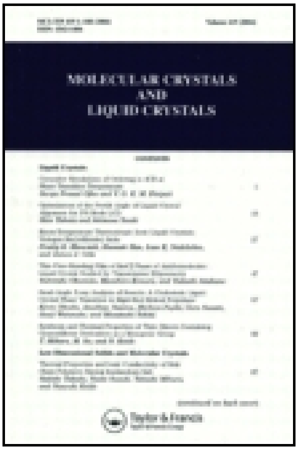

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Nanocarbon-Epoxy Composites as Electromagnetic Shielding Materials

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We present the results of studies of the electromagnetic radiation (EMR) shielding by epoxy-nanocarbon composites (CMs). The EMR frequency range was 25.5–37.5 GHz. Thermoexfoliated graphite and multiwalled carbon nanotubes (CNT) have been used as fillers in CM (the content of a filler was 0.5–2 wt.%). We examined the effect of carbon filler's type in CM on characteristics of the electromagnetic shielding. It is shown that, even for low contents (∼1–2 wt.%) of a nanocarbon filler in CMs, the coefficient of EMR transmission is −(25–27) dB (for $h = 1$ mm). The real ε' and imaginary ε'' parts of dielectric permittivity of the composites under investigation have been determined.

Keywords: carbon nanotube; dielectric permittivity; electromagnetic shielding; nanocarbon filler; porosity

INTRODUCTION

At present, the problem to ensure the environmental safety becomes especially actual because of the rapid development of technique, radiophones, communication facilities, information networks, microwave equipment, intensive computerization, etc. Protective shields and coatings on the base of materials with high attenuation of electromagnetic radiation have been created to avoid the negative action on living matter and electronic equipment.

In this respect, electrically conductive polymer composite materials (CMs) consisting of the polymer matrix and an electrically conductive disperse filler are considered to be the most prospective candidates

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[1,2]. Electrically conductive polymer compositions with the conductive fillers (disperse metallic particles, metallic fibers, carbon filaments, carbon black, etc.) are currently at the sufficiently high technological level which provides their competitiveness with the routine conductive materials (metals). The latter is due to the cheapness of the source materials, low density, manufacturability (high compacting ability and possibility to manufacture articles of arbitrary shape), corrosion resistance, environmental safety, and low production costs. The recent trend in this field is the application of carbon materials such as carbon nanofibers and nanotubes in a polymer matrix, which allows one to create the materials with low filler content and desired electrical and EMR shielding properties [3–7]. These nanocarbon-polymer composites have remarkable structural, mechanical, and electrical properties as compared with those of metals. This study was carried out to examine the effect of carbon filler's type in CM on characteristics of the electromagnetic shielding.

EXPERIMENTAL

Thermoexfoliated graphite (TEG) and two types of multiwalled carbon nanotubes (MWCNT-1 and MWCNT-2) were used as fillers for the preparation of polymer composite materials.

TEG was obtained by a deep thermochemical treatment of natural disperse graphite [8]. The bulk density of TEG powders was $\sim 5\,\mathrm{kg/m^3}$, and the specific surface was $\sim 50\,\mathrm{m^2/g}$.

MWCNT-1 used as a filler in epoxy were produced by the low-temperature conversion of carbon monoxide in a catalytic process through the Bell–Boudoir reaction: $2CO = CO_2 + C$ [9]. CO and hydrogen mixture were flowed over a copper substrate covered with metal catalyst (Co) oxides. These oxides were partially reduced to a pure metal upon the synthesis. The as-prepared NCM specimens contain multiwalled CNTs, particles of amorphous carbon, and particles of the catalyst (Co) [10].

Another type of MWCNT-2 that was used as a filler in epoxy has been prepared during the catalytic decomposition of benzene (as the carbon source) and ferrocene (source of iron) in a tube furnace at different temperatures. The inner diameter of tubes is equal to 5–8 nm, and their length is up to 200 μm [11].

The epoxy-based composites have been prepared by the usual careful mixing of TEG (or MWCNT-1) and epoxy in acetone with the subsequent drying [12] and by the ultrasonic sonication of the mixture of MWCNT-2 and epoxy in acetone for 4 h.

The specimens of nanocarbon-epoxy composites in a form of $7.2 \times 3.4 \times (1\text{–}2)\,\text{mm}^3$ plates were prepared to analyze the interaction of electromagnetic radiation (EMR) with the studied materials. Such sample's shape allows us to totally overlap the cross-section of a rectangular copper waveguide. A P2-65 device (the equivalent of a microwave network analyzer) was used to measure the transmission coefficient within the 25.5–37.5-GHz frequency range. Voltage measurements of the standing wave ratio (SWR) [13] were used to determine the reflection properties and complex dielectric permittivity of the studied specimens. This method allows one to avoid the problems arising due to deviations from the quadratic law of the characteristic of SHF-detectors used in measuring SHF installations.

The essence of the method for the determination of permittivity consists in the following. The CM plate with thickness d_{pl} is placed inside the waveguide and tightly pressed to a metallic plate (shorting device) that overlaps its output. The dielectric plate must overlap the cross-section of the waveguide fully.

At the SHF-signal injection on such a loading, the field as a superposition of the incident wave and two reflected ones is formed before the plate. The first reflected wave is formed as a result of the reflection from the front plate's surface and provides with information about the dielectric permittivity of this plate. The second reflected wave passes through the front plate's surface and is reflected entirely by the back surface because the shorting device (metallic plate) is placed just after the dielectric plate. This wave provides with information about the dielectric permittivity as well as the electromagnetic losses in the investigated material.

RESULTS AND DISCUSSION

Thermoexfoliated graphite, as well as non-purified and purified multi-walled carbon nanotubes (MWCNT-1 and MWCNT-2), have been used as a filler in polymer composite materials. We investigated the influence of the type of a carbon nanofiller and its content on characteristics of the electromagnetic shielding in nanocarbon-epoxy CMs. Table 1 presents the density d, porosity P, and electrical resistivity ρ of the investigated specimens.

The following relations have been used for the determination of specimen's porosity:

$$P = 1 - \frac{d_{CM}}{d_{CM(id)}}, \quad d_{CM(id)} = \frac{d_f \cdot d_p}{C_f^* d_p + (1 - C_f^*) d_f}, \tag{1}$$

where C_f^* is the mass fraction of nanocarbon in CM, $d_{CM(id)}$ is the density of the ideal nonporous CM specimen; d_p, d_f, and d_{CM} are the densities of the polymer, nanocarbon filler, and composite, respectively: $d_{\mathrm{Gr}} = 2.23\,\mathrm{g/cm^3}$, $d_{MWCNT} = 2.045\,\mathrm{g/cm^3}$ [14], $d_{epoxy} = 1.25\,\mathrm{g/cm^3}$.

As seen from Table 1, the value of electrical resistivity sharply decreases from $2.0 \cdot 10^8$ to $7.6 \cdot 10^{-2}\,\Omega \cdot \mathrm{m}$ with the TEG content increasing from 0.5 to 2 wt.%. That is, the sharp percolation transition in the electrical conductivity for CMs occurs, and the percolation threshold in TEG-epoxy is equal to 1.35 wt.% [15]. As for CMs with pure MWCNT, they are also characterized by low values of electrical resistivity for 1–2 wt.% content of MWCNT-2 in comparison with those for epoxy. The nanocarbon fillers (graphite or MWCNT) used in these composites have a high anisotropy of electrical conductivity but, for the CMs with filler content ≤ 2 wt.%, the anisotropy of electrical resisitivity is not observed: The ρ_c/ρ_a ratio is equal to ~ 1. That is why it is possible to assume that the filler particles' distribution is practically uniform and isotropic due to the absence of the preferred orientation of graphite flakes or carbon nanotubes during the specimen's preparation.

The investigations of the electromagnetic shielding efficiency (SE_T) of CMs with various carbon filler contents and different thicknesses have been performed and the results are presented in Figures 1 and 2.

As seen from the figures, the electromagnetic shielding efficiency is high even at a low TEG or MWCNT content in CM (up to 2 wt.%). The EMR transmission coefficient increases from -10 dB/mm for 0.5 wt.% to $-(20–27)$ dB/mm at 2.0 wt.% of nanocarbon. It was found that using TEG or MWCNT-2 as a filler leads to good results on SE_T that are compared with the results of another researchers [2,5,6].

TABLE 1 Characteristics of the Investigated CMs

Filler content					ε'	$tg\delta$	ε''
C, wt.%	ϕ, vol.%	d, g/cm^3	P	ρ_a (293 K), Ω·m	$f = 37$ GHz		
TEG-epoxy							
0.5	0.28	0.86	0.31	$2.0 \cdot 10^8$	6 ± 1	0.08	0.49
1.0	0.56	0.98	0.22	$3.0 \cdot 10^2$	19 ± 1.5	0.10	1.90
2.0	1.1	1.0	0.21	$7.6 \cdot 10^{-2}$	36 ± 3	0.17	3.04
MWCNT-2 + epoxy							
1.0	0.6	1.1	0.12	$1.9 \cdot 10^2$	16 ± 2	0.08	1.28
2.0	1.2	1.1	0.13	8.55	27 ± 2	0.17	4.59
MWCNT-1 + epoxy							
1.0	0.6	0.87		$2.15 \cdot 10^8$	3.4 ± 0.25	0.06	0.27

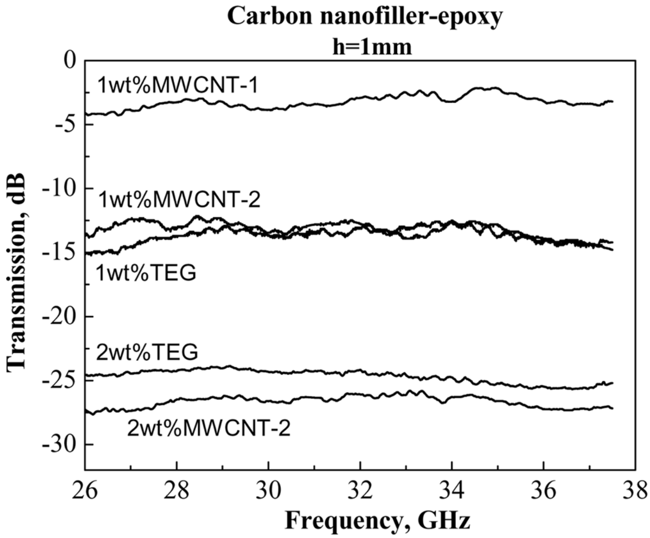

FIGURE 1 Coefficient of EMR transmission for nanocarbon-epoxy CMs.

Thus, we can conclude that TEG is a promising material for the development of novel polymer composites which provide a good electromagnetic shielding. It was shown also that using MWCNT-1 (with high content of amorphous carbon) as a filler in epoxy leads to low values of the electrical conductivity and the EMR transmission index in comparison with those of CMs with TEG or MWCNT-2 as a filler, i.e., the degree of purification of carbon nanotubes essentially influences the electric and EMR shielding properties of nanocarbon-polymer composites.

The distribution of the electric field in a waveguide before loading is studied in order to obtain the relations for the calculation of the dielectric permittivity: the modulus of the reflection coefficient is determined by measuring the standing wave ratio (SWR) κ_{SW} and its phase from a shift of the standing wave minimum $d_{\min}$. For this purpose, the positions of the minimum are fixed at a shorted waveguide without dielectric plate and then with a dielectric plate.

As a result, the reflection coefficient Γ could be expressed as

$$\Gamma = \frac{(\kappa_{SW} - 1)}{(\kappa_{SW} + 1)} \exp[i(4\pi/\lambda_{g0} d_{\min} - \pi)], \tag{2}$$

where $\lambda_{g0} = \lambda_0/\sqrt{\varepsilon_0 - (\lambda_0/\lambda_c)^2}$, λ_{g0} and λ_0 are the wavelengths in the empty waveguide and in free space, respectively, λ_c is the critical

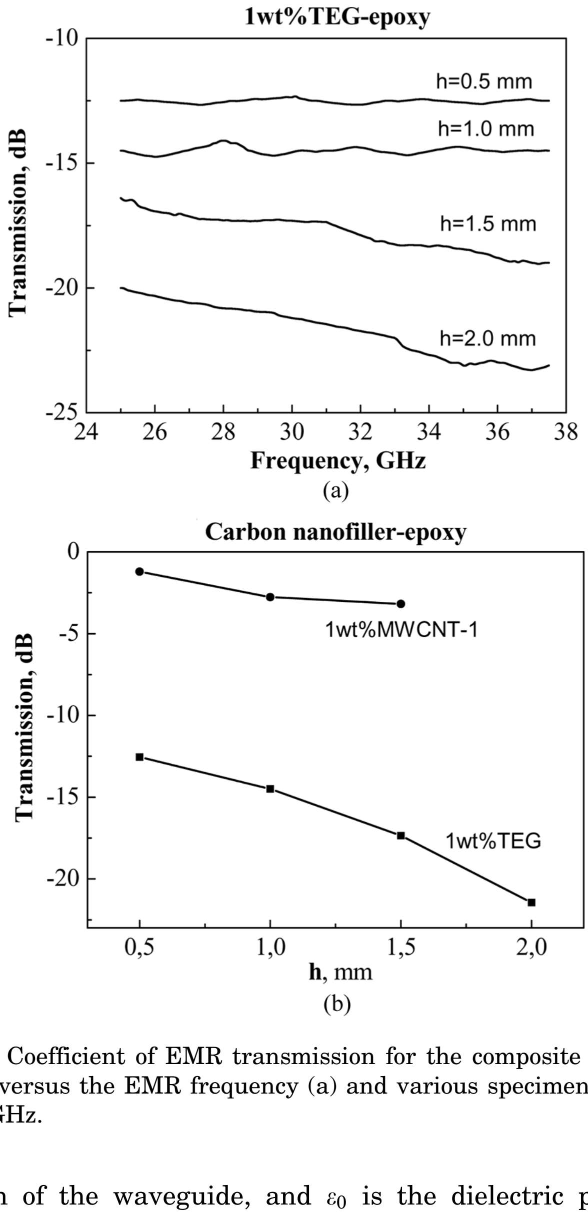

FIGURE 2 Coefficient of EMR transmission for the composite with 1 wt.% TEG-epoxy versus the EMR frequency (a) and various specimen thicknesses h (b) at 37 GHz.

wavelength of the waveguide, and ε_0 is the dielectric permittivity of air.

Since the impedance of the waveguide on the front of a dielectric CM plate should be equal to the input resistance of this plate in a performed experiment, one can derive the equation for the complex propagation constant $\gamma = \gamma'' + i\gamma'$, which allows us to give the analytic expressions for the appropriate parameters of the investigated material:

$$\varepsilon' = [(\gamma_c)^2 + (\gamma'')^2 - (\gamma')^2]/\gamma_0^2, \tag{3}$$

$$tg(\delta) = \varepsilon''/\varepsilon' = 2\gamma'\gamma''/[(\gamma_c)^2 + (\gamma'')^2 - (\gamma')^2], \tag{4}$$

where $\gamma_0 = 2\pi/\lambda_0$, $\gamma_c = 2\pi/\lambda_c$.

The obtained values of ε', $tg\delta$, and ε'' are presented in Table 1. As seen, the values of permittivity and loss tangent $tg\delta$, as well as the electric conductivity of CM, increase with the content of a nanocarbon filler, and no abrupt changes in ε', $tg\delta$, and ε'' were observed for the experimental range of the nanocarbon content (0.5–2 wt.%). It is worth noting that dielectric properties of the composite are determined mainly by the dielectric properties of individual nanocarbon particles, while the electric conductivity is determined both by the electric conductivity of individual particles and the ability of nanocarbon particles to form the chains and an infinite cluster in the polymer matrix.

The relation between transmittance (T), reflection (Γ) and absorbance (A) is known to have the form

$$A + T + \Gamma = 1, \quad \Gamma = \left|E_I^{/}/E_I\right|^2, \quad T = |E_T/E_I|^2, \tag{5}$$

where E_I, E_I', E_T are the electric field strengths of incident, reflected, and transmitted waves, respectively.

The EMR shielding efficiency SE_T is the sum of the SE due to absorption (SE_A) and reflection (SE_Γ):

$$SE_T = -10\lg(T) = -20\ \lg(E_T/E_I) = SE_A + SE_\Gamma \tag{6}$$

Evidently, the material with a low EMR reflection coefficient and a high EMR absorption coefficient could be used as the shielding material with high efficiency. The main task at the development of protection shields is to decrease the reflection of EMR and, at the same time, to provide the required level of shielding. This task can be solved by construction of screens of a special shape, by using of multilayer coatings, etc.

The distinct correlation between the values of electrical conductivity, dielectric permittivity, and SE_T has been revealed for the investigated CMs. Figure 3 presents the imaginary part ε'' of the permittivity (responsible for the EMR absorption in the material) and the EMR transmission coefficient versus $\lg\sigma$ for all specimens under study.

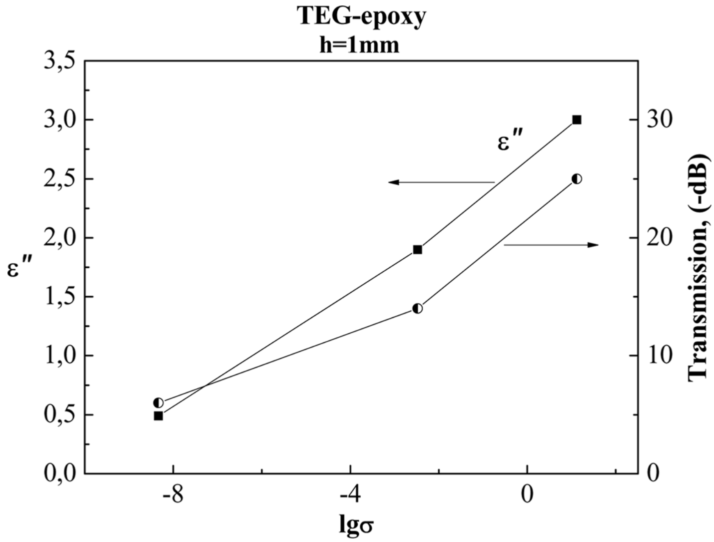

FIGURE 3 Coefficient of EMR transmission and the imaginary part of the permittivity ε'' for TEG-epoxy CMs versus the logarithm of the electrical conductivity, $lg\sigma$.

It is seen that the increase in electrical conductivity leads to high values of ε'' (EMR absorption increase) and EMR transmission coefficient SE_T. It should be noted that SE_T increases also due to an increase of the EMR reflection for the specimens with high electrical conductivity σ. It was shown that the value of SE_T increases almost linearly with specimen's thickness.

From our point of view, the high EMR shielding efficiency of CMs containing TEG as a filler can be explained by the following:

– the presence of a high amount of the graphite-polymer interfaces in TEG-epoxy CMs, as well as the high specific surface of TEG and porosity of the specimens, can considerably increase the contribution to the absorption coefficient due to multiple EMR reflections in the bulk of a specimen.
– the investigated TEG-epoxy CMs are characterized by a low percolation threshold C_{cr} (the abrupt change in the electrical conductivity at $C_{cr} \sim 1.3$ wt.%), which leads to high values of EMR electromagnetic shielding even at low contents of TEG (~ 1 wt.%).

Low shielding efficiency of CMs containing non-purified carbon nanotubes (MWCNT-1) is caused by the fact that this filler contains a high amount of amorphous carbon which is characterized by a relatively low electric conductivity.

CONCLUSION

The basic electromagnetic shielding characteristics for the nanocarbon filler-epoxy CMs have been measured for the first time in the frequency range 26–37.5 GHz. It is found that the characteristics of electromagnetic shielding are high in the case of TEG-epoxy CMs even at low TEG contents (~1–2 wt.%) and compared with that of MWCNT-2 + epoxy CMs: the coefficient of EMR transmission is -25 dB (for $h = 1$ mm). The presence of the amorphous phase of carbon in CMs leads to the worsening of the electric and shielding characteristics. The real ε' and imaginary ε'' parts of the dielectric permittivity have been determined for the composites with low contents of the carbon nanofiller ((0.5–2) wt.% of TEG or MWCNT) in the millimeter range of electromagnetic waves. It is shown that the permittivity increases with the nanocarbon filler content and is determined by the structure and the phase composition of nanocarbon particles.

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