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ELECTROPHYSICAL PROPERTIES OF COMPOSITES BASED ON EPOXY RESIN AND CARBON FILLERS

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Polymeric construction materials based on epoxy resin, carbon fillers, such as graphene nanoplates (GNP), carbon nanotubes (CNT) and fillers of inorganic nature – perlite, vermiculite, sand with improved electrophysical characteristics have been developed. The electrophysical properties of composites obtained in various ways which differ according to the principle of injecting components have been investigated.

GNP were obtained in two ways. Size distribution of GNP obtained by electrochemical method is 50 to 150 nm. The average particle size is up to 100 nm. It occurs that these particles tend to aggregate as it is shown by the method of dynamic light scattering. The GNP obtained by dispersing thermally expanded graphite in water in a rotary homogenizer have a particle size distribution of 400 to 800 nm if very small particles and large aggregates are absent. The second method of obtaining GNP is less energy consuming and requires fewer manufacturing cycles, so it is more cost-effective. Obtaining composites using aqueous suspensions of GNP is environmentally friendly.

Due to the hydrophobic properties of its surface the electrical conductivity of the system which uses vermiculite is higher than one of that which uses perlite for composites with CNT and GNP.

It has been found that the difference of electrophysical characteristics between two systems which contain the same amount of carbon filler is caused by the nature of the surface of dielectric components – sand. By changing the content of dielectric ingredients can expand the functionality of composites if use them for shielding from electromagnetic fields.

Keywords: *electrically conductive composites, percolation threshold, carbon nanotubes, graphene nanoplates, ultrahigh frequency range*

INTRODUCTION

Nanostructural composites with carbon fillers based on thermosetting resins have been introduced in various industries because of their high indices of electrical and thermal conductivity, corrosion resistance, inertness to many chemicals, durability [1–5]. Nano-composites showed increased strength, stiffness [2], significant increase in viscosity during destruction. In papers [3–7] one can find information about the influence of the content of the filler, various methods of dispersing carbon fillers and their injection into a polymeric matrix, an aspect ratio, the area of the specific surface and the functionalization of the component surface.

The main methods of dispersion are the chemical modification of carbon fillers with carboxyl groups and the use of mechanical methods when they are injected into the composite. Various methods of injecting fillers exist, for example, in the form of pre-manufactured concentrated resins, or in the form of suspensions in various solvents [2].

Mechanical methods such as ultrasonic action, centrifugation and mixing at high shear loads let us increase the degree of dispersion of carbon fillers, which in the case of CNT can lead to a decrease of their length.

Expanding the range of nanostructured composites requires their improvement while maintaining the cost, observance of environmental production rules. The properties of composites can be controlled by injecting components of different morphology, as well as changes in composite production technology and method of injecting components. Epoxy composites in this paper are obtained by different methods of introducing components.

The choice of binder for composites is conditioned by the complex of properties of epoxy resins: dielectric indicators and adhesion of the operational level, high mechanical strength, minimal shrinkage. The addition of carbon nanomodifiers (TRG, CNT, GNP) to epoxy resins is explained by a significant improvement in a number of mechanical, electrical, thermophysical properties of epoxy oligomers filled with a small amount (up to 2 % by weight) of nanoparticles

[2, 3, 8]. Expanded perlite, vermiculite are fire-resistant materials with excellent heat conducting and sound insulating properties. The sand was added to the polymer system in order to increase the wear resistance of the initial compositions used in the form of facing material (mostly tiles) to protect buildings and structures from electromagnetic fields.

The aim of this work is to study the electrophysical properties of samples of epoxy composites obtained by different technologies: EC-CNT-perlite, EC-CNT-vermiculite and EC-GNP-perlite, EC-GNP-vermiculite.

METHODS AND MATERIALS

The GNP received in two ways and multilayered CNTs, Epoxide Resin (Epikote Resin 828), hardener – polyethylene polyamine (Telalit 410), expanded perlite of the middle fraction (M-75 marks), vermiculite (GOST 1286-575) and clean sand were used. CNT (TU - in 03291669-009: 2009) obtained by the chemical deposition of the gas phase (CVD) on the $\text{Fe}_2\text{O}_3\text{-MoO}_3\text{-Al}_2\text{O}_3$ catalyst on TM “Spetsmash” [9]. The GNP was obtained by electrochemical dispersion of graphite foil made of EG (TM “Spetsmash”) and dispersion of EG in water by rotary homogenizer (II) [9]. GNP was obtained in the laboratory of electrophysics of nanomaterials of the CISC NAS of Ukraine by electrochemical dispersing anode from graphite foil.

The CNT was injected into the epoxy resin without any additional modifications. GNP was applied to the surface of perlite particles or vermiculite from aqueous suspensions in a rotary evaporator. After drying, the resulting conductive particles were added to the epoxy resin.

The particle size distribution function was studied by a laser correlation spectrometer Zeta Sizer Nano S (Malvern, UK) equipped with a correlator (Multi Computing Correlator Type 7032 CE) by the dynamic light scattering (DLS) [7]. The helium-neon laser LGN-111 was used with the output power of 25 mW and wave-length of 633 nm to irradiate the suspension. The registration and statistical processing of the scattered laser light at 173° from the suspension were performed three times for 120 s at 25°C . The resulting autocorrelation function was treated with standard computer programs PCS-Size mode v.1.61.

For efficient volume distribution of the composite CNT were first dispersed in acetone using an ultrasonic dispersant USD-A. After evaporation (at $T = 50\text{--}60^\circ\text{C}$) of excess acetone: epoxy resin, PEPA hardener, vermiculite or perlite (10 wt. %) were added into a cup with CNT with constant stirring. As a result systems such as ER-CNT-perlite and ER-CNT-vermiculite were obtained. Samples of the same composition but with the addition of sand (30 wt. %) were used to obtain systems such as EC-CNT-perlite-sand and EC-CNT-vermiculite-sand. ER-GNP/perlite, ER-GNP/vermiculite and ER-GNP/perlite-sand, ER-GNP/vermiculite-sand were obtained in a similar way. The application of the graphene layer/layers on the filler particles (GNP/vermiculite, GNP/perlite) was performed manually. The calculated volume of graphene suspension of known concentration had been mixing with perlite particles (vermiculite) for 30 min. Then the samples had been drying at $T = 70^\circ\text{C}$ during 1 day.

Bulk samples for the study (in the case of CNTs and in the case of GNP) were obtained by direct pouring of the compositions into rectangular metal molds measuring $23 \times 10 \times 4$ mm, followed by congelation in molds at room temperature during the day.

The composites were studied using a ultra-high frequency interferometer on the basis of the phase difference meter RFK2-18 and the meter of the stagnant wave ratio and the weakening of P2-60 [10]. The electrophysical characteristics – dielectric constant ε' and specific conductivity σ were measured at low frequencies of 0.1; 1 and 10 kHz using two-contact method with an immittance meter E7-14. The value of ε'_{10} is determined at a frequency of 10 kHz, and σ_1 at a frequency of 1 kHz. The relative measurement error did not exceed $\pm 5\%$.

EXPERIMENTAL RESULTS AND DISCUSSIONS

The values σ_1 of electrical conductivity σ_1 of composites ER-CNT-perlite, ER-CNT-vermiculite and ER-CNT-perlite-sand, ER-CNT-vermiculite-sand have similar values for all concentrations of CNT (Fig. 1).

The dependence of the electrical conductivity of the system with vermiculite is higher than the one with perlite for composites with CNTs (Fig. 1). This repeats the same dependence as with

EG [3] and is explained by the fact that the surface of vermiculite is more hydrophilic.

The electrical conductivity of composites with sand is higher than that of sand-free composites in the range of 0.005–0.02 volume fractions of CNT. The structural role of the inert in the electrophysical sense of the filler (sand) has been shown previously [3].

The values ε' of the real component dielectric constant increased uniformly in the range of CNT concentrations for the ER-CNT-perlite and ER-CNT-vermiculite systems (Fig. 2 a). For systems with sand ER-CNT-perlite, sand and ER-CNT-vermiculite, sand (Fig. 2 b) the values of ε' are higher than for similar systems without sand with a CNT content of up to 0.02 of filler content.

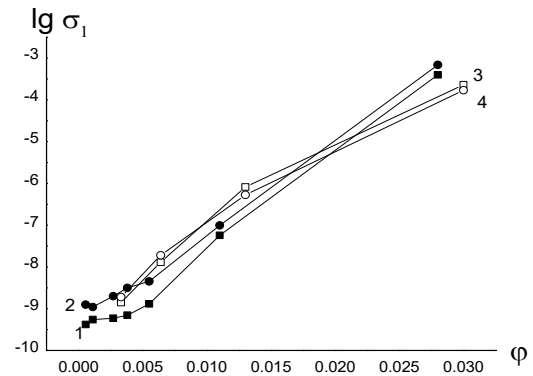
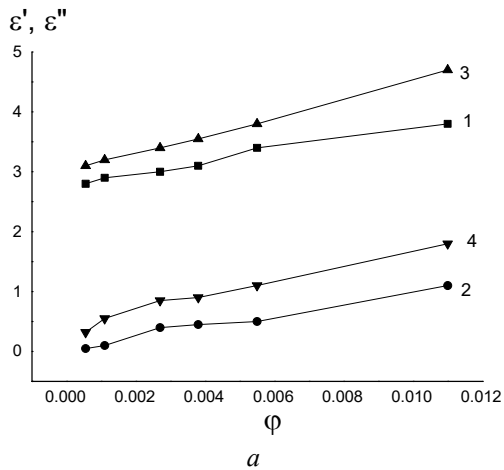


Fig. 1. The electrical conductivity σ_1 to the CNT concentration in composites: ER-CNT-perlite (1) and ER-CNT-vermiculite (2) and respectively in composites containing sand (3 and 4)

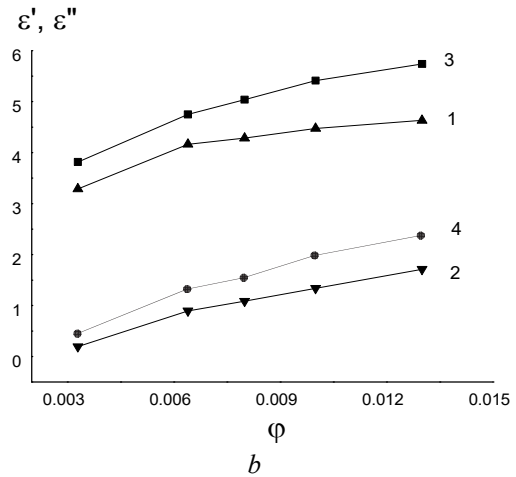


Fig. 2. The real ε' (1, 3) and imaginary ε'' (2, 4) components of the complex permittivity of CNT concentration in systems ER-CNT-perlite (1a, 2a), ER-CNT-vermiculite (3a, 4a) and ER-CNT-perlite, sand (1b, 2b), ER-CNT-vermiculite, sand (3b, 4b) based composites at the frequency of 9 GHz

The technology of manufacturing samples of ER-CNT-filler must ensure uniform distribution of CNT in the mixture. To reduce the agglomerates of nanotubes, they are dispersed by ultrasound in acetone, the presence of which is not desirable in terms of environmental safety requirements. The search for CNT analogues and advanced methods of obtaining composites, with minimal use of organic solvents ended up the choice of GNP. Their synthesis is cheaper, and the technology of injecting them into the composite meets environmental standards.

As it has been shown [8], dimensional effects significantly affect the electrophysical characteristics and other parameters of the

system, particularly, the value of the percolation threshold and the magnitude of the jump in electrical conductivity with increasing concentration of the electrically conductive component. The percolation threshold in polymer systems for CNT is about 0.005, and for GNP it is higher than 0.0075–0.01 by volume depending on the structural features of the source polymer.

The level of electrical conductivity of the system with vermiculite is higher than that for systems with perlite (Fig. 3 curves 1, 2, 5, 6) for composites with GNP (I and II). The same ratio is observed for composites with sand. The values of

electrical conductivity are higher for composites that contain sand (Fig. 3 curves 3, 4, 7, 8).

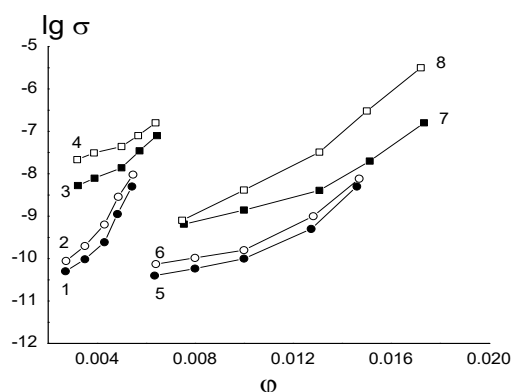


Fig. 3. The electrical conductivity σ at the frequency of 1 kHz on the content of GNP: received by the I method in the systems ER-GNP-perlite (1, 3) and ER-GNP-vermiculite (2, 4) and with sand (3) and (4), respectively; received by the II method, in the systems ER-GNP-perlite (5, 7) and ER-GNP-vermiculite (6, 8) and with sand (7 and 8), respectively

The positive effect on the electrical conductivity of composites of the non-conductive component – sand is explained by the effect of compaction, the narrowing of the layer of epoxy component between the modified GNP filler particles in the composites. The achieved level of conductivity at the content of GNP 0.005–0.006 (I method) and 0.013–0.015 (II method) provides effective absorption of electromagnetic radiation on the microwave, which will allow the use of these systems for the manufacture of radio-absorbing and shielding materials [8, 12, 13].

A more intense and symmetric absorption band is observed in UV-vis spectra of GNP (II) sample (Fig. 4 b), that may be caused by a more homogeneous size distribution of the particles. The shift of the edge of the absorption band in the long-wavelength region (up to 800 nm) may be associated with an increase in the average particle size for this sample.

Using the DLS method, the particle size distribution was determined. The average particle size of GNP (I) is up to 200 nm (Fig. 4 c). The particle size distribution by intensity basis indicates the formation of aggregates up to 1400 nm (Fig. 4 d). The GNP (II) sample is more polydisperse with the average particles size of 400–800 nm (Fig. 4 d). A more homogeneous distribution of particles by volume (Fig. 4 d) and

intensity (Fig. 4 e) basis indicates the absence of both very small particles and large aggregates.

The values of the real component e' of dielectric constant increase abruptly in the range of the optimal concentration of GNP for both systems ER-GNP-vermiculite (Fig. 5 a) and EC-GNP-perlite (Fig. 5 b). Dielectric values for composites with sand are higher than the corresponding values of composites without sand, regardless of the particle size of the GNP. Similar results were obtained for composite systems with TRG and CNT. This dependence for composites containing sand is characteristic of all of the studied systems. Thus, the electrically conductive component forms a more branched framework. As a result, electrophysical parameters of microwave systems reach the percolation threshold at a lower filler content.

The comparing the systems with GNP (I) and (II) indicated, that due to the much larger particle size of GNP (II) the values of e' and e'' reach the same values as for the system with GNP (I) while the content is 2–3 times larger (Fig. 5). Covering the dielectric particles (perlite, vermiculite) with a layer of GNP of a larger size requires a larger number of them.

According to experimental data (Fig. 3) and (Fig. 5), the percolation threshold for the GNP (I) is approximately 0.005–0.006, and for the GNP (II) the percolation threshold is much higher and reaches 0.013–0.015 volume content. The increase in the percolation threshold for the GNP (II) system is associated with larger particles of GNP (II). The injection of sand in composites with GNP (I) and (II) does not lead to a significant increase in the values of the dielectric constant as it is observed for systems with CNT, which is caused by another distribution of the conductive component in the volume of composites.

While comparing the results of studies of these systems with the results of the concentration dependences of electrical conductivity and e' and e'' for the system with CNT (Fig. 1–2), we notice that the percolation threshold for the system with CNT is the same as for the system with GNP (I). Therefore, the considered method of forming composites by applying GNP on the surface of dielectric particles (perlite, vermiculite) is promising because it provides effective absorption of microwave radiation while using electrically conductive nanoparticles with a smaller aspect ratio than CNT.

It is important to note the environmental friendliness of obtaining composites using aqueous suspensions of GNP and applying them to the surface of the dielectric filler instead of organic solvents. Alcohol-acetone mixtures are used for injection into the EG and dispersion of

fillers. In our case, the nanosized filler is dispersed in water without the use of organic solvents, which provides a highly environmentally friendly method of creating and applying coatings and products based on EG, paints, varnishes and nanosized elements.

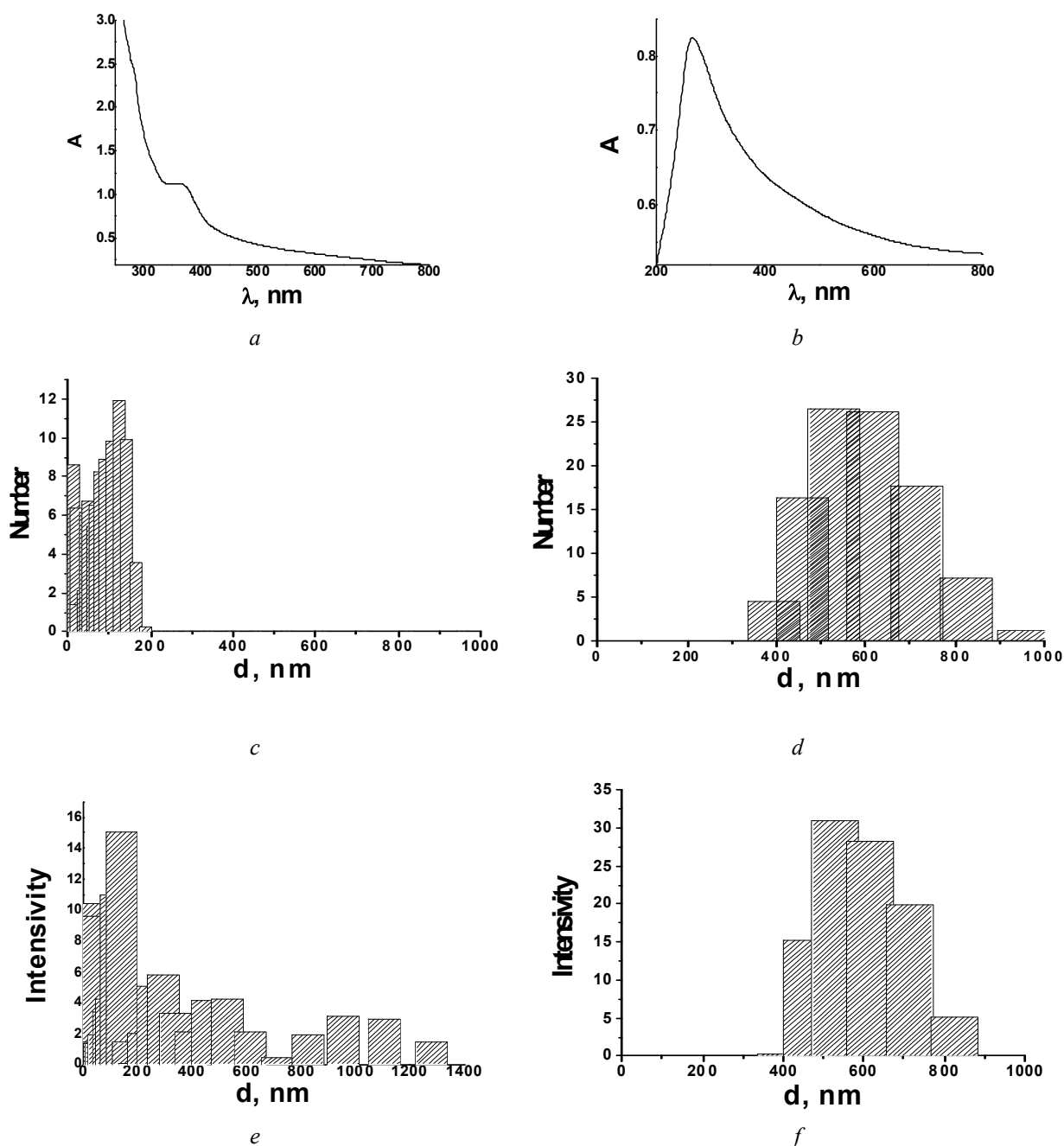


Fig. 4. Optical spectra (*a, b*) and size distribution (DLS method, by number and intensity basis) of GNP particles obtained by the method I (*a, c, e*) and method II (*b, d, f*)

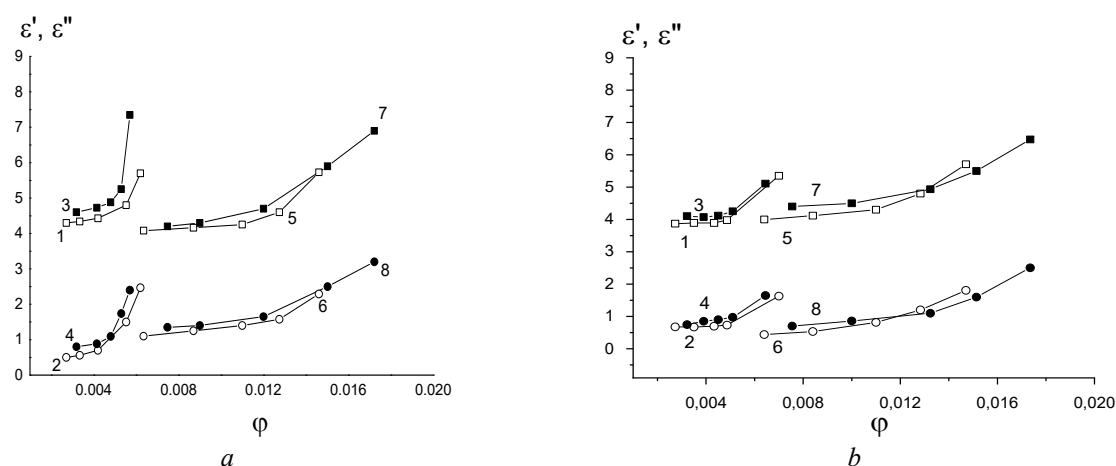


Fig. 5. The real ϵ' (1, 3, 5, 7) and imaginary ϵ'' (2, 4, 6, 8) component of the complex dielectric constant at the frequency of 9 GHz on the content of GNP received by I method in the composites of ER-GNP systems-vermiculite (1a, 2a) and with sand (3a, 4a), ER-GNP-perlite (1b, 2b) and with sand (3b, 4b); received by the II method for systems ER-GNP-vermiculite (5a, 6a) and with sand (7a, 8a), ER-GNP-perlite (5b, 6b) and with sand (7b, 8b)

CONCLUSIONS

The construction materials based on epoxy resin, carbon fillers (carbon nanotubes, graphene nanoplates obtained in two ways) and fillers of inorganic nature – perlite, vermiculite and sand have been developed. GNP (I) was synthesized by electrochemical dispersion of graphite foil made of EG, GNP (II) was performed by dispersing EG particles in water using a rotary homogenizer. In this case, the production of GNP (II) is less energy consuming, requires fewer manufacturing cycles and can be more cost-effective.

The DLS method shows that the particle size of GNP obtained by electrochemical method is from 50 to 200 nm, and the GNP obtained by dispersion of thermally expanded graphite in a rotary homogenizer is 4 times larger. Thus, the average particle size in the first case is much smaller, but in the second one there is a more monotonous particle distribution. Considering the absorption shift in the spectra of GNP (II)

samples, they can be used to create materials with the absorption properties of the IR part of the spectrum.

It has been found that the level of electrical conductivity of composites with CNT and GNP in systems with vermiculite have higher values than those with perlite, both with sand and without, due to higher hydrophobicity. The achieved level of electrical conductivity and dielectric constant of composites at the content of GNP 0.005–0.006 (method I) and 0.013–0.015 (method II) provides effective absorption of electromagnetic radiation on the microwave, which will allow the use of these systems for the manufacture of radio-absorbing and shielding materials.

The dispersion of nanosized fillers in water and their application on the surface of dielectric fillers without the use of organic solvents provides high environmental friendliness of methods of manufacturing coatings and products based on ER, paints, varnishes and nanosized elements.

Електрофізичні властивості композитів на основі епоксидної смоли та вуглецевих наповнювачів

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Розроблено полімерні конструкційні матеріали на основі епоксидної смоли, вуглецевих наповнювачів, таких як графенові нанопласти (ГНП), вуглецеві нанотрубки (ВНТ) та наповнювачів неорганічної природи – перліту, вермікуліту, піску, з покращеними електрофізичними характеристиками. Досліджено електрофізичні властивості композитів, отриманих різними, за принципом введення домішок у суміш зразку, технологіями.

ГНП отримані двома способами. Розмір частинок ГНП, отриманих електрохімічним способом, від 50 до 200 нм, а диспергуванням терморозширеного графіту у воді в роторному гомогенізаторі майже на порядок величини більша, що показано методом динамічного розсіювання світла. Другий спосіб отримання ГНП менш енерговитратний і потребує меншої кількості циклів виготовлення, тому економічно більш вигідний. Одержання композитів з використанням водних суспензій ГНП екологічно безпечно.

Залежність електропровідності системи з вермікулітом має вищі значення, ніж системи з перлітом для композитів з ВНТ та з ГНП, що обумовлено гідрофобними властивостями його поверхні.

Встановлено, що відмінність електрофізичних характеристик двох систем за однакового вмісту вуглецевого наповнювача зумовлена природою поверхні діелектричної складової – піску. Змінюючи вміст діелектричних інгредієнтів, можна розширити функціональні можливості композитів при застосуванні їх для екранування від електромагнітних полів.

Ключові слова: електропровідні композити, поріг перколяції, вуглецеві нанотрубки, графенові нанопласти, надвисокочастотний діапазон.

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