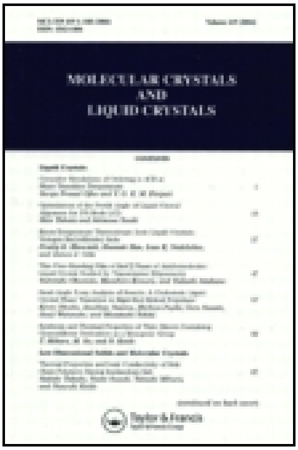


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Electrical and Thermal Conductivity of Polymer-Nanocarbon Composites

A. Lazarenko [a] , L. Vovchenko [a] , D. Matsui [a] , Yu. Prylutskyy [a] , L. Matzuy [a] , U. Ritter [b] & P. Scharff [b]

[a] Faculty of Physics, Taras Shevchenko Kyiv National University, Kyiv, Ukraine

[b] Institute of Physics, Technische Universität Ilmenau, Ilmenau, Germany

To cite this article: A. Lazarenko, L. Vovchenko, D. Matsui, Yu. Prylutskyy, L. Matzuy, U. Ritter & P. Scharff (2008): Electrical and Thermal Conductivity of Polymer-Nanocarbon Composites, Molecular Crystals and Liquid Crystals, 497:1, 65/[397]-75/[407]

To link to this article: http://dx.doi.org/10.1080/15421400802458522

Mol. Cryst. Liq. Cryst., Vol. 497, pp. 65/[397]–75/[407], 2008
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400802458522

Electrical and Thermal Conductivity of Polymer-Nanocarbon Composites

**A. Lazarenko[1], L. Vovchenko[1], D. Matsui[1],
Yu. Prylutskyy[1], L. Matzuy[1], U. Ritter[2],
and P. Scharff[2]**
[1]Faculty of Physics, Taras Shevchenko Kyiv National University,
Kyiv, Ukraine
[2]Institute of Physics, Technische Universität Ilmenau,
Ilmenau, Germany

Thermal and electrical conductivities in composites (CMs) based on various types of polymer matrix – epoxy resin (epoxy) and polyethylene oxide (PEO) have been investigated in the temperature range 150–300 K. A few types of carbon materials have been used as a filler in CMs: thermoexfoliated graphite (TEG) (TEG content was 0.5–10 wt.%), TEG dispersed in an ultrasonic disperser (nano-TEG) (content – 1–2 wt.%), and multiwalled carbon nanotubes (MWCNTs) (content – 1–10 wt.%). It was shown that the ultrasonic dispersion of TEG in the epoxy matrix leads to a shift of the percolation transition in the electrical conductivity to higher values of the graphite content and decreases the thermal conductivity of these CMs. This occurs due to the break down of the worm-like structure of TEG particles, i.e., the already formed fragments of TEG clusters. It is revealed also that the use of epoxy as a polymer matrix and a nondispersed thermoexfoliated graphite as a filler gives the greatest values of the thermal and electrical conductivities of composites in the comparison with others.

Keywords: carbon nanotube; electron microscopy; electrical properties; nanocarbon filler; porosity; thermal properties

INTRODUCTION

Recently, the polymer composites with nanoscaled fillers have been strongly developed due to their interesting characteristics, the possibility of their many potential applications, and the miniaturization of their products. Such nanodimensional fillers as carbon nanotubes,

---

This work was partly supported by the BMBF grant (Ukr 07-003).

Address correspondence to A. Lazarenko, Faculty of Physics Taras Shevchenko Kyiv National University, Kyiv 01033, Ukraine. E-mail: kulich@univ.kiev.ua

nanowires, fullerenes, and nanographite plates [1–4] are most promising in this aspect. For example, the experimental results have shown that the combination of carbon nanotubes with polymers offers an attractive route to obtain new electrical [5] and thermal properties [6]. It is expected that nanocarbon fillers can significantly enhance the electrical and thermal conductivities and the thermal stability of some polymers at high temperatures [7,8]. Moreover, the use of such fillers with the creation of polymer composites gives a possibility to increase considerably their competitiveness in comparison with the traditionally used heat- and electrically conducting materials, such as metals, polymer composites filled with metals, etc. due to low density, manufacturability (high compacting ability, the possibility to manufacture articles of any shape, impact damping properties, etc.), corrosion resistance, environmental safety, and low production costs. Furthermore, these nanodimensional carbon fillers are characterized by the high aspect ratio (100–1000), which makes it possible to lower considerably the three-dimensional percolation threshold, to obtain electrically conducting polymer nanocomposites with very low content of a filler (0.2–1 wt.%), and to preserve the technological characteristics of a polymer matrix in this case.

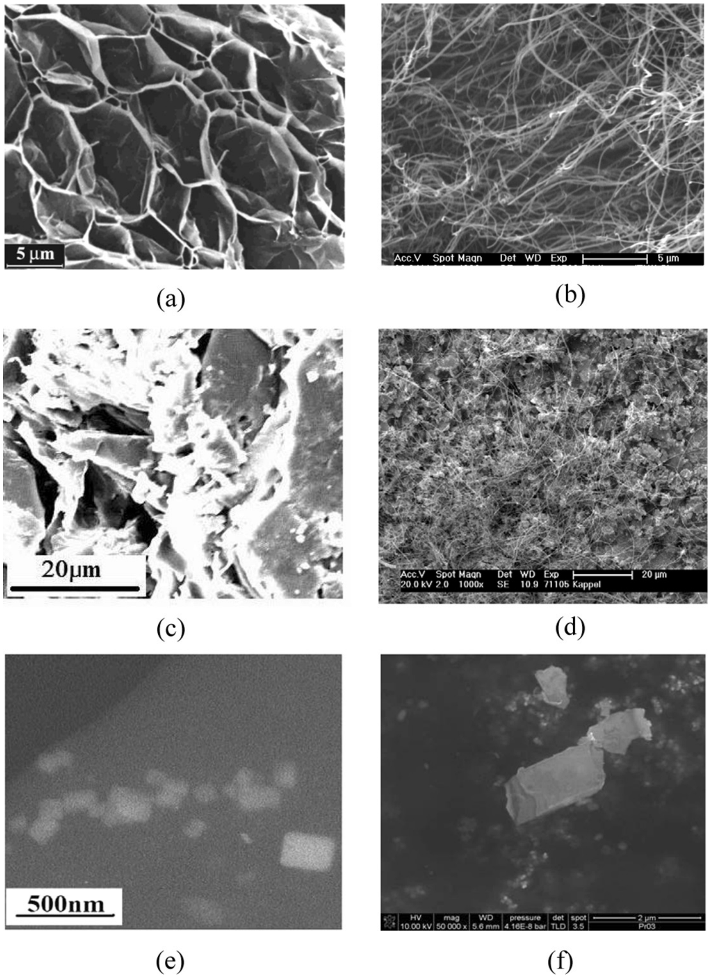
However, the reported results about these properties are frequently conflicting and still far from being satisfactory. The properties of these composites depend on many factors such as the types of nanocarbons, their morphology, structure, the processing method, the type of a matrix, and so on.

Thus, the aim of this study was to determine the influence of the carbon filler type and the processing of a polymer nanocomposite on the electrical and thermal properties of fabricated composites.

EXPERIMENTAL AND SAMPLE CHARACTERIZATION

In the present work, we investigate the composite materials, in which two types of polymers – epoxy ED20 and polyethylene oxide (PEO) – were used as the matrix. Several types of nanocarbon materials – thermoexfoliated graphite (TEG), multiwalled carbon nanotubes (MWCNTs) and MWCNTs containing iron – were used as an electrically conducting filler. TEG is a product of the deep chemical heat treatment of dispersed graphite [9]. It is a high-porosity powder (packing density $\sim 0.03\,\mathrm{kg/m^3}$) with highly developed active surface. It consisted of 1–3-mm particles of cellular structure, the size of cells (pores) was 5–10 mm, and the thickness of the cell walls did not exceed 20–25 nm (Fig. 1a).

MWCNTs have been prepared during the catalytic decomposition of benzene (as a carbon source) and ferrocene (a source of iron) in a tube



(a) (b)

(c) (d)

(e) (f)

FIGURE 1 SEM images for (a) TEG, (b) MWCNTs, (c) TEG + epoxy, (d) MWCNT-PEO, and (e, f) nano-TEG + epoxy CMs.

furnace at different temperatures. The tubes have inner diameter between 5 and 8 nm and the length up to 200 µm. SEM images are presented in Figure 1b. In the same figure, the SEM images for the composites under investigation are presented.

The epoxy and PEO were used with the purpose to study the type of matrix influence on the electrical and thermal properties of CMs. CMs TEG-epoxy have been prepared by using two methods: 1) usual careful mixing of TEG and epoxy in acetone with subsequent drying [10] and 2) ultrasonic sonication of a mixture of TEG and epoxy in acetone during 20 h. As known [3,11], the ultrasonic dispersion leads to the essential fragmentation of worm-like TEG particles on nanocarbon fragments (nano-TEG filler). The samples of composites on the epoxy basis were made by the pouring of the liquid mixtures of TEG-epoxy into the appropriate forms. Figure 1c shows the CMs TEG-epoxy obtained by the usual careful mixing of TEG and epoxy in acetone with subsequent drying. SEM images of a CM fragment preserve the porous structure in the epoxy matrix even with a filler concentration of 1–2 wt.%.

Figures 1e, f present SEM images of a 1-wt.% nano-TEG + epoxy film obtained by the ultrasonic dispersion of a mixture of TEG and epoxy in acetone during 20 h. As can be seen, the essential dispersion of TEG particles is observed. In this case, the particles are uniformly distributed in the volume of a sample. The sizes of the obtained carbon particles are mainly from 0.1 to 1 μm in diameter and from 40 to 130 nm in thickness. There are separate larger particles with a size up to 2 μm (Fig. 1e, f). As can be seen from Table 1, these samples are denser in the comparison with TEG-epoxy obtained by the usual method, because the ultrasonic dispersion significantly destroys the porous structure of TEG particles.

TABLE 1 Characteristics of Nanocarbon-Epoxy CMs

Filler content						
C, wt.%	ϕ, vol. fr.	d, g/cm^3	P	λ_c (293 K), W/(m · K)	$\frac{(\lambda_{CM} - \lambda_p)}{\lambda_p} \cdot 100$, %	ρ_a (293 K), $\Omega \cdot$ m
TEG-epoxy						
0	0	1.20		0.25		$\sim 1 \cdot 10^{13}$
0.5	0.003	1.07	0.15	0.42	68	$2.1 \cdot 10^{8}$
1	0.006	0.85	0.31	0.61	144	$3.3 \cdot 10^{2}$
1.5	0.008	0.92	0.27	0.80	220	$7.6 \cdot 10^{-1}$
2	0.01	1.00	0.20	0.86	244	$8.4 \cdot 10^{-1}$
5	0.03	0.49	0.60	1.60	540	$2.0 \cdot 10^{-2}$
10	0.06	0.7	0.44	2.50	900	$4.3 \cdot 10^{-3}$
Nano-TEG + epoxy						
0.5	0.003	1.1	0.13	0.29	16	
1	0.006	1.13	0.10	0.34	36	10^{11}
1.5	0.008	1.14	0.09	0.39	56	
2	0.01	1.11	0.12	0.37	48	$6 \cdot 10^{10}$
5	0.03	1	0.19	0.8	220	
MWCNT-epoxy						
1	0.006	1.1	0.12	0.38	52	$1.9 \cdot 10^{2}$
2	0.012	1.1	0.13	0.45	80	8.55

TABLE 2 Characteristics of Nanocarbon-PEO CMs

Filler content C, wt.%	d, g/cm^3	λ (273 K), W/(m · K),	ρ_a (293 K), Ω · m
TEG-PEO			
1	0.95	0.34	
3	1.1	0.41	
10	0.96	0.68	
MWCNT-PEO			
1	0.91	0.33	
3	1.07	0.42	0.31
10	1.09	0.53	0.07
MWCNT-Fe + PEO			
1	0.99	0.36	
3	0.97	0.33	
10	1.08	0.32	1.54

CM samples with PEO were produced in the form of tablets with a diameter of 15 mm by the cold molding of PEO-nanocarbon filler powders (Table 2).

The electrical resistance of CM samples was determined by the two-probe (with high values of $R \geq 10^7\,\Omega$) and four-probe ($R \leq 10^7\,\Omega$) methods on the direct current in the range of temperatures 77–300 K. The thermal conductivity of the nanocarbon-epoxy and nanocarbon PEO composites was investigated by the method of dynamical λ-calorimeter in the range of temperatures 150–423 K and 150–323 K, respectively. The above temperature ranges are chosen with regard for both the possibility to use the composites at these temperatures and the thermal stability of a polymer matrix.

RESULTS AND DISCUSSION

Electrical and Thermal Conductivities

This paper presents the investigation of the electrical and thermal conductivities of CMs with low content (<10 wt.%) of nanofillers of various types: MWCNTs, TEG, and nano-TEG. Figures 2–4 present the results of these investigations.

As seen from Figure 2a, the electrical conductivity obeys the percolation dependence, and the percolation threshold is enough low for the all investigated composites. For example, the electrical resistance equals to 8.55Ω · m for 2% MWCNT + epoxy and 0.84Ω · m m for CM 1% TEG-epoxy. C_{cr} for the TEG-epoxy systems equals 1.35 wt.% only.

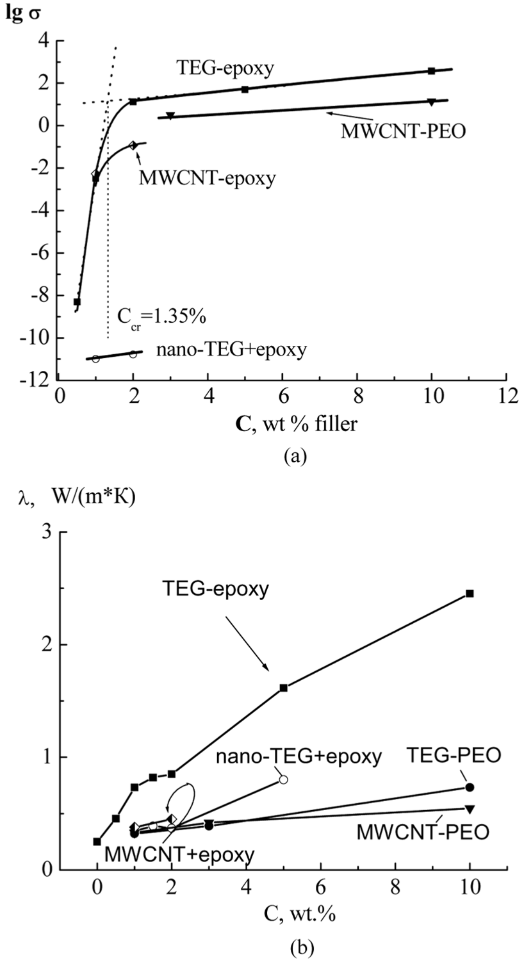


FIGURE 2 Electrical (a) and thermal (b) conductivities versus the filler content for TEG-epoxy, nano-TEG + epoxy, TEG-PEO, MWCNT-epoxy and MWCNT-PEO CMs.

It was shown that the ultrasonic dispersion of TEG particles in the epoxy solution during the CM preparing leads to an essential shift of the percolation threshold in electrical conductivity and to substantially smaller values of electrical conductivity with the same weight TEG content. So, the values of electrical conductivity of CMs with 1 and 2 wt.% non-dispersed TEG are equal to $3 \cdot 10^{-3}$ and 13 $(\Omega \cdot \mathrm{m})^{-1}$, respectively; whereas, for the CMs with the same content of dispersed TEG (or nano-TEG), the value of electrical conductivity does not exceed $(1\text{–}16) \cdot 10^{-11}\ (\Omega \cdot \mathrm{m})^{-1}$. As seen from Figure 3, the all investigated CMs

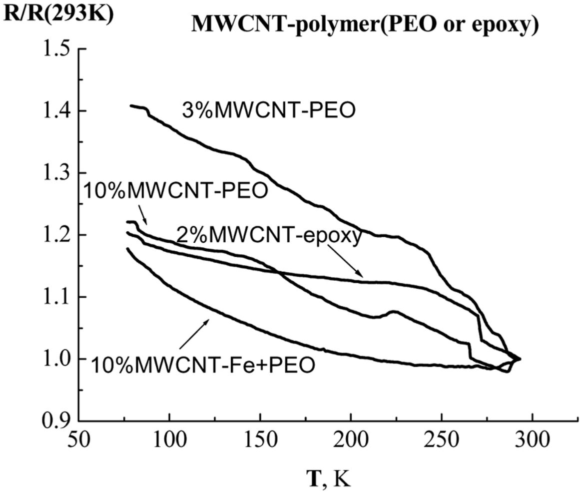


FIGURE 3 Temperature dependences of electrical resistance for polymer-MWCNT.

are characterized by the negative temperature coefficient of electrical resistivity, which can be explained by an increase of the charge carriers concentration and a decrease of the contact electric resistivity between filler particles in CM under heating.

The results of studies of the thermal conductivity are presented in Figure 2b. As one can see, the thermal conductivity approximately linearly depends on the filler concentration for all CMs under investigation. The addition of only 1–2 wt.% MWCNT into epoxy leads to an increase in the thermal conductivity by 50–85% with respect to that of clean epoxy. The more considerable increase of thermal conductivity was observed for the composites with the use of usual nondispersed TEG: with a change in the TEG concentration from 0.5 to 2%, the increase of TEG-epoxy thermal conductivity comes from 68 to 244% (Tables 1 and 2). It was shown that the ultrasonic dispersion of TEG in epoxy resin leads to an essential decrease of the thermal conductivity value. CMs based on PEO are also characterized by low thermal conductivity whether they contain nondispersed TEG or CNT.

Let us consider, in more details, which factors influence the thermal conductivity of CMs under investigation.

First, as was noted above, the thermal conductivity of a polymer CM grows with increase in the content of the heat-conducting graphite component, which agrees with the rule of mixtures for the composites:

$$\lambda_{CM} = (1 - \phi_f)\lambda_p + \phi_f\lambda_f, \quad (1)$$

where λ_{CM}, λ_f, and λ_p are the thermal conductivities of the composite material, carbon filler, and polymer matrix, respectively, and ϕ_f is the volume fraction of a carbon filler.

It is known [1–3] that the nanocarbon fillers used in these composites have a very high anisotropy of thermal conductivity, and, with an increase in their content in CM, the orientation of the macroplates of graphite (in case of the TEG use) or of nanotubes along any specific axis of a sample can occur, which can lead to the essential anisotropy of thermal and electrical properties in the composites. This effect can be essential with high contents of a nanodimensional filler in CM [10,12,13], and also with the forced orientation of filler particles in the polymer matrix [14]. In our case with the filler content ≤ 2 wt.%, it is possible to assume that the distribution of filler particles is practically uniform and isotropic.

Finally, the important parameter which influences the effective thermal conductivity of CM (and electrical conductivity too) is the contact thermal resistance both between the filler particles and on the interface of two phases (polymer – carbon filler). For example, as shown in our paper [15], the total contact thermal resistance between the filler particles in 5 wt.% TEG-epoxy can reach 25% of the overall value of the effective thermal resistance of the composite.

Let us analyze the concentration and temperature dependences of the CM thermal conductivity on the basis of the represented results.

As can be seen from Figure 2b, the dependence of λ_{CM} on the filler concentration is linear and is described, in the first approximation, by the rule of mixtures. However, the values of thermal conductivity are considerably lower, than it would be possible to expect with the use of MWCNTs with high thermal conductivity (indeed, the thermal conductivity of a single MWCNT is very high and equals 3000 W/(m · K) [7]). The authors of paper [4] proposed, in the framework of the effective medium approach (EMA), the following relation for the effective thermal conductivity λ_{CM} of composites with the use of nanotubes:

$$\frac{\lambda_{CM}}{\lambda_p} = \frac{3 + \phi_f \cdot \lambda_f / \lambda_p}{3 - 2\phi_f}, \tag{2}$$

where λ_f is the thermal conductivity of CNT, λ_p is the thermal conductivity of a polymer matrix, and ϕ_f is the volume fraction of CNT. In the case of $\phi \leq 0.02$, we have the simple expression

$$\frac{\lambda_{CM}}{\lambda_p} = 1 + \frac{\phi_f \cdot \lambda_f}{3\lambda_p} \tag{3}$$

This relation must give the sufficiently great values of CM thermal conductivity: 10 and 20 W/(m · K) for CMs with 1 and 2 wt.% of MWCNTs in epoxy. However, the experiment gives a completely different picture – 0.38 and 0.45 W/(m · K), respectively. Such low values of thermal conductivity for the investigated MWCNT-epoxy can be explained by the fact that, according to results in [1,4], it is necessary to consider the contact thermal resistance between the filler particles and also the fact that the curvature of MWCNTa with the CM formation and the formation of MWCNT bundles can occur, which leads to a decrease of the CM effective thermal conductivity. The thermal conductivity of all composites will be determined mainly by the heat transfer by particles of a highly heat-conducting filler. Therefore, the distribution of filler particles in the matrix, their orientation (it is very substantial for the particles with a high aspect ratio 100–1000), the formation of a continuous infinite cluster from filler particles, and interparticle contacts are the basic parameters which influence the value of CM thermal conductivity. So, it was shown [16] that the alignment of nanotubes in the polymer matrix substantially increases the thermal conductivity of the composite: it was shown that, with only a small fraction of aligned CNTs (0.3%) in CM, the enhanced value of thermal conductivity is fairly high (0.65 W/(m · K)); wheras, for the randomly oriented CNT, this enhanced value of thermal conductivity is only 0.03 W/(m · K). The sufficiently high thermal conductivity of non-dispersed TEG-epoxy (1-2 wt.% of filler) in the comparison with those of MWCNT-epoxy and nano-TEG + epoxy is caused by the worm-like structure of TEG particles, i.e., the already formed fragments of TEG clusters consisting of graphite nanosheets well contacting between themselves.

The thermal conductivity of both graphite and carbon nanotubes has the phonon nature (the electron component of thermal conductivity is lost in the noise as a result of the low concentration of free current carriers in comparison with metals) and can be described in the framework of the Debye theory by the relation

$$\lambda = A \cdot C_p \cdot u \cdot L, \tag{4}$$

where A is a geometric coefficient, C_p is the heat capacity of the lattice, L is the mean path length of phonons, and u is the velocity of propagation of elastic waves.

For the investigated CMs, $\lambda(T)$ increases with the temperature in the range 150–425 K (Fig. 4), which is related to an increase of the heat capacity of both the polymer matrix and the nanocarbon filler in this temperature interval [16]. The decrease of the $\lambda(T)$ dependence for higher temperatures (>300 K) is related to the growth of the phonon-phonon scattering.

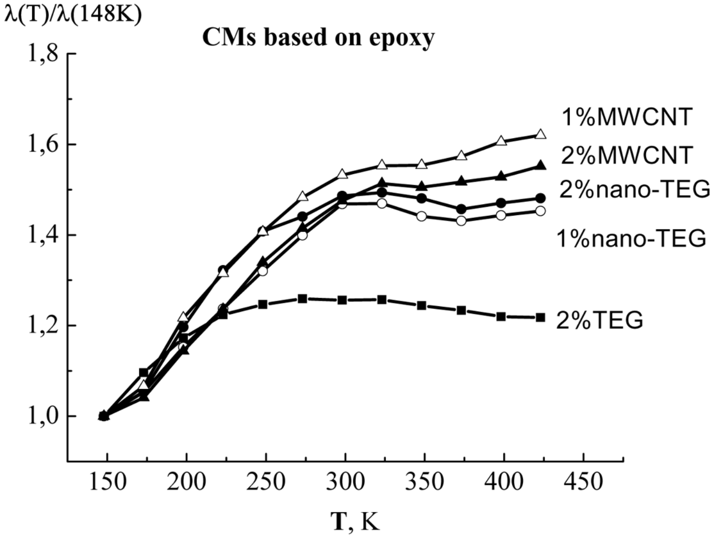


FIGURE 4 Temperature dependences of thermal conductivity for polymer-nanocarbon.

CONCLUSION

The obtained results allow us to conclude that filling the polymeric matrix (epoxy resin or polyethylene oxide) with nanocarbon (thermoexfoliated graphite, multiwalled carbon nanotubes) leads to the essential increase of its electrical and thermal conductivities. The relative changes in the thermal conductivity as compared with that of epoxy are 240 and 80% for the composites with 2 wt.% of TEG or MWCNTs, respectively. The ultrasonic dispersion of TEG in epoxy breaks down the worm-like structure of TEG particles, i.e., the already formed fragments of TEG clusters. This leads to a shift of the percolation transition in the electrical conductivity to higher values of the graphite content and a decrease of the thermal conductivity of these CMs.

REFERENCES

[1] Du, J.-H., Bai, J., & Cheng, H. M. (2007). *Polymer Letters*, *1*, 253.
[2] Biercuk, M. J., Liaguna, M. C., Radosavljevic, M., Hyun, J. K., & Johnson, A. T. (2002). *Appl. Phys. Lett.*, *80*, 2667.
[3] Yu, A., Ramesh, P., Itkis, M. E., Bekyarova, E., & Haddon, R. C. (2007). *Journ. Phys. Chem.*, *111*, 7565.
[4] Nan, C.-W., Shi, Z., & Lin, Y. (2003). *Chemical Physics Letters*, *375*, 666.
[5] Gojny, F. H., Nastalczyk, J., Roslaniec, Z., & Schulte, K. (2003). *Chem. Phys. Lett.*, *370*, 820.

[6] Martin, C. A., Sandler, J. K., Shaffer, M. S., Schwarz, M. K., Bauhofer, W., Schulte, K., & Windle, A. H. (2004). *Comp. Sci. and Tech.*, *64*, 2309.
[7] Kim, P., Shi, L., Majumdar, A., & McEuen, P. L. (2000). *Phys. Rev. Lett.*, *87*, 215502.
[8] Xu, Y. S., Ray, G., & Abdel-Magid, B. (2006). *Composites: Part A*, *37*, 114.
[9] Kharkov, E., Lysov, V., Matsui, L., Vovchenko, L., Tsurule, M., & Morozovskaya, N. (2001). "Arrangement for obtaining of thermoexfoliated graphite", UA Patent 33777A.
[10] Stelmakh, O., Matzui, L., & Vovchenko, L. (2007). *Phys. and Chem. of Solid State*, *8*, 408.
[11] Chen, G., Weng, W., Wu, D., Wu, C., Lu, J., Wang, P., & Chen, X. (2004). *Carbon*, *42*, 753.
[12] Vovchenko, L. L., Matzui, L. Yu., & Kulichenko, A. A. (2007). *Inorg. Mater.*, *43*, 597.
[13] Bonnissel, M., Luo, L., & Tondeur, D. (2004). *Carbon*, *39*, 2151.
[14] Du, F., Fischer, J. E., & Winey, K. I. (2005). *Phys. Rev.*, *72*, 121404.
[15] Vovchenko., L. L., Kulichenko, A. A., & Matzui, L. Yu. (2008). *Perspective Mater.* [in Russian] (to be published).
[16] Huang, H., Liu, C., Wu, Y., & Fan, S. S. (2005). *Advanced Materials*, *17*, 1652.