

Electrical and Thermal Conductivity of Ternary Composites Graphite Nanoplatelets/TiO₂/Epoxy

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The investigation of the electrical and thermal properties of composite materials (CMs) based on epoxy resin L285 and hybrid filler graphite nanoplatelets/titanium oxide particles (GNP/TiO₂) has been performed. The experimental study involved measuring direct current (DC) resistivity in the temperature range 77-293 K and thermal conductivity (within 150-425 K range) of such ternary composite with 0-5 wt. % content of GNP particles and 35 wt. % of TiO₂ ultra-disperse (~130 nm) particles. The decrease of the percolation threshold and enhanced electrical conductivity for the ternary GNP/TiO₂/epoxy CMs compared with binary GNP/epoxy CMs were observed. It was found that the increase of highly conductive GNP content in the composite leads to the increase of electrical conductivity and change in the temperature coefficient of resistance (TCR) from negative to slightly positive in the temperature range 100-293 K. The negative TCR was related to hopping mechanism of conductivity, and the activation energy for low-conductive 2 wt. % GNP/TiO₂/epoxy composite was estimated. The positive TCR for 5 wt. % GNP/TiO₂/epoxy composite may be explained by the changes in tunnel electronic transport under thermal expansion of epoxy matrix. The investigation of thermal conductivity of GNP/TiO₂/epoxy CMs has shown that addition of TiO₂ particles into GNP/epoxy composites doesn't influence the value of thermal conductivity. The changes of the thermal conductivity with increase of GNP content in ternary CMs were considered within a modified Nielsen model and the effective thermal conductivity of each type of filler phase was determined. The role of the thermal interface resistance and interparticle thermal contact resistance in the determination of composite thermal conductivity was also discussed.

Keywords: Titanium oxide, Graphite nanoplatelets, Composite, Electrical conductivity, Thermal conductivity.

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1. INTRODUCTION

One of the promising fields of modern materials science is the development of new polymer composite materials (CMs) that are characterized by a set of enhanced or new quality properties. The use of nanoscale forms of carbon such as carbon nanotubes (CNTs), graphene, graphite nanoplatelets (GNPs), graphitized carbon black (CB), as well as carbon nanomaterials modified with nanoscale metals as fillers in a polymer matrix leads to the creation of CMs with improved physical and mechanical properties, suitable for electromagnetic interference material [1], anti-electrostatic coating [2] and mechanical deformation sensor (piezoresistive) [3] and also as gas sensors for monitoring the chemical environment [4].

Polymer composites filled with ceramic particles such as MoS₂, BaTiO₃, TiO₂, SiO₂ [5, 6] have received considerable attention in the past decade. Favorable features include a high dielectric constant, low dielectric loss, and good compatibility with printed-circuit-boards (PCB), making them promising candidates for embedded capacitors used in passive technology. For example, titanium dioxide TiO₂ is an inorganic filler having a large permittivity and thus used for insulating material in electronics and as a dielectric for capacitors [6]. In addition, TiO₂ nanopowder is increasingly being investigated because it is non-toxic, chemically inert, low cost, has a high refractive index, is a broadband UV filter, kills bacteria by photoirradiation, is corrosion resistant and has a high hardness. Other applications of titania include use as a de-pollutant, self-cleaning agent,

photocatalyst, photovoltaic cell, semiconductor, etc. Composites prepared from titania show increased tensile modulus, tensile strength, hardness, and in some cases, mechanical properties such as the mechanical modulus value are found to decrease with an increase of filler concentration in the polymer matrix [7]. Also, the mentioned advantages of TiO₂ make it an ideal inorganic filler for the development of nanocomposite materials resistant to UV radiation, probably resistant to thermal degradation, and may inhibit the formation of harmful biofilms. For that reason, the addition of TiO₂ nanoparticles could provide the final material with some functional properties of the proper TiO₂ like the UV radiation protection and the bactericidal activity [8]. In [9], the results of a detailed investigation of the electrical and dielectric properties of polyurethane-titania nanocomposites over a wide range of frequency and applied pressure have been reported. It was shown that these composites exhibit excellent piezoelectric behavior and the change in properties with respect to applied stress becomes more and more pronounced at higher titania content and at low frequency. In [10], it was shown that addition of TiO₂ particles in polyester matrix improves the effective thermal conductivity of polyester-25 % TiO₂ composites. Apart from enhancing thermal conductivity (1.2 W/mK), incorporation of TiO₂ results in improvement of glass transition temperature (90-106 °C) (T_g) and reduction in coefficient of thermal expansion (CTE).

In recent years, an increasing interest is for polymer-based composites with hybrid filler systems, for example, a carbon nano-filler combined with inorganic fillers, dielectric (TiO₂, SiO₂, MoS₂, BaTiO₃) or magnetic (Fe₂O₃,

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Fe/Co/Ni). Such a combination of nanocarbon filler and inorganic nanoparticles promotes the further improving the electrical properties and absorption performance of nanocarbon-filled polymers and also enhances the mechanical properties and thermostability. For example, in [11], a good distribution of the ceramic nanoparticles with very little particle agglomeration was observed for polyvinylidene fluoride (PVDF) matrix with hybrid filler barium titanate (BT) nanoparticles/multi-walled carbon nanotubes (MWCNTs). In another paper [12], it is observed that addition of CNTs and TiO₂ seems in PMMA matrix to be beneficial in increasing mechanical strength via increasing the interface dispersed phase. The author of [13] studied the effects of hybrid fillers on the electrical conductivity and electromagnetic interference shielding efficiency (EMI SE) of the polypropylene (PP)/Ni-coated carbon fiber (NCCF) composites with the second fillers, such as MWCNT, CB and TiO₂. Based on the electrical properties of such composites, it was suggested that TiO₂ was the most effective second filler when it was hybridized with the NCCF of the PP/NCCF/TiO₂ composite. Based on the analysis of the flexural modulus, the PP/NCCF/MWCNT composite had a higher flexural modulus than the PP/NCCF/TiO₂ and PP/NCCF/CB composites because of the higher aspect ratio of the MWCNT.

The present investigation deals with the investigation of the effect of the combination of TiO₂ ultra-disperse particles and GNPs filling the epoxy matrix on the electrical and thermal properties of ternary composites GNP/TiO₂/epoxy resin.

2. EXPERIMENTAL

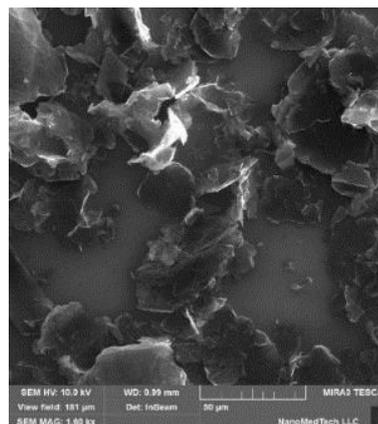
GNPs and disperse TiO₂ particles were used as fillers for the preparation of nanocomposites. GNPs (diameter 0.2-30 μm, thickness 5-65 nm, aspect ratio $AR = 300$) were prepared according to a scheme described in [14]. TiO₂ powder consists of individual particles with an average size of ~130 nm and agglomerated particles with a size of 2 μm. Fig. 1 presents the scanning electron microscopy (SEM) images of GNPs and TiO₂ particles.

Low-viscosity epoxy resin Larit285 (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.

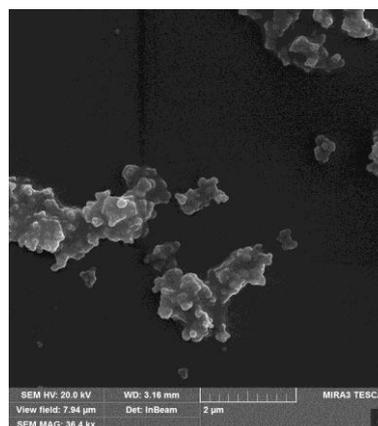
GNP/TiO₂/epoxy CMs with 0, 1, 2, 3, 4, and 5 wt. % of GNPs were fabricated by the method of mixing in solution with additional sonication. At first, the appropriate amount of epoxy resin was pre-dissolved with acetone. Further, TiO₂ and GNPs fillers were introduced into solution and sonication in BAKU ultrasonic bath with the frequency of 40 kHz and power of 50 W was applied for 2 h.

At the next stage, after evaporation of acetone, the curing agent H285 was added in an amount of 40 % by weight of L285. The content of TiO₂ in CMs was in the range of 32.5-34.5 wt. % depending on GNP content.

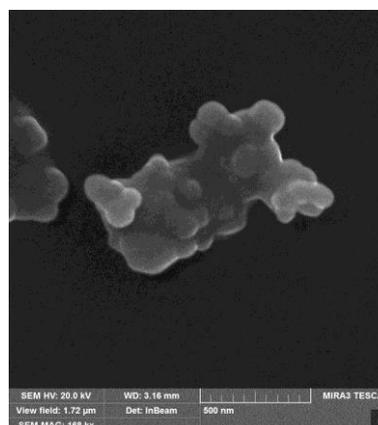
The electrical conductivity of GNP/TiO₂/epoxy was investigated by 2-probe method in the temperature range 77-295 K. The thermal conductivity of the samples was investigated with a dynamical λ-calorimeter in the temperature range from 150 to 423 K.



a



b



c

Fig. 1 – SEM images of GNP (a) and TiO₂ (b, c) particles

3. RESULTS AND DISCUSSION

Table 1 presents the composition, density and porosity of prepared epoxy filled composites.

The porosity of epoxy composites was determined using the following ratios:

$$P = 1 - d_{CM} / d_{CM(id)}, \quad d_{CM(id)} = \left(\sum_{i=1}^n C_i / d_i \right)^{-1}, \quad (1)$$

where d_{CM} and $d_{CM(i)}$ are the CM sample density and density of perfect sample without pores, accordingly, C_i , d_i are the weight fraction and density of the i -th component in composite, consisting of n components.

In determining the porosity of samples using proportions (1), the values of density of GNP, TiO₂ and epoxy were used as follows: $d_{GNP} = 2.20$ g/cm³; $d_{L285} = 1.15$ g/cm³, $d_{TiO_2} = 4.23$ g/cm³ [15].

As seen from Table 1, the density of samples varied within 1.25-1.40 g/cm³ and porosity P of samples is equal to ~ 0.20 .

Table 1 – Composition, density, porosity and electrical resistivity of prepared epoxy filled composites

Sample	GNP content, wt. %	Density d , g/cm ³	Porosity P	ρ_{290} , $\Omega\cdot m$
0GNP/TiO ₂ /L285	0	1.26	0.18	10 ⁸
1GNP/TiO ₂ /L285	1	1.40	0.12	10 ⁷
2GNP/TiO ₂ /L285	2	1.30	0.19	5.1·10 ⁴
3GNP/TiO ₂ /L285	3	1.25	0.23	9.2·10 ⁴
4GNP/TiO ₂ /L285	4	1.31	0.19	2.5·10 ⁴
5GNP/TiO ₂ /L285	5	1.32	0.19	7.9

4. ELECTRICAL MEASUREMENTS FOR GNP/TiO₂/L285 COMPOSITES

Fig. 2 presents the DC conductivity data on investigated CMs versus GNP content. The unfilled epoxy resin L285 exhibits a conductivity of $\sim 10^{-11}$ S/m, the addition of 35 wt. % of TiO₂ leads to increase of conductivity by 3 orders of magnitude, up to 10^{-8} S/m. Such increase of electrical conductivity of epoxy resin contrary to epoxy filled with BaTiO₃ may be explained by semiconductive nature of TiO₂ particles.

The electrical conductivity of individual TiO₂ particles can vary in the range of $1.2 \cdot 10^{-9}$ - $2.6 \cdot 10^{-7}$ S/m depending on parameters of synthesis and chemical treatment. The addition of GNP into TiO₂/L285 increases the conductivity by 3 orders of magnitude for 2 wt. % GNP/TiO₂/L285 composite and percolation threshold may be determined as 1.65 wt. % of GNP that is lower compared to GNP/L285 and GNP/BaTiO₃/L285 CMs.

We can see that GNP/TiO₂/L285 CMs exhibit higher conductivity values with the same content of GNP than GNP/L285 and GNP/BaTiO₃/L285 CMs. So, the results presented in Fig. 2 suggest that TiO₂ produced a synergy effect on the electrical conductivity of the composite and could be an effective filler when hybridized with conductive GNP particles in GNP/TiO₂/epoxy composites. For this case, the electrical transport may be realized due to the presence of various conductive ways, namely GNP-GNP chains, TiO₂ chains, and combined GNP-TiO₂-GNP chains. Electric resistance of composite sample R_{CM} , which is inverse to electric conductivity of composite $\sigma_{CM} \sim 1/R_{CM}$ at first approximation may be presented as [16]:

$$R_{CM} = R_{f-c} / N_{f-c}, \quad (2)$$

where R_{f-c} is the electrical resistance of conductive chain of TiO₂/GNP particles, N_{f-c} is the number of conductive chains.

The electrical resistance of chain R_{f-c} is determined by the electrical resistance of the individual filler particle r_f , the number of particles in the chain n^* , and the value of electrical contact resistance R_k between the filler particles:

$$R_{f-c} = n^* \cdot (r_f + R_k). \quad (3)$$

The contact between filler particles may be via a thin polymer layer or direct at high filler content. Since in GNP/TiO₂/L285 composite we have two sorts of filler particles, the values of r_f and R_k are the average values that are determined by combining semiconductive (TiO₂) and electroconductive (GNP) particles. The presence of large content of TiO₂ particles acts as excluded volume and promotes the formation of the more dense conductive (or semiconductive) network in epoxy matrix. Moreover, the contact electrical resistance between filler particles also decreases due to smaller interparticle distance and possibility of hopping (or tunneling) electron transport in these composites. It is obvious that increase of the content of highly anisometric (with high aspect ratio) electroconductive GNP particles in ternary composites GNP/TiO₂/L285 (for example up to 5 wt. % of GNP) leads to sufficient decrease of both the average value of r_f and average value of R_k (due to formation of GNP-GNP chains), resulting in enhancement of electrical conductivity of composite. The decrease of interparticle distance under increase of GNP content will promote the formation of direct contact between GNP particles and enhances the electrical conductivity.

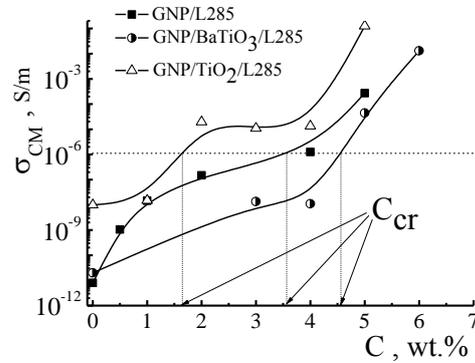


Fig. 2 – Conductivity data for GNP-, GNP/TiO₂- and GNP/BaTiO₃/epoxy CMs versus GNP content

5. TEMPERATURE DEPENDENCE OF DC CONDUCTIVITY FOR GNP/TiO₂/L285 COMPOSITES

In addition to conductivity measurements at room temperature, the temperature dependencies of DC conductivity for three-phase composites GNP/TiO₂/epoxy were measured in the range of 77-295 K. Fig. 3a, b and Fig. 4a, b present the data on electrical resistivity and relative electrical resistivity $\rho(T)/\rho(293)$ versus temperature for CMs filled with 3, 4 and 5 wt. % GNP. The temperature dependence of resistivity for TiO₂/L285 and 1 wt. % GNP/TiO₂/L285 CMs were not investigated because the high values of sample electrical resistance

were outside the measurement limit. As seen from Fig. 3a, for CMs GNP/TiO₂/L285 with 2, 3 and 4 wt. % of GNP the large increase (by few orders of magnitude) of electrical resistivity was observed at cooling from $T = 293$ K down to 77 K.

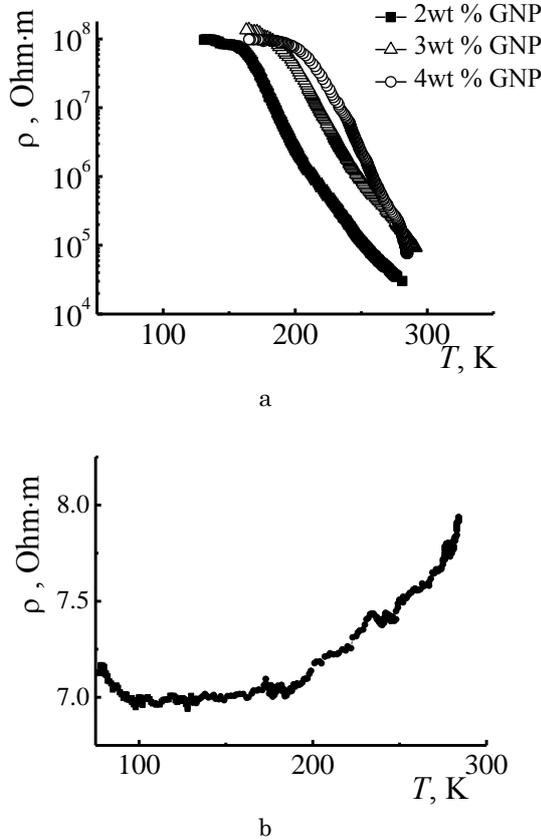


Fig. 3 – The resistivity data $\rho(T)$ for GNP/TiO₂/L285 CMs versus temperature with various GNP content: (a) – 2, 3, and 4 wt. % of GNP; (b) – 5 wt. % of GNP

At $T = 179$ K electrical resistance achieves the maximum value (~ 90 G Ω that corresponds approximately to $\rho \approx 108$ $\Omega\cdot\text{m}$), which can be measured by used arrangement. For these composites, the negative temperature coefficient of resistance (TCR) is observed in a whole temperature range 77-293 K.

In a case of the sample 5GNP/TiO₂/L285 we have observed the sufficiently lower value of electrical resistivity and another type of the temperature dependence of resistivity $\rho(T)$. Under sample cooling from 293 to 100 K the electrical resistivity decreases and then we observe the slight increase of resistivity at cooling up to 77 K.

The similar change of TCR from negative to positive at the increase of GNP content was observed for previously investigated composites with mixed filler GNP/BaTiO₃, the data is presented in Fig. 4b.

Temperature dependence of electrical resistivity (or conductivity) of polymer-filled composites is determined by changes of above-mentioned parameters such as r_f , R_k , $N_{f,c}^*$ (see Eqs. (2)-(3)) with temperature. Depending on the dominant change of any of these parameters, different types of electrical resistance temperature

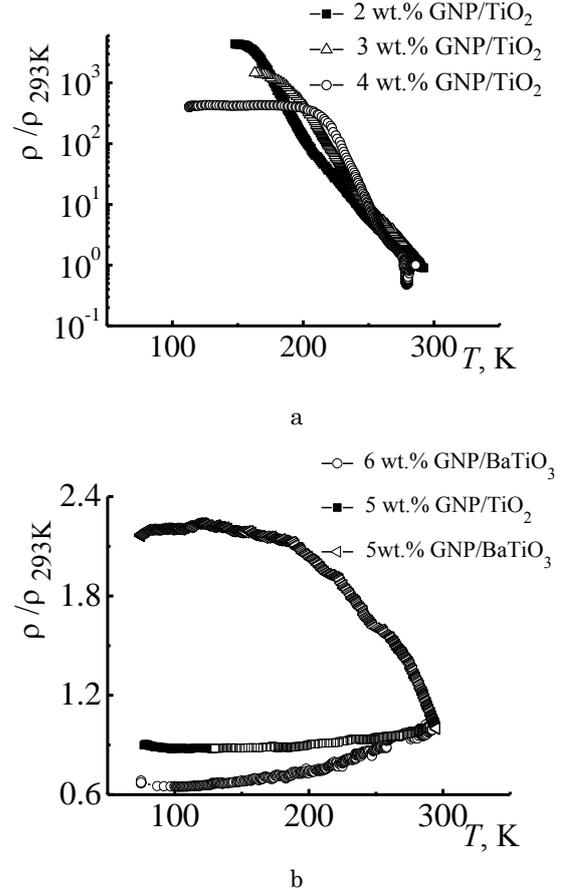


Fig. 4 – The relative resistivity $\rho(T)/\rho(293)$ data for GNP/TiO₂/L285 CMs with various GNP content (2, 3 and 4 wt. %) (a) and 5 wt. % GNP, 5-6 wt. %GNP/BaTiO₃ (b) versus temperature

dependence are observed. The positive TCR for epoxy GNP/TiO₂/L285 CMs with a relatively low content of conductive filler GNP (lower that percolation threshold) may be attributed to thermally activated conduction mechanism [17]. In this case, at first approximation electrical conductivity may be described as:

$$\sigma = \sigma_0 \cdot \exp(-E_a/k_B T), \quad (4)$$

where σ_0 is conductivity at $T = 0$ K, k_B is the Boltzmann constant and E_a is activation energy.

Fig. 5 presents the $\ln(\sigma)$ versus temperature for CMs with 2, 3 and 4 wt. % GNP. As seen from Fig. 5, for low conductive GNP/TiO₂/L285 samples the temperature dependence of conductivity is satisfactorily described by relation (4) for a certain temperature range. The finest agreement between the experimental data and relation (4) was observed for the sample 2GNP/TiO₂/L285, when the process of formation of conductive chains consisting of GNP-GNP particles is not effective due to small amount of GNP particles and electron transport in this composite is realized mainly due to TiO₂ particles chains and maybe GNP-TiO₂ via hopping conduction mechanism. The estimation of activation energy gives a value of 0.27 eV, that agreed with data presented in [17] for PVA-TiO₂ composites.

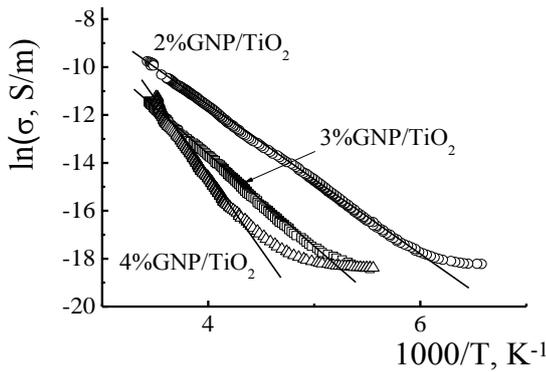


Fig. 5 – The electrical conductivity of GNP/TiO₂/L285 composites with 2, 3 and 4 wt. % GNP versus inverse absolute temperature

The increase of GNP content (up to 4 wt. %) promotes the formation of conductive GNP-GNP pathways and initiation of tunnel mechanism of conductivity along thermally activated electron transport resulting in the more complicated temperature dependence of conductivity. Moreover, the electrical conductivity of individual filler particles also changes with temperature due to semiconductive (TiO₂) and semimetal (GNP) nature of filler particles. However, the electronic transport between filler particles (contact electrical resistance) is the main parameter that determines the value and behavior of electrical conductivity of these composites [16].

The sufficient decrease of electrical resistivity for 5 wt. %GNP/TiO₂/L285 and 6 wt. %GNP/BaTiO₃/L285 and change of TCR (Fig. 3b, Fig. 4b) may be explained by the formation of a large number of conductive GNP chains which are separated by thin gaps (or thin polymer layers) [16] and partially form the direct contacts. At heating, the tunnel contact resistance between these GNP particles increases due to thermal expansion of the epoxy matrix and this effect dominates over the increase of the electrical conductivity of individual GNP particles under increased temperature.

6. THERMAL CONDUCTIVITY OF GNP/TiO₂/L285 COMPOSITES

Fig. 6, Fig. 7 present the data on the thermal conductivity of ternary composite materials GNP/TiO₂/L285 depending on fillers content and its change with temperature in the range 160-423 K.

As seen from Fig. 6, the thermal conductivity of two-phase composite 35 % TiO₂/L285 is slightly higher than for neat epoxy resin L285 and explained by the higher thermal conductivity of TiO₂ particles (~11 W/(m·K)) compared to epoxy resin. The addition of second highly thermoconductive GNP filler leads to an increase of thermal conductivity of GNP/TiO₂/L285 CMs. For comparison in fig. 6 we also presented the data on thermal conductivity for two-phase composites GNP/L285. The thermal conductivity increases almost linearly with the GNP content, the concentration dependence of the thermal conductivity is not percolative, because the ratio of the thermal conductivity of the epoxy matrix and GNP filler is low compared to that of the electrical conductivity and is about 10³. As seen, the addition of

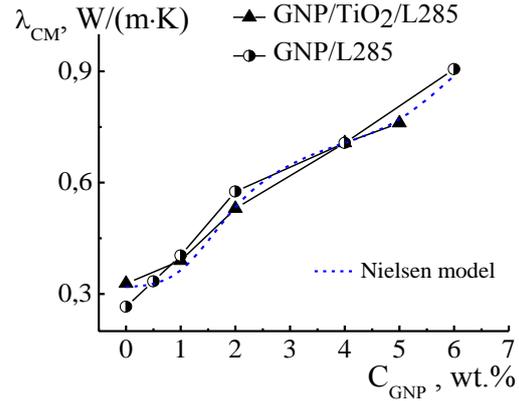


Fig. 6 – Experimental (markers) and calculated (dashed line) dependencies of thermal conductivity λ_{CM} of GNP- and GNP/TiO₂/epoxy CMs versus GNP content

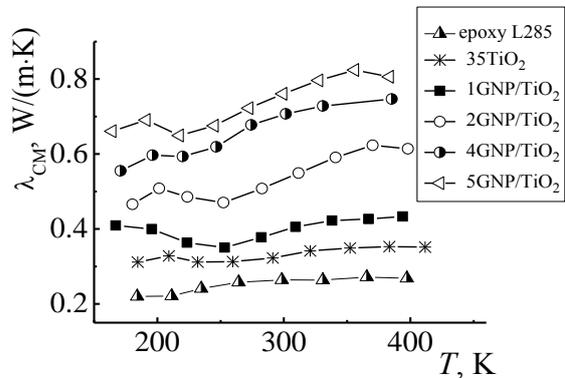


Fig. 7 – Temperature dependencies of thermal conductivity λ_{CM} of GNP/TiO₂/epoxy composites with various GNP content

TiO₂ particles into GNP-epoxy composites doesn't influence the value of thermal conductivity. Such result may be explained by the relatively low thermal conductivity of TiO₂ particles (~11 W/(m·K)) compared to GNP particles and significant role of the thermal interface resistance in the composite [18]. Thermal conductivity of composites with a mixture of few fillers may be described by the modified Nielsen model which combines all the filler contributions into thermal conductivity [19]:

$$\frac{\lambda_{CM}}{\lambda_p} = \frac{1 + \sum_{i=2}^n C_i \cdot B_i \cdot \phi_i}{1 - \sum_{i=2}^n C_i \cdot B_i \cdot \phi_i}, \quad (5)$$

$$B_i = \frac{\frac{\lambda_i}{\lambda_p} - 1}{\frac{\lambda_i}{\lambda_p} + C_i}, \quad \psi_i = 1 + \frac{\phi_p}{\phi_{mi}} [\phi_{mi} \phi_i + (1 - \phi_{mi}) \phi_p], \quad (6)$$

where λ_p is the thermal conductivity of pure polymer, λ_i is the thermal conductivity of each filler component, ϕ_i and ϕ_{mi} are the volume fraction and packing factor of the component i , C_i is a function of the morphology of the filler particles i (aspect ratio A) and their orientation in the polymer matrix, and the parameter ψ_i is related with packing factor of the filler i . Using the equations (5) and (6) and the experimental data on

aspect ratio and packing factor for various fillers (presented in Table 2), the values of the thermal conductivity of the epoxy composites with GNP/TiO₂ fillers were calculated.

Table 2 – Model parameters for the description of the thermal conductivity of GNP/TiO₂/L285

GNP content (wt. %/vol. %)	Effective thermal conductivity of fillers λ_f^* , (W/(m.K))	
	GNP $\varphi_m = 0.05; C = 40$	TiO ₂ $\varphi_m = 0.14; C = 1$
0/0	–	0.4
1/0.7	30	0.4
2/1.46	25	0.4
3/2.21	20	0.4
4/2.96	13	0.4
5/3.73	10	0.4

As seen from Fig. 6, the calculated values of the thermal conductivity agreed with the experimental data at the values of parameter λ_f^* presented in Table 2. It was found (see Table 2) that the effective thermal conductivity of fillers λ_f^* in the composite is much lower than the thermal conductivity λ_f of the individual filler particles which may be explained by the significant role of the thermal interface resistance R_K in the multiphase composite system (strong phonon scattering may occur when the phonons propagate through a phase boundary) and contact thermal resistance R_c between filler particles in heat-conducting chains. The effective thermal conductivity of individual particle of size d including interfacial resistance R_K (Kapitza's resistance) can be written as $\lambda_f^* = \lambda_f / (1 + R_K \lambda_f / d)$ [18].

In a case of very small particles (nanoparticles), the term R_K/d converges to infinity: $R_K/d \rightarrow \infty$, i.e. the filler is not involved in the thermal conductivity, i.e. $\lambda_f^* = 0$. For the large particles, $R_K/d \rightarrow 0$. The thermal resistance of interface layer is the function of the layer thickness and its conductivity, $R_K = l/\lambda_l$ and $R_K \rightarrow 0$ at $l \rightarrow 0$ resulting in $\lambda_f^* = \lambda_f$. Since the λ_f^* values for GNP phase are much larger than for TiO₂ phase, GNP particles provide the main contribution into the value of thermal conductivity of GNP/TiO₂/epoxy composites.

The value of the fit parameter λ_f^* for GNPs in GNP/TiO₂/epoxy composite decreases with increasing content of GNPs (see Table 2). Such a behavior of λ_f^* may be caused by different changes of the thermal resistance between anisometric GNP particles and at the interface of GNP-epoxy due to changes of GNP spatial distribution at increased filler content, namely increasing alignment of the GNP particles in the specimen plane (perpendicular to the heat flow). This GNP alignment may influence not only the C parameter, but also the thermal contact between GNP particles via the change of the contact spot area.

The dependencies of the thermal conductivity on the temperature for the epoxy composite with the hybrid filler GNP/TiO₂ are shown in Fig. 7. As seen, these dependencies are complicated and determined by the changes with the temperature of the matrix thermal conductivity, individual filler particles, and the contact thermal resistances both at interphase boundaries and between the filler particles (GNP-GNP,

GNP-TiO₂ and TiO₂-TiO₂ particles) [19]. The thermal conductivity of the polymer matrix is relatively low and increases slightly while heating. The growth of the number of phonons while heating leads to an increase in the thermal conductivity of GNP phase. On the other hand, the phonon-phonon scattering is also increased at heating leading to the decrease of GNP thermal conductivity and as a result, the temperature dependence of the thermal conductivity of GNP filler has a maximum at one temperature for composites with higher GNP content. At higher filler content the number of direct contacts between the filler particles increases and the temperature dependence of the thermal conductivity of composite, in this case, will approach the temperature dependence of the filler (including the spatial distribution of the GNPs and TiO₂ in the composite).

7. CONCLUSIONS

It was found that ternary GNP/TiO₂/epoxy composites are characterized by the lower percolation threshold and enhanced electrical conductivity compared to binary composites GNP/epoxy. Such behavior of electrical conductivity may be explained by the combination of conductive and semiconductive filler particles in GNP/TiO₂/L285 composites and the electrical transport may be realized due to the presence of various conductive ways, namely GNP-GNP chains, TiO₂ chains, and combined GNP-TiO₂-GNP chains.

It was shown that for low conductive GNP/TiO₂/L285 samples when the process of formation of conductive chains consisting of GNP-GNP particles is not effective due to the small amount of GNP particles (1-2 wt. %), and electron transport in this composite is realized mainly due to TiO₂ particles chains and maybe GNP-TiO₂ via hopping conduction mechanism with negative TCR and the estimated activation energy is equal to 0.27 eV.

The increase of GNP content promotes the formation of conductive GNP-GNP pathways and initiation of tunnel mechanism of conductivity as well as the realization of electron transport via direct contacts between GNP particles at higher GNP content. It was concluded, that the electron transport between filler particles (contact electrical resistance) is the main parameter that determines the value and behavior of electrical conductivity of these composites.

It was observed that the addition of TiO₂ into GNP/epoxy composites doesn't influence the value of thermal conductivity. The analysis of the experimental data on thermal conductivity of the ternary GNP/TiO₂/epoxy composites within a modified Nielsen model has shown that thermal conductivity of each filler phase was strongly affected by thermal interface resistance and interparticle thermal contact resistance. The thermal interface and contact resistance would be decreased with the increase of GNP content, resulting in an increase of GNP phase effective thermal conductivity. The observed decrease of the effective thermal conductivity of GNP phase with increase of GNP content may be explained by the partial alignment of anisometric GNP particles in the samples' plane (perpendicularly to the thermal flow).

REFERENCES

1. K. Sabira, M.P. Jayakrishnan, P. Saheeda, S. Jayalekshmi, *Eur. Polymer J.* **99**, 437 (2018).
2. D.D.L. Chung, *Carbon* **50**, 3342 (2012).
3. P. Dharap, Z. Li, S. Nagarajaiah, E. Barrera, *Nanotech.* **15**, 379 (2004).
4. Z. Zhou, X. Zhang, X. Wu, C. Lu, *Comp. Sci. Technol.* **125**, 1 (2016).
5. P.N. Nikolarakis, I.A. Asimakopoulos, L. Zoumpoulakis, *Hindawi J. Nanomater.* Article ID 7023437 (2018).
6. R. Nasrin, S. Seema, Md.A. Gafur, A.H. Bhuiyan, *Am. J. Mater. Synth. Process.* **3** No 4, 56 (2018).
7. M.F. Abdelkarim, L.S. Nasrat, S.M. Elkhodary, *Eng. Technol. Appl. Sci. Res.* **5**, 775 (2015).
8. E.A. Segura González, D. Olmos, M.Á. Lorente, I. Vélaz, J. González-Benito, *Polymers* **10**, 1365 (2018).
9. S. Nayak, B. Sahoo, T.K. Chaki, D. Khastgir, *RSC Adv.* **3**, 2620 (2013).
10. P.S. Saluja, J.K. Tiwari, G. Gupta, *Int. Res. J. Eng. Technol. (IRJET)* **04** (2017).
11. Y. Jin, N. Xia, R. Gerhardt, *Nano Energy* **30**, 407 (2016).
12. H. Runqin, N. Fenglian, C. Qiuxiang, *J. Exp. Nanosci.* **12**, 308 (2017).
13. D.H. Park, Y.K. Lee, S.S. Park, C.S. Lee, S.H. Kim, W.N. Kim, *Macromol. Res.* **21**, 905 (2013).
14. O. Lazarenko, L. Vovchenko, L. Matzui, Y. Perets, *Mol. Cryst. Liq. Cryst.* **536**, 72 (2011).
15. S. Rajesh, K.P. Murali, V. Priyadarsini, S.N. Potty, R. Ratheesh, P. Mohanan, *Polym.-Plastics Technol. Eng.* **47** No 3, 242 (2008).
16. L. Vovchenko, L. Matzui, Y. Perets, I. Sagalianov, O. Yakovenko, *Adv. Nanotech.* **21**, 1 (2018).
17. A. Hashim, *Am. J. Sci. Res.* **74**, 05 (2012).
18. R. Kochetov, A. Korobko, T. Andritsch, P. Morshuis, S. Picken, J. Smit, *J. Phys. D Appl. Phys.* **44**, 395401 (2011).
19. E. Weber, M. Clingerman, J. King, *J. Appl. Polym. Sci.*, **88**, 123 (2003).

Електро- та теплопровідність потрійних композитів графітові нанопластинки/TiO₂/епоксидна смола

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Проведено дослідження електричних та теплових властивостей композитних матеріалів (КМ) на основі епоксидної смоли Л285 і гібридного наповнювача графітові нанопластинки/оксид титану (ГНП/TiO₂). Експериментальне дослідження включало вимірювання електричного опору на постійному струмі в інтервалі температур 77-293 К і теплопровідності (в інтервалі 150-425 К) для таких потрійних композитів, що містили від 0 до 5 ваг. % ГНП і 35 ваг. % ультрадисперсних (розмір ~ 130 нм) частинок TiO₂. Спостерігалось зниження порогу перколяції і підвищення електропровідності для потрійних КМ ГНП/TiO₂/епоксидна смола у порівнянні із бінарними КМ ГНП/епоксидна смола. Було встановлено, що збільшення вмісту високоелектропровідних частинок ГНП в композиті призводить до збільшення електропровідності і зміни температурного коефіцієнта опору (ТКО) з від'ємного до злегка додатнього в інтервалі температур 100-293 К. Від'ємний ТКО пов'язаний із стрибковим механізмом електропровідності, і для високоомного композиту 2 ваг. % ГНП/TiO₂/епоксидна смола була проведена оцінка енергії активації. Додатній ТКО для композиту 5 ваг. % ГНП/TiO₂/епоксидна смола може бути пояснений змінами у тунельному електронному транспорті при тепловому розширенні епоксидної матриці. Дослідження теплопровідності КМ ГНП/TiO₂/епоксидна смола показало, що додавання частинок TiO₂ в композити ГНП/епоксидна смола не впливає на величину теплопровідності. Зміни теплопровідності при збільшенні вмісту частинок ГНП в потрійних КМ розглядалися в рамках модифікованої моделі Нільсена і визначалася ефективна теплопровідність кожної з фаз наповнювачів. Обговорювалася також роль теплового опору на міжфазних границях і контактного теплового опору між частинками наповнювача у визначенні теплопровідності композиту.

Ключові слова: Оксид титану, Графітові нанопластинки, Композит, Електропровідність, Теплопровідність.