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# On improvement of mechanical and thermo-mechanical properties of glass fabric/epoxy composites by incorporating CNT–$Al_2O_3$ hybrids

Weikang Li [a], Anthony Dichiara [a], Junwei Zha [b], Zhongqing Su [c], Jinbo Bai [a,*]

[a] Laboratoire de Mécanique des Sols, Structures et Matériaux, École Centrale Paris, CNRS UMR8579, Grande Voie des Vignes, 92290 Châtenay-Malabry, France
[b] Department of Polymer Science and Engineering, University of Science & Technology Beijing, Beijing 100083, People's Republic of China
[c] Department of Mechanical Engineering, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong Special Administrative Region

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ABSTRACT

The multi-scale hybridization of carbon nanotubes (CNTs) with micro-particles in polymers offers new opportunity to develop high performance multifunctional composites. In this study, hybrid fillers comprised of CNTs directly grown on alumina micro-spheres by chemical vapor deposition were incorporated into epoxy matrix that was then reinforced with woven glass fibers. The hierarchical composites with 0.5 wt.% hybrid loading was observed to exhibit an improvement of 19% and 11% in flexural modulus and interlaminar shear strength, respectively. Moreover, the glass transition temperature was increased by 15 °C and the storage modulus at 50 °C was enhanced by 20%. These reinforcements are mainly attributed to the improvements of matrix properties resulted from the good dispersion of hybrids and their hindering effect on the formation and development of matrix cracks. This study reveals the potential in improving mechanical and thermo-mechanical properties of the fiber-reinforced composite by using multi-scale carbon hybrids.



## 1. Introduction

Glass fiber-reinforced laminated composites are now widely used as structural materials due to their high specific modulus and strength, providing significant weight reduction relative to metallic materials [1]. The fibers play an important role on the load carrying capacity along the fiber direction, endowing the composites with superior in-plane performance. However, their out-of-plane properties are strongly dependent on the polymer matrix properties and the fiber/matrix interfacial adhesion [2]. In general, the weak out-of-plane properties of fibrous composites are mainly attributed to the matrix dominated cracks at low strain and inefficient stress transfer. As a result, there have been several attempts toward enhancing mechanical properties of the fiber/polymer composites by using modified matrix [3–6].

On the other hand, recent advances and breakthroughs in nanoscale science and engineering have provided new opportunities to develop the composite materials with improved performances. In particular, carbon nanotubes (CNTs) with excellent mechanical properties are considered as attractive candidates for the reinforcement materials [7–9]. Much attention has been paid to the hierarchical composites comprised of the CNTs modified matrix reinforced with the conventional micro-scale fibers [10–13]. These hierarchical composites are synchronously reinforced by both micro- and nano-scale fillers. The presence of CNTs was demonstrated to potentially improve both the in-plane matrix dominated and out-of-plane properties of the composites [14,15]. For instance, the enhanced flexural modulus and strength of carbon fiber/epoxy composites could be obtained by dispersing pristine or modified CNTs into epoxy matrix [16].

However, the incorporation of CNTs into fibrous composites remains a challenging task. One hindrance to prevent the utilization of CNTs from being used for matrix modification is the difficulty in achieving their good dispersion in the matrix, because CNTs tend to agglomerate and entangle due to van der Waals attractions. Moreover, a strong interfacial interaction is required to obtain efficient load transfer from matrix to CNTs. Hence, the poor dispersion and weak interfacial bonding can limit the reinforcing effectiveness of CNTs or even deteriorate the composite properties. Another obstacle is the processing difficulty induced by the increased viscosity of polymer matrix due to introduction of CNTs. Considering these critical issues, a number of approaches, such as stirring, high shear mixing, ultrasonication, chemical functionalization have been proposed [9]. Good dispersion of CNTs not only creates more filler surface for bonding with the epoxy, but

* Corresponding author. Tel.: +33 1 4113 1316.
*E-mail address:* jinbo.bai@ecp.fr (J. Bai).

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also prevents aggregated filler from acting as a stress concentrator which can be detrimental to mechanical performance of the synthesis. Among existing techniques, the addition of amino-functionalized CNTs into the carbon fiber reinforced composites has capacity to improve flexural strength and interlaminar shear strength of the composites [17]. Noteworthy, some researchers proposed the multi-scale hybridization of CNTs with various types of microparticles, where the CNT structure and hybrid organization can be tailored by adjusting synthesis parameters [18–21]. With the addition of hybrids into polymer matrix, the uniform CNT dispersion and improved interfacial properties were achieved [22–25]. It is more recently that the CNT–graphene nanoplatelet (GnP) and CNT–silicon carbide (SiC) hybrids were used as high-performance reinforcements in the composites [26–28]. Nevertheless, the introduction of CNT-microparticle hybrids into the traditional glass fabric composites to prepare multi-scale fibrous composites has not yet been fully reported. Prompted by this, we focus on the potential synergistic reinforcing mechanism between microfibers and hierarchical hybrid fillers, which can facilitate the design and production of high performance composite materials.

Bearing in mind the above deficiencies of existing techniques, the present study aims to develop an insight into the influence of CNT–$Al_2O_3$ addition on both the mechanical and thermo-mechanical properties of traditional glass fabric reinforced composites. As a major ceramic material commonly used for structural applications due to its high specific stiffness, $Al_2O_3$ was selected as the binder for CNTs. CNT–$Al_2O_3$ hybrids comprised of well-aligned CNTs forming six-orthogonal branches on spherical $Al_2O_3$ microparticles were synthesized by chemical vapor deposition (CVD). Combining $Al_2O_3$ with CNTs may be helpful with the dispersion of CNTs in the polymer matrix. Hence, with the help of the ceramic micro-beads 'vehicles', it may be much easier to disperse CNTs by conventional methods. Multi-scale glass fabric/epoxy composites were prepared by incorporating plain woven glass fabric into the epoxy matrix modified with CNT–$Al_2O_3$ hybrids. The fiber/matrix interfacial properties were evaluated by three-point short beam shear test. Flexural properties of the composites were tested by a typical three-point bending method. Dynamic mechanical analysis (DMA) was used to examine thermo-mechanical properties of the composites. Composite morphologies were evaluated by scanning electron microscopy (SEM) to explain the reinforcing mechanism. The potential of CNT–$Al_2O_3$ hybrids as structural reinforcements in fibrous composites was analyzed and discussed.

## 2. Experiment

### 2.1. Materials

Randomly distributed CNTs, reported henceforth as *ran*-CNTs, with 30 nm average diameter and 20 μm average length (Chengdu Organic Chemicals Co., Ltd. China), and $Al_2O_3$ micro-spheres with 3–10 μm in diameter (Performance Ceramic Company, Peninsula, OH, the USA) were used. The CNT–$Al_2O_3$ hybrids with multi-walled CNTs grown on the $Al_2O_3$ particles were synthesized by CVD [19]. Briefly, a quartz plate supporting the homogeneously dispersed $Al_2O_3$ micro-particles was placed in the center of a horizontal quartz tube (45 mm in diameter and 1200 mm in length) heated up by an electrical resistance furnace at 550 °C under argon/hydrogen atmosphere. After 10 min for the system stabilization, a solution of xylene/ferrocene concentrated at 0.05 g/mL was injected at 0.2 mL/min in the form of spray, along with acetylene at 0.05 L/min. The gas flows were controlled by thermal electronic mass flowmeters (Bronkhorst) while the liquid injection was adjusted by a mechanical syringe system fitted with a liquid flow meter (Razel Science, R99-E). The synthesis lasted for 10 min before the furnace was cooled down to room temperature under 1 L/min of argon. As-received plain woven glass fabric (Hexcel Corp) with an areal density of 206 g/$m^2$, warp 51% and weft 49% was employed as reinforcement. Epoxy resin (1080S, Resoltech Ltd., France) was used as matrix material.

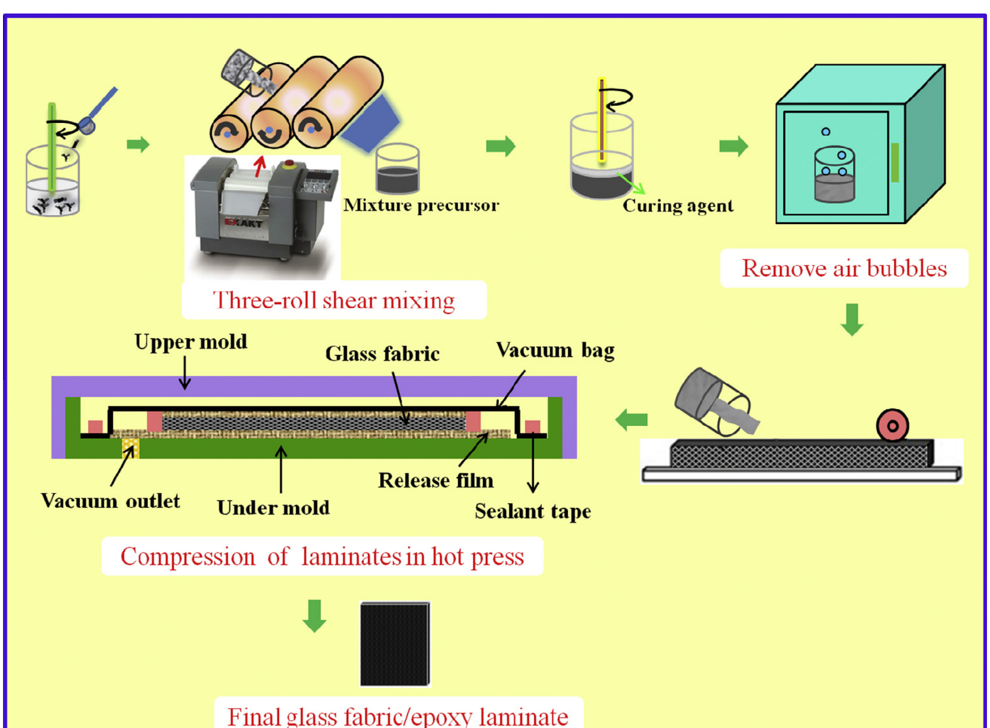


**Fig. 1.** Schematic of filler dispersion in the epoxy matrix and fabrication process of glass fabric/epoxy composite.