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Ultra-low electrical percolation threshold in carbon-nanotube-epoxy composites

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Dedicated to Prof. Ian M. Ward on the occasion of his 75th birthday

Abstract

Epoxy composites based on aligned CVD-grown multi-wall carbon nanotubes with weight fractions ranging from as low as 0.001 up to 1 wt% were produced. The resulting electrical properties were analysed by AC impedance spectroscopy. The composite conductivity σ follows a percolation scaling law of the form $\sigma \propto (p - p_c)^t$ with the critical mean concentration p_c to form a conductive network of approximately 0.0025 wt% and an exponent, t, of 1.2. The results are compared to previous studies investigating the percolation behaviour of entangled carbon nanotubes and spherical carbon black particles in the same matrix processed under similar conditions. The experimental percolation threshold for the aligned nanotubes used in this study represents the lowest threshold observed for carbon-nanotube-based polymer composites yet reported.

Keywords: Carbon nanotubes; Epoxy matrix; Electrical properties

1. Introduction

Market projections for polymer nanocomposite technology show a 160 million lb market for carbon-nanotube-filled products by 2009 [1]. A large part of these nanotube-based polymer composites will exploit carbon nanotubes as a conductive filler for applications ranging from the electronics to automotive and aerospace sector. Depending on the exact application, sufficient matrix conductivity is required to provide electrostatic discharge or electromagnetic-radio interference protection. In most cases, a highly conductive filler is added to the matrix to provide a three-dimensional network of filler particles through the component. This situation is known as percolation and the percolation threshold is characterised by a sharp drop of several orders of magnitude in resistivity.

Percolation theories are frequently applied to describe the insulator-to-conductor transitions in composites made of a conductive filler and an insulating matrix. It has been shown both experimentally and theoretically that the percolation threshold strongly depends on the aspect (length-to-diameter) ratio of the filler particles [2,3]. Hence, it is not surprising that a number of recent experimental studies have verified the potential of carbon nanotubes as a conductive filler resulting in very low percolation thresholds [4,5]. Depending on the polymer matrix and the processing technology as well as the type of nanotube material used, percolation thresholds between 0.05 and 10 wt% have been observed experimentally for thin films [5–9]. In the case of multi-wall carbon nanotubes, optical transparency is generally reduced or lost due to the formation of the conductive network, whereas single-wall nanotube composites can lead to conductive and transparent composites [10]. Most commercial thermoplastic, anti-static, carbon nanotube systems are based on entangled CVD-grown nanotube materials and require between 1.5 and 4.5 wt% loadings [11].

When dispersing conductive particles with diameters below 1 μm in a medium of low viscosity, diffusion processes and particle–particle interaction forces play an important role in the agglomeration and network formation. Electrostatic charging of particles can both aid dispersion and hinder the aggregation required in order to achieve a

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network of touching particles. In certain circumstances, thermal energy alone is insufficient to surmount the potential energy barrier to aggregation and specific measures need to be taken. The application of low shear forces has already been shown to greatly enhance the migration of dispersed carbon black particles and the resulting network formation at loadings below 1 wt% in an epoxy matrix [12,13]. These results clearly indicate that processing conditions play a crucial role in achieving low percolation thresholds in epoxy systems.

In a previous study, we have shown that the use of multi-wall carbon nanotubes in place of carbon black leads to a lower percolation threshold and higher maximum conductivity in bulk samples of an epoxy matrix [4]. The entanglements of the catalytically grown nanotube material were not broken down completely during the shear-intensive stirring process. Nevertheless, macroscopic aggregation of small nanotube clusters occurred at very low weight fractions. Here we show that the use of aligned multi-wall carbon nanotubes from an in-house, chemical vapour deposition (CVD) process leads to a superior dispersion after shear-intensive processing. Such dispersed carbon nanotubes reagglomerate under optimised processing conditions involving an increase in resin temperature and the application of low shear forces when adding the hardener. The experimentally observed bulk composite conductivity increases with increasing nanotube content and is discussed with respect to a percolation scaling law. The percolation threshold is compared to our previous results.

2. Materials and experimental details

The recognition of carbon nanotubes as a new allotrope of carbon in 1991 has provoked an enormous international research effort. Single-wall carbon nanotubes consist of single layers of the graphite lattice rolled into perfect cylinders with a diameter usually in the range of 0.5 to 2 nm. Multi-wall carbon nanotubes consist of sets of concentric cylindrical shells each of which resembles a single-wall nanotube although generally with larger diameters up to tens of nanometres.

The production of nanotubes in large quantities, high purities, and with a uniform size remains a challenge to be solved, but an increasing number of companies are focusing on scaled-up synthesis routes. Although high-crystallinity materials can be most readily grown at high temperatures using electric arcs or laser ablation, large-scale synthesis efforts are mostly based on CVD techniques that use moderate temperatures to decompose hydrocarbons over transition metal catalysts. It should be noted that the various synthesis routes generate nanotubes with very different properties, and it is important to select the appropriate material for a given application.

The aligned multi-wall carbon nanotubes used in this study are produced by an injection CVD method. Nanotube alignment during growth can be achieved by the use of preformed substrates in this process. This approach allows excellent control of the catalyst to carbon ratio and can be used to produce nanotubes with a narrow diameter distribution and a given length by varying the production parameters [14,15]. Furthermore, the carbon nanotube material prepared for this study is relatively straight, unentangled and pure. Electron microscopy revealed that the aligned nanotube material has an average diameter of approximately 50 nm and is 17 ± 3 μm in length. A typical scanning electron microscopy image of the aligned as-grown nanotubes is shown in Fig. 1. The matrix used is an epoxy based on a bisphenol-A resin (ARALDITE LY 556, CIBA GEIGY) and an amine hardener (ARALDITE HY 932, CIBA GEIGY).

Filler weight fractions ranging from 0.001 to 1 wt% were dispersed in the resin by shear-intensive mechanical stirring using a dissolver disk. The mixtures, containing around 30 g of resin, were first stirred at room temperature for one hour at 2000 rpm. In a second step the temperature of the resin was reduced with dry ice to raise the resin viscosity in an attempt to increase the shear forces. Again, the mixtures were stirred at 2000 rpm for one hour. Finally, the resin temperature was raised to about 80 °C and allowed to equilibrate for 10 min. After addition of the hardener at this temperature, the mixtures were stirred for 1 min at 500 rpm followed by 4 min at 50 rpm to allow for a homogeneous dispersion of the hardener and to enhance the nanotube agglomeration process. Rectangular samples were cast in a rubber mould and were subsequently cured in a vacuum oven to remove excess air. Curing was performed for 8 hours at 140 °C.

Strips of about 1 mm thickness were cut from the rectangular specimens and the cross-sectional areas were coated with conductive silver paint. The diameters of circles with equivalent area to the cross-section A were much greater than the distance t between them. 2-terminal AC

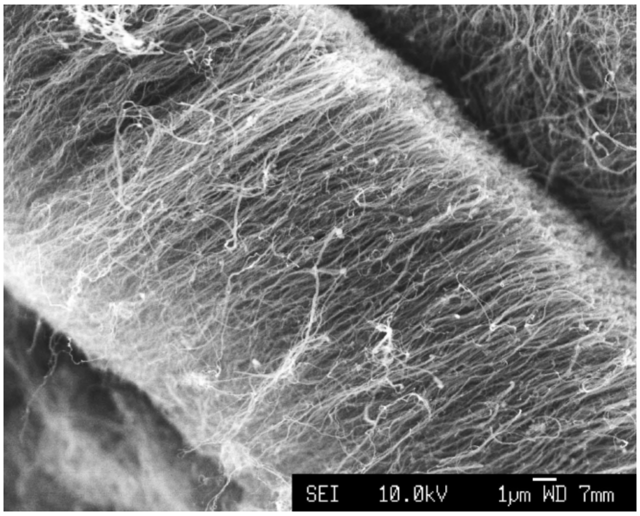

Fig. 1. Typical scanning electron micrograph of the aligned as-grown multi-wall carbon nanotubes used in this study.

impedance spectroscopy was performed using a Solartron 1260 Impedance/Gain Phase Analyzer with a voltage amplitude of 1 V and a DC potential of 0.4 V. The frequency range was set from 1 to 10^6 Hz.

3. Results and discussion

The dispersion process applied in this study differs from the one used for the entangled carbon nanotubes in our previous study [4]. Both processes have been adjusted so that optimum conditions for the incorporation of varying filler weight fractions and the resulting sample homogeneity and nanotube dispersion could be achieved. The entangled carbon nanotubes were found to strongly increase the viscosity of the mixture during the first dispersion step, especially at filler weight fractions above 0.1 wt%. In order to manufacture homogeneous samples without air bubbles, the resin viscosity was lowered by increasing the temperature to 80 °C during the entire production process. In contrast, the aligned carbon nanotubes used in this study do not lead to such a strong increase in resin viscosity as a function of filler content and the resin temperature was lowered to maximise the shear forces during the dispersion step.

The shear-intensive mechanical stirring process leads to well-dispersed CVD-grown multi-wall carbon nanotubes in the epoxy resin. During the final processing step at low stirring rates, following the addition of the hardener, a rapid nanotube aggregation process occurred for the sample with a filler content of 0.0025 wt%. The formation of these nanotube aggregates in the dispersion was already visible during this last production step. It has been shown for carbon black particles dispersed in the same epoxy resin that the application of low shear rates as well as the addition of an electrolyte enhances the network formation of particles [12,13]. The increase in the ionic concentration of the dispersion decreases the repulsive barrier between particles. In our case, the ionic concentration of the amine hardener appears sufficient to allow nanotube agglomeration.

For higher loading fractions, such nanotube aggregates lead, within minutes, to a macroscopic three-dimensional network of darker spots. Only the sample with the lowest nanotube content of 0.001 wt% remained devoid of visible aggregates of nanotubes and retained its optical transparency with just a slight darkening. Fig. 2 shows the development of the nanotube aggregates in the cured samples as a function of nanotube content. It is interesting to note that the distribution of nanotubes within the samples is not uniform even on the millimetre scale. Although, there are light-scattering nanotube clusters present in our samples a level of general transparency is observable up to the highest loading fraction prepared.

Fig. 3(a) shows a fracture surface scanning electron micrograph of the sample containing 0.001 wt% CVD-grown carbon nanotubes. This image confirms that individual nanotubes are dispersed during processing of these nanocomposites. However, at a higher loading of 0.0025 wt%, some reaggregation is seen to occur as shown by the loose clustering apparent at lower magnification in Fig. 3(b). These images highlight the transition from a dispersed to an agglomerated state of carbon nanotubes as a function of concentration and are in agreement with the optical observations of the agglomeration with increasing filler weight fraction shown in Fig. 2.

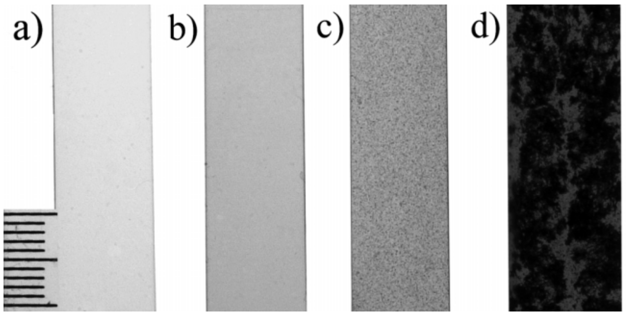

Fig. 2. Optical micrographs of epoxy-nanotube composites; (a) pure epoxy, (b) 0.001 wt%, (c) 0.0025 wt%, and (d) 0.005 wt%. Scale bar is 1 cm and the sample thickness is about 2.2 mm. The formation of small local nanotube aggregates at a loading fraction of 0.0025 wt% can be seen, which then leads to the macroscopic network of nanotubes at higher filler contents.

Fig. 3(c) shows a fracture surface of a nanocomposite containing 0.01 wt% of entangled carbon nanotubes for comparison. As mentioned before, the processing conditions for these samples were different due to a pronounced increase in resin viscosity with the addition of these nanotubes [4]. In contrast to the aligned nanotubes, the entanglements of this nanotube material could not be broken up during processing. Therefore, these nanocomposites revealed densely packed nanotube clusters even at low filler weight fractions. The presence of these clusters and the associated increase in viscosity of the dispersion also required the use of higher shear rates after the addition of the hardener compared to the aligned nanotubes. Nevertheless, both the increase in the ionic concentration due to the hardener and thermal activation energy provided by the final curing step led to the desired network formation. (It should be noted that the entangled carbon nanotubes have an outer diameter of only 8 nm compared to the ≈50 nm diameter of the CVD-grown nanotubes.)

From the AC impedance spectroscopy performed at room temperature, the real and imaginary parts of the complex impedance (Z^*) are obtained as a function of the frequency. The complex admittance ($Y^* = 1/Z^*$) of the nanocomposites can be modelled as a parallel resistor (R) and capacitor (C) and written as a function of angular frequency (ω).

$$Y^*(\omega) = Y' + jY'' = \frac{1}{R} + \mathrm{j}\omega C \tag{1}$$

The specific AC conductivity of the nanocomposites as a function of frequency $\sigma(\omega)$ is calculated from the modulus

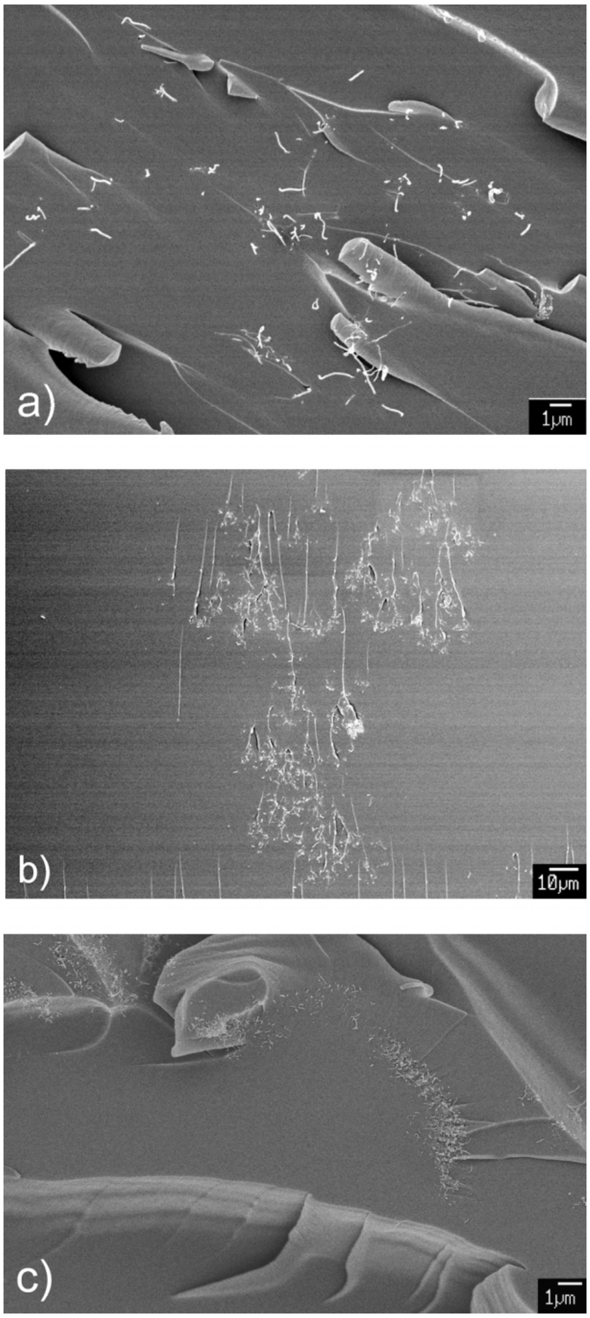

Fig. 3. Comparative scanning electron micrographs of nanocomposite fracture surfaces containing (a) 0.001 wt% and (b) 0.0025 wt% aligned CVD-grown multi-wall carbon nanotubes and (c) 0.01 wt% entangled catalytic carbon nanotubes [4].

of the complex admittance

$$\sigma(\omega) = |Y^*(\omega)|\frac{t}{A} \tag{2}$$

where A is the cross-sectional area and t is sample thickness.

Fig. 4 shows a log–log plot of the specific conductivity of the nanocomposites containing the CVD-grown multi-wall carbon nanotubes as a function of frequency. As can be seen, the sample containing 0.001 wt% of nanotubes reveals an increase in the capacitive component with increasing frequency, similar to the pure epoxy matrix. The observed slope of unity on a log–log scale is in good agreement with the expression $\sigma = \omega\epsilon'\epsilon_0$ which is valid for dieletric materials, where σ is the conductivity, ϵ' is the real part of the dielectric constant, ω is the angular frequency and ϵ_0 is the vacuum permittivity. On the other hand, intrinsic capacitive effects from the AC Impedance Analyser can result in an apparently similar frequency-dependent increase in conductivity for samples with a very high resistance. However, we believe that, in this case, we are within the valid range of impedance values for the Solartron Impedance Analyser used in this study. The sample containing 0.0025 wt% shows a frequency independent conductivity at frequencies below 10 Hz which is then followed by a region of increasing conductivity. This increase is, again, similar to that of the pure matrix.

With further increasing loading fraction of nanotubes, the conductivity becomes frequency independent over the frequency range investigated, indicating a measurable DC conductivity and non-dielectric behaviour. The obtained increase in sample conductivity at a frequency of 1 Hz as a function of filler weight fraction is shown in Fig. 5. Comparison with the DC conductivity of these composites gives identical results. As can be seen, there is an increase in conductivity of about two orders of magnitude when increasing the loading fraction from 0.001 to 0.0025 wt%. A further increase in nanocomposite conductivity to values above 10^{-3} S/m appears for loading fractions of more than 0.005 wt%. This increase in conductivity suggests that an infinite network of percolated nanotubes starts forming above 0.001 wt%, verifying the optical observations of the macroscopic network structure. The conductivity for higher loading fractions can be further analysed with regard to the critical concentration of nanotubes p_c by the following scaling law [16]:

$$\sigma \propto (p - p_c)^t \tag{3}$$

where p is the volume fraction of filler.

The conductivity exponent t generally reflects the dimensionality of the system with values typically around 1.3 and 2.0 for two and three-dimensions, respectively. The insert in Fig. 5 represents a best fit to the experimentally measured conductivity data as a function of $p - p_c$ expressed as weight fraction but otherwise according to Eq. (3). This analysis reveals a percolation threshold of about 0.0025 wt% and a scaling exponent t of 1.2 for these CVD-grown multi-wall carbon nanotubes. The low value of $t = 1.2$ is close to a recent value of $t = 1.36$ reported by Kilbride et al. for dispersed multi-wall nanotube-PVA and PmPV composites where the critical concentration was 0.055 wt% [5].

The low conductivity exponent t does not reflect a reduction in system dimensionality in the present case but rather the aggregation process of the carbon nanotubes during sample preparation. In other words, the formation of these conducting networks is not a true statistical percolation

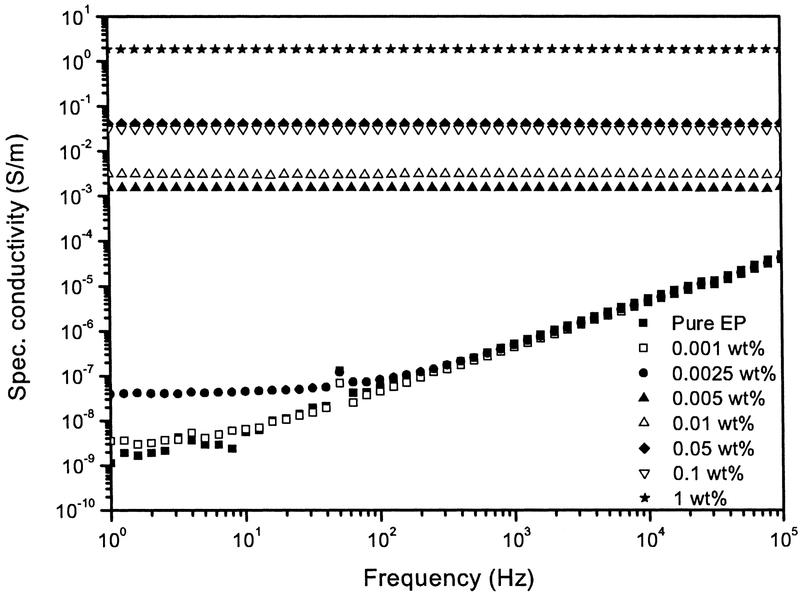

Fig. 4. Log–log plot of the specific conductivity of the nanocomposites as a funtion of nanotube loading.

process based on the random distribution of individual high-aspect ratio fillers, but rather is attributed to the mutual attraction of the nanotubes after the addition of the hardener.

In addition, thermally activated hopping transfers between disconnected or only weakly connected parts of the filler networks through the polymer matrix have been observed previously to reduce the conductivity exponent of an experimental composite system [17]. Some of the individual carbon nanotubes or nanotube clusters in our samples are essentially isolated by a polymer coating, which prevents direct contact. The resulting hopping transfer between the clusters also explains the relatively low maximum conductivity observed. The value of about 2 S/m for a loading fraction of 1 wt% of nanotubes, is orders of magnitude lower than the expected intrinsic nanotube conductivity.

Fig. 6 shows a comparative plot of the specific bulk epoxy composite conductivity processed under similar conditions as a function of filler weight fraction for three different fillers, carbon black particles, catalytically grown multi-wall carbon nanotubes and the aligned CVD-grown nanotubes. The use of carbon nanotubes with their high aspect ratio leads to a lower percolation threshold compared to the spherical carbon black particles. In addition, the maximum composite conductivity that can be achieved is higher for carbon nanotubes than for carbon black. Such an

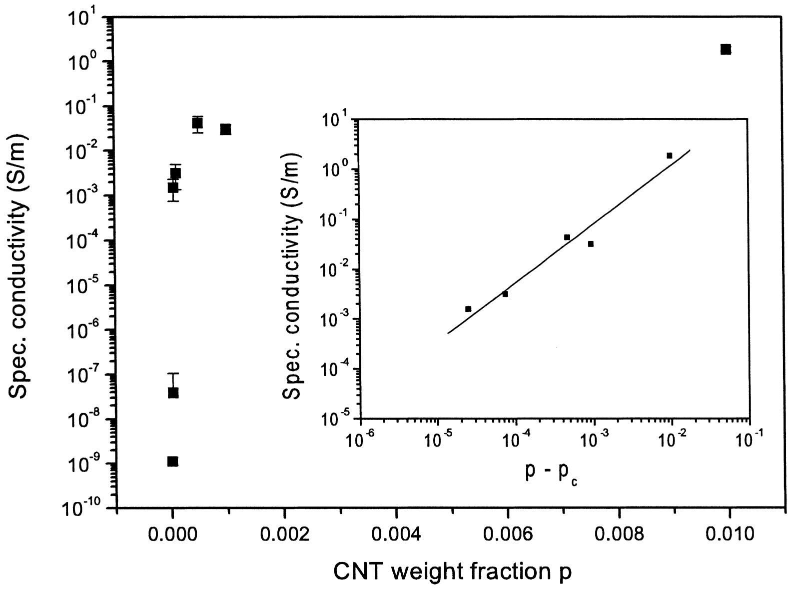

Fig. 5. Semi- log plot of the specific composite conductivity as a function of carbon nanotube weight fraction p. The insert shows a log–log plot of the conductivity as a function of $p - p_c$ with an exponent t of 1.2; the critical weight concentration $p_c = 0.0025$ wt% has been determined from Eq. (3).

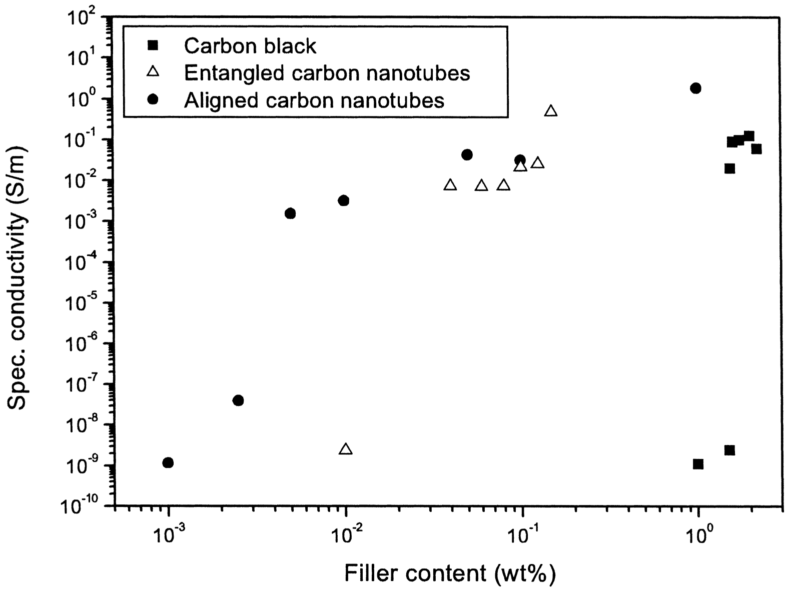

Fig. 6. Epoxy composite conductivity as a function of filler weight fraction for the aligned CVD-grown multi-wall carbon nanotubes compared to results previously achieved with entangled nanotubes and carbon black particles [4].

increase is expected given the reduced number of filler–filler hops required to cross a given distance.

As can be seen, the quality of the initial nanotube dispersion has a pronounced effect on the percolation threshold. For the aligned carbon nanotubes, the formation of local nanotube clusters must be induced by optimising the processing conditions following the addition of the hardener. Such clusters are present for the entangled carbon nanotubes after the dispersion process already. For both filler materials, thermal activation energy during curing then induces the formation of a macroscopic network of nanotube aggregates. The behaviour observed for the aligned carbon nanotubes decreases the percolation threshold by another order of magnitude compared to entangled nanotubes, as shown in Fig. 6.

The experimental percolation thresholds for both types of carbon nanotubes in the epoxy matrix cannot be explained by statistical percolation theories based on an excluded volume approach. Such a theoretical approach considers a random distribution of anisotropic particles within a closed system and determines the likelihood of contact between neighbouring particles. Celzard et al. followed this approach and calculated the percolation threshold for a composite containing randomly oriented conductive fibres in an insulating matrix [2]. Such calculations for an aspect ratio of 500, which is similar to the one measured for our nanotubes, yield a critical nanotube concentration of about 0.5 wt% to form a network of touching particles.

The deviation observed between the real nanotube-epoxy composites and the theoretical calculations further verifies that the percolation of nanotubes is not a purely geometrical problem but rather relates to local improvements in nanotube contacts due to segregation. The shear-induced aggregation of the initially well-separated high-aspect ratio particles, as evidenced by both electron and light microscopy, leads to the formation of a much more efficient network than can occur by random positioning of the particles (although the network remains apparently isotropic). Thus, the strong particle–particle interactions as well as interactions between nanotubes and the polymer matrix are crucially important. This mechanism is in good agreement with results obtained for carbon black filled epoxy and shows that, such systems should be treated by colloid theory [12,13]. Although this process does not reflect true, geometric percolation, it nevertheless shares the key features, namely the generation of a coherent network of particles, leading to a rapid change of properties following a standard sigmoidal curve.

4. Conclusions

Aligned multi-wall carbon nanotubes from an injection CVD process were dispersed as conductive fillers in an epoxy matrix. The resulting electrical properties were investigated by AC impedance spectroscopy and it is shown that sufficient conductivity for anti-static applications can be achieved at an average nanotube loading of approximately 0.005 wt%. The resulting bulk conductivity properties of the nanotube-epoxy composites arise from the formation of macroscopic nanotube aggregates. The experimental conductivity data follows a percolation scaling law.

The use of the aligned multi-wall carbon nanotubes leads to a uniquely low percolation threshold, which is an order of magnitude smaller than best results previously achieved with entangled multi-wall nanotubes. Compared to carbon black particles, the use of nanotubes as a filler represents a significant advance for epoxy systems, allowing anti-static conductivities at loading fractions where the mechanical properties of the matrix are not degraded, as well as higher maximum conductivities. In addition, these ultra-low loading fraction anti-static materials may prove to have interesting, low EM-radiation profiles.

Based on the achievement of initially well-dispersed nanotube-resin mixtures, current work is aimed at establishing the percolation threshold as a function of nanotube aspect ratio as well as determining the nature of the interactions between individual carbon nanotubes as a function of processing conditions.

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