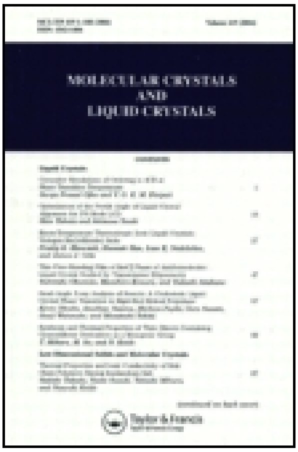

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The Electronic Transport Properties of the Composites with Nanosized Carbon Fillers

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The Electronic Transport Properties of the Composites with Nanosized Carbon Fillers

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Electric resistance of epoxy composite materials where thermally exfoliated graphite (TEG) with different dispersion degree and multi-walled carbon nanotubes (MWCNT) used as fillers has been investigated in the temperature range 77–300 K. The filler content was 5, 10 wt.%. It was shown that the behavior of the resistivity percolation curves of CMs depends on the structure of carbon fillers and becomes more linear with smaller size of particles (nanoTEG). The temperature dependences of electric resistance of CMs depend on the temperature changes of the electrical resistivity of carbon filler and contact resistance between filler particles and electroconductive network formed by fillers in CMs which change as a result of thermal expansion of composite.

Keywords Electrical properties; electron microscopy; linear thermal expansion; nanocarbon filler; porosity

Introduction

Creation of novel functional composite materials based on nanocarbon is one of the directions of modern nanotechnology. The using of superdisperse carbon fillers, such as ultradisperse graphite, thermal exfoliated graphite (TEG), fullerenes, carbon nanotubes, nanographite for the creation of different composites is perspective to make light, durable, corrosion-resisting electroconductive materials. Using of such materials as fillers in polymer matrix allows to provide the necessary functional characteristics of produced polymer CMs (such as electro- and thermal conductivity, mechanical properties, absorption of electromagnetic waves) with low content of electroconductive component and as a consequence keep the elastoplastic characteristics caused by polymer matrix.

Graphene-based polymer composites possess potential applications in radiation and electromagnetic shielding, antistatic, shrinkage- and corrosion-resistant coatings, and other mechanical and functional attributes such as stiffness, barrier, conducting capabilities, light emitting devices, batteries, and other functional applications [1,2].

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Due to high interest there are number of researches of electrophysical parameters dependence of conductive phase concentration in model systems [3]. But the real physical systems have a lot of peculiarities (for example, contact resistance between filler particles) and it significantly differentiates them from number of ideal mathematic models so it is necessary to provide careful experimental researches.

The aim of this work is to investigate temperature dependences of electric resistance of epoxy composite materials based on different carbon fillers, its behavior depending on type of filler, its structure and morphology.

Experimental Details and Sample Characterization

In the present work, we investigate the composite materials, in which epoxy ED20 was used as the matrix. Several types of nanocarbon materials – thermally exfoliated graphite (TEG) with different dispersion degree: TEG, re-oxidated and repeatedly thermal shocked TEG (TEG(2)), TEG(2) ultrasonically dispersed during 3 hours ($TEG(2)_{disp.}$), TEG ultrasonically dispersed during 20 hours (nanoTEG), and multi-walled carbon nanotubes (MWCNT) were used as an electrically conducting filler. To determine the size and morphology of TEG particles surface we investigated our samples using scanning electron microscope JSM-6490LV "JEOL" (Japan) with X-ray microanalysis system "Oxford Analytical Instruments."

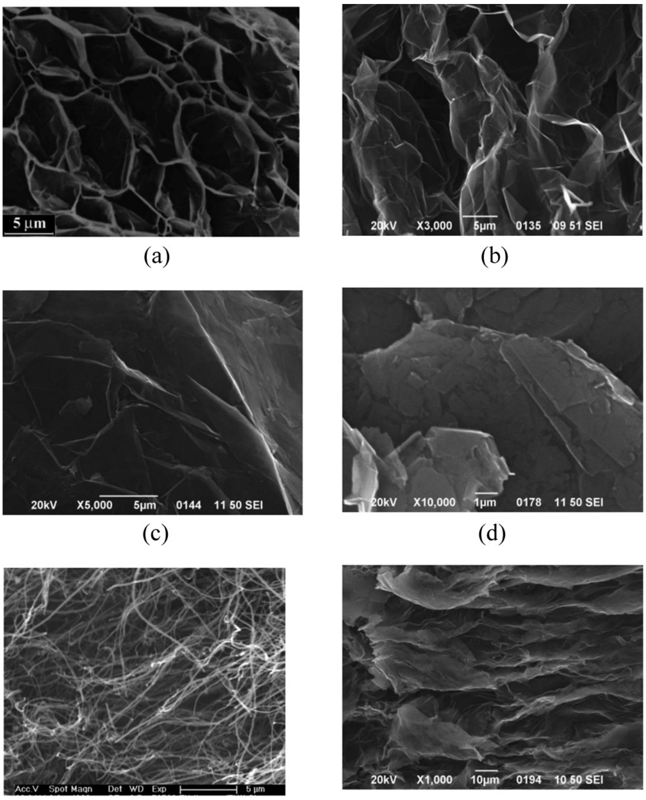
TEG is a product of the deep chemical heat treatment of dispersed graphite [4]. It is a high-porosity powder (packing density – 3–5 kg/m^3 with highly developed active surface. It consisted of 1–3-mm particles of cellular structure, the size of cells (pores) was 5–10 μm, and the thickness of the cell walls did not exceed 40–100 nm (Fig. 1a).

TEG(2) produced by re-oxidation of TEG by sulfuric acid and repeated thermal shock at 900°C.

Electron microscopy investigations of the repeatedly oxidated by sulfuric acid TEG powder have shown its additional fragmentation – the size of macropores in TEG(2) was equal to (3–7) μm, that is significantly lower in comparison with the initial TEG. Besides, as a result of oxidant exhausting while thermal shock the surface of graphite macroplanes became 'wavelike' and hilly. The X-ray diffraction studies of TEG(2) have shown that the line broadening of 002Gr almost two times more in comparison with initial TEG, that indicates the additional fragmentation of TEG crystallites [5].

TEG(2) disp. produced by ultrasonic sonication of TEG(2) during 3 hours. As a result of the ultrasonic effect the structure of TEG(2) particles is grinding. Electron microscope investigations have shown that $TEG(2)_{disp.}$ particles have considerably smaller sizes than initial TEG: less than 600 μm Figure 1(c) also the porosity of particles decreases and pore sizes are not exceed 3 μm.

NanoTEG produced by ultrasonic sonication of a solution of TEG in acetone during 20 h. The ultrasonic dispersion leads to the essential fragmentation of worm-like TEG particles on nanocarbon. In final product the particle sizes change in wide range. As it can be seen from SEM investigation Figure 1(d) the powder consists mainly from small particles ($<$1 μm) which agglomerated due to static field. The particles of themselves are the graphite planes stacks, their thickness changes from 40 to 130 nm. As a result of destroying of carcass structure of TEG the open pores are almost absent.



(a) (b) (c) (d) (e) (f)

Figure 1. SEM images for (a) TEG, (b) TEG(2), (c) TEG(2)$_{\text{disp}}$, (d) nanoTEG, (e) MWCNTs, (f) TEG-epoxy CM.

MWCNTs have been prepared as described in our previous paper [6]. The tubes have inner diameter between 5 and 8 nm and the length up to 200 µm (Fig. 1e).

CMs TEG-epoxy and MWCNT-epoxy have been prepared by methods presented in [7]. SEM images of a CM TEG-epoxy fragment (Fig. 1f) show that the porous structure of TEG is preserved in the epoxy matrix.

The electrical resistance of CM samples was determined by the two-probe (with high values of $R \leq 10^7\,\Omega$) and four-probe ($R \geq 10^7\,\Omega$) methods on the direct current in the range of temperatures 77–300 K. The coefficient of thermal linear expansion (CTLE) of composition materials was investigated by using a dilatometry method in a temperature range of (293–700)K with precision of (5–7)%. The application of high precision temperature regulator VRT-3 allows us to heat the samples at different rates and to maintain the temperature of isothermal annealing with precision of 0.5 K.

Results and Discussion

This work presents the investigation of electric resistance and the coefficient of thermal linear expansion of epoxy CM based on different carbon fillers, its content

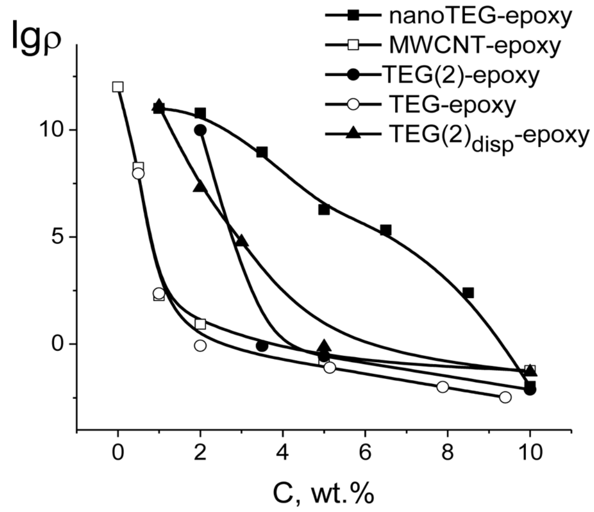


Figure 2. Electrical resistivity dependences on the filler content for epoxy CMs.

is <10 wt.%. As it can be seen from Figure 2 electrical resistivity concentration dependence of CMs has a percolation character. The value of electrical resistivity (conductivity) essentially depends on processing of filler dispersing, particles size and distribution of filler in epoxy matrix, the samples ultrasonically dispersed are more uniform and porous less.

For CMs nanoTEG-epoxy the distinct percolation transition is not observed as the particles sizes are very small and don't have branched carcass structure, as compared with TEG, then the value of $lg(\rho)$ linearly decreases with increasing of filler content. The difference in behavior of concentration dependences of resistivity can be explained by the different aspect ratios of fillers, as the electrical properties of carbon based materials increase with grain and crystallite size [8].

Electrical resistivity for the investigated composites can be described as:

$$\rho_{CM}(\phi) \sim \rho_0(\phi - \phi_{cr})^{-t}, \tag{1}$$

where ρ_0 is the electrical resistivity of carbon component, ϕ is the current volume concentration of carbon component and ϕ_{cr} is the critical threshold concentration, t is the critical index which is equal to 1.7 for the model of three-dimensional electro-conducting net with fixed nodes. The weight C_f and volume φ content (in %) of carbon filler in CMs are related by following expression: $\phi = 1/(100 + C_p \cdot d_f / C_f \cdot d_p)$, where $C_p = 100 - C_f$; d_f and d_p are the densities of carbon filler and polymer, respectively.

Using the relation $lg(\rho_{CM}) = \lg A\text{-}t \cdot \lg(\phi - \phi_{cr})$ and experimental data we have determined the critical index t for the investigated CMs. Table 1 lists the values of ϕ_{cr} and t for CMs.

As it is seen from Table 1, the higher dispersity of TEG leads to higher values of percolation threshold in electrical conductivity of CMs with TEG.

The Figure 3 presents the investigation results of temperature dependences of electrical resistance of CMs. As can be seen, the behavior is different for different

Table 1. Percolation threshold ϕ_{cr} and critical index t for nanocarbon-epoxy CMs

Type of CM	Size and shape of the filler particles	ϕ_{cr}, vol.%	t
TEG-epoxy	Worms, 3–5 mm (length), 50–100 μm (diameter)	0.55	1.90
TEG(2)-epoxy	Particles, 0.3–0.5 mm (thickness), 50–100 μm (diameter)	1.65	1.84
TEG(2)$_{\text{disp}}$-epoxy	Particles, 0.1–0.2 mm (thickness), 50–100 μm (diameter)	1.81	1.87
nanoTEG-epoxy	Platelets, 40–130 nm (thickness); 0.1–10 μm (diameter)	~3.70	2.56
MWCNT-epoxy	Cylinders, 200 μm (length); 5–8 nm (inner diameter)	0.55	1.86

filler and filler content. For CMs with TEG, which was not ultrasonically dispersed and MWCNT, the electric resistance almost linearly decreases with heating, but for the CMs with 5 wt%. of TEG(2)$_{\text{disp}}$. or nanoTEG the positive temperature coefficient of electric resistance $TCR_{CM} = 1/R \cdot dR/dT$ is observed.

We have shown that the CMs with TEG content <10 wt.% are isotropic, and for the electricl resistance of CM R_{CM} in one direction of the sample can be used the next relation:

$$R_{CM} = \frac{A^2\pi \cdot h}{4\phi \cdot K} \cdot (r_{disk} + R_k \cdot B(d)) \quad \text{or} \quad R_{CM} = \frac{A^2\pi \cdot \rho_{Gr}}{4\phi \cdot K}\left(1 + \frac{h}{2a} \cdot B(d)\right) \qquad (2)$$

where ϕ – volume fraction of graphite component, r_{disk} – electrical resistance of separate graphite particle (with disk-shape) with sizes D and h, R_k is the electric resistance of single contact between graphite particles (direct contact, thickness of polymer layer $d = 0 \rightarrow B(d) = 1$). The contact electric resistance can be sufficiently high ($R_k \cdot B$, $B >> 1$) when there are polymer layers d between particles and inverse

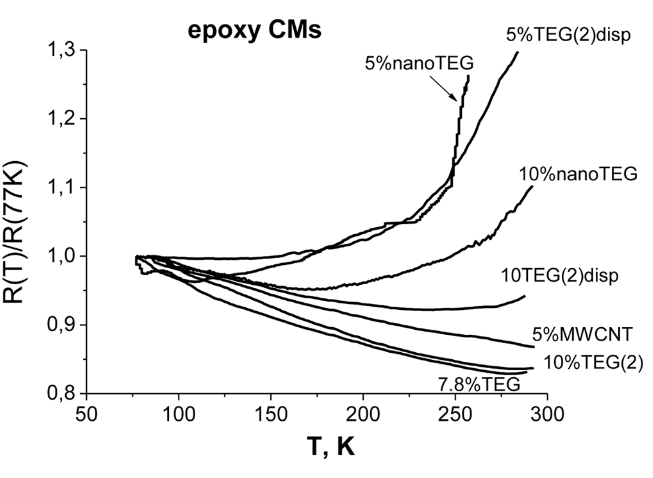


Figure 3. Temperature dependences of electric resistance for epoxy CMs.

to contact surfaces area (contact stain radius a):

$$r_{disk} = \left(\rho_{Gr} \cdot \frac{D}{D \cdot h}\right) = \frac{\rho_{Gr}}{h} \qquad R_k \cdot B = \frac{\rho_{Gr}}{2a} \cdot B(d) \tag{3}$$

The coefficient K can take on values from 0 (state before percolation) to 0.3 (all filler particles create continuous chain structures). In fact, K is a fraction of chains of graphite particles in where electric current transits.

In case when filler particles are elongated flattened ellipsoids, (TEG-particle deformed in polymer matrix at the stage of manufacture of CM, can be imagined like elongated flattened ellipsoid, consisted from n nanodisks of graphite (length of ellipsoid $l = n \cdot D$) with thickness h^* and diameter D) electrical resistance can be represented as:

$$R_{CM} = \frac{A^2\pi \cdot h^*}{4\phi \cdot K \cdot n} \cdot \left(r^*_{disk} \cdot n + R_k \cdot B(d)\right) = \frac{A^2\pi \cdot h^*}{4\phi \cdot K} \cdot \left(r^*_{disk} + \frac{R_k}{n} \cdot B(d)\right) \quad \text{or}$$

$$R_{CM} = \frac{A^2\pi \cdot \rho_{Gr}}{4\phi \cdot K}\left(1 + \frac{h^*}{2a^*} \cdot \frac{B(d)}{n}\right) \tag{4}$$

Notably, if compare relations (2) and (4) it can be seen, that in case of elongated flattened ellipsoids (TEG) or elongated cylinders (MWCNT) the relation between total electrical resistance of graphite particles (nanotube) (first summand) and total contact resistance (second summand) between graphite particles (nanotubes) changes due to the considerable decreasing of the number of contacts between graphite particles in continuous electroconducting chains in comparison with particles with disk shape, in spite of the fact that the thickness of elongated ellipsoids can be significantly less (in 50–100 times), as compared to initial natural disperse graphite. Qualitatively it can be explained by the fact that in case of elongated graphite particles quantity of contact resistances per unit length in n times less than in case of disk shape (disperse graphite and nanoTEG), and ellipsoids thickness decrease to nanosizes compensated by the higher quantity (in the same n times) of graphite particles chains.

Consider the temperature dependences of electrical resistance $R_{CM}(T)$ of CMs with different disperse degree TEG. $R_{CM}(T)$ of CM is determined by the temperature changing of three parameters: 1) electric resistance of graphite particles r_{disk}, 2) contact electric resistance between graphite particles $R_k \cdot B$ and 3) the number of continuous electroconductive chains (current transition paths) K.

1. Electrical resistance of graphite particles decreasing due to increase of the charge carriers concentration (electrons and holes) with higher temperature with mainly temperature-independent charge carriers scattering on crystallite grain boundaries, temperature coefficient of resistivity $TCR_{CM} = 1/R \cdot dR/dT$ is negative, R_{CM} decreases.
2. The contact electric resistance character (increasing, decreasing or constant) with higher temperature relating to the temperature change of electrical resistivity of material (graphite) $\rho_{Gr,}$ contact area and thickness of polymer interlayer d in the contact point (if it exists). This is directly connected with relation between the coefficients of thermal linear expansion of graphite (or pore TEG) α_{Gr} and

Table 2. Characteristics of 5 wt.% nanocarbon-epoxy CMs

Type of CM	P, porosity	α, 10^{-6} 1/K	R_{77K}/R_{293K}
Epoxy resin	0.15	314	
Disperse graphite (monocrystal)		28	
5% TEG-epoxy	0.47	390	1.14
5% TEG(2)-epoxy	0.36	279	1.05
5% TEG(2)$_{disp}$-epoxy	0.43	244	0.77
5% nanoTEG-epoxy	0.13	281	0.8
5% MWCNT-epoxy	0.18		1.15

polymer α_P. If $\alpha_P > \alpha_{Gr}$ then the thickness of polymer interlayer d increases with heating (coefficient B increases), contact area decreases (contact stain radius a decreases) as consequence contact electric resistance increasing, R_{CM} increases.

3. If the thickness of polymer interlayer d or distance between contact filler particles exceeds 2–3 nm due to the thermal expansion the percolation of current is impossible (even tunnelling processes) and electroconductive carbon particles chain excludes from the electroconductive process, coefficient K decreases, R_{CM} increases.

Depending on which of these temperature dependent processes are primary we have positive or negative temperature coefficient of electrical resistance TCR_{CM}.

Table 2 presents characteristics of researched samples: porosity, CTLE and resistance ratio R_{77K}/R_{293K}.

It can be seen that the filler bringing in polymer matrix decreasing CTLE of system in case of porous-less filler according to mixture rule. CM TEG-epoxy has highest porosity ~0.5, as TEG by oneself is high porous and there is the air in its pores, as a result the main factor of system expansion is air expansion in pores, that's why we observe increasing of total CLTE of CM. For CMs with nanographite platelets TEG(2)$_{disp}$ and nanoTEG air expansion in pores is very considerable since fillers by themselves almost porous-less.

In CM with TEG filler creates sufficiently branched carcass electroconductive structure, the number of contacts per unit length between elongated TEG particles in continuous chains are not great and if possible breaking of some chains (due to the thermal expansion) the other connect and average number conductive (K) and isolated ends don't change noticeably. Besides, we have shown that the coefficients of thermal linear expansion of epoxy TEG [9] have close values, since TEG has high porous structure and expands with heating due to expansion of graphite pores. Thus, the changes of electroconductive chains number K and contact electrical resistance are insignificant during heating and negative TCR for CM is observed as consequence of graphite particles electric resistance decreasing with heating.

Ultrasonically dispersed particles of TEG (nanoTEG, TEG(2)$_{disp.}$) are smaller and less porous than initial TEG particles (nanoTEG is almost pore-free) and its CLTE is less than this one of TEG and epoxy resin. As a result, in CMs with low filler content spatial skeleton structure from graphite particles doesn't form, only separate continuous electroconducting clusters form. As a result, in samples with nanoTEG and TEG(2)$_{disp.}$ there is sufficiently high electric resistance and positive TCR as compared with CM with TEG. It can be explained by the mainly role of contact electrical resistance ($R_k \cdot B$ significantly higher than r_{Gr}) in these samples, due to high quantity of contacts per unit length and polymer interlayer in contact points. Besides, CTLE of porous-less epoxy is $65 \cdot 10^{-6}$ 1/K, which is higher than $28 \cdot 10^{-6}$ 1/K for natural graphite.

During the heating of CMs with TEG(2)$_{\mathrm{disp}}$ and notably with nanoTEG, since thermal expansion of epoxy higher than it of graphite (dispersed, nanographite) the thickness of polymer interlayer enlarges (d increases), some of electroconductive chains are breaking (current doesn't transit through them, K decreases) [10], and related with it increasing of electric resistance of composite exceeds decreasing of electrical resistivity of graphite particles since concentration of charge carriers increasing. As a result, the positive TCR is observed.

Conclusions

Obtained results allow some conclusions to be made:

1. It was shown, that the characteristics of percolation transition of electrical conductivity CM nanocarbon-epoxy resin are determined by the structural and morphological peculiarities of carbon filler (particles size, aspect ratio) and the character of its distribution in epoxy matrix. For the TEG-epoxy systems it was observed, that the higher disperse degree of TEG, the less expressed percolation character of resistivity and higher its value.
2. It was determined, that the temperature coefficient of electric resistance (TCR) of investigated composites can be both positive and negative depending on morphology of nanocarbon filler and the type of electroconductive network formed by nanocarbon particles in CM.
3. It was shown, that temperature dependences of electrical resistance of CMs determined by the temperature changing of three parameters: 1) electric resistance of carbon particles $r_{carb,}$ 2) contact electrical resistance between carbon particles $R_k \cdot B$ and 3) the number of continuous electroconductive chains (current transition paths) K. Electrical resistivity of carbon filler has negative TCR, and the changes of last two parameters related with the values of coefficients of thermal linear expansion of components (epoxy and carbon filler) and provides positive contribution in total TCR of investigated CMs.

Acknowledgment

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