



## Epoxy nanocomposites containing magnetite-carbon nanofibers aligned using a weak magnetic field



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### ABSTRACT

Novel magnetite-carbon nanofiber hybrids (denoted by “Fe<sub>3</sub>O<sub>4</sub>@CNFs”) have been developed by coating carbon nanofibers (CNFs) with magnetite nanoparticles in order to align CNFs in epoxy using a relatively weak magnetic field. Experimental results have shown that a weak magnetic field (~50 mT) can align these newly-developed nanofiber hybrids to form a chain-like structure in the epoxy resin. Upon curing, the epoxy nanocomposites containing the aligned Fe<sub>3</sub>O<sub>4</sub>@CNFs show (i) greatly improved electrical conductivity in the alignment direction and (ii) significantly higher fracture toughness when the Fe<sub>3</sub>O<sub>4</sub>@CNFs are aligned normal to the crack surface, compared to the nanocomposites containing randomly-oriented Fe<sub>3</sub>O<sub>4</sub>@CNFs. The mechanisms underpinning the significant improvements in the fracture toughness have been identified, including interfacial debonding, pull-out, crack bridging and rupture of the Fe<sub>3</sub>O<sub>4</sub>@CNFs, and plastic void growth in the polymer matrix.

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### 1. Introduction

Many applications of polymeric materials in electronic devices, fuel storage and transportation, automotive, and aerospace products demand good mechanical properties for structural integrity and high electrical conductivities to dissipate static electricity [1]. Carbon nanomaterials, such as carbon nanotubes (CNTs), carbon nanofibers (CNFs), and graphene nanosheets (GNSs), have emerged as promising nanofillers for polymer nanocomposites due to their outstanding mechanical and electrical properties [2–4]. The introduction of carbon nanofillers into polymers can greatly improve their electrical and mechanical properties [4–6]. The enhancements in these properties can be achieved at relatively low loadings, which arises from their high aspect ratio, leading to them frequently being superior fillers compared to the conventional micrometer-sized fillers [7]. However, the property improvements

achieved to date using carbon nanofillers are still well below the theoretical predictions due to the difficulty in achieving (i) a uniform dispersion of the nanofillers in the polymer matrices, (ii) appropriate interfacial bonding with the polymer matrices [3,5,8], and more importantly, (iii) alignment of the nanofillers. Indeed, aligned carbon nanofillers have been found to produce more significant improvements in the mechanical and electrical properties, in the direction of the alignment, when compared to their randomly-oriented counterparts [9–13].

Different approaches for aligning carbon nanofillers have been reported in the literature, mainly based on mechanical stretching [14,15] or the application of an electric field [16,17] or magnetic field [18–23]. Although using an electric field is recognized as an effective method, this technique is typically restricted to materials with very low electrical conductivity, since the field strength is usually limited to avoid dielectric breakdown of the polymer [23]. Moreover, due to their low magnetic susceptibility [18–21], an extremely strong magnetic field (e.g. of several Teslas) is usually required to align carbon-based nanofillers. For instance, Camponeschi and co-workers [21] employed a magnetic field of up to 25 T

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to orient and align CNTs in an epoxy resin and found that the properties of the resulting nanocomposites were superior to those prepared in the absence of a magnetic field. Another similar attempt was reported by Mahfuz and co-workers [20] who used magnetic fields of up to 28 T to align CNFs in a two-phase toughened epoxy resin system and achieved 21% and 3% increases in the compressive strength and modulus compared to randomly-oriented CNFs. The necessity to employ such high magnetic fields limits the practical application of this method. Therefore, various methods have been reported to functionalise carbon nanofillers with magnetic nanoparticles, especially iron-based nanoparticles, so as to align the nanofiller in a polymer matrix without needing to employ high magnetic fields [24–27]. For instance, magnetite ( $\text{Fe}_3\text{O}_4$ ) decorated single-walled CNTs have been developed using a sonochemical oxidation process and these hybrid nanofillers were successfully aligned in an epoxy using a relatively weak magnetic field [24]. In addition to CNTs, graphene-based magnetic hybrids have also been prepared by attaching  $\text{Fe}_3\text{O}_4$  nanoparticles onto the graphene nanoplatelets and/or graphene oxide, using a wet-chemical co-precipitation method. The graphene hybrids were aligned in an epoxy under a relatively low magnetic field to achieve high thermal conductivity [26] and good gas barrier properties [27].

CNFs have a relatively high aspect ratio and are an excellent low-cost alternative to CNTs [28]. However, most of the reported research efforts on functionalising CNFs by magnetic iron oxide nanoparticles have been either based on complex chemical methods or a very high temperature treatment [29,30]. Moreover, to the best of our knowledge, there is no report on aligning iron oxide-CNFs in an epoxy resin using a relatively low magnetic field to selectively reinforce the epoxy polymer in a preferred orientation.

The present work aims to explore the functionalisation process to coat carbon nanofibers with magnetic iron oxide nanoparticles by co-precipitation and to align the resultant nanofiber hybrids in an epoxy resin for developing epoxy nanocomposites with anisotropic electrical and mechanical properties. The functionalised carbon nanofibers, denoted by  $\text{Fe}_3\text{O}_4$ @CNFs, are first dispersed into a liquid epoxy resin which is then cured under a relatively weak magnetic field of ~50 mT. The electrical conductivity and fracture toughness of the cured epoxy nanocomposites, containing either randomly-oriented or aligned  $\text{Fe}_3\text{O}_4$ @CNFs are measured and compared. Finally, the toughening mechanisms are identified from fractographic studies.

## 2. Experimental details

### 2.1. Materials

Vapour grown carbon nanofibers (VGCNFs) (Pyrograf<sup>®</sup>-III, grade PR-24-XT-HHT) used in the present work are fully graphitized at 2800 °C and contain a very low content of catalyst (iron <100 ppm). They therefore possess a relatively high electrical conductivity and a low magnetic susceptibility. According to material data supplied by the manufacturer, the CNFs have an average diameter in the range of 70–200 nm and a length of between 50 and 200  $\mu\text{m}$ . The epoxy resin used is a liquid blend of bisphenol A and bisphenol F ('105' from West System) together with a slow-curing hardener ('206' from West System) which is a blend of aliphatic amines and aliphatic amine adducts based on diethylene triamine and triethylenetetramine. Concentrated nitric acid (70%) was obtained from RCI Labscan. Iron (II) sulfate heptahydrate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ), anhydrous iron chloride, and ammonia hydroxide ( $\text{NH}_4\text{OH}$ ) were sourced from Sigma–Aldrich, Australia. Carbon fiber composite substrates were manufactured from T700 carbon fiber/epoxy prepreg (VTM 264) supplied by Advanced Composites Group. Twelve

plies of this unidirectional prepreg with dimensions of 300 mm  $\times$  250 mm  $\times$  2.35 mm were used to fabricate the substrates for the fracture toughness tests by curing the prepreg plies in an autoclave at 120 °C and under a pressure of ~650 kPa for 1 h, as recommended by the supplier.

### 2.2. Preparation of the magnetic $\text{Fe}_3\text{O}_4$ @CNFs

To functionalise with  $\text{Fe}_3\text{O}_4$  nanoparticles, the CNFs were first treated with an oxidative mineral acid. Typically, 2 g of as-received CNFs were initially mixed with 200 mL of concentrated nitric acid under vigorous stirring. This mixture was then treated at 100 °C for 6 h under magnetic stirring. After this treatment, the mixture was washed several times by deionized water until reaching a pH value of ~7. The samples were vacuum filtrated and dried in a vacuum oven. After this acid treatment, the CNFs are expected to possess oxygen-containing functional groups, such as carboxylic, lactone and phenolic quinone, on their surfaces and are denoted by CNFs-OX [31].

The  $\text{Fe}_3\text{O}_4$  nanoparticles were fabricated by a facile co-precipitation method [32,33] from the CNFs-OX materials, prepared as described above. Firstly, 0.225 g of the CNFs-OX were dispersed in 200 mL distilled water by ultrasonic sonication for 15 min, into which 0.225 g of  $\text{FeCl}_3$  was added whilst stirring. The mixture was vigorously stirred for 15 min whilst being heated to 50 °C under a nitrogen ( $\text{N}_2$ ) atmosphere. Then, 0.18 g of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  was added, with continuous stirring under a  $\text{N}_2$  atmosphere for 30 min. Next, 15 mL of 8 M  $\text{NH}_4\text{OH}$  aqueous solution was added drop-wise to precipitate ferric and ferrous salts. The pH value of the mixture was kept at ~10 and the reaction was carried out at 50 °C for 30 min under vigorous magnetic stirring, and  $\text{N}_2$  was continuously purged during the reaction to prevent oxidation. The  $\text{Fe}_3\text{O}_4$ @CNFs hybrids were obtained by magnetic separation, washed with distilled water and ethanol, and finally dried under vacuum at 50 °C.

### 2.3. Preparation of the bulk epoxy nanocomposites with $\text{Fe}_3\text{O}_4$ @CNFs

The epoxy nanocomposites containing  $\text{Fe}_3\text{O}_4$ @CNFs were prepared as described below. The  $\text{Fe}_3\text{O}_4$ @CNFs were firstly dispersed in a small amount of acetone by bath sonication for 15 min (the typical concentration being 20 mg/mL). Epoxy resin was then added and the sonication process was continued for 1 h. The acetone was then removed under reduced pressure. Subsequently, a stoichiometric amount of hardener was added and the mixture was poured into a rubber mold for curing. To align the  $\text{Fe}_3\text{O}_4$ @CNFs, the mixture was subjected to a weak magnetic field of ~50 mT generated by a pair of permanent magnets whilst it was being cured. Using a gaussmeter, the intensity of the magnetic field was measured to be approximately 50 mT at a distance of 4 cm between a pair of ferrite magnets which were 150  $\times$  50  $\times$  25.4 mm in size. Initial, exploratory, experiments were carried out using different intensities of magnetic field, ranging from 20 mT to 50 mT by changing the gap between the magnets. Since the alignment of the  $\text{Fe}_3\text{O}_4$ @CNFs needs to be completed prior to gelation of the epoxy (the gel time of the epoxy is around 20–30 min at 25 °C), a magnetic field strength of 50 mT was finally selected so that the  $\text{Fe}_3\text{O}_4$ @CNFs could be highly aligned within approximately 10 min from the application of the magnetic field. Epoxy nanocomposites containing various weight contents (i.e. 0.0, 0.2, 0.4, and 0.6 wt%) of the  $\text{Fe}_3\text{O}_4$ @CNFs were prepared.

### 2.4. Preparation of composite joints

Prior to the application of the liquid epoxy resin mixture as an adhesive to form bonded joints, the surfaces of the carbon-fiber

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