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Effects of sonochemical modification of carbon nanotubes on electrical and electromagnetic shielding properties of epoxy composites

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ABSTRACT

Electrical and electromagnetic interference shielding properties of epoxy/multi-walled carbon nanotube (MWCNTs) composites are studied for low nanotube contents from 0.03 to 0.3 wt.% and different processing conditions. *In situ* chemical modification of carbon nanotube surfaces was achieved by ultrasonic irradiation of carbon nanotubes either in polyethylene polyamine or in liquid epoxy resin, resulting in amine-grafted or epoxy-grafted composites, respectively. Raman, TGA, and SEM analyses indicate a successful grafting of polymer chains to the nanotube surfaces. The amine-grafted MWCNT/epoxy composites show the presence of a thick polymer layer that has formed an extra phase on the carbon nanotube walls, which affects significantly the electrical conductivity and radio frequency response properties. Hence, the amine-grafted composites demonstrate a slightly higher percolation threshold (p_c = 0.08 wt.%) and, at the same time, a lower absolute values of dc-conductivity as compared to that of the epoxy-grafted composites, with p_c = 0.05 wt.%. In the radio frequency range, almost 3 orders of magnitude rise of the values of ac-conductivity was observed for small contents of the amine-grafted MWCNTs in epoxy. The epoxy-grafted composites could be proposed for producing effective antistatic and electrostatic dissipation coatings. Around and above the percolation threshold, the amine-grafting is critical in the radio frequency range for producing coatings with large dielectric losses. The absolute values of microwave attenuation were found to be independent of the surface modification procedure, but strongly dependent on the concentration of MWCNTs and the thickness of the composite layer.

1. Introduction

The use of carbon nanotubes (CNTs) as a filler in epoxy resin has attracted great attention due to the possibility to improve the composite properties for applications ranging from microelectronics to aerospace. The dispersion states of carbon nanotubes, the amount and the aspect ratio determine how easily CNTs can interact with each other to build an interconnecting network of percolation that can transfer phonons and electrons to enhance the properties of the nanocomposite [1–3]. As seen from the reviewed literature [4–8] and our previous studies [9–10], chemical functionalization of nanotube surfaces improved the compatibility of CNTs in epoxy resin and has a positive influence on rheological, electrical, thermal, mechanical, optical and other properties of polymer composites with MWCNTs. Guadagno et al. [8] found that chemical functionalization of MWCNTs leads to the formation of an interface with stronger interaction; this causes a significant decrease in the electrical conductivity of the composite with respect to the untreated MWCNTs which is explained in terms of tunnelling resistance between interacting nanotubes.

A variety of strategies have been developed for surface functionalization of CNTs resulting in bonding of different functional groups on their surfaces [4]. The grafting of polymer brushes to a solid surface is a useful technique which provided a versatile tool for surface modification [3]. A thin polymer brush layer on the solid surface is formed, which determines the surface properties. Recently, the sonochemical method was found to functionalize effectively the CNTs [11], as well as to produce polymer grafted carbon nanotubes [3,12]. The ultrasonic cavitation can produce violent collapse of bubbles and high-energy inter-particle collisions, generating high temperatures and high pressures together with implosion shock waves and micro jets in the liquid media.

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The combined effect is able to provoke chemical reactions on the CNT.

In recent years polymer composites with carbon nanotubes have gained a big momentum due to its potential applications as novel electromagnetic (EM) materials. The analyses of electromagnetic interference (EMI) shielding efficiency (SE) of those composites [13,14] show that the well dispersed CNTs formed electrically conductive network in polymer. The energy of electromagnetic waves was attenuated in network resistors, which is similar to the resistive type of wave absorption materials. The reviewed results confirm that nanocarbon fillers in epoxy demonstrate big potential in industrial applications for microwave absorption [15–19].

To our knowledge, detailed investigations of the sonochemical modification of CNT surfaces in epoxy resin and the effects on the EM performance of the composites have not been reported in the referred literature. The proposed study applies ultrasound irradiation for *in situ* surface modification of CNTs in one step processing of the epoxy nanocomposite. The grafting polyethylene polyamine and epoxy chains to the MWCNT surfaces and the effects on the dispersion, the filler matrix interfacial interactions, and the electrical and electromagnetic shielding performance of composites are studied. Raman and TGA analyses are used to characterize the functionalized MWCNTs. The dispersion states of CNT composites and the interfacial interactions are investigated by rheology and SEM. The combined effects of nanotube content and interfacial interactions on the EM shielding properties in a wide frequency range, as well as the dc- and ac-conductivity are studied in view to the application of these composites.

2. Experimental

Multi-walled carbon nanotubes synthesized by CVD technique [2] having external diameter ~30 nm and approximate length 10–20 μm were used. The D.E.R. 321 (Dow Chemical) chosen as a polymer matrix is ortho-cresyl glycidyl ether diluted standard bisphenol-A based liquid epoxy resin, of extremely low viscosity (η = 500–700 mPa s at 25 °C). The polyethylene polyamine (PEPA) (η = 200–300 mPa s at 25 °C) was used as hardener. A simple sonochemical method was employed for *in situ* surface modification of carbon nanotubes in one step processing. Pristine MWCNTs were mechanically dispersed for 30 min at 9000 rpm in the liquid epoxy resin (which is a standard processing protocol), as well as in the polyethylene-polyamine hardener resulting in two types of dispersions: DER321/MWCNT and PEPA/MWCNT, containing various amount of nanotubes. Then, intensive ultrasonic irradiation of the upper dispersions at 250 W for 60 min in 40 °C temperature bath was applied to provoke grafting of epoxy and polyethylene-polyamine chains to the carbon nanotube surfaces, which resulted in *epoxy-grafted* (MWCNT-e) and *amine-grafted* (MWCNT-a) carbon nanotubes in the respective dispersions. Solid composites were then fabricated by curing of the irradiated dispersions, DER321/MWCNT and PEPA/MWCNT, with the addition to them of appropriate amount of the second component (hardener and epoxy resin, respectively), at the molar ratio 70:30 (DER321:PEPA). The process of curing takes 2 h at ambient conditions, followed by post curing for 2 h at 100 °C. As a result, bulk 1 mm thick samples of *epoxy-grafted* (ER/MWCNT-e) and *amine-grafted composites* (ER/MWCNT-a) were prepared with different nanotube contents varying from 0.03 wt.% to 0.3 wt.%, hereinafter called ER/0.03MWCNT-e – ER/0.3MWCNT-a, where numbers correspond to MWCNT concentration. As it was reported in our previous study [9], dc-conductivity (σ_{DC}) of ER/MWCNT-e composites is somewhat higher than that of ER/MWCNT-a, e.g. 2.1×10^{-8} and 7.5×10^{-6} vs. 3.0×10^{-9} and 2.3×10^{-6} [S/cm] for 0.08 wt.% and 0.3 wt.% of MWCNT inclusions respectively. Along with the higher σ_{DC} absolute values in case of using epoxy-grafted MWCNTs as functional filler, the tendency of shifting the electrical percolation threshold to the higher weight concentrations was also observed, i.e. p_c = 0.03–0.05 wt.% and 0.05–0.08 wt.% for ER/MWCNT-e and ER/MWCNT-a correspondently.

The termogravimetric analysis (TGA), mass spectroscopy and Raman spectroscopy were used to investigate if grafting on the MWCNTs had successfully occurred. A Seteram Labsysis Evo 1600 instrument was used for recording of thermo diagrams from room temperature up to 1000 °C. The heating rate was 10°/min in air atmosphere under an air flow of 20 mL/min in order to determine the released gas phases during the increase of temperature by the mass spectrometer OminStar Preffer vacuum. The following released gas phases are monitored: O_2, N_2, NH_3, H_2O, CO_2, and Ethanol. The Raman spectra were obtained at 632 nm excitation line in the near backscattering geometry on a LabRAM HR spectrometer.

The rheological behavior of the curing dispersions was studied using cone-plate rheometer in an oscillatory mode with angular frequency from 0.1 to 100 s^{-1} and strain amplitude of 0.01 rad, being in the range of linear viscoelasticity.

The fracture morphology of the cured composites was studied by scanning electron microscopy (SEM, FEI Quanta 600F, at CfAM, University of Reading, UK) in micro- and nanoscale at various magnifications. Samples were cut in liquid nitrogen and coated with vacuum evaporated chromium.

Complex dielectric permittivity $\varepsilon = \varepsilon' - i\varepsilon''$ was measured as a function of frequency (1 kHz–1 MHz) at room temperature using an HP4284A precision *LCR* meter. The sample was placed in a home-made furnace between two conductors. The capacitance and loss tangent formalisms were selected to illustrate the obtained data of dielectric analysis.

The microwave measurements were carried out with a scalar network analyzer R2-408R (ELMIKA, Vilnius, Lithuania). 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_a-band). The frequency stability of the oscillator was controlled by frequency meter and it was as high as 10^{-6}. The power stabilization was provided on the level of 7.0 mW ± 10 μW. Measurement range of EM attenuation was from 0 to −40 dB with a basic measurement error of 7% over the range 0–25 dB. The accuracy was controlled by repetitive measurements for different orientations of the sample in the waveguide cross-section. The samples were cut precisely to fit the waveguide of cross-section 7.2 × 3.4 mm. The measurements were performed for free standing 1 mm thick bulk samples.

3. Results and discussion

3.1. Sonochemical modification of MWCNTs

3.1.1. TGA and mass spectroscopy

Ultrasonication is used in this study as an effective method to disperse MWCNTs in low viscosity matrix with a potential to produce *in situ* surface modification by grafting organic chains from the dispersion media to the nanotube surfaces. In order to prove the grafting process the pristine MWCNTs (0.1 g) were dispersed in the liquid epoxy resin DER321 as well as in the polyethylene-polyamine hardener PEPA (100 ml, 0.1% concentration) by mechanical mixing for 30 min at 9000 rpm followed by ultrasonic irradiation at 250 W for 60 min in 40 °C temperature bath. Two dispersions were then dissolved with acetone and filtered. The residue (treated MWCNTs) was washed 5 times with acetone to remove excess disperse matrix and then with distilled water till