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Development of a dispersion process for carbon nanotubes in an epoxy matrix and the resulting electrical properties

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Abstract

To avoid electrostatic charging of an insulating matrix an electrical conductivity above $\sigma = 10^{-6}$ Sm^{-1} is needed. At present, the most common practice to achieve this conductivity is to use a conductive filler such as carbon black. In this work, untreated catalytically-grown carbon nanotubes were dispersed in an epoxy matrix. After curing the epoxy, the electrical properties of the composite were measured in order to relate the filler volume fraction to the electrical conductivity. The intense stirring process used to disperse the carbon nanotubes has made it possible to achieve a matrix conductivity around $\sigma = 10^{-2}$ Sm^{-1} with filler volume fractions as low as 0.1 vol.%. These figures represent an advance on best conductivity values previously obtained with carbon black in the same epoxy matrix. These low filler fractions ensure that the mechanical properties of the matrix are not compromised. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

An increasing number of components are being made from fibre reinforced composites. For example, on aircraft, radomes and the leading edge of the vertical stabilisers are generally made from glass fibre reinforced composites using an insulating epoxy matrix. For these applications, some electrical conductivity is required to provide electrostatic discharge (ESD), and as electromagnetic-radio frequency interference (EMI/RFI) protection. Currently, a highly conductive filler such as carbon black (CB) is added to the matrix in order to ensure electrical conductivity above the required level of $\sigma = 10^{-6}$ Sm^{-1} [1]. This approach reduces the manufacturing and maintenance costs of components as compared with those previously coated with an anti-static paint. The technology is also relevant to other applications where static electrical dissipation is needed, such as computer housings or exterior automotive parts, and where different polymer matrix systems may be involved.

The matrix system investigated in this work is a resin commonly used for fibre reinforced composites for aircraft applications. When dispersing a particulate conductive filler such as carbon black it is important to keep the filler volume fraction as low as possible in order to maintain the fracture toughness and the tensile properties of the matrix. The epoxy matrix can reach a stiffness of about 3–5 GPa, but it is relatively brittle, with an ultimate elongation of about 4%; this strain to failure is only slightly above the critical value required for aircraft applications. The addition of a filler, which is usually harder than the matrix, generally leads to an increase in the Young's modulus, and a reduction in the ultimate elongation of the matrix. High filler contents also lead to an increase in the viscosity which, in turn, reduces processing ease. For these reasons it is important to minimise the conductive filler loading.

To provide a conductive path throughout a component, a three-dimensional network of conductive filler particles is needed, a situation is known as percolation; the percolation threshold is characterised by a sharp drop in the electrical resistance. Many theoretical percolation models have been developed to define the conditions, especially the critical filler volume content, at which a network is formed in conductive polymer compounds. In the most prominent geometrical models, created by Kirkpatrick [2] and Zallen [3], a regular array on which spherical particles are distributed statistically is examined. In their models, the required minimum network of touching particles is 16 vol.%. This value is in approximate agreement with most experimental

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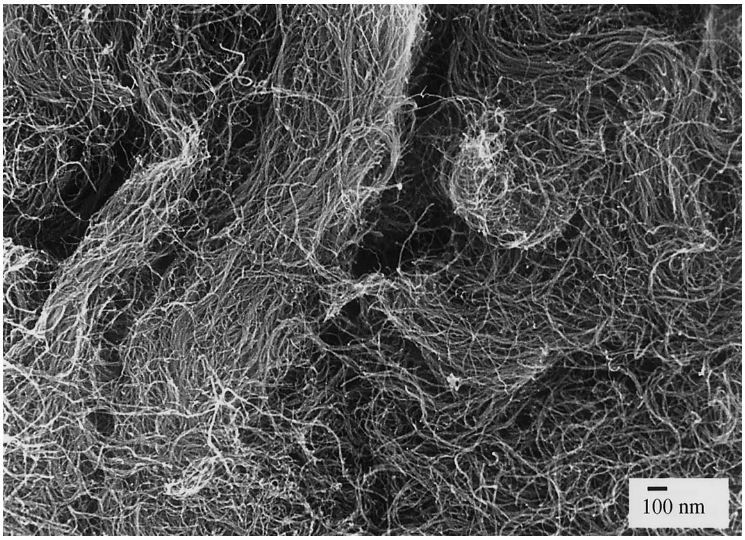

Fig. 1. SEM image of catalytically-grown nanotube matrial, as-supplied.

determinations since for most polymers filled with powdery materials the critical volume fraction for percolation is between 5 and 20 vol.%. However, this model cannot describe the experimentally observed percolation thresholds for carbon black-filled resins that are conductive at filler concentrations as low as 0.5 vol.%.

Colloid theory describes the interactions amongst particles dispersed in liquids as well as the structure and dynamics of agglomeration. Assuming that the carbon black particles are charged during the preparation, and taking the subsequent interactions into account, the agglomeration process of carbon black dispersed in an epoxy resin was described by Schueler [4]. It was found that the percolation threshold not only depends on the particle size and fractal dimension but also on the shearing rate used to disperse the carbon black particles in the matrix. Using this approach it was possible to both achieve and explain a percolation threshold of about 0.3 vol.%. Further optimisation of this dispersion process by adding copper-chloride has led to a matrix conductivity of $\sigma = 10^{-2}\ \mathrm{Sm}^{-1}$ at around 0.06 vol.% [4]. A new preparation method now allows the adjustment of the final resistivity within a range of about seven decades by applying a voltage during the curing of the epoxy [5].

The experimentally observed percolation threshold values strongly depend on the particle shape. Extremely low percolation thresholds have been reported for particles with a high aspect ratio (length to diameter). Dispersing short carbon fibres with an aspect ratio of 280 in an epoxy matrix, Carmona found a percolation threshold of 0.25 vol.% [6]. The recent discovery of carbon nanotubes [7] offers a new opportunity to modify the electrical conductivity of polymer matrix systems. Multi-walled carbon nanotubes are generally conducting [8] and typically have aspect ratios of around 1000. It was expected that a low percolation threshold could be obtained, by dispersing nanotubes in an epoxy matrix using the process developed for carbon black [4].

2. Experimental

The matrix used in this study is an epoxy polymer based on bisphenol-A resin (ARALDITE LY 556, CIBA GEIGY) and an aromatic hardener (ARALDITE HY 932, CIBA GEIGY). The carbon nanotubes used are supplied under contract by Hyperion Catalysis International, Cambridge USA. They are generated by decomposition of hydrocarbon gases [9]. The supplied powder consists, almost exclusively, of balls of loosely aggregated nanotubes that are non-coiled but generally curved. Their outer diameter is about 10 nm and inner diameter of around 5 nm and they have a length of a few microns [10]. Fig. 1 shows a SEM image of typical material.

Weight percentages ranging from 0.0225 to 0.15 wt.% of the untreated catalytically-grown carbon nanotubes were dispersed in the resin. The necessary weight fractions were first dispersed in ethanol in an ultrasonic bath at room temperature for 1 h. After mixing the ethanol-based solution into the resin, the suspensions were stirred for 1 h at 2000 rpm. During the stirring process, the temperature of the resin was kept at 80°C using a silicone oil bath in order to maintain a low viscosity of the resin. In order to evaporate the ethanol the mixtures were placed in a vacuum oven at 80°C for 1 h. The mixtures were then stirred again for 1 h at 2000 rpm. After adding the hardener, the mixtures were stirred at 2000 rpm for 15 min. The epoxy was hardened in a vacuum oven at 140°C for 8 h.

Following curing, the samples were ground on both sides to obtain flat and parallel surfaces. Rectangular specimens

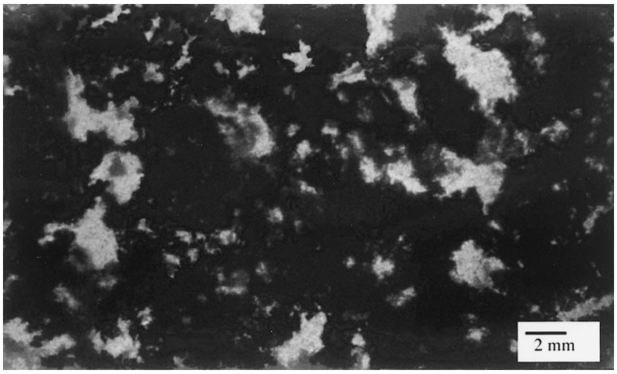

Fig. 2. Magnified transmission light photograph of the sample containing 0.0225 wt.% catalytically-grown carbon nanotubes, highlighting the formation of aggregates. The sample thickness was 0.5 cm.

of about 75 mm length, 20 mm width, and 5 mm thickness were cut, and the cross-sectional areas painted with conductive silver to provide good contact with the filler network within the specimen. First results were obtained from performing 2-terminal DC measurements of the resistance using a Megger M5091 multimeter with a range of resistance from 200 Ω to 20 MΩ. 2-terminal AC impedance spectroscopy was performed using a Solatron 1260 Impedance/Gain Phase Analyzer with a voltage amplitude of 1 V over a frequency range from 1 to 10^6 Hz.

3. Results and discussion

It is not possible to break up all the entanglements of the supplied catalytically-grown carbon nanotube material by the dispersion process used, although the exposure to ultrasound in ethanol and the subsequent intense stirring process of the resin leads to a dramatic improvement in the dispersion of the nanotubes in the epoxy. These aggregated phases then form a conductive three-dimensional network throughout the whole sample. The viscosity of the resin is not affected so much as to negatively influence the processing of the resin at these low filler contents. Furthermore, there is no visible degradation of the surface finish and hence processing methods such as injection molding or extrusion could be applied in the future.

All the cured epoxy samples but the one containing the lowest filler weight fraction of 0.0225 wt.% appeared completely black to the naked eye. It is interesting to note that even on the millimetre scale the distribution of nanotubes is not uniform. Fig. 2 shows that there are regions with a dearth of nanotubes, whilst higher density regions percolate across the sample. The conductivity of the nanocomposites were measured using sample lengths of about 75 mm. This length is more than an order of magnitude larger than the maximum variation in the carbon nanotube density and therefore provides a valid measurement of the bulk conductivity.

From the AC impedance spectroscopy performed at room temperature, the real and imaginary parts of the complex impedance (Z^*) were 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).

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

The specific admittance (y) of the composites was calculated from the modulus of the complex admittance, and was used as a means of comparing the frequency behaviour,

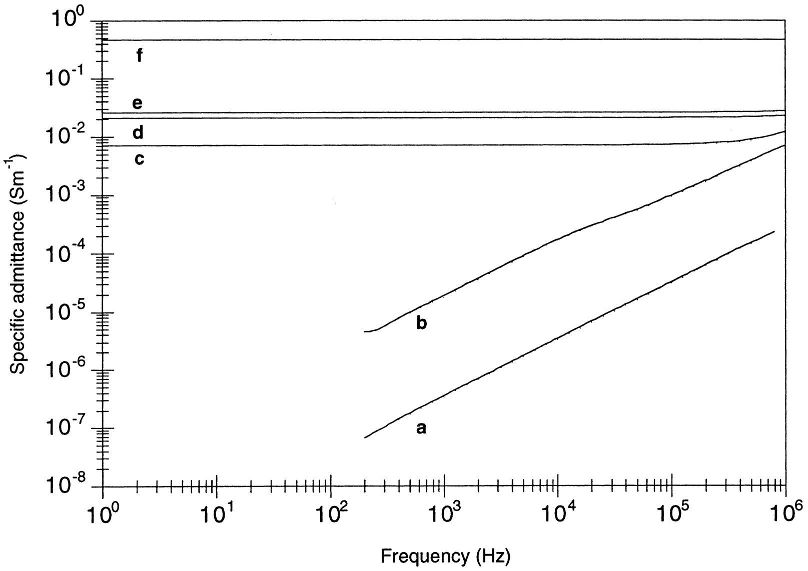

Fig. 3. Log–log plot of the specific admittance of the nanocomposites containing untreated catalytically-grown nanotubes as a function of the frequency. (a) Pure epoxy; (b) 0.0225 wt.% nanotubes; (c) 0.04 wt.%; (d) 0.10 wt.%; (e) 0.13 wt.%; (f) 0.15 wt.%.

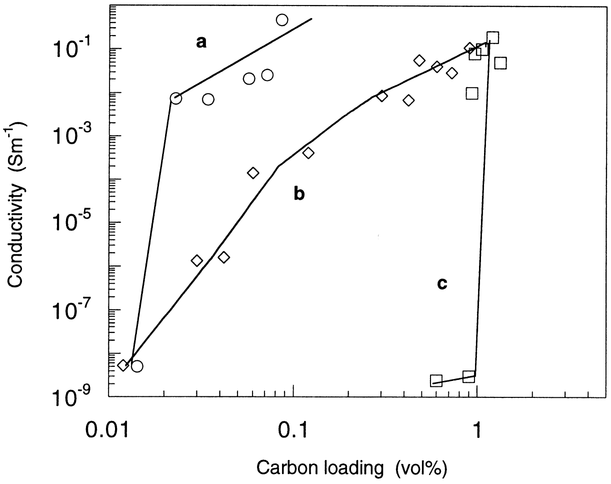

Fig. 4. Comparative log–log plot of the conductivity of nanocomposites containing: (a) Catalytically-grown carbon nanotubes; (b) Carbon black with copper-chloride, and; (c) Carbon black only, as a function of the filler volume content. Lines are included as visual aids.

as described below.

$$y(\omega) = |Y^*| \frac{d}{A}$$

where d is the sample length or distance between the electrodes, and A is the contact area. Values for the AC conductivity were determined from the real part of the complex admittance.

$$\sigma = Y' \frac{d}{A}$$

The values obtained for the AC conductivity at low frequencies were indistinguishable from the DC conductivities.

Fig. 3 shows a log–log plot of the specific admittance of the nanocomposites containing untreated nanotubes as a function of the frequency, measured on sample lengths of 75 mm. The nanocomposites at higher filler contents show a purely ohmic behaviour. In contrast, the pure epoxy is an ideal dielectric material and displays an increase in the capacitive component with increasing frequency. The sample containing 0.0225 wt.% catalytically-grown carbon nanotubes displays similar behaviour. The specific admittance obtained is larger than that of the pure epoxy due to the presence of conductive carbon nanotube aggregates within the specimen. However, the millimetre-scale carbon nanotube aggregates within this sample do not percolate. Below the percolation threshold the admittance of the nanocomposite is dominated by capacitive effects.

Above the percolation threshold the carbon nanotube aggregates provide a conductive three-dimensional path throughout the specimen. All samples containing more than 0.04 wt.% show a purely ohmic behaviour, indicated by the frequency-independence of the specific admittance. The imaginary part of the impedance does not contribute significantly to the admittance of the nanocomposites containing more than 0.04 wt.%. The percolation threshold is therefore taken to be between 0.0225 and 0.04 wt.% for untreated catalytically-grown carbon nanotubes in the epoxy matrix. Fig. 4 shows a comparison of the conductivity values obtained for nanotubes and those previously obtained for composites containing carbon black with and without the addition of copper chloride.

4. Conclusions

Catalytically-grown carbon nanotubes were dispersed as conductive fillers in an epoxy matrix, and the resulting electrical properties compared to those obtained using an optimised process for carbon black. Sufficient matrix conductivity for anti-static applications can be achieved at lower filler concentrations using carbon nanotubes in place of carbon black. The use of carbon nanotubes both reduces the percolation threshold to below 0.04 wt.%, and increases the overall conductivity achieved. At these low filler fractions neither the processing behaviour of the matrix nor the surface finish of the samples are adversely affected.

The samples produced in this study are examples of macroscopic nanotube composites. There is considerable interest in such materials as a result of the excellent mechanical properties that have been predicted for individual nanotubes [8] and in some cases observed [11]. Carbon nanotubes may offer new opportunities to modify both the electrical and mechanical properties of an insulating matrix. Further work will include the application of a voltage during curing to partially align the nanotubes in the epoxy [12] and the development of a conductive glass fibre reinforced composite, containing carbon nanotubes, following a methodology developed for carbon black [13].

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References

[1] Schüeler R. Entwicklung polymerer Verbundwerkstoffe mit elektrischer Leitfähigkeit, PhD Thesis, Technischen Universität Hamburg-Harburg. Hamburg, 1994.
[2] Kirkpatrick S. Review of Modern Physics 1973:45.
[3] Zallen R. The physics of amorphous solids. New York: Wiley, 1983.
[4] Schüeler R, Petermann J, Schulte K, Wentzel H-P. Journal of Applied Polymer Science 1997;63:1741.
[5] Prasse T, Flandin L, Schulte K, Bauhofer W. Applied Physics Letters 1998;72:1.
[6] Carmona F, Prudhon P, Barreau F. Solid State Communications 1984;51:255.

[7] Lijima S. Nature 1991;354:56.
[8] Ebbesen TW. Carbon nanotubes. Boca Raton: CRC Press, 1997.
[9] Hyperion Catalysis Int'l, Inc. US Patent 5, 165, 909, 1992.
[10] Shaffer MSP, Fan X, Windle AH. Carbon 1998;36:1603.
[11] Treacy M, Ebbesen T, Gibson J. Nature 1996;381:678.
[12] Fishbine BH. Fullerene Science and Technology 1996;4:87.
[13] Kupke M, Schulte K, Wentzel H-P. Electrically conductive glass fibre reinforced epoxy resin, ECCM-8, Naples, Italy, 1998.