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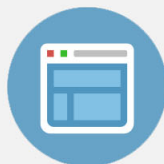
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# Epoxy composites filled with high surface area-carbon fillers: Optimization of electromagnetic shielding, electrical, mechanical, and thermal properties

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A comprehensive analysis of electrical, electromagnetic (EM), mechanical, and thermal properties of epoxy resin composites filled with 0.25–2.0 wt. % of carbon additives characterized by high surface area, both nano-sized, like carbon nanotubes (CNTs) and carbon black (CBH), and micro-sized exfoliated graphite (EG), was performed. We found that the physical properties of both CNTs- and CBH-based epoxy resin composites increased all together with filler content and even more clearly for CBH than for CNTs. In the case of EG-based composites, good correlation between properties and filler amount was observed for concentrations below 1.5 wt. %. We conclude that CBH and, to a lower extent, EG could replace expensive CNTs for producing effective EM materials in microwave and low-frequency ranges, which are, in addition, mechanically and thermally stable.

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## I. INTRODUCTION

Due to the significant progresses of synergistic property improvement in carbon-based polymer composites,<sup>1–6</sup> i.e., improvement of mechanical strength, elastic modulus, and thermal stability along with enhancement of electrical conductivity at a low percolation threshold, etc., carbon-based composites may have great potential for applications in many fields either as structural or functional materials. In particular, polymers filled with carbon nanotubes (CNTs), graphite and its derivatives, carbon black and carbon onions can be widely used as lightweight and ultra-thin effective electric components and sensors, conductive electrodes for solar cells, antistatic coatings, as well as electromagnetic (EM) interference (EMI) shields and filters,<sup>6,7</sup> and conformal materials for structurally integrated RF antennas.<sup>8,9</sup>

The properties of polymer composites filled with nanometer-scale additives are greatly influenced by the dimensions of the constitutive phases (from 1 to 200 nm). Because of the nano-size of the filler and the interaction processes at the carbon particle – matrix interface, nano-structural composites exhibit novel and significantly improved properties. A unique feature of polymer nanocomposites is that a major enhancement of their properties is attained at very low filler contents,<sup>7,10,11</sup> which lead to the development of lightweight materials. The key point is to transfer the outstanding properties of nanofillers to the

polymer nanocomposites. However, to further commercialize carbon/polymer composites, many technical problems need to be overcome. One of them is the good dispersion of nanofillers in polymers, which still remains a challenge. For some particular task one may want to add significant amounts of filler to improve electrical and EM properties. The key question here is whether it is possible to improve continuously the *dc* conductivity and EMI shielding ability, and at the same time not to destroy good mechanical property and thermal stability of the polymer composite. Thus, the question is to find such a critical concentration, corresponding to an optimum between electrical, mechanical, thermal, and electromagnetic properties, depending on possible material application.

Another decisive question is whether it is always necessary to deal with nanocomposites based on relatively expensive fillers, like single-walled or multi-walled CNTs (SWCNTs and MWCNTs, respectively), and whether it is possible to replace them for some particular applications by cheaper nanocarbons, like carbon black, or even with micro-sized carbon, e.g., exfoliated graphite (EG).

The goals of the present communication are (i) to investigate mechanical, thermal, electrical, and EM properties of epoxy resin filled with commercially available both nano-, i.e., SWCNT, MWCNTs, carbon black of high surface area, and micro-carbon (exfoliated graphite); we chose all carbons of high surface area, because they are more effective for EM applications due to skin effect at high frequencies; (ii) to estimate the optimal concentration of carbon filler of each

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type at which the highest values of all mentioned properties exist; (iii) to discuss the possibility of preparing low-cost carbon-based polymer materials depending on the applications.

## II. MATERIAL AND METHODS

### A. Composites fabrication

Commercially available SWCNTs and MWCNTs by Heji were utilized for CNT/resin composite fabrication. The synthesis method of SWCNT and MWCNT was CVD. The SWCNT data are the following: 1–2 nm diameter, mostly in bundles of 8–20 nm; apparent density of 0.3 g/cm<sup>3</sup> at 25 °C, 10–20  $\mu$ m length, 90+% purification degree. The MWCNTs have 20–40 nm diameter, apparent density of 0.5 g/cm<sup>3</sup> at 25 °C, 0.5–200  $\mu$ m length.

ENSACO conductive carbon black was kindly supplied by Timcal Ltd. (Bodio, Switzerland). ENSACO carbon black with a high to very high void volume allows the retention of a carbon network at low to very low filler content. The void volume can originate from the interstices between the carbon black particles, due to their complex arrangement, and from the porosity. Carbon Black of High surface area - CBH (ENSACO 350G; Brunauer–Emmett–Teller (BET) surface area = 770 m<sup>2</sup>/g; oil absorption = 320 ml/100 g) was used.

EG was supplied by Mersen (France) and obtained by intercalation of natural graphite flakes, subsequently submitted to a thermal shock. Accordion-like particles were thus produced, leading to a material of low packing density, around 3 g/l. Typically, the diameter of the EG particles is in the range 0.3–0.5  $\mu$ m, and their aspect ratio is around 20.<sup>12</sup>

EPIKOTE<sup>TM</sup> Resin 828 was used for composites fabrication. EPIKOTE Resin 828 is a medium viscosity liquid epoxy resin produced from bisphenol A resin and epichlorhydrin. It contains no diluent. EPIKOTE 828 provides good pigment wetting and good resistance to filler settling, together with a high level of mechanical and chemical resistance properties in cured state.

A series of CNTs-, CBH-, and EG-based composite samples, using a Epikote 828 epoxy resin, a curing agent called A1 (i.e., a modified Tetraethylenepentamine (TEPA)) and 0.25, 0.5, 1.0, 1.5 and 2.0 wt. % of carbon fillers were fabricated as follows:<sup>13</sup> the resin was degassed under vacuum (1–3 mbar) for 12–14 h, then it was put into an oven at 65 °C. In the meantime, the carbon was dispersed in propanol through ultrasonic bath for 1.5 h. Afterwards the solution of alcohol and carbon fillers was mixed with the resin. The obtained mixture was inserted inside the oven at 130–150 °C for the evaporation of alcohol. The curing agent (A1) was added to the mixture of resin and filler through slow manual mixing for about 7 min. The mix was then poured into 1 cm  $\times$  1 cm  $\times$  7 cm molds, and left as such for 20 h for the curing process at room temperature and then 4 h in oven at 80 °C. When the process was completed, the samples were removed from the molds. The uniformity of distribution of the carbon fillers in the polymer samples was studied by scanning electron microscopy; all fabricated composites demonstrated good homogeneity, carbon inclusions were reasonably well dispersed.

### B. Measurements

Nanoindentations were carried out using Nanomechanical Tester (Bruker, USA). The nanohead of the Nanoindenter performs indentation tests, where the applied load and displacement are continuously monitored, generating load versus displacement data for a test specimen. Young's modulus and hardness are derived from the unload data segments through *in situ* monitoring of the force vs. displacement plot and automatic calculations by utilizing the Oliver-Pharr method.<sup>14</sup> Prior to indentation, the sample surface of the studied composites was polished by means of Leica RM2245 microtome with stereo microscope Leica A60S and diamond knife (Leica Microsystems, Germany).

The software program prepared for this experiment consisted of 4 lines with 12 indentations each (total of 48 indentations) and spacing of 80  $\mu$ m. Each indentation was made with a force of 200 mN. A typical indentation experiment consisted of subsequent steps: (i) approaching the surface; (ii) loading to the maximum force (200 mN) for 15 s; (iii) holding the indenter at peak load for 10 s; (iv) unloading from maximum force (200 mN) to 10% for 15 s; (v) holding at 10% of maximum force for 15 s; (vi) final complete unloading for 1 s (load function 15 s-10 s-15 s trapezoid). The hold step was included to avoid the influence of creep on the unloading characteristics since the unloading curve was used to obtain the elastic modulus of material. The imprints were visualized by use of optical microscope and AFM.

Thermal stability was determined by using thermogravimetric analyzer TGA-1/SF (METTLER TOLEDO, Switzerland). Thermogravimetric analysis (TGA) measurements were performed in air from room temperature (25 °C) to 800 °C with heating rate of 10 °C/min. The average mass of the sample was 10 mg.

Complex dielectric permittivity  $\varepsilon = \varepsilon' - i\varepsilon''$  was measured as a function of frequency at room temperature using an HP4284A precision LCR meter. The sample was placed in a home-made furnace between two conductors. The equivalent circuit of such system was selected as capacitance and loss tangent.

The microwave measurements were carried out with a scalar network analyzer R2-408R (ELMIKA, Vilnius, Lithuania). The system is composed of a sweep generator, waveguide reflectometer, network analyzer and indicator unit (personal computer). The IEC 62431:2008(E) standard specifying the measurement method for the reflectivity of EM materials for normal incidence was used. The EM response of samples as ratios of transmitted/input ( $S_{21}$ ) and reflected/input ( $S_{11}$ ) signals was measured within 26–37 GHz frequency range (K<sub>a</sub>-band). S-parameters were measured by subsequent insertion of the specimen into the waveguide. The measurements were performed with 0.5 mm thick free-standing samples.

## III. RESULTS AND DISCUSSION

### A. Mechanical properties of carbon based epoxy composites

Figure 1 shows examples of optical and AFM micrographs of the indentation imprints after indentation tests.

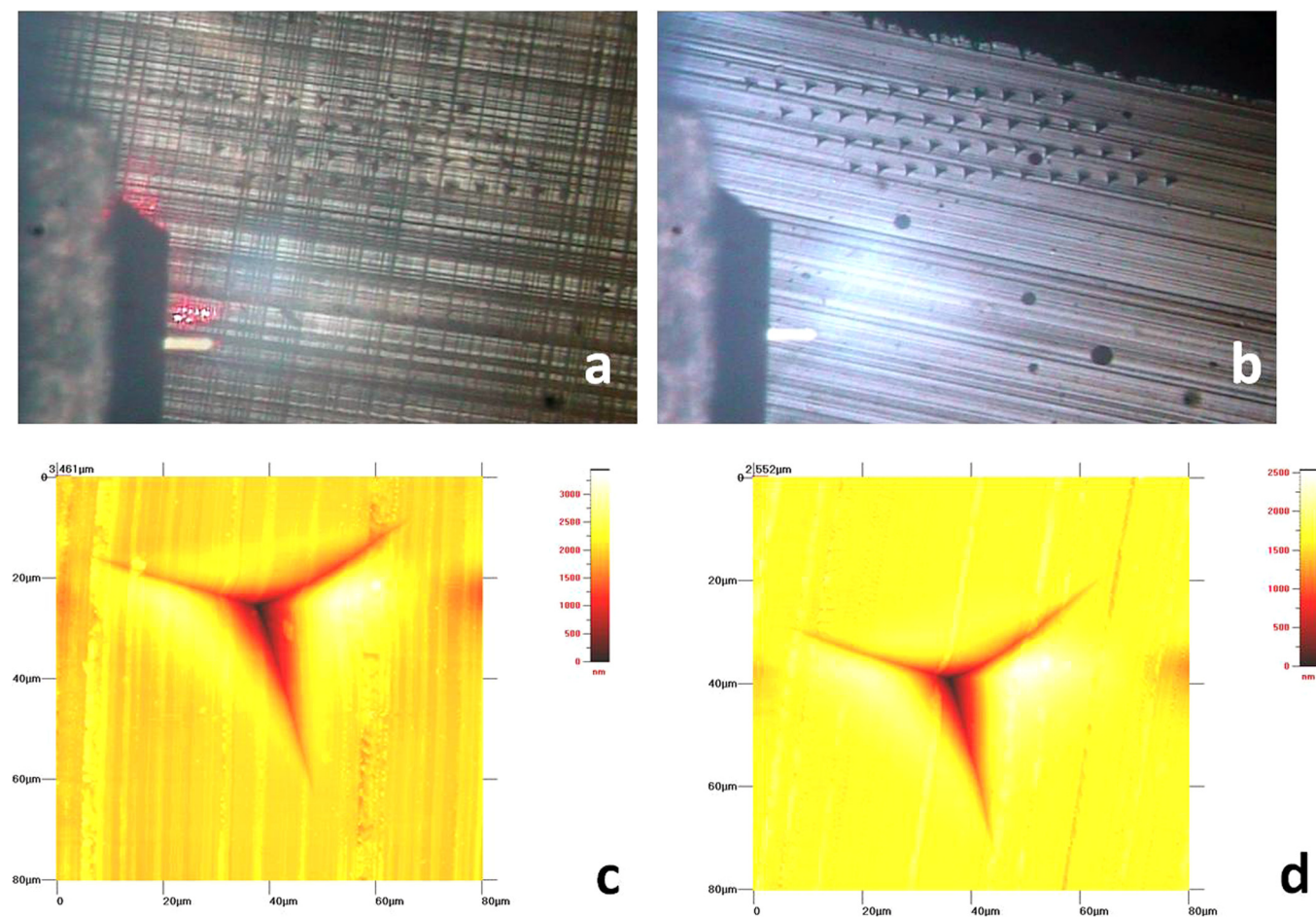


FIG. 1. Optical micrographs obtained after 48 indentations (4 lines of 12 indentations at a distance of  $80\text{ }\mu\text{m}$ ) of (a) neat epoxy and (b) 2 wt. % of SWCNTs in epoxy. (c), (d) AFM images of indentation imprint on (c) a pure bulk epoxy resin sample and (d) epoxy/CBH nanocomposite (0.25 wt. %) with Berkovich nanoindenter tip, at a load of 200 mN.

AFM imaging of the indentation imprint on the sample surface was performed in line with the nanoindentation tests. This technique allows to map different features on the surface and to correlate the obtained results with specific local mechanical properties. AFM images provide information about the brittle–ductile behavior of materials because rigid ones show sink-in indentation imprint and ductile ones show pile-up effect. Both the neat epoxy and all the composites containing 0.25 wt. %–2.0 wt. % of carbon fillers demonstrate low plasticity behavior, in which pile-up effect was not observed in the line profile across the imprint.

Figure 2 shows representative load-displacement curves (a), (c) and values of the apparent elastic modulus and hardness (b), (d) obtained after nanoindentation tests of neat epoxy resin and epoxy/EG (1 wt. %) composite. The maximum load of 200 mN was held for 10 s to ensure that the viscoelastic contribution is negligible and the Oliver-Pharr model is reliable.

As seen from Fig. 2(c) the addition of 1 wt. % of exfoliated graphite shifted the curves to lower penetration depth compared to that of neat epoxy (Fig. 2(a)), i.e., the composite material had better resistance to penetration and increasing the filler loading had a reinforcement effect in the tested composites. Comparison of Figs. 2(b) and 2(d) further confirms the reinforcement effect of EG when used as a filler.

Figs. 3(a) and 3(b) show the concentration dependence of nanohardness and Young's modulus of all series of composites. Composites based on EG show improvement of the hardness and Young's modulus in the concentration range from 0.25 to 1.5 wt. %. Above this concentration, the mechanical properties are degraded. A likely reason for this effect is the non uniform distribution of exfoliated graphite at higher concentrations. Epoxy loaded with CBH demonstrates improvement of the nanohardness in all concentration range while Young's modulus is improved above 0.5 wt. %.

Epoxy/SWCNTs composites show improvement of hardness and Young's modulus up to 0.5 wt. % and 1.5 wt. %, respectively, and above these concentrations, hardness and Young's modulus come close to that of the neat epoxy. MWCNT inclusions influence hardness and Young's modulus insufficiently. Obviously, the best reinforcement effect was obtained with exfoliated graphite, with a maximum improvement of 17.5% of Young's modulus at 1 wt. % of EG.

## B. Thermal stability analysis

Representative TGA data for epoxy/SWCNT and epoxy/CBH composites are gathered in Table I. Weight losses in CBH-loaded matrices can be divided into three parts: 1st minor weight loss region in the temperature range

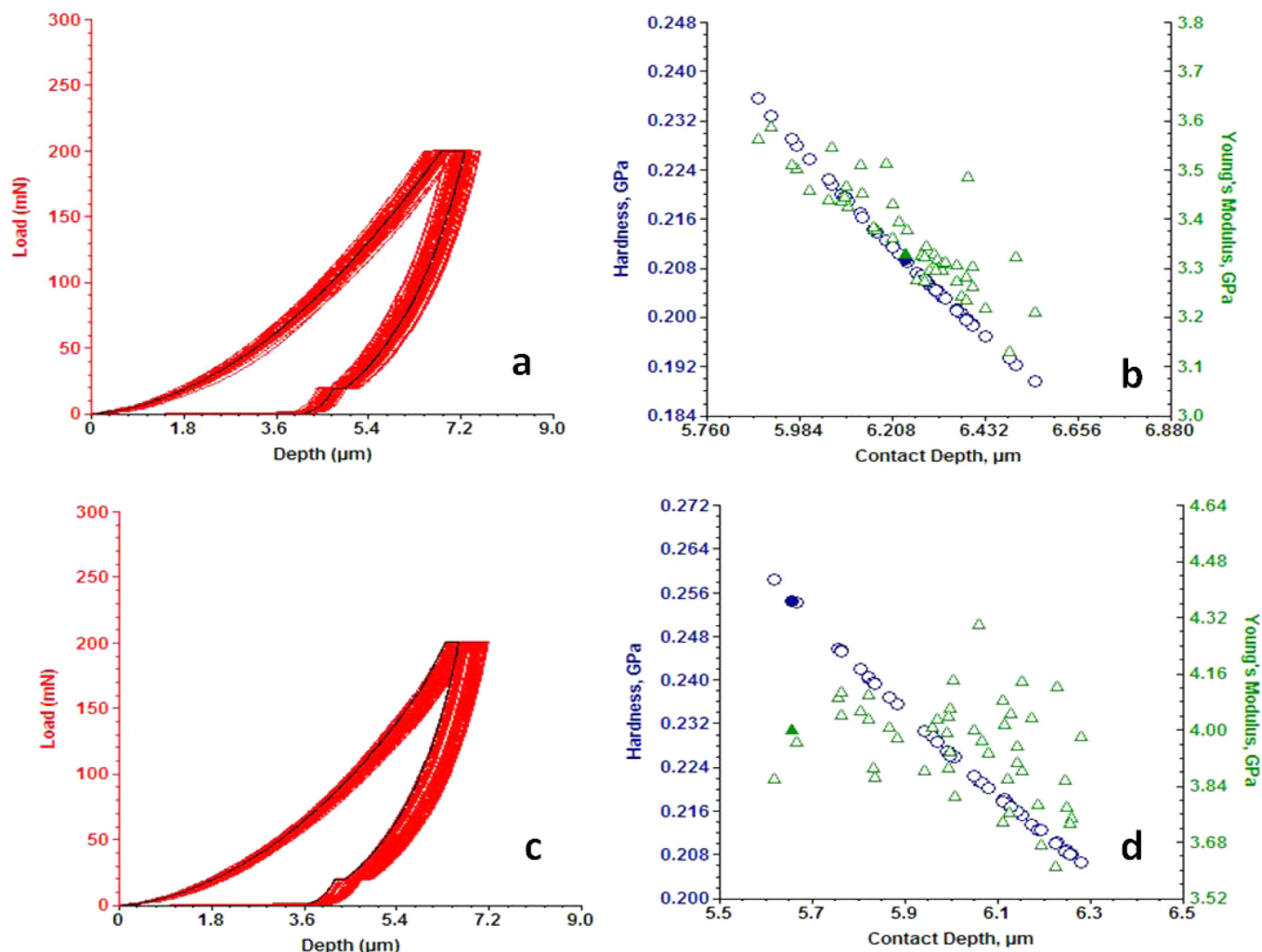


FIG. 2. Representative load-displacement curves (a), (c) and values of apparent elastic modulus ( $\Delta$ ) and hardness ( $\circ$ ) (b), (d) obtained after nanoindentation tests (48 nanoindentations) of neat epoxy resin (Epikote828) (a), (b) and Epikote828/1 wt. % EG composite (c), (d).

from 25 °C to 250 °C; 2nd major weight loss region in the temperature range from 250 °C to 475 °C; and 3rd post-major weight loss region in the temperature range from 475 °C to 800 °C. The 1st minor weight loss region can most

probably be attributed to evolution of moisture and volatile elements, including by-products of polycondensation reactions resulting from incomplete curing of the epoxy resin; 2nd major weight loss region can evidently be attributed to

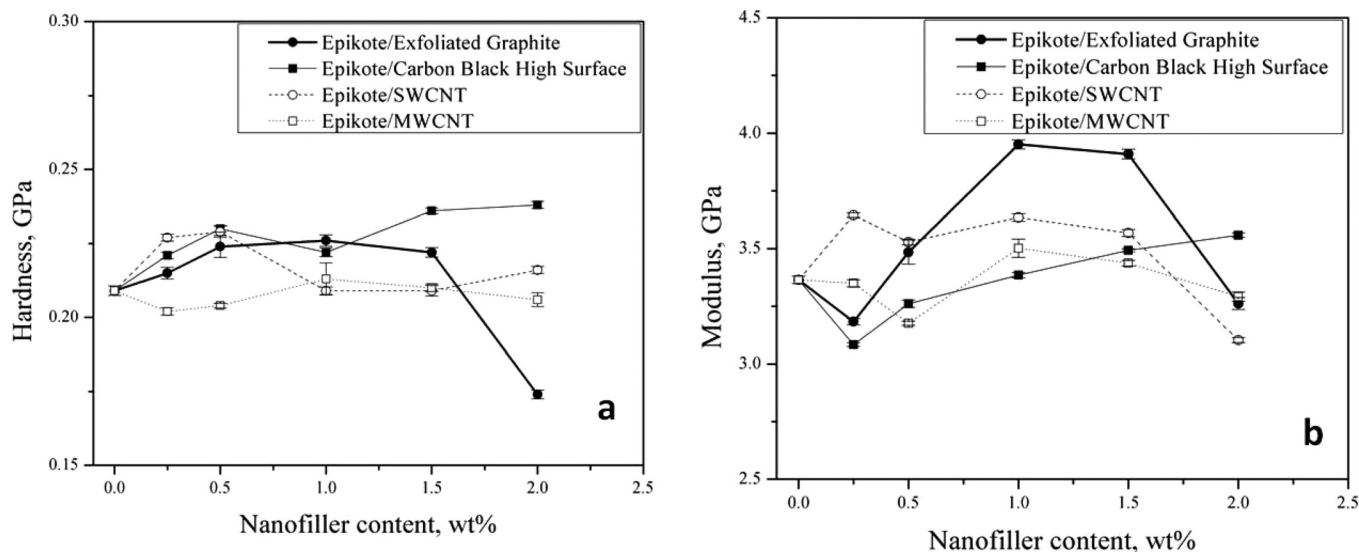


FIG. 3. Concentration dependence of (a) nanohardness and (b) Young's modulus of epoxy filled with SWCNT, MWCNT, EG, and CBH.

TABLE I. Remaining weight of epoxy/carbon composites in the temperature range 40–800 °C.

No.	Material	1st weight loss region		2nd weight loss region			3rd weight loss region			
		100 °C	250 °C	350 °C	400 °C	475 °C	550 °C	575 °C	600 °C	800 °C
1	Epoxy	100	98.4	81.7	32.9	21.7	16.4	11.3	5.6	0.2
2	0.5% epoxy/SWCNT	99.9	98.2	80.3	36.2	19.6	15.3	11.1	5.0	0.2
3	1% epoxy/SWCNT	99.9	97.7	78.6	35.0	23.4	17.5	12.2	5.6	0.2
3	1.5% epoxy/SWCNT	99.9	97.7	78.6	35.0	23.4	17.5	12.2	5.6	0.2
3	2.0% epoxy/SWCNT	99.9	97.7	78.6	35.0	23.4	17.5	12.2	5.6	0.2
1	Epoxy	100	98.4	81.7	32.9	21.7	16.4	11.3	5.6	0.2
2	0.5% epoxy/CBH	100	98.7	83.4	39.0	25.1	16.4	10.1	5.4	0.2
2	1% epoxy/CBH	100	98.7	83.4	39.0	25.1	16.4	10.1	5.4	0.2
2	1.5% epoxy/CBH	100	98.7	83.4	39.0	25.1	16.4	10.1	5.4	0.2
3	2% epoxy/CBH	100	99.3	85.3	37.0	25.6	18.5	12.0	5.9	0.2

degradation of epoxy matrix itself, while 3rd weight loss region is attributed to thermo-oxidation of the remaining degradation products of the epoxy resin. In general as a result of CBH addition, TGA curves are shifted to higher temperatures, whereas modification of the resin with 1 wt. % of nanofiller is relatively more effective than using higher nanofiller concentrations. It should be however mentioned that in the case of the composition containing 2 wt. % of CBH, the thermal stability of the nanocomposite is considerably higher at low and high temperatures. Such behaviour in the low temperature region testifies that curing of the epoxy resin is improved along with increasing CBH content. Similarly, in the high temperature region, diffusion of oxygen to the degradation products of the epoxy resin is reduced along with CBH addition.

Similar thermal stability behaviour is observed also in the case of EG-modified systems (see Fig. 4), revealing that the composition with 1 wt. % of EG fillers in general shows the highest thermal stability. However, increasing carbonaceous filler content above 1 wt. % decreases the thermal stability of the resin-EG system in the major 2nd weight loss region, most probably due to less homogeneous dispersion of EG in the polymer matrix. Higher thermal stability of EG containing composites in comparison to CBH- and SWCNT-modified systems can most probably be associated with

plate-like form of the former filler, offering better thermal barrier characteristics.

In the case of SWCNT-containing systems, TGA curves (see Table I) are somewhat different in comparison to those described previously. Some improvement of the thermal stability is observed only in the 2nd weight loss region. The lower effectiveness of SWCNTs could be explained by their poorer dispersability in the polymer matrix. Besides, the most effective modifier content is somewhat lower (0.5 wt. %) than in the cases of CBH and EG-containing systems. Similar results have been also reported in other works.<sup>15</sup> MWCNT additives do almost not influence the thermal stability of the epoxy resin composite system.

### C. Low frequency analysis

Series of SWCNT-, MWCNT-, EG-, and CBH-based samples with different contents of carbon fillers were investigated in the low-frequency range, in order to observe the effect of carbon additives on complex effective permittivity and electrical conductivity. The concentration dependencies of epoxy filled with carbon additives' *dc* conductivity and real/imaginary part of dielectric permittivity at 129 Hz are presented in Fig. 5. *dc* conductivity  $\sigma_{DC}$  was obtained using fit of frequency spectra of *ac* conductivity  $\sigma_{AC} = \epsilon_0 \epsilon'' \omega$  according to equation

$$\sigma_{AC} = \sigma_{DC} + (\omega/\omega_{cr})^s.$$

Below the percolation threshold, the critical frequency  $\omega_{cr}$  is very low, therefore no *dc* conductivity can be obtained from frequency spectra of *ac* conductivity  $\sigma_{AC}$ . An appearance of *dc* conductivity in conductivity spectra  $\sigma(\omega)$  is a sign of electrical percolation: the following percolation thresholds were determined (Fig. 5(c)) for carbon/epoxy composites: 0.25 wt. % for SWCNT, 0.5 wt% for CBH composites, and 1.5 wt. % for both EG and MWCNT inclusions. Thus, composites with SWCNTs show a lower percolation threshold in comparison with all other investigated samples. At the same time, the absolute values of conductivity of epoxy filled with 2 wt. % of EG are more than two orders of magnitude higher than for all the other investigated composites.

The conductivity of epoxy filled with SWCNT saturates when the filler concentration reaches 0.5 wt. %. The maximal

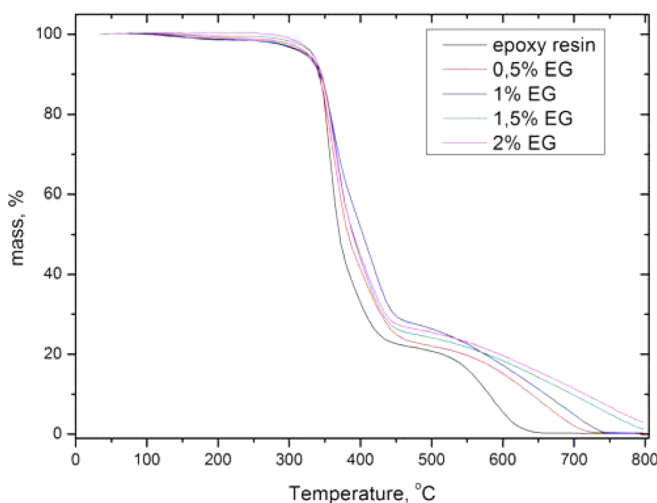


FIG. 4. TGA curves for epoxy filled with EG.

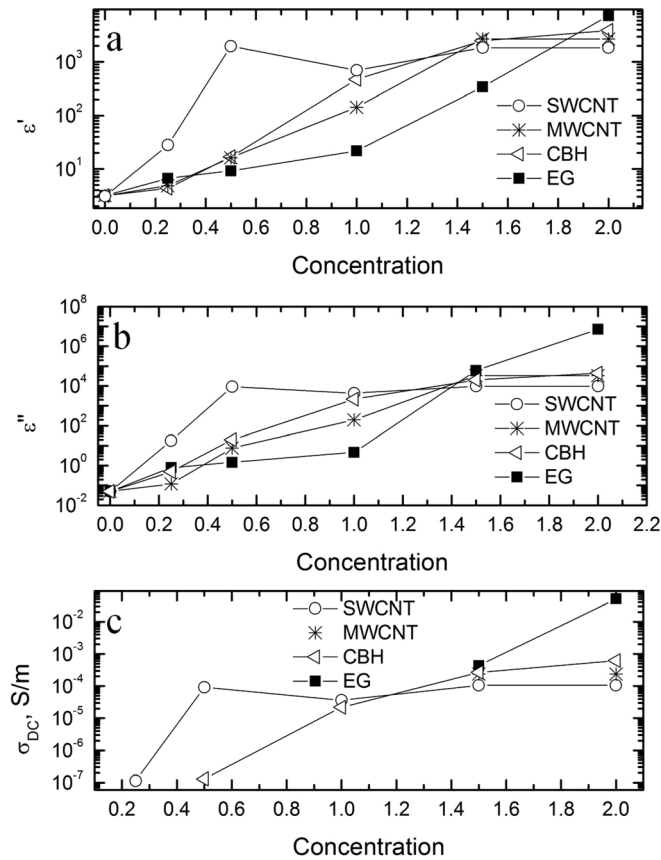


FIG. 5. Concentration (wt.%) dependence of (a) real and (b) imaginary part of the permittivity, and (c) dc conductivity of epoxy filled with CBH, EG, SWCNTs, and MWCNTs at 129 Hz.

value of epoxy/SWCNT conductivities above the percolation threshold is smaller than that of epoxy/MWCNT, epoxy/EG and even of epoxy/CBH samples, filled with 2 wt. % of carbon inclusions. This is because: (i) having higher number of conductive channels, isolated MWCNTs have lower resistance than isolated SWCNT of the same length,<sup>16</sup> (ii) the number of SWCNTs is several orders of magnitude higher than the number of MWCNTs, CBH, and EG particles in the same composites' volume and with the same wt. content of carbon additives. This fact assumes a higher number of contacts barriers between the nanotubes in SWCNT-based composites, which contribute significantly to the composites' resistivity.

#### D. Microwave probing

Experimental data for reflectance ( $R = S_{11}^2$ ), transmission ( $T = S_{21}^2$ ) and absorbance ( $A = 1 - R - T$ ) in K<sub>a</sub>-band are presented in Fig. 6. Microwave experiments show that the most effective additive for producing EM shielding with carbon-based epoxy resin composites is exfoliated graphite at 2 wt. % which is above percolation threshold. It provides almost 100% of EM attenuation due to 30% absorption of microwave power and 70% reflection. At the same time, according to results presented in Sec. III A, 2 wt. % of EG seems to be a critical concentration, considering the degradation of mechanical properties. When the carbon concentrations are relatively small (up to 0.5 wt. %), all functional

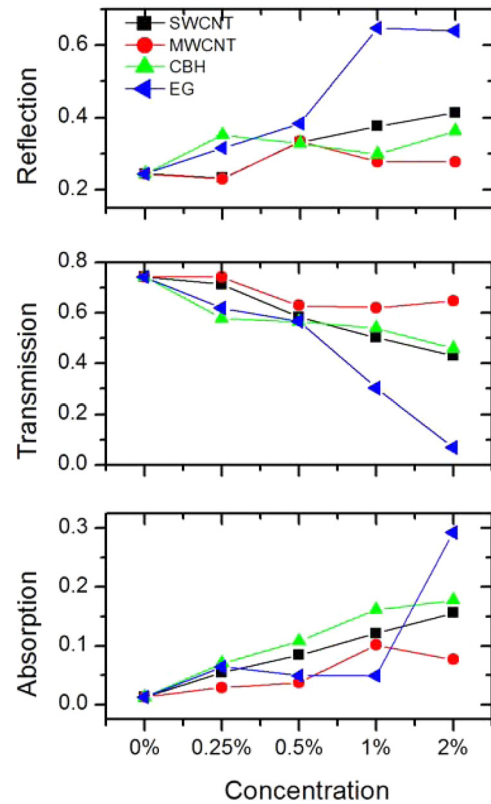


FIG. 6. Reflection, transmission, and absorption of 0.5 mm-thick epoxy filled with CBH, EG, SWCNTs, and MWCNTs at 30 GHz.

fillers provide approximately the same EMI shielding ability at the level of 2.5 dB. SWCNTs within 1.5–2.0 wt. % give attenuation of microwave signal at the level of 55%. It is interesting to point out that almost the same shielding ability is produced by large surface area-CBH particles. Moreover, CBH are also good for mechanical and thermal properties, which means that, if one does not need very high level of EMI shielding efficiency, using CBH could be worthwhile in comparison with much more expensive fillers, like CNTs. Moreover, in microwave frequency range, MWCNTs do not ensure high EM attenuation; their efficiency is lower than that of SWCNTs because of the screening of internal shells by the external ones.<sup>17</sup> Finally, as far as only some 5–10 walls out of 40 interact with microwaves, MWCNTs added to epoxy resin in 2 wt. % concentration produce only 40% of EMI shielding efficiency, which is the worse result out of all investigated carbon materials.

#### IV. CONCLUSIONS

- (i) Carbon fillers were found to improve slightly nanohardness and Young's modulus of epoxy nanocomposites within the studied composition range of 0.25–2.0 wt. % of nanofiller. Exfoliated graphite gave the best reinforcement effect, with a maximum improvement of 17.5% of Young's modulus. However, the mechanical properties of EG-epoxy composites degraded above 1.5 wt. % due to reduced dispersibility. Carbon black produced a continuous improvement of the nanohardness when increasing

the filler amount, reaching about 15% increase of the hardness at the maximum filler content. By comparison, single- and multi-walled carbon nanotubes did not considerably improve hardness and Young's modulus of the epoxy nanocomposites. The nanocomposite materials showed a brittle–ductile behavior.

- (ii) According to TGA data, all the investigated carbons fillers either improved slightly the thermal stability of carbon/epoxy composites or did not deteriorate it. The highest modification effect was observed for EG-containing epoxy composites.
- (iii) Electrical percolation started earlier for SWCNT composites (0.25 wt. % concentration). However, percolation in EG composites at 1.5 wt. % was very sharp and electrical conductivity of 2 wt. % EG/epoxy was two orders of magnitude higher than corresponding values for SWCNT composites. The absolute values of the permittivity as well as the conductivity for composites loaded with high surface area carbon black and MWCNT were very close, which means that, taking into account the observed good mechanical and thermal properties of CBH/epoxy composites, CBH could easily compete with commercial MWCNTs in different electrical and EM applications.
- (iv) EMI shielding efficiency was found to be the largest for EG/epoxy composites with 2 wt. % of filler (approx 12 dB), but this concentration was already critical for mechanical properties. SWCNT and CBH fillers gave similar EM attenuation, around 50% when embedded into epoxy at 2 wt. %. Due to high screening effect of inner shells, relatively thick MWCNTs (20–40 nm in diameter) did not provide effective EM shielding in microwave frequency range.

In conclusion, we found that electrical, EM, thermal and mechanical properties of both CNT- and CBH-based epoxy composites could be improved all together. There is good correlation between improved physical properties of CNT- and CBH-based composites for all investigated concentration ranges (0.25–2.0 wt. %), especially in favour of CBH for which the highest mechanical resistance along with improved ac conductivity and EMI SE ability were observed, being in the same level as those of SWCNT-composites. In the case of EG-based composites, simultaneous improvement of physical properties was observed for concentrations

below 1.5 wt. %. EG could be used for producing very effective thin and lightweight EM material in the  $K_a$ -band when the concentration of fillers reaches 2 wt. %, but for this content the mechanical properties started to degrade, which might perhaps be avoided by improving the fabrication process. Finally, CBH and sometime EG, being effective in microwave and low frequency ranges and at the same time being mechanically and thermally stable, might replace expensive CNTs for producing EM composite layers.

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