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,
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:

\[
\sigma_m = \sigma_\infty(\Phi - \Phi_c)^t
\]

(1)

In Eq. (1) \(\sigma_m\) is the conductivity of the composite, \(\sigma_\infty\) is the conductivity of the filler, \(\Phi\) is the volume fraction of the filler, \(\Phi_c\) 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/(m² 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 VTX-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.
2.3. Carbon nanotube/epoxy sample preparation

Carbon nanotube/epoxy dispersions were produced with weight percentages up to 1.0 wt.%, using Gurit\textsuperscript{\textregistered} C211 Prime 20LV resin, which is a bis-phenol-A epoxy resin, and an aromatic diamine curing agent. The nanotubes were added directly to the resin and high shear mixed using a Silverson L5M lab mixer, with high shear shield attached. The quality of the dispersion was monitored periodically using optical microscopy. A sample of the dispersion was placed on a slide and a covering slip applied on top and observed under minimum magnification. The dispersion was considered ready when no large agglomerates were apparent. Once a good dispersion had been achieved, the dispersions were injected between two plates of glass with a set separation. The samples were cured in accordance to the epoxy manufacturer’s guidelines, for 16 h at 50°C. Initial Differential Scanning Calorimetry (DSC) analysis indicated uncured material once the samples had been removed from the mould, therefore a post-cure process, at 70°C, was applied. Subsequent DSC measured indicated that there was no significant uncured epoxy in the composite.

2.4. Electrical and thermal characterisation

Thermal diffusivity measurements were carried out using the flash diffusivity technique. In preparation for the test, square specimens (13 mm × 13 mm), were cut using a diamond saw and coated with graphite. Testing was performed over a temperature range of 50–200°C using a Xenon light flash diffusivity system (LFA 447 Nanoflash, Netzsch Instruments, Inc.) and the thermal diffusivity obtained from the transient pulse using Cowen analysis. The thermal conductivities were derived using the following equations:

\[ k = \alpha \rho C_p \]  

where \( k \) is the thermal conductivity, \( \alpha \) is the thermal diffusivity, \( \rho \) is the density and \( C_p \) is the specific heat capacity. The density of the samples was measured using the Archimedes method, and the specific heat capacity was obtained using Modulated Temperature Differential Scanning Calorimetry (MTDSC), as described in ASTM E2716-09. Bulk electrical resistivity measurements were carried out following ASTM D4496-04. A simple circuit consisting of a 4 kV precision DC voltage source and an ammeter was used. At lower carbon nanotube loadings, a picoammeter was required, however as the nanotube concentration increased, this was replaced with a standard ammeter. Rectangular test specimens, 40 mm × 10 mm × 3 mm, were cut as with the thermal specimens. Silver-loaded epoxy was used to attach electrodes either end of the sample. A direct voltage was applied to the specimen and the current response was observed using an oscilloscope. The resistivity (\( \Omega \)) was measured by applying the current (\( I \)) directly to the sample at a range of voltages (\( V \)). The bulk resistivity (\( \rho_B \)) in \( \Omega \) cm was derived using Eq. (3), where \( A \) is the cross-sectional area; \( L_{EC} \) is the separation between the electrodes (19).

\[ \rho_B (\Omega - \text{cm}) = \left( \frac{A_{EC}}{L_{EC}} \right) \times \left( \frac{V}{I} \right) \]  

3. Results and discussion

3.1. Sonication-induced scission

Images of the tubes after hourly sonication treatments were captured and the lengths of no less than 200 nanotubes were measured using ImageJ. The intensities of the images have been adjusted to maximise the contrast for measuring. Fig. 2 shows the plot of carbon nanotube length vs. frequency. After 8 h, the mean average length was found to be 5 μm respectively. The results indicate a continual reduction in the length of the nanotubes while showing an increase in the uniformity of the size distribution compared to the as-received carbon nanotubes. A similar saturation point, as previously discussed, was observed in Fig. 2. Further sonication after 8 h yielded no significant reduction in the average length of the tubes.

3.2. Electrical conductivity

The resistivity of the unloaded epoxy resin could not be fully characterised, as it was found to be too resistive, even at voltages lower than 1 kV. Higher applied voltages were required to observe a measurable current response, however as the nanotube concentration increased, the amount of current required to achieve a measurable response decreased. Fig. 2 shows the resistivity of the dispersed nanotubes as a function of voltage.

![Fig. 1. SEM images of (a) as-received long aspect ratio (b) sonicated short aspect ratio carbon nanotubes.](image1)

![Fig. 2. Plot of log average carbon nanotube length vs. normal distribution.](image2)
up to 4 kV. It can therefore be assumed that the resistivity of the pure epoxy exceeds $4 \times 10^3 \Omega \cdot \text{cm}$. Fig. 3 shows a logarithmic plot of electrical conductivity as a function of carbon nanotubes aspect ratio and wt.%. In both the long and the short aspect ratio carbon nanotubes, percolation is observed below 0.1 wt.% samples. Compared with pure epoxy matrix, the short aspect ratio tubes show eight orders of magnitude improvement in the electrical conductivity, and the long tubes show twelve orders of magnitude improvement. Electrical Hazard Management (EMH) scenarios have been included in Fig. 3, which illustrate the regions of conductivity required to achieve electrostatic dissipation (ESD), electromagnetic interference (EMI) and lightning strike protection (LSP) [29]. The longer aspect ratio tubes achieve conductivity for electrostatic dissipation as low as 0.1 wt.% and even reach levels sufficient to protect against electromagnetic interference at 0.5 wt.%. The short aspect ratio carbon nanotubes show much lower levels of conductivity, only reaching electrostatic dissipation levels at 1.0 wt.%. Even though the conductivity of long CNT-based composites was found to be significantly higher than that for the short CNTs, all the long CNTs samples showed very high viscosity (as reported in our previous work, Rahatekar et al. [30]). The short CNTs were easy to process even at as high concentration as 1.0 wt.%. Hence, it may be convenient to use short carbon CNTs for electrostatic dissipation application for improving the processing ability of the composites.

Since percolation has been achieved in both sets of samples, it can be safely assumed that the four orders of magnitude difference between the long and the short aspect ratio tubes are a result of the increase in contact resistance due to the increased number of connections required by the shorter tubes to form a percolating network. While the power law is commonly accepted for the prediction of the effective conductivity of nanocomposites, it doesn’t take into account the aspect ratio of the carbon nanotubes. Deng et al. [30,31] offered an alternative model that aimed to predict the percolation threshold based on the aspect ratio, which was adapted here to evaluate the electrical conductivity. The theoretical percolation threshold is derived using the following equation:

$$f_c = \frac{9H(1-H)}{-9H^2 + 15H + 2}$$

(4)

In this equation, $H$ is the principal depolarisation factor, which takes into account the influence of aspect ratio on the critical volume fraction ($f_c$). $H$ is given by the following equation, where $p$ is the aspect ratio of the carbon nanotubes.

$$H(p) = \frac{1}{p^2 - 1} \left[ \frac{p}{\sqrt{p^2 - 1}} \ln (p + \sqrt{p^2 - 1}) - 1 \right]$$

(5)

According to Eq. (4) conductive fillers with aspect ratios below 50 shows an exponential increase in the critical volume fraction required to form a percolating network. For conductive CNT’s with aspect ratios larger than 50, the effect on the critical volume fraction is less significant.

Since the electrical conductivity is reliant on a percolation network, below the critical volume fraction the conductivity of the composite is governed by the matrix. The following equation evaluates the effective electrical conductivity ($\sigma_e$) for randomly orientated MWCNTs in a polymer matrix:

$$\frac{\sigma_e}{\sigma_m} = 1 + \frac{nf/3}{\pi^2 + H(np)}$$

(6)

where $\sigma_m$ is the conductivity of the matrix, $f$ is the volume fraction of CNTs, $\sigma_1$ is the axial electrical conductivity of a carbon nanotube, and $n$ is a new parameter that describes the effective length of nanotubes in an attempt to account for the waviness of the tubes.

For this model, the parameter has only been applied to the longer aspect ratio tubes, the shorter tubes are considered to be more rigid, as shown in Fig. 1b. Wu et al. [32] used TEM to monitor the effect of carbon nanotube aspect ratio on the extent of flocculation resulting from the degree of entanglement between the tubes. They concluded that as carbon nanotube aspect ratio decreased, fibre rigidity increased. The results from this analytical model have been overlaid on to the experimentally derived electrical conductivities in Fig. 3. The analytical results show good agreement with the trend of the results and show good agreement with the experiment results gathered for the short aspect ratio tubes ($l/d = 50$). The model underestimated the increase in conductivity of the long aspect ratio tubes ($l/d = 500$), however, when the value of the aspect ratio was increased to 5000 the trend begins to show better agreement with the experimentally derived results.

3.3. Thermal conductivity

Using Eq. (2) the thermal conductivities were calculated and plotted. Fig. 4 shows the plot of thermal conductivity vs. carbon nanotube wt.%. The first observation to make is that there is only a modest enhancement in the thermal conductivity of the nanocomposites. With aerospace application in mind, compared to traditional aluminium alloys that can exhibit thermal conductivity up to 234 W/m K, the 1.0 wt.% high aspect ratio carbon nanotube/epoxy exhibits a thermal conductivity of 0.236 W/m K. The orders of magnitude below that of aluminium. While there is an observable difference in thermal conductivities between the long and short aspect ratios, the difference is relatively small compared to the variation in electrical conductivities observed. These findings support the theory that changing the aspect ratio of the tubes,
and therefore the number of contacts required to form a percolating network, has a more profound impact on the phononic conductivity of the composite compared to the electrical conductivity. This is further supported by the 0.1 wt.% sample with the short aspect ratio tubes, where an initial decrease in the thermal conductivity of the sample is observed. Since the thermal conductivity is dependent on the formation of a percolating network, this indicates that at such low loadings, the enhancement in thermal conductivity is dominated by the phononic scattering generated by the interface between the carbon nanotubes and the polymer. Further to their work on analytical modelling to predict electrical conductivity of composites, Deng et al. [33] used the principal depolarisation factor to account for the aspect ratio of carbon nanotubes on the thermal conductivity of a composite. The following equation approximates the thermal enhancement:

\[
\frac{k_e}{k_m} = 1 + \frac{nf}{3 \alpha^2} + H(np)
\]  

(7)

This yields the trends as shown in Fig. 4, for aspect ratios 50 and 500, which has been overlaid over experimentally data collected. The analytical model shows good agreement and fit to the experimentally obtained data.

SEM was carried out to examine the fracture surfaces of the specimens. Compared to the neat epoxy, the addition of carbon nanotubes into the epoxy matrix causes an increase in the surface roughness of the fracture surface, as shown in Fig. 5. As suspected, Fig. 5a shows a poorer dispersion of the long aspect ratio nanotubes, especially as the concentration reaches and exceeds 0.5 wt.%. In Fig. 5b, however, there is a consistently improved dispersion of the short aspect ratio carbon nanotubes observed up to 1.0 wt.%. It is important to mention that while there is a poorer dispersion in the longer aspect ratio tubes, the tubes are not entangled or agglomerated.

4. Conclusions

Sonication-induced scission has been shown to breakdown long aspect ratio carbon nanotubes into shorter aspect ratio tubes. Depending on the diameter of the nanotubes, a technique to quickly monitor the size reduction using optical microscopy has been described. A significant increase in the bulk electrical conductivity of the epoxy resin was observed upon nanotube loading, and has been shown to be strongly dependent on the aspect ratio of the carbon nanotubes. The long CNT-based composites were highly conducting and were suitable for EMI shielding as well as electrostatic dissipation applications. The short CNT-based composites may be a convenient choice for the electrostatic dissipation application as they are easier to process than the long CNT-based composites. Modest increases in the thermal conductivity of both samples were recorded and the results show a sizeable variation in the thermal conductivities between the long and short aspect ratio tubes. Similarly to the electrical conductivity, this can be attributed to the exponential increase in the number of contacts required by shorter aspect ratio tubes to reach percolation resulting in greater phononic scattering and interfacial thermal resistance. The large increase in viscosity, even at these relatively small concentrations, has a profound effect on the processability of the composite. This poses the question: Is it worth tailoring the nanotube aspect ratio to the intended application with regard to electrical conductivity? This way the desired electrical performance can be achieved whilst maintaining shorter aspect ratio to ease the processibility and improve reproducibility. Further studies would help to elucidate an optimal aspect ratio that provides the best enhancement in composite properties with minimal detriment to processability.

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