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Electromagnetic properties of graphene nanoplatelets/epoxy composites

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ABSTRACT

Results of broadband dielectric spectroscopy of epoxy resin composites containing graphene nanoplatelets (GNP) are presented in a wide temperature range (25–500 K). The as-produced composites were heated at temperatures above the epoxy glass transition and subsequently cooled down to room temperature. This annealing was proved to be a simple but powerful process to improve significantly the electromagnetic properties of the GNP-based composites. The dc conductivity of epoxy filled with 4 wt% GNP is 68 times higher after annealing. Another benefit of the annealing is to lower substantially the percolation threshold, from 2.3 wt% for as-produced samples to 1.4 wt%. In composites above the percolation threshold, the electrical conductivity is the result of tunneling between GNP clusters. For a given GNP concentration, the tunnel barrier decreases after annealing.

1. Introduction

Polymer composite mixing bulk specific properties of the matrix—flexibility, resistance to corrosion, good processability, strong adhesion to different substrates, curing ability etc—and conducting properties from the fillers (ferrites, noble metals, carbon and graphite nano- and microstructures) have received a lot of attention during the last two decades [1]. These advanced materials find more and more applications in aerospace, automotive, energy, electronics, defense and health care sectors [2]. Among others, one of the most promising fillers used to produce conductive polymer composites is carbon in various forms: carbon black [3], graphene [4], microsized quartz coated by graphene [5] vapor-grown carbon fibers [6], multi-walled and single-walled carbon nanotubes [7,8], onion-like carbon [9]. A reason for that is the light weight, the chemical resistance and the high dc and ac conductivity of those structures.

To explore the electromagnetic (EM) applications of composites, it is important to measure and analyze their electrical conductivity and effective permittivity. Several theoretical models can be used for the analysis, such as the percolation theory [10], Maxwell–Garnett [11] and McLachlan [12] effective medium theories, and the generalized McLachlan-Jonsher theory [13]. The latter makes it possible to describe the frequency and concentration dependence of the complex effective permittivity. In parallel, computer simulations methods become more and more efficient nowadays to predict the EM properties of composites. Novel methods of calculation allow taking into account the geometry of filler [14] and it influence on AC conductivity of composite [15], make possible performing simulations for a wide range of volume fractions, permittivity ratios and packing conditions [16]. Many researchers have examined this subject by performing *ab-initio* calculations, for example with density functional theory (DFT) [17], or finite-element method (FEM) [18,19] and a combination of FEM and Monte-Carlo simulations [20,21].

Carbon nanotubes (CNT) based composites are extremely interesting for conductive applications. CNTs lead to very low percolation threshold (0.03–0.5 wt% depending on the CNT origin,

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the wall surface quality, the functionalization, the dispersion state) and yield huge effective permittivity and electrical conductivity values at all frequencies [22] including microwave and terahertz ranges. However, a drawback of carbon nanotubes is their higher cost in comparison with other carbon nanostructures such as different derivatives of graphite. Another serious disadvantage is the possible toxicity of CNTs, which has been debated for long [23]. This problem seems less critical with bigger and/or less slender carbon particles such as graphene nanoplatelets (GNP) [24].

GNPs are carbon nanostructures consisting of small stacks of graphene sheets with overall thickness from 1 nm to a few tens of nanometers, and lateral linear dimensions from a few micrometers up to hundreds of micrometers [25]. Graphene nanoplatelets are produced by thermal exfoliation of graphite intercalated compounds [26]. By contrast with CNTs, the GNP production process is easy and cheap. Without a proper surface treatment, GNPs might have poor interfacial adhesion with polymers because of lack of chemical bonding [24,27]. GNP functionalization can lead to better interfacial adhesion to polymer that improves mechanical [28] and thermal [29] properties of resultant composite, but at same time may deteriorate its electrical conductivity. Chemical treatments have been demonstrated improving the strength of interfacial interactions [30,31] without changing significantly the EM properties of their composites [24].

Exploring the EM properties of nanocarbon-based composites at low temperatures (below 300 K) is very important, for it gives information on the main electrical transport mechanism [7,32–34]. Also, the variation of EM properties of polymer/carbon composites with temperature are worth studying due to irreversible processes occurring near and above the glass transition temperature of the polymer matrices [35–37]. In this respect, the hysteresis of electromagnetic properties on heating and cooling cycles has already been reported for composites with carbon black [38], onion-like carbon [9] and CNTs [39]. Moreover, above the room temperature the electrical conductivity and the effective permittivity of composites above the percolation threshold can increase or decrease with temperature [40,41]. These effect can be related with particles redistribution or polymer matrix conductivity.

The objective of the present work was to check with complementary tools whether a thermal treatment may have significant and positive effects on the EM properties of epoxy resin loaded with small amounts of GNPs (up to 4 wt%). The paper is organized as follows: All the experimental details are collected in Section II. The results of broadband dielectric spectroscopy performed at room temperature (subsection A), high (subsection B) and low (subsection C) temperature are discussed in Section III. Conclusions are drawn in Section IV.

2. Experimental

Graphene nanoplatelets were produced by micro-cleavage exfoliation of expanded graphite. Expandable graphite was provided by Asbury® https://asbury.com/. Expandable graphite is manufactured by treating the flake graphite with various intercalation reagents that migrate between the graphene layers in a graphite crystal and remain as stable species. When exposed to a rapid increase of temperature, these intercalation compounds decompose into gaseous products as the result of high interlayer pressure. The internal stress is strong enough to push apart graphite basal planes along the *c* axis. Asbury expandable graphite exhibits a micro and submicron lamellar structure, an example of which revealed by SEM is shown in Fig. 1 (a). After micro-cleavage exfoliation, induced by microwave irradiation [42–46], a porous structure is visible in the SEM micrograph reproduced in Fig. 1 (b). A gentle treatment with ultrasound bath destroys the superstructure, releasing GNP.

In this work, series of composite samples were produced using Epikote 828, a curing agent called A1 (i.e., a modified TEPA) and 0.25, 1, 2, 3 and 4 wt% of GNP filler. The procedure of composite manufacturing is described in details elsewhere [8,38]. In summary, the resin was degassed under vacuum (1–3 mbar) for 12–14 h, then was put into an oven at 65° C. In the meantime, the GNPs were dispersed in propanol, and the suspension was submitted to an ultrasonic bath for 1.5 h. Afterwards, the alcoholic suspension of GNPs 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 molds of dimensions $1 \times 1 \times 7$ cm^3, and left as such for 20 h for the curing process at room temperature, and finally 4 h in an oven at 80° C. When the process was completed, the samples were removed from the molds. After curing at room temperature, the samples were treated for 4 h in an oven at 353 K.

Dielectric properties of the samples where measured in the frequency range 20 Hz–1 MHz with a LCR HP4284A meter. For low-temperature measurements (25–300 K), the samples were placed in the closed-cycle cryostat. Measurements at high-temperature (300–500 K) were performed in a home-made furnace. All measurements were performed in air with heating/cooling rate 1 K/min without isothermal annealing. The samples cut from the $1 \times 1 \times 7\ cm^3$ molded composite had a thickness of about 2 mm and the square-shaped cross section of area 30 mm^2. Silver paste was applied for contacting.

In the frequency range 1 MHz–3 GHz, two different experimental setups were used depending on the GNP concentration. Samples containing 2 wt% and more GNP were analyzed by a coaxial dielectric spectrometer with vector network analyzer Agilent 8714ET. Here, sample with typical area of 2 mm^2 and thickness of 0.3 mm were studied. Epoxy composites with lower GNP concentration were analyzed with E5071C ENA Network Analyzer setup. For measurements of the scattering *S* parameters, an airline cell containing toroidal sample was placed in coaxial line between two ports of the vector network analyzer. The standard procedure was used to convert the *S* parameters into the complex permittivity ε of the material [47].

The microwave measurements in the 26–37 GHz frequency range (K_a-band) were carried out with a scalar network analyzer R2-408R (ELMIKA, Vilnius, Lithuania). For small concentrations (2 wt% and lower), parallelepiped samples of typical thicknesses 1.2 mm were precisely cut to fit the waveguide cross section. Samples with higher concentrations were shaped in cylinders of diameter $d = 0.4$ mm. The EM response of the composites were measured as the ratios of transmitted/input (S_{21}) and reflected/input (S_{11}) signals. The conductivity was recalculated from the *S* parameters via methods described elsewhere [48,49]. For shielding measurements 2 mm thick parallelepiped samples were precisely cut to fit the waveguide cross section 7.2 mm × 3.4 mm. The reflectance(R), the transmittance (T) and the absorbance (A) were calculated from S-parameters in following way: $T = S_{21}^2$, $R = S_{11}^2$, $A = 1 - R - T$.

Measurements at frequencies ranging from 100 GHz to 2 THz were performed in transmission mode using a time-domain THz spectrometer TERAVIL T-SPEC based on an femtosecond laser system. Large-area, polished parallel plates of 0.5 mm-thickness were investigated.