



# Effect of polymer-grafted carbon nanofibers and nanotubes on the interlaminar shear strength and flexural strength of carbon fiber/epoxy multiscale composites

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## ABSTRACT

Multiwalled carbon nanotubes (MWNTs) and vapor-grown carbon nanofibers (VGCNFs) were grafted with poly(styrene-co-maleic anhydride) (SMA) and poly(glycidyl methacrylate) (PGMA) by free radical polymerization, and used as the secondary reinforcing agent for multiscale carbon fiber (CF) reinforced epoxy composites. The polymer-grafted VGCNFs and MWNTs were simply suspended in ethanol and spray-coated onto the surface of CF fabrics to fabricate the multiscale composites. The structures of the polymer-grafted VGCNFs/MWNTs were characterized and their effect on the mechanical properties of multiple composites was compared. Interestingly, polymer-grafted VGCNFs with much larger diameters and lower grafting ratios are more effective than polymer-grafted MWNTs for the reinforcement; and SMA-grafted VGCNFs are more effective than PGMA-grafted VGCNFs. Addition of only 0.4 wt% (on the basis of CF fabrics) of SMA-grafted VGCNFs increases interlaminar shear strength (ILSS) by ~73% and flexural strength by ~21%. The increase of ILSS exceeds those of previously reported functionalized nanotubes/nanofibers, graphene oxide or organoclay nanoplatelets as the secondary reinforcement. The high straightness and large aspect ratio of SMA-grafted VGCNFs and the strong interaction with the matrix play the key roles in the reinforcement. This new and simple method simplifies the fabrication of high-performance multiscale composites for broad applications in the future.

## 1. Introduction

Carbon fiber reinforced polymer (CFRP) composites made of polymer and continuous carbon fibers (CFs) have a wide range of applications in aerospace structures, ground vehicles, sports equipment and etc. When nanofillers are incorporated into common CFRP composites, multiscale composites with hierarchical structures with significantly improved mechanical properties, especially out-of-plane properties, were obtained [1–6]. Vapor-grown carbon nanofibers (VGCNFs) and carbon nanotubes (CNTs) are fiber-like carbonaceous nanomaterials produced by chemical vapor deposition (CVD), with great mechanical properties and electrical conductivities, therefore, are considered as promising nanofillers of polymers and CFRPs, [7–16]. Up to date, several methods have been developed to prepare the multiscale composites, in which the nanomaterials are either directly grown on the surface of CFs, deposited onto the CF surfaces or premixed with the epoxy (EP) matrices. For example, CNTs were grown on CF surfaces by CVD, and zinc oxide nanorods were grown by hydrothermal deposition [17–20]. The CNT/CF/EP multiscale composites showed about 30% enhancement of the interlaminar shear strength (ILSS) compared with

that of common CF/EP composites without CNTs. Bekyarova et al. [21] deposited multi- and single-walled CNTs on woven CF fabrics by electrophoresis. The CNT/CF/EP composites showed about 30% enhancement of ILSS. Rodriguez et al. [22] fabricated multiscale composites by electrophoretic deposition of carboxylic acid- or amine-functionalized CNFs on the surface of CF layers and found that amine-functionalized CNFs increased ILSS by 12% and the compressive strength by 13%. Yokozeki et al. [23] directly added VGCNF powder at the mid-plane of CFRP laminates, which improved the interlaminar mechanical properties including higher critical load and fracture toughness. Functionalized CNTs [24–26], nanoclays [27–32], graphene oxide (GO) and other graphene derivatives [33–36] have also been premixed with the resin matrices to prepare multiscale composites, which is a relatively simple method. With the addition of only 0.1 wt% and 1 wt% CNFs in the epoxy matrices, ILSS of the multiscale composites is increased by 6% and 25%, respectively. The flexural strength and modulus are increased by 16–20% and 23–26%, respectively [20]. CNTs with carboxyl and hydroxyl groups improve the in-plane shear strength of the CF/EP composites by 15% [36]. ILSS is 86% higher when electrospun carbon fibers are used to fabricate multiscale CF/EP composites [37,38]. Zhao

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et al. [39] grafted CNTs onto CF surface using polyhedral oligomeric silsesquioxanes as a linkage to improve the interfacial properties between CFs and epoxy matrix. The interfacial shear strength between the CNT-grafted CF and epoxy resin evaluated using single fiber pull-out testing was 105% higher than that between bare CF and epoxy resin. The functionalized CNTs were usually prepared by oxidation to prevent the aggregation of CNTs and increase their interfacial interactions with the matrices and achieve uniform dispersion.

In these studies, surface modification of CNTs and CNFs is usually required to improve the dispersion uniformity and the filler-matrix interfacial interactions, which are crucial for the improvement of the composite properties [14,40–45]. Oxidation by the mixture of concentrated sulfuric and nitric acid is the commonly used method for the surface modification of CNTs and CNFs. Further modifications of the oxidized CNTs and CNFs are also widely investigated. For example, Nie et al. [46] treated oxidized CNFs with 3-glycidoxypropyltrimethoxysilane and dispersed the modified CNFs into epoxy resin to improve the mechanical properties. On the other hand, modification of CNTs with polymers by free radical addition reaction and graft polymerization has also been extensively studied [47–50]. In contrast to the chemical oxidation of carbon nanomaterials by strong oxidants, free radical polymerization does not introduce significant defects in the sidewalls of VGCNFs and CNTs, and the reaction is conducted under mild conditions. However, to the best of our knowledge, polymer grafted CNTs or CNFs have not been used as the secondary reinforcement for multiscale CFRPs.

In this work, we report the multiscale composites with polymer-grafted VGCNFs and multiwalled CNTs (MWNTs) spray-coated onto the surface of CF fabrics. The structure of the polymer-grafted VGCNFs and MWNTs were characterized. The influences of polymer-grafted VGCNFs and MWNTs on the mechanical properties, including ILSS and flexural strength, and the structure of the multiscale composites were characterized. The polymer-grafted VGCNFs and MWNTs were prepared by free radical polymerization and can be readily dispersed in ethanol and sprayed onto the surface of CF fabrics. Two polymers, i.e. poly(styrene-co-maleic anhydride) (SMA) and poly(glycidyl methacrylate) (PGMA), that are reactive with epoxy were selected for the modification. Compared with CVD, hydrothermal deposition and electrophoretic deposition, spraying is an industrially preferred method, which is operated under ambient conditions, time-saving and is applicable to large-area surfaces. The multiscale composites of epoxy and the CF fabrics coated with the polymer-grafted VGCNFs and MWNTs were fabricated by hand lay-up and hot pressing process. SMA-grafted VGCNFs (VGCNFs-g-SMA) was found to be the most effective reinforcing reagent for the multiscale composites.

## 2. Experimental

### 2.1. Materials

VGCNFs with diameters ranging from 50 to 200 nm and an average length of about 15  $\mu\text{m}$  were obtained from Taiwan Unitetek international Co., Ltd. (Taiwan, China). MWNTs of 10–20 nm in diameter and purity above 97% were supplied by Shenzhen Nanotech Port Co., Ltd. (Shenzhen, China). Tetraglycidyl diaminodiphenyl methane (TGDDM) was purchased from Shanghai Research Institute of synthetic resins (Shanghai, China). Glycidyl methacrylate (GMA), styrene (St), maleic anhydride (MAH) and azodiisobutyronitrile (AIBN) were offered by Shanghai Lingfeng Chemical Reagent Co., Ltd. (Shanghai, China). 3,5-Dimethylthio-2,4-toluenediamine (DMTDA), the curing agent was purchased from Tianjin Zhongxin Chemtech Co., Ltd. (Tianjin, China). Unidirectionally aligned CF fabrics (T700-12K) were provided by Toray (Japan). Other chemicals were of reagent grade and purchased from Shanghai Chemical Reagents Company (China).

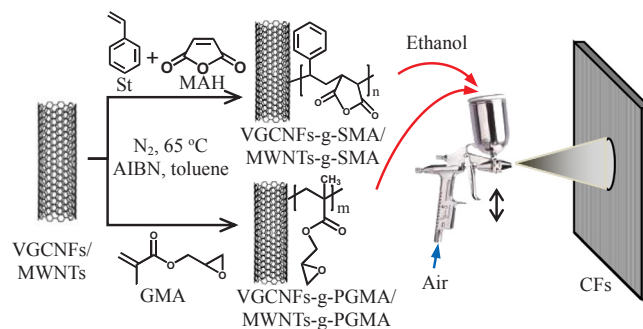


Fig. 1. Schematic illustration for the synthesis and spraying of the polymer-grafted VGCNFs and MWNTs.

### 2.2. Preparation of SMA-grafted VGCNFs and MWNTs

The synthesis and spraying of the polymer-grafted VGCNFs and MWNTs are presented in Fig. 1. VGCNFs or MWNTs (0.5 g), St (6.25 g, 60 mmol) and MAH (8.5 g, 90 mmol) in toluene (200 mL) were added into a three-necked flask. After 10 min of ultrasonication, the flask was purged by nitrogen to remove oxygen dissolved in the solution. 0.5 g of AIBN was added and the reaction was held at 65 °C under ultrasonication for 2 h and then mechanically stirred for 10 h. The solid was separated by filtration and thoroughly washed with acetone. Finally, the product was dried in a vacuum oven at 80 °C to obtain SMA-grafted SMA-grafted VGCNFs (VGCNFs-g-SMA) and MWNTs (MWNTs-g-SMA).

### 2.3. Preparation of PGMA-grafted VGCNFs and MWNTs

VGCNFs or MWNTs (0.5 g) and GMA (9.53 g, 60 mmol) in toluene (200 mL) were added into a three-necked flask. The conditions for the preparation of PGMA-grafted VGCNFs (VGCNFs-g-PGMA) and PGMA-grafted MWNTs (MWNTs-g-PGMA) were the same as those for the above-mentioned preparation of VGCNFs-g-SMA and MWNTs-g-SMA.

### 2.4. Fabrication of the multiscale composites

CF sheets with the size of 10 × 15 cm<sup>2</sup> were dried at 80 °C for 2 h. Pristine VGCNFs, MWNTs and the polymer-grafted VGCNFs and MWNTs were suspended in ethanol at a concentration of 0.5 mg/mL by ultrasonication. In about 10–20 min after the ultrasonication, the ethanol suspensions were spray-coated onto the surface of CF sheets by spraying through an air-spray gun (K3, Wufa Air Tools Co. Ltd., Taizhou, China), as shown in Fig. 1. The CF sheets were placed on a hot plate and heated to 60 °C to make sure the rapid drying of the coating. The pressure of operating air was controlled at 0.8 MPa by an air compressor (YL-8022, Shanghai Luodi, China). The distance between the nozzle and the CF sheets was kept at 20 cm and the coating area was controlled to be about 15 cm<sup>2</sup>. The spray gun was smoothly moved back and forth at a moving speed of about 5 cm/s during the spray-coating process to make sure the complete and uniform coverage. Typically, 6 mL solution was needed to cover an area of 100 cm<sup>2</sup>. The amount of the nanomaterials on the surface of CF sheets was determined by the volume of the suspensions. After spraying, the fabrics were dried at 80 °C in a vacuum oven for 2 h. TGDDM and the curing agent DMTDA were mixed and coated onto the two sides of the CF sheets to obtain the CF prepreps. 10 pieces of the CF prepreps were then stacked and degassed under vacuum at 80 °C for 2 h, hot compressed at 10 MPa at 120 °C for 0.5 h, 150 °C for 0.5 h, 170 °C for 2.5 h and then post-cured at 200 °C for 1 h. The weight percentage of the VGCNFs and MWNTs was based on the weight of CF sheets in the composites. The content of epoxy resin in the final composites was measured to be about 34 wt%.

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