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The electronic transport properties and microstructure of carbon nanofiber/epoxy composites

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Abstract

Carbon nanofibers (CNF) were dispersed into an epoxy resin using a combination of ultrasonication and mechanical mixing. The electronic transport properties of the resulting composites were investigated by means of impedance spectroscopy. It was found that a very low critical weight fraction ($p_c = 0.064$ wt%) which may be taken to correspond to the formation of a tunneling conductive network inside the matrix. The insulator-to-conductor transition region spanned about one order of magnitude from 0.1 to 1 wt%. Far from the transition, the conductivity increased by two orders of magnitude. This increase and the low value of the conductivity were explained in terms of the presence of an epoxy film at the contact between CNF. A simple model based on the CNF–CNF contact network inside the matrix was proposed in order to evaluate the thickness of that film.
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1. Introduction

Carbon nanofibers (CNF) are hollow cylinders with diameters around one hundred nanometers and lengths of a few tens of microns giving high aspect ratios (length/diameter > 100). CNF are the cheaper counterpart of carbon nanotubes (about 3–500 times cheaper, respectively, when compared to multi-wall (MWNT) or single-wall carbon nanotube (SWNT)). They have a larger diameter (2–100 times, respectively, compared to MWNT or SWNT) and are less crystalline (with a kind of cup-stacked or stacked coins structure), while keeping acceptable mechanical and physical properties (Young modulus ~500 GPa, tensile strength ~3 GPa, electrical conductivity ~10^3 S/cm, thermal conductivity ~1900 W m^{-1} K^{-1}). They are expected to be a promising nanofiller for the preparation of composites with multiple enhanced properties. Many studies related to the enhancement of the mechanical properties of an epoxy matrix by the introduction of CNF have been conducted [1–6,10]. Some studies were dedicated to the electrical properties of CNF/epoxy composites [8–13] and a general review of the properties of CNF-based composites has been published [7]. Because of their high aspect ratio and of van der Waals attractive interactions arising at the nanoscale, CNFs are tangled and form aggregates of different sizes which makes their homogeneous dispersion inside the matrix one of the main hurdles. For this reason, most of the research work published so far on the electrical properties of CNF-based composites focused on relatively high loadings, usually higher than 2 wt%, and aimed to obtain a high conductivity without determination of the critical weight fraction at which the system becomes conductive. In the literature, different preparation methods have been used to disperse CNF inside an epoxy resin and they led to different levels of electrical conductivity of the composites. The use of ultrasonication [10,11] gives a higher level of conductivity, up to 1.2×10^{-2} S/cm at 10 wt% loading [10], compared to mechanical mixing [8,9] giving rise to a maximum conductivity of 2×10^{-5} S/cm at 8 wt% loading [8]. Almost no data were published for

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CNF loading lower than 1 wt%. In the present paper, a method combining ultrasonication and mechanical mixing was used to prepare composites at different weight fractions, from 0.066 to 9 wt%, and their electrical properties were investigated by impedance spectroscopy. A complete picture of the electrical properties of a CNF/epoxy composite is given, including the vicinity of the insulator-to-conductor transition and the region far from the transition.

2. Experimental

2.1. Materials

Heat treated graphitized CNF (Pyrograf III PR24LHT) with diameters in the range of 60–150 nm and lengths between 30 μm and 100 μm, were obtained from ASI (Fig. 1). A low viscosity diglycidyl ether of bisphenol-A (DGEBA) epoxy resin ($\eta \sim 0.7$ Pa s) with triethylenetetramine (TETA) hardener (Epofix, Struers) was used. The stoichiometric ratio was 100:12 (w/w) epoxy resin:hardener.

2.2. Sample preparation

The as-received CNF powder contained many large clumps with sizes in the mm range. Sieving as reported elsewhere [13,14] was used as a standard debulking method. The CNF powder was manually pushed through a 0.5 mm sieve. Carbon nanofibers were then dispersed in acetone in a concentration of 0.3 vol% using tip ultrasonication in pulse mode (30 pulses per min) combined with mechanical mixing. The epoxy resin was diluted in acetone (1:4 in volume) and then added to the CNF solution. The mixture was again submitted to ultrasonication in pulse mode (30 pulses per min) combined with mechanical mixing for 4 h. Solvent was removed by heating under continuous mixing. A masterbatch containing 10 wt% of CNF was obtained in that way. Composites with different CNF loadings ranging from 0.066 to 9 wt% were prepared by dilution of the masterbatch with the right amount of resin. The mixture was mixed under vacuum with a Thinky mixer at 2000 rpm. The hardener was added, the mixture was again mixed under vacuum, then cast into a mold and cured at 120 °C for 2 h. Disk-shaped samples with diameter 25 mm were obtained and polished down to a thickness around 1 mm.

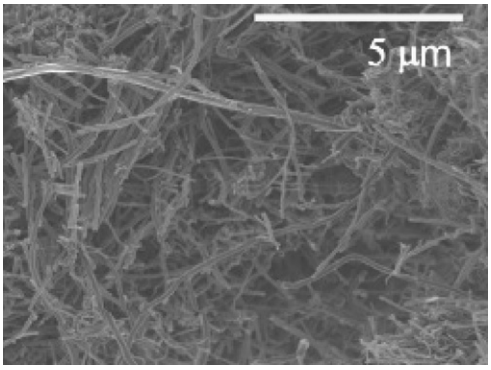

Fig. 1. Scanning electron micrograph of the carbon nanofibers.

2.3. Impedance spectroscopy

The electrical properties were investigated using a dielectric analyzer (TA Instrument DEA 2970) in ceramic parallel plate mode. All experiments were performed at room temperature and at testing frequencies ranging from 1 to 10^5 Hz. Nitrogen gas was used to provide an inert environment at a flowing rate of 500 ml/min. The sample was placed between two gold electrodes, a load (300 N) was applied and the thickness was measured with the built-in LVDT (linear voltage–displacement transducer) with a precision of 1 μm. A low amplitude sinusoidal voltage (V_{applied}) was applied and the current (I_{measured}) through the sample was measured. The AC conductivity is given by

$$\sigma_{\text{AC}} = \frac{I_{\text{measured}}}{V_{\text{applied}}}(\cos\delta)\frac{e}{A}$$

with δ being the phase angle shift, e being the thickness and A the surface area of the sample.

3. Results and discussion

3.1. Microstructure

Light transmission optical micrographs at low magnification permitted the observation of the gradual formation of a complex network and the global homogeneity of the sample. As the weight fraction increased, the aggregation appeared more refined and highly structured, as can be seen in Fig. 2a. At a higher magnification (Fig. 2b), the interconnected network of CNF is revealed. It can be observed that CNF have different lengths ranging from 1 to 10 μm. As previously reported [13], when using mechanical mixing for dispersing CNF in epoxy, isolated aggregates with size around 30 μm remained. This size almost corresponds to the length of the CNF, as a consequence, it is difficult to break these aggregates without CNF breakage and length reduction. The effect of fiber breakage is to shift the CNF critical fraction at which the composite becomes conductor to higher values. In this work, the effect of fiber breakage is negligible compared to the beneficial effect of disaggregation as the critical fraction is reduced from 1 to less than 0.1 wt%. The better the dispersion the lower the critical fraction.

3.2. Electrical conductivity

The electrical conductivity, σ, as a function of frequency is plotted in Fig. 3 for the composites at different CNF loadings. For each loading, at least three samples were tested and the reproductibility is good. As expected, the standard deviation is higher in the transition region. The unfilled epoxy resin showed a typical insulating behavior

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