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Multiscale carbon nanotube-woven glass fiber reinforced cyanate ester/epoxy composites for enhanced mechanical and thermal properties

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ABSTRACT

Electrophoretic deposition (EPD) was employed as a method to deposite amine – functionalized multi-wall carbon nanotubes (A-MWCNTs) onto insulating woven glass fiber and A-MWCNT-glass fiber layers were prepared. Then multiscale A-MWCNTs-woven glass fibers reinforced cyanate ester/epoxy (GFRP) composites were manufactured using the A-MWCNT-glass fiber layers. Mechanical and thermal properties of the A-MWCNTs reinforced GFRP composites were characterized at different temperatures. Results show that interlaminar shear strength and thermal conductivity of A-MWCNTs composites are significantly improved compared with those of pure GFRP composites. Meanwhile, the reinforcing mechanism was investigated and enhanced interfacial bonding between A-MWCNT, matrix and glass fibers were demonstrated.

1. Introduction

Glass fiber reinforced polymer (GFRP) composites have shown excellent performance combined with high strength, high stiffness and low moisture absorption so that they have been widely used for structural and functional applications at room temperature (RT) and cryogenic temperatures [1–3]. However, with the development of many industries such as aerospace systems, superconducting magnet and cryogenic equipment, the properties in terms of mechanical strength and thermal conductivity were proposed higher requirement. In particular, the interfacial bonding between glass fiber and matrix is usually weak so that interlaminar shear strength (ILSS) is an important factor for these composites. Meanwhile, these GFRP composites usually show low thermal conductivity which limits their applications in many areas.

Carbon nanotubes (CNTs) have been considered as candidate fillers for enhancing properties of GFRP composites, owing to their intrinsic outstanding mechanical properties (high aspect ratio, high Young's modulus and high tensile strength) and thermal conductivity [4,5]. Many researchers focused on addition of CNTs to improve properties of GFRP composites. Gojny et al. [6] have found that ILSS increased compared with the matrix-dominated ILSS with addition of 0.3 wt% double-wall carbon nanotubes (DWCNTs) into GFRP composite and the electrical conductivity of the system was also enhanced. Shen et al. [7] have shown that the flexural stress and the thermal conductivity of GFRP laminates was improved with the addition of multi-wall carbon nanotubes (MWCNTs). The conventional preparation method for manufacturing GFRP composites is vacuum-assisted resin transfer moulding (VARTM). To ensure a homogeneous resin distribution in GFRP composites, relative low viscosity and long pot-life are required for impregnation. Meanwhile, uniform dispersion of CNTs and strong interfacial bonding between the CNTs, matrix and glass fibers are necessary to ensure high performance of composites. One of the most widely used methods in preparation composites is impregnation of a CNT/resin suspensions into the woven glass fibers [8,9]. Unfortunately, this method was suitable for limited CNT contents because the viscosity of CNT/resin suspensions increases at a large amount of CNTs so that it is difficult to degas. Meanwhile, high viscosity of resin suspensions is contributed to weak fluidity of resin suspensions during impregnation using the VARTM. Moreover, at a large amount of CNTs, CNTs tend to be agglomerated together even through CNT surface was functionalized [10]. Many techniques have been developed to overcome such shortcomings [11–14]. Qian et al. [12] used a chemical vapor deposition method to grow CNTs onto fiber surface and manufactured CNT-grafted carbon fiber/epoxy composites, and a dramatic improved interfacial shear strength of CNT-grafted carbon fiber/epoxy composites was observed. Hou et al. [14] immersed carbon fiber fabric into CNT

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aqueous solution followed by freeze drying process and thermal treatment. A continuous and uniformed CNT network was achieved on carbon fiber fabric.

Electrophoretic deposition (EPD) has been one of the effective methods to manufacture GFRP composites at a large loading of CNTs. During an EPD process, surface charged CNTs were uniformly dispersed into a liquid medium and deposited onto woven layers with an electric field. Bekyarova et al. [15] deposited CNTs onto woven carbon fabric and manufactured composites. Enhancement of the ILSS and out-of-plane electrical conductivity were observed for the CNT/carbon fabric/epoxy composites. Rodriguez et al. [16] deposited amine functionalized CNTs onto carbon fiber fabric and prepared composites. Results showed that the ILSS and compressive strength were improved. Recent researches involved in depositing CNTs onto conducting carbon fiber fabric, while few investigations were focused on depositing onto insulating woven glass fiber fabric. Zhang et al. [17] deposited functionalized MWCNTs onto a single insulating glass fiber and they found that interfacial shear strength of the composites had been significantly improved. Our research was focused on uniformly depositing CNTs onto insulating woven glass fiber. Moreover, in previous study, interfacial bonding between CNTs and fiber fabric was not taken into consideration. Strong interfacial bonding between CNTs and fiber fabric plays an important role to ensure a uniform distribution of CNTs on fabric and an effective reinforcement. In this study, the epoxy group functionalized woven glass fibers were used, and MWCNTs was amine group functionalized. Thus, chemical bond may be formed between epoxy group and amine group as the temperature increases.

In this work, a homogenous suspension was prepared by dispersing amine-functionalized MWCNTs (A-MWCNTs) into water with addition of a surfactant. A-MWCNT-glass fiber layers were prepared by the EPD process. A-MWCNTs–glass fiber layers were subsequently impregnated with cyanate ester/epoxy resin using the VARTM method. Mechanical properties and thermal conductivity of the composites were investigated at different temperatures.

2. Experimental

2.1. Materials

The resin matrix used in this work is the blends consisting of 60 wt% epoxy resin and 39.9 wt% cyanate ester with 0.1 wt% catalysts ($Co(acac)_2$). The epoxy resin and the cyanate ester were diglycidyl ether of bisphenol-F (DGEBF, GY285 from Huntsman) and 1,1-Bis(4-cyanatophenyl)ethane (DCBE, Primaset LECy from Lonza), respectively. The catalyst, acetylacetone cobalt(II) ($Co(acac)_2$), was provided by Alfa Aesar. The glass fiber woven is a boron free, 240 g/m^2 plain weave, with 18 threads/cm in the warp (length), 14 threads/cm in the fill (width), treated by a silane agent (RW220-90 from Sinoma Science and Technology Co. Ltd., China). The mechanical and thermal properties of cyanate ester/epoxy resin and glass fibers used in this work are provided in Table 1.

The as-received MWCNTs were provided by Chengdu Organic Chemicals Co. Ltd., which have dimensions of 30–50 nm in external diameter and 10–20 μm in length. The silane coupling agent used in this research is 3-Aminopropyltrimethoxysilane purchased from Acros. Surfactant Cetrimonium Bromide (CTAB, Tianjin Jinke Chemical Research Institute, China) was used to improve dispersion of A-MWCNTs in water.

2.2. EPD process

The well dispersed solution was required for a successful deposition. The MWCNTs were treated by the silane coupling agent 3-Aminopropyltrimethoxysilane. 0.5 g as-received MWCNTs were ultrasonic dispersed into 80 ml ethanol and 400 μl silane coupling agent was added. Then the suspensions were refluxed for 3 h at 80 °C. Thus, amine groups were introduced on MWCNT surface, so that the surface of MWCNTs was positive charged. 50 mg A-MWCNTs were dispersed into 200 ml deionized water and then sonicated for 10 min. 5 mg CTAB were added into the solution and sonicated for 20 min. Finally the well dispersed solution was prepared. The concentration of A-MWCNTs was 2.5×10^{-4} wt% and the CTAB concentration was 2.5×10^{-5} wt%.

Considering insulated property of glass fiber, the woven glass fiber was fixed on a steel plate and used as a negative electrode so that the positive charged A-MWCNTs could migrate toward the negative electrode. Another steel plate was employed as a positive electrode. The process of the deposition and the installation of EPD are illustrated in Fig. 1 (Stage 1). The EPD process was carried out at a constant voltage of 45 V and an electrode distance of 50 mm. The reverse side of the woven glass fiber was deposited under the same condition. After deposition, the MWCNT-glass fiber layers (MGL) were dried at 60 °C overnight in a vacuum oven. Two kinds of MWCNT-glass fiber layers were prepared and the deposition time was 3 min and 10 min, respectively.

2.3. Preparation of composites

The impregnation method employed in this study was VARTM. 20 layers of as-received woven glass fiber layer and MGL were piled into a metal mould which had been coated releasing agent, respectively. The schematic illustration was shown in Fig. 1 (Stage 2). The metal mould together with woven glass fiber was dried at 100 °C for 10 h. The blends consisting of 60 wt% epoxy resin and 39.9 wt% cyanate ester with 0.1 wt% catalysts ($Co(acac)_2$) were premixed in a 250 ml beaker and degassed with a vacuum pump at 45 °C. The bubble freed cyanate ester/epoxy blends were impregnated into the preheated mould and were cured at 100 °C for 6 h, 120 °C for 4 h and then 150 °C for 16.5 h.

Based on the density of A-MWCNT composites and pure GFRP composites, the A-MWCNT content was estimated to be 4 wt% and 2 wt% for 10 min EPD duration and 3 min EPD duration, respectively. The volume fractions of the composites are calculated according to ASTM D2734-09. The volume fraction of glass fiber is consistent for before and after deposition for the thickness of the specimen is remained 4 mm. The volume fraction of glass fiber in composites is estimated to be 53.7 vol%. The volume fraction of A-MWCNTs in composites is estimated to be 3.74 vol% and 1.82 vol%, respectively and the void content is calculated lower than 0.5 vol%.

Table 1
Properties of cyanate ester/epoxy resin and glass fibers used in this work.

	Tensile modulus (GPa)	Tensile strength (MPa)	Thermal conductivity (W/m/K)
Matrix resin	2.91	81.5	0.185
Glass fiber	72.8	3550	1.03