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Probing of polymer to carbon nanotube surface interactions within highly aligned electrospun nanofibers for advanced composites

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ABSTRACT

By electrospinning poly(ethylene oxide) (PEO)-blended sodium dodecyl sulfate (SDS) functionalized carbon nanotube (CNT) solutions, we engineered single- and double-walled nanotubes into highly aligned arrays. CNT alignment was measured using electron microscopy and polarised Raman spectroscopy. Mechanical tensile testing demonstrates that a CNT loading of 3.9 wt% increases the ultimate tensile strength and ductility of our composites by over a factor of 3, and the Young's modulus by over a factor of 4, to ~260 MPa. Transmission electron microscopy (TEM) reveals how the aligned nanotubes provide a solid structure, preventing polymer chains from slipping, as well as polymer crystallisation structures such as 'shish-kebabs' forming, which are responsible for the improved mechanical properties of the composite. Differential scanning calorimetry (DSC) and small angle X-ray scattering (SAXS) reveals micellar and hexagonal columnar structures along the axis of the fibers, some of which are associated with the presence of the CNT, where these hexagonal structures are associated with the SDS functionalization on the CNT surfaces. This work demonstrates the benefits of CNT alignment within composites, revealing the effectiveness of the electrospinning technique, which enables significantly improved functionality, increasing the utility of the composites for use in many different technological areas.

1. Introduction

Carbon nanotubes (CNT) are of interest due to their outstanding mechanical, thermal and electrical properties, combined with their high aspect ratio: nano-sized diameters and typically microns in length [1]. It has been well documented that, due to the difficulty in growing continuous CNT material to macroscopic lengths [2], an easier route to harnessing their unique properties on a larger scale is to align and connect or combine the individual tubes [3]. A high degree of CNT alignment will result in the magnification of the uniaxially excellent properties of individual nanotubes to macroscopic length-scales. This scalable alignment technology therefore is a strong candidate for large-area manufacturing of highly-conductive light-weight CNT yarns/wires [4] and advanced composite materials [5]. A secondary challenge is to ensure a good, strong chemical bond between the matrix and the CNT content, to enable both the transfer of mechanical strain but also to improve electrical and thermal conductivity between the matrix and the CNT [6]. Although there are several successful methods of CNT alignment [7], one simple and elegant method is electrospinning, which forms nanofibers based on the uniaxial stretching of a viscoelastic solution, utilising electrostatic forces to extend the solution as it solidifies, before collection [8,9]. Furthermore, the stretching and shear flow occurring during the travel of the electrospun polymer from the source to the collector can lead to controlled crystallisation of the polymer chains [10]. When they are introduced, CNT incorporation has been observed to promote crystallisation along their surfaces as a regular structure known as 'shish-kebab' [11], where the CNT acts as the central directional nucleation point, which promotes the polymer to form spherulites along the nanotubes length, resembling similarity of meat layers along a kebab stick. This crystalline formation facilities load transfer from the polymer to the embedded nanotubes, whilst

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improving the electrical and thermal conductivities of the resulting composite.

Electrospinning (see Fig. 1, diagram A) has been commonly used for nanofiber manufacture since its inception in 1887 [12], with modern utilisation of the nanofibers covering a vast range of applications, such as polymer textiles, air filters, tissue-growth substrates, etc. [13]. Various publications report on how electrospinning CNT loaded solutions, dispersed within a suitable polymer, can be used to produce arrays of aligned fibers, containing the embedded, aligned nanotubes [9,14–17]. These CNT-embedded polymer nanofibers exhibit improved properties, depending on the polymer and type of CNT reinforcement, but few studies explore the polymer/CNT interactions which result in the overall material enhancement. By using high-quality, long nanotubes (>1 μm) functionalized with sodium dodecyl sulfate (SDS), the electrospinning process was used to align nanotubes within poly(ethylene oxide) (PEO) nanofibers (a water-soluble polymer), producing a nano-composite material. Furthermore, we will demonstrate that not only are the electrospun fibers well-aligned, but also that the CNT content is also well aligned. The inclusion of the highly-aligned nanotubes within the PEO was found to enhance the mechanical properties of the material by a significant factor, increasing the Young's modulus by up to 430%. This we attribute to be the result of the CNT functionalization promoting the growth of polymer nanocrystalline structures in their vicinity, due to the shear flow and stretching experienced during the electrospinning process [18]. Thermal analysis revealed that although the CNT presence lowered the overall crystal content as well as the melting temperature, it promoted crystal growth and initiated crystallisation at a higher temperature on cooling. This change in crystallisation behaviour was evidenced by electron microscopy and X-ray scattering exposing how although the CNT presence lowers overall crystalline content, they equally promote the growth of an alternative crystalline structure, oriented with the nanofibers, as a rigid support for the polymer chains, allowing for the efficient transfer of mechanical stress from the polymer matrix to the CNT loading.

We analyse the CNT distribution inside the polymer fibers, their degree of alignment and reveal the polymer crystallisation around the nanotubes using: Raman spectroscopy to assess CNT quality and alignment, scanning transmission electron microscopy (STEM) to image CNT interaction and positioning within the nanofibers, differential scanning calorimetry (DSC) to probe crystallinity, and small-angle X-ray scattering (SAXS) to evaluate nanomorphology. In particular, SAXS is able to look at macroscopic-sized materials, as opposed to inferring polymer crystallisation from individual nanotubes in single polymer fibers [18,19]. We assess the mechanical properties of the composite using tensile testing, for different CNT loadings.

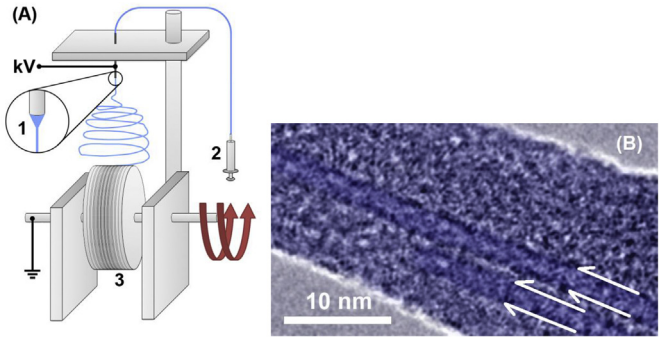

Fig. 1. (A) A schematic diagram of the electrospinning setup used, showing 1) the single needle spinneret, 2) a pumped syringe and 3) the grounded high-speed collector. (B) A false-colour transmission electron micrograph of the SDS-coated CNT material embedded within the PEO electrospun nanofiber. This image demonstrates how the electrospinning technique aligns the CNT within the polymer nanofiber (direction of CNT walls arrowed). (A colour version of this figure can be viewed online.)

2. Experimental section

PEO supplied by Sigma Aldrich (Merck) was chosen as the spinnable polymer in this study, with an average molecular weight of ~2,000,000 M_v. It provided the necessary viscoelastic properties required for electrospinning, while being low-cost and water-soluble. The single/double-wall CNT material was manufactured by Thomas Swan & Co. Ltd. using a chemical vapour deposition (CVD) process [20], and supplied as their Elicarb® 'wet-cake' product (3.7% wt. CNT in an aqueous solution, forming a 'caviar'). Raman analysis revealed that the CNT wet-cake contained single- and double-walled with predominant diameters of 1.23 nm and 1.07 nm (± 0.05 nm) for the single-walled tubes, and 1.61 nm (± 0.05 nm) for the double-walled tubes (see Supplementary Information Fig. S1). The CNT content was dispersed with sodium dodecyl sulphate (SDS) at a weight-ratio of 1:10, CNT to SDS respectively, previously reported as being the ideal ratio of surfactant to CNT [21,22]. Two aqueous solutions were mixed, containing 0.004% and 0.1% weight CNT material. These dispersions were blended with PEO after the CNT dispersion, so as to prevent the ultra-sonic irradiation destroying the polymer chains, which would render the solution unsuitable for electrospinning [23]. After all the solvent evaporates during and after electrospinning, these solutions will effectively produce PEO nanofibers containing a CNT content of 0.7% and 3.9% weight respectively. Fig. 1, image B (bright-field transmission image taken on a Hitachi HD-2300A STEM), illustrates how the embedded CNT material has been pulled into alignment by the whipping/drawing effect exerted on the polymer during the electrospinning process. This drawing/stretching effect not only pulls the polymer chains and subsequently the CNT loading into alignment, but also reduces the diameter of the electrospun fibre, so that it is much smaller than the length of the CNT, forcing it to align.

In some situations, such as tensile testing and SAXS, it was necessary to first roll the aligned CNT nanofibers into ropes or yarns. This was done by hand, rolling the nanofibers parallel to the direction of the fibre, producing a rope with diameters ranging from 200 to 300 μm, comprised of thousands of nanofibers (see Fig. 2). Cross-sectional area of these ropes was measured using both a micrometre gauge and a high-powered optical microscope.

Polarised Raman spectroscopy was conducted using a Renishaw micro-Raman spectrometer equipped with a 785 nm (red) laser. Before measuring the samples, the laser's plane of polarisation, and the spectrometers grating calibration were confirmed using a silicon reference sample. For polarised Raman analysis on the rolled CNT ropes, the incident laser polariser was fixed at the laser's measured plane of polarisation and the specimen rotated, enabling measurements to be taken with the laser polarisation both parallel and perpendicular to the nanofiber axis.

To conduct mechanical testing, the nanofiber ropes were secured into a 'TA XT Plus Texture Analyser' using the clamps provided. Each sample was analysed using a test rope length of 4.0 ± 0.1 cm. Each test was conducted at a recorded room temperature of 21 °C, at a testing speed of 0.5 mm/s, where measurements were taken 50 times a second.

DSC was used to probe crystallinity of the various nanofiber samples, this was conducted on a TA Instruments Q1000 DSC. Each sample of approximately 5 mg was tested using a heat-cool-heat method from 0 °C to 100 °C at 10 °C/min. This allowed for the initial crystallinity of the as-spun nanofibers to be compared to a sample if it was simply blended and set, giving an indication of any crystal structures produced during the electrospinning process.