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Study of composite joint strength with carbon nanotube reinforcement

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Abstract In order to strengthen the interface of a composite scarf joint, this study investigated the benefits of using locally applied carbon nanotubes to reinforce a carbon fiber composite scarf joint. The effect of carbon nanotubes on enhancing the fracture toughness and interface strength was investigated by performing Mode I and Mode II fracture tests with and without carbon nanotubes applied locally at the joint interface. Furthermore, the effects of seawater absorption and different carbon nanotube concentration values on Mode II fracture were investigated. Finally, a partial application of carbon nanotubes only near the crack tip area was considered. During the study, the image correlation technique was used to examine the fracture mechanisms altered by the introduction of carbon nanotubes. The experimental study showed that an optimal amount of carbon nanotubes could increase the fracture toughness of the composite joint interface significantly, especially for Mode II, including a physical change in the fracture mechanism.

Introduction

In recent years, large composite structures have been incorporated into naval vessels to increase operational performance while lowering the ownership costs [1]. The trend continued with new projects, such as the superstructure for DDG 1000. In particular, carbon fiber-reinforced composite material provides high strength and stiffness while maintaining low weight. The joints of these large composite structures are the weakest point due to discontinuity of fiber reinforcement so that the joints have the largest failure rate [2]. Strengthening the composite joint will increase the strength of the entire composite structure. Research has shown that varying joint geometry can increase the joint strength [3]. However, changing the joint geometry depends on the loading condition. Ship structures undergo a variety of different loading conditions. Therefore, varying the geometry is not always an ideal method of strengthening the joint. Another type of reinforcement is required. Carbon nanotubes, with high strength and stiffness, may provide a means to locally reinforce the joint while not sacrificing the integrity of the composite material.

Carbon nanotubes (CNT) are allotropes of carbons with a hexagonal lattice structure like graphite. The lattice structure forms a tube with a nano-sized diameter. CNT can be several millimeters long. They are either single-walled or multi-walled, meaning an inner cylinder lies within an outer cylinder [4]. Although many strides have been made in producing CNT, they are still quite expensive.

The elastic moduli of CNT are generally greater than 1 TPa, and CNT are 10–100 times stronger than the steels [5]. The CNT have high strength and relatively low weight which makes them a prime candidate for composite material reinforcement. Much research has been performed to document the ability of CNT to reinforce a variety of matrix materials such as polymers and ceramics [6–10]. One such study found high interfacial shear stress and stronger interfacial adhesion between multi-walled CNT (MWNT) to epoxy than epoxy to epoxy. The same study

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found no increase in tensile strength due to MWNT reinforcement [10]. Another study explored the use of several different types of carbon nanotubes in a polymer composite and found that elastic modulus was doubled as a result of the reinforcement. The same study indicated that multiwalled carbon nanotubes of a small diameter were ideal for CNT reinforcement due to their surface area characteristics [9].

Many studies have also been conducted to determine the type of bonds formed between the CNT and the epoxy [10–15]. The general conclusion is that CNT bond in three main ways: micromechanical interlocking, chemical bonding, and non-bond interactions like electrostatic and van der Waals bonding. While the CNT surface is quite smooth, it has been proposed that there are local non-uniformities in the CNT such as kinks, bends, and changes in diameter. It is at these local non-uniformities where micromechanical interlocking occurs [10]. Chemical bonding has been considered possible from a quantum mechanics prediction [12], but it is not guaranteed. Finally, non-bonding like van der Waals and electrostatics forces certainly occurs, but are relatively weak bond forms [10, 11]. One study also proposed the effects of thermal properties. The coefficient of thermal expansion of CNT is much lower than that of the polymer matrix. As a result, residual thermal stress is present after the polymer matrix hardens. This thermal stress results in closer contact between the CNT and polymer, which in turn increases micromechanical interlocking and non-bond interactions [10].

While most of the studies investigated the effects of global incorporation of carbon nanotubes within polymer materials, much less work documented the results of local reinforcement of CNT into polymeric composites. One study focused on a local CNT introduction on a composite scarf joint. Several types of CNT were tried, including various multi-walled CNT as well as bamboo structured CNT. Additionally, two different CNT concentrations were used. The study found that under compression testing, the carbon fiber composite scarf joint was stronger when locally reinforced with CNT [16].

The research presented in this article was built on the aforementioned study [16]. Widespread use of carbon nanotubes throughout a composite ship superstructure is too costly. However, local reinforcement of the structure at its weakest points is possible. The fracture toughness of the locally reinforced joint must be studied to determine the impact of reinforcement. The purpose of this research is to determine the critical energy release rate, G, and crack propagation characteristics of CNT reinforced and non-reinforced carbon fiber/vinylester composite samples for Mode I and Mode II fractures. Additionally, the effects of seawater absorption on Mode II critical energy release rate were studied. Finally, a study was conducted to determine the effects of CNT concentration and a local CNT reinforcement near the crack tip on the interface strength.

Composite sample construction

Multiple sets of carbon fiber samples were constructed during the course of this research. Each set of samples had joint interfaces with and without CNT reinforcement, respectively, so that results could be compared. The basic sample construction remained the same throughout the research. Samples consisted of carbon fiber-reinforced composite specimens with a secondary bond at the interface layer and a pre-existing edge crack, as shown in Fig. 1. The presence of the secondary bond was required to mimic the scarf joint construction. When constructing the scarf joint, one plate was constructed and cured. Then, the next plate was constructed directly on top of the previous plate and cured.

The vinylester matrix base, DERAKANE 510-A was used with TORAY T700CF carbon fiber weave. Hardening chemicals were required to cure the resin. The hardening chemicals were Methyl Ethyl Ketone Peroxide (MEKP) and Cobalt Naphthenate (CoNap). These chemicals were used in concentrations recommended by the manufacturer of DERAKANE 510-A. A hardening time of 60 min was selected to allow ample time for sample construction. With ambient temperature between 20 °C and 25 °C, the combination of hardeners consisted of 1.25 wt% MEKP and 0.20 wt% CoNap so as to achieve the desired hardening time.

The Vacuum Assisted Resin Transfer Molding (VARTM) technique was used to fabricate the composite specimens with or without CNT at the interfaces. A description of the VARTM procedure is provided below. The VARTM technique involves pulling the resin through the layers of carbon fiber with a vacuum. Samples were constructed such that a bottom carbon fiber plate, consisting of five layers of fabric, was constructed first and cured using VARTM. Then the bottom plate was sanded and cleaned with acetone. Before constructing the top plate on the already-made bottom plate, a Teflon film of thickness 0.0051 cm (0.002 in) was used as

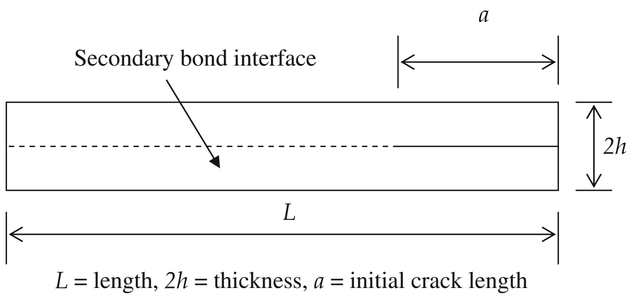

Fig. 1 Sample geometry

the initial crack insert between the top and bottom plates. Acetone was again used as the dispersing agent for applying CNT and its surface concentration was varied. After the acetone was dried, layers of carbon fiber fabric were stacked on the bottom plate and infused with resin. After curing, samples were cut using the Jet Edge waterjet cutter. Samples then underwent a post-cure treatment at 60 °C for 6 h.

There was some concern that the CNT would be displaced when pulling the resin through the layers of carbon fiber fabrics. However, the CNT remained in place. This was a significant finding, since VARTM has been a popular method for constructing carbon fiber composites in industry. No special technique is needed when applying CNT locally. The CNT can simply be dispersed on the desired area and VARTM can be conducted.

Testing for fracture toughness

Samples were tested using an Instron Tension/Compression Machine (Model Number: 4507/4500) with 10 kN load cell. Series IX computer software was used to control displacement and record displacement and load values. All tests were performed at the rate of 2.54 mm displacement per minute. Additionally, a Digital Image Correlation (DIC) system was employed to record images during testing at the rate of one image per second. The DIC System was also used to measure strain fields around the crack during the crack initiation and growth.

The applicable ASTM Standard was followed for Mode I testing. Mode I testing consisted of a Double Cantilever Beam (DCB) test as shown in Fig. 2 [17]. Piano hinges, used to apply the load, were attached to each sample using a commercially available two-part epoxy. The following equation was used to determine critical energy release rate, G_{Ic}, through the modified beam theory method [17]:

$$G_{\mathrm{Ic}} = \frac{3P\delta}{2b(a + |\Delta|)} \tag{1}$$

where P is the load when the crack propagates, δ is the point displacement, b is the sample width, a is the crack length, and Δ is the horizontal axis intercept from a versus $C^{1/3}$ curve. Here C is the compliance of the DCB.

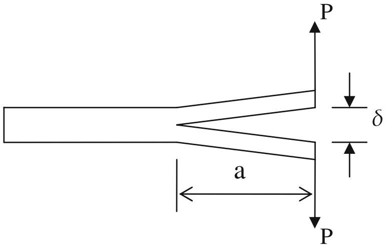

Fig. 2 Double cantilever beam test for Mode I (i.e., crack opening) fracture

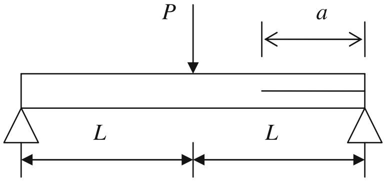

Fig. 3 Three point bending test for Mode II (i.e., shearing mode) fracture

No applicable ASTM Standard exists for pure Mode II fracture toughness testing. Mode II testing consisted of a three point bending test as shown in Fig. 3. Because the crack lies in the midplane of the beam, only shear stress was applied to the crack. The following equation was used to determine Mode II critical energy release rate, G_{IIc} [18]:

$$G_{\mathrm{IIc}} = \frac{9P^2a^2C}{2b(2L^3 + 3a^3)} \tag{2}$$

where P is the critical load when the crack propagates, C is compliance, a is the initial crack length, b is the sample width, and L is a half of the span length.

In order to test the effects of seawater absorption on local CNT reinforcement and fracture toughness, samples were soaked in seawater until saturation and then tested in Mode II. Seawater was mixed using substrate conforming to ASTM Standard D1141-98 and samples were soaked at room temperature, nominally at 20 °C [19]. Dimensions and weight of each sample were recorded prior to soak. Seawater absorption was tracked by periodically weighing each sample during soaking. When weight no longer changed significantly, the samples were determined to be saturated and Mode II testing was conducted as described previously.

Results and discussion

Crack opening mode (i.e., Mode I) test results showed a modest improvement in the critical energy release rate G_{Ic} when the joint interface was reinforced with CNT. Figure 4 compares the average values of normalized G_{Ic} for resin only samples (i.e., without CNT reinforcement) and CNT reinforced samples. Standard deviation is also shown in the figure. Unless otherwise mentioned, 5–7 samples were tested repeatedly for the average value and standard deviation. The average G_{Ic} value increased about 10% with CNT reinforcement. However, the characteristics for Mode I crack propagation were observed with no discernable difference between the CNT reinforced and non-reinforced samples. The DIC System was used to observe the crack

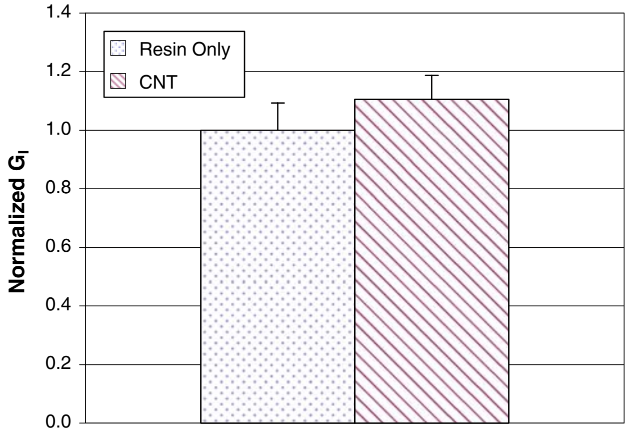

Fig. 4 Normalized G_{Ic} values for Mode I

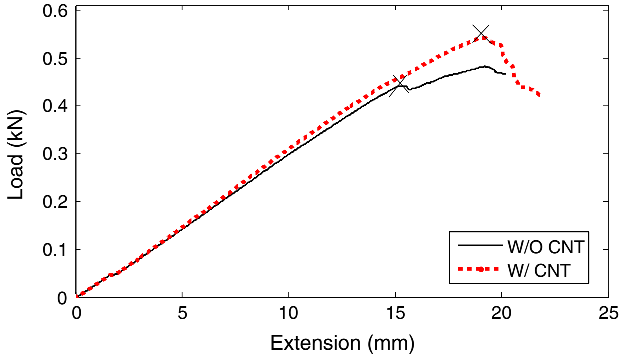

Fig. 6 Representative load versus extension plot for Mode II testing of non-reinforced sample and CNT reinforced sample (The points of crack propagation are marked with an X)

growth in both the CNT reinforced and non-reinforced specimens and their images were very similar.

After testing, the samples were fully broken to inspect the cracked surface. Mode I samples revealed little difference between CNT reinforced and non-reinforced samples. Both CNT reinforced and non-reinforced samples had crack growth through the resin layers where the initial cracks were located.

Mode II (i.e., shearing mode) testing resulted in a significant increase in the critical energy release rate G_{IIc} for the samples reinforced with CNT. Figure 5 shows the normalized average values of G_{IIc} for the specimens. Again, standard deviation is also shown in the figure. As shown by the standard deviation, the lowest CNT reinforced value is higher than the highest non-reinforced value. The average G_{IIc} value for CNT reinforced samples was 32% higher than the average G_{IIc} value for non-reinforced samples.

The G_{IIc} values were computed from the compliance of the load versus displacement curves. Representative plots of load–displacement are shown in Fig. 6. The point of crack propagation is marked with an X. As shown in the figure, the CNT reinforced sample increased the crack propagation load when compared to that of the non-reinforced sample.

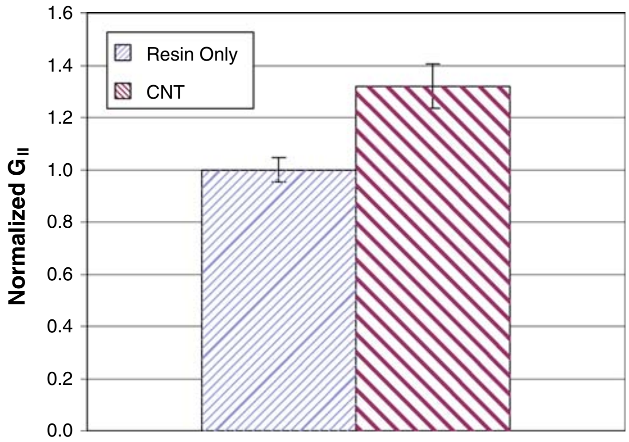

Fig. 5 Mode II normalized G_{IIc} values

Qualitatively, the observed crack propagation for Mode II was significantly different between the CNT reinforced and non-reinforced samples. For the non-reinforced samples, crack propagation began at the tip of the initial crack and went through the interface resin material. However, for CNT reinforced samples, a crack began to nucleate away from the initial crack tip, perhaps in an area of lower CNT concentration, i.e., a weaker strength zone. Eventually, this newly formed crack grew to connect to the initial crack. This result was widely observed in the CNT reinforced samples. Representative images from the DIC system are shown in Fig. 7. Without CNT reinforcement at the joint interface, the initial crack propagated through the interface all the way as shown in Fig. 7a. On the other hand, CNT reinforcement resulted in a tougher joint interface so that the crack path deviated away from the joint interface as seen in Fig. 7b.

After testing, the samples were fully broken to inspect the cracked surface. All non-reinforced samples had a clear fracture through their secondary bonding layers. For some of them, the joint interface bond was broken through the resin, while in others the bonding failed between the resin and fiber interface. However, the CNT reinforced samples failed much differently. The CNT reinforced the resin at the bonding interface, making it stronger. The CNT themselves did not fracture. The CNT were bonded to the resin, blocking crack propagation. As a result, the crack propagated by breaking neighboring fiber bundles of the bonding interfaces and at times through a different layer than the initial crack layer. The critical energy release rate for CNT reinforced samples became higher because the crack propagated through the carbon fibers vice resin interface. Figure 8 shows the fractured surfaces with and

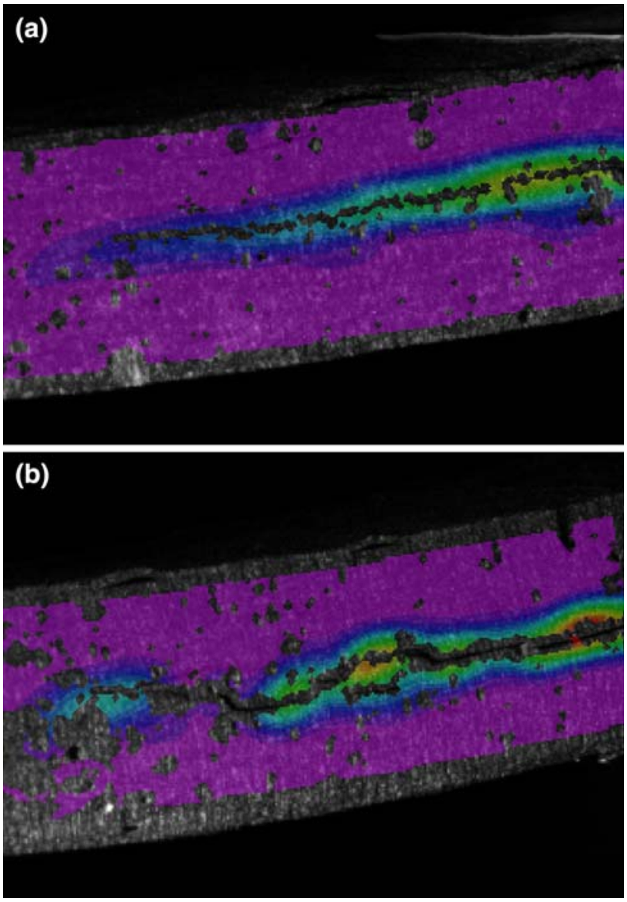

Fig. 7 Images of crack growth: **a** Without CNT reinforcement, the crack propagated through the joint interface plane. **b** With CNT reinforcement, the crack path showed deviation away from the joint interface

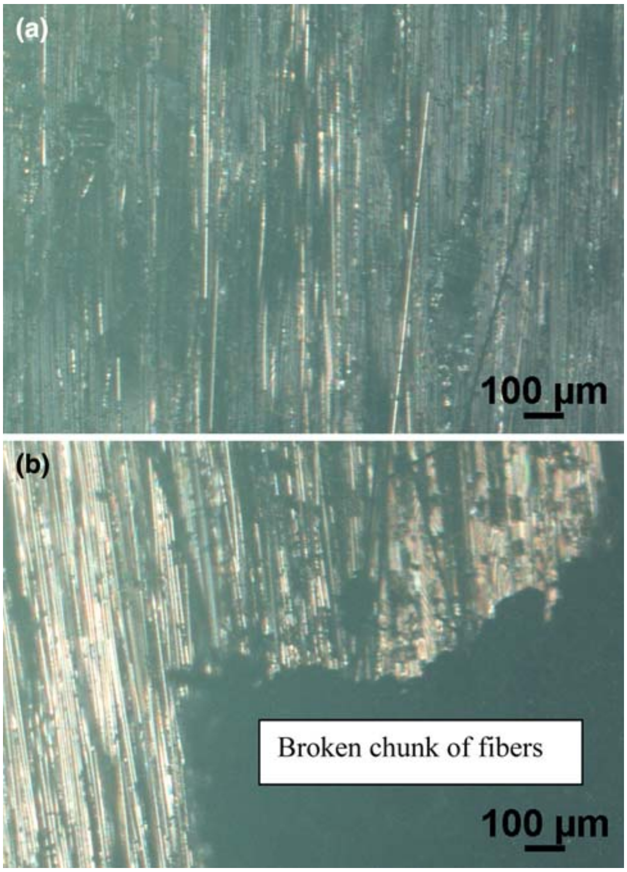

Fig. 8 Optical microscopy pictures of fractured surfaces without (**a**) and with (**b**) CNT reinforcements at the interface

without CNT reinforcement, which were obtained using an optical microscope. The fractured interface without CNT has a very clean surface as shown in Fig. 8a where all fibers are aligned well without interruption. On the other hand, Fig. 8b shows a broken chunk of fibers with CNT reinforcement, which was stuck to the other side of the bonding interface.

CNT reinforcement was more significant for Mode II fracture than for Mode I. A possible explanation is given below for the application of CNT as an interface bond. The CNT is not believed to have a strong chemical bonding with the resin material. Instead, CNT are considered to have a mechanical interlocking with possible local non-uniformity of CNT as described in Ref. [10]. Such a mechanical interlocking is more effective in resisting the shearing force of Mode II than the normal force of Mode I. Therefore, the fracture toughness of Mode II becomes much higher with CNT reinforcement.

Composite samples were also tested to determine the effect of seawater absorption on Mode II critical energy release rate. Weight of each sample was tracked periodically during soaking in seawater at the room temperature. The average weight changes of CNT reinforced and non-reinforced samples are plotted in Fig. 9. The samples were deemed saturated when no significant weight change occurred. In this case, the samples were tested after 91 days of soaking. Samples were removed from the seawater, patted dry, and tested. It should be noted that the

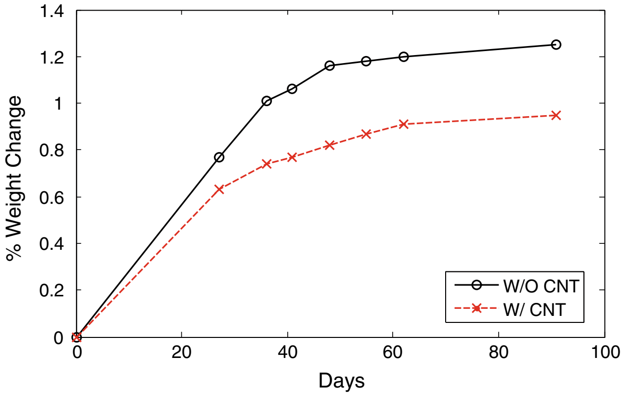

Fig. 9 Weight change of samples caused by seawater absorption as a function of soaking days

CNT reinforced samples absorbed slightly less seawater, resulting in a smaller percentage weight change.

The results of moisture effect testing showed that there was little difference between the seawater soaked and dry specimens for the interface strength regardless of CNT reinforced or not. In other words, both dry and wet specimens had almost the same fracture toughness for the CNT reinforced specimens. For non-reinforced cases, dry samples had slightly higher strength than the wet samples. As a result, the Mode II energy release rate for wet specimens was 36% higher for the CNT reinforced specimens than non-reinforced ones. This data indicated that soaking the carbon fiber composite samples in seawater had a minimum effect on Mode II interface fracture toughness. This result qualitatively agrees with that in Ref. [18]. In that study, a carbon/epoxy composite, T000H/3631, showed less than 8% decrease in the fracture toughness with a little over 2% weight increase from an 80 °C wet condition. The present samples had a lower weight change and were under a lower temperature. As a result, the effect of moisture was less than that in Ref. [18].

The main purpose of the last set of testing was to determine the effect of the surface concentration of CNT, i.e., the mass of CNT per unit CNT reinforced surface area of interface. To achieve this goal, three concentrations of CNT were used: 5, 7.5, and 10 g/m^2. As with all sample sets, non-reinforced samples were constructed and tested as a reference point. Mode II testing was completed since prior phases determined CNT reinforcement significantly affected Mode II fracture toughness. The results of Mode II testing are shown in Fig. 10 along with the standard deviation. As shown, 7.5 g/m^2 of CNT was the best concentration among the three choices, which is consistent with the previous study on compressive strength improvements with CNT reinforcement [16]. Again, the lowest value of G_{IIc} for samples reinforced with 7.5 g/m^2 CNT was higher than the highest value of non-reinforced samples.

The higher concentration of 10 g/m^2 resulted in slightly lower critical energy release rate than the 7.5 g/m^2 concentration. On the other hand, interface toughness with the CNT concentration of 5 g/m^2 was even lower than that of non-reinforced specimens. This result suggested that a lower amount of CNT at the interface did not provide proper mechanical interlocking while serving as a localized defect because of a lower bonding between CNT and polymers. More elegant studies are needed to investigate the relationship between CNT dispersion/alignment and the interface fracture toughness. In the present study, there was no effort to control the alignment of CNT. Therefore, they were expected to be randomly orientated with certainly not a perfectly uniform dispersion.

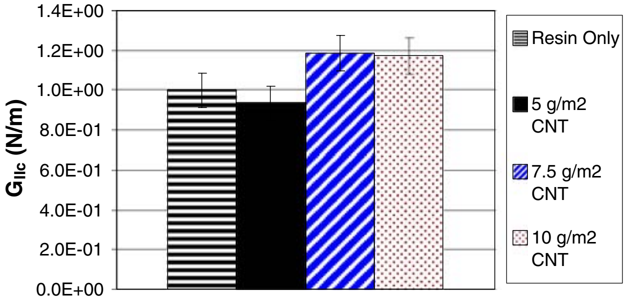

Fig. 10 Normalized G_{IIc} values for different concentration of CNT

The secondary purpose of the last set of testing was to determine the effect of "banding" CNT. "Banding" refers to only reinforcing a part of the interface area on the sample. All other sample sets involved using CNT to reinforce the entire secondary bond between the top and bottom plates. However, samples for the present tests were only reinforced in the area extending 6 cm from the initial crack tip. "Banding" CNT may be applicable to repair of carbon fiber composite components when only a localized area requires reinforcement. The Mode II critical energy release rate resulted in 19% increase due to CNT reinforcement with 7.5 g/m^2 CNT concentration. The drop from roughly 30% found in previous sample sets was due to "banding" the CNT vice reinforcing the entire secondary bond.

Conclusions

Interface critical energy release rates and crack propagation characteristics of pre-existing cracks were studied in carbon fiber composite samples with and without CNT reinforcement at their secondary bonding interfaces. Mode I (i.e., opening mode) and Mode II (i.e., shearing mode) crack propagation were studied. Mode I testing determined a modest significant increase in G_{Ic} due to CNT reinforcement. No difference in crack propagation behavior was observed. However, Mode II testing indicated a significant increase in G_{IIc} due to CNT reinforcement. Additionally, two qualitative differences were noted during Mode II testing as stated below:

1. CNT reinforced samples displayed crack nucleation and growth away from the initially existing crack tip. As load increased, these cracks propagated to meet the existing initial crack. For non-reinforced samples, crack propagation occurred from the existing initial crack tip.
2. Crack propagation occurred across the fibers deviated from the original interface in CNT reinforced samples. Conversely, crack propagation in non-reinforced samples occurred along the original interface with resin failure.

Additional research was conducted to determine the effect of seawater absorption and to optimize the concentration of CNT. Seawater absorption was found to have a minimal effect on Mode II fracture toughness. The optimal concentration of CNT was found to be 7.5 g/m^2. Applying CNT to a part of the joint interface area was also proved to be effective. Finally, the VARTM technique was implemented to ensure local CNT reinforcement was feasible using current manufacturing practices. It was determined that the dispersed CNT remained in place while the carbon fiber layers were infused with resin.

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