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ENHANCING ELECTRICAL CONDUCTIVITY OF MULTIWALLED CARBON NANOTUBE/EPOXY COMPOSITES BY GRAPHENE NANOPLATELETS

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The need of high performance integrated circuits and high power density communication devices drives the development of materials enhancing the conductive performances by carbon nanoparticles. Among nanocomposites, the ternary hybrid carbon nanotubes/graphene nanoplatelets/polymer composites represent a debatable route to enhance the transport performances.

In this study hybrid ternary nanocomposites were manufactured by direct mixing of multiwalled carbon nanotubes (MWCNTs) and graphene nanoplatelets (GNPs) at a fixed filler content (0.3 wt.%), but different relative combination, within an epoxy system. MWNT/epoxy nanocomposites were manufactured for comparison. The quality of dispersion was evaluated by optical and scanning electron microscopy (SEM). The electrical properties of hybrid composites were measured in the temperature range from 30 up to 300 K.

The synergic combination of 1D/2D particles did not interfere with the percolative behaviour of MWCNTs but improved the overall electrical performances. The addition of a small amount of GNPs (0.05 wt.%) led to a strong increment of the sample conductivity over all the temperature range, compared to that of mono filler systems.

Keywords: graphene nanoplatelets, multiwalled carbon nanotubes, epoxy resin, hybrid nanocomposites, electrical conductivity

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1. Introduction

Epoxies are an indispensable class of thermosetting polymers widely used in modern industry. These materials are ubiquitous, due to the fact that scientists and engineers from a wide range of disciplines use them in various applications. Carbon nanomaterials such as carbon nanotubes (CNTs) and graphene nanoplatelets (GNPs) are among the most utilized nanomaterials due to their electrical, mechanical and thermal properties. The result of combining the insulating epoxy as a host matrix and conducting carbon nanomaterials as fillers is the material with a whole new set of properties that are not found in individual components [1, 2]. Conducting polymer composites are mainly applied as electromagnetic coatings, radar waves absorbing materials, and as antistatic materials [3–5]. In electronics, conductive polymer composites find applications as adhesives and circuit elements [6].

Electrical conductivity of polymer composites depends on the filler concentration. For a low filler content the distance between conductive particles is large and the conductivity is limited in an insulating polymer matrix. Increasing the content of filler composites evokes a non-linear increase of the electrical conductivity as a function of the filler concentration. At a certain filler concentration, known as the percolation threshold (φ_c), the electrical conductivity suddenly increases by several orders leading

a composite from an insulator to a conductor. Sometimes addition of a very small amount of conducting particles makes a filler to form an effective conducting path thus making the whole composite conductive. CNTs and GNPs, as effective fillers, could be used to produce a conductive polymer composite with a very low percolation threshold [7]. The typical percolation threshold values that were reported in literature vary from 0.002 to over 2 wt.% [8–10] for MWCNT composites and from 1 to 8 wt.% for GNP composites [11, 12]. Such large variations of percolation threshold values show that the nanofiller content, aspect ratio, dimensions and geometrical arrangement, and also composite processing conditions are important [13, 14].

The main problems limiting the expected improvement of epoxy resin are that such nanoparticles increase viscosity and form agglomerates due to van der Waals forces [2, 15, 16], and the sufficient network is not created in the polymer matrix which leads to a higher percolation threshold. The agglomeration could be decreased by improving the dispersion state of the filler in the polymer matrix. One of the most promising solutions is to attempt combining two carbon fillers into a hybrid structure which could lead to a potentially new multifunctional material in research and application as the result of synergy effect of both fillers, improving mechanical [17, 18], thermal [13] and electrical [14] characteristics. A small size of nanofillers with a different shape results in a large surface area, thus increasing the amount of the polymer in contact with the filler. When the volume content of the nanofiller is large enough, the inter-phase becomes the dominant phase in the composite. In addition, the use of different shape (1D – CNT and 2D – GNP) nanoparticles allows one to increase the efficiency at a smaller filler content. For the same filler content of particles with various geometrical arrangements of the chains, different results of particle lengths and shape can be achieved. Therefore, it is hard to predict theoretically the final results. Physical properties of a composite filled with carbon nanoparticles in a different filler content and combination should be experimentally investigated in order to determine the optimal nanoparticle content, the filler combination and the ratio which would maximally improve certain physical properties of the composite, reduce production costs, enhance multifunctionality and application possibilities. The synergistic effect of carbon nanofillers on improving the thermomechanical and electrical properties of the material is not clearly determined as well. Moreover, usually electrical properties of hybrid composites were investigated only at room temperature [19], while investigations in a wide temperature range are needed to determine the electrical transport mechanism [20].

The aim of this work is to systematically investigate hybrid nanocomposites at different MWNTs/GNPs ratios to highlight synergic effects on the electrical conductivity. In this paper electrical conductivity measurements were performed in a wide frequency and temperature range starting from cryogenic temperature (30 K) to room temperature (300 K) in order to determine the electrical transport mechanism at different temperatures.

2. Materials and methods

Composites were prepared with multiwalled carbon nanotubes (MWCNTs) and graphene nanoplatelets in an epoxy resin matrix. The epoxy resin is a monocomponent thermosetting resin RTM6 (HexFlow®), which is already degassed. It is a premixed epoxy-amine system for service temperatures from –60 up to 180 °C, specifically developed to fulfill the requirements of aerospace industries in the advanced resin transfer moulding process. This resin is characterized by a high ultimate glass transition temperature (200 °C) and a low viscosity (50 MPa) within the range 100–120 °C.

MWCNTs N7000 were purchased from *Nanocyl* (Belgium) and they were produced via the catalytic carbon vapour deposition process. The mean length of a MWCNT is 0.1–10 μm, the diameter 10 nm. The MWCNT filler content is 0.015–0.30 wt.%. Graphene nanoplatelets (GNPs) were purchased from *PuntoQuantico* (Italy). The average particle (lateral) size is 20–50 μm, the specific surface area is 60–80 m^2/g, and the average density is 2.43 g/cm^3. Filler contents 0.015–3.0 wt.% were chosen. According to the data sheet, the electrical conductivity of particles is $\approx 5 \cdot 10^{-5}$ W·cm, but the thermal conductivity is 3000 W/m·K. Using both carbon nanofillers, hybrid nanocomposites with the filler content 0.30 wt.%, the ratio of MWCNTs and GNPs being selected as 1:1, 1:2, 1:5, 2:1, 5:1, were produced.

Epoxy resin/carbon nanofiller nanocomposites were prepared using 150 g of resin mixed with carbon particles in different contents for a constant time (70 min) at 85 °C temperature with a nominal

speed of 6000 rpm. The mixer used in this work was a T 25 digital ULTRA-TURRAX high-performance disperser by *IKA* with the output power 500 W and the frequency 50 Hz. A disperser horn was directly put into a resin and MWCNT mixture warmed up to 60 °C. The disperser used produces extremely strong shear and thrust forces due to high accelerations acting on the material, and additionally a high turbulence occurs in the shear gap between the rotor and the stator, which provides an optimum mixing of the components.

The structure and dispersion of the filler in the polymer matrix were determined using microscopic methods – optical microscopy and scanning electron microscopy (SEM). Optical microscopy analysis was carried out by using an *Olympus* system type BX51 in transmitted light configuration. The homogeneity of composites was checked with a scanning electron microscope *Helios* NanoLab 650.

Dielectric properties of the composites were measured in a wide frequency range (from 20 Hz to 3 GHz) at room temperature and at low frequencies (20 Hz – 1 MHz) in the temperature range from 30 to 300 K. In the frequency range from 20 Hz to 1 MHz measurements were performed using a LCR meter (HP4284) measuring the capacitance and the loss tangent. For low temperature measurements a helium closed cycle cryostat was used. In the frequency range from 1 MHz to 3 GHz reflection and phase were measured using the coaxial line technique with a vector network analyzer (*Agilent* 8714 ET). The samples were of a cylindrical shape with different thickness and diameter for different technique. In the frequency range 20 Hz – 3 GHz the height and radius were 3 and 6 mm and in the frequency range 1 MHz – 3 GHz they were 3 and 1 mm, respectively. Silver paste was used for contacts. The real part of the electrical conductivity is calculated using the formula $\sigma' = \varepsilon_0 \varepsilon'' \omega$, where ε_0 is the vacuum permittivity, ε'' is the imaginary part of the dielectric permittivity and ω is the frequency.

3. Results and discussion

3.1. Structure characterization

Microscopy methods were used to characterize and determine the dispersion and interactions of carbon nanoparticles in the polymer matrix. Using the optical microscopy analysis the samples with MWCNTs and GNPs were characterized by nominal dimensions of 10 × 10 mm with a thickness varying in the range 200±50 μm (Fig. 1).

The image in Fig. 1(a) shows an uneven distribution of MWCNTs in the epoxy resin. There are areas with a high concentration and agglomerated MWCNTs and small areas with an almost negligible

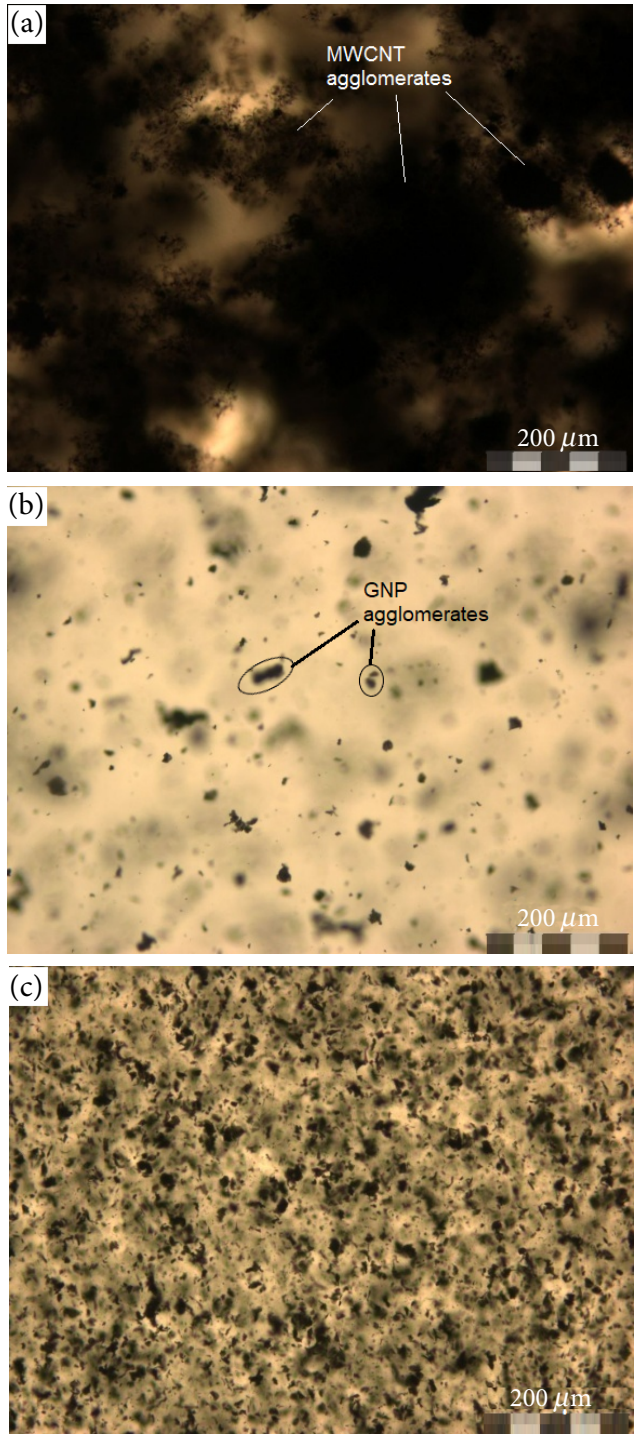

Fig. 1. Optical microscopy images of epoxy resin filled with (a) 0.03 wt.% of MWCNTs; (b) 0.03 wt.% of GNPs; (c) 1.00 wt.% of GNPs, at 10× magnification.

concentration of the carbon nanotubes. The agglomerates could be related to strong van der Waals forces between the carbon nanotubes. The images of the GNP composites in Fig. 1(b) and (c) of the GNP composites show large agglomerates of the GNPs due to interactions between the sheets of graphene nanoplatets. A smooth surface of the GNPs could result in a weak interfacial bonding with the polymer [7]. For further structural investigations the SEM images are performed (Fig. 2).

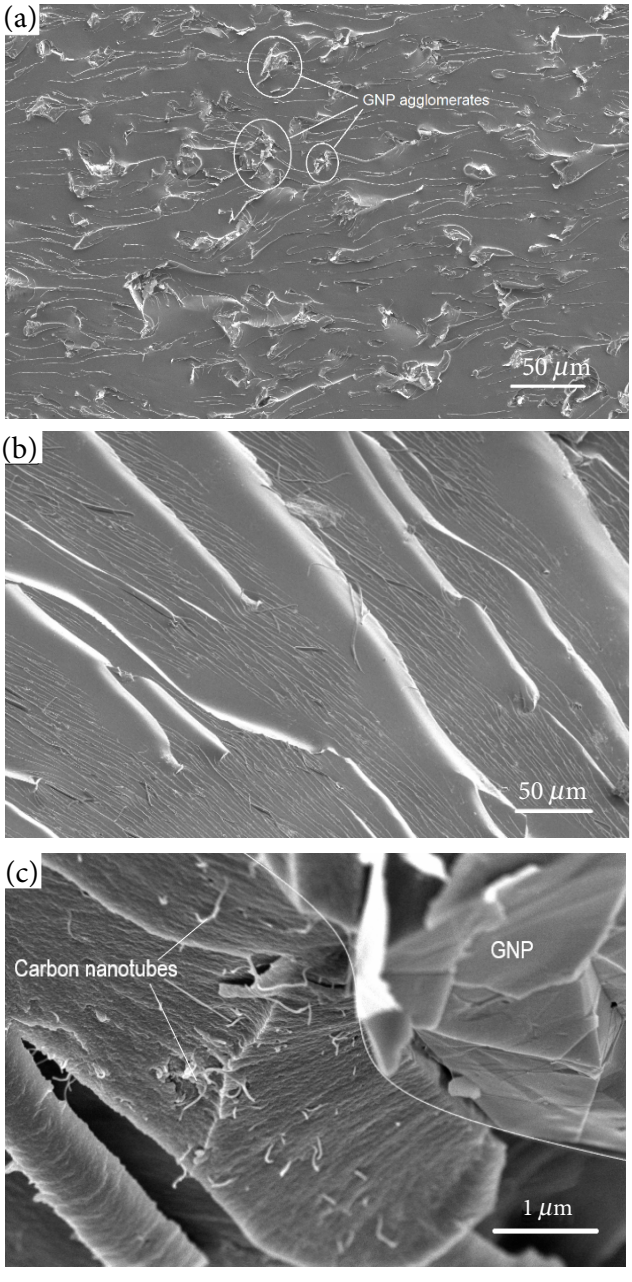

Fig. 2. SEM images of epoxy resin composites filled with (a) 0.3 wt.% of GNPs, magnification 500×; (b) MWCNTs/GNPs (5:1), magnification 500×; (c) MWCNTs/GNPs (5:1), magnification 35000×.

Figure 2(a) shows the surface of a composite containing 0.3 wt.% GNPs. GNP agglomerates of varying size are randomly dispersed in the polymer matrix. In contrast, the surface of hybrid filler composites is smoother with no visible large agglomerates of GNPs or MWCNTs, and carbon nanotubes likely reduce the size of GNP aggregates. The magnification of the SEM images in Fig. 2(a) and (b) is 500×. The SEM image (magnification 35000×) in Fig. 2(c) shows that smaller GNP agglomerates can still be found, but the dispersion of MWCNTs is much more even.

3.2. Electrical properties

The dielectric and electrical properties of the composites containing MWCNTs, GNPs and hybrid nanocomposites with different combinations of MWCNTs/GNPs are compared in a wide frequency and temperature range.

The frequency dependences of the dielectric permittivity and the electrical conductivity at room temperature for the composites containing only MWCNT and GNP fillers are presented in Fig. 3. The values of dielectric permittivity and electrical conductivity increase sharply close to the percolation threshold. Moreover, above the percolation threshold in the frequency dependence of the conductivity a frequency independent plateau is observed.

The theoretical percolation threshold for GNP particles could be calculated from the excluded volume theory [21, 22]

$$\varphi_c = \frac{21.2}{A_{\mathrm{GNP}}}, \tag{1}$$

where A_{GNP} is an aspect ratio of round shape particles. As the average aspect ratio value for GNP particles is $A_{\mathrm{GNP}} = 1500$, the percolation threshold is 1.41 volume % or 3 wt.%. However, considering the experimental data (Fig. 3), the dielectric permittivity and the electrical conductivity of GNP composites are low enough and similar to pure epoxy resin properties even with the highest available filler concentration (3 wt.%). It indicates that the percolation threshold in GNP composites is higher than 3 wt.% and somewhat higher than the value of percolation threshold calculated from the excluded volume theory. Such high

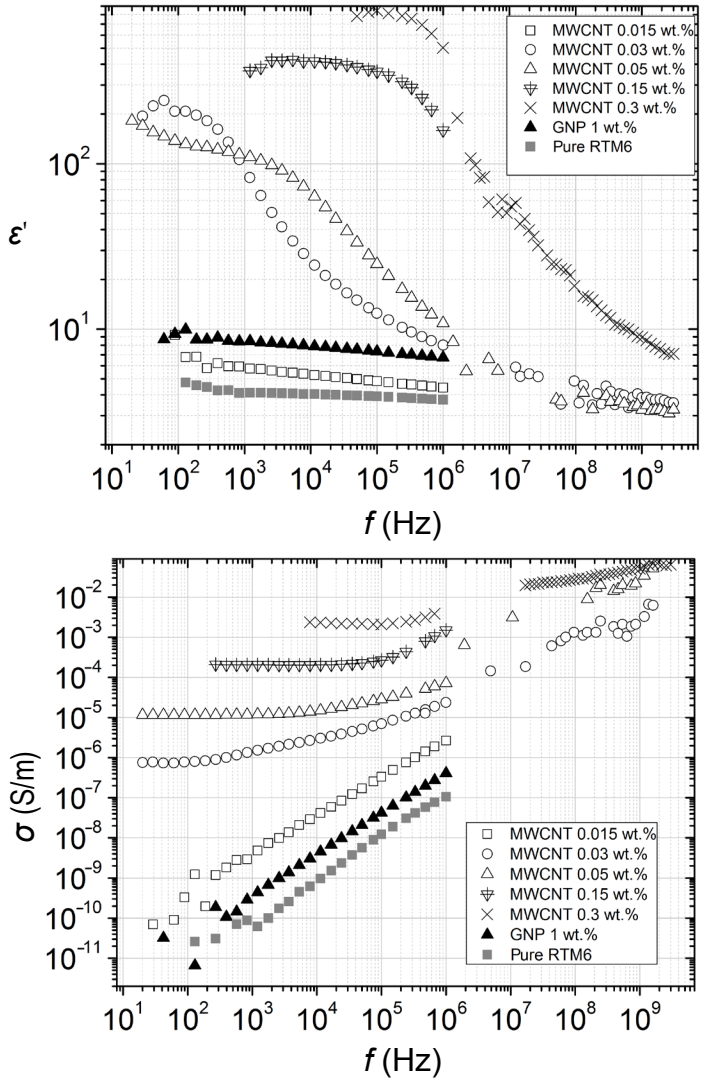

Fig. 3. Frequency dependence of the dielectric permittivity and the electrical conductivity of GNP and MWCNT composites.

experimental percolation threshold value could be attributed to the uneven distribution and large aggregates of GNPs in the polymer matrix. Similar percolation threshold values were already observed in GNP/epoxy composites [23, 24]. At low filler concentrations aggregated particles do not form a conductive path.

According to the excluded volume theory, the theoretical percolation threshold for rod-like particles could be calculated by the formula [21, 22]

$$\varphi_c = \frac{0.5}{A_{\mathrm{MWCNT}}}, \tag{2}$$

where A_{MWCNT} is the aspect ratio, and the average aspect ratio for MWCNT is $A_{\mathrm{MWCNT}} = 505$. The percolation threshold for MWCNT composites is 0.1 volume % or 0.14 wt.%. Moreover, the experimental percolation threshold for MWCNT composites is close to 0.03 wt.%.

The dielectric permittivity and the electrical conductivity of mixed MWCNT/GNP composites with various proportions and the total 0.3 wt.% concentration are presented in Fig. 4. All investigated composites with hybrid nanofillers are above the percolation threshold because the frequency independent conductivity plateau is very well expressed in conductivity spectra. This is quite expected because according to the excluded volume theory the following relation should be valid for mixed MWCNT/GNP composites:

$$\frac{m_{\mathrm{MWCNT}}}{p_{c,\mathrm{MWCNT}}} + \frac{m_{\mathrm{GNP}}}{p_{c,\mathrm{GNP}}} = 1. \tag{3}$$

Here m_{MWCNT} and m_{GNP} are mass fractions of MWCNTs and GNPs, respectively, and $p_{c,\mathrm{MWCNT}}$ and $p_{c,\mathrm{GNP}}$ are mass percolation thresholds in composites filled with MWCNTs and GNPs, respectively.

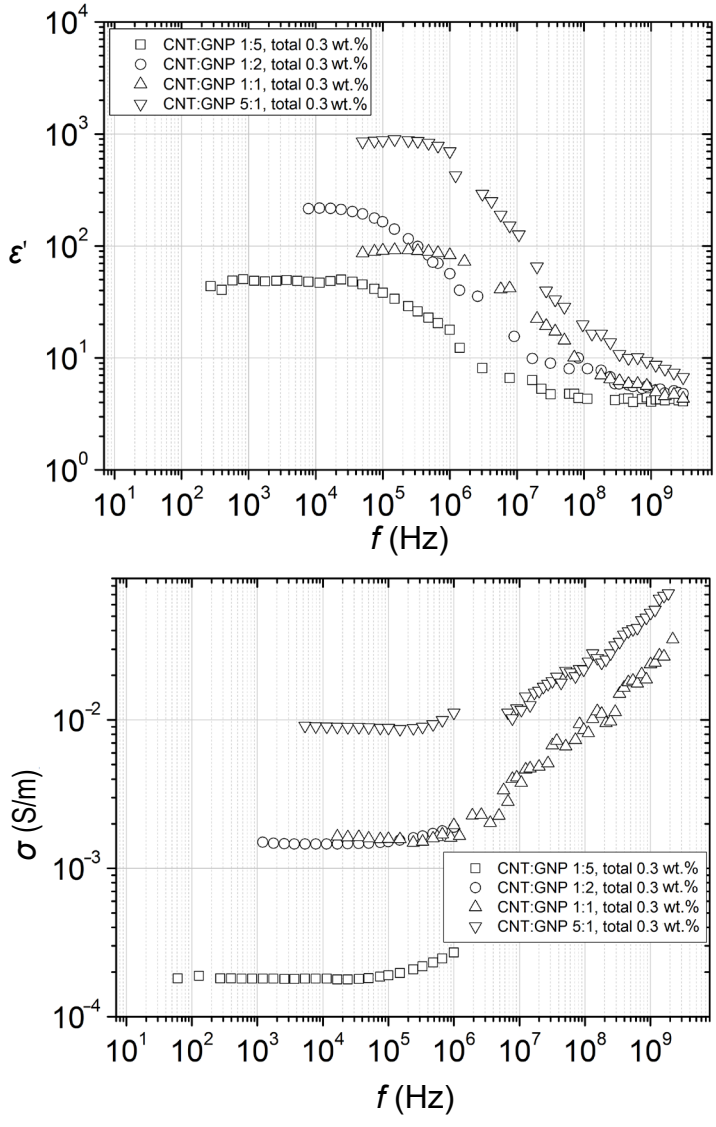

Fig. 4. Frequency dependence of the dielectric permittivity and the electrical conductivity of hybrid MWCNT/GNP composites.

$m_{\mathrm{MWCNT}} > p_{c,\mathrm{MWCNT}}$ composites will be above the percolation threshold for any m_{GNP}.

For mixed composites the electrical conductivity and dielectric permittivity increase with the increase of the MWCNT concentration.

Above the percolation threshold the frequency dependence of electrical conductivity could follow the Jonscher equation [25]

$$\sigma'(\omega) = \sigma_{\mathrm{DC}} + A\omega^n, \tag{4}$$

where σ_{DC} is the DC conductivity and $A\omega^n$ is the AC conductivity. The values of electrical conductivity as a function of the filler concentration of single filler MWCNT and hybrid filler composites are presented in Fig. 5. Above the percolation threshold the DC conductivity follows the power law [26]

$$\sigma(p) \propto (p–p_c)^t, \tag{5}$$

where p_c is the percolation threshold and t is the critical exponent.

The highest DC conductivity value 8.9 mS/m is observed in MWCNT:GNP mixed filler composites with proportions 5:1 (total content 0.3 wt.%) and it is increased by four orders of magnitude over that of composites containing 0.3 wt.% MWCNTs. Such high value is clearly higher than can be predicted by a simple rule of mixtures (ROM) theory [27]

$$\sigma = \frac{1}{\Sigma_{i=0}^{n} V_i} \Sigma_{i=0}^{n} \sigma_i V_i, \tag{6}$$

where V_i and σ_i are the volume and the conductivity of the ith component. Indeed, the conductivity of composites only with MWCNTs is much higher than the conductivity of composites only with

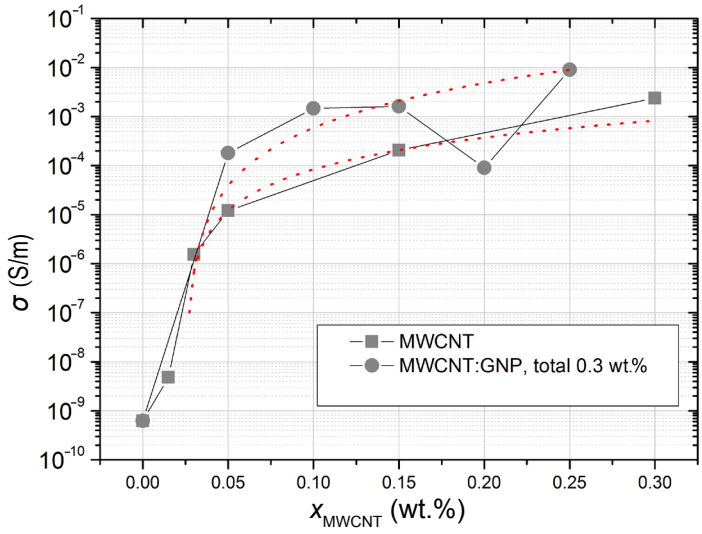

Fig. 5. Concentration dependences of the electrical conductivity at 1 kHz frequency for composites containing MWCNTs only and mixed MWCNT:GNP fillers. Dotted lines are the fits of the power law.

GNPs, therefore the conductivity of mixed composites clearly overcomes the values predicted by the ROM theory in all frequency range, including microwaves (Eq. 6), while in other works a similar effect was observed only at low frequences below 1 MHz [28]. An increase could be attributed to the formation of a more effective conductive network due to combining 2D MWCNT and 1D GNP conductive particles.

The electrical transport in mixed MWCNT/GNP composites can occur via 1) hopping and tunnelling of electrons in the MWCNT subsystem, 2) hopping and tunnelling of electrons in the GNP subsystem, and 3) tunnelling of electrons between the GNP and the MWCNT subsystems [29]. Increase of the conductivity with the increase of the MWCNT concentration for hybrid composites with the total 0.3 wt.% concentration of nanofillers indicates that the second conductivity mechanism is negligible in comparison with the first and third ones. Therefore, the electrical conductivity in mixed composites increases because of the better distribution of MWCNTs and the tunnelling of electrons between the GNPs and the MWCNTs.

Temperature dependences of the DC conductivity are presented in Fig. 6. Above the percolation threshold the DC conductivity below room temperature fits the electrical tunnelling model [30]

$$\sigma_{DC} = \sigma_0 \exp\left[\frac{T_1}{k(T+T_0)}\right], \quad (7)$$

where T_1 is the energy for an electron to cross the insulator gap between the conductive particles, T_0 is the temperature above which thermally activated conductivity over the barrier occurs. The obtained tunnelling model fit parameters are listed in Table 1. The tunnelling model parameters T_1 and T_0 are related with the microscopic parameters [30]

$$T_1 = wA\beta_0/8\pi k \quad (8)$$

and

$$T_0 = 2T_1/\pi\chi w, \quad (9)$$

where $\chi = (2mV_0)^{0.5}/h$ and $\beta_0 = V_0/ew$, m and e are the electron mass and charge, respectively, V_0 is the potential barrier amplitude, w is the interparticle distance (gap width), and A is the area of capacitance formed by the junction. From Eqs. (8) and (9) it follows that T_1/T_0 is proportional to the gap width w and the potential barrier V_0 amplitude. The ratio T_1/T_0 decreases with the MWCNT concentration in single and hybrid composites (Table 1). Thus the interparticle distance and the potential barrier amplitude can decrease with the decrease of the MWCNT concentration for both single and hybrid composites. The gap width is approximately proportional to $p^{-1/3}$ in single composites [31]. The dependence T_1/T_0 is very similar in hybrid and single composites. However, the ratio T_1/T_0 is higher in single composites. According to SEM investigations, the smallest distance between nanoparticles is in mixed composites (Fig. 2). Therefore the ratio T_1/T_0 is lower in hybrid composites due to the better distribution of nanoparticles.

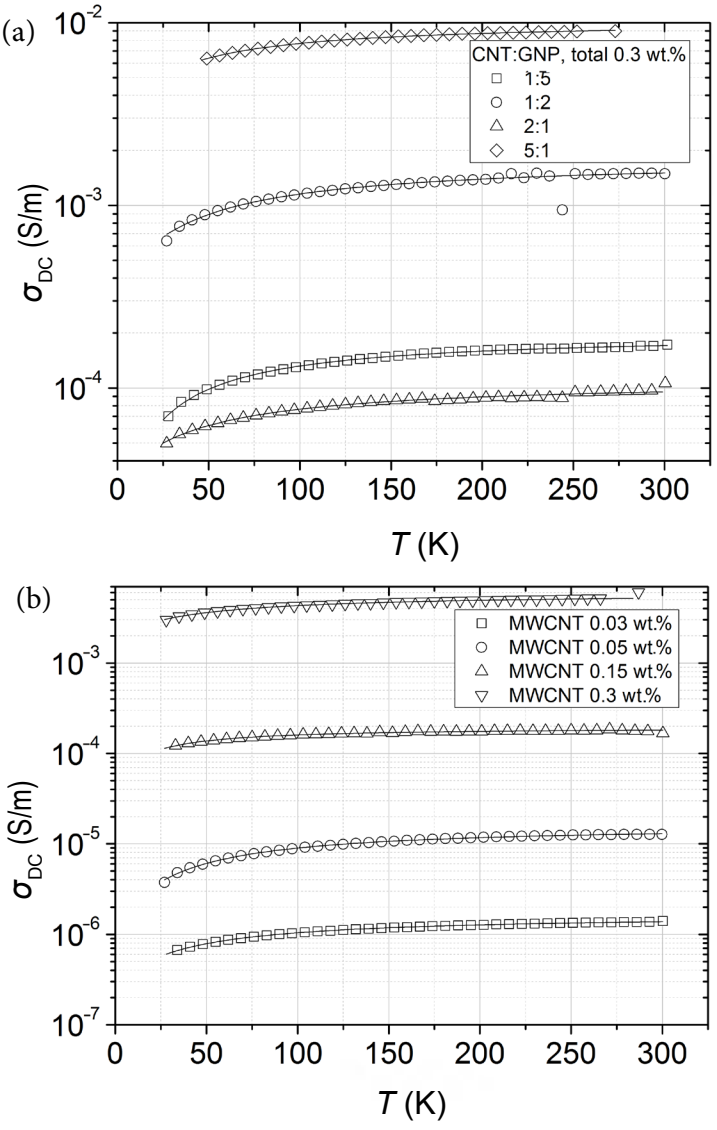

Fig. 6. Temperature dependence of DC conductivity for composites filled with (a) MWCNTs, (b) MWCNTs/GNPs; total concentration is 0.3 wt.%. Solid lines are fits of the tunnelling model.

Table 1. Tunnelling model fit parameters.

MWCNTs (wt.%)	σ_0 (S/m)	T_1 (K)	T_0 (K)
0.03	$1.6 \cdot 10^{-6}$	63	34
0.05	$1.5 \cdot 10^{-5}$	77	27
0.15	$2.1 \cdot 10^{-4}$	22	15
0.3	$6.1 \cdot 10^{-3}$	46	41
CNTs:GNPs (total 0.3 wt.%)			
1:5	$2.1 \cdot 10^{-4}$	50	20
1:2	$1.8 \cdot 10^{-3}$	61	37
2:1	$1.1 \cdot 10^{-5}$	52	41
5:1	$1.1 \cdot 10^{-2}$	36	27

4. Conclusions

MWCNT/epoxy and GNP/epoxy nanocomposites with different filler contents (0.015–0.3 wt.%) and hybrid epoxy nanocomposites filled with CNTs/GNPs in a total reinforcement of 0.3 wt.% were fabricated, and the effects of varying individual CNT/GNP contents and combination on electrical properties were evaluated.

The lowest electrical percolation threshold is observed in MWCNT composites (0.03 wt.% concentration). Although the percolation threshold in mixed MWCNTs/GNPs can be described by the excluded volume theory, the electrical conductivity of mixed composites is substantially higher in comparison with that of single composites. The electrical conductivity of hybrid nanocomposites containing 0.3 wt.% MWCNTs and GNPs in ratio 5:1 exhibits the highest value of 0.009 S/m, which is more than 4 times higher than that of composites containing only 0.3 wt.% MWCNTs (0.002 S/m). The concurrent 1D and 2D

particles did not affect the percolative behaviour of MWCNTs but led to an outstanding increment in the final electrical conductivity. That could be considered as a synergistic effect between GNPs and MWCNTs due to the better distribution of MWCNTs and the tunnelling of electrons between GNPs and MWCNTs.

Acknowledgements

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EPOKSIDINĖS DERVOS KOMPOZITŲ SU DAUGIASIENIAIS ANGLIES NANOVAMZDELIAIS ELEKTRINIO LAIDUMO GERINIMAS GRAFENO DALELĖMIS

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Santrauka

Tobulėjant technologijoms ir didėjant našesnių bei mažesnių matmenų prietaisų poreikiui reikalingos naujos medžiagos, atitinkančios kylančius reikalavimus. Vienos iš tokių medžiagų yra polimeriniai kompozitai su anglies nanodalelėmis, kurie pasižymi geromis mechaninėmis, terminėmis ir elektrinėmis savybėmis.

Straipsnyje aptariami mišraus užpildo kompozitų su anglies nanovamzdeliais ir grafeno dalelėmis elektrinio laidumo tyrimai. Anglies nanovamzdeliai ir grafenas sumaišyti įvairiomis proporcijomis, kai bendra dalelių procentinė masės dalis kompozite – 0,3 %. Palyginimui pagaminti kompozitai su anglies nanovamzdeliais, kurių procentinė masės dalis buvo nuo 0,025 iki 0,3 %.

Užpildo dalelių pasiskirstymas polimero matricoje įvertintas optinės mikroskopijos ir skenuojančios elektroninės mikroskopijos metodais. Elektrinių savybių tyrimai atlikti plačiame dažnių (20 Hz – 3 GHz) bei temperatūrų intervale (30–300 K).

Nustatyta, kad įterpiant nedidelį kiekį grafeno dalelių (0,05 % masės dalies) į kompozitus su anglies nanovamzdeliais, kai bendra užpildo dalelių koncentracija 0,3 %, elektrinis laidumas padidėja keturis kartus, palyginti su kompozitais, užpildytais tik anglies nanovamzdeliais esant tokiai pačiai dalelių koncentracijai. Tai gali būti siejama su geresniu vienmačių ir dvimačių dalelių tarpusavio pasiskirstymu mišraus užpildo kompozito polimerinėje matricoje.