The electromagnetic absorbers based nano-structured granular polymer-composites at gigahertz frequencies.

D Savelev¹, E Grushevski¹, N Savinski², M Soloviev, V Turov¹ and V Krenev¹

¹ Department of Nanotechnology in Electronics P.G. Demidov Yaroslavl State University, Sovetskaya Street 14, 150003, Yaroslavl, Russia.
² Valiev Institute of Physics and Technology of Russian Academy of Sciences, Yaroslavl Branch, 150007, Universitetskaya Street 21, Yaroslavl, Russia.

dmitriy.savelev9@mail.ru

Abstract: The rapid increase in electromagnetic interference has received a serious attention from researchers who responded by producing a variety of radar absorbing materials especially at high gigahertz frequencies. Ongoing investigation is being carried out in order to find the best absorbing materials which can fulfill the requirements for smart absorbing materials which are lightweight, broad bandwidth absorption, stronger absorption etc. Therefore, this article introduces the electromagnetic wave absorption mechanisms and then reveals and reviews those parameters that enhance the absorption performance.

1. Introduction

With the development of electromagnetic technology, the problem of electromagnetic hazard is becoming more and more serious. So, the roles of electromagnetic absorption are attracting more attention in the military and civilian. Electromagnetic wave absorption coating, as an important means of radar wave absorption material, has a wide range of application. Because few materials in nature can respond to THz frequency, and because there is a lack of effective THz sources and detectors, it still remains a big challenge to effectively manipulate THz waves. Recently, graphene has been demonstrated as a viable alternative in realizing THz absorbers because of its high THz absorption and tenability of surface conductivity [1]. The absorption of electromagnetic energy (EME) is due to dielectric, magnetic and conductivity losses, which are trying to maximize to achieve the maximum efficiency of shielding. Composite materials appear to provide the most attractive and promising solution to demands for lightweight, high-performance structures. Since composite materials have high specific strength and stiffness compared with bulk materials, the range of their applications is rapidly expanding from aerospace and military use to commercial activities. On the other hand, the use of polymers to protect the electronic devices from EME is popular due to the light weight, flexibility and cost-effectiveness. Here we report a method based on generation of materials with a wide range of adjustable electrical and magnetic properties: conductive polymers (polyanilines), flaky nanographite, nano-structured granular composites.
2. Experiment

2.1. Materials

2.1.1. Polyaniline (PANI). The main problem of PANI is that it is poorly soluble in most common solvents, hampering experimental studies and limiting its industrial exploitation. The matrix polymerization of aniline neutralized by polymeric acids is of prime significance as a method of preparing soluble materials combining electrophysical properties of polyaniline (PANI) and the mechanical properties of polymer materials. We used poly (2-acryl-amino-2-methyl-1-propane) sulpha acid (PAMPSA) [2], are distinguished by the regular distribution of sulpha acid groups along the main chain of macromolecules. It was assumed that, upon protonation of aniline by the above polyacids, the resulting PANI macromolecules would be located along polyacid macromolecules and form a two-strand macromolecular structure of the interpolymer complex. In this case, the conformations of polyacid and PANI macromolecules are changed to adjust each other. The synthesis was performed at room temperature while successively mixing solutions of PAMPSA, aniline, and ammonium persulphate in water. The ratio of PAMPSA to aniline in the reaction mixture was 1 : 1 mole-unit/mole, and that of aniline to oxidant 1 : 1.25 mole/mole. The concentration of aniline and PAMPSA in the reaction mixture 0.034 M/L. The conducting emeraldine salt (ES) form can be obtained by oxidative doping of leucoemeraldin base (LB), or by protonation of EB. The electroconductivity of film determined by of polyaniline synthesized by the method of template synthesis with PAMPSA, which was spinning on transparent glass electrode ITO from an aqueous solution at 3500 rpm. An electroconductivity, was measuring by the four-probe method at room temperature, was equal to 0.25 S cm⁻¹.

2.1.2. Ferrites. Ferrites are considered to be the best magnetic material for electromagnetic wave absorbers due to their excellent magnetic and dielectric properties, but they are expensive and heavy. Moreover, nowadays, research interest is focusing on and towards higher gigahertz frequency, nanoparticles, ferrite incorporated into polymers, over a single layer, wide bandwidth and to achieve higher and higher absorption. In this study, ferrites produced by JSC «Ferros» Yaroslavl were used. The barium ferrite was used in the form of small magnetized balls, with a diameter of 3 mm and in the form of a powder with a dispersion of 30 microns.

2.1.3. Nanographite Graphite exfoliation. Typically, graphite exfoliation was performed in a two-electrode system, whereby graphite foils were used as working anodes (commercial graphite foil Graflex RF) and platinum foils as counter electrodes. To avoid short circuits (connections between the graphite and Pt foils) during exfoliation, graphite foils were rolled like rods. The Pt foils were placed parallel to the graphite electrodes at a fixed distance of 2 cm. The electrolyte for the graphite exfoliation was prepared by dispersing ammonium sulfate crystals (3.0 M) and DMSO (dimethyl sulfoxide) in DI water. When the electrodes were immersed in the electrolyte, a static potential of 10 V was applied to start the electrochemical exfoliation process. When the exfoliation was complete, the suspended graphene sheets were collected with a 0.2 μm PTFE membrane filter and washed alternatively with DI water and ethanol by vacuum filtration. The washing process was repeated three times to clear any chemical residues. Later, the dark-gray product was dispersed in N, N - dimethylformamide (DMF) via mild sonication (15 min). This homogeneous suspension sat overnight to remove un-exfoliated flakes and large particles. Then, the supernatant was taken out for further measurement and ultimately device fabrication.

2.2. Preparation of microwave-absorbing coatings
As a target, fiberglass was used in the form of an isosceles triangle with an edge 300 mm long, 0.8 mm thick, with an area of ~390 cm², and a mass of 33 g. The coating was applied in bulk and with a brush, in the form of several layers with successive drying in a drying cabinet at 80°C. As a binder, a 30%
(by dry residue) aqueous solution of polyvinyl acetate emulsion DF50/5H was used. Dispersion of solid substances in the emulsion was carried out using a laboratory mechanical dispersant for 20 minutes. If necessary, the emulsion was diluted with deionized water. In the case of sample 5, the dispersant Synthanol 10 at a concentration of 1% by weight was used to improve wetting. The thickness of the coatings was 50-170 microns.

2.3. Measurement
Microcosmic morphology of nanostructured granular polymer-composites and cross section of polymer matrix filled with and GNs were performed using scanning electron microscopy (SEM, SUPRA - 40). The polyaniline particles have a structure similar to «raspberries», small grains have a size of 27-29 nm, large «berry» have a size of 150-160 nm. Phase analysis of the products of exfoliation graphite was done via X-ray diffraction on an ARLX’Tra X-ray diffractometer under the following conditions and parameters: CuKα radiation with a wavelength of nm; λ = 0.15418nm accelerating voltage of 35 kV; and an incandescent current of the X-ray tube of 40 mA. The elemental composition of the samples was determined via Rutherford backscattering spectrometry. Three tablets of a compressed product of exfoliation were used as samples and a graphite plate was used as a reference. The measurements were made on the λ = 0.15418 K2MV (HVEE) facility. We used He+ ions with an energy of 1.0 MeV at normal beam incidence. Scattered ions were detected at angle θ = 150° using a surface barrier semiconductor detector with a resolution of 13 keV. The spatial angle of the detector was 3.415 msr. The radiation dose in all experiments was 54 μCl at an ion current of 40 nA on each sample. X-ray diffractometry of our graphite foil samples and products of electrochemical exfoliation revealed the presence of two crystallographic phases: hexagonal 2H and orthorhombic 3R. X-ray diffractometry and electron microscopy showed the exfoliated graphite samples contained crystallites of virtually half the normal size that had 30–50 graphene layers each and could be classified as nanographites. Our Rutherford backscattering spectrometry study confirmed the substantial oxidation of graphite samples during electrochemical exfoliation, due to the generation of a strong oxidizer (a hydroxyl radical) [3,4]

3. Results and discussion

3.1 Factors influence the electromagnetic wave absorption
The general scheme of the processes occurring when electromagnetic radiation falls on the coating is illustrated in Figure 4.

3.2 Measurements of absorption properties
The portable radar was used to study the absorption properties of electromagnetic radiation. The radar signal was processed using the consistent filtering method. The consistent filtering assumes finding the filter response in the form of convolution of the radar input signal x(t) and the pulse characteristic of
the filter \( h(t) \), consistent with the probe radar signal. With this processing in the output signal of the matched filter (SF) \( z(t) \), the maximum signal-to-noise ratio is achieved by the accumulation of the useful signal energy and suppression of out-of-band noise. Additional measures may be used to suppress possible interference [6]. The test sample (target) was located so as to be in the Fraunhofer zone (far field) at a distance from two pairs of broadband radar antennas with a circular aperture of 5 cm and a beam half-width of 20°. The reflection measurements were carried out at incidence angles of 0°, 60°, 120° to the normal. For each sample, values were averaged over 100 parallel signals; the obtained data were averaged over 32 more polarizations and over 3 angles of incidence. The received data were normalized by the average reflection value of the sample of a fiberglass substrate without an absorbing coating.

**Figure 4.** Schematic illustrations of the absorption mechanisms when incident wave enters into coating [5].

**Figure 5.** Photo of a portable radar for measuring the electromagnetic characteristics of coatings.

### 3.3. Grain sizes (nanometer vs micrometer and the effects of particle size upon the EM wave properties)

The relationship between thickness, permeability and frequency of minimum reflection loss can be explained using the following equation

\[
 f_m = \frac{c}{2\pi \mu' d} \tag{1}
\]

where \( f_m \) : matching frequency with minimum reflection loss; \( c \) : velocity of light; \( d \) : sample thickness; \( \mu' \) : imaginary part of permeability.

Thus, from this equation it is easy to tell that the matching frequency \( f_m \) shifts towards lower frequency with increasing sample thickness [7]. More results have been reported on the fact that increasing thickness causes the resonance frequency to move towards lower frequency [8].

Nanomaterials which have a new wave absorption mechanism lead to an excellent electromagnetic wave absorber performance in the GHz range with the effects of small size, surface and shape anisotropy. According to the natural –resonance equations [9],

\[
 2\pi f_r = H_a r_a \tag{2}
\]

where \( H_a \):

\[
 H_a = \frac{4|K_1|}{3\mu_0 M_S} \tag{3}
\]

where \( r_a \) is the gyromagnetic ratio, \( H_a \) is the anisotropy field and \( K_1 \) is the anisotropy coefficient. It demonstrates that the resonance frequency of the magnetic materials shifts to higher frequency when \( H_a \) increases due to the small size effect. It is believed that the anisotropy energy of small size materials, especially on nanometer scale, would be remarkably increased due to the increased surface anisotropic field induced by the small size effect.
3.4 Electromagnetic characterist

Table 1. Types of polymer matrix, filler, filler's particle size and its absorbing properties.

| №  | Structure                                                                 | Filler's particle size  | Coating density (g/cm² 10⁻²) | Reflection loss (dB) at 10 GHz | Absorbed energy % |
|----|--------------------------------------------------------------------------|-------------------------|-------------------------------|-------------------------------|------------------|
| 1  | Ferrite in the form of small balls, 3 mm in one layer (magnetized balls) | Barium ferrite 3 mm.    | 94                            | -14.3                        | 96,3             |
| 2  | BaFe₁₂O₁₉ (1: 1 by mass to mass of 30% emulsion)                         | Barium ferrite 30µ      | 10                            | -11.2                        | 92,4             |
| 3  | Nanographite: 1: 1 by mass to mass of 30% emulsion, 0.1% Syntanol-10     | Nanographite 10-100µ    | 4.7                            | -14.4                        | 96,4             |
| 4  | Aluminum Powder PAP2 1: 1 by mass to mass of 30% emulsion                | Aluminum powder 20-30µ   | 4.6                            | -11.8                        | 93,4             |
| 5  | PANI (Emeraldine salt, sulfonic acids)                                   | Polyaniline 27-29 nm    | 3.7                            | -13.3                        | 95,3             |
| 6  | Ultra-wide flexible radar absorbing material based on nanostructured ferromagnetic microwire [10] | JSC «CDB RPM» МЫПК-1Л | 10                            | -17                          | 98               |

4. Conclusion

As a result, the nanographite coating has a power reflection coefficient of -14.4 dB. This value is close to the material МРПК-1Л (-17 dB) [10]. But the advantage of nano-structured granular composites, particularly, nanographite is that coating thickness and weight less than competitors with the same degree of reflection and absorption an electromagnetic waves. It is shown that on the basis of granular nanostructures it is possible to create magnetic materials with close complex magnetic and dielectric permittivity at a magnitude of magnetic losses several times higher than traditional ferrite magnetic materials. These materials can be the basis for the creation of effective broadband electromagnetic wave absorbers with a thickness of hundreds of microns.

Acknowledgements

This research was financially supported within the framework of the state assignment of the Valiev Institute of Physics and Technology of the Russian Academy of Sciences Yaroslavl Branch of the Ministry of Education and Science of the Russian Federation on the topic No. 0066-2019-0003 and the state assignment of P.G. Demidov Yaroslavl State University No. 0856-2020-0006. Some experimental results were obtained on the equipment of the Center for Collective Use "Diagnostics of Micro-and nanostructures" with the support of the Ministry of Education and Science of the Russian Federation.

We would like to thank A. Dubov an application ferrites of JSC «Ferros» Yaroslavl.

References

[1] Moradiani F, Farmani A, Yavarian M, Mir A and Behzadfar F 2020 Physica E: Low-dimensional Syst. and Nanostructures 122 114159
[2] Savinsky N G 2012 Bulletin of the Yaroslavl State University P. G. Demidov Natural and Technical Sciences series 4 53-64.
[3] Solov’ev M E, Raukhvarber A B, Savinskii N G and Irzhak V I 2017 Russian journal of general chemistry 87 N 4 805-811.

[4] Savinsky N G, Melesov N S, Parshin E O, Vasiliev S V, Bachurin V I and Churilov A B 2020 Bulletin of the Russian Academy of Sciences: Physics 84 N 6 732–735.

[5] Duana Y, Liua Y, Cuia Y, Mab G and Tongmina W 2018 Progress in Organic Coatings 125 89–98.

[6] Turov V E 2011 Radar warfare. Construction and noise protection of basic correlation systems of passive location: Monograph.-M (Vuzovskaya kniga) 205

[7] Mohd F, Idris, Hashim M, Abbas Z, Nazlan R and Ibrahim I 2016 Journal of Magnetism and Magnetic Materials 405 197–208.

[8] Liu L D, Duan Y P, Ma L X, Liu S H and Yu Z 2010 Appl. Surf. Sci. 257 842–846.

[9] Kong J, Liu J, Wang F, Luan L, Itoh M and Machida K 2011 Appl. Phys. 105 351–354.

[10] Patent RU 2322735 C1, H01Q 17/00 (2006.01) electromagnetic wave absorber / Ustimenko L G , Vladimirov D N, Smirnov G A, Suslov L M and Khandogina E N; OAO "TsKB RM"; Applic. 2006125655/09 ; Date of public. 20.04.2008 Bull. 11