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Microstructure, elastic and electromagnetic properties of epoxy-graphite composites

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A set of epoxy resin-based composites filled with 0.25 – 2.0 wt.% of commercially available exfoliated graphite (EG) and thick graphene (TG), prepared by suspending EG particles in cyclohexane, and submitting the suspension to a series of grinding and ultrasonic dispersion steps, was produced. The microstructure of such epoxy-graphite composites has been studied by the impulse acoustic microscopy technique. According to acoustic microscopy data, exfoliated graphite microparticles have been well dispersed in the epoxy matrix. TG nanoflakes demonstrated persistent tendency to clustering and formation of agglomerates. The addition of graphite particles in small amount (0.25 – 2.0 wt.%) did not influence the bulk elastic properties of epoxy-graphite composite materials. Being extremely lightweight, 0.003 g cm^{-3}, EG had a lower percolation threshold than TG, at the level of 1-1.5 wt.% against 2.1-3.2 wt.%, respectively. As a result, epoxy composites filled with 1.0-2.0 wt.% EG provided high electromagnetic (EM) interference shielding both at microwave and THz frequencies. In contrast, no significant influence of TG loading was observed at low weight fraction (up to 2 wt.%) on the EM performance of epoxy composites. [http://dx.doi.org/10.1063/1.4922872]

I. INTRODUCTION

Conductive polymer composites find large-scale applications as antistatic materials, in printed electronics, supercapacitors, organic solar cells, biosensors, flexible transparent displays, etc.[1] Despite practical limitations due to limited processability and high manufacturing cost, *dc* and *ac* conductive composites are rapidly gaining attention in new applications such as packaging for electronics and chemical industry, metal replacement, heating elements and fuel cells. Conductive composites are also highly interesting for electromagnetic (EM) applications such as shielding and absorption in GHz and THz frequency ranges where traditional radar materials, if not completely inapplicable,[2] lose their attractiveness due to rising consumer wants. Efficient control of the parameters of THz and microwave radiation is a time-consuming task for applications such as homeland security, communications and medical imaging. One way of developing new advanced EM materials is to achieve the synergy of well-known properties of host polymers with new potentialities originating from the fillers. For a variety of applications, the nondestructive control of the structural and morphological properties of fabricated composites is necessary.

Graphite derivatives, i.e. expanded graphite and graphene nanoplatelets, have recently been proved to improve thermal conductivity, dielectric, mechanical and rheological properties of epoxy composites with up to 3 wt.% filler content.[3–5] The present communication is devoted to the preparation and to the characterization of epoxy resin filled with two types of graphitic particles, *viz* exfoliated graphite (EG) and "thick graphene" (TG), consisting of a few tens of graphene monolayers. The microstructure and elastic properties of the resultant composites were investigated by nondestructive impulse acoustic microscopy technique. The correlations between microstructure and elastic and EM properties of epoxy-EG and epoxy-TG composites were discussed.

II. MATERIALS AND METHODS

A. Composites preparation

EPIKOTE™ Resin 828 was used as composite matrix. 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 and high mechanical and chemical resistance in the cured state. Two series of composite samples, using Epikote 828, a curing agent called A1 (i.e., a modified TEPA) and 0.25, 0.5, 1.0, 1.5 and 2.0 wt.% of graphite fillers were fabricated as follows.[6] The resin was degassed under vacuum (1–3 mbar) for 12-14 h, and then was put into an oven at 65°C. In the meantime, the carbon filler was dispersed in propanol, and the suspension was submitted to an ultrasonic bath for 1.5 h. Afterwards, the alcoholic suspension of carbon was mixed with the resin. The obtained mixture was placed inside an oven at 130–150°C for evaporating the alcohol. The curing agent A1 was added to the mixture of resin and filler through slow manual mixing for about 7 min. The blend was then poured into moulds of dimensions 1 cm × 1 cm × 7 cm, and left as such for 20 h for the curing process at room temperature, and finally for 4 h in an oven at 80°C. When the process was completed, the samples were removed from the moulds.

The following graphite particles were used as fillers in epoxy resin:

- Exfoliated graphite (EG), see Fig. 1(a), was purchased from Mersen (France). It is a material of extremely low apparent density, around 0.003 g cm^{-3},[7] based on highly porous, accordion-like particles. Typically, the diameter of the EG particles is in the range 0.3-0.5 mm, and their aspect ratio is around 20.
- Thick graphene (TG), see Fig. 1(b), was prepared by suspending EG particles in cyclohexane, and submitting the suspension to a series of grinding and ultrasonic dispersion steps. After freeze-drying, disk-shaped particles, having diameter and thickness around 2-10 and 0.01 μm, respectively, were obtained.[8]

B. Impulse acoustic microscopy

The internal microstructure of epoxy-graphite composites was investigated with an impulse acoustic microscope SIAM-1 designed and produced by the Institute of Biochemical Physics, RAS. Long-focus (low-aperture) objectives at operation frequencies of 50 and 100 MHz were used to visualize the bulk microstructure of epoxy-graphite composites.

Acoustic imaging is based on using focused high-frequency ultrasonic probe beams and the raster (point-by-point) principle of image formation.[9] The bulk visualization is implemented in reflection mode of operation, i.e., the same ultrasonic focusing system is employed to generate a focused probe beam in immersion liquid and to receive echo signals reflected from an object. The application of ultra-short probe pulses provides selection of echo pulses reflected at different depths inside the object by their arrival time.[9,10] To get acoustical images, a plane-parallel object is placed into an immersion liquid (water) nearby the focal plane of the probe beam. A probe impulse of focused ultrasound partly reflects at the immersion-object interface, partly penetrates into the object and leads to echo pulses from elements of bulk microstructure and from the specimen bottom. Reflected radiation is received by the acoustic focusing system as a set of wavelets separated by

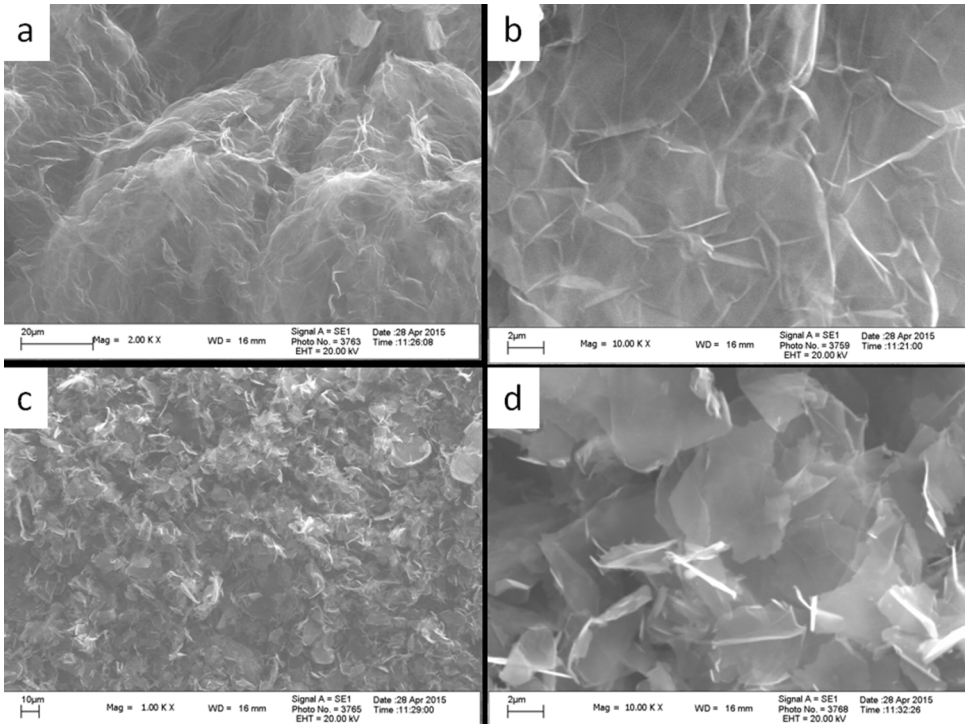

FIG. 1. SEM images of (a,b) EG, and (c,d) TG particles at different magnifications.

time intervals equal to the double of the time spent by the probe pulse to run the difference in depth positions of two corresponding structural elements. Acoustical images (C-scans) are formed by 2D scanning of the probe beam spot over the specimen surface. A pair of special switches in the electronic system of the microscope ("electronic gate") is used to set depth and thickness of any imaged layer inside the specimen bulk.

Elements of internal microstructure inside the object volume are seen in acoustic images as bright points, lines, or extensive spots against the dark background. Bright elements are formed by ultrasound reflected at interfaces or scattered by inclusions. The dark background corresponds to areas without any structural elements or defects. Acoustic images in epoxy/graphite composites are formed by longitudinal elastic waves only, transverse waves do not participate in imaging because of a very high level of their attenuation in epoxy.

The dimensions of exfoliated graphite (EG) particles (300 – 500 μm) are comparable with, or exceed, the ultrasound wavelength (30 – 60 μm). The interaction of incident radiation with EG particles is ordinary ultrasound reflection at the epoxy-EG particle interface. EG particles, as it is seen in scanning electron microscopy images (Fig. 1(a)), possess 3D cellular structure with micron-sized air-filled units. Such obstacles are excellent reflectors and scatterers of ultrasonic radiation because of the high difference between the acoustic impedances of epoxy matrix and hollow graphite particles. Therefore, the internal microstructure of EG-based composites was observed in acoustic images as a result of probe beam interaction with individual EG particles.

On the contrary, individual TG particulates could not be seen in acoustic images. TG thickness is $d \sim 80 – 120$ nm whereas its lateral size is up to 2 – 10 μm, which is significantly smaller than the wavelength of probe ultrasound. When the distribution of TG particles is uniform, there are no reflected or scattered signals coming from the nanocomposite interior. In this case, acoustic images should be uniformly dark. The occurrence of visible elements in these images indicates nanoparticle agglomeration in the composite bulk. Agglomeration of nanoparticles leads to clusters whose sizes exceed the planar dimensions of individual TG particles, but which remain small with respect to the ultrasonic wavelength. Agglomerates generate scattered radiation similar to point scatterers. In acoustic images, they appear as bright points or small spots.

Finally, there are essentially different mechanisms to form acoustic images of the inner microstructure of carbon nanocomposites, depending on both geometrical characteristics and nature of graphite particles used as filler. The structure observed in acoustic images of epoxy-EG composite interior is a distribution of large EG inclusions all through the composite bulk. For nanometrically-thin TG filler, acoustic imaging is an effective method for revealing nanoparticle agglomeration processes and characterizing the inhomogeneity of the composite material caused by nanoparticle clustering.

C. Electromagnetic characterization

The complex dielectric permittivity $\varepsilon^* = \varepsilon' - i\varepsilon''$ was measured by a LCR meter HP4284A in the frequency range 20 Hz – 1 MHz. The electrical conductivity σ was deduced from the following equation $\sigma = i\omega\varepsilon_0\varepsilon''$, where $\omega = 2\pi\nu$ and ν is the measurement frequency. The microwave measurements were provided by a scalar network analyzer R2-408R (ELMIKA, Vilnius, Lithuania), including sweep generator, waveguide reflectometer and indicator unit (personal computer). The IEC 62431:2008(E) standard, specifying the measurement method for the reflectivity of EM materials, was used. The EM response of samples was measured as ratios of transmitted/input (S_{21}) and reflected/input (S_{11}) signals in the 26-37 GHz frequency range (K_a-band). The accuracy was controlled by repetitive measurements for different orientations of the sample in the waveguide cross-section. Experimental reflectance (R), transmission (T) and absorbance (A) at room temperature were reconstructed according to the simple expressions $R = S_{11}^2$, $T = S_{21}^2$, and $A = 1\text{-}R\text{-}T$, respectively. In the frequency range from 100 GHz to 3 THz, measurements were performed by time-domain terahertz spectrometry (EKSPLA, Vilnius Lithuania) based on femtosecond laser (wavelength 1 μm, pulse duration less than 150 fs) and GaBiAs photoconductive switch as THz emitter and detector.

III. RESULTS AND DISCUSSION

A. Bulk microstructure

Bulk microstructure of epoxy-graphite specimens have been observed in 1.0 – 1.7 mm-thick plane-parallel specimens. Fig. 2 - 4 present typical internal microstructures of pure epoxy resin (Fig. 2), and of epoxy filled with EG (Fig. 3) and TG (Fig. 4).

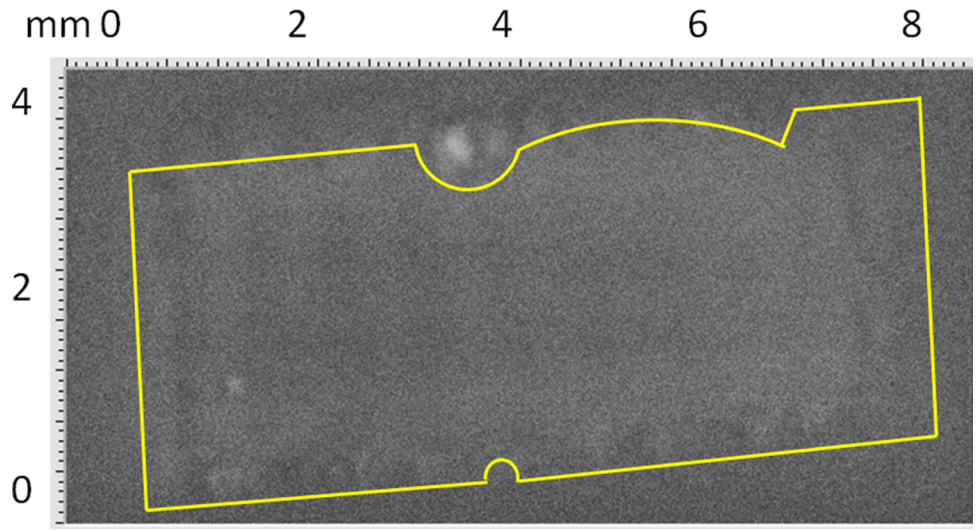

FIG. 2. Bulk structure of a 1.77 mm-thick pure epoxy resin specimen. The thickness of the imaged layer, located inside the specimen interior at the depth of 0.54 mm beneath specimen surface, was 190 μm. The yellow figure gives the specimen contour. No microstructural details are seen inside the imaged layer.

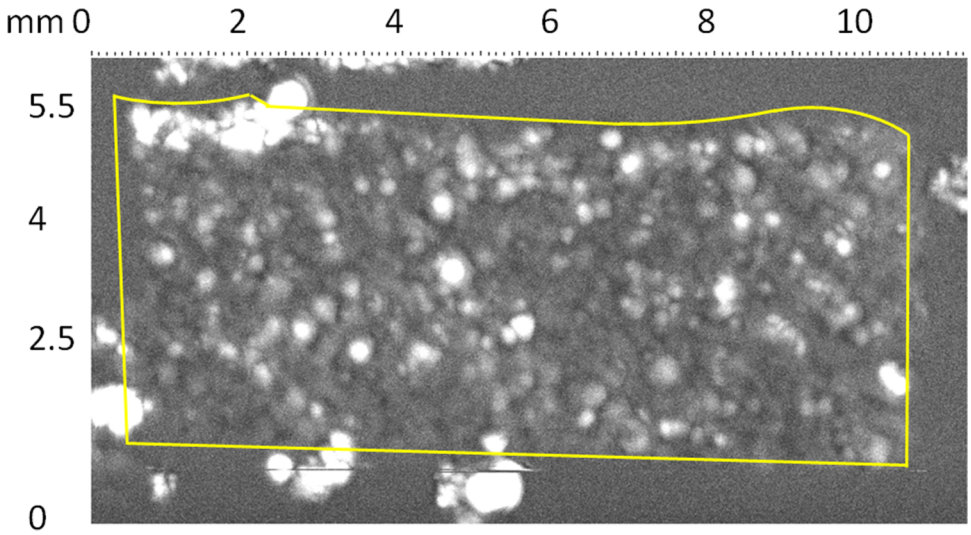

FIG. 3. Bulk microstructure of a 1.43 mm-thick epoxy + 1.5 wt.% EG composite specimen. The image gives the structure of a layer ≈ 220 μm thick at a depth of 0.41 mm beneath the specimen surface. The yellow figure gives the specimen contour. The many bright spots correspond to exfoliated graphite particles dispersed in the epoxy matrix.

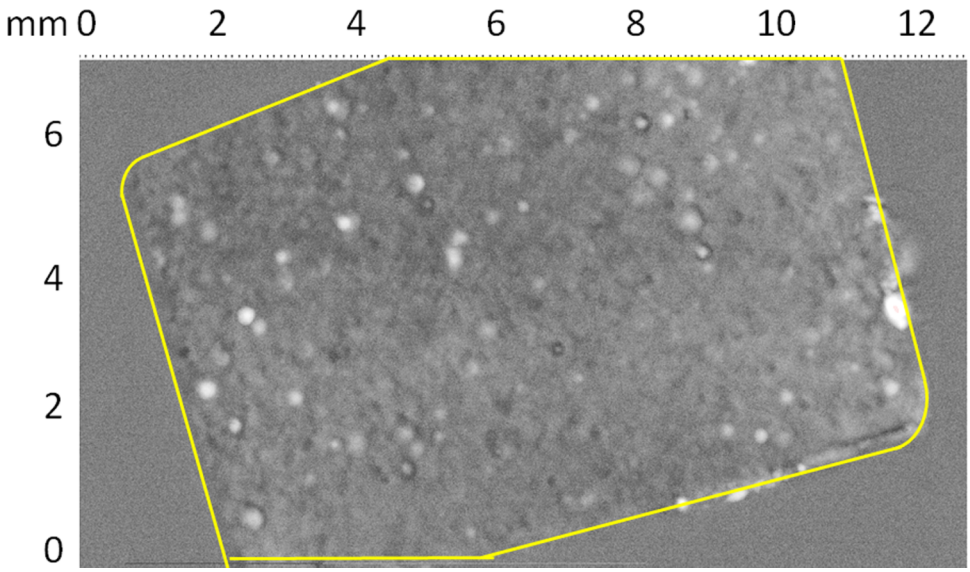

FIG. 4. Bulk microstructure of a 1.37 mm-thick epoxy+ 1.5 wt.% TG composite specimen. The imaged layer was 175 μm thick and at a depth of ~ 0.30 mm beneath the specimen surface. The yellow figure gives the specimen contour. Numerous agglomerates of graphene flakes in the material volume are seen.

The bulk microstructure of a pure epoxy sample was studied to estimate the contribution of epoxy matrix imperfections (air bubbles, inclusions, inhomogeneity induced by non-uniformity of epoxy curing process, etc.) in acoustic imaging of epoxy-based composites. As seen in Fig. 2, no visible details were observed in the bulk microstructure. This means that the matrix material has a negligible contribution to the bulk microstructure of nanocomposites. All details of acoustic images of bulk microstructure in epoxy-EG and epoxy-TG specimens therefore originate from probe beam interaction with graphite filler.

Peculiarities of bulk microstructure of the epoxy filled with 1.5 wt.% EG are shown in Fig. 3. The image gives the expected bulk microstructure of this material, showing large and medium-sized particles of exfoliated graphite distributed all through the specimen bulk. Most particles are bigger

than the probe radiation wavelength, and all particles are excellent ultrasound reflectors and scatterers because of their pore microstructure.

The most intriguing picture is represented in Fig. 4 for the bulk microstructure of the epoxy loaded with 1.5 wt.% TG. Numerous small bright spots distributed inside the specimen contour are seen in the image. Each spot corresponds to a particular scatterer situated inside the imaged layer. As justified above, individual flakes of TG cannot be seen in acoustical images, at least, at the frequency range that has been used in the present experiments. The occurrence of the "night sky picture" in Fig. 4 means that the bulk microstructure of the specimen under investigation includes numerous minute scatterers, whose sizes are substantially smaller than the probe ultrasound wavelength. Such scatterers could arise only owing to agglomeration of TG particles into porous clusters in which air remained trapped. The same high number of scatterers is present in the acoustic images of the internal microstructure of all TG-based nanocomposites in a wide range of TG flakes content, from 0.5 up to 2.0 wt.%. Agglomerates are not occasional defects of the composite preparation technology employed in our case. Graphene particle agglomeration processes are caused by natural reasons – much higher affinity of graphene particles between themselves, compared with their affinity with the matrix material – epoxy. Thus, the observation of the inner microstructure of nanocomposites provides the feasibility of investigating the agglomeration processes of 2D graphite nanoparticles in the bulk of such nanocomposites.

The obvious trend of 2D graphene nanoparticles to form micron-sized agglomerates differently affects the main physical properties of nanocomposites. For instance, agglomeration processes poorly changes their microwave properties, but there is a critical dependence of their *dc* conductivity on filler agglomeration. The conductivity is indeed intimately related to the formation of a continuous path made of graphene flakes in the material bulk. Therefore, flake agglomeration, i.e., poor dispersion, reduces its formation probability. Agglomeration should also affect the mechanical properties of nanocomposites. Enhancement of elastic and strength properties is usually connected with changes in the supramolecular structure of the polymer matrix nearby nanofiller particles.[11,12] Agglomeration of nanofiller might prevent such mechanism.

B. Elastic properties

Impulse focused ultrasound has been applied for measuring local values of the sonic velocity c in epoxy-graphite composites. The technique is based on the measurement of a delay time interval τ between echo pulses reflected from the specimen upper and lower surfaces within the focal zone of the probe ultrasonic beam. Such time interval corresponds to the round-trip time of probe pulse propagation through the specimen thickness and back. Independent data of the specimen thickness d allows finding a local value of the sonic wave velocity within the focal spot area in the specimen face: $c = 2d/\tau$. In our experiments, this experimental procedure was applied to measure the longitudinal elastic wave velocity c_L, presented in Table I.

As seen from Table I, the addition of graphitic filler did not change significantly the value of longitudinal sonic velocity c_L with respect to its value in pure epoxy resin. The same values of c_L were observed for all concentrations of both fillers (EG and TG).

Longitudinal sound velocity was derived from the longitudinal elastic modulus B using the equation: $c_L = \sqrt{B/\rho}$, ρ being the material's density. The modulus is a linear combination of two basic elastic characteristics, i.e., the bulk modulus K (inverse of the bulk compressibility β:

TABLE I. Elastic properties of epoxy-EG and epoxy-TG composites.

Material	Specimen thickness *d, mm*	Time delay of the L echo signal τ_L, μs	Calculated value of the longitudinal sound velocity c_L, km/s
Epoxy	1.74 ± 0.01 mm	1.20 ± 0.01 μs	2.90 ± 0.06 km/s
Epoxy + 1.5% TG	1.43 ± 0.01 mm	0.98 ± 0.01 μs	2.92 ± 0.06 km/s
Epoxy + 1.5% EG	1.37 ± 0.01 mm	0.95 ± 0.01 μs	2.88 ± 0.06 km/s

$K = 1/\beta$) and the shear modulus G. It reads:

$$B = K + \frac{4}{3}G.$$

In polymers, the shear modulus is essentially lower than the bulk one, i.e., $K >> G$. Correspondingly, the value of the measured sonic velocity c_L is essentially controlled by the bulk modulus K. Finding c_L values independent from the carbon filler content means that the addition of carbon particles did not lead to any enhancement of bulk elastic properties for the resultant composites. It is possible (see Refs. 13 and 14) that the shear elastic modulus G is more sensitive to presence and amount of carbon filler in epoxy matrix.

C. Electromagnetic characterization

It was found that the influence of graphene filler on physical and mechanical properties substantially depends on the average size (the aspect ratio of lamellar nanofillers) of dispersed fillers.[4,5] Here the percolation threshold of composites filled with graphite fillers has been estimated[10,11] according to procedures described in details in Refs. 15–19, based on either percolation or on effective-medium theories. All the size/geometry data of used graphite fillers along with the estimated percolation thresholds are gathered in Table II. The very low percolation thresholds in EG-based composites are mainly due to the very high porosity of the EG filler (higher than 99%).

The results of measured and reconstructed data of real and imaginary parts of dielectric permittivity at fixed frequencies in quasistatic (129 Hz), microwave (30 GHz) and THz (1 THz) regimes are presented in Table III. The standard procedure was used to convert measured *S*-parameters to dielectric permittivity spectra in the microwave frequency range.[20]

The *ac* conductivity of the same samples is presented in Fig. 5. It can be seen that, in the low-frequency range, the *ac* conductivity increased significantly for EG concentration above 1.0 wt.%. The conductivity indeed jumped by 9 orders of magnitude, with respect to the neat resin, for epoxy filled with 2 wt.% of EG. At the same time, TG-based composites did not demonstrate the percolation behavior expected from our theoretical estimations (see Table II). Microwave probing did not feel the influence of TG particles addition up to the highest concentrations analyzed in our experiments. In contrast, at high frequencies, 30 GHz, electromagnetic coupling already took place between particles, as the rise of the *ac* conductivity of EG-based samples already started at 0.25 wt.% and strongly increased with concentration up to 12 S/m at 2 wt.% of EG loading. The same trend was observed in the THz range, where the conductivity increased by ten times from 11 to 110 S/m for composites filled with 0.25 wt.% and 2 wt.% of EG, respectively. For all frequencies,

TABLE II. Fillers' lateral dimension, aspect ratio and estimated percolation thresholds.

Filler type	Lateral size, μm	Aspect ratio	Percolation threshold, vol.%	Percolation threshold, wt.%
EG	300-500	20	16-23	1-1.5
TG	2-10	100	1.1-1.7	2.1-3.2

TABLE III. Real \ imaginary parts of dielectric permittivity of EG- and TG-based composites at fixed frequencies in quasistatic (129 Hz), microwave (30 GHz) and THz (1 THz) regimes.

	EG			TG		
	129 Hz	30 GHz	1 THz	129 Hz	30 GHz	1 THz
0%	3.16\ 0.05	2.75\ 0.06	1.17\ 0.22	3.16\ 0.05	2.75\ 0.06	1.17\ 0.22
0.25%	6.68\ 0.79	3.58\ 0.20	1.65\ 0.35	3.59\ 0.125	2.97\ 0.06	1.14\ 0.15
0.50%	9.18\ 1.47	4.02\ 0.17	1.34\ 0.72	4.7\ 0.178	2.97\ 0.06	1.11\ 0.35
1%	21.8\ 4.69	6.93\ 0.42	1.63\ 1.01	6.03\ 0.205	3.33\ 0.07	1.09\ 0.47
2%	7406.6\7.14×10^6	30.48\ 12.38	1.15\ 3.65	9.14\ 0.4	3.84\ 0.09	1.10\ 0.38

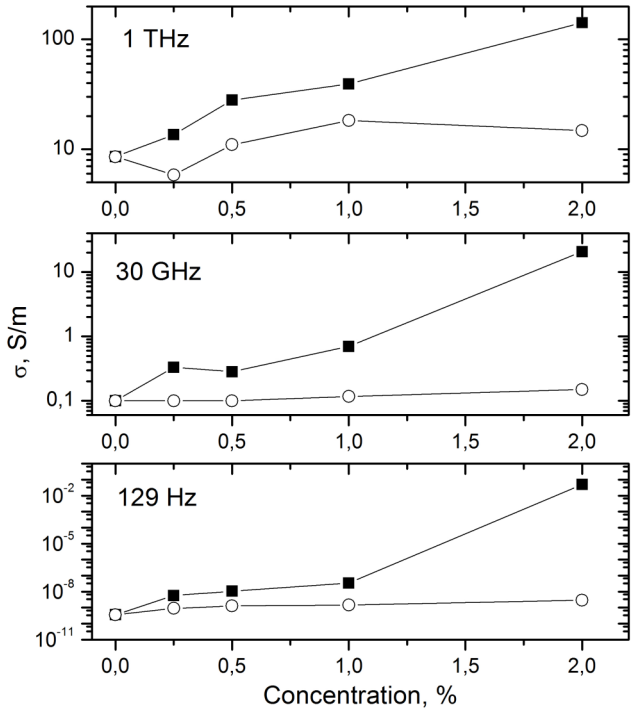

FIG. 5. *ac* conductivity (S/m) of epoxy-EG and epoxy-TG composites vs filler concentration in quasistatic (129 Hz), microwaves (30 GHz) and THz ranges (1 THz). Black squares and white circles correspond to EG and TG filler, respectively.

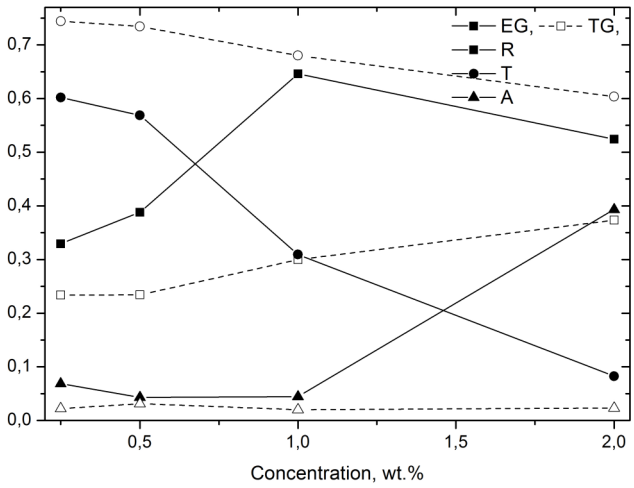

FIG. 6. Absorption (A), reflection (R) and transmission (T) of epoxy-graphite composites vs filler concentration at 30 GHz.

the TG concentrations investigated here were not high enough for observing high *ac* conductivities. In particular, at microwave frequencies (see Fig. 6), only 10% of microwave radiation could penetrate 0.5 cm-thick epoxy + 2 wt.% EG composite, whereas epoxy + 2 wt.% TG allowed 65% transmittance of microwave power.

IV. CONCLUSIONS

A set of epoxy resin composites filled with 0.25-2.0 wt.% of either commercially available exfoliated graphite (Mersen, France) or thick graphene (prepared by suspending EG particles

in cyclohexane, and submitting the suspension to a series of grinding and ultrasonic dispersion steps) was produced. The bulk microstructure of the epoxy-graphite composites was studied by the impulse acoustic microscopy technique. According to acoustic microscopy data, the interior of the epoxy-EG composites presents a sufficiently uniform dispersion of exfoliated graphite microparticles in the epoxy matrix. Acoustical images of the epoxy-TG composite interior evidenced a dense distribution of micron-sized scatterers that should be treated as agglomerates of graphene nanoparticles in view of the fact that acoustic microscopy is not able to display individual nanoparticles. Large-size agglomerated structures are not defects of the nanocomposite preparation technology used here, as TG nanoflakes demonstrate persistent tendency to clustering and formation of nanoparticle agglomerates. Local elastic measurements at micron resolution were performed to study bulk elastic properties of carbon-based composites and fillers distribution all through the material bulk. It was shown that the addition of graphite particles in different amounts (0.25 – 2.0 wt.%) did not influence the bulk elastic properties of epoxy-graphite composite materials. The elasticity of nanocomposites remained uniform in spite of the agglomeration of TG fillers.

Being extremely lightweight, 0.003 g cm^{-3}, EG has a lower percolation threshold than that of TG particles, 1-1.5 wt.% against 2.1-3.2 wt.%, respectively, which was supported by results of dielectric spectroscopy in the low-frequency range. As a result, epoxy composites filled with 1.0-2.0 wt.% EG should be very interesting materials for producing EM coatings for microwave and THz frequencies. A very important point is that such concentrations of EG are still acceptable for retaining good mechanical and thermal properties,[3–5,21–23] as the elastic properties of the epoxy composites remain the same as for the neat resin. The effect of higher percolation threshold for TG-based composites did not allow us to observe a significant influence of TG loading on the EM performances at low filler content (up to 2 wt.%).

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