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Structure and Thermal Stability of the Polymer - Magnet Nanocomposites

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It is studied a structure and thermal behavior of the hybrid polymer magnetic composites based on a high dispersive magnetite and polystyrene - butyl acrylate copolymer obtained by suspension polymerization. According to structural studies, the nanostructure of composite is formed in results of encapsulating of the magnetite particles by the polymer shells. A thermal behavior of the hybrid composite indicates the several stages of thermal decomposition process and significant reduction in the thermal stability of the copolymer matrix under the influence of magnetite.

Key words: hybrid nanocomposites, magnetite, styrene - butyl acrylate copolymer, thermal destruction, structure.

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Introduction

Nowadays, the magnetic nanocomposites are of great importance because of their potential application in the different fields of industry. They are part of electrical, optical or magnetic components in sensors, electro-magnetic shields and displays in microelectronics and even in biomedicine [1 - 4]. Those composites are expected to have novel properties due to reduction in particles size and the dispergation of the particles in a polymer matrix which protects them from degradation. Furthermore, the matrix also allows to regulate an interparticle interaction and size distribution and, therefore, it is possible to tune the final properties of the composite.

Among the intensive investigation in the field of the magnetic polymer composites a question on the interconnection between their structure and thermal stability is not finally solved. In the series of investigations was observed the effect of magnetite both on increasing and decreasing of thermal stability [3, 4]. So, in the each case for polymer-magnetic composites an investigation of the thermal stability is necessary. In the present work we studied the structure and thermal behavior of the polymer-magnetite composites synthesized on the basis of styrene - butyl acrylate copolymer and magnetite particles with high degree of dispersity.

I. Experimental

Polymer magnetic composites were obtained by suspension copolymerization of styrene (St) with butyl ester of acrylic acid (BA) in the presence of high dispersion magnetite (Fe₃O₄), the peroxide initiators of polymerization and the stabilizers as described in [5]. The magnetite nanoparticles were synthesized by alkaline hydrolysis of iron (II) and iron (III) salts and stabilized by sodium salt of oleic acid. Content of magnetite in composition was from 10 to 30 % (mass) in relation to monomer quantity. St and BA monomers were in mass ratio of 85:15. The polymerization was carried out at the temperatures of 65 – 80 °C during 8 – 10 hours. Obtained products were separated, rinsed by water and dried at the temperature of 60 °C to constant mass. In result the dispersive powders with specific density from 1.05 to 1.25 g/cm³ were prepared.

XRD powder diffraction data were collected on automatic diffractometer DRON-2.0M (Bragg-Brentano geometry, $q/2q$ -scanning; Fe $K\alpha$ radiation, 2θ -range $15.00 \leq 2\theta \leq 130.00$ ° with step 0.025 °; scan time 1.5 s/step). X-ray phase analysis was performed using the Powder Cell and LATCON programs. Structural investigations of the obtained composites was carried out with help of the atomic force microscope "Solver P47 – PRO" at a semi-contacting regime.

Thermal decomposition of composites was investigated with a derivatograph Paulic-Paulic-Erday

system “Q – 1500 D” in air atmosphere in a temperature from 20 to 500 °C. Heating rate was 10 degree/min. Al₂O₃ annealed at 1000 °C was used as a standard. In all cases the sample mass was provides the polymer content in composites was equal to 100 mg. The specific density of the composites was defined by the pycnometric method [6].

II. Results and Discussion

A typical XRD powder pattern of synthesized nanoparticles of magnetite Fe₃O₄ (Fig. 1,a) shows the broadened diffraction peaks of semi-amorphous samples and confirms the presence of cubic Fe₃O₄-phase of spinel-type structure [7], space group *Fd-3m*, lattice parameter $a = 8.3490(3)$ Å. Micro-structural analysis, i.e. determination of the average apparent size and average max strain of grains, was performed by simplified integral breadth methods, using the profile fitting procedure, gives the calculated average grain sizes of Fe₃O₄ to be (75.5 ± 7.3) Å or near 8 nm. This value is in

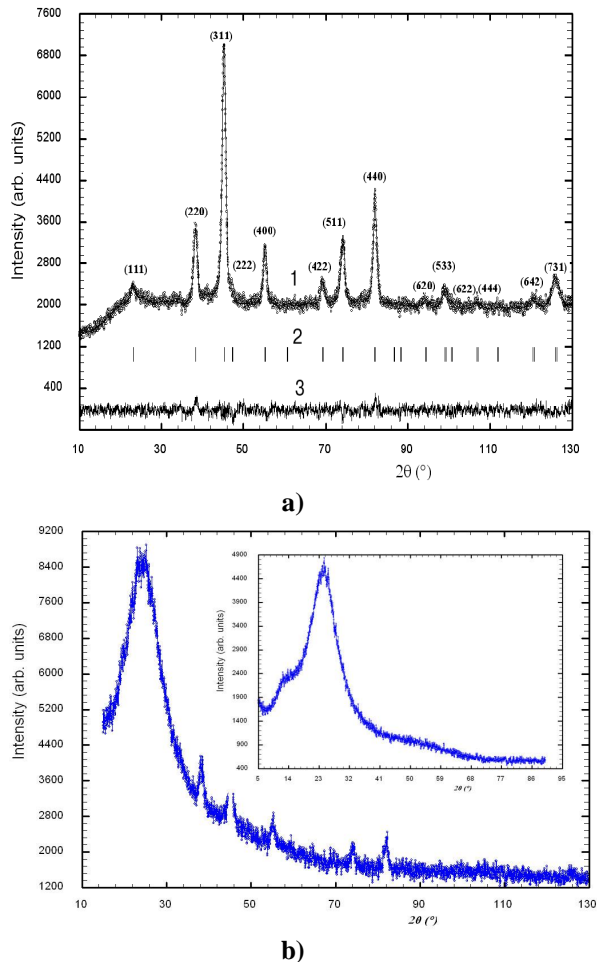


Fig. 1. (a). Observed (circles), calculated (solid line) and difference (bottom) X-ray powder profiles with hkl indices for sample Fe₃O₄ stabilized by sodium oleate; (b) X-ray diffractogram of (St-BA) copolymer-magnetite composite with magnetite content of 12 mass.%. Inset: X-ray diffractogram of the (St-BA) copolymer.

a good agreement with data of [8] for the magnetite synthesized by alkali hydrolysis of ferric salts. For the magnetite nanoparticles stabilized by sodium oleate as surfactant an average size of grain is $89.4 (\pm 5.7)$ Å due to adsorption of surfactant molecule around the magnetite nanocrystals.

XRD powder patterns of the copolymer-magnetite samples (Fig. 1,b) confirm the formation of Fe₃O₄ – copolymer hybrid nanocomposites. While the polymer matrix provides only an amorphous halo (Fig. 1,b, inset), X-ray diffractograms of composites are also characterized by the presence of crystalline peaks of the magnetite (Fig. 1,b).

It is found that lattice parameter a approximately equal within the range of standard uncertainties, but for composite samples it has a higher value of $a = 8.351(3)$ Å. From the other hand the low intensity diffraction peaks of cubic Fe₃O₄-phase (e.g. (222), (620), (622), (444), (642)) practically do not appear on powder patterns of composites (see Fig. 1,a, b). The determined average apparent size of grains for these samples is greater than size of Fe₃O₄-nanoparticles and achieves 110 – 120 Å. This can be explained as a result of encapsulation of magnetite by the copolymer shell.

The grains of the synthesized composites dispersed in water demonstrate ability to some nanoscaled agglomeration of multiple nanoparticles [9] with formation the aggregates by spherical form. This aggregation stopped at certain length scale probably because the presence of thin polymeric shells

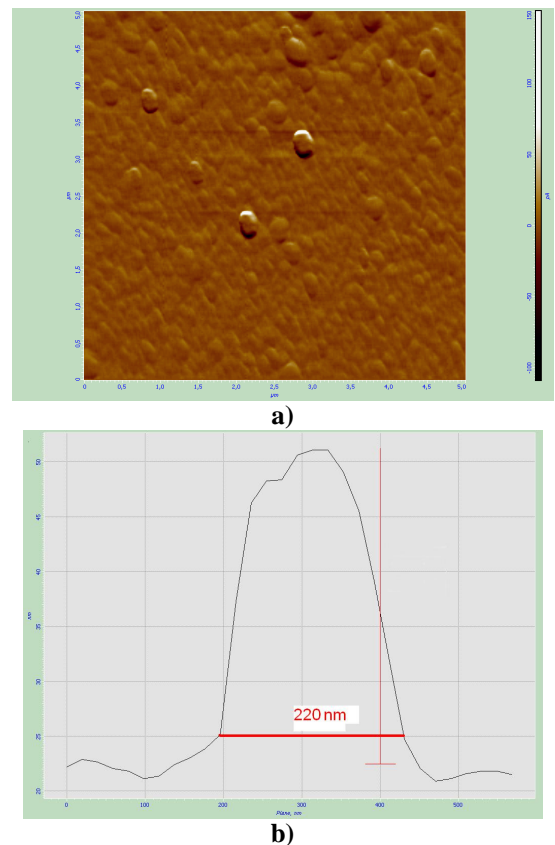


Fig. 2. AFM image of copolymer-magnetite nanocomposite (a) and histogram of size distribution of nanoparticles (b).

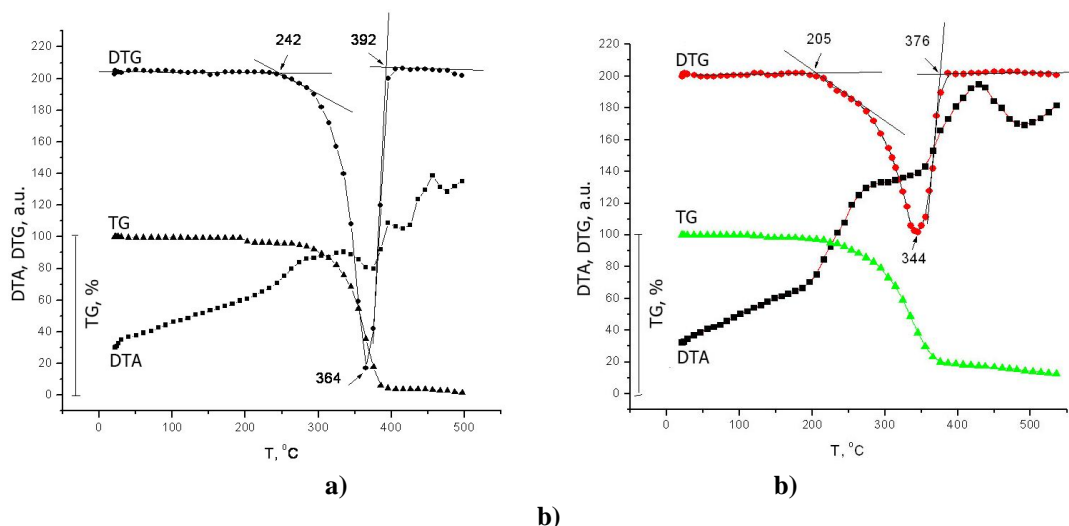


Fig. 3. Derivatograms of thermal decomposition of (a) poly(St-BA) (85:15) copolymer and (b) copolymer-magnetite nanocomposite at magnetite content of 25 mass %.

Table 1

Characteristic temperature of thermal destruction of St-BA copolymer (85:15) and it's composites with magnetite

Magnetite content, mass %	Characteristic temperatures and mass loss (Δm)					
	T_{init} , °C	Δm , %	T_{max} , °C	Δm , %	T_{fin} , °C	Δm , %
0	242	2,2	364	62,5	392	98
12	223	2,3	351	63,8	378	87
25	205	2,2	344	60,5	376	75
28	207	2,5	336	67,8	376	72

surrounding the particles prevented them from further approaching to each other. Fig. 2 presented the AFM image of the polymer-magnetite composite precipitated from water dispersion. A size distribution of composite particles indicates that main part of the nanospheres has a size between 200 and 220 nm (Fig. 2,b).

It was found that content of magnetite in polymer matrix has effect on the all complex of physical - chemical properties of the composites — their microhardness, specific density and thermo-mechanical characteristics in comparison to non-filled copolymer [5]. It provides a reason to suggest that magnetite has effect also on the thermal stability of the copolymer matrix and hybrid composites in overall.

It found that pure St-BA copolymer under heating in the interval of 20 – 500 °C begins to decompose at 242 °C (Fig. 3,a) and demonstrates an endothermic peak at $T = 364$ °C. This peak position is in a good agreement with maximum rate of mass loss of the copolymer (extremum on *DTG* curve). A residual mass of the copolymer samples at 500 °C is 2.2 - 2.5 % from initial mass, a degree of the thermal destruction determined as relative mass loss of samples (Δm , %) for St-BA copolymer is 98 %. Practically full destruction of copolymer is achieved at 390 – 392 °C independently on copolymer composition, because a thermal decomposition of these polymers followed by radical-

monomer mechanism through $-\text{CH}_2-\text{CH}_2-$ bonds [10].

As shown by thermogravimetric analysis, formation of hybrid polymer-magnet composites has a certain effect on the process of thermal decomposition of copolymer matrix (Fig. 3,a, b). In particular, the start temperatures of polymer backbone destruction (T_{init}) are noticeable shifted to the lower temperature values in comparison with a pure copolymer. As one can see from the Table 1, for composites $T_{init} = 205 - 207$ °C, while for copolymer $T_{init} = 242$ °C, which indicates on the sharp decreasing of the thermal stability of polymer matrix. Maximum of mass loss for composites observed at $T_{max} = 344 - 346$ °C. Beside this, on *DTG*-curve (Fig. 3,b) it is observed a clear assymetry of the descending branch of *DTG* maximum, which is evidence of several stages of the thermo-destruction process.

This phenomenon perhaps has an adsorption nature, connected with existence of two forms of copolymer matrix in the composites, namely, copolymer, attached to the magnetite surface by adsorption, which primarily undergoes to process of thermooxidative destruction, and copolymer in the bulk of the composite. In this case a thermal behaviour of polymer is connected only with polymer nature and strength of the chemical bonds.

Practically full destruction of copolymer in the composites is achieved at 376 - 380 °C, the residual mass (25 – 28 %) corresponds to mass fraction of the

magnetite with a high thermal stability [3, 4].

While we deal with thermooxidative destruction, a sharp decreasing the thermal stability of the polymer backbone in the presence of magnetite probably caused by a catalytic effect of the magnetite nanoparticles [10]. It may be suggested, Fe_3O_4 as other metal oxides with variable valence act as effective catalysts for the processes of oxidation and thermal destruction of the polymer matrix.

Conclusions

The obtained hybrid composites were formed by encapsulating of magnetite by the polymer shell in the condition of suspension copolymerization of styrene and butyl acrylate in the presence of magnetite nanoparticles. A thermal behavior of the hybrid composites indicates the several stages of thermal decomposition process and significant reduction in thermal stability of the copolymer matrix under the influence of magnetite.

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Структура і термічна стабільність полімер-магнітних нанокмполітiв

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Вивчено структуру і термічну поведінку гібридних полімер-магнетних композитів на основі високодисперсного магнетиту і полістирен-бутилакрилатного кополімеру, отриманих методом суспензійної полімеризації. За даними структурних досліджень при формуванні композиту відбувається утворення наноструктур за рахунок інкапсуляції магнетиту полімерними оболонками. Термічна поведінка гібридних композитів вказує на стадійність процесу термічного розкладу та суттєве зменшення термічної стабільності полімерної матриці під впливом магнетиту.