Interface Interaction as a Factor of Dielectric Properties of Epoxy-based Composites with Graphite Nanoplatelets

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The paper is devoted to the investigation of the physical properties of graphite nanoplatelets / epoxy composite materials with a modified level of interface interaction due to pre-irradiation of the filler with ultraviolet light. The influence of interface interaction at the filler / matrix interface in polymer-carbon composite materials on their electrodynamic properties is determined, which is the basis for the development of composite materials with an adjustable set of physical properties. By analyzing within the model, which takes into account the volume fraction of the interface region, it has been shown that the increase of dielectric constant in composites, where pre-irradiated with ultraviolet light graphite nanoplatelets were used as a filler, occurs due to an increase of the dielectric constant of the interface layer, which is associated with a change in the chemical composition of the surface of graphite nanoplatelets.

Keywords: Graphite nanoplatelets, Composite material, Dielectric permittivity, Dielectric loss, Interface interaction.

1. INTRODUCTION

The development of modern technologies requires the development of new materials, mainly with modified properties. Polymer-based composites may serve in the role of such materials, which, in particular, play an important role in obtaining coatings for absorption and shielding of electromagnetic radiation. An epoxy resin (ER) often acts in the role of polymer. Graphite nanoplatelets (GNP) are the product of deep chemical-thermal treatment of disperse graphite, followed by dispersing, and GNP are distinguished among other types of carbon fillers with relatively low cost and rather high aspect ratio. The value of dielectric permittivity of such materials determines the spectrum of their functional applications. Therefore, the perspective area is the development of composites that contain carbon fillers, in which unique electrical, electrodynamic, sorption properties are combined.

Carbon materials stand out among the other possible fillers for conductive composite materials (CM) with high propensity to agglomeration due to Van der Waals interactions, which prevent the uniform distribution of carbon filler in the polymer matrix. Thus, the value of the percolation threshold increases and the mechanical properties of the CM decrease as a result of the deterioration of the interfacial adhesion of the material components and the accumulation of mechanical stresses at the points of filler agglomeration. Among the methods for increasing the surface activity of carbon filler and its better cross-linking with a polymer, the chemical functionalization of carbon particles, which provides the required number of functional groups on the surface of carbon for uniform distribution and, accordingly, interaction with the polymer matrix, is proposed. However, chemical functionalization is referred to aggressive methods of structure modification, which can lead to the destruction of graphene *sp*-bonds, and is also

dangerous for the environment. An alternative method for introducing additional functional groups on the surface of carbon and its cleaning of insulating contaminants is the treatment with ultraviolet (UV), which can be used for both the filler and the composite. In addition to the impact on the composite's morphology, preliminary treatment of the filler with UV light leads to changes in the electrical properties of the material [1, 2], namely, it improves the electrical conductivity of the GNP / ER composite if pre-irradiation of GNP with UV for 20 min, which is the optimal exposure time, has been applied. An increase in the electrical conductivity of GNP / ER composites when UV-irradiated GNP are used can be associated with the removal of insulating contaminants from the surface of GNP and with an increase in the content of functional groups on the GNP's surface.

The aim of the present work was to investigate the electrodynamic properties of GNP / ER composites with different morphology and surface modification of GNP. For this, GNP, which were obtained by ultrasound dispersion (USD) of thermo-expanded graphite in various liquid media such as water, isopropyl alcohol, acetone and pre-treated with UV, were used in the manufacture of CM.

2. OBJECT AND METHODS OF THE STUDY

Frequency dependence of complex permittivity and dielectric loss tangent was investigated at low frequencies (0.2-2 MHz) for GNP / ER CM with a fixed content of GNP (i. e. 5 wt. %) in cases where the filler was produced by USD of thermoexfoliated graphite (TEG) in various liquid media: water, isopropyl alcohol or acetone.

GNP powders were obtained from TEG by a technique, which includes USD with the help of Baku 9050 device with a maximum output power of 50 W and an ultrasound frequency of 40 kHz. After drying, the ob-

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tained GNP were divided into two parts, one of which was subjected to UV irradiation, and the other was left in the initial state.

UV treatment was carried out using an installed in a fume cupboard arc mercury tubular high pressure lamp (DRT-1000), which is a powerful source of UV radiation. DRT-1000 lamp emits an UV flux in the wavelength range of $240 \div 320$ nm with a power of 50 W. The distance between the tube of the UV lamp and the shelf with irradiated powders of GNP was 11 cm. The initial GNP powders were subjected to UV treatment for 20 min.

GNP / ER CM were manufactured by the method of mixing in solution with subsequent pouring into plastic molds for polymerization of samples.

Investigation of dielectric properties of the composites was carried out using dielectric relaxation spectroscopy (DRS) method which is implemented on the basis of the impedancemeter Z-2000 in an alternating current at an amplitude of 0.125 V. Alternating current which passed through the sample is measured after which the values of the variable sinusoidal voltage and current are converted to the values of real (Z') and imaginary (Z'') parts of the impedance by Fourier analysis. The measuring device is connected to a dielectric cell with a two-electrode circuit. The construction of a dielectric cell is similar to a flat capacitor covers, between which a test sample in the form of a thin plate is placed instead of an insulator layer.

Complex impedance Z^* can be represented through electrical module M^*:

$$Z^* = Z' + iZ'',$$

$$M^* = M' + iM'',$$

$$M' = \varepsilon'/(\varepsilon'^2 + \varepsilon''^2),$$

$$M'' = \varepsilon''/(\varepsilon'^2 + \varepsilon''^2),$$

$$Z' = M''/(\omega C_0),$$

$$Z'' = M'/(\omega C_0),$$

where ε' is the real part of dielectric permittivity, ε'' is the imaginary part of dielectric permittivity, ω is the angular frequency, C_0 is the capacity of free capacitor.

Dielectric loss tangent is determined by the following formula: $tg\ \delta = \varepsilon''/\varepsilon'$.

3. RESULTS AND ANALYSIS

The US dispersion process in the appropriate liquid media has been applied until then a worm porous structure of TEG was destructed into separate GNP scales, the thickness and diameter of which depend on the type of dispersant liquid media and the duration of US treatment. A detailed study of the morphology of GNP, depending on the medium of US dispersion of TEG, was carried out in our paper [1] by methods of optical, scanning electron, atomic force microscopy. Results of the study of GNP's particles morphology depending on the media of USD are presented in Table 1.

Thus, USD of TEG in various liquid medium results in obtaining GNP with different characteristic dimensions and defective structure. However, the aspect ratio of the filler (p) is one of the defining parameters for predicting the electrical properties of the CM. In [1], the research results of infrared spectroscopy (IR) about the functional composition of the surface of graphite nanoparticles which were obtained in various liquid media are given. The process of USD of TEG in acetone, isopropyl alcohol and water can be considered as a non-covalent functio-nalization, during which hydrorophobic interactions or hydrogen bonds between carbon atoms and functional groups are formed. A redistribution of the intensities of absorption peaks of functional groups on the surface of UV-treated GNP in comparison with the initial ones is noted. UV-irradiation leads to an increase in the content of oxygen-containing functional groups, including ethers, hydroxyl, carboxylic and carbonyl groups on the GNP's surface. For GNP obtained by USD in acetone, the functionalization of their surface is different from others due to manifestation of the valence oscillations of the $C = O$ bond in the COOH group near $1725\ \text{cm}^{-1}$. It was also noted that the UV-treatment of GNP significantly reduces the intensity of absorption bands by $C_{sp}2$-H at $2926\ \text{cm}^{-1}$ and $C_{sp}3$-H at $2852\ \text{cm}^{-1}$ bonds. In addition, for GNP obtained by USD in water, inversion of the $C = C$ bond was observed. Such changes can be explained by cleaning of the GNP surfaces of organic and weakly bound substances, which is stimulated by ozonolysis. To this conclusion, in particular, the authors of the work [3] came, who note the purification of the boundaries between the basic graphite planes due to their treatment with UV light.

Table 1 – Morphology of GNP, depending on the media of US dispersion of TEG

Designation of received particles	Type of liquid medium of US dispersion	Time of dispersion	Lateral dimensions of GNP particles	Thickness of GNP	Maximum of the curve of GNP thickness distribution	Aspect ratio of the obtained GNP
GNP1	water	20 hours	$100 - 1500$ μm, individual GNP have a diameter of $1 - 3$ μm	$25 - 100$ nm	50 nm	$\sim 10^3 - 10^4$
GNP2	isopropyl alcohol	1,5 hours	$20 - 50$ μm	$22 - 36$ nm	32 nm	$\sim 10^3$
GNP3	acetone	3 hours	$1 - 3$ μm, individual GNP have a diameter of $5 - 10$ μm	$15 - 45$ nm	30 nm	$\sim 10^2$

The frequency dependence of the real part of the complex permittivity, ε', for the GNP / ER composites where the particles of GNP1, GNP2, GNP3 were used as fillers (see Table 1) is presented in Fig. 1a. As shown in Fig. 1a, ε' remains practically unchanged with the increase of the EMR frequency when ε'' (see Fig. 1b) decreases, as it is for dielectric loss tangent (Fig. 1 c), which decreases for all of the investigated samples at an increase of the EMR frequency.
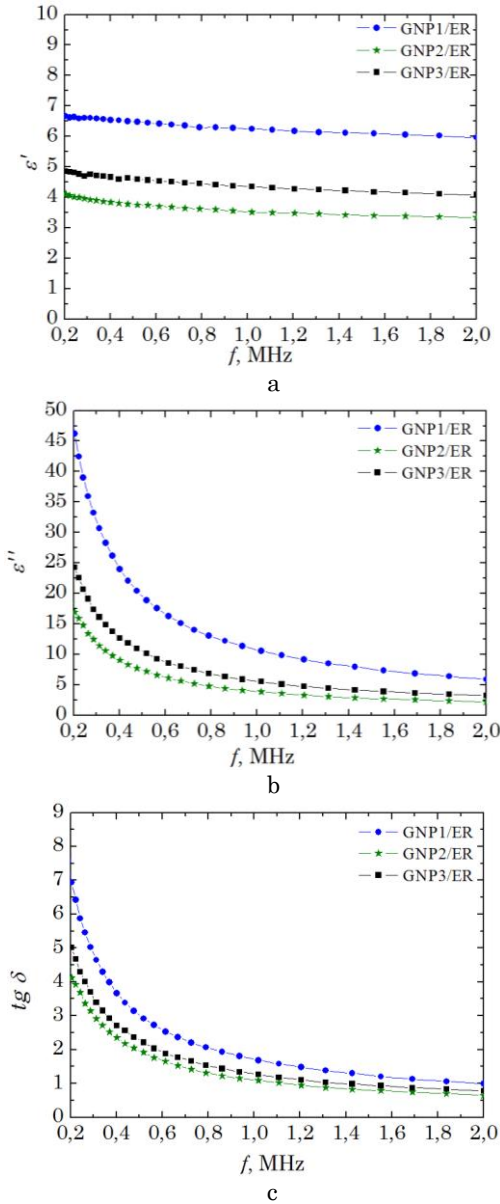
a

b

c

Fig. 1 – Frequency dependences of the real part of dielectric permittivity (a), the imaginary part of dielectric permittivity (b) and dielectric loss tangent (c) for CM 5 wt. % GNP/ER

Besides, the highest value of ε' was observed for composites, where obtained by dispersion of TEG in water GNP1, which have the highest value of the aspect ratio ($\sim 10^4$), were used as filler.

Qualitatively, this behavior of ε' can be explained in terms of the Maxwell-Garnett model [4, 5], where the permittivity of the composite components as well as the volume content and shape of the conductive filler particles is taken into account. In the Maxwell-Garnet model, the dielectric permittivity of a CM with an isotropically distributed filler is described by the following expression:

$$\varepsilon_{eff} = \varepsilon_p + \varepsilon_p \frac{\dfrac{\phi}{3}\sum\limits_{j=x,y,z}\dfrac{\varepsilon_i - \varepsilon_p}{\varepsilon_p + N_j(\varepsilon_i - \varepsilon_p)}}{1 - \dfrac{\phi}{3}\sum\limits_{j=x,y,z}\dfrac{N_j(\varepsilon_i - \varepsilon_p)}{\varepsilon_p + N_j(\varepsilon_i - \varepsilon_p)}}, \qquad (1)$$

where ε_{eff} is the effective dielectric permittivity of CM, ε_i and ε_p are the dielectric constants of the filler and polymer, respectively, ϕ is the volume fraction of filler in CM, N_j is the the depolarization factor of particles in the form of ellipsoids in x, y, z directions.

However, as can be seen from the results presented in Fig. 1, the dielectric permittivity of the CM with the use of GNP3 as filler, for which p is 10^2, exceeds the value of the dielectric permittivity of the CM with the use of GNP2 as filler, for which p is 10^3. This means that, in addition to the aspect ratio of the filler, there are other important factors that determine the dielectric constant of the CM.

As shown in the study [6], among the factors that determine the value of ε_{eff} in the GNP / ER CM, a particular attention should be paid to the uniform distribution of GNP in the epoxy matrix and to the level of interface interaction due to the presence of the "interface" area at the boundary of the filler and the polymer [7-9]. Composite system where the filler phase, the matrix and the interface areas are conditionally highlighted is illustrated in Fig. 2.
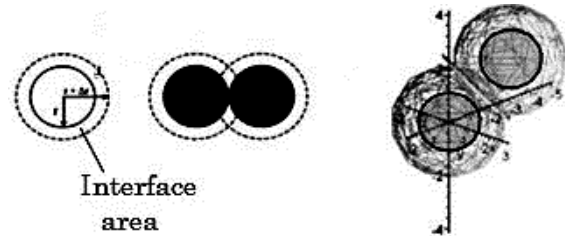

Fig. 2 – Schematic image of the interface area around the filler particles in the composite [10]

The interphase region is formed from polymer molecules, which are bound or somehow oriented on the matrix-filler boundary. This boundary between phases is conventionally called as "interface region", the characteristics of which are modified due to the fact that the particles of the filler limit the motion of polymer molecules in the matrix. The polymer chains in the matrix phase take random orientation configurations in the composite volume, since there the polymer chains and side groups are relatively free to movement – stretching, spin and twist, which minimizes their conformational energy and maximizes their internal entropy [10].

However, polymer molecules are limited in movement in the case of their binding to the filler molecules. Changes of polymer's ε in the interface region is proportional to the decrease or increase of the dipole polarization [10].

According to a model that takes into account a volume fraction of the interface area (Interphase Power Law model), which is based on the expansion of general model of the power law, composite systems with the filler, the matrix, and the interface area phases should be considered as special three-component composite systems consisting of two main components (matrix and filler) and interface area, whose properties are derived from the characteristics of the filler and matrix components [7, 11].

Dielectric permittivity of the composites containing the interface area is described by the expression:

$$\varepsilon_n^{\beta} = \varphi_f \varepsilon_f^{\beta} + \varphi_i \varepsilon_i^{\beta} + \varphi_m \varepsilon_m^{\beta}, \qquad (2)$$

where φ_f, φ_i and φ_m determine volume fractions of the filler, the interface area and the matrix in CM, respectively, ε_c, ε_f, ε_i and ε_m are the complex dielectric permittivities of the composite, the filler, the interface area and the matrix in CM, respectively. For fillers in the form of thin discs: $\beta \cong 0.3$ [6]. The volume fraction of the filler, φ_f, is a known value for each composite. Volume fraction of the matrix phase is given by:

$$\varphi_m = (1 - \varphi_f - \varphi_i). \qquad (3)$$

The volume fraction of the interface area, φ_i, depends on the volume fraction of the filler, the surface area of the filler and the thickness of the phase region which surrounds each particle of the filler. Thus, for monodisperse, spherical particles φ_i is determined by the expression [8]:

$$\varphi_i = (1 - F) S_f \Delta r \rho_f \varphi_f, \qquad (4)$$

where S_f is the specific surface area of the filler (measured in m²/g) and ρ_f is the filler's density (measured in g/m³). The probability of interfacial areas overlap F is a function of the folllowing values: the filler's volume fraction, the interfacial layer's thickness, the shape and size of filler particles, and, according to [12], is defined as:

$$F = \left(\frac{6\varphi}{\Pi}\right)^3. \qquad (5)$$

Then, taking into account conditions (3) and (4), the equation for dielectric permittivity (2) can be represented as follows:

Then, taking into account the data on the volume fraction of the interfacial layer, which are given in Table 2, we can assume that the increase in the dielectric permittivity of GNP1 / ER CM in comparison with the dielectric permittivity of GNP3 / ER CM is associated, first of all, with a larger value of the dielectric permittivity of the interface layer in GNP1 / ER CM. The analysis shows that this condition will persist, even if we assume that the value of Δr in these CM is 2-3 times greater than the value of Δr in GNP3 / ER CM.

The role of the dielectric permittivity of the interfacial layer in the formation of effective dielectric permittivity of CM becomes clearer after analysis of the results of investigation of the dielectric permittivity of CM with UV-treated GNP. As shown in Fig. 3, where the frequency dependences of dielectric permittivity of CM where GNP1 and GNP1 (20 minutes UV) (Fig. 3a), GNP2 and GNP2 (20 minutes UV) (Fig. 3b) were used as fillers, UV treatment for 20 minutes results in the increase of ε' for all the investigated samples. Taking into account that the size of the particles and the value of Δr practically do not change after processing of the fillers with UV, which was evidenced by the results of the study of the temperature dependence of the electrical resistivity of the CM (the value of temperature at the minimum point on $\rho(T)$ dependences practically does not change

$$\varepsilon_n^{\beta} = \varphi_f (\varepsilon_f^{\beta} - \varepsilon_m^{\beta}) + \varphi_i (\varepsilon_i^{\beta} - \varepsilon_m^{\beta}) + \varepsilon_m^{\beta}. \qquad (6)$$

Let's estimate the volume fraction of the interface area for CM GNP / ER when using GNP obtained in various dispersing media with the use of an average values of the GNP's particle size, which were obtained by optical and atomic force microscopy (see Table 1). It is known that the thickness of the interfacial layer is of the order of one molecular radius and the value of it is 5÷20 nm [13, 14]. Then, in the first approximation, we use the following value for calculations: $\Delta r = 10$ nm. Results of the calculation of the volume fraction and dielectric permittivity of the interface layer in GNP / ER CM within the framework of the model, which takes into account the volume fraction of the interface area, are given in Table 2.

Table 2 – Calculation of the volume fraction and dielectric permittivity of the interface layer in CM GNP / ER

Composition	ε'	φ_i, vol. fr	ε_i'
GNP1/ER	6.02	0.89×10^{-2}	53.4
(GNP1+UV)/ER	7.42	0.89×10^{-2}	68.73
GNP2/ER	3.32	1.35×10^{-2}	13.6
(GNP2+UV)/ER	4.37	1.35×10^{-2}	26.7
GNP3/ER	4.11	1.50×10^{-2}	18.67

Bearing in mind that the volume fraction of carbon filler in the studied CM GNP / ER with GNP1, GNP2, GNP3 fillers is the same, as the values of ε_f^{β} and ε_m^{β} are, the difference between the dielectric permittivity of GNP / ER samples with the use of GNP, which were obtained in different dispersing media of TEG, can be represented as following:

$$\varepsilon_{c(GNPn/EC)}^{\beta} - \varepsilon_{c(GNPm/EC)}^{\beta} = \varphi_{i(GNPn/EC)}(\varepsilon_{i(GNPn/EC)}^{\beta} - \varepsilon_m^{\beta}) - \varphi_{i(GNPm/EC)}(\varepsilon_{i(GNPm/EC)}^{\beta} - \varepsilon_m^{\beta}). \qquad (7)$$

when using UV-treated GNP as a filler [2], it can be argued that the increase of ε' for all the investigated samples is observed solely because of increasing permittivity of the interfacial layer, which is associated with a change in the chemical composition of the GNP particles surface.

Thus, from the analysis of the frequency dependence of the complex permittivity of GNP / ER composites it is seen that the preliminary irradiation of the filler with UV light leads to an increase in the effective dielectric permittivity of the CM, which correlates with an increase in their electrical conductivity.

4. CONCLUSIONS

It has been experimentally shown that in the frequency range of 0.2-2 MHz the dielectric permittivity of the CM with the use of obtained by TEG dispersion in acetone GNP3 as filler, for which p is 10^2, exceeds the value of the dielectric permittivity of the CM with the use of obtained by TEG dispersion in isopropyl alcohol GNP2 as filler, for which p is 10^3, although, in general, the dielectric permittivity of CM increases with an increase of the filler's particles aspect ratio. To explain this behavior of ε, it is suggested to take into account the dielectric permittivity of the interface layer in the forma-tion of effective dielectric permittivity of CM. It was shown that
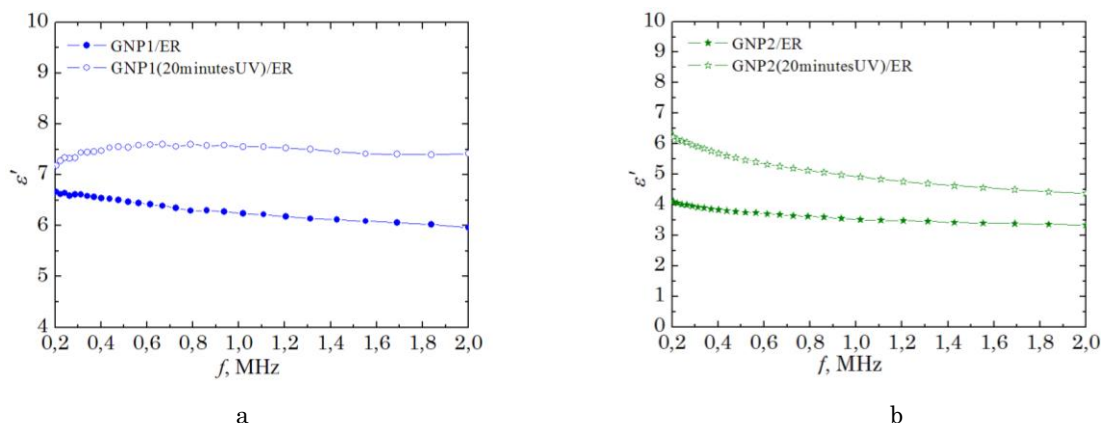
a   b

Fig. 3 – Frequency dependence of the dielectric permittivity of CM 5 wt. % GNP/ER and 5 wt. % GNP (20 minutes UV)/ER (GNP were obtained by USD in water (a) and isopropyl alcohol (b))

UV-treatment of GNP for 20 minutes resulted in an increase of ε' of CM GNP/ER, which is due to an increase in the dielectric permittivity of the interface layer of CM, which, in turn, is due to a change in the chemical composition on the GNP's surface after UV-irradiation.

It was found that the real part of dielectric permittivity of 5 wt. % GNP/ER composites, where the UV-irradiated GNP were used as filler, is higher than the real part of dielectric permittivity of composites with non-irradiated filler, which, as shown by the analysis within the framework of the model taking into account the volume fraction of the interface region (*Interphase Power Law model*), is solely due to an increase of ε of interfacial layer, which is due to the change in the chemical composition of the GNP's particles surface.

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Міжфазна взаємодія як чинник діелектричних властивостей композитів на основі епоксидної смоли з графітовими нанопластинками

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Робота присвячена дослідженню фізичних властивостей композитних матеріалів графітові нанопластинки / епоксидна смола із зміненим рівнем міжфазної взаємодії за рахунок попереднього опромінення наповнювача ультрафіолетом. З'ясовано вплив міжфазної взаємодії на границі наповнювач / матриця в полімер-вуглецевих композитних матеріалах на їх електродинамічні властивості, що є основою розробки композитних матеріалів із регульованим набором фізичних властивостей. Аналіз в рамках моделі, що враховує об'ємну частку міжфазної області, показав, що підвищення діелектричної проникності в композитах, де в ролі наповнювача було використано опромінені ультрафіолетом графітові нанопластинки, відбувається за рахунок збільшення діелектричної проникності міжфазного шару, що пов'язано із зміною хімічного складу поверхні графітових нанопластинок.

Ключові слова: Графітові нанопластинки, Композит, Діелектрична проникність, Діелектричні втрати, Міжфазна взаємодія.