diffraction pattern of an oxide–cellulose composite subjected to thermal treatment at temperatures lower than the onset temperature of the exothermic effect (260°C) contains no iron phase.

As follows from the DSC data, the magnitude of the exothermic effect, found from its area, in thermal decomposition of samples with Fe_3O_4 mass fraction of 0.21, 0.27, and 0.54 is 10 940, 13 990, and 15 730 J g^{-1}, respectively, in terms of the cellulose base, which exceeds the corresponding value for cellulose (7600 J g^{-1}). In other words, the cellulose–iron oxide composite is a more efficient energy carrier than cellulose. In this context, an attempt was made to subject the composite to thermal treatment by its initiated firing. The experiments performed demonstrated that, in initiated firing of oxide–cellulose composites with varied weight fraction of Fe_3O_4 (including the maximum mass fraction of 0.54), the cellulose base completely burns out at the combustion front to give α-Fe_2O_3 with L = 30.0 nm according to X-ray diffraction data (Fig. 2, curve *2*). The annealed sample reproduces the texture of the starting fabric and, on being touched, crumbles without special dispersion into a dark red, loose soft, by touch, powder of anisotropic particles, microfibers. This circumstance is important, e.g., when oxides are used as pigments for polymers [10] or as synergists of fire-retardant additives to polymers [11], because, in this case, oxide microfibers arranged along chains of polymer macromolecules impair the performance characteristics of the polymer to a lesser extent than do spherical particles of oxides [12].

Thus, the oxide–cellulose composite, which is a microheterogeneous system with numerous phase boundaries, is less thermally stable than cellulose. Serving as a carrier matrix in the composite, modified cellulose fibers execute in combustion, because of the vigorous gas evolution, an additional function of a dispersant and homogenizer of the forming final degradation product, oxide stock. The thermal transformations of the composite in air are accompanied by a stronger exothermic effect than those in the case of cellulose. This circumstance enables synthesis of finely dispersed α-Fe_2O_3 in the self-propagating combustion mode, similar to the known self-propagating high-temperature synthesis [13].

CONCLUSIONS

(1) A cellulose–iron(II, III) oxide composite material was synthesized. The material combines the magnetic properties characteristic of Fe_3O_4 with the elastic-

ity of cellulose, which enables its use as magnetic shields.

(2) The relative amounts of cellulose and Fe_3O_4 in the composite, necessary for its complete transformation in thermal treatment in a vacuum into an almost single-phase product having the form of α-Fe with the fabric texture of the precursor composite, were determined. The specific magnetization of the single-phase product is an order of magnitude higher than that of the composite.

(3) The possibility of conversion of the composite into α-Fe_2O_3 in air at the self-propagating combustion front was demonstrated.

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