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One-step amino-functionalization of milled carbon fibre for enhancement of thermo-physical properties of epoxy composites

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ABSTRACT

Development of new chemical approaches for preparation of engineered carbon-based fillers is critical for high-performance applications. Herein, an efficient method for covalent functionalization of polyacrylonitrile-based carbon fibre through azo radical addition under mild condition is demonstrated. In this way, isobutyronitrile radicals *in situ* produced from thermal decomposition of 2,2′-azobisisobutyronitrile (AIBN), were covalently grafted on milled carbon fibre (MCF) surface, assisted by microwave irradiation, as evidenced by FTIR, Raman, and TGA analysis. The grafted isobutyronitriles on MCF surface (*n*-MCF) were applied for further MCF amino-functionalization (*a*-MCF) via nucleophilic reaction of an amine-rich compound. Then, both pure MCF and *a*-MCF were incorporated into epoxy matrix; and its curing process and thermo-physical properties were investigated using DSC, rheometry, DMA, TGA, and flexural analysis. The T_g and flexural strength of epoxy/*a*-MCF composites, compared to epoxy/MCF, increased by ~3.5% and ~10.2%, resulting from good adhesion between *a*-MCF and epoxy matrix which confirmed by SEM observations.

1. Introduction

For decades, polyacrylonitrile-based carbon fibres have been widely employed in carbon fibre reinforced epoxy (CFRE) composites because of owning a unique combination of excellent mechanical, physical and chemical properties, such as high strength, high modulus and low density (1.65–2.00 g/cm^3) [1]. CFRE composites with their promising strength-to-weight and stiffness-to-weight ratios are considered ideal for low-weight high performance materials in different applications, such as sports goods, automotive and aerospace industries. In spite of all merits related to composites reinforced with continuous carbon fibre, the increasing demand leads to an increasing amount of waste associated with fabrication of these composites [2–5]. Moreover, carbon fibres are costly products, both in terms of energy consumed during manufacturing (up to 165 kW h/kg) and raw material price (up to 40 £/kg). Manufacturing waste is around 40% of all such composite waste caused, whereas woven trimmings hold more than 60% to this number [6,7]. Carbon fibre waste recycle are often accompanied with different stages including surface heat treatment, mechanical grinding, sieving, milling, and drying. The resulting material will be milled carbon fibre (MCF) which has the advantage of being inexpensive and free from any sizing and binder [8,9].

The mechanical performance and thermal characteristics of carbon-reinforced composite materials are highly governed by interfacial characteristics and physicochemical interactions between reinforcements and resin matrix, because a strong interfacial adhesion and good wettability ensure effective transition of stress across filler-matrix interface [10–12]. However, a large number of studies have shown that the low surface energy as well as the inertness characteristics of carbon fibre surface can limit its performance in CFRE composite due to its poor adhesion to most organic resin matrices [13–18]. Hence, resin modification and carbon fibre surface treatment are the well-known approaches to improve the interfacial adhesion via different mechanisms such as chemical bonding, Van der Waals bonding, mechanical interlocking and surface wetting [19–23].

Carbon fibre surface treatment mainly is categorized into two groups; oxidative and non-oxidative treatments. Oxidation treatments consist of liquid-phase, gas-phase, and plasma oxidation. On the other hand, non-oxidative approaches involve either deposition of more active forms of nanomaterials on carbon fibre surface i.e. CNTs, graphene oxide, and POSS [24–26] or organic reactions e.g. *in-situ* generated diazonium salts [13,27,28]. Most

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of these approaches for introduction of organic molecules on carbon fibre surface are limited and hindered either by side effects of oxidation process or several chemical steps with difficult purifications. Most recently, development of non-oxidative organic reactions having high reactive intermediates for chemical functionalization of carbon fibre surface under mild conditions have been extensively examined. Among these chemical approaches, addition of free radicals having different functional groups to carbon based structures were extensively investigated for functionalization of fullerene, CNT, and graphene nanomaterials [29–32].

In this work, for the first time, the free radicals produced from azo compounds was utilized to functionalize the graphitic structures of milled carbon fibre (MCF) surface which is inherently more stable than other type of carbon based materials e.g., CNT and graphene. This method was then applied for preparation of an amine rich MCF surface which could be heralded for its ability to reinforce epoxy-based composites through improvement of interfacial adhesion. For this purpose, the epoxy composites containing surface-functionalized MCF were prepared and its features, such as thermal, mechanical, and morphological properties, were systematically studied.

2. Experimental

2.1. Materials

The epoxy system used was diglycidyl ether bisphenol A, trade name: D.E.R. 332, with an epoxy equivalent weight of 175 g/eq and the hardener was *m*-phenylenediamine (PDA) which were obtained from Sigma-Aldrich. Polyacrylonitrile-based milled carbon fibres with density of 1.65–1.75 g/cm^3, diameter of 7 μm, mesh of 50–800, and carbon content of ⩾98% was supplied by Fibertech Korea Company. The microscopy image of the milled carbon fibre used in this work is presented in Fig. 1. Azobisisobutyronitrile (AIBN) solution, tetraethylenepentamine (TEPA) and 4-(trifluoromethoxy)aniline (TFMA) were purchased from Sigma and used as received. All the solvents used in this study were also provided from Sigma-Aldrich.

2.2. Amino-functionalization of MCF

Firstly, the received MCF was rinsed by stirring in acetone for 48 h under reflux condition. The pure MCF was repeatedly washed with copious ethanol and acetone, and then the fibres were vacuum dried at 200 °C prior to use. In a one-step experiment, pure MCF (1 g) was dispersed in 100 ml dry *n*-methyl-2-pyrrolidone (NMP) and ultra-sonicated for 30 min. Then, it was poured into a two-necked round bottom flask containing 100 ml solution of 12 wt% AIBN in acetone and the mixture was stirred at 75 °C for 48 h under a continuous nitrogen flow, followed by microwave irradiation (500 W) for 10 min. Afterwards, a large excess of TEPA (100 ml) was added to the above mixture, followed by further heating at 110 °C for 12 h under reflux condition. After cooling to room temperature, the resulting mixture containing aminated MCF (*a*-MCF) was filtered under vacuum and washed with acetone and ethanol to remove the un-reacted chemicals.

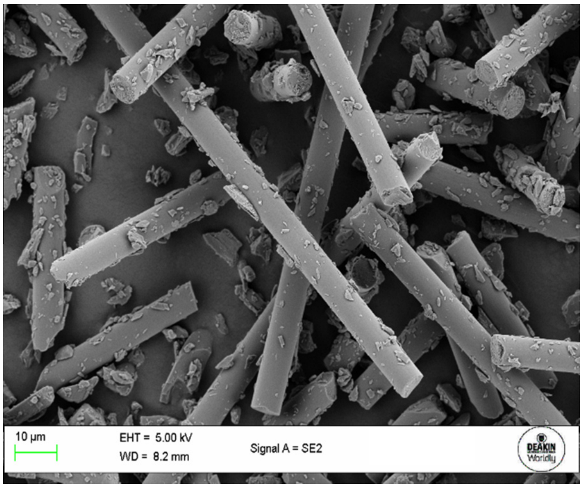

Fig. 1. SEM image of milled carbon fibres. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

2.3. Fluorine tagging of n-MCF

The MCF functionalized with isobutyronitrile radicals (*n*-MCF) was firstly obtained by the same conditions in previous section. After completing the reaction and microwave irradiation, the solution containing MCF/NMP/AIBN in acetone was filtered and washed three times with NMP and acetone. To tag the *n*-MCF surface with fluorine atoms, *n*-MCF (500 mg) was heated at 85 °C into 150 ml dry NMP solution containing TFMA (5 g) for 18 h under reflux condition. After cooling to room temperature, the resultant mixture (F-tagged MCF) was filtered under vacuum and washed with abundant acetone.

2.4. Composites fabrication

To fabricate the carbon fibre-epoxy composites, 1 wt% pure MCF or *a*-MCF (with respect to the total composite weight) were dispersed in acetone (20 mg/ml) using an ultrasonic bath for 30 min. The epoxy was then added in and the suspension was ultra-sonicated for further 30 min and stirred at 70 °C for 2 h. To remove acetone, the above mixtures were placed in a vacuum oven at 60 °C for 15 h. Then, stoichiometric amounts of hardener were added to the mixtures and then poured into containers. The curing process was conducted on the above-mentioned compositions according to the following schedule: (a) at 80 °C for 6 h under vacuum, and (b) postcuring of the samples at 100 °C for 90 min.

2.5. Measurements

FTIR spectra were obtained using a FTIR spectrophotometer (Bruker Optics) using the KBr pellets. Raman measurements were conducted using a Renishaw InVia Raman Microspectrometer (Renishaw, Gloucestershire, UK) with diode laser at 514 nm at room temperature. TGA experiments were carried out using a TA Instruments Q50 TGA in N_2 atmosphere at heating rate of 10 °C/min from room temperature to 750 °C. DSC measurements were performed using TA Q200 DSC in high purity N_2 atmosphere. The samples were heated in the temperature range of 25–300 °C at various heating rates. Rheological measurements were conducted on a TA Instruments HR-3 Rheometer with cone–plate geometry at 30 °C. A cone with a diameter of 40 mm and a tilt angle of 2° was used, and gap width was set to be 150 μm. The shear rate was carried out between 100 and 1000 1/s. The specimens placed between the cone and plate and were soaked for two minutes. Dynamic mechanical properties of the produced materials were measured using a TA Instruments Q800 DMA. The samples were polished to ~30 mm × 10 mm × 1 mm before being mounted on a single cantilever clamp. The DMTA tests experimental conditions were: temperature range, 25–250 °C; frequency of 1 Hz; and heating rate 5 °C/min. 3-point bending tests were conducted according to ASTM D790-02 using an Instron universal testing machine with a 10 kN load cell at a cross-head speed of 2 mm/min and the span-to-depth ratio was maintained at 16:1. At least five specimens