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Composite Materials Based on Foam Polyurethane and Graphene Nanoplates Effectively Screening Electromagnetic Radiation

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Abstract

Composite materials based on polyurethane foam and graphene nanoplates (**GNP**) for shielding from electromagnetic radiation in the frequency range from 2 to 12 GHz were made by impregnation. The use of phenol-formaldehyde resin (**PFS**) as a binder component promoted good adhesion of graphene to the polymer matrix and made it possible to obtain samples of composites with a high graphene concentration of ~ 50 wt %. An increase in the shielding efficiency of composites was found both with an increase in the frequency of electromagnetic radiation and with an increase in the concentration of GNP in them. The maximum shielding value was 75 dB at a frequency of 12 GHz and graphene concentration of 50 % by mass. It is concluded that the impregnation method proved to be promising for the manufacture of flexible and lightweight composite foams effective for shielding electromagnetic interference in the range from 2 to 12 GHz.

Keywords

Nanocomposite; graphene nanoplates; electromagnetic radiation; phenol-formaldehyde resin; shielding coefficient; polyurethane foam.

Introduction

Due to the widespread use of various electrical and electronic devices in everyday life and work, pollution by electromagnetic interference is becoming a serious problem today, since they have an adverse effect on human health [1–4]. Of particular importance is the problem of individual protection of people when they perform various jobs in conditions of high-frequency electromagnetic radiation (**EMR**). Depending on the frequency, the EMR has a different penetration depth into various materials. The human body is no exception [1]. As a result, certain tissues and organs can be exposed to an electromagnetic field (**EMF**) [1, 3, 4]. When EMR is absorbed, the temperature of the object rises. For biological objects, and especially for humans, an increase in temperature by 1–5 degrees can cause numerous malformations, temporary infertility in men, brain damage and changes in the chemical composition of blood [1]. Even a slight increase in temperature by about 1 °C in the human body can lead to a change in hormone production and suppression of the immune response [1, 5].

Of course, the most effective solution to the problem is to combat the cause, namely, reducing the intensity of electromagnetic radiation. Thus, the European Union funded the project "Networks with a low level of exposure to electromagnetic fields" (**LEXNET**) [6] under the FP7 program, in order to reduce at least 50 % the impact on the population of electromagnetic fields without compromising the quality of communication and data transfer [2].

However, there are areas where it is impossible to exclude the effect of electromagnetic radiation on humans and biological objects. Therefore, the urgent task is to develop materials that can be used in personal protective equipment against electromagnetic radiation. Materials should effectively shield EMI (SE EMI of at

least 20 dB), be lightweight and flexible [7]. Using foamed polymer composites, it is possible to create shielding products with high service characteristics compared to materials based on metal [7–9]. To ensure high shielding characteristics, it is necessary that the polymer material possesses high electrical conductivity [7, 10]. Among non-metallic fillers, carbon nanotubes (**CNTs**) and graphene are the most effective, since possess the highest values of electrical conductivity in comparison with other carbon nanostructures [11, 12]. The main advantage of graphene over nanotubes is its high reflectivity of EMR, which is preserved when used in polymer composites as a shielding component [13].

The use of absorbing EMR materials, in particular nanotubes [14–17], in personal protective equipment will cause them to heat up, and therefore, discomfort during human use. CNTs are also rather difficult to evenly distribute in a polymer matrix because of their confusion [18, 19]. Therefore, graphene nanoplates can be effectively used as a modifying component, since they are efficiently distributed in most polymer matrices, can be a concomitant surfactant (in oxidized form) [20], and can also provide shielding properties for polyurethane matrices. To achieve a high degree of shielding, it is necessary to increase the concentration of graphene in polyurethane foam, as was shown in [7–9]. Therefore, the development of production methods and the study of highly concentrated polyurethane foam composites is relevant.

Thus, the aim of the work was to obtain a highly effective shielding material based on polyurethane foam and graphene nanoplates.

Method

To study the shielding from electromagnetic radiation, five polyurethane foam samples were prepared with a mass graphene content of 10, 20, 28, 40, and 50 % by weight of the polyurethane foam.

The procedure for obtaining these samples consisted of the following stages.

Obtaining GNP modified with phenol-formaldehyde resin (GNP / FFS)

An experimental batch of water paste GNP / FFS was used, manufactured by Ltd NanoTechCenter (Russia, Tambov). Manufacturing technology includes oxidative intercalation of natural graphite GSM-2, mixing intercalated graphite with an aqueous solution of phenol-formaldehyde resin type Fenotam GR-326 (non-volatile residue 50 %, production – Krata PJSC, Tambov, Russia), ultrasonic treatment. Under these conditions, at least partial grafting of oligomeric FFS molecules to the surface of oxidized graphene were occurred (under these processing conditions, graphene nanoplates contain 10–13% of oxide groups). The degree of exfoliation of graphite to graphene during ultrasonic processing was controlled by the light absorption coefficient of samples diluted with water according to the procedure described in [21]. After ultrasonic treatment, the suspension was filtered to a paste state.

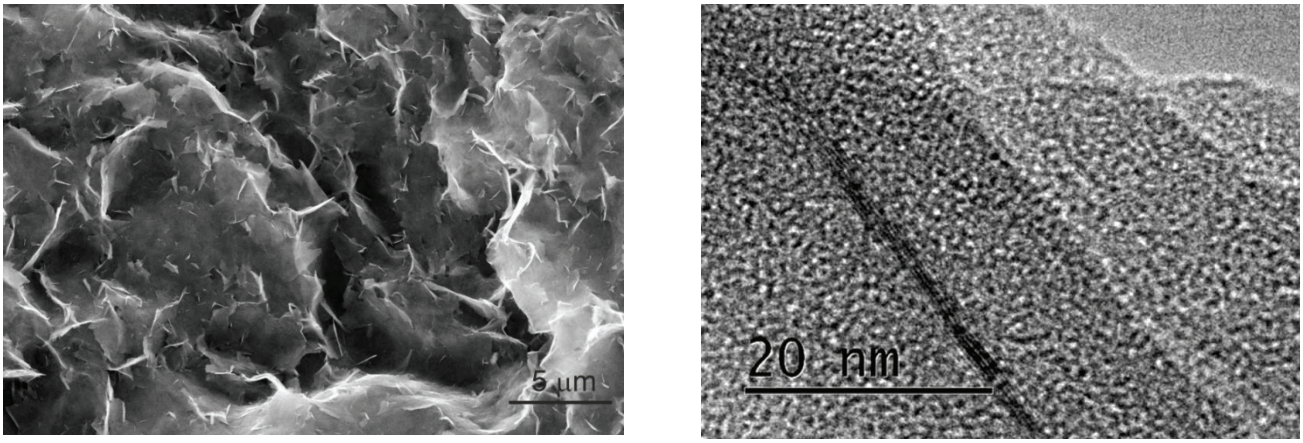
In the resulting aqueous paste, the mass content of graphene was 5.5–6.0 %, the content of PFS 30–50 % by weight of graphene. Typical images of the obtained GNP in a scanning and transmission electron microscope are shown in Fig. 1.

Obtaining samples of polyurethane foam, modified GNP / FFS

Polyurethane foam plates of 10 × 220 × 220 mm in size were used as the substrate material. The initial mass of such a plate was about 8.3 g.

The GNP / FFS paste was diluted with a small amount of water and processed on a homogenizer for several minutes, which allowed to obtain a homogeneous suspension. The mass of graphene paste was chosen so that the amount of dry graphene in it was 10, 20, 28, 40, and 50 % of the mass of the initial sample of polyurethane foam. The amount of water for diluting graphene paste was chosen so that the entire solution was absorbed into the pores of the polyurethane foam without residue. After impregnation, the samples were dried in a stream of hot air under a fan heater, rotating the sample all the time so that the impregnating solution would not flow in one direction. The completeness of the drying was controlled by weight (up to constant weight). Due to the presence of the phenol-formaldehyde component acting as glue, the samples prepared in this way hold graphene firmly, it does not get dirty and does not crumble upon mechanical action on the sample.

After impregnation and drying, the thickness of the samples was about 7 mm, i.e., the samples shrinked compared to the initial thickness of 10 mm.



a) *b*)

Fig. 1. Images of graphene nanoplates modified with FFS:
a – SEM; *b* – TEM

Characterization and research methods

The morphology and microstructure of the GNP surface, as well as individual plates, were studied using a Carl Zeiss Merlin scanning electron microscope (**SEM**) and a JEOL JEM 2100F transmission electron microscope (**TEM**).

The electrodynamic characteristics (screening and reflection coefficients) of composite polyurethane foams were measured on a measuring stand (Fig. 2) in accordance with the procedure described in [22]. In this case, filtering of noise in the time domain was used.

When measuring the screening coefficient (**CE**), the transmitting antenna was A1, the receiving one was A2. To determine the FE, reference measurements were carried out: without installing the test sample (empty window) and with the installation of a metal diaphragm of sufficient thickness, and measurement with the installation of the test sample in the equipment of the measuring stand. CE (**SE**) was determined by the ratio:

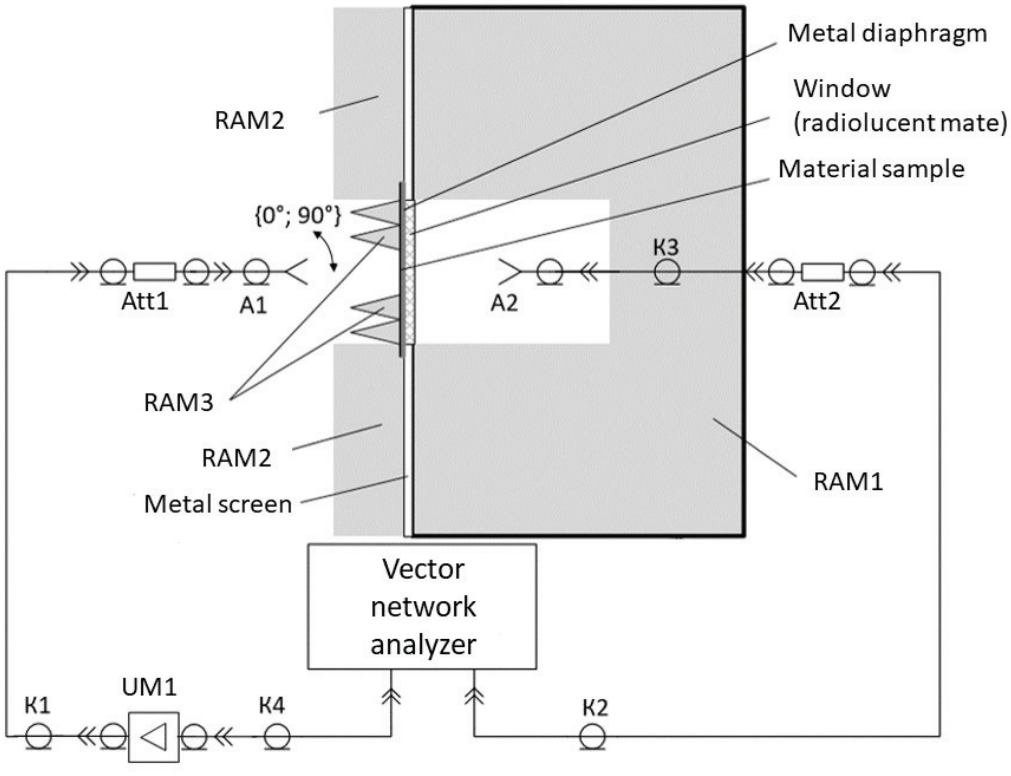


Fig. 2. Diagram of a measuring stand for studying the electromagnetic characteristics of samples

$$SE = -20\lg\left|\left(S_{21,\,obr} - S_{21,\,m}\right)\right| + 20\lg\left|\left(S_{21,\,v} - S_{21,\,m}\right)\right|,$$

where $S_{21,obr.}$ – complex transfer coefficient with the test sample installed in the equipment; $S_{21,\,m}$ – complex transfer coefficient with a metal screen of sufficient thickness installed in the equipment; $S_{21,\,v}$ – complex transfer coefficient with an empty window.

When measuring the reflection coefficient on metal R_{Me}, a sample of material was laid on a sheet of metal of sufficient thickness. The measurements were carried out on a single antenna A1, which worked on the transmission and reception. To determine R_{Me}, reference measurements were carried out: without installing the test sample (empty window) and with the installation of a sheet of metal of sufficient thickness, and measurement with the installation of the test sample on a sheet of metal of sufficient thickness. R_{Me} was determined by the ratio:

$$R_{Me} = 20\log\frac{\left|U_{obr} - U_{fon}\right|}{\left|U_{Me} - U_{fon}\right|},$$

where U_{obr} – the complex value of parameter S_{11} for a sample on a metal sheet; U_{Me} – the complex value of parameter S_{11} for a sheet of metal; U_{fon} – the complex value of parameter S_{11} for an empty measuring cell.

The value R_{Me} characterizes the loss of electromagnetic energy in the sample.

Results and discussion

Fig. 3 shows the dependences of the screening coefficient SE of the samples on the EMR frequency.

An increase in the efficiency of shielding of composites was found both with an increase in the frequency of electromagnetic radiation and with an increase in the concentration of GNP in them.

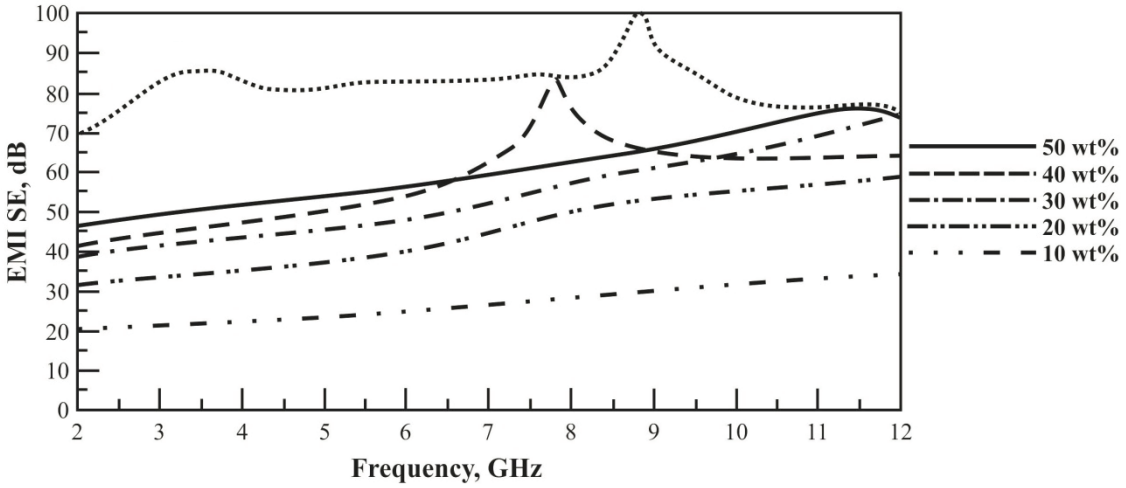


Fig. 3. Screening coefficient dependences (EMI SE) of the studied samples of polyurethane foam composites on the frequency of EMR

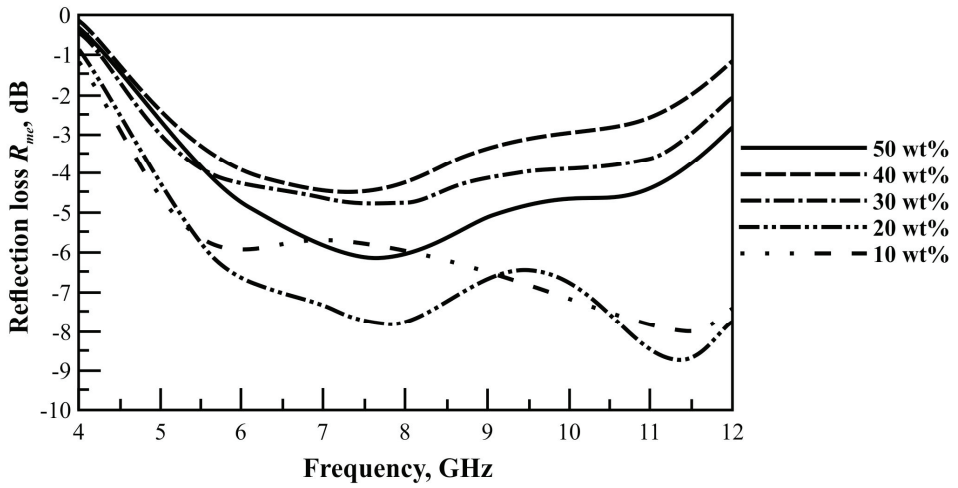


Fig. 4. Reflection coefficient dependences on the metal R_{Me} of the studied samples of polyurethane foam composites on the frequency of electromagnetic radiation

Table 1

Comparative characteristics of shielding foamed polymer composites (X EMR frequency range)

Polymer	Graphene content, wt %	Thickness, mm	EMI SE, dB	References
TPU	50	7.0	75	This work
TPU	6.5	1.8	21.8	[7]
TPU	20	2.4	20	[9]
PS	30	2.5	29	[23]
PMMA	5	2.4	19	[24]
PEI	10	2.3	13	[25]

An increase in graphene concentration logically leads to an increase in the screening coefficient (Fig. 3), which is probably associated with an increase in the electrical conductivity of the samples [7, 10]. The maximum shielding value was 75 dB at a frequency of 12 GHz at a graphene concentration of 50 % by mass.

To study the absorption capacity of material samples, studies of the coefficient R_{Me} of reflection on the metal were conducted, the results of which are presented in Fig. 4.

As can be seen from the dependency graphs (Fig. 4), the resulting composites have low absorption characteristics (R_{Me} values do not exceed minus 9 dB). In a compartment with high SE values, this indicates that the studied samples of materials mainly reflect EMR, which opens up prospects for their use in personal protective equipment.

Table 1 compares the shielding characteristics for the samples obtained in our work and existing analogues (foamed polymer composites).

Obtained material has comparable shielding characteristics compared to analogues (Table 1), and in some cases surpasses them, however, the developed method for producing foamed polyurethane composites is simpler.

Conclusion

Composite materials based on polyurethane foam and graphene nanoplates were successfully fabricated using a simple impregnation method. With an increase in the GNP content in polyurethane foam, the screening coefficient of the samples increased. The screening coefficient increases from 45 to 75 dB with an increase in the frequency of electromagnetic radiation from 2 to 12 GHz.

As a result, a technique was developed for producing light gas-permeable composites that have low absorbing properties and high shielding effect, which can be successfully used in personal protective equipment against electromagnetic radiation and other applications.

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