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Colloidal processing, hot pressing and characterisation of electroconductive MWCNT-alumina composites with compositions near the percolation threshold

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Abstract

Multiwall Carbon Nanotubes (MWCNT)-alumina nanocomposites have been fabricated by colloidal processing and uniaxial hot pressing.

In the nanotube sols, the electrical conductivity is particularly high, even for low concentrations (≤0.7 vol.%). Classical conductivity models fail to explain this particular behaviour, which is likely to be related to the high aspect ratio of the nanotubes (>70).

Aqueous colloidal processing was performed optimising electrostatic repulsion and conserving the homogeneity by freeze-drying. Inhomogeneities of about 50 μm appeared in the composites and a thermodynamic explanation is suggested based on the free volume of elongated and spherical particles, respectively and considering the persistence length of the nanotubes.

The densification after hot pressing is incomplete (92–93%) even for the low nanotube concentrations considered (<1.4 vol.%).

The composites show electrical conductivity (2.5 S/m) and the percolation threshold is ≤0.6 vol.%.

The conductivity is maintained up to 500 °C in air, degradation of the nanotubes due to oxidation at higher temperatures is likely to occur, decreasing the conductivity.

Keywords: Nanocomposite; Nanotube; Suspension; Persistence length; Electrical conductivity; Al_2O_3

1. Introduction

When electrically conducting particles are dispersed in an electrically isolating matrix, the composite will become conducting at the so called percolation threshold.[1] Indeed, from this concentration limit, a continuous connectivity of the dispersed phase appears in the composite, which in turn becomes conducting. When the dispersed particles are spherical, the critical volume fraction (ϕ_c) above which percolation occurs is 16 vol.%. This value can be largely modified by the geometry of the particles. For instance, the elongated geometry of fibres leads to a high excluded volume, defined as the volume around an object (fibre) into which another similar object is not allowed to enter if overlapping of both objects is to be avoided.[2] If the excluded volume of two conducting fibers overlap, there is a certain probability that they will form a conducting link. Therefore, the critical volume fraction for electrical conductivity decreases as the excluded volume increases.

Carbon nanotubes (CNT) are characterised by a very big length to radius ratio (100 and more). When (semi)-conducting nanotubes are introduced in a poorly conducting ceramic matrix, a much lower percolation threshold can be expected, as shown in the literature.[3,4] However, nanotubes are difficult to process as they have unfavourable geometrical characteristics for colloidal processing,[5] due to a high excluded volume and short interaction distances. As a consequence, they also show electrical conductivity in the sol state for very low nanotube concentrations. However, this is not reflected by any known model up to now as we will show in this paper.

Furthermore, we propose a colloidal processing route, based on electrostatic repulsion between particles, combined with densification by hot pressing in order to study the electrical properties of alumina-MWCNT nanocomposites.

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2. Experimental

Nanocyl®-7000 thin Multiwall Carbon Nanotubes (MWCNT) were used. According to the producer specifications, the nanotubes have an average diameter of about 10 nm and lengths between 0.1 and 10 μm with a mean length of 1.5 μm, as determined from TEM observations. The carbon purity after the Catalytic Chemical Vapour Deposition (CCVD) process is 90%, the remaining impurity being basically encapsulated metal or oxide particles. The surface area specification is between 250 and 300 m^2/g.

Water-based suspensions from Nanocyl, stabilised at pH 4 and with 1 wt.% nanotube content, were used in this study.

As α-alumina raw material, P172SB powder (Alcan Speciality Alumina Europe, Fr; particle size ~0.4 μm, purity ~99.7%) was used. An aqueous sol containing 10 wt.% of alumina was prepared at the same pH as that of the nanotube sol.

The grain size distribution of the nanotubes was assessed by laser diffraction granulometry (Malvern Mastersizer). In order to assess the length distribution of the nanotubes, the distribution function, calculated, first, from the diffraction spectrum using a Fraunhofer diffraction model, was recalculated assuming that nanotubes have a fixed diameter of 10 nm.

Mixing of aqueous alumina sols with MWCNT sols (0.6 and 1.4 vol.% nanotubes with respect to the alumina content) was achieved after controlling and optimising the ζ potential and grain size distribution by electroacoustic and attenuation measurements of each sol, respectively (Acoustosizer II, Colloidal Dynamics, USA).

In order to preserve the homogeneity of the mixture, the suspension was rapidly frozen with liquid nitrogen and drying was carried out by freeze-drying.

The dried powder mixtures were densified by uniaxial hot pressing (KCE, Ge) under argon and the shrinkage was followed up by a Linear Variable Displacement Transducer (LVDT). All samples prepared for resistivity measurement were densified at 1450 °C during 30 min under 30 MPa uniaxial load. The final density was measured by Archimedes' method.

The homogeneity of the densified samples was assessed by Scanning Electron Microscope (SEM) observation of gold-coated rupture faces obtained after three point bending tests with a span of 15 mm and a crosshead speed of 0.1 mm/min. The microstructure was further assessed by Field-Effect-Gun Scanning Electron Microscope (FESEM). In order to assess the critical defect size, the critical stress intensity factor (K_{IC}) was measured using the Single Edge Notched Beam (SENB) technique.

Impedance measurements were assessed on plane grinded samples, in order to achieve parallel faces, and after platinum coating of the cylinder faces by sputtering. The resistivity was assessed at 100 Hz, from room temperature up to 550 °C.

3. Results and discussion

3.1. Characterisation of the aqueous nanotube suspension

The grain size distribution of the nanotubes is shown in Fig. 1. Particles have calculated lengths between 0.7 and 10 μm. The mean volume diameter is calculated to be 1.67 μm which is close to the mean value measured by Transmission Electron Microscope (TEM) by the producer (1.5 μm). Considering the particle diameter to be equal to the mean value (10 nm) the length to diameter ratio therefore varies between 70 and 1000.

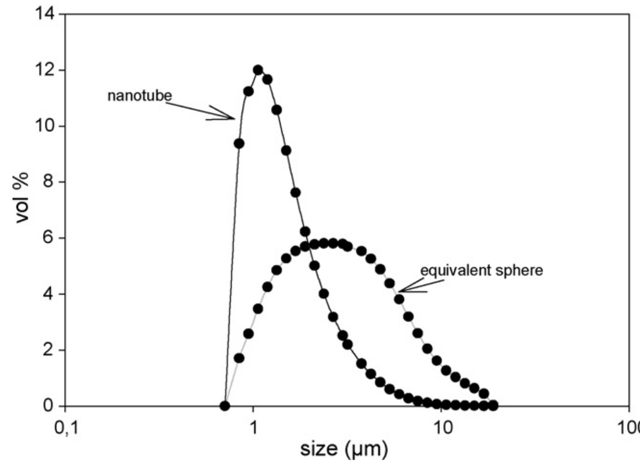

Fig. 1. Calculated length distribution function of the nanotubes.

The ζ potential of the MWCNT sol, calculated from the acoustic response measured by acoustosizer, was −33 mV. The parameters introduced in the model developed by R.W. O'Brien for calculating the complex dynamic mobility[6,7] was a density of 1.4 g cm^{-3}, obtained from the technical data sheet of the producer, whereas the dielectric constant did not significantly influence the result.

The measured electrical conductivity of the nanotube suspension was 0.8 S/m.

The concentration dependence of the electrical conductivity of the nanotube sol was assessed. In order to measure at constant ionic strength, KCl was added in order to have a fixed background of 0.01 M electrolyte concentration with an intrinsic electrical conductivity $\sigma_0 = 0.12$ S/m.

The electrical conductivity, σ, of the sol increases as the nanotube concentration increases (Fig. 2).

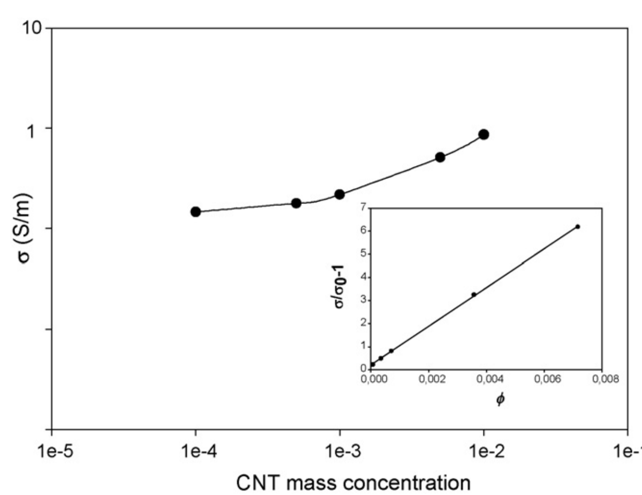

Fig. 2. Concentration dependence of electrical conductivity of the nanotube sol.