Reducing dispersity of mechanical properties of carbon fiber/epoxy composites by introducing multi-walled carbon nanotubes

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1. Introduction

Since the discovery of Carbon nanotubes (CNTs), they have been considered as ideal fillers for high performance polymer composites, owing to their low density, nano-scale diameter, high aspect ratio, and more importantly, extremely high mechanical strength and modulus \([1,2]\). Over the last decade, CNTs based polymer nanocomposites have been fabricated by adding CNTs into various polymer matrices using different processing techniques \([3,4]\). Though some technical and economical issues still need to be overcome, including the difficulty of obtaining homogeneous and stable dispersion of CNTs, tuning the CNT-polymer interfacial adhesion, and reducing the cost of CNTs, the results obtained so far are promising. A unique level of mechanical property enhancement is gained even at low CNT content. However, the transfer of the outstanding properties of CNTs into the polymer composites with superior mechanical properties can be used for large-scale composite structures is still challenging. Currently, the closest to structural applications are the attempts that have been made to use CNTs loaded matrices in reinforcing conventional fibers, like carbon fibers (CFs) and glass fibers (GFs), reinforced composites. Various parameters, such as processing techniques, matrix, CNT aspect ratio, CNT types and surface properties, have been considered by these previously reported studies on CNTs based multi-scale composites \([5–10]\). By adding CNTs, matrix-dominated composite properties, such as interlaminar shear strength (ILSS), fracture toughness, through-thickness conductivity, glass transition temperature \((T_g)\), can be improved. For instance, Gojny et al. \([11]\) got an increase in ILSS by nearly 20% through adding amine groups functionalized CNTs into the matrix. Fan et al. \([5]\) reported a even higher degree of increase in ILSS by aligning the CNTs perpendicular to the fiber fabric surface. Benefits of CF reinforced composites, fabricated by a prepreg technique, from the dispersion of cup-stacked CNTs between fiber mats were reported by Yokozeki et al. \([6]\). A delay of matrix crack onset that results in the improvement of fracture toughness was found. Similar positive effects of CNTs on mechanical properties of fiber/polymer composites were also obtained by other researchers \([7,8,12]\).

Several localized mechanisms of energy dissipation brought by CNTs have been investigated and discussed for CNTs based polymer as well as multi-scale (fiber reinforced) composites. These are CNT pullout, CNT rupture, CNT/matrix debonding, and crack bridging \([13,14]\). These studies, however, mainly focused on the efficiency of these enhancing mechanisms on the bulk mechanical properties of the composites. The focus of the present study is to evaluate the effect of these enhancing mechanisms on reducing the dispersity of bulk mechanical properties of the fiber reinforced polymer composites.

As is well-known, fiber reinforced polymer-matrix composites are generally microscopically inhomogeneous, consisting of reinforcement phase, matrix phase and interfacial phase between them. At the microscopic level, the types of defects, such as resin-rich areas or resin-poor areas, micro-voids, and internal micro-cracks, are complex and random. These features result in multi-modes of failure mechanisms under applied loadings.
result, the mechanical properties of the fiber reinforced polymer-matrix composites are rather more dispersed and hard to predict than conventional metal materials [15,16]. Considering this fact, the allowed load for composite structures is usually lower than their ultimate load. Consequently, the design safety factor is quite high for composite structural materials, especially for aircraft structures [16], and the weight saving of using composite structures still need future optimization.

In this study, CF and CNTs co-reinforced epoxy composites were fabricated using the prepgrep technique. The prepgrep technique is chosen to minimize the technical difficulties in dispersing CNTs, which is more difficult for resin transfer molding technique, in which CNTs will be blocked and agglomerated while flowing through closely packed fibers. Localized energy dissipation mechanisms, as well as the influence of CNTs on fiber–matrix interface quality, are discussed. No major but conclusive results were obtained, indicating a positive effect of CNTs on reducing dispersity of the bulk mechanical properties of fiber reinforced polymer composites.

2. Experimental

2.1. Materials

Resin and curing agent used in this study was a bisphenol A epoxy (CYD-128) and Ethylamine Boron Trifluoride (EBT), both purchased from Balin Petrochemical Company, Inc. Toray T700 CF produced in Japan was used. Multi-walled carbon nanotubes (MWCNTs) were provided by the Shenzhen Nanotech Port Co., Ltd., with diameters range from 10 to 30 nm and lengths range from 1 to 5 µm (Fig. 1).

2.2. Composite manufacturing

The MWCNTs were first acid treated according to the methods described in detail elsewhere [17], in order to tailor the dispersion and interfacial interaction with the matrix. The obtained functionalized MWCNTs were then dispersed in acetone by high-intensity ultrasonication. Meanwhile, the epoxy was dissolved in acetone with a weight ratio of 1:1 in a separate vessel. The curing agent EBT was also added. The epoxy solution and MWCNT suspension were subsequently mixed in a bath ultrasonic together with stirring for 60 min. The weight ratio of epoxy, curing agent and MWCNTs was kept constant to 100:3:1.

Unidirectional CF prepgrep layers were manufactured by filament wind (Drum-winder) process using the above matrix system.

Fig. 1. A typical SEM image of the MWCNTs.

Pure epoxy/acetone solution with the same concentration was also used to reduce the variation in the viscosity of the resin system, which could introduce the variations in the final fiber areal weight. Speed of the drum rotation (10 r/m, diameter of the drum is 500 mm), and speed of the drum translation (2 mm/r, axial movement of the drum during rotation) were set to be constant to ensure the certain areal weight of fibers in the prepgrep. Once the prepgrep layers were prepared, they were removed from the wind mould and dried for several hours to get rid of the acetone. Later they were cut into dimensions 350 mm by 350 mm and eight such layers were laid up into a flat mould in unidirectional fiber orientation. The prepgreps were cured at 80 °C for 1/2 h, and at 120 °C for 4 h, followed by a post curing step at 140 °C for 4 h. The cured panels with the final fiber volume fraction about 60% were machined for mechanical testing.

2.3. Mechanical and micro-structural characterizations

Tensile tests were performed using a universal testing machine (MTS810), and the ILSS was measured via three-point-bending test using the short-beam method. Typical specimen dimensions were 250 mm in length, 14 mm in width, 2 mm in thickness for tensile tests, and 25 mm in length, 7 mm in width, 2.2 mm in thickness for ILSS tests. Around 50 specimens for each composite system were cut from different locations at both neat and nano-modified composite panels to make sure that the measured distribution of mechanical properties is close to that of the composites. Microstructures of the composites were investigated using scanning electron microscopy (SEM) (KYKY-2800, 25 kV and FEI Quanta-200, 25 kV).

3. Results and discussion

Tensile properties and ILSS of the composites were investigated and the results are shown in Fig. 2. Curves of the distributions of Young’s modulus (a), fracture strength (b), fracture strain (c) and ILSS (d) of the composites were fitted by Gaussian distribution to evaluate the dispersity of the mechanical properties.

Interfacial characteristics between the MWCNTs and the polymer matrix have been studied by researchers using both experimental and computational methods [18–20]. The stress transfer efficiency of CNT-polymer interface is estimated to be much larger than that of the conventional CFs or GFs. Thus, MWCNTs with high aspect ratio can act as bridges at micro-crack initiation sites or propagation paths. During the failure process, the bridge effect will efficiently delay the crack initiation and propagation in the form of MWCNT pullout or rupture. Evidences of MWCNT pullout (or rupture) were commonly found and typical ones are shown in Fig. 3. The white filaments are the pulled-out or broken end of MWCNTs. The CNT pullout and rupture mechanisms are energy dissipative and increase the toughness of the matrix [8]. Consequently, the tensile strength and strain of the composites increased, as shown in Fig. 2b and c. In fiber/epoxy composites, the fiber–matrix interface debonding is another main failure mechanism. During the fabrication process, defects (mainly voids) are produced and tend to occur at the interface[21], and these defects are common crack initiation sites. Under applied loadings, the deformation of fibers also initiates cracks near the fiber–matrix interface. MWCNTs near the fiber–matrix interface can also prevent the crack initiation or propagation along the interface. Fig. 4 illustrates scenarios where MWCNTs bridge cracks near the interface. All these micro-mechanisms contribute to the increase of bulk mechanical properties of the composites, as shown in Fig. 2.

Dispersion of mechanical properties of the composites is mainly affected by the inhomogeneity (mainly brought in by defects and
residual stress), commonly located at stress concentration area inside the matrix or near the fiber–matrix interface. The MWCNT bridging, pullout and rupture mechanisms discussed above are also expected to reduce the influence of defects by hindering the initiation and propagation of micro-cracks. In addition, the embedded MWCNTs can reduce the residual stress inside the matrix [22]. Hence, dispersity of the mechanical properties of nano-modified composites can be decreased as a result of the added MWCNTs, as shown by the narrower curves of property distributions for nano-modified composites in Fig. 2.

From Fig. 2a, it can be seen that the mean tensile modulus of the nano-modified composites increased, while the dispersity of modulus did not change much. This behavior can be attributed to the following two main effects: First, the modulus of the composites is mainly dominated by the modulus of the CFs rather than the matrix. Hence the dispersity of modulus of the composites is mainly determined by the dispersity of modulus of the CFs. Second, the dispersion of MWCNTs in the matrix is not perfectly homogenous. The modulus describes the resistance to elastic deformation which is reversible, and is much more sensitive to the defects brought by MWCNT agglomeration (as shown in Fig. 5). The sensitivity of modulus to defect concentration for other materials, such as plasma sprayed deposits and MWCNTs, has also been discussed [23,24]. The effect of agglomeration defects counteracted the effects of the above mentioned mechanisms in reducing the dispersity of the modulus.

Typical fracture modes of neat and nano-modified composites were shown in Fig. 6. Lots of tiny and fragmentary matrix blocks presented at the fracture surface of the neat composites, showing...
multi-modes of damages. Compared with the fracture surface of the neat composites, the fracture surface of the nano-modified composites is much smoother and the fractured matrix blocks are much bigger and more uniform, indicating a much more homogeneous structure. This phenomenon also indicates that adding MWCNTs into the matrix leads to the decrease of dispersity of mechanical properties of the composites.

From Fig. 2d, it can be seen that the ILSS of the composites improved and the dispersity decreased with the introduction of MWCNTs. Generally, interlaminar shear failure involves several fracture mechanisms that occur during delamination, including matrix deformation and fracture, fiber pullout and fiber bridging, and fiber–matrix interface debonding [25]. Above mentioned matrix and interface enhancing mechanisms for tensile properties also contribute to the increase of ILSS which is a matrix-dominated property. Besides, MWCNTs contribute to the ILSS improvement through another two effects: First, the MWCNTs are randomly dispersed in the matrix. Part of the MWCNTs that oriented perpendicular to the CF cloth layer plane can act as inter-plane bridges and enhance the ILSS effectively [5], as shown schematically in Fig. 7. Second, delamination along the fiber–matrix interface is one of the major failure modes and hence the interface characteristic is critical for the ILSS [26]. Researchers explained that presence of nano-particles could reduce the residual stresses at the fiber–matrix interfaces [27,28].
SEM pictures of three-point-bending test sample fracture surface are given in Fig. 8. The neat composites possessed a poor interface bonding with matrix for the fiber surface is rather clean (Fig. 8a). In contrary, the fracture surface of nano-modified composites shows a thin film of matrix adhered to the fibers (Fig. 8b), indicating a stronger fiber–matrix interface. It can be also seen in Fig. 8c and d that the inner matrix surface left by fiber pullout of the neat composites is smooth, while that of the nano-modified composites is much rougher. The stronger fiber–matrix interface contributes to the observed higher ILSS.

Though the increase of ILSS is not as high as that reported by Gojny et al. [11] and Fan et al. [5], for the absence of tube surface modification or alignment of the MWCNTs, the reduction of dispersity of the ILSS is observed. The main reason is believed to be the improved matrix and fiber–matrix interface qualities, which reduced the stress-induced cracks, as well as the influence of defects.

![Fig. 6. Fracture surfaces of the composites.](image)

![Fig. 7. Schematic of MWCNTs between CF cloth layers that could enhance the ILSS.](image)

![Fig. 8. Interfacial surfaces of the fiber and matrix.](image)
All the mechanisms have a positive effect on the enhancement of ILSS and reduction of dispersity of the ILSS.

4. Conclusions

Multi-scale MWCNT/CF/epoxy laminated composites were fabricated by traditional filament winding and prepreg laying up technique. Enhancing mechanisms of the MWCNTs, in the form of MWCNT bridging, pullout and rupture, are discussed. These micro-mechanisms reduce the influence of matrix defects and micro-cracks on mechanical properties of the composites. Evidences for the improvement of the quality of fiber–matrix interface are also found. All these contribute to the increase of bulk mechanical properties, and more importantly, the reduction of dispersity of bulk mechanical properties of the composites. The obtained no major but conclusive results leave us scope for future improvement and optimization in the CNT/CF/polymer multi-scale composites.

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