Interlaminar Shear Properties of CFRP Composites with CNF-Bucky Paper Interleaves

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Abstract

This paper reports the effects of bucky paper interleaves made from carbon nanofiber (CNF) on mechanical properties of carbon fiber reinforced epoxy composites (CFRPs). The CNF bucky papers were fabricated by vacuum filtration of functionalized CNF-acetone dispersion. Three different techniques were used to impregnate the bucky papers with epoxy resin, including simple soaking, hot compression and vacuum infiltration. Partially cured bucky papers containing about 10wt% CNFs were then integrated into carbon fiber prepregs to produce CFRP hybrid composites with bucky paper interleaves.

It is revealed that the vacuum infiltration technique resulted in the best quality of polymer intercalation among the three methods used to impregnate the bucky papers. The mode-II fracture toughness of the corresponding CNF bucky paper interleaved hybrid composites increased by about 104% whereas the corresponding interlaminar shear strength improved by about 31% compared to the composites without interleaves. Fracture surfaces were examined on a SEM and an optical microscope to identify the pertinent mechanisms involved in toughening and strengthening of CFRP composites.

The significance of this paper is that the technique developed here can be used to incorporate CNFs of high contents to strengthen/toughen at failure prone locations in CFRP composites, which has not been possible previously because of the high viscosity caused by simple dispersion of randomly-oriented CNFs in a polymer resin.

1. Introduction

CFRP composites have been extensively used in the aerospace, military, automotive and sporting goods industries owing to their high specific strength and stiffness. However, these laminated composites can experience premature failure because of interlaminar stresses caused by cracks present between layers of different orientations especially under impact loading. The delamination process represents a fundamental weakness of all laminated composite materials [1]. Several techniques have been successfully devised to improve the delamination resistance [2,3], namely designing 3D fabric architecture, transverse stitching or pinning the fabric, fiber hybridization, toughening the matrix resin, and placing an interleaf, typically of thermoplastic material, in the interplay regions of the laminate. These methods enhanced the interlaminar properties but at the cost of in-plane mechanical properties. Thus, it is ideal to find an effective technique to improve the through-thickness properties without compromising the basic in-plane properties.

Carbon nanotubes (CNTs) have shown great potential as multifunctional nanofillers for polymer composites due to their excellent mechanical, electrical and thermal properties. Considerable improvements in various mechanical properties of polymer have been reported with a small CNT content, most often in the range of 0.5–1.0%. A higher concentration is required for large-scale composite structures that are intended to replace conventional fiber composites. However, the incorporation of high CNT contents is severely limited by the difficulties of CNT dispersion in most polymer resins with a high viscosity.

CNTs in a sheet form or bucky paper offers a platform to eliminate the above issue in fabricating composites with high concentration CNTs. Bucky papers show a great promise for many potential applications [4], such as super capacitors, electrodes,

actuators, sensors, field emitters and hydrogen storage materials. In this work, partially cured CNF-epoxy bucky papers are interleaved in CFRP composites and their effects on the interlaminar shear properties, such as the mode-II fracture toughness and interlaminar shear strength, are specifically evaluated.

2. Materials and experiments

2.1 Materials

The carbon nanofibers (CNFs, supplied by Hodogaya Chemical Co) used in this study had an outer diameter ranging between 60-80nm and length between 7-10 μm. A nonionic surfactant, polyoxyethylene octyl phenyl ether (Triton X-100, supplied by VWR International) was used to functionalize CNFs to improve the interfacial interactions with the epoxy matrix [5]. The epoxy resin system consisted of LY 1564, Aradure 1571, Accelarator LME1181 and Hardener XB 3404 (all supplied by Huntsman). The carbon fiber roving (Pyrofil TR 30S, supplied by Mitsubishi Rayon, Japan) with a filament count of 6K was used as the main reinforcement.

2.1 Fabrication and resin impregnation of bucky Papers

The as-received CNFs were functionalized by a UV-ozone treatment for 30 min to create the oxygen containing functional groups on the CNF surface, which in turn helped uniform dispersion of CNF agglomerates into individual CNFs. The oxidized CNFs were further functionalized in a mixture of acetone and a nonionic surfactant, polyoxyethylene octyl phenyl ether (Triton X-100) with the critical micelle concentration (CMC) value of 10CMC for 2 hr to improve the interfacial interactions with the epoxy matrix, followed by sonication using an ultrasonicator (Branson 2510) for 2 hr to disperse CNFs. The mixture was then vacuum filtered through a filter paper of pore size 4 μm using a vacuum pump. After filtration, the CNF bucky paper was carefully peeled off and dried in a vacuum oven for 12 hr at 50 ^{o}C.

Three different techniques were used to impregnate the bucky papers with epoxy resin, namely simple soaking, hot compression and vacuum infiltration. For simple soaking, the bucky paper was immersed in the resin bath for 2 hr. After impregnation, the bucky paper was removed from the bath and placed between metal sheets with a Teflon spacing frame and cured in an oven at 120 ^{o}C for 3 hr.

For infusion technique, a vacuum pressure of 0.1 MPa was applied to the system to infiltrate the bucky paper with epoxy resin. A porous release film was placed below the bucky paper for demolding and a sealant tape was placed around the edge of bucky paper. The resin was placed over the bucky paper and allowed to infiltrate through the paper in the thickness direction under the vacuum. The bucky paper was then cured in an oven at 120 ^{o}C for 3 hr.

The third infiltration technique employed was compression method using a hot press. In this approach, the bucky paper was directly placed in a Teflon dam of required thickness and epoxy resin was poured onto the bucky paper. A pressure of 0.3 MPa was applied through steel plates for 2 hr at 40 ^{o}C followed by complete curing at 120 ^{o}C for 3 hr. In all cases, the final thickness of the bucky paper-epoxy composite film was approximately 200 μm containing about 10 wt% CNF loading, which was measured by weighing the bucky papers before and after resin impregnation.

2.2 Fabrication of composite laminate

CFRP composite prepregs were prepared on a lab-scale prepregger (Model 40 Research Tool Corp.) via a solventless prepregging process [6]. 3.5 mm thick laminates consisting of 12 layers of unidirectional prepregs $[0]_{12}$ were fabricated by hand lay-up. For composites with bucky paper interleaves, partially cured bucky paper was placed in the mid-plane of the laminate for the end notched flexural (ENF) test and in the central three planes for the short beam shear (SBS) test. A Teflon film of about 25 μm was placed in the mid-plane of the ENF test specimens as the starter crack. The CFRP composites with and without CNF-bucky paper interleaves were cured in a vacuum hot press (CARVER No. 4122) at 120 ^{o}C for 3 hr at a pressure of 0.4 MPa. The final thickness of the bucky paper interleaf in the fully consolidated CFRP hybrid composites was 160$\pm$20 μm.

2.3 Characterization and mechanical testing

The young's modulus of the impregnated bucky paper composites was measured with a dynamic mechanical analyser (DMA 7, Perkin Elmer). The composite films of size 20 x 3 mm were subjected to

a tensile force at a ramp rate of 0.10 N min^{-1} at room temperature. The SBS tests were conducted according to the specification, ASTM D 2453, to determine the interlaminar shear strength (ILSS) that was calculated from the maximum load and the known dimensions of the specimens. The mode-II interlaminar fracture toughness, G_{IIC}, was measured using the ENF test. G_{IIC} was determined using the direct beam theory according to the following equations:

$$G_{IIC}=\frac{9P^2a^2}{16Eb^2h^3}=\frac{9P^2Ca^2}{2b(2L^3+3a^3)}=\frac{9Pa^2\delta}{2b(2L^3+3a^3)}$$

where P is the peak load, C is the compliance, a is the crack length, and L is the half-span length. E is the flexural modulus, δ is the displacement and h is the half specimen thickness.

3. Results and discussion

3.1 Morphologies and elastic moduli of bucky paper-epoxy interleaves

The Tensile moduli of bucky paper–epoxy interleaves impregnated in three different techniques are presented in Fig. 1. In all cases, the moduli of the nanocomposites were higher than that of the neat epoxy indicating effectiveness of all three resin impregnation techniques. The vacuum infiltration technique resulted in the highest increase of about 67% in elastic modulus amongst the three, followed by an increase of 41% and 10% for hot-compression and soaking techniques, respectively. The difference in modulus precisely reflected the quality of bucky paper wetting with epoxy resin. The SEM images in Fig. 1 indicate that the impregnation by soaking method resulted in many voids throughout the composites. These voids that varied in size from sub-micrometer to a few micrometers are a consequence of poor wetting in the absence of pressure during impregnation. On the other hand, both the hot-compression and vacuum infiltration techniques exhibited high quality impregnation of bucky paper. Nevertheless, a few smaller voids were observed in the hot-compressed samples at a high magnification, indicating its less effectiveness than the vacuum infiltration method.

The comparison of experimental results with the predictions based on the Halpin-Tsai model indicates significantly lower measured modulus values. The modulus and aspect ratio of CNF were assumed to be 500 GPa and 130, respectively, for the prediction. The perfect dispersion of the fillers as well as the perfect load transfer between the fillers and resin assumed in prediction were mainly responsible for the large disparity in the comparison.

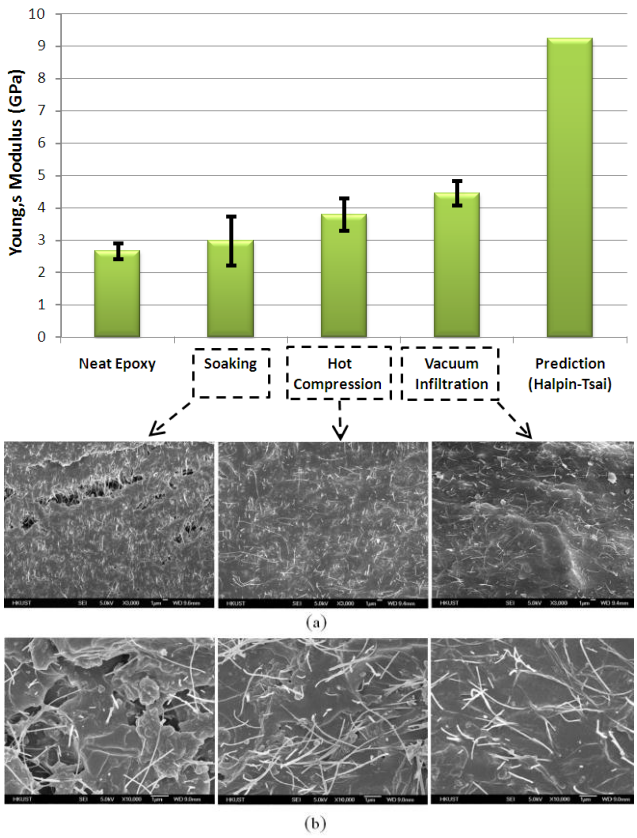

Fig. 1. Comparison of Young's moduli and the corresponding SEM micrographs at (a) low and (b) high magnifications showing the overall qualities of CNF bucky papers prepared by different impregnation techniques

3.2 Interlaminar Shear Strength

The average ILSS values of the CFRP hybrid composites are given in Fig. 2. Incorporation of CNF-interleaves was clearly beneficial and there was a significant increase of about 31% in ILSS.

To understand the mechanisms responsible for the enhancement of ILSS, the fracture surfaces of the specimens were examined by SEM, as shown in Fig. 3.The matrix in the neat CFRP composites was typically separated from the fibers, as evidenced by the clean fiber surfaces without any trace of attached

resin particles, indicating weak interfacial adhesion and debonding being a primary mode of failure in these composites. Meanwhile, the matrix material had significant plastic deformation between the separated fibers as indicated by the large shear lips. In contrast, the majority of the fiber-matrix interface in the composite containing CNFs was intact after fracture (Fig. 3a and c), indicating strong interfacial adhesion and failure mainly arising from resin cracking and deformation within the CNF rich matrix interlayer.

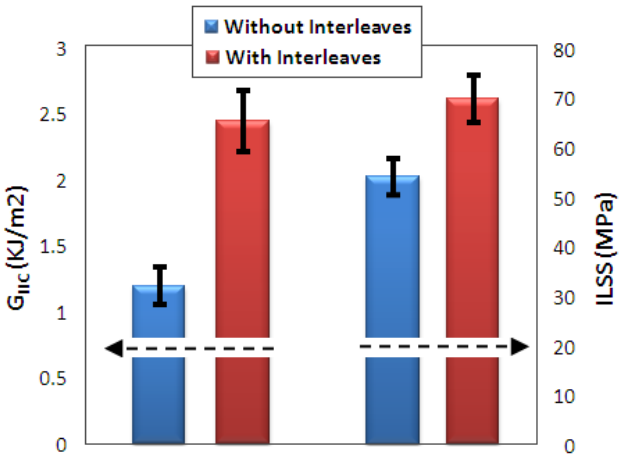

Fig. 2. Comparison of interlaminar properties of composites with and without interleaves

It is well known that the interlaminar shear strength (ILSS) of FRPs depends on both the fiber-matrix interfacial bond and the shear properties of matrix material [1]. The CNFs acted as reinforcement to the matrix rich interface and improved matrix shear properties by offering resistance to matrix cracking (Fig. 3b). The observed mechanism of crack bridging by CNFs (Fig. 3b) hindered the crack initiation and propagation, requiring a higher load for failure. It is worth noting that CNFs altered completely the morphology at interphase area around the carbon fibers, Fig. 3c and 4c. The extremely long CNFs not only reinforced the matrix near the carbon fiber, but also extended across the carbon fiber, thus effectively strengthening the interphase and interlaminar properties. In addition, the non-ionic surfactant applied to the CNT surface may have also contributed to the enhancement of the fiber-matrix interfacial adhesion, allowing a more efficient load transfer leading to increased shear strength.

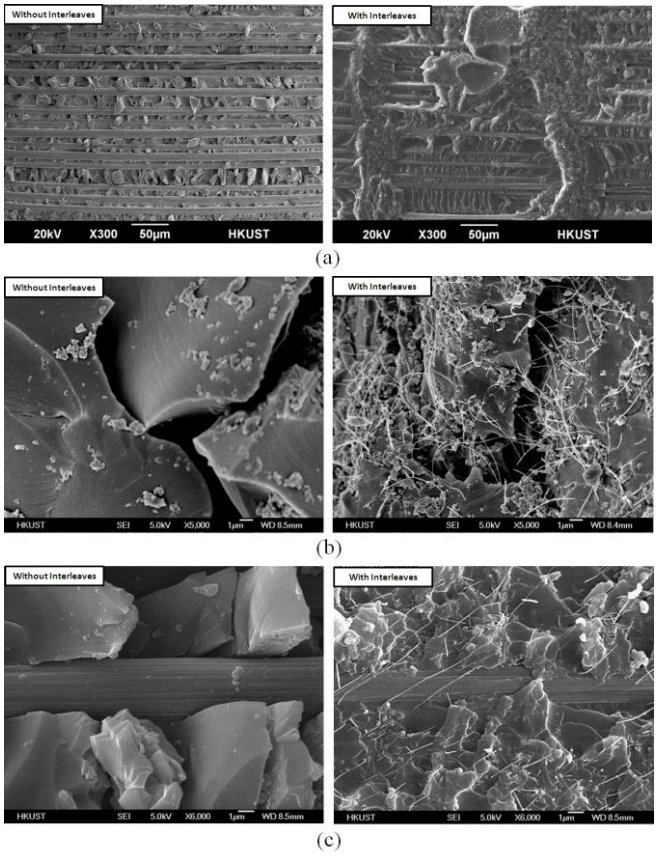

Fig. 3. SEM micrographs of the fracture surfaces of short beam shear test specimens without and with bucky paper interleaves, showing (a) global view at a low magnification, (b) matrix cracking behavior and (c) fiber/matrix interfacial region.

3.3 Mode II Interlaminar Fracture toughness

The average mode II interlaminar fracture toughness values, G_{IIC}, of the CFRP composites with and without a bucky paper interleaf are presented in Fig. 2. The incorporation of a CNF-interleaf to CFRP composites resulted in a remarkable 104% increase in G_{IIC} compared to the composite without interleaf. The fracture surfaces were examined at two different regions using SEM; Fig. 4(a) represents the crack initiation site and Fig. 4(b) the propagation site. Fig. 4(a) shows highly deformed matrix region near the crack starter film in the composite with an interleaf, suggesting higher resistance to delamination initiation. In contrast, such a deformation zone was absent in the composite without an interleaf. Closer examination of the fracture surfaces in the

propagation region, Fig. 4(c), revealed large shear lips for the neat composite, typical of epoxy based FRP composites, while the composites with a bucky paper interleaf showed entirely different morphologies. The matrix between the reinforcing fibers became coarser and rougher, evidence of higher energy absorption during fracture due to the presence of CNFs. The matrix appeared to be well bonded to the carbon fibers suggesting strong interfacial adhesion and crack propagation mainly through the matrix material within the interlayer region. Indeed, the microscale carbon fibers were surrounded by a network of nanoscale CNFs embedded in the matrix, creating multidirectional, multiscale CFRP hybrid composites. Such reinforcements may also lead to mechanical interlocking between the fibers and the matrix through CNFs [7].

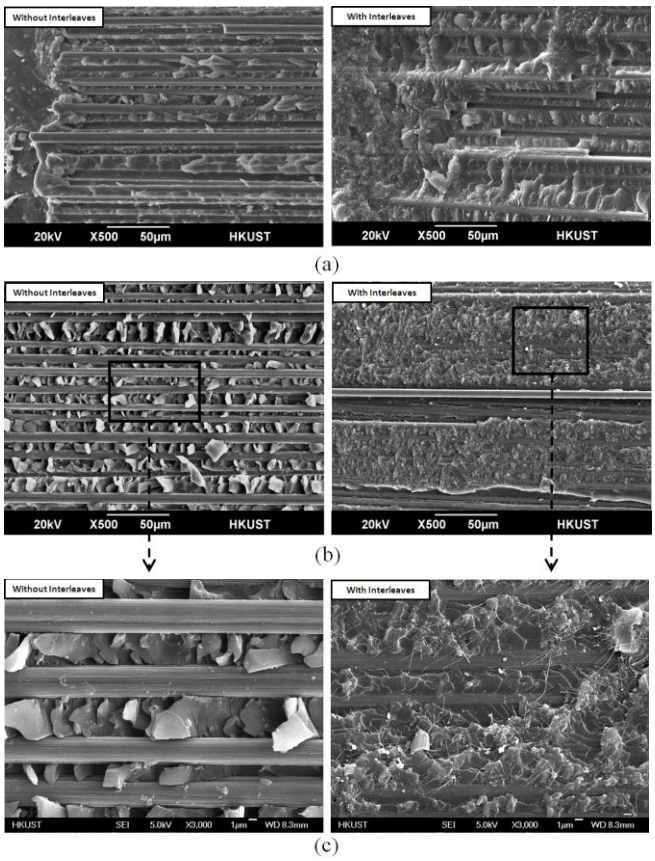

Fig. 4. SEM micrographs of the fracture surfaces of ENF test specimens without and with bucky paper interleaves, showing (a) crack initiation region , (b, c) crack propagation region taken at low and high magnifications. Crack growth from left to right.

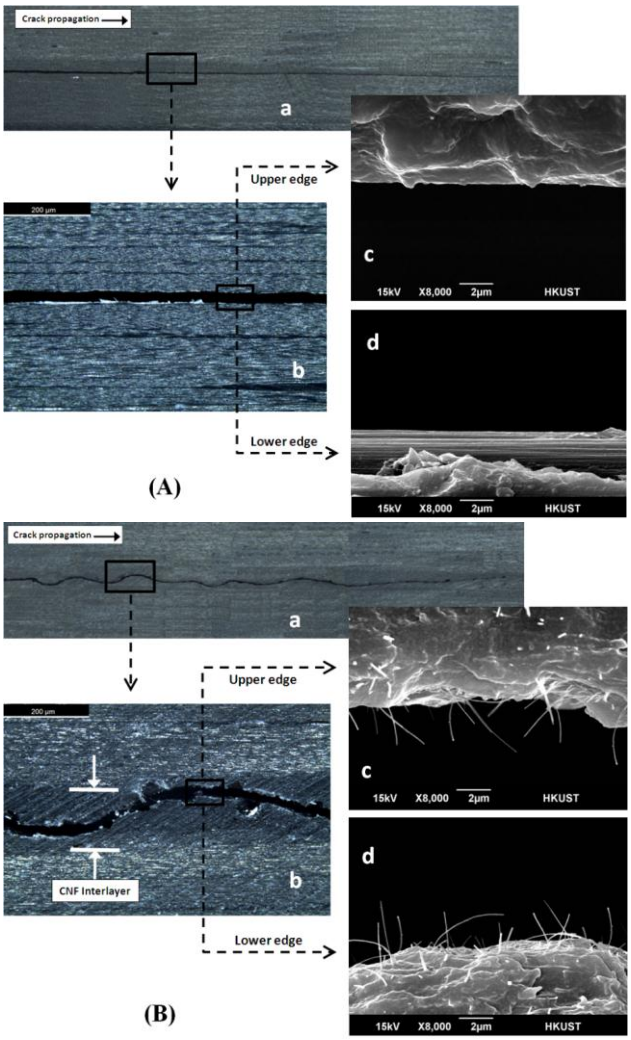

Fig. 5. OM and SEM images of crack path (edge views); (A) without interleaf (B) with interleaf. Crack growth from left to right.

A clear difference in the crack propagation pattern of the CFRP composites with and without a bucky paper interleaf was identified in Fig. 5. The cracks in the neat CFRP composite followed a straight path without deflection or kinking (Fig. 5A(a,b)), suggesting that there was no significant resistance to propagation. The images taken at a high magnification (Fig. 5A(c,d)) confirmed that cracks propagated mostly along the fiber/matrix interface in a brittle manner, typical of CFRP composites. The cracks in the CFRP composites with an interleaf propagated in a zig-zag manner showing meandering paths (Fig. 5B(a,b)). Such deflections required a higher driving force and caused a larger fracture area, and thus higher fracture toughness. The

enhanced interlaminar fracture toughness of CFRP composites containing CNTs or nanoclay was attributed to the increased fracture surface area due to crack deflection [8-9].

The images taken at a higher magnification indicate that the crack propagated within the CNF interleaf, avoiding crack growth along the boundary between the interlaminar regions, Fig. 5B(b). This observation suggests a strong adhesion between the CNF interleaf and the adjacent fiber-rich laminae. The images of the crack edges (Fig. 5B(c,d)) revealed the expected toughening mechanisms in operation. The presence of pulled out CNFs on both sides of the crack face provided direct evidence of crack bridging and eventual pulling out during fracture. Barber et al. [10] performed nanoscale pull-out tests of MWCNT/PE composites under an atomic force microscope and concluded that tougher composites may result from the increased interfacial fracture energies in CNT-polymer composites.

4. Concluding Remarks

The present study demonstrated the effectiveness of strengthening and toughening CFRP composites with CNF bucky paper interleaves. The following can be highlighted:

1. The vacuum infiltration technique resulted in the best quality of epoxy impregnation among the three methods used to impregnate the bucky papers.
2. The interlaminar shear strength of the hybrid composites containing CNF bucky paper interleaves increased by about 31% whereas the corresponding mode-II interlaminar fracture toughness by about 104% compared to the composites without interleaves.
3. The interlaminar region was reinforced by the randomly-oriented network of CNFs with improved matrix shear properties and the fiber/matrix interfacial adhesion, which were responsible for the improved ILSS.
4. CNF pullout and bridging mechanisms on the microscopic scale, as well as crack deflection and meandering on the macroscopic scale were responsible for the improved interlaminar fracture toughness.

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