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Length-dependent electrical and thermal properties of carbon nanotube-loaded epoxy nanocomposites

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ABSTRACT

Sonication-induced scission was used to obtain carbon nanotubes (CNTs) with aspect ratios averaging 50 (short CNTs) and 500 (long CNTs). A series of carbon nanotube/epoxy nanocomposite samples with CNT content up to 1.0 wt.% were prepared using these tubes. Electrical and thermal characterisation was conducted to identify changes in such properties and the extent of these changes as a function of aspect ratio and CNT content. Results show significantly enhanced electrical conductivities and a modest increase in the thermal conductivities in both sets of samples. Further analysis of electrical conductivity of the long CNT and short CNT-based epoxy nanocomposites was carried out in order to understand their viability for EMI shielding and electrostatic dissipation applications. The processing behaviour of the long and short CNT-based composites and the corresponding electrical properties is also discussed which will help the researchers to select the right type of carbon nanotube aspect ratio achieve specific electrical properties as well as good processing behaviour.

1. Introduction

The last decade had seen a significant increase in the usage of carbon fibre-reinforced polymer (CFRP) materials in commercial aviation. The Boeing 787 "Dreamliner", currently entering service, and the Airbus A350 XWB, which is due to enter service in the near future, are boasting in excess of 50% composites by weight.

There is a growing focus on the potential enhancements of nanoparticle reinforcements to further augment the mechanical and physical properties of such materials for use in aerospace application. These new materials could be employed in a range of novel applications such as erosion resistance, de-icing, structural health monitoring or lightning strike protection [1]. Compared to lightning strike applications; electromagnetic shielding, electrostatic discharge and antistatic dissipation do not require high levels of conductivity and therefore are well suited to CNT/polymer composites at relatively low filler loadings [2].

Carbon nanotubes have attracted considerable research attention over the past two decades owing to the remarkable physical and mechanical properties that have been quoted by experimental and theoretical studies. Such studies suggested that carbon nanotubes would make ideal candidates as reinforcement materials [3–6]. It is widely accepted that multiwall carbon nanotubes (MWCNTs) exhibit metallic electrical conductivity, while single-wall carbon nanotubes (SWCNTs) can exhibit either metallic or semiconductor electrical conductivity, depending on the hexagonal lattice orientation of the nanotube main axis. Chiral tubes, that have helicity indices where m–n are a multiple of 3 exhibit metallic electrical conductivity, whereas other lattice configurations exhibit semiconductor electrical conductivity [7]. The electrical conductivity of metallic carbon nanotubes has been measured in the order of 10^4 S/m. Furthermore, carbon nanotubes exhibit extremely high current-carrying capacities, with metallic tubes exhibiting current densities up to 10^9 A cm^2 [8]. Thermal conductivity values have been reported to be around 3000 W/mK for MWCNTs [9]. A variety of mechanical properties have been published over the years, for example, The Young's modulus is reported to be 1 TPa, and tensile strength is considered to be ~30 GPa [10].

Compared to traditional conductive fillers, such as carbon black or metallic powders, where high filler loadings are required to achieve desired conductivity, the high aspect ratios of carbon nanotubes allow for conductive or percolating networks to form at much lower loadings. The key to effective reinforcement is to achieve a high degree of dispersion, alignment and optimised bonding between the reinforcement and the polymer matrix. Such problems revolve around the ability to process carbon nanotubes,

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to achieve homogenous dispersions, anisotropic alignment of the tubes and to improve the load transfer efficiency between the matrix and the nanotube at the interface.

While the effect of weight or volume fraction of carbon nanotubes in epoxies has been studied intensely over the years, less attention has focused on the effect of aspect ratio, and such studies typically focus on theoretical predictions of physical and mechanical enhancement potential [11,6,12]. Modelling of nanocomposite properties, especially electrical conductivity, has traditionally applied percolation theory to define the threshold whereby there is a transition from insulator to conductor. This threshold describes a critical concentration that is required to form a continuous conductive network. Above the percolation threshold it is widely accepted that the enhancement in electrical conductivity follows a simple power law:

$$\sigma_m = \sigma_h(\Phi - \Phi_c)^t \quad (1)$$

In Eq. (1) σ_m is the conductivity of the composite, σ_h is the conductivity of the filler, Φ is the volume fraction of the filler, Φ_c is the percolation threshold and t is a critical exponent. Percolation theory relies on statistical geometric assumptions that are accounted for by applying "universal" values for t, which have been quoted between 1.7 and 2 for three-dimensional networks, however, values greater than 2 have also been reported [13]. A number of approaches have attempted to account for the shape, size and aspect ratio [14] of the fillers to improve the accuracy, which are often based on an excluded volume theory.

In addition to theoretical studies, a rather limited experimental work has been carried out to investigate the influence of carbon nanotube aspect ratio various composite properties, including: flammability [15], fatigue behaviour [16], electrical behaviour and a variety of mechanical properties of different polymer-based nanocomposites [17,18,20,21]. Ayatollahi et al. [18] investigated the effect that changing carbon nanotube aspect ratio had on electrical and mechanical properties of epoxy composites. Instead of changing the length, however, Ayatollahi et al. focussed on varying the diameter of the nanotubes. The results indicated that the best response in electrical conductivity and fracture toughness were observed in samples containing higher aspect ratio carbon nanotubes.

Park et al. [19] investigated the stress transfer and electrical self-sensing in carbon nanofiber epoxy nanocomposites using various concentrations of carbon nanofibers with different aspect ratios. Using comparative electrical resistivity measurements across individual samples, it was possible to indirectly qualify the dispersion of the carbon nanofibers on a macroscopic scale. The resistivity measurements clearly indicated that the dispersion of nanofibers was not homogenous across the composite. Furthermore, the degree of dispersion was found to decrease with increasing concentrations of nanofibers. This was attributed to the increase in electrical contacts.

Results from Park et al.'s mechanical tests indicated improved stress transfer between the matrix and nanofibers with lower aspect ratios. This was attributed to an increase in surface contact resulting from improved alignment of the short nanofibers enhancing the interfacial adhesion between the matrix and the reinforcement.

Further rheological studies conducted by Rahatekar et al. [22,23] on carbon nanotubes of various aspect ratios showed that the shear-induced agglomeration effects were more pronounced in longer aspect ratio tubes. Observations highlighted that while the aspect ratio improved network formation at lower weight percentage, the higher degree of entanglement lead to an increase in the yield stress. This has a significant effect on the process efficiency of longer aspect ratio carbon nanotube polymer melts compared to their shorter aspect ratio counterparts.

With regards to the thermal conductivity enhancement of nanocomposites, results from previous studies have shown that the enhancements in thermal conductivity, as predicted by theoretical studies, fall well below prediction. Huxtable et al. [24] attributed these differences to the thermal conductance of the nanotube–polymer interface, quoted as 12 MW/(m^2 K). This represents a high interfacial thermal resistance, which arises due to energetic constraints in converting high-frequency phononic conduction modes within the carbon nanotubes to low-frequency modes from phonon–phonon coupling when being exchanged with the surrounding medium.

In a review on the thermal conductivities of carbon nanotubes/polymer nanocomposites, Han and Fina [5] concluded that the electrical and thermal conductivities should not be treated as analogous. While they both rely on percolation, the difference between the phononic and electronic conduction mechanisms is a significant consideration. Singh et al. [25] carried out theoretical studies to investigate the effect of nanotube size and interface on the thermal conductivity.

2. Materials and methods

2.1. Materials

As part of this study, as-made multiwall carbon nanotubes without any chemical post treatment were supplied by the Department of Materials Science and Metallurgy at University of Cambridge (Cambridge, UK). The nanotubes were produced by a thermal chemical vapour deposition-based method described by Singh et al. [26] that produces highly aligned "carpets" of multiwall carbon nanotubes of good quality. The high alignment makes dispersion of the nanotubes easier compared to other commercially available nanotubes that are often highly entangled and those entangled nanotubes suffer most in terms of shortening during the processing stage. The average length was found to be 50 μm, and diameters ~100 nm.

2.2. Sonication-induced scission

The long aspect ratio tubes were used as received, while the shorter aspect ratio nanotubes were produced by using ultra high-frequency sonication using a SONICS VCX-750 sonicator with a half wave extender. Two grams of the as-received tubes were sonicated at 65% amplitude in 600 ml ethanol for 8 h at 1-h intervals. The size reduction was monitored using optical microscopy. Following sonication, the nanotube dispersion was added dropwise to 5 ml 1% Sodium DodecylBenzyl Sulphonate (SDBS) solution, until the solution had a grey tint. The size reduction was characterised using a Leica DMI3000B inverted optical microscope at 40× magnification, using phase contrast to improve the resolution of the tubes. Images were captured and, after setting the scale of the image, a segmented line was overlaid on each nanotube and the length recorded. The results were analysed and distribution was plotted. Prakash et al. [27] reported that phase contrast techniques enabled larger carbon nanotubes to be observed using optical microscopy. Kerr et al. [28] and Rahatekar et al. [23] used the same method to reduce the aspect ratio of carbon nanotubes. One conclusion that Kerr made from the study was that a length saturation point was achieved depending on the diameter of the tubes. The long and short aspect ratio tubes were imaged using SEM. Further length analysis was carried out of the electron micrographs to characterise and validate the size reduction of the sonicated nanotubes. The results of the analysis show good agreement with those obtained from optical microscopy.