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Concentration and Temperature Dependences of the Thermal and Electrical Conductivity of Polymer Hybrid Composites Graphite Nanoplatelets/Fe/Epoxy

Yu. S. Perets, O. S. Yakovenko, L. L. Vovchenko, T. A. Len,
O. V. Turkov, and L. Yu. Matzui

*Taras Shevchenko National University of Kyiv,
60, Volodymyrska Str.,
UA-01033 Kyiv, Ukraine*

The concentration and temperature dependences of the electrical and thermal conductivity of epoxy-based (L285) composite materials (CM) with a combined graphite nanoplatelets/carbonyl iron (GNP/Fe) filler are studied. The content of GNP is varied from 0.7 to 4.0% vol., and the content of Fe was 5.6% vol. As found, the addition of Fe particles in the GNP/L285 composite leads to a decrease in thermal conductivity and a more complex dependence of thermal conductivity on the concentration of GNP. Such changes in thermal conductivity for three-phase CM can be related to an increase in thermal contact resistance at the interfacial boundaries of the matrix–filler, the number of which increases significantly with the addition of Fe particles. Experimental concentration dependences of thermal conductivity of two- and three-phase CM with GNP filler are described in the framework of the combined model of mixtures. The features of the temperature dependences of the thermal conductivity of two-phase CM GNP/L285, Fe/L285 and three-phase composites GNP/Fe/L285 are determined by increasing the concentration of phonons and increasing phonon–phonon scattering when heated. As found, the addition of 5.6% vol. of dispersed Fe particles in a two-phase GNP/L285 composite has almost no effect on the percolation threshold, the value of which is $\phi_c = 1.8\%$ vol. This means that electrically conductive chains are formed mainly from GNP particles in the hybrid composite, and electrically conductive particles

Corresponding author: Olena Serhiyivna Yakovenko
E-mail: alena-ya@ukr.net

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do not form individual continuous chains and can only act as ‘bridges’ connecting GNP particles in electrically conductive chains. For concentrations of hybrid filler above the percolation threshold, the number of electrically conductive chains and the value of contact electrical resistance between GNP particles are estimated within the framework of model of the effective electrical resistance. It is shown that in CM with GNP content which is less and near the percolation threshold electronic transport in composites is carried out mainly due to the hopping mechanism of conductivity, and at GNP concentrations above the percolation threshold the tunnelling mechanism of conductivity is realized due to the formation of a large number of electrically conductive chains with a small gap between the conductive particles.

Key words: iron, graphite nanoplatelets, three-phase composite, thermal conductivity, electrical conductivity.

Було досліджено концентраційні та температурні залежності електропровідності та теплопровідності композитних матеріалів (КМ) на основі епоксидної смоли (L285) з комбінованим наповнювачем графітові нанопластинки/карбонільне залізо (ГНП/Fe). Вміст ГНП варіювався від 0,7 до 4,0% об., а вміст Fe — 5,6% об. Виявлено, що додавання частинок Fe в композит GNP/L285 приводить до зменшення теплопровідності і більш складної залежності теплопровідності від концентрації ГНП. Такі зміни теплопровідності для трьохфазних КМ можуть бути пов’язані зі зростанням теплового контактного опору на міжфазних границях матриця–наповнювач, число яких значно зростає при додаванні частинок Fe. Експериментальні концентраційні залежності теплопровідності дво- і трифазних КМ з ГНП описано в рамках комбінованого моделю сумішей. Характер температурних залежностей теплопровідності двохфазних КМ ГНП/L285, Fe/L285 і трьохфазних композитів ГНП/Fe/L285 визначається збільшенням концентрації фононів і зростанням фонон-фононного розсіяння при нагріванні. Виявлено, що додавання 5,6% об. дисперсних частинок Fe у двохфазний композит ГНП/L285 майже не впливає на поріг перколяції, величина якого складає $\phi_c = 1,8\%$ об. Це означає, що електропровідні ланцюжки формуються переважно з частинок ГНП у трифазному композиті, а електропровідні частинки не формують окремих неперервних ланцюжків і можуть виконувати лише роль «містків», що з’єднують частинки ГНП в електропровідних ланцюжках. Для концентрацій гібридного наповнювача вище порогу перколяції в рамках моделю ефективного електроопору було оцінено кількість електропровідних ланцюжків та величину контактного електроопору між частинками ГНП. Показано, що в КМ із вмістом ГНП менше та в околі порогу перколяції електронний транспорт в композитах здійснюється, головним чином, за рахунок стрибкового механізму провідності, а при концентраціях ГНП вище порогу перколяції реалізується тунельний механізм провідності внаслідок утворення великої кількості електропровідних ланцюжків з невеликим проміжком між провідними частинками.

Ключові слова: залізо, графітові нанопластинки, трифазний композит, теплопровідність, електропровідність.

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1. INTRODUCTION

Epoxy resins, due to their chemical and electrical resistance, are used for the manufacture of adhesives, protective coatings, potting, casting and composites in the electrical industry [1]. Polymers typically have inherent thermal conductivity much lower than that of carbons, metals, or ceramic materials, and their applications are limited by their low thermal conductivity. However, polymers with high heat-conducting properties are already known [2]. The thermal conductivity of polymers has traditionally been enhanced by the addition of thermally conductive fillers, including but not limited to graphite and carbon nanotubes [3, 4]. Many applications will benefit from the use of dielectric polymers with increased thermal conductivity. For example, when used as heat sinks in electrical or electronic systems, a thermal conductivity of 1 to 30 W/(m·K) is required [5]. However, obtaining of composites which have both, conventional polymer machinability and thermal conductivity above 4 W/(m·K), is a very challenging task [6]. The addition of electrically conductive particles to epoxy resins also makes it possible to significantly increase the electrical conductivity of the composite materials (CM) and vary it over a wide range by changing both, the type of filler and its concentration in the CM.

To improve electrical and thermal conductivity of the polymer matrices the use of conductive metal particles has been investigated [7, 8]. And, at the same time, lightweight and cost-effective process ability of polymers are stored. Among metals, gold and silver stand out the most in terms of the electrical and thermal characteristics, but their price forces to look for other, more affordable options. Thus, copper is characterized by the highest conductivity of metals at room temperature, which, in turn, is much cheaper than gold and silver.

The effect of copper nanowires (CuNWs) and copper nanoparticles (CuNPs) on the thermal conductivity of dimethicone nanocomposites was established in [9]. The authors conclude that due to the high aspect ratio of 1D CuNWs, they can construct thermal networks more effectively than CuNPs in the composite, resulting in higher thermal conductivity. Therefore, the shape of the filler particles is important for thermal conductivity, as well as for many other characteristics of a nanocomposite. Besides, the extent of thermal conductivity enhancement depends upon various factors, such as types, morphology, and concentration of nanosized fillers. A smaller size nanoparticle enhances the thermal conductivity of nanocomposite to a larger extent to their bigger counterpart [10, 11]. The enhancement in thermal conduction of nanocomposite upon the shape of nanoparticles might be due to the fact that the surface to volume ratio would be different for different shapes of the same nanoparticles [12]. The influence of crystallinity, phonon scattering, filler/matrix interfaces on thermal conductivity,

ty is discussed in detail in [13].

The interface area between the matrix and the filler phase in nanocomposites is usually an order of magnitude larger than for conventional composite materials. As a result, a relatively small amount of nanosized fillers can have a noticeable effect on the properties of the composite at the macro level.

Series of metal oxide nanoparticles, including TiO_2 , SiO_2 , iron oxide, zinc oxide (ZnO), gallium oxide (Ga_2O_3), nickel oxide (NiO), copper oxide (CuO), *etc.*, were used to improve thermal conductivity of composites. They have different morphologies such as spherical, triangular, star, nanowires, nanotubes, nanorods, *etc.* Thermal conductivity of PCM-metal oxide nanocomposites was improved by 147.5%, 62.5%, 55% and 45% by the addition of 0.5% wt. TiO_2 , ZnO , Fe_2O_3 and SiO_2 , respectively [14].

Metals in the role of fillers have advantages not only in the study of thermal and electrical conductivity, but also in dielectric properties enhancement. Besides, thermal conductivity has become an important parameter for new technologies, especially in aerospace and aeronautics, where the combination of excellent thermal, electrical, mechanical and dielectric properties is required. Authors [15] report that CuNW/PVDF had higher dielectric permittivity and lower dielectric loss than the MWCNT/PVDF nanocomposites at room temperature. It is known that magnetic metals (Fe, Co, Ni) and their oxides are rather good microwave absorbing materials because of their large saturation magnetization and high Snoek's limit. They can significantly weaken the electromagnetic radiation by natural ferromagnetic resonance, exchange resonance, as well as eddy current effect in the high frequency range [16]. Up to now, many magnetic metals with various structures and morphologies have been prepared as microwave absorbing materials and considerable amount of researches have been devoted to the study of high frequency properties of magnetic metal or alloy nanoparticles [17–21]. Synergistic effect between dielectric and magnetic constituents of filler (double-loss mechanisms) are needed to satisfy the strict requirements of excellent microwave-absorption performance in composites. Combination of nanocarbon materials and different metal nanoparticles can serve for these purposes [22].

Besides, incorporation of metals into polymer matrix can protect their nanoparticles against oxidation, dissolution in acids and agglomeration, which are one of the main disadvantages of such fillers. Filled with metals and their oxides composites are an extremely important class of materials from both a scientific and technological viewpoint. However, the absolute control over the shape and size distribution of metal oxide particles in composite remains a challenge.

Carbon-based fillers are promising fillers due to their high electrical and thermal conductivity, as well as due to their low specific gravity.

There is a vast amount of publications on two-phase graphene/epoxy resin composites and their applications [23–28]. Graphite nanoplates in the thickness range of 10–100 nm has aroused interest due to their good thermal conductivity of $\lambda \approx 1800 \text{ W}/(\text{m}\cdot\text{K})$ [29] at room temperature and cost of production corresponding to industrial production [30]. Recently, much attention has been paid to the development of new composite materials where multicomponent fillers are used: nanocarbon particles in combination with various inorganic fillers, such as BaTiO_3 , TiO_2 , MoS_2 with high dielectric constant and in combination with magnetic ones— $\text{BaFe}_{12}\text{O}_{19}$, oxides of Fe, Co, Ni, *etc.* [31–33]. Such multiphase composites have already shown themselves to be quite promising for use as shields and absorbers of microwave radiation [34, 35]. At the same time, it is also necessary that the introduction of multiphase fillers into the polymer matrix to obtain improved microwave characteristics of CMs does not lead to a deterioration in their electrical, thermal, and mechanical properties, which are especially important for their practical applications. The challenge is then to improve the thermal conductivity significantly and to achieve the properties required for wide type of application. This requirement leads us to study and reconsider thermal conductivity mechanisms in composite materials to understand how to enhance this property by combination of fillers.

The aim of this work was to study the effect of fillers (graphite nanoplates GNP, carbonyl iron Fe) with different structural and morphological characteristics on the concentration and temperature dependences of thermal and electrical conductivity of three-phase composites GNP/Fe/epoxy resin.

2. EXPERIMENTAL/THEORETICAL DETAILS

2.1. Materials and Methods

Low-viscosity epoxy resin Larit285 (L285) (viscosity of 600–900 mPa·s, density of 1.18–1.23 g/cm³ at 25°C) with hardening agent H285 (viscosity of 50–100 mPa·s) were used as polymer matrix.

Graphite nanoplatelets (GNPs) and particles of Fe were used as fillers for the preparation of nanocomposites. Graphite nanoplatelets (diameter 0.2–30 μm , thickness 5–65 nm, aspect ratio $AR = 300$) were prepared according to a scheme described in [36]. Fe powder consists of individual particles with an average lateral size of 3–7 μm , while their thickness is varied from 0.6 to 2 μm . Figure 1 presents the scanning electron microscopy (SEM) images of GNP and Fe particles.

GNP/Fe/L285 CMs with 0–5% wt. (1, 2, 3, 4, 5% wt.) of GNPs and 30% wt. of Fe were fabricated by the method of mixing in solution with additional sonication. At first, the appropriate amount of epoxy resin was pre-dissolved with acetone. Further, Fe and GNPs fillers

were introduced into solution and sonication in BAKU ultrasonic bath with the frequency of 40 kHz and power of 50 W was applied for 2 hours. After evaporation of acetone, the curing agent H285 was added in an amount of 40% by weight of the L285. The volume content of GNPs in final three-phase composites accounting the samples porosity ($\sim 10\%$) were of 0.7, 1.2, 1.8, 2.2, 3.4% vol. and the volume content of Fe was of 5.6% vol.

The electrical conductivity of the samples was investigated by 2-probe method in the temperature range 77–295 K. The thermal conductivity of the samples was investigated with a dynamical λ -calorimeter in the temperature range of 150 to 423 K.

2.2. Theoretical Background

2.2.1. Combined Model of Mixtures for Thermal Conductivity

To explain the behaviour of the thermal conductivity depending on the concentration of mixed filler in the polymer composite, a combined model of mixtures can be used [37]. In the combined model of mixtures, composites are considered as structures with a set of heat conductive planes. These planes are formed of chains of filler particles. The chains are oriented in a certain way in the matrix of the polymer in relation to the heat flux. According to this model, the thermal conductivity of hybrid CMs can be described by the following equation:

$$\lambda_{\text{CM}} = \frac{(\phi_p \lambda_p + \sum_{i=1}^n \phi_i \lambda_i^*)^u}{(\phi_p / \lambda_p + \sum_{i=1}^n \phi_i / \lambda_i^*)^{1-u}}, \quad (1)$$

where λ_i^* is the effective thermal conductivity of i -th filler particles forming the chains in composites; λ_p is the thermal conductivity of polymer matrix; ϕ_i is the volume fraction of i -th filler, the parameters $(1 - u)$ and u determine the part of chains from filler particles, oriented perpendicular or along the heat flow, respectively.

If all chains of filler (the particles of filler) are oriented along the heat flux, $u = 1$ and Eq. (1) transforms into the usual mixture model:

$$\lambda_{\text{CM}} = \phi_p \lambda_p + \sum_{i=1}^n \phi_i \lambda_i^*, \quad (2)$$

when all conductive chains are oriented perpendicularly to the heat flow, $u = 0$, Eq. (1) transforms into inverse mixture rule:

$$\lambda_{\text{CM}} = (\phi_p / \lambda_p + \sum_{i=1}^n \phi_i / \lambda_i^*)^{-1}. \quad (3)$$

In the case of the isotropic structure, $u = 0.5$.

λ_i^* is determined by the thermal conductivity of the filler particles, by the orientation of highly anisotropic particles of filler in chains (orientation angle θ) and the contact thermal resistance P_k between the particles of filler, moreover, in our case, the contact can be also through the polymer and air layer. So, $\lambda_i^* = f(\lambda_i, \theta, P_k)$. The character of the connection of the anisometric filler particles with high aspect ratio AR (such as GNPs, CNTs) in the chain and their orientation substantially influence the value of the thermal conductivity of the chain, since these fillers are characterized by the sufficiently high anisotropy of the thermal conductivity.

2.2.2. Electrical Properties of Polymer-Filled Composites

The electrical conductivity in the sample plane ($\sigma_{CM(ab)}$) of composites filled with dispersed conductive components above the percolation threshold ϕ_c ($\phi_c \leq \phi \leq F$), where F is the packing parameter of the filler) can be described within the model of an effective electrical conductivity proposed in [38]:

$$\sigma_{CM(ab)} = \frac{L_{(ef)}^2 \sin^2 \theta F}{\gamma^2 V_{f(ef)}} \left(\frac{\phi - \phi_c}{F - \phi_c} \right)^t \frac{1}{(r_{f(ef)} + R_{k(ab)ef})}, \quad (4)$$

where $L_{(ef)}$ is the length of the larger side of the filler particles (diameter D for disk-like particles), $V_{f(ef)}$ is the volume of the individual filler particle, F is the packing parameter of the fillers, $\phi = \phi_1 + \phi_2$ is the volume content of the fillers, $R_{k(ab)ef}$ is the electric contact resistance between the filler particles in the chains in plane of the sample. The subscript 'ef' means that values are determined by the volume ratio be-

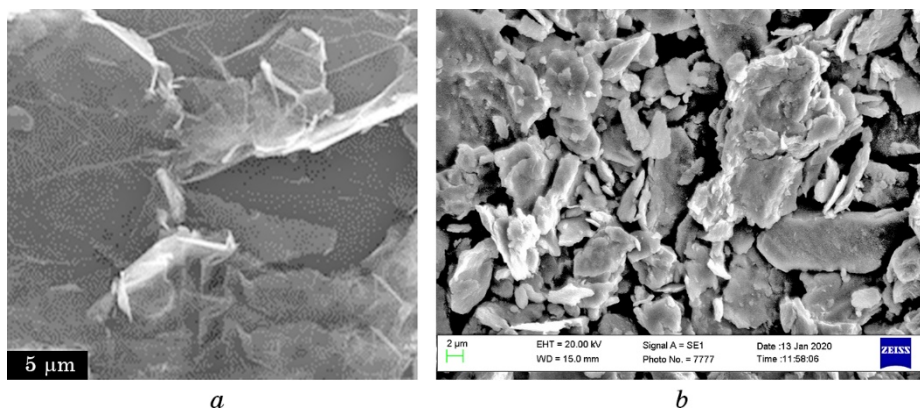


Fig. 1. SEM images of GNP (a) and Fe (b) particles.

tween fillers of various sorts. As it is seen from Eq. (4) the orientation of anisometric filler particles in the plane of a composite specimen (an increase of angle θ between the long axis of the particle and the vertical axis of the sample (perpendicular to the plane ab of the sample) leads to the increase of in-plane electrical conductivity.

As it is seen from Eq. (4) the conductivity follows the power law, as in the case of the classic percolation model [39]:

$$\sigma_{\text{CM}} = D(\phi - \phi_{\text{cr}})^t, \quad (5)$$

where the term D is determined by the morphology of filler particles, their ability to form the conductive chains and the contact resistance between the conductive filler particles [38].

The value of contact resistance between filler particles in chains depends on the nature of the filler particles' contact (direct contact or through the polymer layer) and defines the mechanisms of electrical transport in CM. In a case of direct contact, the resistance is proportional to the electrical resistivity of the filler ρ_f and the contact spot radius a [40]:

$$R_{\text{k (direct)}} = \rho_f / 2a \text{ for } a \gg l, \quad (6)$$

where l is the mean free path of carriers in the carbon material.

In the case of tunnel contacts resistance is a function of the temperature-dependent height of the barrier λ_b , barrier width δ and cross-section of tunnelling w [41]:

$$R_{\text{k(tunnel)}} = \frac{h^2 \delta}{we^2 \sqrt{2m\lambda_b}} \exp\left(\frac{4\pi\delta}{h} \sqrt{2m\lambda_b}\right), \quad (7)$$

where e and m are charge and mass of the electron, h is Planck's constant.

3. RESULTS AND DISCUSSION

3.1. Concentration and Temperature Dependences of the Thermal Conductivity of Graphite Nanoplatelets/Fe/Laric CMs

Figure 2 shows the concentration dependences of the thermal conductivity of GNP/L285 composite and GNP/Fe/L285 hybrid composite. As can be seen from Fig. 2, in the presence of only Fe (5.6% vol.), the thermal conductivity did not increase much in relation to L285 values (see Fig. 2 and Table 1). The addition of 60% wt. of Fe (which corresponds to 16.7% vol. of Fe) to the epoxy leads to an increase in the

thermal conductivity of the epoxy to $0.45 \text{ W}/(\text{m}\cdot\text{K})$, but this increase is not as significant as one might expect, given that the thermal conductivity of iron is sufficiently large, namely, $89 \text{ W}/(\text{m}\cdot\text{K})$ [42]. Such a volume content of Fe particles in CM is insufficient for the formation of continuous chains for efficient heat transfer, and the high interfacial thermal resistance at the Fe-polymer boundaries levels out the contribution of Fe particles to the increase in thermal conductivity.

For CM with combined filler, GNP/Fe/L285, the concentration dependences of thermal conductivity were more complex compared to two-phase GNP/L285 composite: initially, there is almost independent of the content of GNP (0–2.2% vol.) low thermal conductivity of CM at $0.33\text{--}0.4 \text{ W}/(\text{m}\cdot\text{K})$, and it is less than the thermal conductivity of 16.7% vol. Fe/L285 CM. Starting from the GNP content of 2.2% vol., the thermal conductivity increases and is $0.93 \text{ W}/(\text{m}\cdot\text{K})$ (increase on 244%) for composites which contain 3.4% vol. of GNP and 5.6% vol. of Fe. It should be noted that since Fe particles have a plate shape and their lateral size is comparable to the lateral size of GNP ($10 \mu\text{m}$), at the formation of CM will be the mutual influence of GNP and Fe on their spatial distribution in the composite matrix. It can be assumed that the orientation of the plate particles will be random.

The analysis of concentration dependences of thermal conductivity using Eq. (1) showed that the experimental data on thermal conductivity versus GNP content in two-phase and three-phase epoxy-based composites are satisfactorily described within the combined model of mixtures taking into account the significant influence of thermal interface resistance on the thermal transport in the composites.

When calculating the thermal conductivity of the composite within

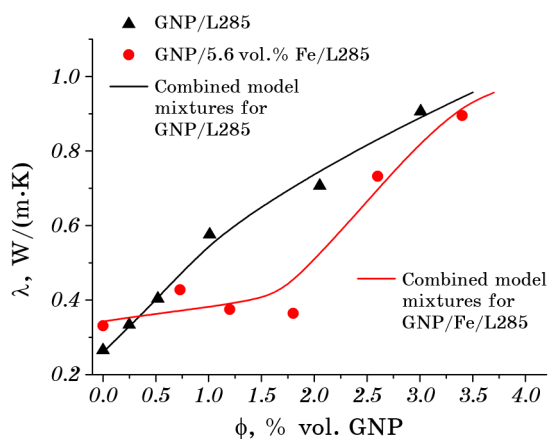


Fig. 2. Concentration dependences of the thermal conductivity of the two-phase composite GNP/Larit and three-phase composite GNP/Fe/Larit; symbols are experimental data; solid lines are calculation using Eq. (1).

TABLE 1. Characteristics of CMs specimens: effective thermal conductivity of fillers $\lambda_{f(\text{GNP})}^*$, $\lambda_{f(\text{Fe})}^*$ and parameter u .

CMs	$\phi_{\text{GNP}}, \phi_{\text{Fe}}, \%$ vol.	$\lambda_{f(\text{GNP})}^*$, W/(m·K)	$\lambda_{f(\text{Fe})}^*$, W/(m·K)	u	$((\lambda_{\text{CM}} - \lambda_{\text{p}})/\lambda_{\text{p}}) \cdot 100$, %
GNP/L285	0.2	30	–	0.5	11
	0.5	50	–		35
	1.0	80	–		92
	2.1	80	–		135
	3.0	80	–		201
Fe/L285	5.6	-	3	0.5	27
Fe/L285	16.7	-	3	0.5	69
GNP/Fe/L285	0	10	3	0.5	65
	0.7	10	3		44
	1.2	10	3		40
	1.8	15	3		182
	2.6	50	3		244
	3.4	75	3		

the framework of the model, the effective thermal conductivity λ_{GNP}^* and λ_{Fe}^* for each of the phases was sought as an adjustable parameter. The effective thermal conductivity for each phase of the filler is a function of the number of filler particles heat-conducting chains in the composite (we do not take into account here that these chains can be mixed GNP–Fe–GNP, *etc.*), the type of thermal contact between the filler particles (direct or through polymer layer).

The parameter u , which characterizes the type of distribution of filler particles in the matrix of CM, was taken to be 0.5, which corresponds to an isotropic structure with a random distribution of filler particles in the polymer matrix.

The effective thermal conductivity of the filler λ_f^* is considered in this model as a whole for two fillers. As can be seen from Table 1, the value of λ_f^* for both two-phase and three-phase composites increases with increasing GNP concentration. For a three-phase GNP/Fe/L285 composite at low GNP concentrations (up to the percolation threshold) the effective thermal conductivities of the fillers are rather low: for Fe $\lambda_{f(\text{Fe})}^* \sim 3$ W/(m·K), and for GNP $\lambda_{f(\text{GNP})}^*$ is 10 W/(m·K) for low GNP concentrations and increases to 75 W/(m·K) for high GNP concentrations. The low values of the effective thermal conductivity of the filler particles in the composite compared to the thermal conductivity of iron (89 W/(m·K) [42]) and graphene (~ 1800 W/(m·K) [29]) are explained

by the significant effect on the total thermal conductivity of the thermal resistances of the interfacial boundaries of the polymer–GNP, polymer–Fe, Fe–GNP and contact resistances between GNP particles in direct contacts.

Analysing the data, it can be assumed that the addition of Fe particles to the GNP/L285 composite worsens the thermal conductivity of the hybrid composite due to phonon-phonon scattering and high thermal resistance since the Fe particles in the L285 polymer matrix are isolated and randomly distributed. The thermal resistance R_k at the filler–polymer phase boundary is also high when heat is transferred through the polymer layer from particle to particle. Fe particles in the GNP/Fe/L285 composite can also serve as bridges between GNP particles, but the role of interfacial thermal resistances is still dominant in the formation of heat transfer in the composite.

Figure 3 shows the temperature dependences of the thermal conductivity of pure L285 epoxy resin and of GNP/L285, Fe/L285 and GNP/Fe/L285 composites.

Composites with Fe filler have a small minimum on the temperature dependence of thermal conductivity (at 250 K and 300 K for concentrations of 16.7% vol. and 5.6% vol., respectively), and the increase in thermal conductivity is only 27% and 69% for concentrations of Fe of 16.7% vol. and 5.6% vol., respectively. That is, we can conclude that Fe particles, even with a high concentration, slightly affect the value of thermal conductivity of the composite and its temperature dependence.

Thus, the presence of Fe particles along with graphite nanoplatelets leads to a change in the character of the temperature dependences of thermal conductivity in comparison with two-phase GNP/L285 composites.

When analysing the temperature dependences of the thermal conductivity of CM, it is necessary to take into account a number of parameters, such as: thermal conductivity of the filler, filler concentration, contact thermal resistance between particles, thermal conductivity of the polymer, matrix/filler interfacial thermal resistance, phonon-phonon scattering, porosity, spatial distribution of the filler in CM, and *etc.*

The thermal conductivity of the solid phase of graphite has a phonon character and can be described within the framework of the Debye theory by the following relation [43]:

$$\lambda_{\text{GNP}} = \frac{1}{3} C v_s L_{\text{ef}}, \quad (8)$$

where C is heat capacity of graphite, L_{ef} is phonon mean free path, v_s is velocity of propagation of elastic vibrations.

With an increase in temperature, the number of phonons increases,

which leads to an increase in the phonon heat capacity, on the other hand, phonon-phonon scattering increases significantly (that is, a decrease in the mean free path of phonons) and the phonon thermal conductivity decreases (see formula (8)). Thus, the changes of the thermal conductivity with temperature in both, the filler and the composite as a whole, is determined by two competing processes: an increase in the number of phonons (thermal conductivity increases) and an increase in phonon-phonon scattering (a decrease in thermal conductivity) with increasing temperature.

As can be seen from Figure 3, for two-phase Fe/L285, GNP/L285 composites and for three-phase GNP/Fe/L285 CM with GNP content up to 1.8% vol., the thermal conductivity decreases (or changes slightly) when heated to a certain temperature (~ 250 K), after which starts to increase slowly. This character of the temperature dependences of the thermal conductivity indicates the predominant influence of phonon-phonon scattering on the heat transfer (at $T < 250$ K), while at $T > 250$ K it indicates an increase in the number of phonons.

For two-phase GNP/L285 composites with a GNP content above 1.8% vol., already at low temperatures (up to 220–250 K), the increase in the number of phonons with increasing temperature is unambiguously predominant, and the higher the GNP concentration, the greater the thermal conductivity and its increase with increasing temperature. The temperature dependences of the thermal conductivity have a maximum at $T = 220$ –250 K, and with a further increase in temperature, a decrease in thermal conductivity is observed. It is associated, as noted above, with an increase in phonon-phonon scattering.

For three-phase GNP/Fe/L285 composites with a GNP concentration above 1.8% vol. up to a temperature of 250 K, phonon-phonon scattering (a decrease in thermal conductivity) is predominant, and with an increase in temperature above 250 K in these composites, the effect on thermal conductivity from an increase in the number of pho-

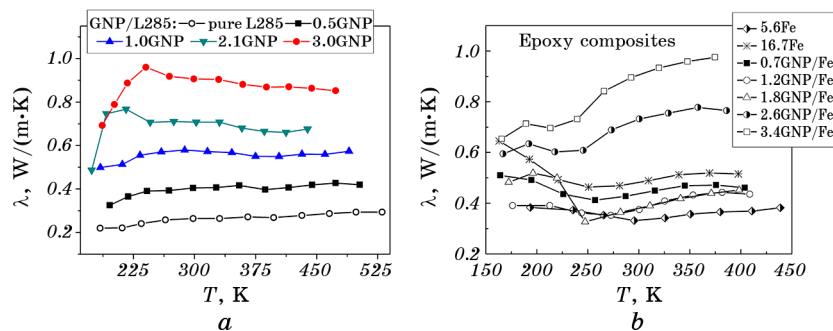


Fig. 3. Temperature dependencies of the thermal conductivity of CMs Fe/L285 (a) and GNP/Fe/L285 (b) with various GNP content.

nons prevails over an increase in phonon–phonon scattering, which leads to an increase in thermal conductivity in general.

3.2. Concentration and Temperature Dependences of the Electrical Conductivity of Graphite Nanoplatelets/Fe/L285 CMs

When using heavy metal Fe particles of micron size with a low aspect ratio, the percolation threshold is quite high and can be 21% vol. [44]. Obviously, the use of Fe particles in combination with light graphite nanoplatelets with a high aspect ratio will lead to a significant decrease in the percolation threshold.

Figure 4 shows the concentration dependences of the electrical conductivity of GNP/L285 and GNP/5.6% vol. Fe/L285 composites. As we can see from Fig. 4 and Table 2, the curves have a percolation character.

The critical concentration is $\phi_c = 1.8\%$ vol. for both two-phase and three-phase composites (formula (7)), *i.e.*, the addition of 5.6% vol. Fe to the GNP/L285 system does not change the value of the percolation threshold.

The parameters σ_f , t were fitted using the method of mean squared error minimization (Fig. 4, *b*, Table 2). As we see from Table 2, the parameter t is lower for the hybrid composite. In the classical percolation theory (formula (7)) $t \approx 2$, and for the GNP/5.6% vol. Fe/L285 composite, this parameter is $t \approx 1.9$. The critical index t strongly depends on the aspect ratio of the filler particles, their distribution and the formation of conductive chains for electric transport. It is obvious that the presence of electrically conductive particles with a low aspect ratio along with GNP particles will affect the nature of their spatial distribution and the process of forming a conductive network in the composite matrix and, accordingly, the percolation transition parameters.

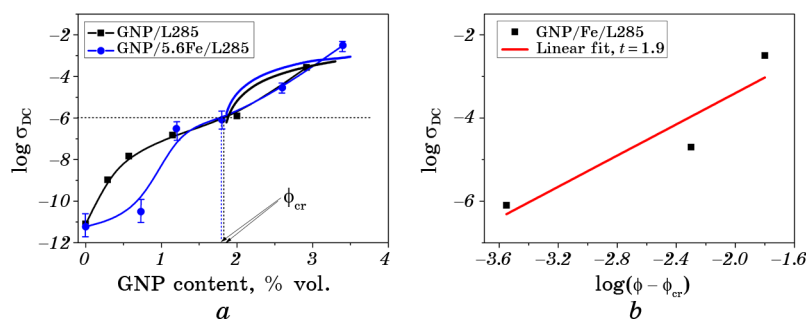


Fig. 4. Experimental and calculated concentration dependences of the conductivity of GNP/L285 and GNP/Fe/L285 CM (*a*) and determination of the critical coefficient t for three-phase CMs (*b*).

TABLE 2. Percolation parameters of the two- and three-phase CM.

Composite	ϕ , vol.%	ϕ_{cr} , % vol.	t	σ_t	$N_{\text{filler_chain}}$, cm ⁻³	R_k (293 K), Ω
	1.9				$6.2 \cdot 10^3$	$1.7 \cdot 10^8$
GNP/L285 [18]	2.7	1.8	2.1	3.6	$9.9 \cdot 10^5$	$7.1 \cdot 10^8$
	3.2				$3.1 \cdot 10^6$	$2.7 \cdot 10^8$
	1.8				–	–
GNP/Fe/L285	2.6	1.8	1.9	3.2	$6.2 \cdot 10^5$	$2.2 \cdot 10^9$
	3.4				$5.7 \cdot 10^6$	$1.8 \cdot 10^8$

Using the model of the effective electrical resistance (formula (8)) and the experimental results, the number of electrically conductive chains in the composite $N_{\text{filler_chain}}$ and the average contact electrical resistance between particles in the chain R_k were estimated. The calculations are shown in Table 2.

Therefore, in the model of the effective electrical resistance (formula (8)), only chains of GNP particles are considered in calculations, although Fe particles in three-phase CM can act as ‘bridges’ between fragments of GNP chains. But, since at a concentration of micron Fe particles of 5.6% vol., their number is an order of magnitude smaller than the number of GNP particles, this does not introduce a significant error in determining the number of electrically conductive chains. As can be seen from the table, there were no significant differences in the number of electrically conductive chains and contact electrical resistance between the filler particles in the chains for two-phase and three-phase epoxy CMs.

The next stage of our research is the temperature dependence of the resistivity of GNP/Fe/L285 hybrid composite with different content of fillers. Figure 5 shows data on DC electrical resistivity of GNP/Fe/L285 CMs with various GNP contents for the temperature range of 77–293 K.

As seen from Figure 5, for three-phase CMs with GNP content of $\phi \leq 2.6\%$ vol. electrical resistivity decreases on few orders of magnitude after heating from 77 to 293 K. Such a strong temperature dependence of the electrical resistivity for GNP/Fe/L285 CMs may be explained by the poor conductive network formed by the electroconductive GNP and Fe particles. The electrical transport for this case is realized via the variable range hopping (VRH) mechanism [45].

If the interaction between charge carriers is neglected, the dependence on temperature of DC conductivity follows the formula [45]:

$$\sigma_{DC} = \sigma_0 \exp[-(T_2 / T)^\nu], \quad (9)$$

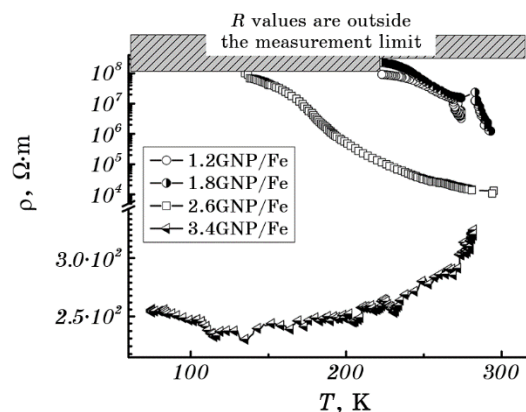


Fig. 5. Temperature dependences of resistivity of three-phase GNP/Fe/L285 CMs with different GNP content.

where the parameter σ_0 can be considered as the limiting value of conductivity at infinite temperature, T_2 is the characteristic temperature that determines the thermally activated hopping among localized states at different energies and is considered as measure of disorder and the exponent γ is related to the dimensionality d of the transport process via the relation $\gamma = 1/(1 + d)$, where $d = 1, 2, 3$. In the conventional VRH model the parameters σ_0 and T_2 are functions of the localization length and density of states.

The applicability of the VRH model is examined by plotting the experimental results for the GNP/Fe/L285 CMs with GNP content 1.2–2.6% vol. in the form of $\ln \sigma_{DC} = f(T^{-\gamma})$ and it was found the good agreement for $\gamma = 1/3$, fitting data are presented in Fig. 6. Thus, it may be supposed that the conductive filler network corresponds to 2D conduction process. T_2 values for these CMs are high, namely, the values are of $(1.2\text{--}2.7) \cdot 10^7$ K for CMs with GNP content 1.2–1.8% vol. indicating the low-conductive nature of the system and structural disorder due to agglomerates and conductive clusters dead ends. For CM with GNP content 2.6% vol. parameter T_2 increases up to $5.5 \cdot 10^6$ K, that can be related to better conductive filler network and more effective electric transport between conductive filler particles.

3.4% vol. GNP/Fe/L285 composite shows sufficiently lower electrical resistivity and weak dependence of resistivity versus temperature. In addition, in the temperature range from 77 to 300 K, this composite is characterized by a minimum of electrical resistance at 140 K, and then a monotonic increase in electrical resistance is observed. A similar change in temperature coefficient of resistance (TCR) from negative to positive with an increase in the GNP content was observed for previously studied composites with a combined filler, GNP/BaTiO₃ and

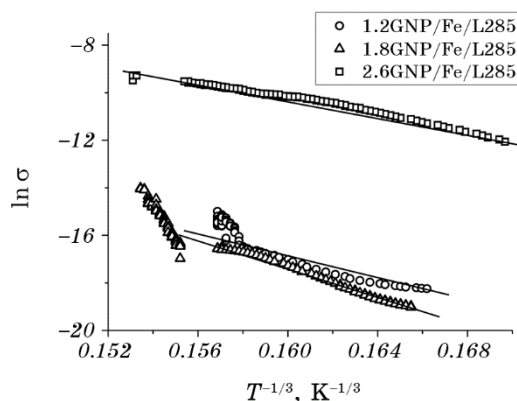


Fig. 6. The electrical conductivity of composites GNP/Fe/L285 with 1.2, 1.8 and 2.3% vol. of GNP versus temperature.

GNP/TiO₂ [46].

Such changes in electrical resistivity with the increase of GNP content are explained by the increased probability of connection among the filler particles leading to the formation of a branched conductive network and the transition from the activated electronic transport to the tunnelling electronic transport. For this case, the electrical resistivity can be described within the model of an effective electrical conductivity (Eq. (4)).

The change in resistivity in this case is determined by the change with temperature of such basic parameters as electrical resistance of individual filler particle r_{filler} , contact resistance between filler particles R_k and the number of parallel-connected electroconductive chains $N_{\text{chain in CM}}$. Depending on which of these three parameters listed above changes are dominant, one or another type of temperature dependence of the electrical resistance is observed for the composite: the TCR can be negative over the entire temperature range (77–300 K), or it could be changed from negative to positive when the composite is heated.

When 3.4% vol. GNP/Fe/L285 composite is heated, due to the greater thermal expansion of the epoxy resin than for GNP, the thickness of the polymer interlayers between the filler particles in the chain increases, and, in some electrically conductive chains, contacts may open (there is no current through them, $N_{\text{chain in CM}}$ decreases) and, as a consequence, an increase in electrical resistance upon heating is observed.

The electrical resistance of individual filler particles also changes with temperature due to the metallic (Fe) and semi-metallic (GNP) nature of the filler particles. However, electron transport between filler particles (contact electrical resistance) is the main parameter that determines the magnitude and behaviour of the resistance of these compo-

sites.

4. CONCLUSION

1. The experimental studies of the thermal conductivity of three-phase epoxy composites filled with graphite nanoplates/iron showed that their thermal conductivity decreases compared to two-phase epoxy composites with GNP filler only. This is due to the significant influence of contact and interfacial thermal resistance on heat transfer processes, which increase significantly with an increase in the number of interfacial boundaries GNP–epoxy resin, Fe–epoxy resin, GNP–Fe. The experimental concentration dependences of thermal conductivity are satisfactorily described within the framework of the combined model of mixtures and it is shown that the effective thermal conductivity of each phase of the filler (GNP, Fe) decreases significantly due to the high interfacial thermal resistance, the effect of which decreases with increasing GNP content in the composite.

2. The temperature dependences of the thermal conductivity of epoxy composites with GNP and GNP/Fe fillers are determined both by the thermal conductivity of the filler particles themselves and by the number of heat-conducting chains formed by them and the values of contact and interfacial thermal resistances in CM. The increase in the content of GNP leads to the manifestation of the maximum on the temperature dependence of the thermal conductivity of CM, which is the result of increasing the number of phonons when heated and, on the other hand, increasing phonon-phonon scattering.

3. It has been shown that the addition of carbonyl iron along with GNP particles does not change either the percolation transition or the electrical conductivity values in three-phase GNP/Fe/L285 CMs compared to two-phase GNP/L285 CMs. The analysis carried out within the framework of the model of the effective electrical resistance showed that the number of electrically conductive chains and the value of the contact electrical resistance between the GNP particles differ insignificantly for three-phase and two-phase CMs.

4. It has been established that in three-phase GNP/Fe/L285 CMs with a GNP concentration of 0.7–2.6% vol., the hopping mechanism of conduction is predominant and the temperature coefficient of resistance is negative. For the 3.4% vol. GNP/Fe/L285 composite, in addition to the thermally activated conduction mechanism, the tunnel conduction mechanism is added. This is due to the formation of a larger number of electrically conductive chains with a small gap between the conductive particles, which leads to a more complex temperature dependence of the electrical resistance.

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