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ScienceDirect
Scripta Materialia 58 (2008) 69–72
Scripta MATERIALIA
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Comparison of carbon nanotubes and nanodisks as percolative fillers in electrically conductive composites

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Received 2 March 2007; revised 20 August 2007; accepted 23 August 2007

Composites based on polyvinylalcohol have been fabricated from solution with either carbon nanotubes or carbon nanodisks as fillers. Addition of both filler types resulted in conductivity scaling with volume fraction according to $\sigma = \sigma_0(p - p_c)^t$. The nanotube-based composites displayed percolation thresholds of 0.4 vol.% compared to 2.1 vol.% for the nanodisks, which is higher than expected due to disk alignment. Maximum conductivities observed were ~1 S m^{-1} for both composite types. Values of σ_0 of 20 and 40 S m^{-1} were calculated for nanotubes and nanodisks, respectively.

Keywords: Percolation; Electrical properties; Nanocomposite

For more than 30 years composites fabricated from polymers filled with carbon have been widely used in the sports, aviation and automotive industries to produce strong, stiff, conducting plastics. While carbon black (CB) [1] and carbon fibres [2] are routinely used in huge volumes, carbon nanotubes [3–6] and graphene [7,8] have attracted considerable attention recently due to their unique combination of mechanical and electrical properties.

One fundamental difference between carbon black, graphene and carbon nanotubes is dimensionality. In general, the physical properties of most composites depend to some degree on the dimensionality of the filler. This is most obvious in the case of the percolation threshold, the critical volume fraction of conducting filler which renders a material conductive, a quantity that depends strongly on the filler aspect ratio [9]. Both carbon nanotubes and graphene sheets have large aspect ratios, resulting in composites with very low percolation thresholds [6,8].

Several groups have studied electrical properties of composites made from various types of polymer [4–6,10–13] and nanotubes [6]. However, no direct comparison has yet been made on the difference between planar and rod-like fillers in the same polymer–solvent system. In this work, the electrical conductivities of polyvinylalcohol (PVA)-based composites have been investigated using rod-like (multiwalled carbon nanotubes (MWNTs)) and planar (carbon nanodisks [14] (CNDs)) carbon nanomaterials as fillers. The results were analyzed using percolation theory and show that lower percolation thresholds can be obtained using nanotubes as conductive fillers.

CNDs were prepared by pyrolysis of hydrocarbons in a carbon arc [14] and purchased from n-Tec (www.n-TEC.no), while MWNTs prepared by chemical vapour deposition (CVD) were purchased from Nanocyl (www.nanocyl.be, Product code 3100). Scanning electron microscopy (SEM) images of both filler materials are shown in Figure 1. The MWNTs shown in Figure 1A are typical of CVD-grown nanotubes in that they are relatively long and contain significant quantities of defects. The CNDs (Fig. 1B), however, generally appear well graphitized, with a well-defined disk shape. Note also the presence of small quantities of nanocones. Stock solutions of PVA ($M_w = 30$–70 kg mol^{-1}, Aldrich: P8136) in water were prepared at a concentration of 30 mg ml^{-1}. The solutions were sonicated for 10 min using an ultrasonic tip (GEX600, 60 kHz, 120 W), followed by 2 h in a low-power sonic bath (70 W) and a further 10 min with

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doi:10.1016/j.scriptamat.2007.08.025

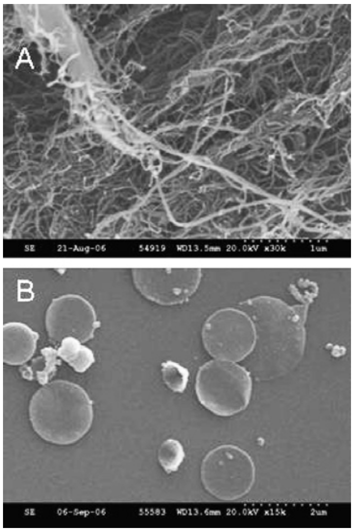

Figure 1. SEM images of (top) MWNTs and (bottom) the CNDs used in this work. Note that a small population of nanocones exist in addition to the disks.

the sonic tip. Composite dispersions were prepared by adding MWNTs and CNDs to separate PVA–water solutions with partial concentrations, *C*, of 7.5 and 10.5 mg ml^{-1}, respectively (due to their more compact geometry it was possible to disperse higher levels of disks compared to nanotubes). These were then sonicated using the same regime as before. The solutions were left to sediment for 72 h and then decanted. The mass fractions, after decantation, were found by comparison of the optical absorbance, *A*, before and after settling. Assuming the absorption coefficients of the dispersed and sedimenting nanotubes are the same we can apply the Lambert–Beer law to write: $A_b/C_b = A_a/C_a$, where the subscripts b and a represent before and after sedimentation. Calculation of the new concentrations after sedimentation, C_a, then allows the calculation of the new mass fractions to be ~16% and ~20% for the MWNT and CND samples, respectively. These two stock dispersions were then used to prepare a range of composite dispersions with different filler contents.

The stock dispersions were diluted by addition of polymer solution to provide a range of dispersions with different nanodisk/nanotube mass fractions. Free-standing films were drop-cast in standard weighing boats (3 cm × 3 cm × 1 cm, polystyrene) and the water evaporated in a oven at a temperature of 60 °C. The film thicknesses were ~65 μm on average as measured using a digital micrometer. This relatively high thickness is in order to ensure a minimum sample dimension, significantly greater than 10 times the longest filler dimension as specified by Foygel et al. [15]. The films were peeled off the substrates, cut into 12 mm × 12 mm squares and then gold contacts were evaporated onto either side, yielding six sandwich-structure devices with an active area of ~6 mm^2. In this geometry we measure the bulk conductivity perpendicular to the film. The volume fractions, *p*, were calculated from the mass fractions [16] taking the densities to be 1300, 1800 and 2000 kg m^{-3} for the polymer, nanotubes and nanodisks, respectively. DC measurements were made using a Keithley Model 2400 sourcemeter in the voltage range 0–4 V. AC measurements were made using a Zahner IM6e impedance spectrometer over a frequency range of 1 Hz to 1 MHz with applied alternating voltage of 20 mV. MWNT and CND powder conductivities were determined by loosely packing the powder into a cylindrical holder with electrodes on each end. Thin films were prepared by vacuum filtration of dispersions of the nanotubes/nanodisks in *N*-methylpyrrolidone onto Teflon filter papers. Conductivity measurements were made by measuring the film resistance as a function of film length.

In all cases, current–voltage curves (not shown) were ohmic in the voltage range studied. Conductivities were calculated from the slopes of the current–voltage curves and are presented in Figure 2. For both fillers, the conductivity increases rapidly as the volume fraction is increased. However, the onset of the conductivity occurs at higher volume fraction for the disks compared to the MWNT samples. Furthermore, the disks reach slightly higher conductivities than the MWNTs. In systems such as these, the onset of conductivity occurs at the percolation threshold, p_c. The frequency dependence of the conductivity moduli are shown in Figure 3. At low volume fraction, the conductivity scales linearly with volume as is appropriate for a dielectric. At higher volume fractions the conductivity becomes frequency independent at low frequency, indicating conducting behaviour. The transition between these regimes gives the range in which the percolation threshold is located. In addition, Cole–Cole plots (not shown) display one semicircle for all mass fractions, in both sets of samples, indicating film homogeneity.

The type of non-linear behaviour displayed in Figure 2 can be modelled (above the percolation threshold) using the percolation scaling law [17]:

$$\sigma \cong \sigma_0 (p - p_c)^t, \tag{1}$$

where σ is the conductivity, *p* is the volume fraction, p_c is the percolation threshold, and σ_0 and *t* are constants. The conductivity data for both tubes and disks were fitted to Eq. (1) in Figure 2 (inset). In both cases a good fit was obtained. The fit parameters obtained are presented in Table 1 where they can be compared with typical results from the literature for polymers filled with carbon black [1] (spheres), graphene [8] (sheets) and carbon fibres [18].

The percolation thresholds for disks and tubes were found to be 2.1 and 0.4 vol.%, respectively. The latter value is typical for composites filled with nanotubes

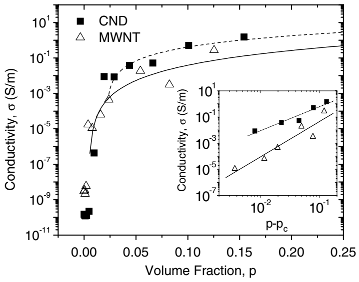

Figure 2. DC conductivity versus volume fraction, *p*, for both MWNTs and CNDs as fillers in PVA-based composites. Inset: conductivity plotted versus $p - p_c$. The lines are the fits to Eq. (1).