



## Toughening of epoxies by covalently anchoring triazole-functionalized stacked-cup carbon nanofibers



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### ARTICLE INFO

#### Article history:

Received 27 March 2013  
Received in revised form 10 May 2013  
Accepted 13 May 2013  
Available online 31 May 2013

#### Keywords:

Carbon nanofibers  
A. Polymer–matrix composites (PMCs)  
B. Fracture toughness  
B. Interface  
B. Thermomechanical properties

### ABSTRACT

Novel triazole-functionalized carbon nanofibers (m-CNFs) were prepared by one-step arylation with diazonium salts generated in situ. Microscopic observations indicate that m-CNFs exhibit significantly improved dispersibility in a high-performance epoxy resin compared with pristine CNFs (p-CNFs). The results of DSC and SEM show evidence of interfacial reaction and a more robust interface between m-CNFs and the epoxy matrix. Thermal and mechanical properties of two CNF/epoxy composites were systematically studied at different filler loadings. The results show that both CNF fillers could reinforce the epoxy matrix without sacrificing their thermal properties. Benefiting from the improved dispersibility and interfacial interaction, the ability of m-CNFs in toughening the epoxy resin is clearly superior to p-CNFs. The addition of only 0.4 wt% m-CNFs gives 41% and 80% enhancement in critical stress intensity factor ( $K_{IC}$ ) and the critical strain energy release rate ( $G_{IC}$ ), respectively.

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### 1. Introduction

Toughening of brittle epoxy thermosets has long been a subject of intense research since the inherent brittleness and poor resistance to crack propagation of epoxy resins greatly restrict their widespread applications in industries. The incorporation of a second phase, either rigid or soft, into epoxy matrices is presently a well-established strategy for improving the fracture toughness of epoxies. In these systems, phase-separated morphology can initiate various toughening mechanisms to dissipate a portion of energy available for crack propagation [1,2]. To date, the use of numerous micro-sized and nanosized second phases such as rubber [3], thermoplastics [4], ceramic particles [5], carbon-based nanomaterials [6–8] and their combinations [9–12] in toughening epoxy thermosets has been demonstrated.

Recently, the potential applications of stacked-cup carbon nanofibers (CNFs) as reinforcing fillers for polymer-based composites have attracted considerable attention due to its nanoscale diameter, high aspect ratio, and excellent intrinsic mechanical, thermal and electrical properties. Although the overall properties of the CNFs are slightly inferior to those of carbon nanotubes (CNTs), the manufacturing cost of CNFs are much lower (about 3–500 times lower than that of CNTs) [13,14]. More importantly, Brinson et al. recently demonstrated that the unique stacked-cup

structure of CNFs can bring out sacrificial bonding behaviors, which are not found in the systems with CNTs or graphene [15]. Their mechanical testing results revealed that the addition of only 0.68 wt% stacked-cup CNFs would increase the critical strain energy release rate ( $G_{IC}$ ) by approximately 43–112% in reinforcing epoxy resins with various blend.

There is, however, still a strong need to further enhance the toughening efficiency of CNFs. The challenges of achieving optimum properties of epoxy/CNF composites at even lower CNF loadings lie primarily in two areas. One is that CNFs tend to agglomerate in epoxy matrices due to their high aspect ratio and surface energy, leading to inhomogeneous dispersion. The other is the lack of interfacial forces between CNFs and epoxy matrices so that the CNFs can be easily pulled out, lowering the efficiency of load transfer from the matrices to the reinforcement [16–18]. In general, covalent incorporation of CNFs into epoxies through chemical modification and functionalization of CNFs is considered to be a feasible method for solving the above issues as it can both provide chemical affinity for efficient dispersion and improve interfacial interactions through chemical bonding. Several functionalization methods for CNFs have already been reported, such as carbonylation by Friedel–Crafts (F–C) reaction [13,19], carboxylation by strong acid ( $HNO_3$  or/and  $H_2SO_4$ ) as well as subsequent functionalization [20–22]. Although all these functionalized CNFs show improved dispersibility and interfacial interactions in epoxy matrices and thus give rise to significantly enhanced stiffness, their toughening effects have not yet been reported in literature to the

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best of our knowledge. Therefore, there remains a need to clarify whether the interfacial chemical bonds would really have significant influence on fracture toughness of the CNF-reinforced epoxy composites.

Motivated by the aforementioned issues, we prepared novel triazole-functionalized CNFs (m-CNFs) by one-step arylation with diazonium salts generated in situ. Unlike the modification using strong acid, this method is milder and less destructive to the CNF structure, allowing the CNFs to maintain their good intrinsic properties. The m-CNFs were subsequently introduced into an aerospace-grade anhydride-cured epoxy resin. The grafted triazole groups could initiate localized curing reaction directly from the surfaces of m-CNFs and thus the modified CNFs could be covalently anchored onto the epoxy network during the cure process [23]. Thermal and mechanical properties of the CNF/epoxy composites were systematically investigated. Pristine CNF (p-CNF)/epoxy composites and neat epoxy samples were also prepared as reference materials in order to study the influences of functionalization on the dispersion state of CNFs and interfacial interaction between CNFs and epoxy matrix, which are closely related to the stiffening and toughening efficiencies of CNFs.

## 2. Experimental

### 2.1. Materials

Pyrograf-III CNFs (PR-24-XT-LHT) with diameter of 70–200 nm and length of 50–200  $\mu\text{m}$  were obtained from Applied Science Inc. (USA). All solvents and reagents were purchased from Sigma–Aldrich Chemicals Inc. (USA) and used as received, unless otherwise specified. 1-(4-Aminobenzyl)-1,2,4-triazole was purchased from Combi-Blocks Inc. (USA). Tetra-functional epoxy (Resin XB 9721) and anhydride hardener (Aradur<sup>®</sup> 917) were supplied by Huntsman Advanced Materials (USA). Zinc acetylacetonate was used as catalyst (or so-called accelerator) and supplied by Sigma–Aldrich Chemicals Inc. (USA). The chemical structures of Resin XB 9721 and Aradur<sup>®</sup> 917 are given in Fig. 1.

### 2.2. Synthesis of m-CNFs

In a typical experiment, 0.5 g of p-CNFs were dipped into 150 ml of DMF, and sonicated in an ultrasonic bath for 2 h. Separately, 1-(4-aminobenzyl)-1,2,4-triazole (9.1 g,  $\approx 4$  equiv/mol of carbon) was dissolved in 150 ml acetonitrile, and then this arylamine solution was added in the CNF suspension. After degassing with argon for 30 min, isopentyl nitrite (10.7 ml) was quickly added by a syringe and the suspension was stirred at 60 °C for about 15 h in an argon atmosphere. After cooling to room temperature, the

suspension was filtered using a PTFE (0.45  $\mu\text{m}$ ) membrane and washed extensively with DMF. The functionalized CNFs were further purified by repeated sonication and washing with DMF, and then acetone. Finally, the obtained m-CNFs were dried in a vacuum oven at 60 °C for 48 h.

### 2.3. Preparation of CNF/epoxy composites

A desired amount of p-CNFs or m-CNFs were first dispersed in low viscosity anhydride hardener, and the mixture was sonicated using a Sonic & Materials model VCX-750 (1  $\text{cm}^2$  Ti horn at 20 kHz, 750 W) at 50% amplitude for 30 min (pulse: 2s on and 2s off) in an ice bath. Then, the mixture was subjected to a bath sonication for another 4 h. Separately, epoxy monomer and catalyst (1 wt% of the total weight) were mixed homogeneously with rotary evaporator at 80 °C for half an hour. Then, all the components were uniformly mixed together and the weight ratio of epoxy/hardener was 100/141 as recommended by the supplier. Finally, the mixture was poured into a self-made silicone mold and degassed for 1 h at a vacuum approaching about 0.1 mbar. All samples were cured using the following profile: 120 °C for 2 h, 160 °C for 2 h and 200 °C for 2 h. Samples for mechanical testing were obtained by curing in the silicone mold with specific dimensions.

### 2.4. Characterization

Fourier transform infrared (FTIR) spectra were obtained using a Perkin Elmer Instruments Spectrum GX FTIR spectrometer at room temperature in a wave-number range from 600 to 4000  $\text{cm}^{-1}$ . All of the samples were prepared as pellets using spectroscopic grade KBr. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Kratos Analytical AXIS His spectrometer with a monochromatized Al K $\alpha$  X-ray source (1486.6 eV photons) and Shirley functions were used to correct the baseline. Elemental analysis was performed using a Perkin Elmer Instruments CHNS-O Analyzer. The weight percentage (%) composition of Carbon, Hydrogen and Nitrogen were measured. Differential scanning calorimetry (DSC) was recorded on a TA Instruments DSC Q10 using N<sub>2</sub> as purge gas at a heating rate 3 °C/min. Thermal gravimetric analysis (TGA) were performed on a TA Instruments TGA Q 500 under a nitrogen or air atmosphere over a temperature range of 25–800 °C at a heating rate of 10 °C/min. Dynamic mechanical analysis (DMA) was conducted on a TA Instruments DMA Q800 at a heating rate of 3 °C/min and frequency of 1 Hz under an air atmosphere. The tests were carried out using the single cantilever mode on the specimens with dimension of 40  $\times$  13.0  $\times$  2.0  $\text{mm}^3$ . Tensile tests were performed using an ITW Instron Tester 5567 with a 3 kN load cell at a crosshead speed of 1 mm/min. The

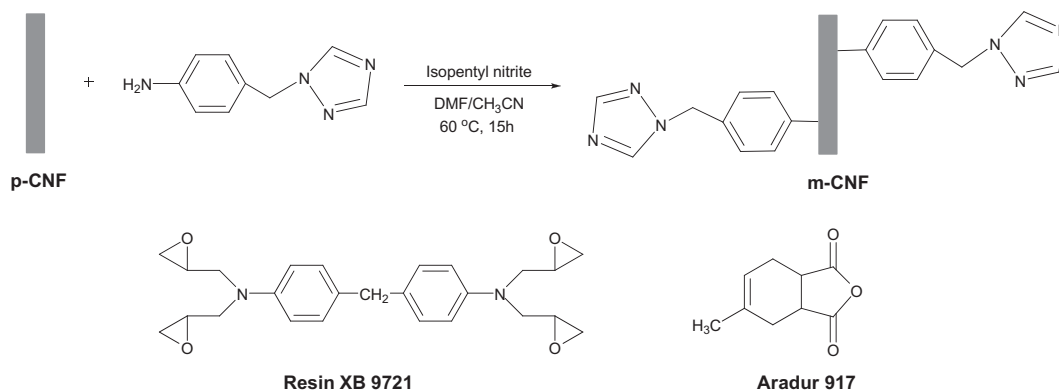


Fig. 1. Synthesis route of m-CNFs and formulas of epoxy and hardener used in this study.

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