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O.G. Sirenko, S.M. Makhno, O.M. Lisova, G.M. Gunya, P.P. Gorbyk

ELECTROPHYSICAL PROPERTIES OF COMPOSITES BASED ON THE EPOXY RESIN AND EXPANDED GRAPHITE

Chuiko Institute of Surface Chemistry of National Academy of Sciences of Ukraine
17 General Naumov Str., Kyiv, 03164, Ukraine, E-mail: elenasirenko@ukr.net

The composites of epoxy resin-expanded graphite(EG)-vermiculite and epoxy resin-expanded graphite-perlite were obtained and their electrophysical properties were analysed at low frequencies and in the microwave range.

High values (> 30) of real and imaginary components of the complex permittivity for both systems were achieved with a content of EG of less than 2 wt. %. The values of the percolation threshold and critical index of systems were defined: for a system with vermiculite the percolation transition ($\varphi_c = 0.0018$); and for a system with perlite ($\varphi_c = 0.0039$). The method of impedance spectroscopy (10^{-2}–10^6 Hz) shows that for all investigated composites there is no dependence of electrical conductivity to frequency, but up to a value of 10^3 Hz, indicating a low level of ionic conductivity.

It was found that the difference in electrophysical characteristics of two systems with the same content of the expanded graphite arises due to the nature of the surface of the dielectric components. The best indicators, namely, the lower percolation threshold and the achievement of maximum electrical conductivity values at lower EG, are in the system with vermiculite. It is due to the hydrophobic properties of the surface the filler particles, as well as the effect of the flow of a dielectric particle of vermiculite by a suspension of an epoxy resin-EG, while the particles perlite is impregnated with it.

Changing the content of such dielectric ingredients allows us to expand the functionality of composites when used for shielding from electromagnetic fields.

Keywords: *conductive composites, percolation threshold, expanded graphite, microwave range*

INTRODUCTION

Filled composites based on thermosetting resins and expanded graphite (EG) are used in various industries due to high conductivity and thermal conductivity, corrosion resistance, inertness in relation to many chemicals, durability and affordable prices [1–4]. However, the intensive development of technology constantly corrects the requirements for the properties of conductive composite materials (CM), which requires a change in the functional composition of the composite and the application of new methods and technologies for their receipt.

Polymeric CM based on epoxy resins belongs to structural materials: plastic, chemically resistant to alkalis, salts, oxidizers, organic solvents, but are combustible. Therefore, the use of fillers to reduce the combustibility of composites with an epoxy matrix is very relevant. In most cases fillers of inorganic nature are used and they are administered in a significant amount, more than 20 %, which reduces the concentration of resin in the composite. So its thermophysical characteristics and conditions of heat and mass exchange during combustion are changed.

The purpose of this work is to determine the optimal concentration of expanded graphite, for two systems: perlite - epoxy resin, vermiculite – epoxy resin.

METHODS AND MATERIALS

In researches there were used: expanded graphite (GOST 1286-575, TU U 26.8-30969031-013-2007), epoxy resin (Epikote 828), hardener – polyethylenepolyamine (TELALIT 410), expanded perlite of middle fraction (Mark M-75), expanded vermiculite (GOST 1286-575), cleared annual sand.

The epoxy resin (ER) was heated to a temperature of 60–70 °C, to a rarefied state. A powder of EG (from 0.1 to 2 % by weight) was added to the resulting melt while stirring for 5–10 min, hardener was added and then the impurity was added: perlite or vermiculite (9 % by weight), and sand (30 % by weight).

In order to obtain bulk samples, a rectangular mold with dimensions of

23×10×4 mm was used. Samples in the form were kept at room temperature during 24 h.

The composites were studied using an ultra-high frequency interferometer on the basis of a phase difference meter RFK2-18 and a meter of the stagnant wave ratio and the weakening of P2-60 [5]. Frequency dependences of the complex specific conductivity of composites were determined by calculating the impedance spectra in the frequency range 10^{-2}–10^{6} Hz obtained on a Solartron SI 1260 impedance spectrometer [6].

Electrophysical characteristics – dielectric permittivity ε' and specific electrical conductivity σ were measured at low frequencies of 0.1; 1 and 10 kHz by two-contact method with the help of an immittance meter E7-14. The value of ε'_{10} is determined at the frequency of 10 kHz, and σ_1 is at the frequency of 1 kHz. The relative error of measurements did not exceed ±5 %.

EXPERIMENTAL RESULTS AND DISCUSSION

The dependence of the real component ε' of the dielectric constant at low frequencies has a nonlinear dependence on the concentration of EG for ER-perlite-EG and ER-vermiculite-EG systems (Fig. 1 *a*, *b*) and reaches high values already at 2 % of the content of the filler.

The values ε' and the conductivity σ of the source materials without EG are similar. With an increase in the content of the EG, the corresponding characteristics for the composites containing vermiculite are significantly higher than those containing perlite, and reach the maximum values more quickly. The electrical conductivity of a vermiculite system is three times the order of magnitude at the concentration of 0.6 %, although this difference is leveled when the content of the filler increases.

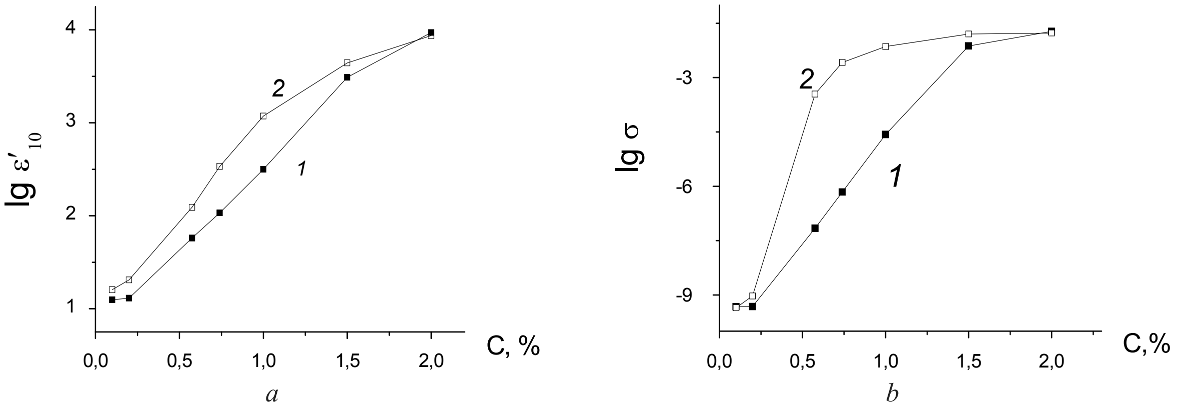


Fig. 1. Dependence of the logarithm the real component ε'_{10} the dielectric constant (*a*) and of the conductivity σ_1 (*b*) on the EG concentration of in perlite (*1*) and vermiculite (*2*) based composites

Using the percolation theory, the following expressions for describing the dependence of the electrical conductivity σ on the content of the filler:

$$\sigma_i \sim \sigma_n(\varphi - \varphi_c)^t, \quad (1)$$

where: t is the critical index of the percolation theory, σ_i is the electrical conductivity of the composite, σ_n – conductivity of the filler, φ – the volume fraction of the filler.

According to the dependencies, the value of the percolation threshold and critical system indices are determined. For a system with vermiculite, the mass content, at which there is a percolation transition is 0.35 % ($\varphi_c = 0.0018$), correlation length $t = 1.4$, effective specific conductivity $\sigma_i = 119$ Ohm^{-1}cm^{-1}, for a system with perlite 0.75 % ($\varphi_c = 0.0039$), $t = 2.1$, $\sigma_i = 770$ Ohm^{-1}cm^{-1}.

Consequently, for a system with perlite, the value of percolation threshold is twice as high as that with vermiculite. This indicates that in a system with vermiculite, continuous cluster is formed with less content of the EG.

The initial values of components of the complex permittivity are the same for both systems under study (Fig. 2) and at high frequencies. After the percolation threshold in each system, there is a rapid increase of ε' and ε'' due to the formation of a continuous cluster. These values for the vermiculite system are higher. Such a difference may be due to the fact that the surface of vermiculite is less hydrophilic than perlite. Around the particle of vermiculite, a shell of «epoxy resin-EG» is created, the electrical conductivity of which is much higher than the electrical conductivity of vermiculite. A leading volumetric mesh is formed in a vermiculite composite, while perlite is leaked by a EG suspension.

The dependence of the logarithm of the real component of the conductivity on the logarithm of frequency for samples with the content of EG 1 and 1.5 % of the ER-perlite-EG system (Fig. 3 *a*) and samples 0.5; 0.7; 1; 1.5 % of the ER-vermiculite-EG system (Fig. 3 *b*) is linear and does not depend on the frequency. For other samples, such independence of frequency is maintained up 10^3 Hz, which indicates a high level of electronic conductivity, as well as a relatively low level of ionic conductivity [6].

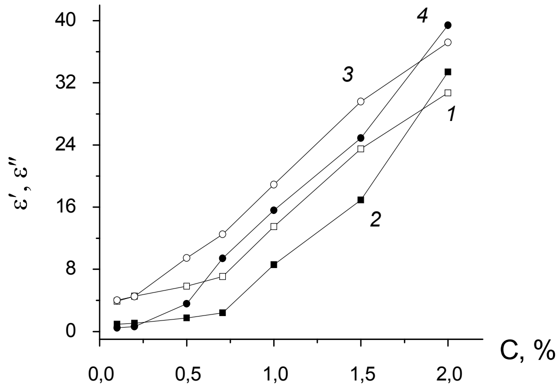
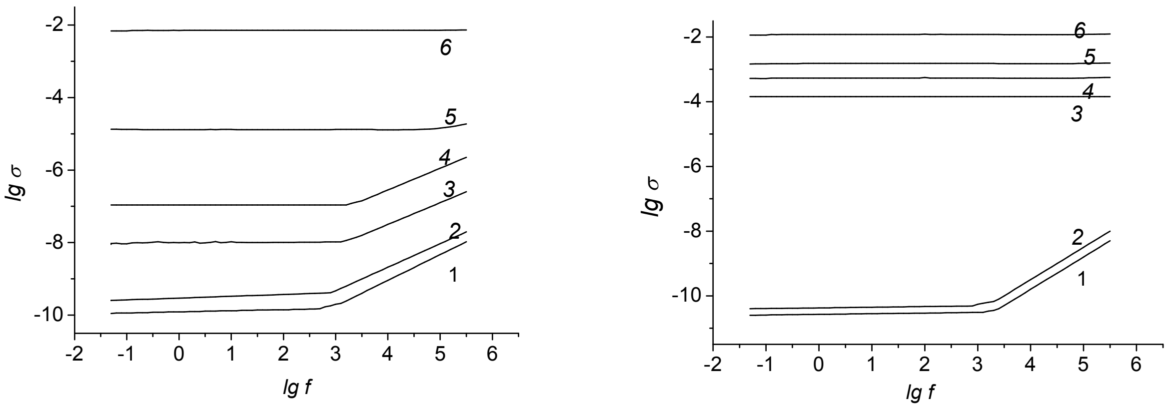


Fig. 2. Dependence of the real ε' (*1, 3*) and imaginary ε'' (*2, 4*) components of the complex permittivity on the EG concentration in ER-perlite-EG (*1, 2*) and ER-vermiculite-EG (*3, 4*) based composites at the frequency of 9 GHz



a *b*

Fig. 3. Dependence of the logarithm conductivity to of the logarithm frequency for the systems ER-perlite-EG (*a*), ER-vermiculite-EG (*b*) for EG concentrations: *1* – 0.1, *2* – 0.2, *3* – 0.5, *4* – 0.7, *5* – 1, *6* – 1.5 %

Sites of smooth growth of conductivity values at an increase in frequency above 1000 Hz are observed for specimens with a content of EG from 0.1 to 0.2 % for both systems, which occurs due to the jumper conduction mechanism [7] and is satisfactorily described by the equation:

$$\sigma = \sigma_0 \cdot \left(1 + \left(\frac{f}{f_0} \right)^n \right), \qquad (2)$$

where σ_0 – the initial value of the conductivity, f_0 – the value of the frequency at which there is a change in the angle of inclination of the electrical conductivity of the frequency, n – power index.

According to data obtained for the composites of both systems, $n \approx 0.8$.

Consequently, the difference in the electrical properties of the two systems is significantly different only in the region of the EG content of 0.2–1.5 %, which corresponds to the area of the percolation threshold. The best indicators, namely, the lower percolation threshold and the achievement of maximum electrical conductivity values at lower EG, in the system with vermiculite. They are due to the hydrophobic properties of the surface the filler particles, as well as the effect of the flow of a dielectric particle of vermiculite by a suspension of an epoxy resin-EG, while that of the particles of perlite is impregnated with it.

CONCLUSIONS

Two systems of ER-perlite-EG and ER-vermiculite-EG were obtained, a combined study on electrophysical properties of composite systems was carried out.

Percolation threshold value and critical system indices were defined. For a system with vermiculite, mass content, which undergoes a percolation transition 0.35 % ($\varphi_c = 0.0018$), $t = 1.4$, $\sigma_i = 119$ Ohm^{-1}cm^{-1}, for a system with perlite, 0.75 % ($\varphi_c = 0.0039$), $t = 2.1$, $\sigma_i = 770$ Ohm^{-1}cm^{-1}.

The difference in electrophysical characteristics of the two systems with the same content of the EG is due to the nature of the surface of the dielectric components. Changing the content of such dielectric ingredients allows us to expand the functionality of composites when used for shielding from electromagnetic fields.

Електрофізичні властивості композитів на основі епоксидної смоли та терморозширеного графіту

О.Г. Сіренко, С.М. Махно, О.М. Лісова, Г.М. Гуня, П.П. Горбик

Інститут хімії поверхні ім. О.О. Чуйка Національної академії наук України
вул. Генерала Наумова, 17, Київ, 03164, Україна, elenasirenko@ukr.net

Розроблено полімерні конструкційні матеріали на основі епоксидної смоли, терморозширеного графіту (ТРГ) та наповнювачів неорганічної природи – перліту, вермікуліту з покращеними електрофізичними характеристиками. З метою визначення оптимальної концентрації ТРГ, для двох композитів: перліт – епоксидна смола, вермікуліт – епоксидна смола досліджено електрофізичні властивості композитів обох систем на низьких частотах методом імпедансної спектрометрії та в надвисокочастотному діапазоні за допомогою надвисокочастотного інтерферометра.

Високі значення (> 30) дійсної та уявної складових комплексної діелектричної проникності для обох систем досягаються при вмісті ТРГ менше 2 мас. %. Визначено значення порогу перколяції та критичні індекси систем: для системи з вермікулітом поріг перколяції становить $\varphi_c = 0.0018$, для системи з перлітом $\varphi_c = 0.0039$. Залежність логарифму дійсної складової електропровідності від логарифму частоти для зразків з низьким вмістом ТРГ до порогу перколяції носить лінійний характер і не залежить від частоти, що свідчить про високий рівень електронної провідності, а також про відносно низький рівень іонної провідності композитів.

Встановлено, що відмінність електрофізичних характеристик двох систем за однакового вмісту ТРГ обумовлена природою поверхні діелектричних складових. Вищі значення має система з вермікулітом, що обумовлено гідрофобними властивостями його поверхні і проявом ефекту обтікання діелектричної частинки суспензією епоксидна смола–ТРГ, а частинки перліту частково просочуються суспензією. Змінюючи вміст діелектричних інгредієнтів, можна розширити функціональні можливості композитів при їх застосуванні для екранування від електромагнітних полів.

Ключові слова: *електропровідні композити, поріг перколяції, терморозширений графіт, надвисокочастотний діапазон*

Электрофизические свойства композитов на основе эпоксидной смолы и терморасширенного графита

О.Г. Сиренко, С.Н. Махно, О.М. Лисова, Г.М. Гуня, П.П. Горбик

Інститут химии поверхности им. А.А. Чуйко Национальной академии наук Украины
ул. Генерала Наумова, 17, Киев, 03164, Украина, elenasirenko@ukr.net

Разработаны полимерные конструкционные материалы на основе эпоксидной смолы, терморасширенного графита (ТРГ) и наполнителей неорганической природы - перлита, вермикулита с улучшенными электрофизическими характеристиками. С целью определения оптимальной концентрации ТРГ, для двух композитов: перлит - эпоксидная смола, вермикулит - эпоксидная смола, исследованы электрофизические свойства композитов обеих систем на низких частотах методом импедансной спектрометрии и в сверхвысокочастотном диапазоне с помощью СВЧ интерферометра.

Высокие значения (> 30) действительной и мнимой составляющих комплексной диэлектрической проницаемости для обеих систем достигаются при содержании ТРГ менее 2 масс. %. Определены значения порога перколяции и критические индексы систем: для системы с вермикулитом порог перколяции составляет $\varphi_c = 0.0018$, для системы с перлитом $\varphi_c = 0.0039$. Зависимость логарифма действительной составляющей электропроводности от логарифма частоты для образцов с низким содержанием ТРГ к порогу перколяции носит линейный характер и не зависит от частоты, что свидетельствует о высоком уровне электронной проводимости, а также об относительно низком уровне ионной проводимости композитов.

Установлено, что отличие электрофизических характеристик двух систем при одинаковом содержания ТРГ обусловлена природой поверхности диэлектрических составляющих. Высшие значения имеет система с вермикулитом, что обусловлено гидрофобными свойствами его поверхности и проявлением эффекта обтекания диэлектрической частицы суспензией эпоксидная смола-ТРГ, а частицы перлита частично пропитываются суспензией. Изменяя содержание диэлектрических ингредиентов, можно расширить функциональные возможности композитов при их применении для экранирования от электромагнитных полей.

Ключевые слова: *электропроводные композиты, порог перколяции, терморасширенный графит, сверхвысокочастóтный диапазон*

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