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Hybrid Composites with Low Reflection of IR Radiation

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The conditions of formation and properties of hybrid organic-inorganic composites based on epoxy polymer matrix and a mixture of magnetic and polymeric fillers were studied.

Based on the study of physicochemical properties of fillers and composites, it was found that the introduction of a dispersion of magnetite modified with polymer shells and polyaniline doped with toluene sulfonic acid in the thermosetting epoxy composition in the amount of 2 - 6 wt.% provides the ability of composites to significant absorption and low reflection of IR and microwave range.

It was found that the optimal content of the composition corresponds to the best mechanical properties of the obtained coatings, in particular, high microhardness. This makes it possible to use the proposed composition to obtain on its basis composite films and coatings for anti-radar purposes, which reduce the intensity of microwave radiation acting on the object and at the same time act as protective coatings on the surface of metals.

Keywords: hybrid composites, IR radiation, magnetite, polyaniline, microhardness.

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Introduction

In many practical applications, especially solar energy and military equipment there is a demand for surface coatings that effectively absorb IR radiation. Such coatings may substantially improve electromagnetic energy harvesting in both photovoltaic and thermal solar systems. On the other hand, those materials can be used for stealth technologies, thus providing survivability of weapons [1, 2].

Composite materials consisted of dielectric matrix and ferromagnetic material attract great attention over last decades. Ferromagnetic materials are known for their ability to absorb electromagnetic waves of near IR and microwaves ranges [3-5]. It is expected that nano- or micro-particles of filler will enhance the interaction between composite and electromagnetic radiation thus providing desired practical results [6].

Analyzing open-source scientific literature one can conclude that thermoreactive polymer composites based on epoxy resin, hardener and magnetic filler (carbonyl iron, ferrite, nanosize magnetite) [3, 4] and conductive carbon dopants (carbon fibers, carbon nanotubes) [5, 7] are mainly used for the fabrication of protection coatings capable to strongly interact with IR radiation. However, exploitation of magneto-dielectric materials as fillers results in substantial increase of the temperature of a coating due to the transformation of electromagnetic energy into thermal one [4], while introduction of nanosized magnetic particles cannot provide effective IR scattering. At the same time, the use of expensive carbon nanoparticles as conductive component increases market price of the composite. Alternatively, the conductive part of the composite can be represented by conductive conjugated polymer, namely polyaniline (PAN) that will help to decrease reflected (scattered) IR radiation [6].

In present work, we aimed to fabricate composite coating with high absorption and low reflectivity in the IR spectral range. Since the first IR transparency window occurs within 0.8…1.6 μm wavelength range where most

of laser guiding systems operate, we limited our studies to that spectral range. Besides its desired IR properties, the potential coating should satisfy some other technological conditions, such as easy of fabrication and covering of the surface, mechanical strength, anticorrosion properties and low cost [7].

Among other dielectric compounds we suggest to explore epoxy resin as a matrix containing Fe_3O_4 particles along with conductive conjugated polymer – polyaniline (PAN) [8]. Iron oxide Fe_3O_4 (magnetite) serves as an absorber of IR radiation, whereas conductive polymer may provide a synergetic effect, i.e. enhance electromagnetic energy absorption and improve anticorrosive properties of the metal surface. In order to enhance the interaction between IR radiation and material we use magnetite in a form of near-spherical particles with an average diameter of 1 - 2 μm. Since that size is comparable with the wavelengths of near IR range the particles not only absorb electromagnetic radiation but also effectively scatter it reducing overall intensity of the reflected IR signal.

I. Experimental technique

Highly dispersed magnetite Fe_3O_4 was synthesized by alkaline hydrolysis of iron II and iron III salts with sodium oleate as a stabilizer [9]. In order to provide better compatibility of the magnetic part with epoxy matrix the surface of magnetite nanoparticles was modified with polymer shell during suspension polymerization of styrene according to the procedure described in [10]. Dispersed magnetite - polymer composite in a form of spherical particles (granules) with the size of about 1 - 2 μm were separated by magnetic decanting from the suspension.

Polyaniline (PAN) was synthesized by oxide polymerization of aniline solution under the action of equimolar amount of the oxidizer ammonium persulfate. 0.1 M aqueous solution of toluenesulfonic acid (TSA) was used as reactive medium [11]. The obtained product was dried at the dynamic vacuum conditions at the temperature of 60°C until its mass remains unchanged (6 hours) following by grinding in ceramic mortar.

To prepare the thermosetting polymer composition 2 g of epoxy α-resin ED-20 was mixed with 0.05…0.015 g of magnetite powder. After that 0.05…0.15 g of polyaniline powder doped with TSA was added and carefully stirred following by sonication for 10 minutes at the temperature 20 ± 1 ºC. Curing agent (amine hardener) PEPA in the amount of 0.24 g was added to the prepared mixture and stirred thoroughly. The resulting polymer composite was spilled onto flat Teflon or steel substrate forming 0.2 mm film. The film was kept for 2 hours to complete hardening process and then annealed at 40 - 50°C for one hour in the thermostat for final curing. After final curing the film was peeled off the surface and free standing film was obtained.

Polymer composites were characterized by X-ray (DRON-2, FeK_α-radiation). X-ray phase analysis was performed using the PowderCell and LATCON software [12]. The crystal structure was refined from powder diffraction data by the Rietveld method using FullProf.2k software. Micro-structural analysis, i.e. determination of the average size and average maximum strain of the grains was performed by simplified integral breadth methods using the profile fitting procedure with Voigt approximation supported by WinPLOTR software [13].

Molecular structure of PAN-TSA composite was studied by FTIR spectroscopy using AVATAR-320N spectrophotometer in 400 - 4000 cm^{-1} wave number range. The spectra were acquired on the polymer samples compressed together with KBr into pellets.

Raman spectroscopy studies were performed using Jobin Yvon T64000 spectroscope connected to Olympus microscope equipped with 50× lens. Ar laser (LEXEL) operated at 514.5 nm wavelength was used for the sample excitation. The output laser power was 10 mW that converts to 1 mW near the sample's surface.

Measurements of the specific volume conductivity and temperature dependence of resistivity were carried out at dynamic temperature change with 5 K/min rate. Powder sample was placed in quartz cylinder (d = 5 mm, h = 2 mm) between two nickel disc contacts with built-in thermocouple under pressure of 10 N/cm^2.

Mechanical properties of the composites were studied by Heppler consistometer. Microhardness (F_p) or conic flow point was determined using the area (S) of immersion of conical-end rod (h) into the sample under the defined load (G):

$$F_p = \frac{G}{S} = \frac{4 \cdot G \cdot 10^4}{\pi \cdot h^2}$$

Composite samples for microhardness studies were prepared by pouring of fluid composition into Teflon cylinder with diameter of 0.5 cm and 0.8 cm depth. The composite was hardened at ambient temperature for two hours and at T = 50°C for 1 hour.

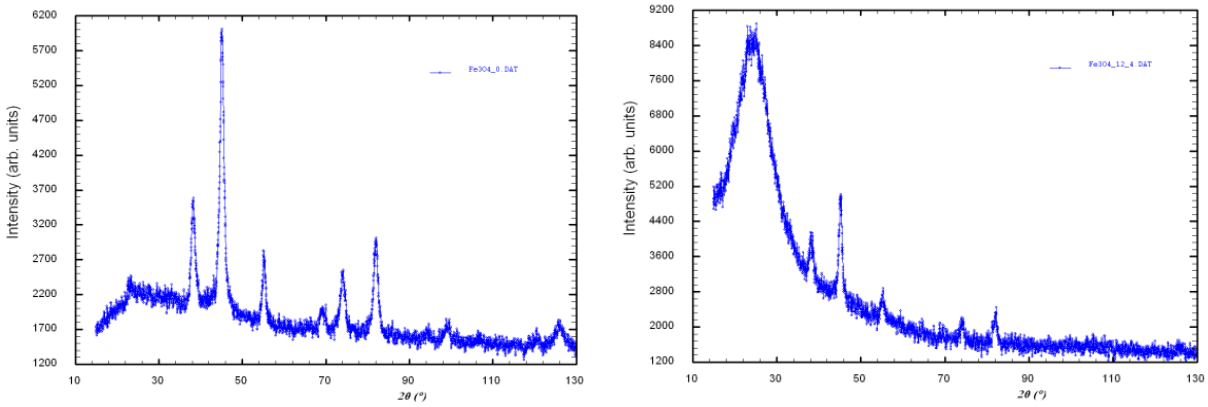
The IR absorption and reflectance spectra of the samples were acquired using MDR-23 monochromator equipped with a halogen lamp as a light source. The samples were formed as films with an area of 1 cm^2 and a thickness of 0.2 mm by watering the resulting composition on the surface of Teflon, curing at 50 ºC and separation from the surface with the formation of "free" films.

II. Results and discussion

Magnetic and electric properties of hybrid nanocomposite materials depend on the nature of the initial components, the amount of ferromagnetic and conductive fillers as well as polyaniline dopants, and obviously the preparation procedure. Composite films with low level of conducting polymer prepared in the presence of ferromagnetic nanoparticles with special properties can be a good alternative to metal-containing systems due to improved properties and lower price.

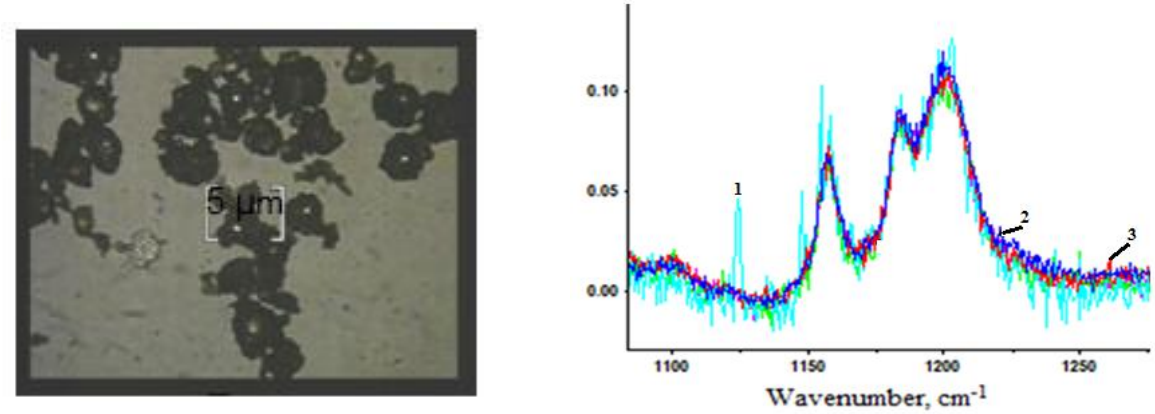
We suggest to use magnetite particles coated with polymer shell as magnetic filler in the composite and polyaniline doped with toluenesulfonic acid (TSA) as conductive component.

Fig. 1a depicts diffractogram of the synthesized magnetite. The peaks denoted with hkl indices indicate the presence of cubic phase Fe_3O_4 with spinel structure and cell parameter a = 8.3490(3) Å. Microstructure



a **b**

Fig.1. X-ray diffractogram of Fe_3O_4 (a) and polymer/magnetite composite (b).



a **b**

Fig. 2. (a) Micrograph of magnetite dispersion encapsulated into polymer shell ("Olympus" microscope); (b) Raman spectra of hybrid polymer/magnetite composite at different levels of magnetite content: 6.3 (curve 1), 9.5 (2), 12.4 (3) mass %**.**

studies reveal to determine the average size of the Fe_3O_4 granules that amounts 75.5(± 7.3) Å. The diffractogram of the composite polystyrene/magnetite is shown in Fig. 1b. The amorphous halo observed for magnetite modified with polymer shells is associated with polystyrene, while the set of diffraction reflections is associated with magnetite. At the same time, diffraction peaks of cubic Fe_3O_4 phase with low intensity for powder diffraction are practically vanishing.

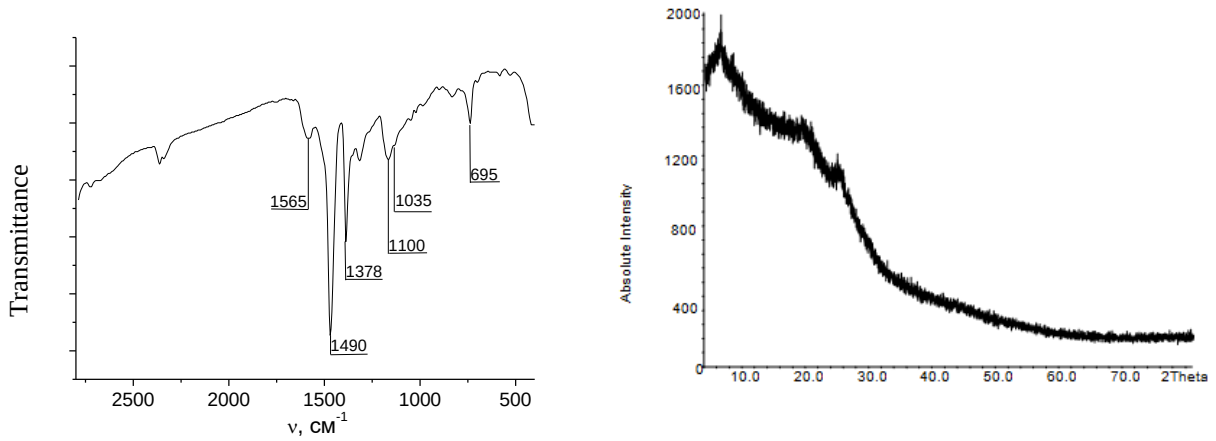
It was found that the cell parameter *a* almost the same for both samples within standard deviation but it has a bit larger value of a = 8.3491(12) Å for the composite. It is important that determined average size of the composite granules exceeds one for Fe_3O_4 samples prepared without polymer that confirms the formation of polymer shell around magnetite particles. The observed phenomena can be explained by the formation of nanocomposite with magnetite structure encapsulated into polymer shell. Partial aggregation of magnetite grains and formation of polymer shell on their surface results in the appearing of spherical core-shell particles with the average size of 1.5 - 2 μm (Fig. 2a).

According to Raman spectroscopy data Raman shifts that are characteristic for polymer and magnetite in polymer matrix are observed for all samples. From those spectra one can see broadening of 1590 - 1595 cm^{-1} peak base at relatively high magnetite content that is typical for encapsulated systems [15]. Low frequency Raman spectrum associated with magnetite is observed in 275 - 300 cm^{-1} range.

It is worth noting that encapsulation of magnetite into polymer shell weakly affects magnetic susceptibility of magnetic filler [16]. Thus, fabricated composites are capable for effectively absorption of IR and microwave electromagnetic radiation [3].

In order to enhance absorbing ability of antiradar coatings a conductive material that facilitates electromagnetic radiation scattering can be added [4-6]. We use conductive dopant such as polyaniline doped with TSA due to its high conductance and excellent compatibility with epoxy.

FTIR spectroscopy of doped PAN-TSA polymer confirms the emerging of conductive emerald salt of polyaniline [11]: peak at 1490 cm^{-1} corresponds to



a **b**

Fig. 3. (a) FTIR spectrum of PAN-TSA polymer; (b) X-ray powder diffractogram of PAN-TSA.

benzene ring, double peak at 1090–1100 cm^{-1} can be attributed to bending mode of C–H bond vibrations. Absorption bands at 1378 and 1565 cm^{-1} are associated with stretching modes of C–N and C=N bonds respectively. Spectral bands at 1035 and 695 cm^{-1} confirm the presence of toluenesulfonic acid (Fig. 3a).

X-ray diffraction studies reveal the prevailing amorphous structure of PAN-TSA with some crystalline reflections at 2θ = 6°.80, 19°.60, 22°.60. The degree of crystallinity was determined by integration of crystalline maxima as well as amorphous halo and amounts 8 - 10 %. The average size of the crystallites is about 25 - 27 Å.

It was found that PAN-TSA samples possess high magnitude of conductivity σ = 0.4 - 0.5 S/m that exceeds the value of conductivity for a majority of acid doped PAN almost by the three orders of magnitude [17]. As the temperature of the sample increases resistivity ρ of the composite decreases that is typical for semiconductors. As can be seen from the figure 4, the temperature dependence of the resistance of PAN-TSA is characterized by two parallel sections. The abrupt change of resistance occurs at temperatures T = 370 - 373 K (about 100 ^{0}C), which corresponds to the desorption of chemisorbed moisture. Temperature dependence of the resistivity excellently fitted by the equation $\rho = \rho_0 \exp(E_a/2kT)$ within 273 - 373 K temperature range. Activation energy of conductivity can be determined from $\ln\rho = f(1/T)$ plot that yields E_a = 0.17 - 0.19 eV (Fig. 4).

Therefore, the use of PAN-TSA as conductive dopant in antiradar coatings is promising since it facilitates scattering of absorbed electromagnetic energy and prevents heating up of the composite [5, 6]. Also, doping of polyaniline with TSA that has high surface activity provides effective wetting of the filler by epoxy oligomer.

On the other hand, the influence of the fillers on the mechanical parameters of protective coatings, microhardness in particular, is an important issue in polymer composite applications. Fig. 5 depicts typical dependences of microhardness (F_p) as a function of load (G) for the samples of different composition. It can be seen from Fig. 5a, b that the plot $F_p = f(G)$ exhibits plateau where the microhardness saturates at a particular load.

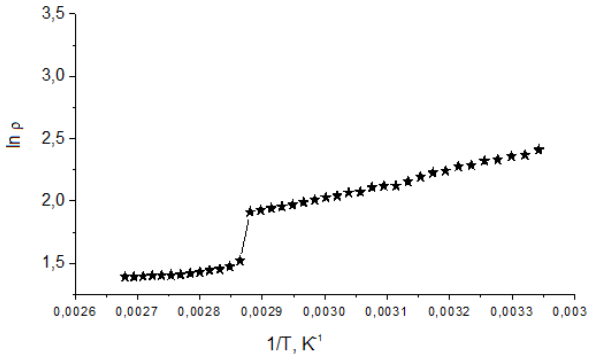


Fig. 4. Dependence of lnρ vs 1/T for PAN-TSA sample.

The determined values of F_∞ as yield point for the composites being studied illustrate that microhardness depends on the amount of polymer filler as well as on its chemical nature. The magnitude of F_∞ is $7.7 \cdot 10^8$ N/m^2 at the load G > 5 N for the composite based on epoxy and hardener without fillers (Fig. 5a). Doping of epoxy with PAN-TSA filler results in substantial increase of F_∞. At the same time, the dependence of F_∞ on the amount of fillers is quite complex and for PAN-TSA dopant reaches maximum at 5 w% (Fig. 5c). Doping with magnetite also results in the increase of microhardness (Fig. 5d).

The most prominent increase of F_∞ up to $67 \cdot 10^9$ N/m^2 is observed when both PAN-TSA and magnetite fillers are introduced to the composite (Fig. 5b). That indicate on synergetic effect when the influence of one component is enhanced by another one and proves the formation of a hybrid structure. Note that at high content of fillers more than 10 - 15 % microhardness of the composite decreases due to loosening effect or even breaking of the sample. Thus, 5 % level of doping can be considered as optimal since it provides not only the highest hardness but also exceptional anticorrosion properties [16].

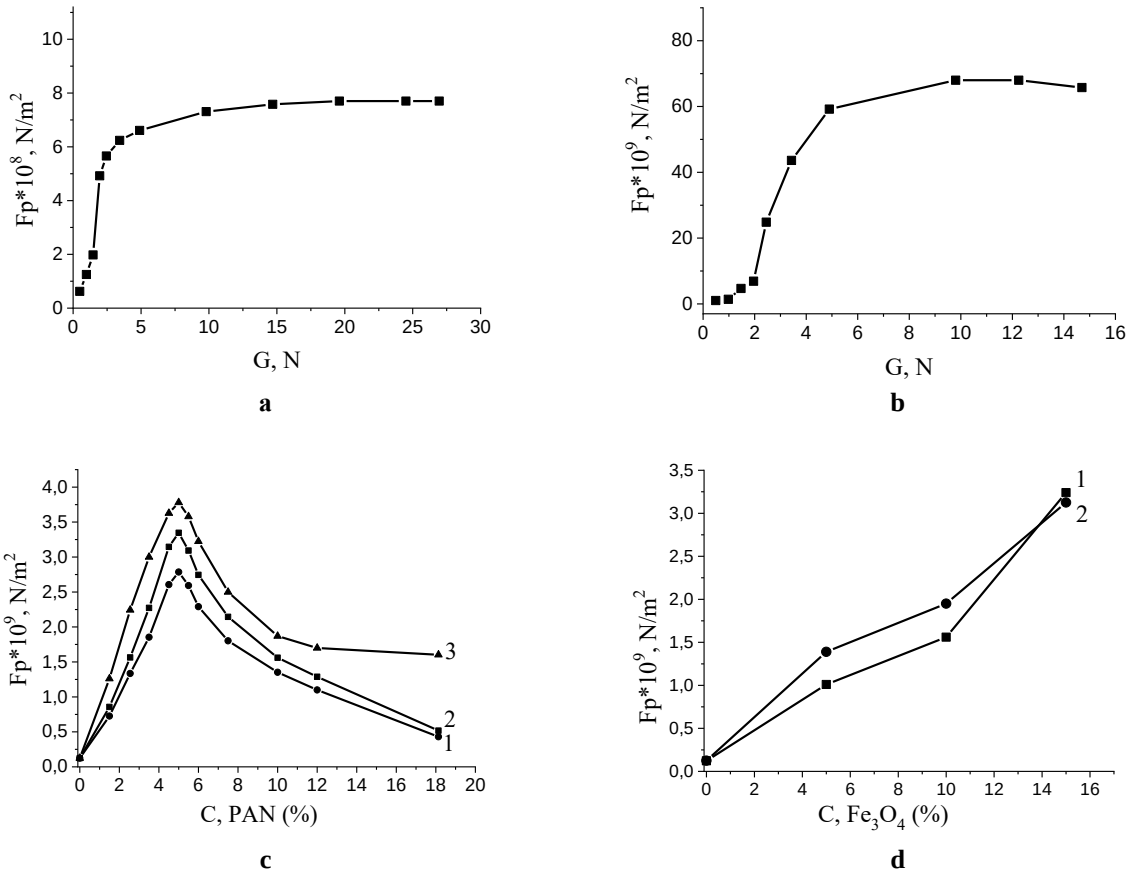


Fig. 5. Microhardness as a function of applied load: for ED-20+PEPA composite (a); for composite filled with 5 % PAN-TSA and 5 % Fe_3O_4 (b). Microhardness of the composites as a function of filler content at different loads: PAN-TSA – 1) 0.49 N; 2) 0.98 N; 3) 1.47 N (c); magnetite – 1) 0.49 N; 2) 0.98 N (d).

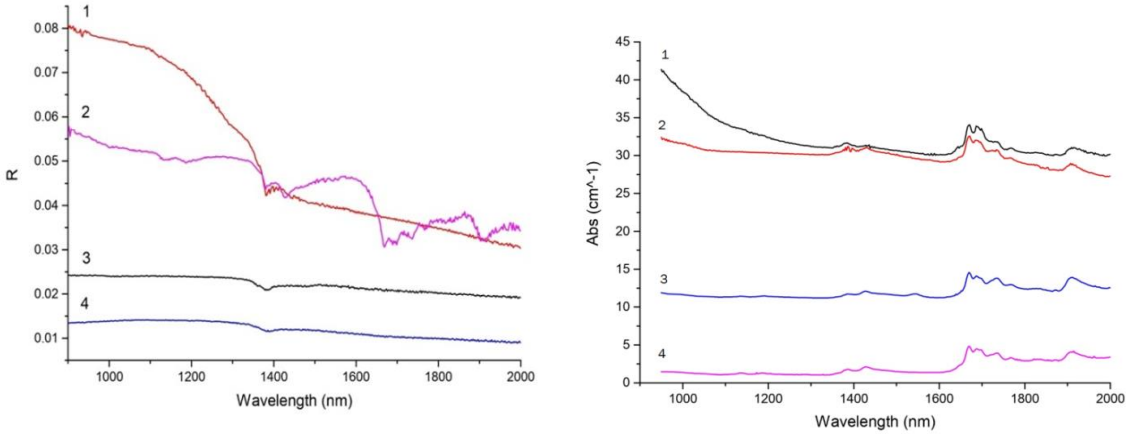


Fig. 6. (a) IR reflectance spectra of polymer-magnetite composite with various filler content, w.%: 1 – without fillers, 2 – 10 Fe_3O_4; 3 – 5 Fe_3O_4 +5 PAN; 4 – 10 PAN; (b) IR absorption spectra of the composite films with various filler content, w.%: 1 – 10 (5 Fe_3O_4 +5 PAN); 2 – 15 magnetite; 3 – 10 PAN; 4 – without fillers.

To study reflectivity and absorption of the composites in near IR range film samples of different composition were prepared. The IR reflectance and absorption spectra of the samples with various filler abundance are shown in Fig. 6.

Our studies reveal that the composite containing magnetic microparticles and particles of polyaniline doped with toluensulfonic acid at 1:1 ratio exhibits the strongest IR absorption $A = 35.2\ cm^{-1}$ and low reflectivity $R = 0.22$ (see Table). At the same time, this composition exhibits excellent anticorrosive properties and high microhardness.

Table 1

The influence of fillers on IR absorption and reflectivity

Sample №	Magnetite, w.%	PAN-TSA, w.%	Reflectivity, *R* (at λ = 1200 nm)	Absorption coefficient, *A*, cm^{-1}
1	0	0	0.082	3.5
2	5	5	0.022	35.2
3	10	0	0.056	31.7
4	0	10	0.014	14.8

As it is seen from IR spectra and data in the Table 1 the composite containing only conductive PAN-TSA component has low level of both reflectivity and absorption ($R = 0.014$ and $A = 14.8\ cm^{-1}$ respectively). The composites doped only with 10 % of magnetite exhibit high absorption and reflectivity that is not desired for protective coatings. Doping of the composite with both PAN and magnetite fillers leads to the desired result, namely high absorption and low reflectivity.

Conclusions

Studies of physical and chemical properties of composite materials and fillers reveal that doping of epoxy with dispersed magnetite in a form of spherical particles 1 - 2 μm in diameter that is comparable with near IR wavelengths results in effective absorption and scattering of electromagnetic radiation. Additional doping with conductive PAN-TSA enhances those processes due to synergetic effect observed within narrow concentration range at the 1:1 ratio. At the same time, that optimal composition possesses excellent mechanical properties, hardness in particular.

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Гібридні композити з низьким відбиттям ІЧ-випромінювання

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Вивчено умови формування і властивості гібридних органо-неорганічних композитів на основі епоксидної полімерної матриці та суміші магнітних та полімерних наповнювачів.

На основі вивчення фізико-хімічних властивостей наповнювачів та композитів встановлено, що уведення дисперсії магнетиту, модифікованого полімерними оболонками, та поліаніліну, легованого толуенсульфокислотою, до складу термореактивної епоксидної композиції у кількості 2 - 6 мас.% забезпечує здатність композитів до значного поглинання та низького відбивання хвиль ІЧ та СВЧ діапазону.

Знайдено, що оптимальному складу композиції відповідають найкращі механічні властивості отриманих покрить, зокрема, висока мікротвердість. Це дає змогу застосувати пропоновану композицію для отримання на її основі композиційних плівок і покрить антирадарного призначення, які зменшують інтенсивність діючого на об'єкт мікрохвильового випромінювання та одночасно діють як захисні покриття на поверхні металів.

Ключові слова: гібридні композити, ІЧ-випромінювання, магнетит, поліанілін, мікротвердість.