UNDERSTANDING INTERLAMINAR TOUGHENING MECHAMISMS IN STRUCTURAL CARBON FIBER/EPOXY COMPOSITES INTERLEAVED WITH CNT VEILS

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Abstract

The susceptibility to delamination is one of the main concerns in fiber reinforced polymer composites. Carbon nanotubes carry the promise of enhancing this poor out-of-plane mechanical performance, although their integration has been challenging. In this work, macroscopic CNT veils with controlled nano-meso structure were fabricated and integrated into woven carbon fiber/epoxy matrix composites utilizing a facile and scalable approach. Interlaminar fracture toughness of the resulting composites was determined in Mode-I (opening mode) test. Additionally, crack propagation and interlaminar toughening mechanisms were systematically analyzed by means of optical microscope, SEM and Raman analysis. The results show that interlaminar crossing play a paramount role in toughening mechanism. The crack front alternatingly propagates above and below the CNT-toughened interlayer, significantly improving the fracture toughness of resultant laminates.

1. Introduction

Several approaches for integrating CNTs into FRP structural composites have been studied [1-3]. Among all these methodologies, dispersing CNTs entirely throughout the composite matrix is, to date, the predominant route due to its relative simplicity. Yet, the main problem of this approach is that the viscosity of a CNT-modified matrix increases dramatically with increasing CNT content, leading to incomplete matrix infusion [4]. Also, it is difficult to get a homogeneous dispersion of extra phases into the epoxy matrix and final laminate [5].

Using pre-formed veils of CNT yarns [6, 7] offers an alternative method which avoids the problems related to increased viscosity and the inhomogeneous dispersions of the aforementioned route, as these veils can be easily and readily deposited in between the primary reinforcing fiber layers before infusion. Thus, the viscosity of the composite matrix is not affected.

In this paper, a new strategy is proposed to integrate macroscopic fibers and home-made CNTs fiber veils into structural laminate composites. Meanwhile, commercial CNT veils were used and compared. In the following sections, we will discuss how to use optimized Vacuum Assisted Resin Transfer Molding (VARTM) to manufacture CNT toughened epoxy/carbon fiber composites. By selecting appropriate manufacturing parameters, we could manufacture satisfactory composite specimens for mode-I delamination tests according to standard test methods. The critical energy release rate of mode-I delamination (G_{IC}) of the CNT toughened CFRPs composites were then compared with that of conventional CFRPs combined with a deep analysis of toughening mechanisms.

2. Experimental

2.1. Materials

As-produced CNT veils were synthesized by the direct spinning process from the gas-phase during growth of CNTs by floating catalyst chemical vapor deposition (FCCVD) [6], as schematically illustrated in **Fig. 1a**. Commercial CNT veils with a thickness of 10 µm (**Fig. 1b**) were kindly provided by TORTECH. They were not optimized for this application. The carbon fabrics used in this study was a Hexcel woven fabric with a weave style of 5H satin. DERAKANE 8084 was chosen as matrix which is provided by Ashland Inc. Both the MEKP hardener and Cobalt octoate catalyst were available from Plastiform S.A. By using a recommended concentration of precursors (100:1.5:0.3), the mixture will reach its gel point after 30-60 min.

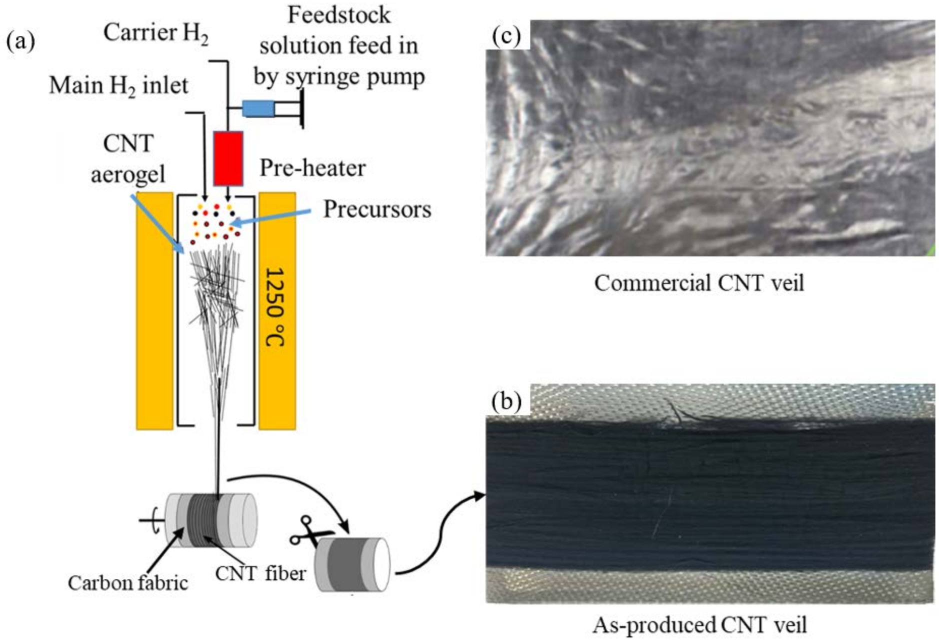

Figure 1. (a) Schematic of direct spinning of CNT fibers from the gas phase by FCCVD; (b) CNT fiber were directly grown on the surface of carbon fabric forming a fluffy/cotton-like structure; (c) Commercial CNT veil.

2.2. Laminate preparation

VARTM method was employed to make the CF/CNT veil/epoxy hierarchical laminate. The impregnation driving force comes from the pressure differential between the inlet and outlet gates and the resistance to resin flow is controlled by the permeability of the porous fiber bed and the rheological properties of the fluid. After completing the infusion process, the inlet and outlet of the system was closed off and cured at room temperature for 24 hours and then post cured at 60°C for 2 hour.

2.3. Characterization

The DCB tests were carried out in accordance with ASTM Standard D5528-01 [8], which specifies either hinges or end blocks for load introduction. Measurements were conducted in a standard testing machine (Instron 3384) at loading rate of 1 mm/min. Force was detected by utilizing a 500 N load cell and the displacement recorded by load frame, both of which were digitally stored by the machine.

Crack growth was visually observed every millimeter and listed in an experimental sheet. C-Scan was performed to determine the quality of the panel and to localize manufacturing defects. Scanning electron microscopy was used to investigate the morphology of CNT fiber veils as well as the fracture surfaces of the laminates. An optical microscope was used to visualize the distribution of CNT veils in the cross section of the composite laminates. Raman spectroscopy (530 nm wavelength) analysis was also performed to identify constitutents at the fracture surface.

3. Results and Discussion

3.1. Method exploration and optimization

Even though the VARTM method is a very mature method in the area of laminate manufacturing, the production of high-quality composites requires good control of multiple factors. These include infusion time, resin-degassing time and curing time etc. Infusion time exerts a profound influence on the quality of laminate. Switching off the vacuum outlet too early will finally lead to obvious thickness variation along the direction of resin flow. **Fig. 2a** and **c** showed the C-scan image and cross-sectional image of laminate in which non-degassed resin was used. Apparently, there were many macro voids inside, most of which were possibly induced during resin-mixing process. While resin-degassing is strongly suggested before infusion, it should be kept in mind that there is an intrinsic trade-off between degassing time and infusion time because the gel time of resin is fixed when finishing the final mixing step. The best practice is to choose a suitable mix proportion of precursors, realizing a relatively long gel time without mechanical penalty when fully cured.

The final optimized VARTM protocol included 10 minutes of resin-degassing and using 2 layers of distribution medium, etc. C-Scan picture (**Fig. 2b**) combined with cross sectional micrograph (**Fig. 2d**) of final CNT toughened laminate proves that there is no macro void inside. Furthermore, the CNT veil maintains its shape after infusion and is fully integrated, leaving no gap between the two plies, a prerequisite to reinforce the interface between the two lamina.

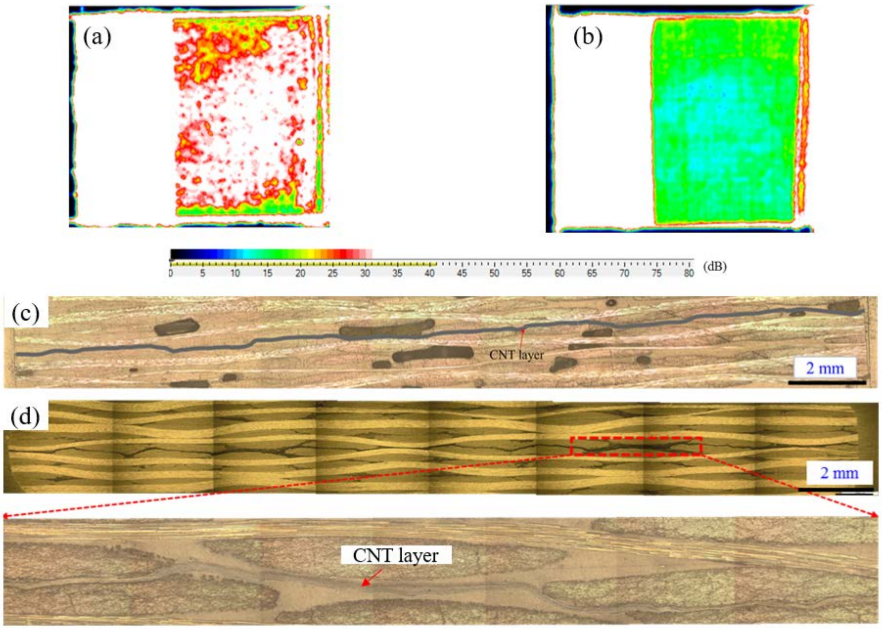

Figure 2. (a) C-scan image and (c) Cross-sectional image of laminate made from resin without degassing; (b) and (d) correspond to the laminate made from resin with degassing process.

3.2. Fracture toughness

The influence of CNT veils on the fracture toughness of the CFRP composites shows that even at relatively low CNT concentration (~0.3 wt.%), there is a significant improvement in the fracture toughness (**Fig. 3**). **Fig. 3a and b** present representative examples of load-extension curves and R-curves, respectively, for a control sample without CNTs, one with CNTs produced in-house and directly deposited onto the CF fabrics, and the third using commercial CNT veils as interleaves. It is clear that there is no significant amount of CF bridging existing in the woven laminates, resulting in a relatively flat R-curve. It is also noteworthy that there is 1.3 times as much area in load-extension curve of as-produced CNT-toughened sample as in that of baseline (**Fig. 3a**), which means the former consumes much higher energy than the latter during the crack propagation. Additionally, the propagation value of fracture toughness increased ~60% compared with the initiation value (G_{in}), which can be attributed to pull-out, interleaving or toughening mechanism of CNT [9]. However, laminates integrated with commercial CNT show a poor interlaminar fracture behavior, which could be attributed to the poor infiltration of resin (see **Section 3.3.**). Average fracture toughness values for the three types of samples are included in **Fig. 3c**.

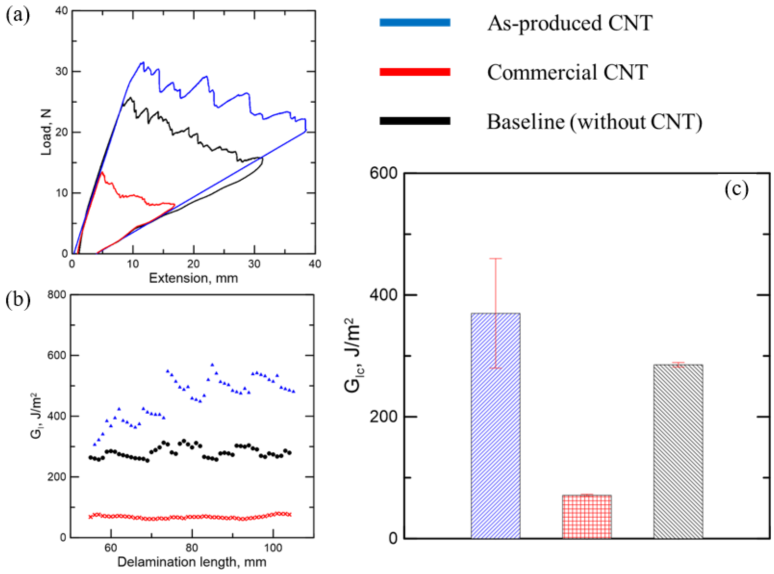

Figure 3. Representative Load-extension curves (a) and R-curves (b) of specimens with and without CNT veils; (c) comparison of Mode I interlaminar fracture toughness for CNT-toughened composites and baseline

3.3. Fractography

The fracture surfaces of tested specimen were examined by SEM (**Fig. 4**). Typical features of brittle Mode-I fracture were observed in the reference specimen (**Fig. 4a**), showing a very smooth matrix fracture surface and no fiber-bridging, in line with its flat R-curve (**Fig. 3b**). When integrating fluffy as-produced CNT veils into resin-rich layer, the case is totally different. Overall, the epoxy matrix is modified by the addition of CNTs, which participate in delaying the crack initiation or hindering the crack propagation by deflection, blocking or crack bridging. These mechanisms help increase the absorption of the applied energy. The extensive CNT breaking and pull-out, as shown in micrographs of **Fig. 4c**, are well in agreement with the prior explained toughening mechanisms. **Fig. 4b** showed a typical fracture surface of laminate interleaved with densified commercial CNT veils, in which extensive sheet-like peeling were observed. This is principally because most of the commercial CNTs films were densified with solution before they appeared on the market. Although this kind of densification, to some extent, does not disrupt the CNT bundle network [10], the structure after shrinkage may be not suitable for the infiltration of solution especially for the resin with high viscosity (i.e. epoxy resin), thus resulting in poor interlaminar toughness.

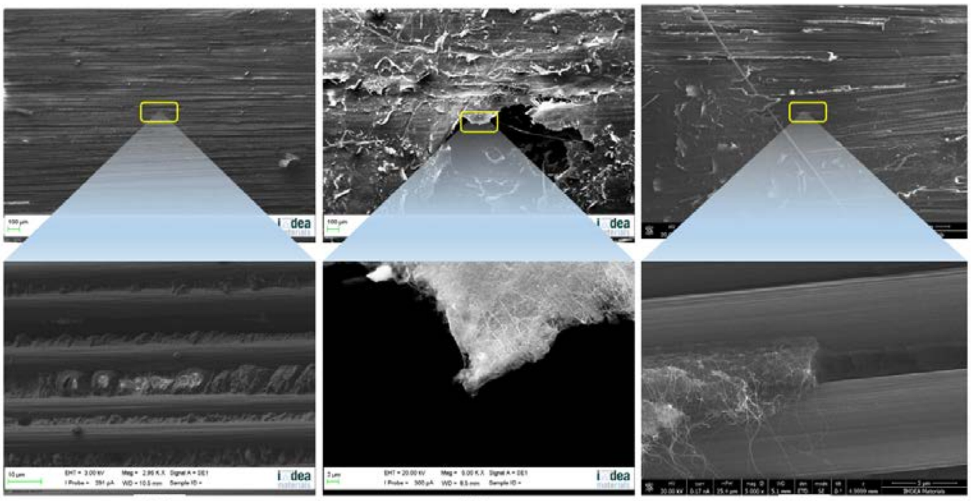
(a) (b) (c)

Figure 4. (a) Comparison of fracture surfaces: (a) baseline, (b) laminate interleaved with commercial CNT veils (c) laminate interleaved with as-produced CNT veils

3.4. Crack propagation

Toughening effect, to a considerable degree, depends on crack behavior. Several surface analysis technologies were used in order to get a deep insight into the crack initiation and propagation behaviors as well as the toughening logics. Three distinct regions were observed on the whole fracture surface of laminate toughened by as-produced CNT, named as shiny, grey and dark part respectively. By means of Raman spectroscopy analysis, the main component of each part could be readily determined. With this information, we determined that a crack propagation during the opening test, as schematically illuminated in **Fig. 5**. This saw-like interlaminar crossings result in a crack through the nanotoughened epoxy triggering thousands of nano-bridgings, which is usually claimed to consume additional energy and hence contribute significantly to the enhanced matrix toughness and thus fracture behaviors.

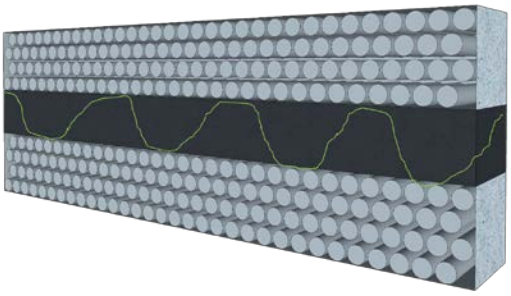

Figure 5. Schematic of the crack propagation in a laminate integrated with CNT fiber veils produced in-house

4. Conclusions

Assembling micro CNTs to macro fiber veils is a promising way to fully explore the excellent properties of these nanomaterials on a macroscopic scale. Furthermore, since there is no need to disperse them into the matrix, there exists no disadvantages such as an increased viscosity or inhomogeneous dispersion which makes them suited candidates for most laminate manufacturing routes.

A facile and scalable infusion protocol was successfully built to make CNT/CF/epoxy composite, by which void-free laminates can be manufactured without utilizing expensive techniques.

The analysis results showed that interlaminar crossing play a paramount role in toughening mechanism. The crack front alternatingly propagates above and below the CNT-toughened interlayer, significantly improving the fracture toughness of resultant laminate.

Acknowledgments

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