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A contribution from dielectric analysis to the study of the formation of multi-wall carbon nanotubes percolated networks in epoxy resin under an electric field

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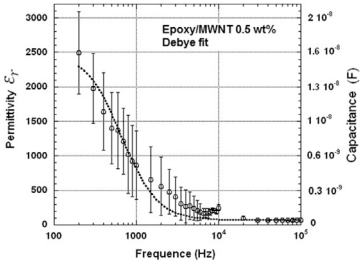
HIGHLIGHTS

- We report the formation of percolating networks of MWNTs under AC electric field.
- MWNT/epoxy dielectric properties were measured by impedance spectroscopy.
- Lower percolation thresholds were obtained for composites with aligned CNTs.
- Application of AC electric field helps the debundling of CNTs.
- CNT/Epoxy with percolated networks presents interfacial and hopping polarizations.

GRAPHICAL ABSTRACT



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ABSTRACT

The formation of percolation networks in epoxy matrix nanocomposites reinforced with multi-wall carbon nanotubes (MWNT) during the curing process, at different MWNT contents, was studied by using a parallel plate cell subjected to a 300 V/cm AC electric field at 1 kHz. The percolation was verified by the electrical current output measured during and after the resin curing. The behavior of electric dipoles was characterized by impedance spectroscopy and followed the Debye first order dispersion model, by which an average relaxation time of 6.0×10^{-4} s and a cut-off frequency of 1.7 kHz were experimentally found. By applying the theory of percolation, a critical probability, p_c, equal to 0.038 vol% and an exponent of conductivity of 2.0 were found. Both aligned and random samples showed dipole relaxation times typical of interfacial and/or charge-hopping polarization, while the permittivity exhibited an exponential decrease with frequency. This behavior can be related to the increased ability to trap electrical charges due to the formation of the carbon nanotubes network. Optical and electron microscopies confirm the theoretical prediction that the application of an electric field during cure helps the process of MWNT debundling in epoxy resin.

1. Introduction

Carbon nanotubes (CNTs) are cylindrical structures with very high aspect ratio and surface area, having unique transport and mechanical properties [1,2]. CNTs can present conducting or

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semiconducting properties [3,4], which allows a wide range of applications in electronic materials, such as polymer matrix nanocomposites with electromagnetic shielding (EMI) and electrostatic discharge (ESD) properties, presenting bulk conductivities between 10^{-9} S/m and 10^{-1} S/m [5,6].

The electrical conductivity in polymer/CNT nanocomposites is generally explained by nanotube network formation, allowing the percolation of electric currents through the material. Even at low concentrations (<1 wt%), CNTs can increase the conductivity of epoxy matrices up to ESD levels [7,8]. However, to achieve high electrical conductivities at low CNT contents and better capability to shield electromagnetic waves, the alignment of CNTs is important [9–11].

Several experimental studies [12–15] show that AC or DC electric fields can help alignment and separation of nanotubes dispersed in polymer matrices, since these particles may be polarized and could be able to rotate or to translate in the presence of an electric field. The observed polarization can be attributed to the delocalized vibration of π electrons of the sp^2 carbon atoms and should increase the process of repulsion between two parallel CNTs [16]. An outstanding review on this topic has been recently published [17].

Most of the alignment methods are based on AC external electric fields that can induce a dipole moment on metallic CNTs [18], which tend to align parallel to the field [19]. For a more comprehensive understanding of the process, and to know how the electric field influences charge migration and electric dipole reorientation in the nanocomposites, the measurement of the dielectric properties, such as permittivity, dielectric constant, and relaxation time, is essential. Another important factor is related to the cut-off frequency, which indicates the frequency at which the induced dipoles still respond to AC electric fields stimuli. At higher frequencies the alternating field is much faster than the speed of interfacial charges thus undermining the process of polarization and the possibility of jumping or tunneling of charges between sites [13,14]. Moreover, AC fields can promote, in addition to the nanotube alignment, a better dispersion of CNTs in the matrix, when compared to DC fields [10,12]. This is also a relevant issue, as one of the major technological obstacles for using CNTs is to debundle them, which is a serious limitation for making nanocomposites, nanocircuits and nanotransistors.

Yet many other factors influence the electron conductivity of the nanocomposites, including the polymer crosslinking process, which is directly linked to the matrix stiffness, and the interaction between the nanotubes and the matrix [8,19–21].

Nevertheless, there is a gap in the literature about the determination of the dielectric parameters (permittivity, relaxation time, cut-off frequency) for aligned multi-walled carbon nanotubes (MWNT) networks in epoxy nanocomposites over a wide frequency range. Thus, in this work, epoxy/MWNT systems were submitted to sinusoidal AC electric fields, during the curing process, to induce the alignment of nanotubes and to evaluate the influence of the crosslinking degree and CNT content on the formation of carbon nanotube networks. The systems were further characterized by electrical measurements (AC and DC electrical conductivity, electric hysteresis, electric permittivity, relaxation time of dipoles and capacitance) and morphological analyses (optical, transmission and scanning electron microscopies). The percolation threshold of the systems was determined according to the classical theory of percolation.

2. Experimental

2.1. Materials

The carbon nanotubes (MWCNT - CVD), used in this work were produced by Bayer Baytubes® and have a purity of 95%. Their diameters range from 5 to 20 nm and lengths of 1–10 μm. The polymer matrix consisted of bisphenol-A-based epoxy resin (Araldite GY 251) with an amine-based hardener (Aradur HY 956), obtained from Huntsman Advanced Materials. The solvent used was analytical grade acetone (Cinetica Quimica-Brazil).

2.2. Preparation of nanocomposites

Initially, the MWNT were dispersed in acetone by sonication (Sonics 750 W) and magnetic stirring, for 30 min at a power of 166 W. The epoxy resin was then added, followed by sonication and magnetic stirring for 40 min at a power of 250 W. The removal of solvent was carried out by heating the system under vacuum for 2 h. The samples were then cooled down to room temperature and the curing agent was added, at a 5:1 (w/w) epoxy:hardener ratio, and the system homogenized for 5 min.

The epoxy/MWNT dispersion was transferred to a polytetrafluoroethylene circular cell (6 mm thick) with two aluminum electrodes with an area of 45.4 cm^2. Samples introduced into the cell were subjected to sinusoidal electric fields with a frequency of 1 kHz, during the curing process.

2.3. Characterization

The electrical properties investigated in this work were: AC bulk conductivity during the curing process, DC conductivity (after curing), electrical permittivity (relaxation time of induced dipoles), and electrical capacitance.

Fig. 1 shows the experimental scheme used to determine the AC bulk electrical conductivity of the sample during the curing process (4 h). A sinusoidal generator with adjustable amplitude and frequency linked to an amplifier power (gain of 50 V/V and bandwidth of 200 kHz) was used to provide the electric field. The acquisition of the electric current was performed by using a True RMS ET-2907 Multimeter (Minipa) attached to a PC computer.

The DC electric conductivity was carried out through a DC voltage generator and an ammeter (Minipa). The measurements of voltage and electric current were made with sputtered gold electrodes (26 mm^2) in epoxy/MWNT systems with thickness of 1 mm, using three different samples for each composition. The permittivity values were obtained through phase analysis between voltage and current with the support of a Tectronics 2024B oscilloscope. DC conductivity and permittivity measurements were carried out at room temperature after 48 h of the curing process.

Characterization and comparison of clusters morphology were made by transmission optical microscopy (TOM) using an OLYMPUS CX31 microscope. Transmission electron microscopy

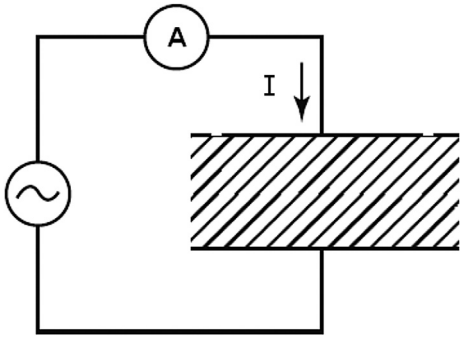

Fig. 1. Experimental scheme used to determine the AC electrical conductivity during the curing of epoxy/MWNT systems.