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Preparation of continuous carbon nanotube networks in carbon fiber/epoxy composite

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ABSTRACT

In order to optimize carbon nanotube (CNT) dispersion state in fiber/epoxy composite, a novel kind of CNT organization form of continuous networks was designed. The present work mainly discussed the feasibility of preparing continuous CNT networks in composite: Fiber fabric was immersed into CNT aqueous solution (containing dispersant) followed by freeze drying and pyrolysis process, prior to epoxy infusion. The morphologies of fabric with CNTs were observed by Scanning Electron Microscope. The relationship between CNT networks and flowing epoxy resin was studied. Properties of composite, including out-of-plane electrical conductivity and interlaminar shear strength (ILSS), were measured. The results demonstrated that continuous and porous CNT networks formed by entangled CNTs could be assembled in fiber fabric. Most part of them were preserved in composite due to the robustness of network structures. The preserved CNT networks significantly improved out-of-plane electrical conductivity, and also have an effect on ILSS value.

1. Introduction

Carbon fiber/epoxy composite exhibits good electrical and mechanical properties, which has obtained applications in many realms. Relative to reinforcing fibers, epoxy and interface between fibers and matrix are considered to be fatal bottlenecks constraining the further improvement of overall properties [1–4]. The main reasons are summarized as follows: (1) Pure epoxy matrix has low electrical conductivity, strength and/or toughness relative to fibers. However, its volume percent is as high as 30–50% in composite; (2) Original carbon fibers possess inert surface. Thus epoxy resin is not easy to combine with fibers closely. It means that weak interface exists in fiber/epoxy composite. While weak interface always result in large interface resistance and serious physical defects (such as cracks) on a micro level as well as low electrical conductivity along the through-thickness direction and modest mechanical performances of interlaminar composite in macro.

As nanoscale material, CNTs offer possibility to solve these problems discussed above benefiting from their exceptional electrical and mechanical properties [5–14]. On one hand, the introduction of CNTs in interface by the method of CNT aqueous solution immersion [5], electrophoretic deposition [6,7] or sizing technique [8] can ameliorate the bonding state between fiber and matrix. Interfacial reinforcing mechanisms are divided into several types, such as increase of fiber surface roughness and formation of chemical bond between fiber and CNTs [5,6]. On the other hand, the presence of CNTs in epoxy has direct influence on crosslinking density, toughness, stiffness and electrical conductivity of matrix [15–18]. Above all, the CNTs in different positions affect the properties of composite from different perspectives. But in most of the pre-existing processes, CNTs always separately disperse on fiber surface (in interface) (as shown in Fig. 1a) or in matrix (as shown in Fig. 1b) when CNT loading is low, thus could not ameliorate properties of matrix and interface between fiber and matrix simultaneously. While CNTs with high content are inclined to aggregate resulting from their characteristics of small diameter in nanometer scale with high aspect ratio and large surface area. The aggregates always weaken the modifying effects of CNTs on composite [13,16]. Furthermore, even though the CNTs might be disordered in the region between fibers in fiber/CNTs preform, the CNT orientation would be changed to be parallel to fibers due to the viscous forces of fluid epoxy resin and the weak interactions between CNTs during the infusion process (as shown in Fig. 1c) [6,19]. But the change is not beneficial for the improvement of electrical and mechanical performance of composite [6]. Therefore, proper dispersion state and organization form of CNTs in composite need to be designed.

Previously, we have applied freeze drying technique to disperse CNTs in three-dimensional (3D) carbon fiber felt/epoxy composite [20]. Compared with heat drying method which is commonly used, freeze drying displays an obvious advantage in ameliorating CNT dispersion state. It is interesting that the utilization of freeze

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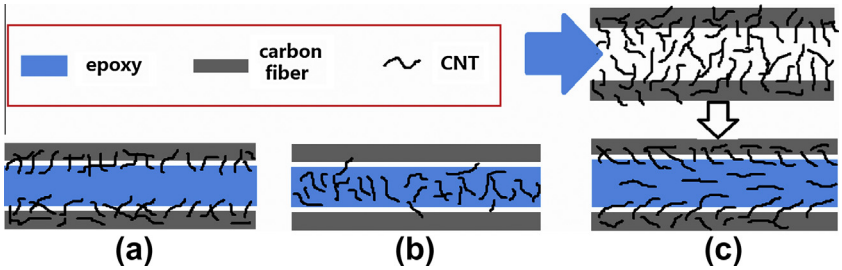

Fig. 1. Dispersion state of CNTs in fiber/epoxy composites: mainly in interface (a) and mainly in matrix (b); morphology of CNTs between fibers before (upper) and after (lower) epoxy was introduced into fabric (c). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

drying is helpful to assemble partial and porous CNT networks formed by entangled CNTs between fibers which are close to each other (the distance between them are less than several micrometers). Considering that the distance between fibers in unidirectional or two-dimensional (2D) fiber fabric mainly ranges from hundreds of nanometers to tens of micrometers, continuous CNT networks are more promising to be assembled through the method of freeze drying in theory, thus might have a positive effect on composite.

In the present work, we discussed the feasibility of preparing continuous CNT networks in 2D fiber fabric reinforced composite in the situation that freeze drying method was adopted. CNT aqueous solution with different concentration was introduced into fiber fabric. Then the fabric was dried by freeze drying and heat treated (pyrolysis process of removing dispersant) to prepare fabric/CNTs preform. The composite would be obtained after epoxy resin was added to the preform. The characteristics of outcomes of each step during the preparation of composites were detected to analysis the morphological transformation of CNT organization and its effect on the properties of composite.

2. Experimental

2.1. Materials

The reinforcement was polyacrylonitrile-based carbon fiber (with sizing on surface. The density of carbon fiber was 1.76–1.78 g/cm^3) plain cloth woven in a 0°/90° satin-weave (yarns of 1000 filament count. The areal density of cloth was 130 g/m^2) from Shenzhou Carbon Fiber Co., Ltd. (Jilin Province, China). CNT paste was made by Shenzhen Nanotech Port Co., Ltd. The weight ratio of CNTs: water: dispersant (polyvinyl pyrrolidone, abbreviated to PVP) is about 5:95:1. The CNTs were synthesized by chemical vapor deposition. The diameter and length ranged between 10–30 nm and 1–5 μm, respectively. Glycidyl epoxy resin and curing agent used to produce composite was SK-0430 and methylnadic anhydride, respectively, purchased from Changzhou SUNCHEM High Performance Polymer Co., Ltd. (Jiangsu Province, China). The mix ratio of curing agent to epoxy resin was 135 to 100 g. The viscosity of the mixture is very high at 25 °C (room temperature), and it will decrease to a certain extent when temperature rises to 90 °C. Therefore, introducing epoxy to fiber fabric was always operated at 90 °C in this work. Freezing dryer (model: FD-1-50), with high ultimate vacuum (<20 Pa) and low operating temperature (<−55 °C), was made by Beijing Boyikang Co., Ltd.

2.2. Preparation of carbon fiber fabric with CNT networks

Before preparation of the fiber fabric with CNT networks, the CNT paste was diluted with deionized water. CNT aqueous solutions with different concentration of 1 wt% and 2.5 wt% were prepared. The stability of such solution was examined by static test for days. Obvious layering or coagulation was not observed after 30 days, revealing that these solutions were stable. $[0]_8$ carbon fiber clothes (fabric) with rectangle shape was fixed by glass slides and immersed into CNT solution under vacuum. Then the fabric was dried by freeze drying method consisting of freezing at −20 °C for 24 h and subsequent drying in freezing dryer. In particular, when the vacuum of freeze drying system was lower than 17 Pa, fabric was took out and heat treated from 400 to 650 °C with a rate of 1 °C/min under argon atmosphere to remove PVP in fabric. The procedures of preparing fiber fabric with CNT networks (noted as CF/x%CNTs: x% stands for the concentration of CNT solution. x = 1 or 2.5) was illustrated in Fig. 2.

2.3. Characteristics of fiber fabric with CNT networks

The characteristics of carbon fiber and CNT paste before and after heat treatment (400–650 °C with a rate of 1 °C/min under argon atmosphere) were detected by Scanning Electron Microscope (SEM), Transmission Electron Microscope (TEM) and Fourier Transform Infrared Spectrometer (FTIR). The morphologies of CNT networks in fiber fabric before epoxy infusion were also observed by SEM.

2.4. Preparation of composite for electrical conductivity and ILSS tests

Epoxy resin was introduced into three types of $[0]_8$ carbon fiber fabric (as-received fiber fabric, CF/1%CNTs and CF/2.5%CNTs) by means of vacuum assisted infusion model at 90 °C. The infusion of liquid epoxy resin was performed along the direction of X axis as defined in Fig. 2. Then, the fabric containing liquid epoxy resin was cured at 120 °C for 1 h, at 180 °C for 4 h and finally at 200 °C for 4 h. Three types of composites (noted as CF/x%CNTs/EP: the meaning of x% is as same as what has been defined in Section 2.2. Carbon fiber/epoxy composite without CNTs was noted as CF/EP) kept the same thickness of 1.8 mm during curing process. Following the method utilized in previous researches [6,14], the volume fraction composition of varying composites were established from weight changes in the fiber fabric after CNT deposition and from density measurements and nitric acid digestion of the prepared composites.

Out-of-plane electrical conductivity of specimen was tested by CHI660D electrochemical workstation (made by CH Instruments, Inc.) to evaluate the dispersion state of CNTs in composite and its effect on electrical performance. The surface of specimen was beforehand polished to expose fibers sufficiently. ILSS tests followed ASTM D2344 guidelines. Five specimens were tested for each set of conditions. The opened surface around cracking of laminated composite was observed by SEM.

3. Results and discussion

3.1. Effect of heat treatment on fiber and CNTs

The SEM images of carbon fiber (Fig. 3a and b) indicate that the distance between fibers in one bundle ranges from hundreds of