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POLYMER-MAGNETITE THERMOSETTING COMPOSITES WITH PROTECTIVE AND ANTIRADAR FUNCTIONS

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ABSTRACT

The hybrid polymer-magnetite composites with antiradar and anticorrosive properties based on the thermoreactive epoxy resin filled with magnetite Fe_3O_4 particles and conductive conjugated polymer have been prepared. Dispersed magnetite Fe_3O_4 in a form of spherical particles with the diameter near 2 μm capable of not only absorb but also effectively scatter electromagnetic radiation served as magnetic filler for composites. The magnetite particles were stabilized via polystyrene shell that results in the formation of self-assembled molecular aggregates and provides overall stability of the system. Prepared polymer composites were characterized by X-ray and EDAX-analysis and by measuring of some physical properties. Variation in the size of Fe_3O_4 particles and their concentration in the composites has some effect on the elementary cell parameters of magnetite and has a complex effect on the magnetic susceptibility and microhardness of polymer-magnetite composites. It was found that composite containing magnetic microparticles and particles of polyaniline doped with *p*-toluene sulfonic acid in 1:1 ratio exhibits the strongest microwave absorption. At the same time this optimal composition provides high microhardness and anticorrosive properties of the coating on the surface of steel. The value of the relative water absorption of the composite coatings during 30 days of exposure in a moist chamber with a humidity of 95% turned out to be 5-6 times less as compared to an unfilled epoxy composition. The electrochemical potential of the steel surface coated with the developed thermosetting composition exhibits significant anode shift (by 0.3-0.4 V) at soaking in 3% aqueous NaCl solution, while the surface state of the coatings remained unchanged more than 30 days. The obtained results confirmed the sufficient corrosion resistance of the coatings and will be used for development of composites with special purpose.

***KEY WORDS**: magnetite-polymer composition, microhardness, corrosion, water adsorption.*

INTRODUCTION

Composite materials containing dielectric or semiconductor nanoparticles of a particular shape as well as periodical micro- and nanostructures capable of spatial redistribution of scattered electromagnetic radiation in desired directions are perspective for that task. Iron oxides, magnetite or Fe_3O_4 in particular are especially interesting among other components due to their ability to absorb electromagnetic waves of near IR and microwaves ranges [1]. Carbon threads or carbon nanotubes inclusions in magnetite-based composites may provide a synergetic effect, i.e. enhance electromagnetic energy absorption and improve anticorrosive properties of the metal surface [2, 3]. Successful applications of such coatings in atmospheric conditions and under the influence of periodical mechanical factors require high anticorrosion properties of those materials. To enhance the protective properties of polymer coatings based on thermosetting epoxy matrix the nanoparticulate magnetite is often used [3, 4]. We suggest filling in the composite with magnetite particles having a diameter commensurate with microwave's length that may provide an effective reflection and radiation scattering. In the present work the hybrid polymer-inorganic composite were prepared with microparticles of magnetite stabilized with polymer shell [5] during the process of synthesis. Instead of expensive and scarce nanotubes, we used a conductive polymer, polyaniline, as an organic additive.

The goal of presented work is to study an influence of magnetite and polyaniline content on the structure, morphology, mechanical and protective properties of thermosetting hybrid composition.

MATERIALS AND METHODS

Dispersed magnetite Fe_3O_4 in a form of spherical particles (granules) with the size of about 2 μm were separated by magnetic decanting from the magnetite suspension stabilized via polystyrene shell providing overall stability of the system [5-7].

To prepare the thermosetting polymer composition 2 g of epoxy α-resin ED-20 was mixed with 0.05 g of magnetite powder. After that 0.05 g of polyaniline powder doped with toluensulfonic acid (TSA) was added and carefully stirred followed by sonication for 10 minutes at room temperature 20 ± 1°C. To cure the obtained composition 0.24 g amine hardener PEPA was added to the prepared mixture and stirred thoroughly. The resulting composition formed a coating on the surface of steel with a thickness of 0.2 mm. The coating was kept for 2 hours for monolithization, and then annealed at 40–50 °C for one hour in the thermostat for final curing.

Prepared polymer composites were characterized by X-ray (DRON-2, FeKα-radiation), EDAX-analysis (REMMA-102-02), optical microscopes "Olimpus" and "Nicomed". Magnetic susceptibility was measured by Faraday method at room temperature. Microhardness of magnetite nanogranules and composites was measured by Heppler consistometer. The absorption spectra of the IR irradiation were obtained using a spectrometer MDR-23. The value of the relative water absorption of the composite coatings was estimated in the process of their exposure in a moist chamber with a humidity of 95 %. Measurement of the stationary potential of the coated specimens (relative to the Ag/AgCl) was performed in 3 % NaCl solution at 20 ± 2°C.

RESULTS AND DISCUSSION

The microparticles obtained after polymerization of styrene in the presence of magnetite Fe_3O_4 dispersion have a form of spherical particles (granules) with an average size of 2±0.5 μm (Fig. 1). XRD powder patterns of the magnetite dispersion stabilized via polystyrene shell (Fig. 2) indicate the formation of Fe_3O_4–PS composites. The diffraction peaks of cubic Fe_3O_4-phase with low intensity (e.g. (222), (620), (622), (444), (642) [5]) practically do not appear in powder patterns at the same time significant amorphous halo corresponding to PS is observed. This can be explained as a result of formation of a composite structure of magnetite particles capsulated by polymer shell [6, 7]. Variations in the size of Fe_3O_4–PS particles have some effect on the parameters of the elementary cell of magnetite and have a complex effect on the magnetic susceptibility and microhardness of magnetite–polymer composite (Table 1).

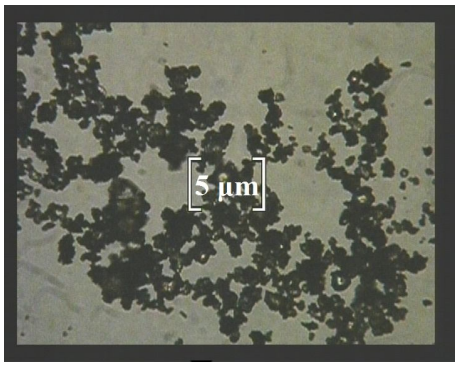


Fig. 1. Micrograph of the dispersion of magnetite stabilized by polystyrene shells. Average diameter of micro granules is 2 ±0.5 μm.

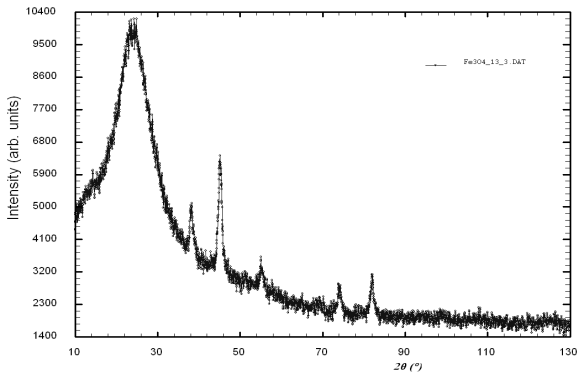


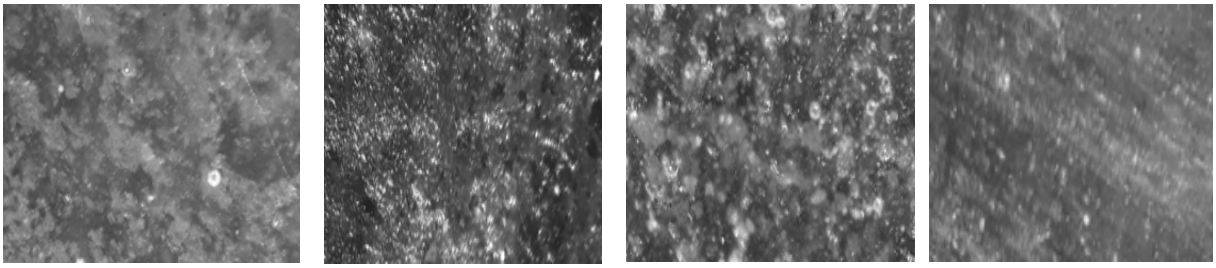
Fig. 2. X-ray diffraction spectrum of polystyrene-magnetite composite with magnetite content of 12.4 %.

Table 1. Physical properties of magnetite-polystyrene granules

Sample №	Granule size of Fe_3O_4 -PS composite, μm	Magnetic susceptibility $\chi \cdot 10^{-6}$, cm^3/g	Period of elementary cell, Å	Microhardness $F_\infty \cdot 10^{-8}$, N/m^2
1	1,5-1,7	1797	8,36(2)	2,45
2	1,7-2,0	1969	8,357(9)	2,47
3	2,0-2,5	2822	8,333(9)	3,03
4	2,2-2,5	2589	8,35(2)	3,89
5	2,5-3,0	2123	8,36(2)	2,78

Granules of Fe_3O_4-PS with the size of about 2 μm were used as magnetic filler for preparation of thermosetting polymer composites exhibiting antiradar and protective functions [2]. We suggest using a polyaniline doped with TSA as a complementary component that possesses intrinsic electron conductivity. This polymer is characterized by high specific conductivity at the level of $(3.0\pm0.3)\times10^{-2}$ S/cm, which provides a possibility to form the conducting channels inside the composite structure, that is necessary to enhance absorption and scattering of the electromagnetic radiation [1, 2].

Composite polymer prepared from thermosetting mixture based on epoxy resin, amine curing agent, different fillers and their mixture exhibits noticeable changes in microstructure of the coatings (Fig. 3, *a-d*). As one can see from the micrographs, the best uniform structure is observed for the composite contained mixture of fillers at their overall concentration of 10 % and weigh ratio 1:1 (Fig. 3, *d*). Probably, in this case better interaction of the components inside of composite takes place due the compatibility of magnetite microgranules surrounded by polystyrene shell and PANI doped with TSA (plasticizer) with hydrophobic epoxy matrix.



a *b* *c* *d*

Fig. 3. Micrographs of composites based on epoxy resin ED-20 cured with PEPA for different amount of fillers: *a* – magnetite 10 %; *b* – PANI-TSA powder (10 %); *c* – magnetite 10 % + PANI-TSA powder (10 %); *d* – magnetite 5% + PANI-TSA powder (5 %).

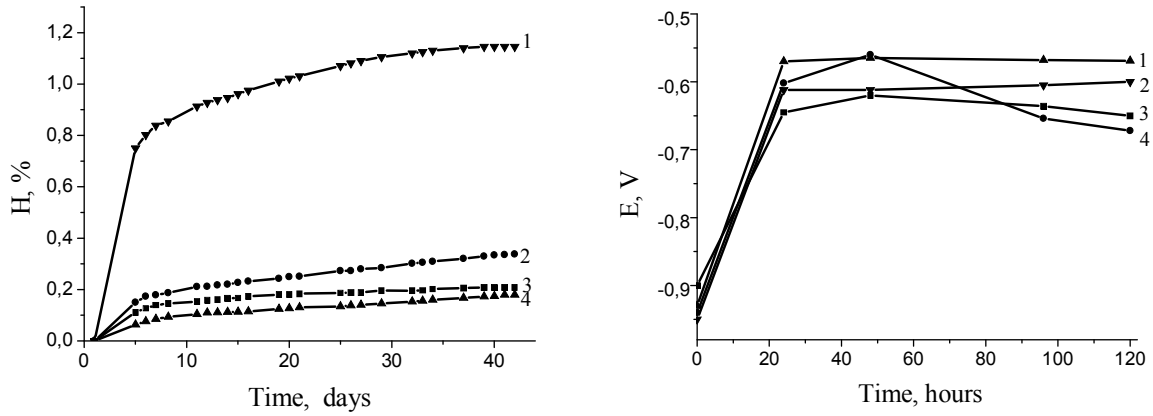
The presence of such interaction leads to a significant increase in the microhardness of the filled composites contained mixture of fillers at their overall concentration of 10 % – up to 18.7×10^9 N/m^2 compared to the unfilled epoxy composite (1.25×10^9 N/m^2) and composition containing more filler: 6.26×10^9 N/m^2 for 10 % magnetite and 10 % PANI-TSA (Table 2).

Table 2. Effect of filler content on the microhardness and IR-absorbtion of epoxy composites

Sample №	Magnetite, w.%	PANI-TSA, w.%	Microhardness $F_\infty\cdot10^{-9}$, N/m^2	Absorption coefficient, A, cm^{-1}
1	0	0	1.25	3.5
2	5	5	18.7	35.2
3	10	0	10.4	31.7
4	0	10	15.7	14.8
5	10	10	6.26	–

It was found that composite containing magnetic microparticles and particles of polyaniline doped with TSA at 1:1 ratio and 10% overall fillers content exhibits the strongest microwave absorption [2]. In the range of wavelengths from 1000 to 2000 nm absorption coefficient (A, cm^{-1}) for all studied composites has the absorption bands in the spectral interval 1380–1420 nm, 1670–1680 nm and 1900–1950 nm. The highest value of A at 1680 nm is observed for composites containing 5 % magnetite + 5 % PANI-TSA (A = 35.2 cm^{-1}) and 10 % magnetite (A = 31.7 cm^{-1}). For epoxy composite without filler and that containing 10% of PANI-TSA the absorption coefficient amounts only 3.5 cm^{-1} and 14.8 cm^{-1} respectively.

At the same time the discovered optimal filler amount in thermosetting composition (5 % magnetite + 5 % PANI-TSA) provides not only high microhardness and IR-absorption but good water protection and excellent anticorrosive properties of the coating on the surface of steel. The value of the relative water absorption of the composite coatings during 30 days of exposure in a moist chamber with a humidity of 95 % turned out to be 5-6 times less than that for unfilled epoxy composition (Fig. 4, *a*).



a *b*

Fig. 4. (*a*) Time dependence of water absorption at 95 % humidity for composite coatings of epoxy resin ED-20 cured with PEPA at various fillers content: *1* – without filler; *2* – 5 % magnetite + 5% PANI-TSA; *3* – 10 % magnetite; *4* – 10 % PANI-TSA; (*b*) Change of stationary potential in time in 3 % NaCl solution of composite coating on steel with various filler content: *1* – magnetite 10 %; *2* – 5 % magnetite + 5 % PANI-TSA; *3* – 10 % PANI-TSA; *4* – unfilled.

The electrochemical potential of the coated steel surface based on the developed thermosetting composition exhibits significant anode shift (by 0.3–0.4 V), while the surface state of the coatings remained unchanged. The obtained results confirmed the sufficient corrosion resistance of the coatings in comparison with the known analogues [4]. Method of the composite formation with special purpose would be further developed based on the obtained results.

CONCLUSION

Synthesized magnetite microgranules stabilized by polystyrene shells with a particle size of about 2 microns and electrically conductive polyaniline doped with TSA were used to prepare composite coatings with antiradar properties. The best properties, in particular high microhardness and corrosion resistance are achieved by the combined application of magnetic and conductive components due to the synergetic effect observed in the composition at the concentration of the filler mixture near 10 % that corresponds to the optimal composition.

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