



Thermosetting nanocomposites with high carbon nanotube loadings processed by a scalable powder based method



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ABSTRACT

A powder based processing route was developed to allow manufacturing of thermosetting nanocomposites with high (20 wt%) carbon nanotube (CNT) loading fractions. Adaptation of high shear mixing methods, as used in thermoplastic processing, ensured that the CNTs were well distributed and dispersed even at the highest loadings. By minimising flow distances, compression moulding of powders ensured that the CNTs did not agglomerate during consolidation, and yielded a percolated CNT network in a nanocomposite with excellent electrical and thermal conductivities of 67 S m^{-1} and $0.77 \text{ W m}^{-1} \text{ K}^{-1}$, respectively. Unusually, the CNTs provided effective mechanical reinforcement at even the highest loadings; embrittlement is minimised by avoiding large scale inhomogeneities and the maximum measured Young's modulus (5.4 GPa) and yield strength (90 MPa) could make the nanocomposite an attractive matrix for continuous fibre composites. The macromechanical measurements were interpolated using micromechanical models that were previously successfully applied at the nanoscale.

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1. Introduction

Carbon nanotubes (CNTs) have been scrutinized for over a decade as a constituent in thermoset based nanocomposites (NCs) due to their exceptional intrinsic multifunctional properties [1]. One of the major challenges in the field has been to distribute and disperse high loading fractions of CNTs in epoxy resins by a route that is scalable to high throughput. The choice of processing route is critical to determining the microstructure and hence properties of the composite; agglomeration of CNTs is often particularly problematic [2].

Large CNT loadings have been relatively easily achieved in thermoplastics by shear mixing [3,4], as they benefit from broad processing windows. For thermosets, traditional dispersion techniques such as simple stirring and sonication have produced good

quality NCs for low CNT loadings, but have been ineffective at CNT volume fractions beyond a few percent [5–7]. At high loadings, techniques such as layer-by-layer (LBL) deposition [8], resin infiltration of buckypapers [9], drawing, aligning and stacking CNT sheets [10] or resin infusing continuous and aligned CNT forests [11,12] have been successfully employed to manufacture high quality thermosetting composites. In one promising example, highly aligned and crystalline CNT arrays were infused with epoxy and shown to be an effective reinforcement (16.5 wt%), improving stiffness from 2.5 to 20.5 GPa, strength from 89 to 231 MPa, and electrical conductivity (σ_{DC}) similar to that of amorphous carbon ($\sim 10^3 \text{ S m}^{-1}$) [10].

Three roll milling has been identified as a promising approach for dispersing high fractions of CNTs in epoxy resins in large volumes [13]. This technique has been successfully used to produce NCs containing up to 5 wt% multi walled carbon nanotubes (MWCNTs) that also have enhanced mechanical, electrical and thermal properties [14]. The highest CNT loading reported in epoxy with this method is 8 wt% [15], but since the aim was maximum σ_{DC} , the NC was only moderately sheared to allow the formation of

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a dense, interconnected CNT network, which is not optimal for mechanical performance. However, in principle, mixing CNTs and thermosets using large shear forces as done in thermoplastic based NCs could yield good CNT dispersions at high loadings.

This work draws on the potential of readily scalable, shear mixing techniques to make excellent isotropic dispersions of CNTs in epoxy matrices. The aim was to avoid agglomeration on the 10–100 μm scale, which is typically the limitation to introducing large CNT fractions in the resin. The approach uses thermoplastic processing techniques, specifically extrusion; the excellent dispersion was maintained during consolidation by minimising the flow distance using a powder-based, vacuum-assisted compression moulding technique. The resulting NCs were characterised mechanically, electrically and thermally to determine the success of the processing route and the resulting properties.

2. Experimental

2.1. Materials and nanocomposite preparation

The CNTs (NC 7000, Nanocyl™) were industrial grade, highly entangled and catalytically grown. According to the manufacturer's datasheet, the CNTs were about 1.5 μm long, 10 nm in diameter and contained 10 wt% metal oxide catalyst; the catalyst content was confirmed by thermogravimetric analysis (TGA) in air. Raman spectroscopy confirmed [16] a large proportion of defects in the otherwise graphitic walls ($I_G/I_D = 0.86$). The matrix consists of a Bisphenol-A and Bisphenol-F epoxy blend (EPIKOTE™ 1001) cured using a dicyandiamide (Dyhard® 100S) hardener with an average particle size of 10 μm . Both components were generously provided by Hexcel Composites (Duxford, UK).

When choosing this resin system, there were two considerations. The first was to upgrade the properties of a low-cost resin so that it could be used for structural applications. The second was that the NC should be moulded as a fine powder in order to minimise flow distances during consolidation thus minimising re-agglomeration and difficulties associated with high viscosities. EPIKOTE™ 1001 was chosen because it is a relatively inexpensive coating resin and remained as a powder at ambient temperatures rather than fusing. Dicyandiamide (DICY), a latent curing agent, provides a broad processing window so that CNTs can be initially mixed into the epoxy at high temperature and shear without the undesired onset of gelation [17].

DICY was weighed out at 4% by weight of resin and 2.4, 4.8, 9.1, 13 and 20% CNTs by weight of the composite. Control samples were prepared without any CNTs. The raw materials were mixed using a co-rotating twin screw extruder (PRISM TSE 16 TC, Thermo Scientific) in two passes at speeds of 100–200 RPM (residence time of 2–5 min) and barrel temperature of 70–125 °C to maintain constant torque.

The NC product was then ground into a powder using a cryogenic ball mill (Cryomill, Retsch). The milling process was adjusted by varying the duration and frequency of the grinding cycles to reduce the median powder particle size, and obtain a narrow particle size distribution. The powder particle sizes were measured from surfactant stabilised suspensions (0.5% Triton X-100 by weight of water) in deionised water using a laser diffractometer (Mastersizer 2000, Malvern Instruments), which produces a distribution of particle diameters based on refraction angles, with larger particles having smaller refraction angles.

The powder was consolidated by compression moulding into dogbones according to the ASTM D638 Type V specification with a $3 \times 3 \text{ mm}^2$ gauge section. The mould assembly containing the powder was covered with peel ply, breather cloth, and a vacuum bagging sheet sealed to a metal plate with tacky tape. Vacuum was

applied for 30 min to remove air, then held while the mould was heated to 125 °C on the platen of a hydraulic hot press (Moore Presses) to allow the powder to melt. Once the desired temperature was reached, 14.5 bar of pressure was applied and the mould was heated to 150 °C to cure for 12 h. The control sample was cured following the same temperature profile, but in a vacuum oven and without a plunger since the low viscosity epoxy melt flowed easily; overflow during degassing was thus prevented.

2.2. Nanotube and nanocomposite microscopical characterisation

SEM (LEO Gemini 1525 FEG, Carl Zeiss) and TEM (2100, JEOL) of over 100 CNTs were used to determine their length and diameter distributions, respectively. Samples for TEM were prepared by dipping a holey carbon grid into an ethanol solution containing as-received nanotubes dispersed by bath sonication (USC300T, VWR), and imaged at an accelerating voltage of 200 kV in bright field. Samples for measuring CNT lengths by SEM were prepared by dissolving in acetone the uncured resin from NCs that had been extruded and cryomilled, filtering (0.1 μm hydrophilic PTFE membrane, Millipore) and washing the nanotubes with acetone (ACS, VWR), suspending them in dimethylformamide (DMF) (Rectapur, VWR) by bath sonication and pipetting the suspension onto polished SEM stubs. Images were collected at an accelerating voltage of 10 kV, and analysed with the ImageJ software.

SEM of fractured tensile samples was also used to characterise the dispersion and distribution of the CNTs in the epoxy system and measure their pull-out length. Fractured samples were mounted onto aluminium stubs and sputter coated with a 5 nm thick layer of chromium to prevent charging. The specimens with the highest CNT loading were sufficiently conductive and were not sputter coated so as to allow observation of the CNT-resin interface. Samples were imaged at an accelerating voltage of 3 kV.

The morphology of the NC microstructure was characterised by differential interference contrast (DIC) optical reflective microscopy (AX10 with AxioVision, Zeiss) using fragments from the grips of tensile test specimens that were mounted in epoxy, then ground and polished to 1 μm with a rotary polishing machine (Motopol 12, Buehler).

2.3. Chemical and physical characterisation

The composition of the NCs was determined by TGA (Pyris 1, PerkinElmer) in N_2 at a ramp rate of 5 °C/min from 100 to 850 °C using segments taken from spent mechanical test specimens. Densities of the NC dogbones were measured by the gas displacement method with a pycnometer (Accupyc 1330, Micrometrics GmbH).

The curing behaviour of the NC was investigated using differential scanning calorimetry (DSC) (TA Q2000, TA Instruments). The extent of reaction was determined from integrating the heat flow against time as measured from isothermal scans at 150 °C [18] and normalising it to the integrated heat flow of the control sample. The heat flows were normalised for the mass fraction of resin, as the CNTs are not believed to participate in the crosslinking reaction. The glass transition temperature (T_g) of the cured NCs was measured from dynamic DSC scans at 10 °C/min between 20 and 150 °C.

Samples for conductivity measurements were sectioned from the grip regions of spent mechanical test specimens and polished to remove gripping damage. The electrical conductivities in three axes were deduced from volume resistances measured with a two point probe and an ohm meter (DM9C, Amprobe). Silver paste was applied to the probe and the contact points on each sample to minimise contact resistance. The thermal conductivity (k) was

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