Macromolecular Nanotechnology

A comparative study on the mechanical, electrical and piezoresistive properties of polymer composites using carbon nanostructures of different topology

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ABSTRACT

The mechanical properties, electrical conductivity and piezoresistive response of thermosetting polymer nanocomposites comprising carbon nanotubes (CNTs, one-dimensional topology, 1D), few-layer thermally reduced graphene oxide (FLG, two-dimensional topology, 2D), cubic-shaped few-layer graphene shells (CGSs, three-dimensional topology, 3D), and hybrid combinations of them (1D-2D and 1D-3D) are investigated. It is observed that the most electro-conductive materials are formed when CGSs, CNTs or a hybrid combination of both are used, likely because of the lower defect density of CGSs and the higher aspect ratio of CNTs. The mechanical properties and piezoresistive sensitivity are higher for composites comprising CNTs or a 1D-2D hybrid combination of CNTs and FLGs. While the increased mechanical properties for these two groups of composites are attributed to the higher aspect ratio/lateral size, higher number of dangling bonds and functionalities, and higher specific surface area (for the case of FLGs) of their fillers, the increased piezoresistive sensitivity is explained in terms of their higher excluded volume within the composite.

1. Introduction

The concept of piezoresistivity (change of electrical resistance driven by a change in mechanical stress/strain) using carbon nanostructures as polymer fillers has been widely reported for the development of flexible electronics, motion, and strain sensors, among other novel applications [1–5]. Earlier works in this field refer to the use of carbon fibers, carbon black and graphite [6–10]. More recently, a vast amount of research efforts have been devoted to the development of piezoresistive strain and pressure sensors using carbon nanotubes (CNTs) embedded in a variety of polymers [11–19]. Given their large aspect ratio, CNTs can be considered as one-dimensional (1D) materials, and this topological property is one of their biggest advantages to form electrically percolated networks at very low concentrations in polymer composites, see e.g. [20,21]. For two-dimensional (2D) nanostructures, the fact that graphene (single layer) is too

difficult to synthesize and maintain energetically stable as a monolayer inside a polymer, has probably hindered the development of true graphene polymer composites. However, recent developments of novel synthesis routes to produce a family of few-layer graphene materials [22–26] targeting comparable structural quality and analogous properties to graphene, have brought about a host of interest in polymer composites filled with several 2D forms of few-layer graphene and exfoliated graphite [27–33]. Another family of carbon nanostructures of particular interest is the family of three-dimensional (3D) nanostructured few-layer graphene (hollow) shells. These novel 3D materials are commonly produced by using a metal, oxide or carbide nanoparticle as a template, which is then removed by chemical digestion or carburization [34,35]. After removing the template particle, the resulting carbon nanostructure becomes typically a round or cubic shell, depending on the morphology of the templating particle [35]. Because of their novelty, research on the piezoresistive properties of

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polymer nanocomposites filled with this kind of 3D carbon nanostructures is probably inexistent to date. It has also been recently proposed that the use of 1D-2D hybrid nanostructures may benefit the mechanical, electrical and piezoresistive properties of polymer composites [12,36,33] but more research is needed to confirm such preliminary observations. Therefore, this work investigates the electrical, mechanical and piezoresistive properties of a vinyl ester polymer composite filled with CNTs, few-layer graphene oxide platelets (FLGs), few-layer graphene shells of 3D cubic morphology (CGSs), and hybrid combinations of them (CNT-FLG and CNT-CGS). Basic characterization of the carbon nanostructures is provided in an attempt to better understand the property-structure relationships in this kind of novel carbon nanocomposites, advancing towards the development of strain/pressure-sensitive smart materials.

2. Materials and methods

2.1. Materials

Commercial MWCNTs (Cheap Tubes Inc., Vermont, USA) with purity > 95%, 4–6 nm inner diameter, 15–40 nm outer diameter (d_{CNT} = 29.1 nm as mean of the diameter distribution), interlayer distance $\sim$ 0.34 nm, and 1–6 μm length (L = 2.59 μm as mean of the length distribution) were used. Dedicated length and diameter distributions of these MWCNTs have been previously reported in [37]. All MWCNTs were chemically oxidized using a solution of H_2SO_4/NHO_3 at 3 M (each) for 2 h following the procedure described in [38]. Raman characterization (Renishaw InVia Reflex, using a 532 nm green laser) of these MWCNTs showed that the average ratio of intensities of their D-to-G bands (I_D/I_G) is 0.71 and the average ratio of their areas (A_D/A_G) is 0.72. Measurements of N_2 adsorption-desorption isotherms at 77 K (Quantachrome 2000 equipment) by the Brunauer-Emmett-Teller (BET) method yielded a specific surface area of 110 m²/g, as detailed in Table 1.

The FLG sheets were synthesized from a top-down synthesis approach by expanding natural graphite using the Brödie's method to oxidize the carbon layers, followed by thermal exfoliation/reduction at 1000 °C, as detailed elsewhere [23]. This produced FLG sheets of approximately 315 (± 160) nm planar dimensions, comprising 4–6 individual sheets with an interlayer distance of $\sim$ 0.60 nm [23,39], as summarized in Table 1. Raman characterization of the FLG sheets yielded I_G/I_D = 0.76 and A_D/A_G = 2.16, and its measured BET surface area was 727 m²/g.

The cubic graphene shells (CGSs) were synthesized using a bottom-up chemical vapor deposition (CVD) method described in detail in [35]. The synthesis used cubic MgO nano-crystals as template particles for graphene growth which were then removed by refluxing in diluted HCl, to leave hollow (mostly cubic-shaped) shells comprising 2–5 layers of graphene with interlayer distance $\sim$ 0.34 nm and $\sim$ 100–200 nm side-length. Transmission electron microscope images of the three carbon

Table 1
Physico-chemical characteristics of the three carbon nanostructures used as fillers.

Property	CNT	FLG	CGS
Length (*L*, μm)	2.59	–	–
Diameter (CNT) or side-length (*d*, nm)	29.1	~315	~150
Number of graphene layers	> 20	4–6	2–5
Raman I_D/I_G	0.71 (± 0.05)	0.76 (± 0.07)	1.0 (± 0.08)
Raman A_D/A_G	0.72 (± 0.03)	2.16 (± 0.11)	1.12 (± 0.11)
Specific BET surface area (m²/g)	110	727	592

Table 2
Nomenclature used for the nanocomposites.

Label	Filler composition (wt.%)	Total filler content (wt.%)
A	0.5 CNT	0.5
B	0.5 FLG	
C	0.5 CGS	
D	0.25 CNT + 0.25 FLG	
E	0.25 CNT + 0.25 CGS	
F	0.5 CNT + 0.5 FLG	1.0
G	0.5 CNT + 0.5 CGS	

nanostructures were investigated and comparison of their Raman spectra is included in Appendix A.

A vinyl ester Hetron 992 FR resin from Ashland composites (Dublin, OH, USA) was used as polymer matrix. This resin has low viscosity, good mechanical, properties and is commonly used for manufacturing large scale composites using vacuum-assisted processes. Methyl ethyl ketone peroxide in a proportion of 0.6 wt% and 0.2 wt% Cobalt naphthenate were used to initiate and promote the polymerization reaction. Tensile testing of five specimens of the neat matrix yielded an elastic modulus of 2.27 ± 0.1 GPa and a tensile strength of 70.2 ± 4.0 MPa.

2.2. Manufacturing of nanocomposites

Vinyl ester nanocomposites were fabricated by a process based on mechanical stirring and ultrasonic dispersion. Carbon nanostructures (CNSs) were first stirred in the resin for 30 min and then dispersed by a (cooled) ultrasonic bath (42 kHz and 70 W) for 3 h, before adding the initiator and catalysts and pouring into dumbbell silicon molds. After curing, specimens were post-cured first at 50 °C and then at 100 °C for 2 h each step. Seven groups of nanocomposites were fabricated in this way, which will be hereafter identified with letters *A* to *G* as detailed in Table 2. Specimens *A* to *E* contain the same total concentration of filler (0.5 wt%) while specimens *F* and *G* double the total filler concentration of specimens *A-E*, both containing 0.5 wt% of MWCNTs and 0.5 wt% of other carbon filler. Specimens *A* to *C* contain only one filler, while specimens *D* to *G* are hybrids.

2.3. Electrical and electro-mechanical tests

Electrical resistance was measured using 10 mm long specimens of 3 mm by 3 mm square cross section, with 2 mm thick lines of silver paint at the specimen ends (lengthwise) to define the electrodes. Electrical resistance (*R*) measurements were conducted using a Keithley 6517B electrometer and converted to volumetric (direct current) electrical conductivity using the effective specimen length (6 mm) and cross sectional area (9 mm²). Four specimens (replicates) per group were measured, reporting the average and one standard deviation.

The electro-mechanical (piezoresistive) uniaxial tensile tests were conducted by using Type V dumbbell specimens according to the D638 ASTM standard [40]. Electrodes for two point measurements were defined by a pair of copper wires running around the periphery of the specimen cemented by 2 mm thick sliver paint lines. The electrodes were centered on the specimen separated 6 mm. A table-top Shimadzu AGS-X universal testing machine equipped with a 1 kN load cell was employed. The crosshead displacement rate of the universal testing machine was 0.5 mm/min and the strain was calculated from the crosshead displacement. *In situ* electrical measurements were conducted