

# Interfacially reinforced methylphenylsilicone resin composites by chemically grafting multiwall carbon nanotubes onto carbon fibers

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## ABSTRACT

Both silane and multiwall carbon nanotubes (CNTs) were grafted successfully onto carbon fibers (CFs) to enhance the interfacial strength of CFs reinforced methylphenylsilicone resin (MPSR) composites. The microstructure, interfacial properties, impact toughness and heat resistance of CFs before and after modification were investigated. Experimental results revealed that CNTs were grafted uniformly onto CFs using 3-aminopropyltriethoxysilane (APS) as the bridging agent. The wettability and surface energy of the obtained hybrid fiber (CF-APS-CNT) were increased obviously in comparison with those of the untreated-CF. The CF-APS-CNT composites showed simultaneously remarkable enhancement in inter-laminar shear strength (ILSS) and impact toughness. Moreover, the interfacial reinforcing and toughening mechanisms were also discussed. In addition, Thermogravimetric analysis and thermal oxygen aging experiments indicated a remarkable improvement in the thermal stability and heat oxidation resistance of composites by the introduction of APS and CNTs. We believe the facile and effective method may provide a novel interface design strategy for developing multifunctional fibers.

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## 1. Introduction

CFs reinforced polymer composites mainly served as ideal structural materials have been used widely in marine, aerospace and automobile industries because of their superior properties, such as strong specific strength, high rigidity, light weight and superior fatigue resistance [1–6]. However, applications of fibers reinforced materials are restricted due to the poor interfacial adhesion between the fibers and matrix [7]. To satisfy the various technological demands, a sufficient and appropriate interfacial adhesion between fibers and matrix is of crucial importance [8–10]. Interfacial adhesion of composites depends largely on interfacial structures and interfacial interactions [11]. As a result, a variety of surface treatments of CFs are developed such as oxidation treatments, chemical grafting, polymer sizing, high energy irradiation, etc [12–17]. All these surface treatments increase the surface wettability, surface roughness or chemical bonding aiming to improve the interfacial performance.

MPSR is going through increasing development in the field of advanced heat resistant composites like the automotive and aerospace industries, which is used as thermal protection coatings to protect structural materials such as aeroplane and interceptor missiles from aerodynamic heating due to excellent thermal stability and heat oxidation resistance [18,19]. MPSR is semi-inorganic thermosetting resin with the main backbone siloxane structures, which can be easily used with CFs to prepare reinforcement composites. The CFs reinforcements can enhance greatly the mechanical strength and thermal properties of the resulting composites. Unfortunately, a weak interfacial adhesion between CFs and MPSR leads to low mechanical and thermal properties of composites. To ensure that the MPSR composites can be used safely under complicated environmental conditions and utilize the outstanding thermal performance effectually, it is necessary to improve the interfacial properties of CFs/MPSR composites.

The outstanding mechanical, electrical and thermal properties of CNTs make them ideal hierarchical reinforcements in advanced nanocomposite fields [20–22]. Very recently, several researchers have made effort for the chemical grafting of CNTs onto CFs based on different bridging agents by realizing chemical bonding between CFs and CNTs aiming to enhance the interfacial properties. For example, Li et al. [23] have reported a facile chemical method of

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grafting CNTs onto CFs by 1,3-propanediamine as the coupling agent. Peng et al. [24] introduced CNTs onto CFs using poly(amido amine) (PAMAM) as the bridging agent to prepare a new CF-CNT hierarchical reinforcement. The results showed that CF-CNT hierarchical reinforcements by the two grafting methods could lead to remarkable enhancement of interfacial properties. However, the used agents mentioned above are too expensive or the grafting processes are too complicated. Furthermore, both of the two bridging agents are not suitable for preparing the heat resistant interface between CFs and MPSR.

Silane coupling agents with the Si–O bond have led the samples to form a SiO<sub>2</sub> passivation layer, which protects the underlying polymer from further thermal degradation. The bifunctional structures of silane coupling agents have also been of interest in applying them to create chemical bridges between the fibers and hot matrix [25,26]. Therefore, APS with both amino and ethoxyl groups is selected as the bridging agent in this study. Efforts to improve significantly the mechanical performance of the CFs reinforced MPSR composites and to figure out the factors in influencing the interfacial adhesion are important and emergent targets. However, the usage of APS as the bridging agent to be grafted onto CFs has not been reported for the introduction of CNTs onto CFs to enhance the interfacial performance and heat resistance of the MPSR composites.

In this paper, we proposed a multifunctional interphase consisting of APS and CNTs in CFs/MPSR composites by chemical grafting. The microstructure, interfacial properties, impact toughness and heat resistance of CFs with and without surface treatment were systematically characterized and investigated. The results suggested that the modified CFs composites with simultaneously improved interfacial, impact toughness and heat resistance could be prepared using the facile method proposed herein.

## 2. Materials and methods

### 2.1. Materials

CFs (T300, tensile strength 3500 MPa and diameter about 7 μm) used in the study were purchased from Toray Industries, Inc. The CNTs (purity >97%, diameter 10–40 nm, length 1–5 μm) were obtained from Shenzhen Nanotech Port Co., Ltd. Hydroxyl-terminated MPSR was purchased from ShangHai Chemicals Co. 3-aminopropyltriethoxysilane (APS) and Lithium Aluminium Hydride (LiAlH<sub>4</sub>) were received from TCI Ltd. All other chemicals (acetone, thionyl chloride, toluene, concentrated sulfuric acid, concentrated nitric acid, pyridine, tetrahydrofuran, ethanol) obtained from Tianjin Bodi Organic Chemicals Co. Ltd. were reagent-grade.

### 2.2. Preparation of CF-APS-CNT

Cutting by acid and surface functionalization of CNTs by SOCl<sub>2</sub> were performed using the method similar to the procedure described in previous studies [27,28]. The CF-APS-CNT hybrid reinforcement was prepared via following several steps of chemical reactions. Firstly, the CFs were refluxed in acetone for 24 h to remove the polymer sizing and pollutants (denoted as untreated-CF). Secondly, the CFs were oxidized in concentrated HNO<sub>3</sub> at 353 K for 4 h to generate some oxygen-containing functional groups. The oxidized CFs were taken out and washed with deionized water until the pH value reached 7 and then dried under vacuum to get CF-COOH. In order to reduce carboxyl groups to hydroxyl groups, the CF-COOH was submersed in LiAlH<sub>4</sub>-THF saturated solution, and allowed to react under reflux for 2 h. The obtained fiber (CF-OH) provides the reactive sites of

homogeneously hydroxyl groups for further functionality with APS. After being washed with ethanol and dried, the CF-OH was reacted with APS (0.5 mL) in toluene (100 mL) at 373 K for 10 h to obtain APS functionalized carbon fibers (denoted as CF-APS). Finally, CF-APS was mixed with CNT-COCl (0.1 g) in dry THF (100 mL) under sonication for 30 min to form a homogeneous dispersion, and then reacted at 333 K for 24 h under N<sub>2</sub> atmosphere. The obtained sample (CF-APS-CNT) was washed by excel THF under sonication to remove unreacted CNTs. The whole grafting processes used to prepare CF-APS-CNT are schemed in Fig. 1.

### 2.3. Preparation of CFs/MPSR composites

The compression molding method was employed to prepare CFs reinforced MPSR composites. The unidirectional prepreg of CFs and MPSR was cast into a mold to make composites. Typically, the CFs/MPSR composites were fabricated by heating the specimens 120 °C and 150 °C for 1 h without pressure, a pressure of 20 MPa was applied at 180 °C for about 2 h, followed by post curing at 250 °C for 4 h under 20 MPa. When the curing process had finished, the mould was cooled to room temperature with the pressure being maintained. The content of the resin in the composites was kept in the range of 30–40 mass%, and all the samples were 6 mm in width and 2 mm in thickness.

### 2.4. Characterization of CFs and composites

The surface functional groups of CFs were analyzed by FTIR spectrophotometer (Nicolet, Nexus670, USA) using powder-pressed KBr pellets. The FTIR spectra were acquired by scanning the specimens for 64 times in the wavenumber range of 400–4000 cm<sup>-1</sup> with the resolution of 2 cm<sup>-1</sup>.

XPS (ESCALAB 220i-XL, VG, UK) was performed on a monochromated Al Kα source (1486.6 eV) at a base pressure of 2 × 10<sup>-9</sup> mbar. The XPS was energy referenced to the C1s peak at 284.6 eV. The XPS peak version 4.1 program was used for data analysis.

The surface morphologies of CFs before and after modification were observed by SEM (Quanta 200FEG, Hitachi Instrument, Inc. Japan). The samples were coated with a thin conducted gold layer

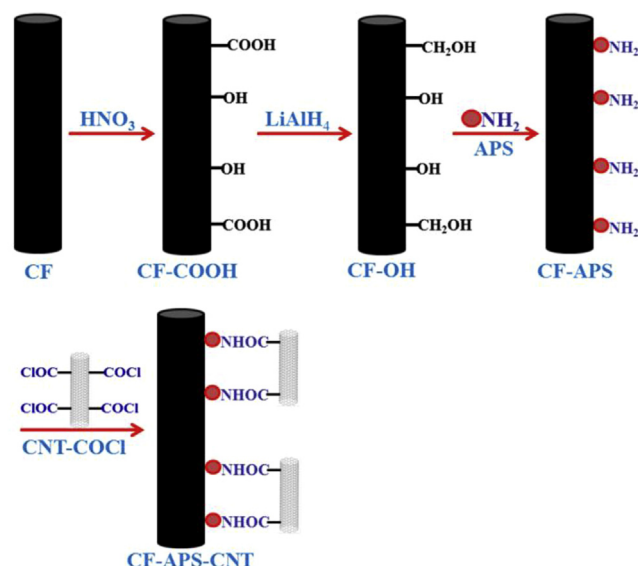


Fig. 1. The schematic illustration of CFs covalently bonded with CNTs.

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