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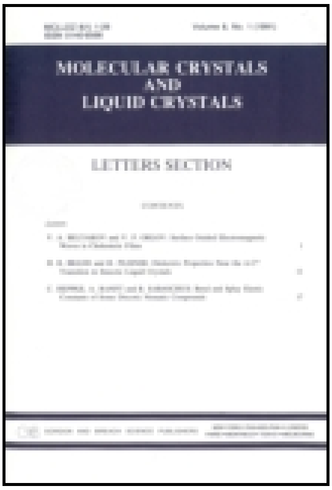

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Transport Properties of Epoxy-Binary Filler Composites

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Transport Properties of Epoxy-Binary Filler Composites

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This paper presents the results of changes in electrical resistivity and thermal conductivity of polymer composites (CMs) with two-component filler. It is shown that thermal conductivity of epoxy CMs strongly depends on structural and morphological characteristics of carbon fillers. The synergistic effect in electrical and thermal conductivities of the studied CMs is observed upon addition of boron nitride BN. The presence of a sufficiently large number of BN particles in CMs promotes a more efficient formation of chains of carbon filler and reduces thermal (electrical) contact resistance between the filler particles by decreasing the distance between particles of the filler.

Keywords Electrical conductivity; Nanocarbon filler; porosity; thermal conductivity; boron nitride

Introduction

Polymer composite materials are investigated since the late 1980s. Today, the CMs based on epoxy [1], phenolic, polyurethane, and polyamide resins are widely used in various fields. These resins have a low density, low polymerization temperature, high strength and sufficient adhesive strength with the main types of reinforcing fibers, and good technological properties. Mainly used reinforcing materials are various fibers - glass, carbon, boric, organic, plate nanocarbon [2], boron nitride [3], and metal wire. Reinforcing materials can be in the form of individual fibers or filaments, strands [4], films, and multilayer tissues. However, those CMs contained a reinforcing filler of only one type [5], while the addition of the second filler in a composite allows one to extend the range of variation of physical properties of composites and, hence, to extend the field of applications.

One of the main tendencies of the last years is the development of new composite materials with synergistic effect, i.e. the properties of these composite materials are improved due to a combination of several fillers [6].

The addition of multicomponent fillers in a polymer matrix promotes the interaction process between the fillers and allows one to obtain materials with new range of the electrical [7] and thermal characteristics [8]. But, currently, the nature of the improvement of CMs characteristics under addition of the second filler is not clear, which motivates the study of multicomponent polymer CMs.

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This paper presents the results of investigations of the changes of electrical and thermal characteristics in polymer-carbon composites under addition of dielectric component - boron nitride (BN).

Experimental and Sample Characterization

The two types of a polymer matrix - epoxy resin (ED-20) and epoxy resin modified by organosilicon components (SEDM-2) - were used for the fabrication of polymer composites. ED-20 is dianic epoxy resin with low molecular mass, and it consists at least of two epoxy groups (α-oxidized). SEDM-2 is epoxy, in which the mass fraction of the volatile matter (dry residue) is 98.5%, and the mass proportion of epoxy groups - at least 14% and 5% silicon. Graphite nanoplatelets (GNPs) prepared by the scheme described in [9] and the multiwalled carbon nanotubes (MWCNTs), purchased from Cheap Tubes Inc. with purity $\geq$90% were used as fillers of epoxy resins.

The morphologies of used carbon filler particles are different. So, GNPs can be considered as disks (diameter D = 0.2–30 μm, thickness h = 5–65 nm), while MWCNTs can be presented as cylinders (diameter d = 10–30 nm, length l = 10 μm). There are different aspect ratios A for GNPs and MWCNT: for GNPs, A = D/h is equal to 40–500, and, for MWCNTs, A = l/d is equal to 330–1000, respectively. The concentration C of the nanocarbon filler in polymer matrices ranged from 2 wt.% to 10 wt.%.

For the arising of the synergistic effect in the thermal and electrical conductivities of the studied nanocarbon-epoxy CMs, we have used disperse boron nitride (BN) as the second filler. BN powder consists of plate-like particles 5–50 μm in diameter and 50–260 nm in thickness that corresponds to the aspect ratio equal to 100–200. The boron nitride content in the polymer matrix was 20 or 27 wt.%.

Epoxy CMs were obtained by the careful mixing of the components in an acetone solution of epoxy resin, followed by the ultrasonic dispersion of the mixture for 15–30 min. It was cured initially at T = 293 K (24 h) and then heated from 313 to 353 K (5 h). The CMs specimens for thermal measurements were fabricated in the form of tablets with a diameter of 15 mm, and specimens in the form of plates with size $10 \times 3.5 \times 2.5$ mm^3 were used for electrical measurements.

The electrical resistance of CM samples was measured by the two-probe (with high values of $R = 10^4 - 10^9\ \Omega$) and four-probe ($R \leq 10^4\ \Omega$) methods on the direct current in the temperature range (77−300) K. The thermal conductivity of nanocarbon-ED20, nanocarbon-SEDM-2, and nanocarbon-SEDM-2 + 27%BN composites was investigated by the method of dynamical λ-calorimeter in the temperature range (150–423) K.

Results and Discussion

The results of investigation of the electrical and thermal conductivities of polymer CMs depending on the content of different nanocarbon fillers with and without the addition of boron nitride are shown in Table 1 and in Figs. 1 and 2. As can be seen from Table 1, the average porosity P of the prepared CMs samples is equal to 15–20%, and it is 30% for 10%GNP+SEDM-2+27%BN CM.

As can be seen from Figs. 1 and 2, the thermal conductivity increases almost linearly with the nanocarbon filler content, the concentration dependence of the thermal conductivity is not percolative, because the ratio of the thermal conductivities of the matrix and the filler is low compared to that of the electrical conductivities and is about 10^3. The comparative analysis of the results of measurements of the thermal conductivity showed that GNP is

Table 1. Characteristics of CMs specimens: density *d*, porosity *P*, effective thermal conductivity of filler λ_f^*, electrical conductivity σ_{dc} and percolation threshold ϕ_c.

CMs	C, wt.%	d, g/cm^3	P	λ_f*, W/(m·K)	((λ_{CM} -λ_p) /λ_p)·100,%	σ_{dc}(293K), S·m^{-1}	ϕ_c, vol.fr.
				GNP + polymer			
GNP+epoxy	0	1.04	0.13	—	0	$1.8 \cdot 10^{-12}$	0.022
	3	1.11	0.09	142	188	$1.1 \cdot 10^{-9}$	
	5	1.11	0.09	143	252	$3.8 \cdot 10^{-6}$	
	10	0.97	0.23	194	479	$4.4 \cdot 10^{-1}$	
GNP+SEDM-2	0	1.2	—	—	0	$2.8 \cdot 10^{-11}$	0.024
	3	0.73	0.27	57.2	75	$1.0 \cdot 10^{-9}$	
	5	1.06	0.14	126.2	207	$7.8 \cdot 10^{-8}$	
	10	1.11	0.11	268.3	507	$1.6 \cdot 10^{-1}$	
GNP+SEDM-2 +20%BN	5	1.26	0.05	137.7	223	$4.5 \cdot 10^{-6}$	—
	10	1.17	0.14	169	378	$8.7 \cdot 10^{-1}$	
GNP+SEDM2 +27%BN	3	1.17	0.16	330	234	$8.7 \cdot 10^{-9}$	0.021
	5	1.2	0.14	276.5	274	$1.4 \cdot 10^{-5}$	
	10	1.0	0.30	338.5	458	32	
				MWCNT + polymer			
MWCNT+ SEDM-2	3	—	—	2.75	5	$3.8 \cdot 10^{-8}$	0.017
	5	1.01	0.17	10.3	30	$1.3 \cdot 10^{-4}$	
	10	1.05	0.16	13.7	69	$1.7 \cdot 10^{-1}$	
MWCNT+ SEDM-2 +27%BN	3	1.11	0.2	48.5	57	$3.5 \cdot 10^{-3}$	0.01
	5	1.12	0.2	48.1	86	$1.2 \cdot 10^{-1}$	
	10	1.22	0.14	49.65	157	2.3	

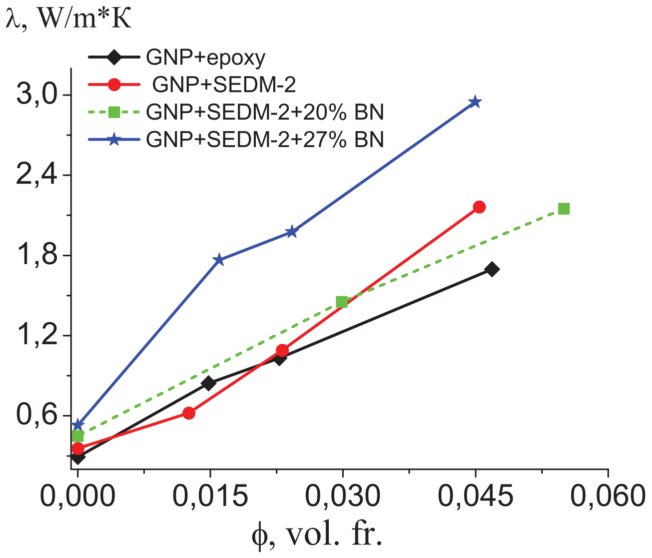

Figure 1. Dependence of thermal conductivity versus GNPs content for CMs with BN and without it.

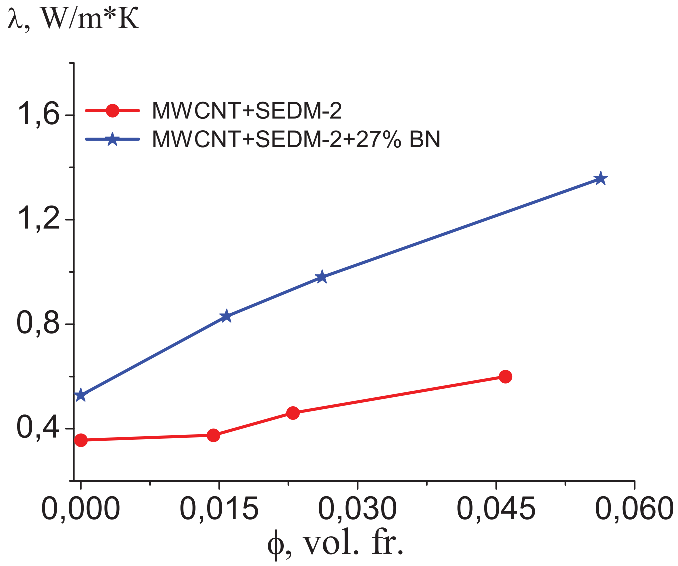

Figure 2. Dependence of thermal conductivity versus MWCNTs content for CMs with BN and without it.

a more efficient filler in terms of increasing the thermal conductivity of the epoxy matrix than carbon nanotubes.

For example, the lowest value of thermal conductivity is observed for CM 10%MWCNT+SEDM-2: thermal conductivity compared with that of pure polymer increases by 69% (see Table 1). Moreover, as can be seen from Table 1, the opposite pattern is observed for the elecrtical conductivities of CMs with GNP and MWCNT: in CMs with MWCNT, the percolation threshold is much lower (0.0017 vol. fr.), than that in the CMs with GNP, where the percolation threshold is 0.0022 vol. fr. As shown in Figs. 1 and 2, the addition of 27 wt.% BN increases the thermal conductivity of both epoxy matrix (from 0.36 W/(m·K) for pure SEDM-2 and 0.53 W/(m·K) by adding BN) and epoxy composites with GNPs and MWCNTs. So, the addition of BN in CM with 3 wt.% GNP increases the thermal conductivity by 234%, while, without BN, this increase was only 75% (see Table 1). A similar pattern was observed for the CMs with MWCNT, so adding BN to CM 10%MWCNT+SEDM-2 increases the thermal conductivity by 157% relative to that of pure resin SEDM-2. Hence, the thermal conductivity of epoxy CMs strongly depends on the structural and morphological characteristics of nanocarbon fillers and, thus, on the nature of their spatial distribution in the polymer matrix and the orientation relative to the heat flow in the CM. Adding boron nitride particles in the CMs with carbon filler greatly enhances the effect of increasing the thermal conductivity of the epoxy matrix with increasing the content of carbon nanofillers, i.e. those CMs reveal the synergistic effect by combining two different types of fillers. In the electrical conductivity of the investigated CMs, the manifestation of the synergistic effect upon the addition of dispersed BN as the second filler is even more significant (see Table 1), although BN is an insulator. For example, in CM with 5 wt.% GNP, σ_{dc} increases by 180 times at the adding of BN, and, for CM with 5 wt.% MWCNT, by 920 times.

The observed concentration dependences of the thermal conductivity of CMs (GNP-epoxy, MWCNT-epoxy with and without BN) can be described within the model described in [10]. In frame of this model, CM is considered as a structure with a set of plates (string) filling in some way and oriented in the polymer matrix relative to the heat flow. According to this model, the thermal conductivity of CM can be described by the relation

$$\lambda_{CM} = \frac{\left[(1-\phi)\cdot\lambda_p + \phi\cdot\lambda_f^*\right]^u}{\left(\frac{1-\phi}{\lambda_p} + \frac{\phi}{\lambda_f^*}\right)^{1-u}}, \qquad (1)$$

where λ_f^* is the effective thermal conductivity of the filler particles forming the chains in composites; λ_p is the thermal conductivity of the polymer matrix; ϕ is the volume fraction of a filler, the parameters (1-u) and u determine the part of chains from GNP or MWCNT, oriented perpendicularly or along the heat flow, respectively; $u = 1$, when all chains from the filler (the particles of filler) are oriented along the heat flux; $u = 0$, when all chains are oriented perpendicularly to the heat flow; and $u = 0.5$ corresponds to the isotropic structure.

λ_f^* is determined by the thermal conductivity of particles (λ_{Gr}, λ_{CNT}, and λ_{BN} are the thermal conductivities of graphite, carbon nanotube, and boron nitride, respectively), the orientation of highly anisotropic particles of a filler in chains (orientation angle θ), and the contact thermal resistance P_k between the particles of a filler. Moreover, in our case, the contact can be also through the polymer layer. So, $\lambda^*{}_f = f$ (λ_{Gr} (or λ_{CNT} and λ_{BN}), θ, P_k). The character of the connection of the nano-platelets of graphite in the chain and their orientation substantially influence the value of thermal conductivity of the graphite chain, since the graphite platelets, as well as nanotubes and boron nitride, are characterized by a sufficiently high anisotropy of the thermal conductivity:

As was shown in [10], when the content of a filler did not exceed 10 wt.% (0.06 vol. fr.), the studied CMs can be considered as isotropic, i.e. the parameter $u = 0.5$. In the proposed model (Eq. (1)) with the use of the experimental values of λ_p and λ_{CM} for CMs with different contents of fillers ϕ, the concentration dependences of the effective thermal conductivity have been determined for all studied systems, and the results are presented in Table 1. As is seen from Table 1, λ_f^* increases with ϕ for all systems, and the value for λ_f^* for CMs GNP-epoxy is significantly higher than λ_f^* CMs MWCNT-epoxy. This difference in values can be associated with a significantly large value of the thermal contact P_k between nanotubes in the chain in comparison with the value of P_k between GNPs. While increasing the filler content, P_k are reduced due to a decrease in the distance between particles of the filler. The addition of disperse boron nitride into epoxy-nanocarbon CM increases λ_f^*, both for the CMs with GNPs and MWCNT fillers. As was shown in [11], such increase of λ_f^* can be related with an enhancement of the chemical bonding of the polymer matrix and the nanocarbon filler. In addition, the boron nitride is characterized by a high thermal conductivity in comparison with the thermal conductivity of the epoxy matrix. It is obvious that the addition of BN to CMs will result in the increase of the effective thermal conductivity of CMs. In addition, the relatively high amount of dispersed boron nitride in CM has a positive effect on the character of formation of the heat-conducting chains of the carbon filler and reduces the thermal contact resistance P_k between particles of the filler due to reducing the distance between the filler particles under a significant increase in the total content of fillers - nanocarbon+BN.

Figure 3 presents the temperature dependence of the thermal conductivity $\lambda_{CM}(T)$ of polymer CMs with 5 wt.% GNP and MWCNT, with and without the addition of 27 wt.% BN.

It is clearly seen from Fig. 3 that the temperature dependences $\lambda_{CM}(T)$ for the epoxy matrix and CMs with 5 wt.% of GNP's are similar and more or less monotonous. The

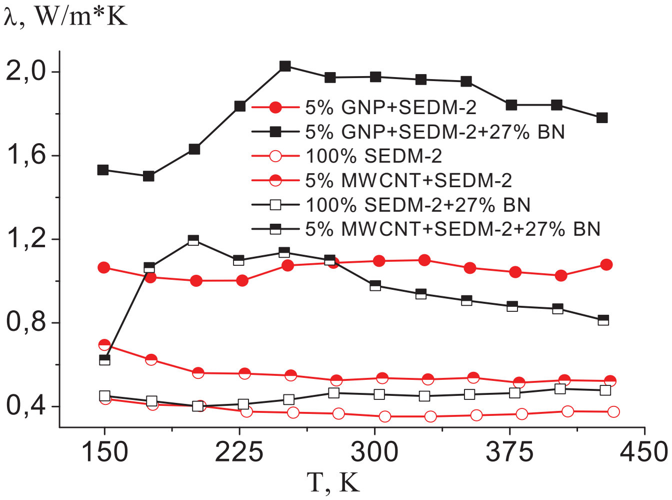

Figure 3. Temperature dependences of thermal conductivity for 5%GNP+SEDM-2, 5%GNP+SEDM-2+27%BN, 5%MWCNT+SEDM-2, 5%MWCNT+SEDM-2+27%BN.

adding of BN particles increases the values of thermal conductivity, and the character of the temperature dependences becomes more complex: a broad maximum at $T = 220$–250 K is observed in the temperature dependences $\lambda_{CM}(T)$. Increasing the value of thermal conductivity of CMs GNP-epoxy and MWCNT-epoxy under adding BN indicates a more effective participation of the fillers in the heat transfer. The maximum in the temperature dependence $\lambda_{CM}(T)$ is a result of changes of the thermal conductivity of the filler due to increasing the number of phonons and the value of phonon-phonon scattering, as well as the changes of the thermal contact resistance between the filler particles and at phase boundaries due to the thermal expansion of the matrix and the filler particles.

Conclusions

It is shown that the thermal conductivity of epoxy-based CMs strongly depends on the structural and morphological characteristics of carbon fillers, the character of their distribution in the polymer matrix, and their orientation with respect to the heat flow in CM. The lower value of thermal conductivity of CMs MWCNT-epoxy in comparison with CMs GNP-epoxy can be explained by a significantly higher value of thermal contact resistance P_k between nanotubes in a chain in comparison with the value P_k for GNPs.

It is established that the adding of BN particles in the CMs with carbon filler greatly enhances the effect of increasing the thermal conductivity of the epoxy matrix with increasing the content of carbon nanofillers, i.e. the synergistic effect is observed in the studied CMs under combining two different types of fillers.

It is shown that the synergistic effect in the electrical conductivity of the studied CMs upon the addition of dispersed BN, as the second filler, is even more significant, despite the fact that BN is an insulator.

The presence of a relatively high amount of disperse boron nitride in CM promotes a more efficient formation of chains of carbon filler and reduces the thermal (electric) contact resistance P_k (R_k) between particles of the filler due to a decrease of the distance between filler particles under a significant increase in the total content of fillers - nanocarbon+BN.

Acknowledgment

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