



Melnyk L.

RESEARCH OF ELECTRICAL PROPERTIES OF EPOXY COMPOSITE WITH CARBON FILLERS

Проведено дослідження основних фізичних властивостей вуглецевих наповнювачів. Досліджено вплив виду та вмісту вуглецевого наповнювача на електричні та діелектричні властивості епоксидного композиту. Показано, що при збільшенні концентрації наповнювача в полімерній матриці зростає величина діелектричної проникності, а перколяційний поріг для систем епоксидна смола – вуглецевий наповнювач коливається в межах ~1–5 мас. %.

Ключові слова: вуглецеві нанотрубки, епоксидний композит, терморозширений графіт, питомий опір, діелектрична проникність.

1. Introduction

The development of modern technology is associated with the creation of new materials with specified properties. One way to solve this problem is production of polymer composite materials (PCMs). However, they must have strictly regulated physical and mechanical characteristics, such as: high impact strength, low water permeability, appropriate thermal and electrical conductivity and at the same time maintain tightness and good adhesion. To obtain the necessary characteristics, polymeric composite materials with fillers of various natures are used.

Currently, epoxy oligomers are one of the most common binders. The complex of valuable properties of epoxy resins – excellent adhesion, good physical and mechanical properties, minimal shrinkage, – low level of internal stresses [1]. The main field of application of epoxy resins is sealing and repair materials, protective coatings.

Among inorganic fine- and medium-dispersed fillers, carbon fillers are widely used. These materials are of interest because they have many properties of metals (high electrical conductivity and thermal conductivity) and characteristics such as low specific gravity, corrosion resistance, and inertness to many chemicals [2].

A special place among carbon-graphite materials is occupied by thermally expanded graphite obtained by deep thermochemical treatment of natural disperse graphite. Thermally expanded graphite (TEG) is a specific material that inherited high resistance to temperature and chemical attack from graphite and acquired additional properties of flexibility and compressive and tensile strength [3]. These properties make it an excellent material.

In recent decades, one of the most promising approaches is the addition of nanomodifiers (carbon nanotubes, nanodiamonds) into epoxy resins [4]. Applied interest is explained by a significant improvement in a number of mechanical, thermophysical and other properties of epoxy oligomers filled with a small amount (up to 2 wt. %) of nanoparticles.

2. The object of research and its technological audit

The objects of research in this work are epoxy composite materials with different types of carbon filler. The

technological process of manufacturing epoxy compositions is carried out in accordance with the technological regime (Table 1).

Table 1

The norms of the technological mode of manufacturing epoxy compositions

Stages of the process	Parameters
I. Filler preparation: Ultrasonic grinding in acetone Dispersing time Ultrasound frequency	≥2 h 50 kHz
II. Composition preparation: Ultrasonic dispersing with epoxy resin Dispersing time Ultrasound frequency Viscosity of epoxy varnish (B3-4)	≥5 h 50 kHz 30–45 s
III. Composition obtaining Ultrasonic dispersion of the obtaining composition with the addition of a plasticizer and hardener Dispersing time Ultrasound frequency	0.5 h 50 kHz
IV. Composition curing Curing temperature	20 °C

Bulk samples for the study are obtained by directly pouring the composition into fluoroplastic forms, followed by solidification in molds under ordinary conditions.

One of the most problematic places in the technology of composite materials production is the considerable porosity of the investigated carbon fillers. Therefore, ultrasonic grinding is one of the solutions to the problem – the production of coatings based on research systems.

3. The aim and objectives of research

The conducted studies aimed to determine the effect of multilayered carbon nanotubes and thermally expanded graphite on the electrical properties of epoxy composites.

To achieve this aim, the following tasks are accomplished:

1. To investigate the basic physical and chemical properties of carbon fillers.
2. To determine the electrical conductivity of epoxy composites with carbon fillers.
3. To investigate the dielectric properties of epoxy composites with carbon fillers.

4. Research of existing solutions of the problem

Electrically conductive adhesives are used in a variety of applications for attaching bare matrices and other electronic components, such as resistors or capacitors, to the base. For example, lead frames, printed circuit boards (flexible electronics), ceramic substrates (LTCC) or DCBs and the like. Such devices, for example, are used for communication (for example, mobile phones, tablets, computers), power conversions (for example, power electronic modules), lighting (for example, LEDs), etc. To this end, there are a number of requirements for electrically conductive glue. It must be mechanically compatible and highly conductive. It is necessary to have low processing temperatures and compatibility with a wide range of substrates. Other requirements include elasticity and flexibility, biocompatibility, stable physical and chemical properties, good temperature stability, low cost, and so on.

However, the basic requirement is obviously the low electrical resistivity of the material and good contact with the substrate and electronic components [5].

Despite the electrical conductivity, heat conduction is also important in some applications, especially if the material is used for bonding, for example, a heat conductor with electronic components. Although some of the known adhesives have good bulk thermal conductivity, they show limited thermal conductivity when used. It is believed that some of these problems are related to the contact between the conductive adhesive and the electronic component or base.

There are studies of epoxy compositions with increased heat resistance using boron nitride as filler with preliminary treatment of its surface with siloxane modifiers [6–9].

Although there are a number of different electrically conductive adhesives, there is still a need for electrically conductive adhesives with improved properties. Cured epoxy resins have a microheterogeneous structure of the globular type, and the formation of the structure is already observed in the liquid phase at the initial stages of curing. Structures of other types in epoxy polymers are not detected [10]. Globules in epoxy resins consist of a more dense substance than the surrounding matrix. The size of globular particles (of the order of 10^3 Å) depends on the structure of the composition, the type of hardener and the curing conditions (the particle size decreases with increasing temperature). The presence of globules in epoxy systems can be associated with the heterogeneity of the curing process. As the size of the globules decreases, the electrical strength of the polymer increases, and its density decreases. As the distance between grid nodes decreases, the glass transition temperature, compressive strength, chemical heat resistance increase, but the polymer's brittleness is usually increased [11].

More importantly characteristics of fillers are their morphology and specific surface, on which the effectiveness of interaction with the polymer matrix depends [6]. This is especially important when polymeric materials are treated with surfactants, modifiers and plasticizers or hardeners.

Among inorganic fine- and medium-dispersed fillers, carbon fillers, chalk, kaolin, natural silicon dioxide are the most widely used [12].

Carbon is not one of the most abundant elements in nature – it accounts for only 0.14 % of the total number

of atoms in the earth's crust. However, this element is the basis of the structure of the entire animal and plant world. Therefore, among the chemical elements, carbon occupies a special place.

In recent years, new forms of carbon nanotubes (CNTs), diamond nanopowders, which have their own atomic structure, size, morphology, and have manifested a wide variety of physicochemical properties, have found their distribution.

Carbon nanotubes are cylindrical structures ranging in diameter from one to several tens of nanometers, consisting of one or more hexagonal graphite planes (graphene) folded into a tube and ending usually with a hemispherical head [13]. Carbon nanotubes is artificially obtained structure, is a set of atoms in the form of tubes with a cavity inside a length of up to 100 nm and a diameter of 1–2 nm. The tubular form has three contact surfaces: the outer surface, the inner surface and the ends of the tubes [14].

CNTs are not only strong, but also flexible, and remind of their behavior is not brittle straws, and rigid elastic tubes. With a mechanical load exceeding the critical, under the influence of heat and radiation, they do not tear and do not break down, but simply rebuilt, «self-cured». This is due to the fact that with a strong deformation of the hexagonal structure, a defect is formed in the form of a condensed pair of a five-membered or seven-membered ring. Such defects, moving along the surface, regroup atoms. In this way, the primary form of the nanotube surface is restored [15].

TEG occupies a special place among other forms of graphite [16]. This is due to the peculiarities of the crystal structure and morphology of its particles. The distinctive properties of thermally expanded graphite are the vermiform shape of the particles.

Thermally expansion of the natural graphite leads to a decrease in the bulk density by a factor of tens, and hence to an increase in the total porosity and specific effective surface, which leads to an increase in the strength of the epoxy composite. And the introduction of carbon nanotubes provides an increase in strength by 50–80 %. Even at low concentrations (up to 1 %), strength, elasticity, thermal stability, and other properties of the compositions increase [16]. Large surface energy leads to aggregation (coalescence) of nanoparticles. The problem of addition of nanoparticles into the polymer matrix has not been completely solved for today. To achieve the maximum positive effect of the modification, it is first of all necessary to ensure an even distribution of the particles in the polymer matrix and to break down aggregates of particles formed when the components are combined. As a method for increasing the uniformity of particle distribution and dispersing aggregates, ultrasonic treatment of the composition is often used [17].

When processing the composition by ultrasound (US), two conflicting factors must be taken into account. On the one hand, the increase in the power of ultrasound makes it possible to more efficiently break up aggregates of particles and evenly distribute the fractions in the volume, which positively affects the characteristics of the material. On the other hand, ultrasound affects the structure of the thermoset matrix, and the increase in its power, possibly, can lead to the destruction of individual bonds. For the epoxy composition, the recommended intensity of ultrasonic vibrations is 30 kW/m².

TEG also has a sufficiently high electrical conductivity (about $105 (\Omega \cdot m)^{-1}$), which makes it possible to use TEG as electrically conductive fillers when creating electrically conductive polymer composites [18].

Epoxy composites with a TEG concentration more than 2.5 wt. % are conductors of an electric current. It should be noted that epoxy composites modified with TEG have sufficiently low percolation thresholds (about 3 wt. %) and percolation transition occurs in a narrow range of TEG concentrations.

Intensive development in the development of new electrically conductive polymer compositions using nanodispersed carbon fillers (nanotubes, ultradispersed graphite forms, carbon fibers and filaments) is due to the wide possibilities of using these materials. Despite a significant amount of research in this area, the problem has not been fully investigated and requires additional research, so the topic is promising.

5. Methods of research

The objects of research in this work are epoxy composite materials. The epoxy resin ЕД-22 (GOST 10587-84), the plasticizer ДБФ (GOST 8728-88), the ПЕПА hardener (TU 2413-357-00203447-99) are chosen as the matrix. The following are chosen as the carbon filler:

- multilayered carbon nanotubes (TU U 24.1-03291669-009:2009);
- TEG, obtained from graphite ГAK-2 by the method [19], clean and after ultrasonic (US) grinding in acetone using ultrasonic bath BK-9050 (PRC) for 2 hours.

The tasks are solved using the main provisions of composite materials science. Experimental studies on obtaining epoxy composite materials and evaluating their electrophysical properties are performed using modern methods of physical and chemical research. Measurements of the electrical resistance are carried out by a four-point potentiometric method at constant voltage [3]. The determination of dielectric permittivity and dielectric losses is carried out in accordance with GOST 6433.4-71. Investigation of the physical and chemical properties of fillers is carried out in accordance with the methods of [20].

6. Research results

6.1. Investigation of the basic physical and chemical properties of carbon fillers. The structure and properties of the filler affect the properties of the polymer composition, and given the considerable extended surface of the carbon fillers, it is expedient to determine their physical properties (Table 2).

Table 2

Physical properties of carbon fillers

Parameters	TEG	TEG with US grinding	CNTs
Bulk density, g/cm ³	0.006	0.061	0.0431
True specific gravity, g/cm ³	0.550	1.243	0.267
Total porosity, %	94.35	44.26	70.46
Specific effective surface, m ² /h:			
For air permeability	60.2	71.2	18.5
For wetting with water	43.1	27.6	132.9
For wetting with benzene	13.7	6.3	45.2

The data in Table 2 indicate that ultrasonic grinding of TEG leads to an increase in order of bulk density, an increase of 2 times the true specific mass, a decrease in the total porosity twice. The specific effective surface is growing:

- for wetting with water from 43.1 to 71.2;
- for wetting with benzene from 13.7 to 27.6 m²/h.

CNTs and TEG are much better wetted with benzene (12–16 times) than with water, which indicates the high hydrophobicity and low energy state of their surface.

The low value of the density of carbon fillers indicates a significant internal porosity of their particles. In other words, the main part of the volume of the filler particle is represented by pores.

The fact that the pycnometric specific gravity of carbon fillers is much larger than its bulk density is indisputable evidence that the pores are mostly open. The large specific surface area of carbon fillers is due to the fact that the linear pore sizes are much smaller than the linear dimensions of the material particle, and the pore walls are thin compared to the linear pore size. The pycnometric specific gravity is studied in order to assess the total porosity of carbon fillers.

The structure of CNTs and TEGs differs significantly in both size and shape and packing density, which affects their electrophysical properties. The CNTs particles have a tubular shape (the particle size of the TEG is on the average: an outer diameter of 10–40 nm, a length of several hundred nm). The particles of TEG are worm-like (the particle size of the TEG is on the average: length 4 mm, diameter 0.3 mm). The particles with an average size of 15 μm (medium dispersed filler) are obtained by ultrasonic grinding. The presence of significant differences in the structure of carbon nanotubes and thermally expanded graphite has a very significant effect on their electrophysical and mechanical properties. It is found that the resistivity in the direction perpendicular to the pressing axis for various TEGs at room temperature can reach $7.5 \cdot 10^{-6} \Omega \cdot m$, while for carbon nanotubes this value is $5.1 \cdot 10^{-8} \Omega \cdot m$.

There are at least three factors that can significantly affect the electrical properties of the compositions: the average size of an electrically conducting cluster, the number of active centers on the surface of graphite filler particles, and the content of non-conductive inclusions.

An analysis of the results presented for TEG allows to assume that the most extended surface has a TEG with ultrasonic grinding. It can be assumed that during the formation of TEG (during heat treatment), active centers appear on the surface, probably due to structural defects and deformations of the crystal lattice. In addition, further ultrasonic grinding and mixing with the epoxy matrix cause the destruction of TEG particles, at which free radicals and energetically active surfaces are formed. Grinding graphite and possible deformations in the basal plane can increase the number of π-electrons, as a result of which the adsorption activity of TEG particles with ultrasonic grinding increases. So, grinding promotes the formation of spatial structures in the polymer matrix and the growth of the dimensions of the electrically conductive clusters.

6.2. Electrical conductivity of epoxy composites with carbon fillers. Electrophysical properties of PCMs based on carbon fillers of compositions depend on many factors [1]. Despite this, it was advisable to investigate the effect of the content of carbon filler on electrical conductivity.

The electrophysical characteristics of PCMs are estimated from the change in electrical resistivity at room temperature. The parameters of the prototypes for studying the electrical conductivity averaged $5 \times 5 \times 0.25$ cm.

The results of an investigation of the electrical resistance (Table 3, 4) and the dependence of the electrical resistance on the concentration of CNTs and TEG are shown in Fig. 1, 2.

Bulk electrical resistance of epoxy compositions filled with carbon nanotubes

CNTs content, wt. %	0	0.25	0.5	0.75	1	1.5	2	2.5
Electrical resistance, $\Omega \cdot \text{m}$	5.37×10^{14}	8.13×10^{12}	4.36×10^9	6.60×10^7	1.51×10^4	2.29×10^2	18.62	0.28

Table 3

Bulk electrical resistance of epoxy compositions filled with thermally expanded graphite

TEG content, wt. %	0	2,5	5	10	30	50	70
Electrical resistance, $\Omega \cdot \text{m}$	$5,37 \times 10^{14}$	1,39	$7,90 \times 10^{-2}$	$9,86 \times 10^{-3}$	$9,05 \times 10^{-5}$	$3,85 \times 10^{-5}$	$3,22 \times 10^{-5}$

Table 4

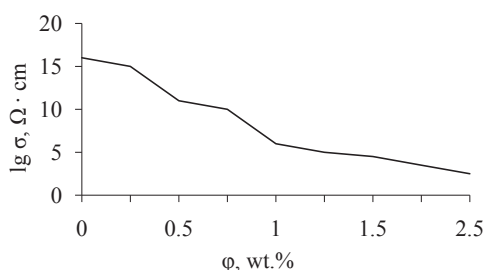


Fig. 1. Dependence of the logarithm of the bulk electrical resistance on the concentration of carbon nanotubes

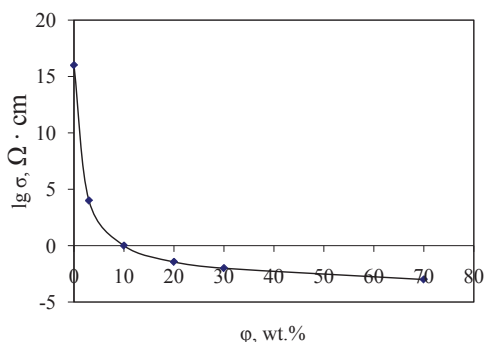


Fig. 2. Dependence of the logarithm of the bulk electrical resistance on the concentration of thermally expanded graphite

It is shown that with increasing the content of CNTs and TEG, the electrical resistance of composites decreases, and this means that their conductivity increases.

Dependences of the logarithm of the resistance of PCMs samples on the concentration of carbon fillers have a power-law form, therefore, it is expedient to use the percolation theory for their description. According to this theory, the structure of polymer composites with filler is prone to self-organization with the formation of clusters. From the point of view of percolation theory, an epoxy resin-carbon filler system is similar to a three-dimensional grid model with electrically conductive components of filler particles and blocked nodes from polymer particles. With a small content of carbon filler, its particles propagate in an epoxy matrix in an arbitrary manner and do not form a grid that conducts an electric current. With an increase in

the content of the carbon filler, its particles begin to interact with each other, the clusters join together forming a continuous cluster, that is, a grid that pervades the volume of the composite.

Near the percolation threshold, there is a sharp decrease in the electrical resistivity (the so-called percolation transition), i.e. the properties of the composite vary from insulator to conductor.

Epoxy composites filled with CNTs have very low percolation thresholds and percolation transition is observed with a CNT content of about 1 wt. %. Epoxy composites filled with TEG also have sufficiently low percolation thresholds and percolation transition occurs in a narrow range of concentrations, with a TEG content of about 5 wt. %.

If compare these carbon fillers, then it can be said that CNTs will be better electrically conductive filler than TEG. The percolation transition of epoxy composites filled with CNTs occurs in a smaller concentration range than for TEG. But CNTs have one significant drawback: the addition of CNTs into epoxy binders in amounts of more than 2.5 wt. % will not be advisable, because at such concentrations the physical and mechanical parameters of the composites decrease, and the cost price increases. And so, nevertheless, when using TEG in large quantities, it is possible to obtain epoxy compositions with large values of electrical conductivity.

6.3. Dielectric properties of epoxy composites with carbon fillers. Epoxy resin refers to polar dielectrics. A special feature of the dielectric is its ability to polarize in an electric field. There are several mechanisms for the polarization of dielectrics. The main of these are orientational and electronic polarizations. In the general case, in a dielectric, several polarization mechanisms occur simultaneously, the quantitative characteristic of which is the permittivity ϵ . The permittivity ϵ depends on the frequency of the change in the external electric field. This is due to the fact that all the processes of displacement and orientation of the particles of the dielectric in an alternating electric field will take place as long as the time constant of these processes is less than the half-period of the variation of the external field. In real dielectrics, several dispersions of ϵ can be observed, depending on which kinds of polarization take place.

In epoxy compositions, particles of carbon filler, when an external electric current is applied, become macrodipoles, the reduced (induced) dipole moment of which changes depending on the frequency of the alternating current. In this case, the migration (Maxwell-Wagner) polarization occurs, which is accompanied by the transformation of a part of the electrical energy into heat due to the occurrence of microcurrents in the particles. The physical reason for the appearance of migration polarization is the presence of volumetric phases with different electrical conductivity in inhomogeneous materials. This leads to the collection of free charge carriers at the boundaries of the more leading phase and the creation of the corresponding

macro-dipoles. When heterogeneous materials are introduced into the electric field, free electrons begin to move within each inclusion, forming polarized regions. The processes of establishing and removal of migration polarization are slow compared to slow and can last for seconds, minutes and even hours. The dispersion of migration polarization is the lowest frequency and manifests itself in the frequency range 10^{-4} – 10^4 Hz. Next, the relaxation mechanisms of polarization are switched off, with the installation of which is 10^{-11} – 10^{-6} s. In the last turn, the deformation modes of polarization are turned off, the most high-frequency of which is the electronic elastic polarization. Its dispersion is observed at frequencies of 10^{13} – 10^{16} Hz.

The influence of the frequency of the alternating current on the real and imaginary part of the dielectric constant is shown in Fig. 3, 4.

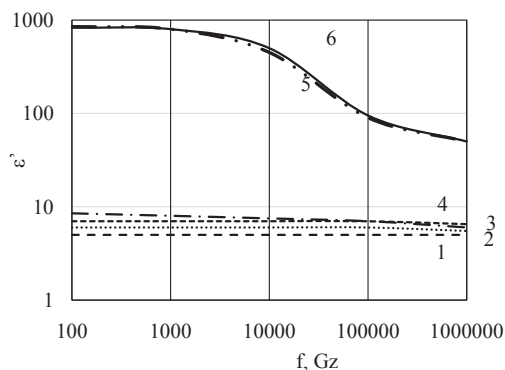


Fig. 3. Dependence of the real part of the permittivity of ϵ' of epoxy composites based on carbon nanotubes on the frequency of alternating current f with the content of carbon nanotubes:

1 – 0 wt. %, 2 – 0.25 wt. %, 3 – 0.5 wt. %, 4 – 1 wt. %, 5 – 1.5 wt. %, 6 – 2 wt. %

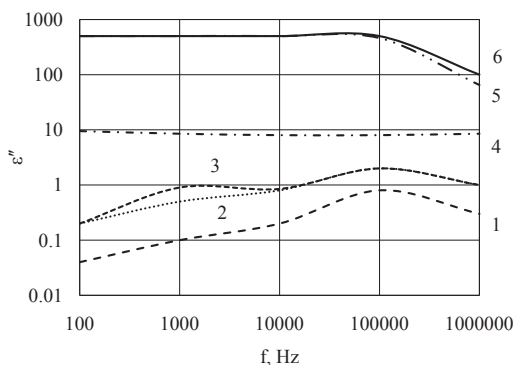


Fig. 4. Dependence of the imaginary part of the dielectric constant ϵ'' (dielectric losses) of epoxy composites based on carbon nanotubes on the frequency of alternating current f with the content of carbon nanotubes: 1 – 0 wt. %, 2 – 0.25 wt. %, 3 – 0.5 wt. %, 4 – 1 wt. %, 5 – 1.5 wt. %, 6 – 2 wt. %

A violation of monotonicity as a function of the filler concentration (Fig. 3) is observed considering dielectric permeability of epoxy composites using the example of a CNT-based composite. It can be assumed that with a small content of CNTs (up to 0.5 wt. %), the net structure of the composite begins to form, the size of the CNT dipoles is small, and the permittivity increases due to orientational polarization. However, with an increase in concentration and a large difference in the surface energy of epoxy resin and nanotubes, the structure of the composite becomes unstable and nanotubes form agglomerates which surface

is smaller than the total surface of their nanotubes. As a result, the orientation polarization decreases. Further growth of the dielectric constant with increasing filler concentration in the composite is explained by an increase in the number of agglomerates and bundles of nanotubes, reduces the dielectric layer between the leading structures and leads to an increase in capacity. A sharp increase in the permittivity is observed with a CNT concentration of 1 %. This can be explained by the fact that with a CNT content of about 1 wt. % separate clusters of CNTs are connected in a continuous grid and it becomes possible to form a current-conducting chain, while the length of macro-dipoles increases. The dielectric constant increases due to migration polarization. The process of migration polarization is established very slowly and does not succeed in changing the magnitude and direction of the electric field. Therefore, migration polarization decreases with increasing frequency and, therefore, an increase in dielectric losses (migration losses) is observed.

An increase in the dielectric losses of the orientational polarization is observed as the frequency of the alternating current increases to 10^5 Hz (Fig. 4). With increasing concentration of CNT, the role of orientational polarization decreases and the dielectric losses are almost independent of the frequency of the alternating current. As the concentration of CNTs increases, the composition becomes heterogeneous, migration polarization processes predominate, which are established very slowly and there is an increase in migration losses.

As regards the influence of the type and content of the filler on the dielectric constant and the dielectric losses of the research compositions (Fig. 5, 6), it can be noted that the systems have similar dependencies.

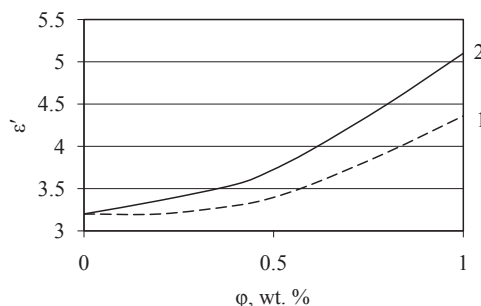


Fig. 5. Dependence of the real part of the permittivity of ϵ' of epoxy composites on the concentration of carbon filler ϕ at a frequency of 10 kHz: 1 – with the content of thermally expanded graphite, 2 – with the content of carbon nanotubes

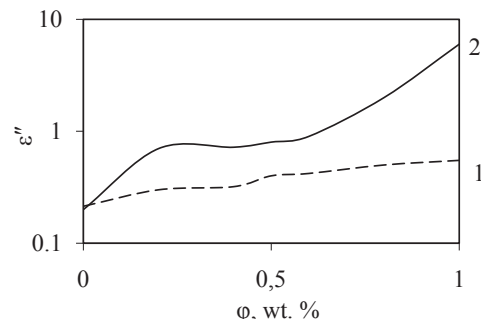


Fig. 6. Dependence of the imaginary part of the dielectric constant ϵ'' (dielectric losses) of epoxy composites on the concentration of the carbon filler ϕ at a frequency of 10 kHz: 1 – with the content of thermally expanded graphite, 2 – with the content of carbon nanotubes

It should be noted that the intensity of the dependence of the dielectric loss and the permittivity is slightly higher for systems based on carbon nanotubes. This can be explained by the fact that processes of orientational polarization predominate at low concentrations in TEG-based systems.

7. SWOT analysis of research results

Strengths. The use of ultrasound in the technology of obtaining composite materials based on epoxy binders and carbon fillers will make it possible to obtain conductive coatings in a thin layer with extended filler surface. This will ensure current conductivity at low filler concentrations. Also, the use of an epoxy binder as a polymer matrix will provide excellent adhesive properties of the composite.

Weaknesses. The use of ultrasound technology increases the preparation time of the composition and requires additional energy and water.

Opportunities. In the future, it is necessary to pay attention to the mechanical properties of research systems, which will make it possible to use the developed systems and as free films.

Threats. There are similar systems based on other polymer binders that can create competition for this development, but it is the use of epoxy to provide cold curing of the product and excellent adhesion. The use of ultrasound destroys the structure of the carbon filler, but at the same time, the specific surface remains sufficiently extended.

8. Conclusions

1. The physical properties of carbon fillers have been analyzed, which allows to consider that carbon nanotubes with the most extended surface contribute to the formation of spatial structures in the polymer matrix and to the growth of the dimensions of electrically conductive clusters. It is determined that it is much better (by 12–16 times) that CNTs and TEG are wetted with benzene than with water, which indicates the high hydrophobicity and low energy state of their surface.

2. It has been experimentally established that the resistivity in the direction perpendicular to the axis of formation of samples containing graphite thermal expansion is normal. And after ultrasonic grinding at a temperature can reach $7.5 \cdot 10^{-6} \Omega \cdot \text{m}$, and when using carbon nanotubes is $5.1 \cdot 10^{-8} \Omega \cdot \text{m}$. The percolation threshold for epoxy resin systems – thermally expanded graphite is ~5 wt. %, and for epoxy resin systems – carbon nanotubes is ~1 wt. %.

3. The dielectric properties of epoxy composites with carbon fillers have been studied. A sharp increase in the dielectric constant of research systems is observed with a CNT concentration of 1 %. An increase in the dielectric losses of the orientational polarization is observed as the frequency of the alternating current increases to 10^5 Hz.

References

1. Trenisova, A. L. Poluchenie kompozitsionnykh materialov na osnove epoksidnogo oligomera i nanonapolnitelei [Text]: PhD thesis: 05.17.06 / A. L. Trenisova. – Moscow, 2009. – 16 p.
2. Meleshko, A. I. Uglerod, uglerodnye volokna, uglerodnye kompozity [Text] / A. I. Meleshko, S. P. Polovnikov. – Moscow: SAINS-PRESS, 2007. – 192 p.

3. Melnyk, L. I. Zakonomirnosti formuvannya i zastosuvannya termostiikykh strumoprovodnykh syloksanhravitovykh materialiv [Text]: PhD thesis: 05.17.06 / L. I. Melnyk. – Kyiv, 2009. – 167 p.
4. Asai, K. Crystallization behavior of nano-composite based on poly(vinylidene fluoride) and organically modified layered titanate [Text] / K. Asai, M. Okamoto, K. Tashiro // Polymer. – 2008. – Vol. 49, № 19. – P. 4298–4306. doi:10.1016/j.polymer.2008.07.037
5. Epoxy resin-based electroconductive composition [Electronic resource]: WIPO Patent Application WO/2016/018191 / Hagedorn H.-W., Lower Y., Dickel T., Stenger K., Yong L. X., Teo K. W., Fritzsche S., Schafer M.; Assignee: Heraeus Deutschland GMBH&Co. Kg, Heraeus Materials Singapore Pte., Ltd. – Appl. № SG2015/000131, Filed June 19, 2015, Publ. February 04, 2016. – Available at: \www/URL: http://www.sumo-brain.com/patents/wipo/Epoxy-resin-based-electroconductive-composition/WO2016018191A1.html
6. Chung, S.-L. Thermal Conductivity of Epoxy Resin Composites Filled with Combustion Synthesized h-BN Particles [Text] / S.-L. Chung, J.-S. Lin // Molecules. – 2016. – Vol. 21, № 5. – P. 670. doi:10.3390/molecules21050670
7. Gu, J. Thermal conductivity epoxy resin composites filled with boron nitride [Text] / J. Gu, Q. Zhang, J. Dang, C. Xie // Polymers for Advanced Technologies. – 2011. – Vol. 23, № 6. – P. 1025–1028. doi:10.1002/pat.2063
8. Wattanakul, K. Effective surface treatments for enhancing the thermal conductivity of BN-filled epoxy composite [Text] / K. Wattanakul, H. Manuspiya, N. Yanumet // Journal of Applied Polymer Science. – 2010. – Vol. 119, № 6. – P. 3234–3243. doi:10.1002/app.32889
9. Kim, K. Fabrication of thermally conductive composite with surface modified boron nitride by epoxy wetting method [Text] / K. Kim, J. Kim // Ceramics International. – 2014. – Vol. 40, № 4. – P. 5181–5189. doi:10.1016/j.ceramint.2013.10.076
10. Gladkikh, S. N. Heat-conducting adhesives based on modified epoxy resins [Text] / S. N. Gladkikh, L. I. Kuznetsova, L. I. Naumova, A. I. Vyalov // Polymer Science. Series D. – 2009. – Vol. 2, № 4. – P. 238–242. doi:10.1134/s1995421209040108
11. Shirshova, N. Composition as a Means To Control Morphology and Properties of Epoxy Based Dual-Phase Structural Electrolytes [Text] / N. Shirshova, A. Bismarck, E. S. Greenhalgh, P. Johansson, G. Kalinka, M. J. Marczewski, M. S. P. Shaffer, M. Wienrich // The Journal of Physical Chemistry C. – 2014. – Vol. 118, № 49. – P. 28377–28387. doi:10.1021/jp507952b
12. Kats, E. A. Fullereny, uglerodnye nanotrubki i nanoklastery: Rodoslovnaia form i idei [Text] / E. A. Kats. – Moscow: LKI, 2008. – 296 p.
13. Diachkov, P. N. Uglerodnye nanotrubki: stroenie, svoistva, primeneniia [Text] / P. N. Diachkov. – Moscow: BINOM, Laboratoriia znaniia, 2006. – 293 p.
14. Harris, P. J. F. Carbon Nanotubes and Related Structures: New Materials for the Twenty-first Century [Text] / P. J. F. Harris. – Cambridge University Press, 1999. – 279 p. doi:10.1017/cbo9780511605819
15. Suhno, I. V. Uglerodnye nanotrubki [Text]. Part 1. Vysokotekhnologichnye prilozheniia / I. V. Suhno, V. Yu. Buzko. – Krasnodar: KubGU, 2008. – 55 p.
16. Chernysh, I. H. Pryrodnyi hrait ta materialy na yoho osnovi [Text] / I. H. Chernysh // Khimichna promyslovist Ukrainy. – 1994. – № 4. – P. 4–8.
17. Melnyk, L. I. Structure, physical and chemical properties of natural and reinforced graphites [Text] / L. I. Melnyk, R. P. Volynets, D. O. Budya // Research Bulletin of NTUU «KPI». – 2010. – № 6. – P. 141–146.
18. Melnyk, L. I. Strumoprovodni kompozitsii na osnovi vuhletsevykh napovniuvachiv i epoksyidnoho zviazuiuchoho [Text] / L. I. Melnyk, D. O. Budya, O. O. Vasyliieva // Tezy dopovidei VI Mizhnarodnoi naukovy-tekhnicnoi web-konferentsii «Kompozitsiini materialy». – Kyiv, 2012. – P. 165–167.

19. Method for obtaining metallized thermally expanded graphite [Electronic resource]: Patent of Ukraine № 40256, МРК С01В31/04 / Tsurul M. F., Kharkov Ye. Y., Matsui L. Yu., Vovchenko L. L., Morozovska N. O. – Appl. № 2000116217, Filed. 02.11.2000, Publ. 16.07.2001, Bull. № 6. – Available at: \www/URL: <http://uapatents.com/3-40256-sposib-oderzhan-nya-metalizovanogo-termorozshirenogo-grafitu.html>
20. Kariakina, M. I. Laboratornyi praktikum po ispytaniiu lako-krasochnyh materialov i pokrytii [Text] / M. I. Kariakina. – Moscow: Khimiia, 1977. – 240 p.

ИССЛЕДОВАНИЕ ЭЛЕКТРИЧЕСКИХ СВОЙСТВ ЭПОКСИДНОГО КОМПОЗИТА С УГЛЕРОДНЫМИ НАПОЛНИТЕЛЯМИ

Проведено исследование основных физических свойств углеродных наполнителей. Исследовано влияние вида и со-

держания углеродного наполнителя на электрические и диэлектрические свойства эпоксидного композита. Показано, что при увеличении концентрации наполнителя в полимерной матрице растет величина диэлектрической проницаемости, а перколяционный порог для систем эпоксидная смола – углеродный наполнитель колеблется в пределах ~1–5 мас. %.

Ключевые слова: углеродные нанотрубки, эпоксидный композит, терморасширенный графит, удельное сопротивление, диэлектрическая проницаемость.

Melnyk Liubov, PhD, Senior Lecturer, Department of Chemical Technology of Composites, National Technical University of Ukraine «Ihor Sikorsky Kyiv Polytechnic Institute», Ukraine, e-mail: luba_xtkm@ukr.net, ORCID: <http://orcid.org/0000-0001-5139-3105>

UDC 621.791.927

DOI: 10.15587/2312-8372.2017.105637

Blokhyna I.

INVESTIGATION OF SURFACED PRESS MOLDS MADE ITS WORKING RESOURCE

Показано, що при ремонті і виготовленні виробів необхідне зміцнення поверхонь, працюючих при термоциклічних навантаженнях в хімічно агресивних середовищах. Проведено дослідження структурної неоднорідності наплавленого металу і її вплив на працездатність прес-форм. Проаналізовано всі варіанти наплавлення способом плазма-МІГ наплавлення і на основі проведених досліджень прийняте оптимальне рішення, що дозволяє істотно підвищити швидкість кристалізації наплавленого металу.

Ключові слова: плазма-МІГ наплавлення, порошковий дріт, структурна неоднорідність наплавленого металу, працездатність прес-форм.

1. Introduction

One of the most important tasks of industrial production in Ukraine is to improve the quality of products, reduce labor, energy and materials. The possibility of using different methods of surfacing for the purpose of repairing and obtaining surfaces of tools and parts operating under extreme conditions has a great importance [1]. Such products include press molds for the production of glass insulators, as well as equipment for hot working with non-ferrous metals [2]. The working surface of the press mold is exposed not only to high temperatures and their sudden drop, but also to the chemical attack of the corrosive medium. Therefore, to restore worn surfaces, special attention is paid to both the composition and structure of the weld metal and its high-quality application to the surface of the product. With the help of the conducted researches it is possible to reduce the probability of cracks formation in the deposited layer by means of plasma-MIG surfacing.

2. The object of research and its technological audit

The object of research is the repair of press molds with the help of plasma-MIG surfacing.

Plasma-MIG process with the use of a flux-cored wire ensures maximum uniformity of the deposited layer and its specified chemical composition in one pass. This is explained by the features of the process, which allows to get a shallow and wide weld pool. However, when repairing previously welded press molds that have worn out their working life, a new layer of surfacing material is applied after machining by the plasma-MIG method on the previously treated surface (in the manufacture) with the thermal action of the plasma. Therefore, the weld metal on the repaired press molds wears out unevenly, has different structure and hardness, which is characteristic of multilayer surfacing of alloyed steels. This shows that research in this direction is necessary.

3. The aim and objectives of research

The aim research is investigation of the structural heterogeneity of the weld metal and its effect on the operability of the press molds to ensure uniform hardness over the section of the welded metal layer.

To achieve this aim, it is necessary to perform the following tasks:

1. To establish, with what step it is necessary to conduct surfacing at restoration of the press molds working at thermocyclic loadings.