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Flame synthesis of carbon nanotubes onto carbon fiber woven fabric and improvement of interlaminar toughness of composite laminates

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ABSTRACT

A simple flame synthesis method was utilized for grafting functional carbon nanotubes (CNTs) onto carbon fiber fabrics. Functional organic groups found on CNTs were formed after the flame growth process. Results from electrochemical tests also showed that the accessible surface area was improved by more than 50 times after the carbon fiber fabrics were grafted with CNTs for 3 min. Hence, mode I and mode II interlaminar fracture toughness of these composite laminates, wherein carbon fiber fabrics were grafted with CNTs, increased by ~67% and ~60%, respectively.

1. Introduction

The incorporation of nanofillers, such as carbon nanotubes (CNTs) or carbon nanofibers (CNFs) into the matrix of composites has been developed as an efficient method for improving the mechanical and multifunctional properties of carbon fiber reinforced polymer composites (CFRPs) [1,2]. Two typical routes have been used to incorporate CNTs or CNFs into CFRPs. One utilizes the CNTs or CNFs as reinforced fillers in polymer matrices of CFRPs to improve their mechanical properties. The challenge of this route is that uniform dispersion of CNTs or CNFs in the polymer is hard to achieve, especially at high concentrations, due to the dramatically increased viscosity of the resin. Highly viscous resins with agglomerated CNTs or CNFs are very difficult to process and always lead to poor performance of the polymer nanocomposites [3]. Another route is to attach CNTs or CNFs directly onto CFs to build up a hierarchical reinforcement. Several techniques were successfully developed [1,2]. CNTs could be applied on the fiber surface by spreading CNT powder [4] or CNT-solvent paste [5], and transferring CNT arrays [6]. Grafting of CNTs onto CFs could also be achieved by chemical reaction between the pre-modified functional groups on the surfaces of both CNTs and CFs [7,8]. The electrophoresis technique could be used [9–11], where CNTs were uniformly deposited on the surface of carbon fiber fabric from the CNT dispersion in an applied electric field.

The concept of *in situ* growing CNTs onto the surfaces of CFs has also been introduced to increase the interfacial shear strength (IFSS) of CFs in the matrix [12]. Chemical vapor deposition (CVD) was the most utilized method for growing CNTs on carbon fibers [12–18]. The growth of CNTs on the surface of CFs leads to the formation of two interfaces: one between CF and CNT and another between CNTs and matrix. Outstanding adhesion between CNTs deposited by CVD and CFs has been obtained [16–18] and a dramatic increase in IFSS was achieved after CNTs were grafted onto CFs [17,18]. In a recent study [19], we showed strong adhesion of *in situ* flame synthesized CNTs onto CF substrate using an atomic force microscope (AFM) to measure the peel force for a single CNT from a CF [19]. This result indicates a potentially effective method to increase the IFSS and delamination toughness of CFRPs by flame synthesis of CNTs onto carbon fiber fabrics.

A problem with CNTs fabricated by normal CVD techniques is their poor affinity with many polymer matrices due to their inert chemical properties. Hence, further functionalization is required to introduce some functional groups on the CNT surface [20]. However, this is not an issue with flame synthesis as oxygen-functional groups are formed on the CNT surface during the growth process [21,22]. Thus, glass fiber/vinyl ester composite laminates with flame synthesized CNTs in the matrix have improved mechanical properties compared to those with CNTs formed by CVD owing to the abundant functional groups present on the flame synthesized CNTs [21]. Hence, the interface between CNTs and matrix in CFRPs can also be promoted by flame synthesized CNTs onto carbon fabrics.

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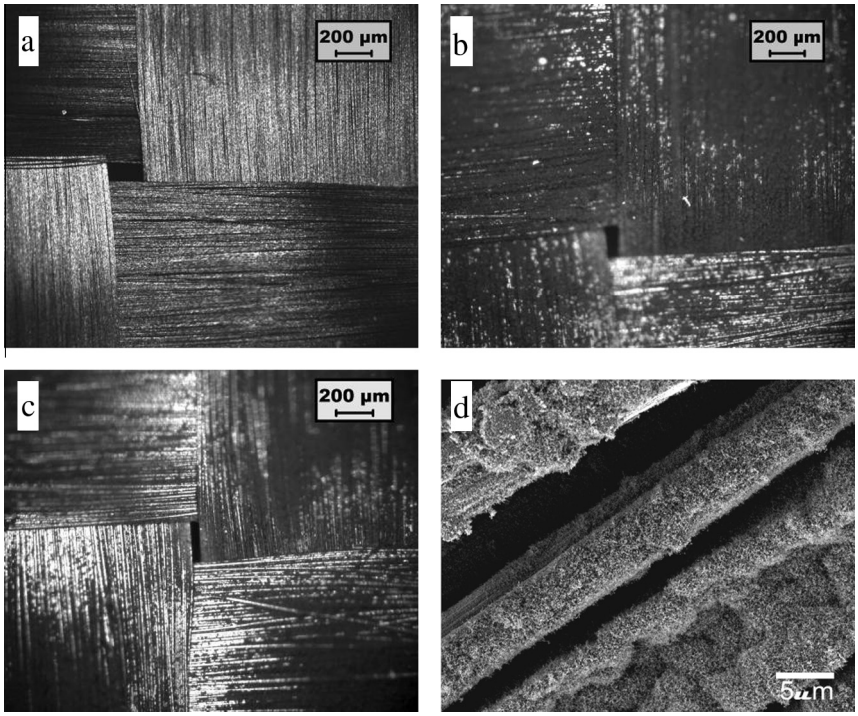

Fig. 1. (a) Optical image of carbon fiber fabric (CF); CNTs on CF grown for (b) 3 min, and (c) 1 min. (d) SEM image of CNT/CF grown for 3 min.

Based on the abovementioned improved interface properties of CNT/CF and CNT/matrix owing to the flame synthesis technique, we expect the mechanical properties of such CFRPs will be substantially enhanced. Herein, we show that this simple method allows the CNTs to be readily grafted onto the CFs, thus increasing the delamination toughness of woven CFRPs. Compared to CVD, which is an energy intensive batch process requiring costly reagents and equipment, the flame synthesis of CNTs on CFs decreases significantly the growth time and its simple open-environment deposition process facilitates easy industry scale-up.

2. Experimental work

2.1. Materials

Carbon nanotubes were *in situ* deposited onto the plain woven CF fabric (Inter-Turbine Advanced Logistics Pty Ltd) according to our recent developed flame synthesis method [19]. $NiCl_2$ (0.2 mol/L) was used as a catalyst precursor and ethanol flame the carbon source. Briefly, the plain woven carbon fabric applied with the nickel chloride catalyst precursor was mounted on a metal frame and inserted into the core of the flame at ~500–700 °C for 1 and 3 min to grow the CNTs. Plain woven fabrics with or without CNTs were utilized as the main reinforcement in the CFRPs. Araldite-F (diglycidyl ether of bisphenol A, Huntsman) and piperidine (Sigma–Aldrich) in weight ratio of 100:5 were used as the matrix. Laminates having 16 plies of woven fabrics were prepared by the hand lay-up method. The whole process was maintained at 80–90 °C to ensure the low viscosity of epoxy to fully impregnate the fiber mats. A 25 μm thick polyimide film was inserted in the mid-plane of the laminates to act as the initial crack. The laminates were then wrapped with bleeders and release film within a vacuum bag, first vacuumed in a chamber for 0.5 h followed by curing in a hot-press at 120 °C for 16 h under a pressure of 200 kPa. The fiber volume fraction in the final composite laminates was ~58%.

2.2. Characterization

Scanning electron microscopic (SEM) images were taken on a Zeiss ULTRA Plus and optical images on a Leica microscope. Transmission electron microscope (TEM) and HRTEM images were recorded on the Philips CM12 (120 kV) and JEOL 2200FS (200 kV), respectively. Fourier transformed infrared (FT-IR) spectra were obtained by a FT-IR spectrometer (Bruker) and differential scanning calorimetry (DSC) datas taken by a TA modulated DSC 2920 in nitrogen. Electrochemical characterization was performed on a CHI1202 Electrochemical Analyzer (CH Instruments). A three-electrode electro- chemical cell was used for the measurements, where the counter electrode was a Pt foil and the reference electrode was a saturated calomel electrode (SCE). Plain woven CF fabric with or without flame synthesized CNTs was directly used as the working electrode.

Mode I and mode II interlaminar fracture toughness values were measured using double-cantilever-beams (DCB) and three-point end notched flexure (ENF) tests at room temperature on an Instron 5567 machine, following ASTM D5528 for mode I interlaminar fracture toughness tests [23] and the ESIS protocol [24] for mode II interlaminar fracture toughness tests, respectively. For samples modified with CNTs, only the 8th and 9th plies were modified by the flame synthesized CNTs, since the fracture behavior of interest was along the laminate mid-plane in the delamination tests. At least three samples were tested for each reinforced composites system. The mid-plane deflection of the ENF specimens was controlled by a crosshead rate of 1 mm/min and the initial crack length was 25 mm. For Mode I DCB delamination tests, the crack mouth opening displacement rate was 1 mm/min. To ensure the same testing conditions for both neat carbon fabrics and those modified with CNTs, DCB specimens with synthesized CNTs 20 mm ahead of the pre-crack were also prepared (as shown in Fig. 4b later). The delamination toughness results of these specially designed DCBs were obtained and compared with those of normal specimens without the 20 mm bare CF area.