

NANOSTRUCTURED FIBRE SURFACE AND COMPOSITE INTERPHASE

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Abstract

We report the use of graphene nanoplatelets (GNPs) and carbon nanotubes (CNTs) in fibre surface coatings and composite interphases to integrate both mechanical and electrical functionalities. The nanostructured fibres demonstrated enhanced wear protection and tensile strength. The electrical conductivity is introduced to the nonconductive glass fibre and polymer matrix composites. Multifunctional fibre surface and composite interphase are realized with monitoring abilities of water wetting/dewetting and polymer curing processes. The unidirectional composites fabricated via the CNT-glass fibres exhibit extremely high anisotropic electrical conductivity and relative permittivity. The fibres may find applications in many fields, such as ‘smart’ composite fabrication, chemical reaction or liquid detection, wear prevention, among many other potential applications at nanoscale.

1 Introduction

The development of material surface with both mechanical protection and sensory function is a fundamental issue of scientific and practical importance. The use of graphene nanoplatelets (GNPs) and carbon nanotubes (CNTs), as ideal reinforcements, has attracted academic and industrial interest because of their unique capacity to produce a dramatic improvement in mechanical properties, and simultaneously to introduce sensing abilities at very low filler content. The nanostructured functional materials have wide applications in the fields such as smart textiles, artificial muscles, flexible touch screens, wear protections and others.

A great progress has been achieved in this area, e.g., nanocomposites with maximum tolerance of flaws [1], solid lubrication coatings [2], smart responsive skins [3] and human-like sensing materials [4]. While most of the studies are devoted to bulk solids, thin films or powders, the functionalization of fibres or composite interphases are now drawing more and more attention from interdisciplinary fields. Recently, we have focused on integration of multiple functions into traditional glass fibres [5-9]. In this work, our approach intends for further bridging traditional materials and nanomaterials based on a simple dip-coating or ‘adhesion-orientation’ methods to form multi-functional GNPs or CNT networks on glass fibre surfaces (Fig. 1) and composite interphases.

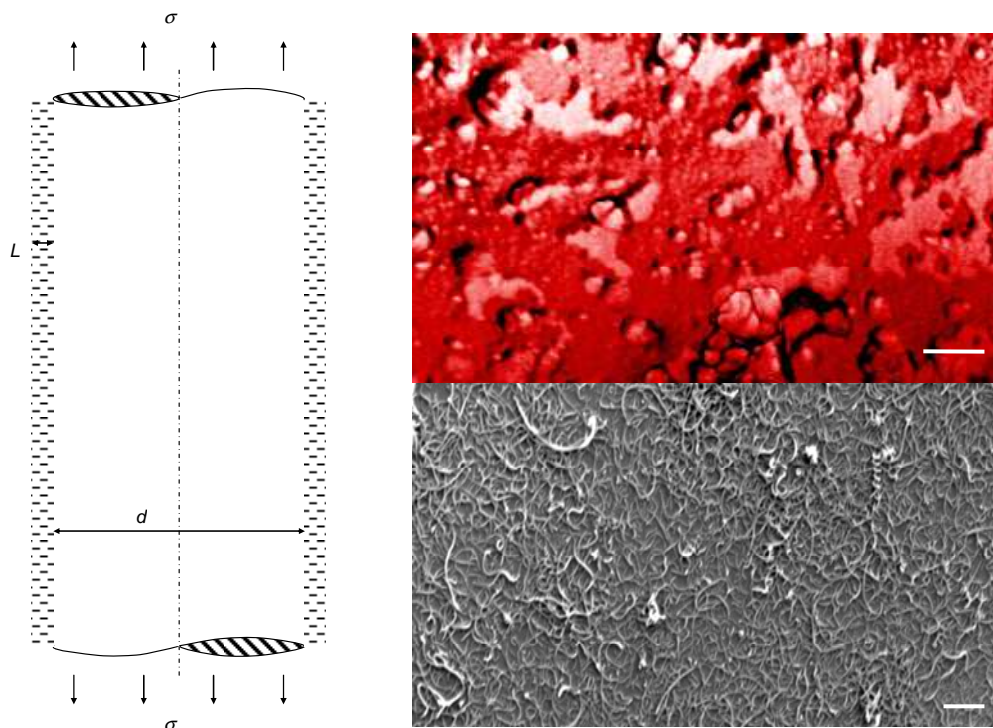


Figure 1. Cross-sectional illustration of a glass fibre coated by GNPs/epoxy (AFM phase image, right up) or CNT networks (SEM image, right bottom). Scale bars, 200 nm.

2 Materials and testing methods

The alkali-resistant glass fibres (ARG) with an average diameter of 17 μm were made at our institute by a continuous spinning process. We used commercial GNPs (xGnP-M-15, XG Science, USA) and carboxyl functionalized multi-walled CNTs (NC-3101, Nanocyl S.A., Belgium) produced via the chemical vapor deposition (CVD) process. The GNPs have average thickness of 6 nm and surface area of 135 m^2/g and the CNTs have average diameter of 9.5 nm and average length of 1.5 μm . We developed a simple ‘adhesion-orientation’ method to fabricate the GNP-glass fibres. Specifically, the single fibre initially imbedded in the epoxy resin/hardener mixture was drawn between two soft substrates where the GNPs were distributed in ‘dry’ stage without the need of a solvent, thus, the GNPs were shifted to the fibre surface by adhesive force and in turn the platelets were oriented along fibre surface direction by fluid deformation and friction/shear forces. Based on the AFM images, our initial approach achieved surface coverage rate of GNPs is about 20-50%, which could be further improved when the process is repeated layer by layer. To avoid complex effects from temperature variation, a room-temperature curing epoxy (UHU plus endfest 300, UHU GmbH & Co. KG, Germany) was used for the GNPs coatings. The epoxy resins for CNTs coatings were commercial products DGEBA resin (EPR L20, Momentive Specialty Chemicals, Germany) with hardener EPH960. We have previously reported in detail of either the continuous spinning process with aqueous sizings consisting of CNTs and film formers, or the dip-coating process with aqueous dispersion consisting of stabilized and individualized CNT without polymers [5-9].

The fibre surface morphologies were studied using atomic force microscopy (AFM, a Digital Instruments D3100, USA) and scanning electron microscopy (FE-SEM Ultra 55, Carl Zeiss SMT AG, Germany). The abrasive wear resistance of a single GNP-glass fibre was determined by the relative friction displacement (sliding between two surfaces) S , where it

contacts and abrades over the surface of abrasive paper (p2500 SiC, Buehler GmbH, Düsseldorf, Germany) on a rotating rod up to the fibre breakage (see Fig. 2a, insert). The tensile strength of single fibre was measured using the Favigraph semiautomatic fibre tensile tester (Textechno, Germany) equipped with a 1 N force cell. The gauge length is 20 mm and the cross velocity is 10 mm/min according to specification EN ISO 5079. Four-point conductivity measurements were carried out with a Keithley 2000 multimeter, to in-situ monitor the DC electrical resistance changes for the single CNT-glass fibres which were either wetted by a drop of distilled water or imbedded in the epoxy/hardener mixtures at three different ratios by weight (100:25 or 34 or 45). The direct current (DC) electrical resistance and alternating current (AC) frequency dependences of relative permittivities of unidirectional CNT-glass/epoxy composites, ϵ_r , are measured in directions parallel and perpendicular to the fibre axis at room temperature on a LCR-digital multimeter (VC-4095) and an Agilent 4263 LCR meter (Agilent Technologies Deutschland GmbH, Germany), respectively. The composites with a wide range of CNT weight fractions ($1.9 \times 10^{-4} \sim 1.45$ wt%) were used for the DC resistance measurement and the composites with 1.45 wt% of CNT were used for the relative permittivity measurement.

3 Results and discussion

3.1 Mechanics

The first set of experiments investigated how the nanostructured coatings enhance materials' wear durability and tensile strength. We characterised the abrasion resistance of single glass fibres by using the friction displacement on the abrasive paper until the fibre breakage occurs. Fig. 2a shows that the GNP coating systems lead to significant increase up to 200% in the friction displacement. The sample with epoxy coating, however, yields only about 50% improvement. Despite the test features causing a large data scatter, the mean values provide a ready implication for the ability of the GNPs to serve as solid lubricant nanoparticles for further optimize functional surface.

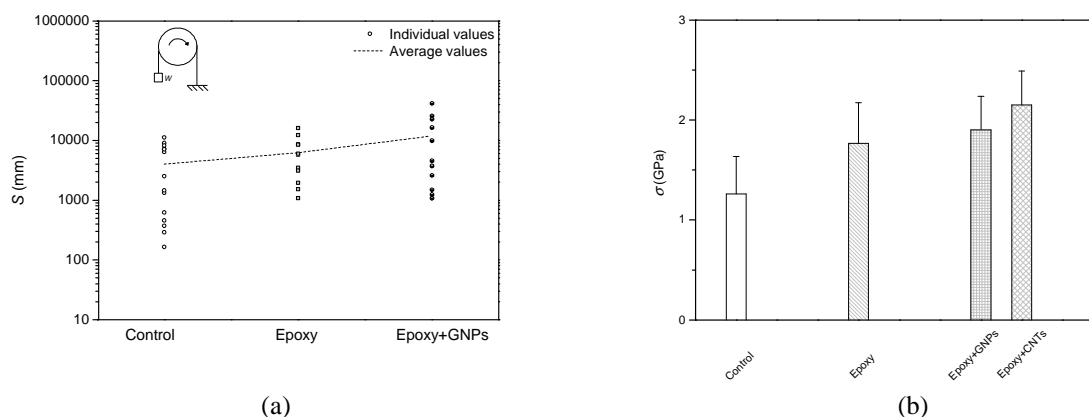


Figure 2. Comparison of (a) friction displacement S , and (b) tensile strength σ of a single glass fibre without or with epoxy or nanoparticles/epoxy coatings.

Because the critical flaws which limit the strength of fibres are located at the fibre surface, the fibre fracture behaviour is strongly affected by the variation of coating properties. As shown in Fig. 2b, the glass fibres coated with either GNPs or CNTs have higher tensile strength values than the control or the epoxy coated fibres. By using relative homogeneous distributed 1 wt% CNTs in the coatings, the CNT-glass fibre achieves remarkably 70 % increase in fibre strength, reflecting the high efficiency in healing surface flaws. In contrast to the

aforementioned wear durability, however, the GNP-glass fibre has marginal improvement in the tensile strength, possibly owing to the inhomogeneous and insufficient coverage of GNPs.

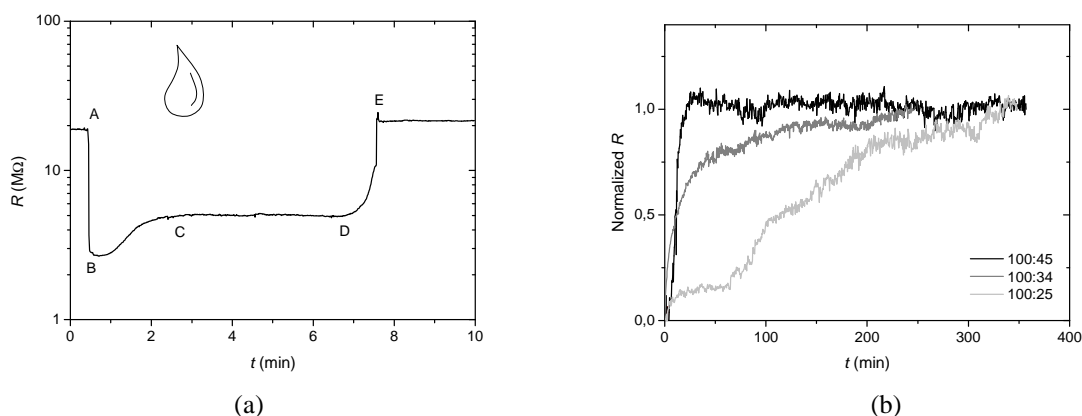


Figure 3. Change in the electrical resistance of a single CNT-glass fibre with time upon exposure to (a) a drop of water during wetting (A-D) and dewetting (D-E) processes, and (b) epoxy/hardener mixtures with three ratios.

3.2 Sensors

The second set of experiments developed an ultrathin CNT network sensor using a single CNT-glass fibre without polymer coatings (Fig. 1). The interconnected CNT networks on the glass fibre surface show typical thickness of a few tens to a few hundreds of nanometers and achieved conductivity of $10\text{--}10^4$ S m $^{-1}$ [6]. We first performed experiments to characterise the electrical responses of the entangled CNT networks to a small distilled water droplet on fibre surface. The typical electrical resistance variation of CNT networks exposed to water from wetting to dewetting processes under ambient conditions is presented in Fig. 3a. The immersion of water molecules reduces resistance and vice versa in the case of evaporation. The water immersion causes an initial sharp decrease in resistance (A-B) within two seconds, followed by a slower increase (B-C) for about one to three minutes and then a stable stage (C-D).

Several principles of mechanisms can be employed to understand the whole process. As we know, pure water has ions H_3O^+ and OH^- and ordinary distilled water in equilibrium with carbon dioxide of the air has even more ions in solution. The observed sharp decrease in the resistance is attributed to the movement of electrically charged ions in water that help to pass electricity from one tube to the next one without physical contact. On the other hand, the reverse mechanism claimed previously that the physisorbed molecules also influence the electrical properties of isolated CNT [10-11]. Since CNTs usually exhibit a hole transport like p-type semiconductor, the adsorbed water molecules transfer electrons to CNTs and in turn deplete the concentration of holes in CNTs, resulting in an increase of resistance. The current data of decreasing resistance demonstrates that the resistance of the thin CNT network is predominantly determined by the contact resistance of crossing tubes, rather than by the resistance of CNT segments in water.

A possible mechanism for the slow increase of resistance (B-C), ΔR_{BC} , is attributed to permanent loss of Ohmic contacts between part of nanotubes, since the original surface forces (such as those from hydrogen bonding, electrostatic and Van der Waals forces) imposed on the liquid were varied and capillary forces were introduced. We also found that the resistance exponentially increases in the course of desorption where the water molecules and associated ions are removed. The resistance value in the final stage, however, cannot be fully recovered

to the value in the initial stage. Interestingly, the amount of resistance increase after water evaporation (A-E) is almost the same with the above resistance difference (B-C), $\Delta R_{AE} \approx \Delta R_{BC}$, suggesting that the unrecovered part is possibly caused by those of permanent disconnected nanotube–nanotube junction points during the liquid immersion.

Further insight into the fibre sensing ability was gained from the response to chemical composition. The strong influence of epoxy/hardener mixtures to the electrical resistance of a single CNT-glass fibre is shown in Fig. 3b. The CNT networks increasing resistance with time can be attributed to the cross-linking reactions and increasing viscosity, which reduce the concentration of ions and limit mobility of free ions in the surrounding environment. An initial sharp increase followed by a slower phase is found, particularly in systems with higher hardener concentration. This can be understood by a faster formation of non-conducting layers between nanotubes and reduction of ions concentration or mobility as aforementioned. Our functional fibre with substantial role of inter-tube contacts, achieving higher sensitivity towards the cross-linking reactions or crystallization in comparison with traditional methods, will be reported in detail elsewhere [12]. Such surface/interphase with high sensitivity to environmental factors may find applications in integrated functional devices.

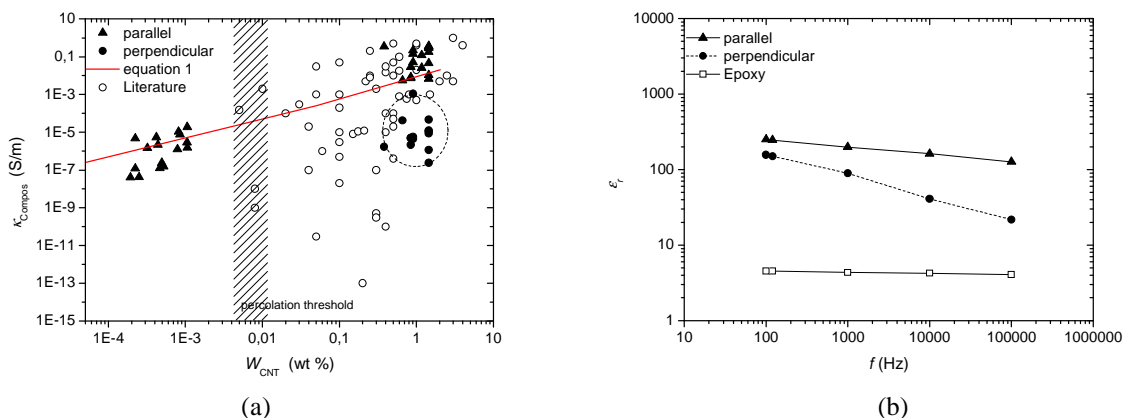


Figure 4. Anisotropic electrical properties of CNT-glass fibre/epoxy composites in the directions parallel and perpendicular to fibre axis. (a) Dependence of DC electrical conductivity on CNT content of composites. The data in the parallel direction to fibres are in close agreement with theoretical expectations (red line) by Equation 1. All the data (open circles) of various nanotube/epoxy composites from a review literature [13] distributed in the right side of the electrical percolation threshold. (b) Frequency dependence of the relative permittivities ϵ_r of epoxy resin and CNT-glass fibre/epoxy composites.

3.3 Electricity

To examine whether the unique conductive composite interphases help to introduce electrical anisotropy to the composites, we finally tested a series of unidirectional CNT-glass fibre/epoxy composites with different nanotube concentrations (Fig. 4a). The measured conductivity normal to the fibre axis, K_{\perp} , is extremely low which is attributed to very few contacts between neighbouring fibres. Thus, the conductivities along the direction of glass fibres, K_{\parallel} , are typically four orders of magnitude higher than those perpendicular to them, achieved the highest anisotropic ratio (K_{\parallel}/K_{\perp}) among the reported values of various CNTs/polymer composites. The exceptionally anisotropic property could be controlled flexibly by glass fibre direction and volume fraction, which allows for the conduction of electricity in one direction but not the others. For a 3D resistor network that contains randomly distributed CNTs in the polymer matrix, the transition nature of electrical properties with CNT concentrations normally shows a percolation threshold (Fig. 4 a) described by the classical percolation theory. It is defined as the least concentration at which a composite with

conductive inclusions is capable of conducting direct current. It is crucial to note, however, that our approach predicts that specific conductivity of composites along the fibre direction, K_{\parallel} , gradually increases with increasing fibre/nanotube concentration following a hyperbl function:

$$K_{\parallel} = K_o \rho_o / \{ \rho_1 [(W_o/W_{CNT}) - 1] + \rho_o \} \quad (1)$$

where W_o and W_{CNT} are the weight fraction of nanotubes in CNT-glass fibre and composites, ρ_o and ρ_1 are the density of epoxy and glass fibre, respectively. The specific conductivity of single CNT-glass fibre in epoxy, K_o , can be experimentally obtained. The plot using Equation 1 in Fig. 4a shows a fairly good agreement with the experimental data. Thus, our globally anisotropic network of nanotube rich interphase paves the possible way to make conductive composites at extremely lower nanotube loading than the previously reported percolation threshold values.

To substantiate further the role of conductive interphase in forming anisotropic electricity of composites, we carried out experiments to investigate the frequency-dependent dielectric properties under AC electric field. Figure 4b shows the relative permittivities of epoxy and CNT-glass fibre/epoxy composites in the directions parallel and perpendicular to the fibre axis. Towards low frequency and the electrical field in the parallel direction to the fibres, the relative permittivities of the composites with only 1.4 wt% of CNTs increase to about $\epsilon_{\parallel} \approx 250$, which is more than 50 times higher than that of the pure epoxy ($\epsilon \approx 4.5$). Because the microstructure of CNT enriched interphase between glass fibre and epoxy can be considered as sea-island structure characterised by a conductive region surrounded by a thin insulating barrier, the individual or aggregated CNTs behaved similar to mini-capacitors charged in an AC electric field leading to the largely enhanced dielectric properties.

The composites also exhibit highly anisotropic dielectric permittivity according to the fibre alignment. As clearly shown by the data of $\epsilon_{\parallel}/\epsilon_{\perp} > 6$ at $f=100$ MHz, the significantly higher dielectric values in the parallel direction than those in the perpendicular direction is observed. It should be noted that the relative permittivity decreases dramatically with increasing the frequency for the composite in the perpendicular direction. The flow of free charge from fibre to fibre is blocked by insulating matrix, where the charge polarisation decreases with frequency due to the inertia of the charge with respect to the change of polarization under the applied AC field. However, the relative permittivity shows only a slight correlation to the frequency for the composites in the parallel direction, suggesting the CNT networks behave as good conductor. In this geometry, all the conductive interphases are arranged across the entire length of composite in electric field direction and so the effect of epoxy and glass fibre upon the permittivity is trivial. Overall, the composites with relatively high and anisotropic dielectric constant combine the advantages of ferroelectric ceramics and polymer composites, and represent a novel type of dielectric material that is flexible, strong and easy to process.

4 Conclusions

A simple approach to effectively integrate both mechanical reinforcements and electrical sensitivities to a single glass fibre and composites is studied. We found that the surface nanostructured glass fibres using either graphene nanoplatelets or carbon nanotubes have enhanced wear protection and tensile strength. The ultrathin CNT networks on glass fibre surface introduce the electrical conductivity to the nonconductive glass fibres and composites. The networks present high sensitivity towards the liquid wetting/dewetting processes and polymer cross-linking reactions, owing to the out-put signal from the charge-transfer inside materials. The unidirectional composites fabricated via the CNT-glass fibres exhibit

extremely high anisotropic electrical conductivity and relative permittivity. The nanostructured fibres and composites can be employed as functional materials in many fields, such as wear prevention, chemical reaction or liquid detection, artificial nerves/muscles, “smart skins”, high charge-storage capacitors, among other potential applications at nanoscale.

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