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# Enhanced Fracture Properties of Carbon Reinforced Composites by the Addition of Multi-Wall Carbon Nanotubes

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**ABSTRACT:** In the present study, the fracture energy of hybrid carbon fiber reinforced polymers was investigated. The composites were modified by the addition of multi-walled carbon nanotubes into the matrix material. The interlaminar fracture properties under Mode I and Mode II remote loading were studied as a function of the carbon nanotube content in the matrix. With the addition of carbon nanotubes in the epoxy matrix, a significant increase in the load bearing ability as well as in the fracture energy was observed, for both Mode I and Mode II tests. It is speculated that carbon nanotubes due to their large aspect ratio have a significant toughening effect since extra energy is needed in order to pull them out from the matrix and start the crack propagation following a kinking out pattern at nanoscale.

**KEY WORDS:** carbon nanotubes, fracture toughness, Mode I, Mode II, carbon fibers.

## INTRODUCTION

**P**OLYMER MATRIX COMPOSITES are extensively used in structural applications. Their combination of high stiffness and strength and low density makes them attractive materials for all transport modes on land, in the air and at sea. The structural performance of a fiber-reinforced composite depends on the fracture resistance to various modes of crack propagation. Since a critical design criterion for fiber composites is sufficient fracture energy absorption capability, there have been a number of attempts to improve the fracture toughness. These include the use of various methods, e.g., interleaving, hybridization, stitching, short-fibers and z-pinning [1,2]. Nowadays, nano-scaled fillers such as carbon nanotubes (CNT) and carbon nanofibers (CNF) offer new possibilities

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towards this direction. Taking into consideration their high axial Young's modulus, high aspect ratio, large surface area, and excellent thermal and electrical properties [3,4] these fillers can be used as modifiers for the polymer matrices of the carbon fiber reinforced polymers (CFRPs) leading to advanced mechanical behavior. Improving the fracture behavior of a CFRP has also other positive side-effects, e.g., increased fatigue life and better impact performance. Previous work by the authors [5,6] has demonstrated dramatic increase on Young's modulus and fracture energy in Mode I, of CFRP laminates by the incorporation of CNFs in the epoxy matrix.

Apart from the well-known graphite, carbon can build closed and open cages with honeycomb atomic arrangement. First such structure to be discovered was the C<sub>60</sub> molecule by Kroto et al. [7]. Although various carbon cages were studied, it was only in 1991, when Iijima [8] observed for the first time tubular carbon structures. The nanotubes consisted of up to several tens of graphitic shells (known as multi-walled carbon nanotubes (MWNTs)) with adjacent shell separation of 0.34 nm, diameters of 1 nm and large length/diameter ratio. Carbon nanotubes can be visualized as a sheet of graphite that has been rolled into a tube. Two years later, Iijima and Ichihashi [9] and Bethune et al. [10] synthesized single-walled carbon nanotubes (SWNTs). All the types of CNTs are produced mainly by three techniques: arc-discharge, laser-ablation, and catalytic growth.

This study was directed towards the systematic investigation of the influence of MWNTs on the fracture behavior of unidirectional CFRPs. The nanotubes were incorporated in the epoxy matrix of the laminates in various concentrations. Mode I and Mode II tests were carried out and the fracture energy as a function of the MWNT content was evaluated.

## EXPERIMENTAL

MWCNTs produced by catalyzed CVD, were supplied by ARKEMA, France. Their diameters were 10–15 nm and they were more than 500 nm long. The nanotubes were used as received, i.e., no treatment or functionalization took place. In order to eliminate any present humidity the nanotubes were placed in an oven overnight prior to use. The epoxy system used for the fabrication of CNT doped resins was the Araldite LY564/Aradur HY2954 from Huntsman Advanced Materials, Switzerland. The dispersion of the MWCNTs in the epoxy took place in a torus-mill device (VMA Getzmann GmbH). The torus-mill introduces high shear forces by a high-speed rotating disk and reduces the nanoparticle agglomerates due to the milling effect generated by zirconium dioxide beads. The beads have a diameter of 1.2–1.7 mm and cause strong shear action and collision effects. The dissolver-disk provides additional shear forces and maintains the vortex flow. The compound is stirred in a vacuum container to avoid air inclusion. The vortex flow achieved by the geometry of the disk leads to continuous mixing of the compound. During processing, temperature, rotational frequency, energy input and time are controlled and recorded for reproducible test conditions. The mixing speed was 2000 rpm for 6 h. Doped resin compounds with three different MWCNT contents of 0.1, 0.5, and 1 wt%, respectively, were produced. The manufacturing of CFRPs with the above resins as matrix material was the next step. The carbon fiber (CF) laminas were chosen to be unidirectional (UD) by HEXCEL, France with weight of 160 g/m<sup>2</sup>. Each panel had 16 plies of carbon fibers and was hand laid-up and then processed in an autoclave, using the vacuum bag technique. A 50 mm wide and 13  $\mu$ m thick PTFE film was added in the middle plane in order to generate the starter crack. The curing cycle was 1 h at 80°C and 8 h at 140°C.

Fracture toughness experiments were performed at an MTS 858 testing machine. The Mode I interlaminar fracture toughness was measured using the double cantilever beam (DCB) method according to the ASTM standard (D5528-94a). The specimens were approximately 25 mm wide and 250 mm long. The edges of the specimens were painted in white and scaled in order to enable the observation of the crack growth. The fracture specimens were pulled apart in tension with a rate of 2 mm/min until the crack was propagating to about 120 mm. The Mode II interlaminar fracture toughness was measured using the three-point end-notched flexure (3ENF) method [11,12]. The test-pieces were 140 mm long and 20 mm wide. The overall starter film length was 50 mm and the initial crack length  $\alpha$ , was around 25 mm. Before the tests, the crack was carefully wedged open and extended about 2 mm beyond the insert in order to achieve a natural starter crack [13]. The distance between the supports (span length) was 100 mm and the rate of the cross-head was 2 mm/min. For all the fracture tests performed, at least six specimens were tested. The volume fraction was measured using a light microscope and Image J software on polished cross-sections and the values can be seen in Table 1. The same analysis showed that no voids were present.

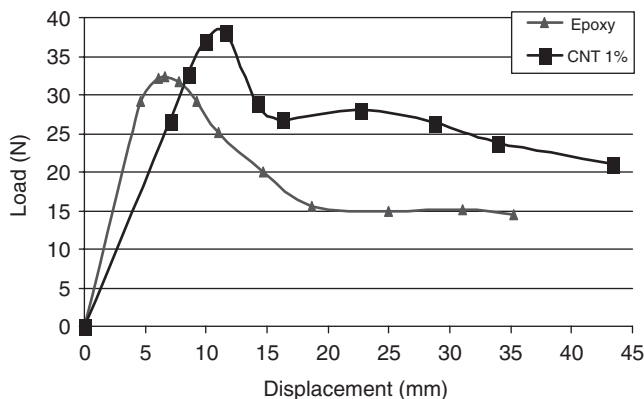
## RESULTS AND DISCUSSION

### Mode I Results

Figure 1 shows typical load–displacement curves during Mode I loading for neat epoxy and CNT doped matrix CFRP. The maximum load,  $P_{max}$ , is significantly

**Table 1. Summary of the volume fraction of the composite panels manufactured.**

Composite	Volume fraction (%)
Epoxy	56.82
1% CNT	55.51
0.5% CNT	55.38
0.1% CNT	56.69



**Figure 1.** Load vs. Displacement for (a) CFRP with neat epoxy matrix and (b) CFRP with epoxy matrix doped with 1 wt% MWCNTs.

increased in the case where the EP matrix is doped with 1 wt% CNTs. The fracture energy of the CFRPs was calculated using the modified beam theory (MBT) in accordance with:

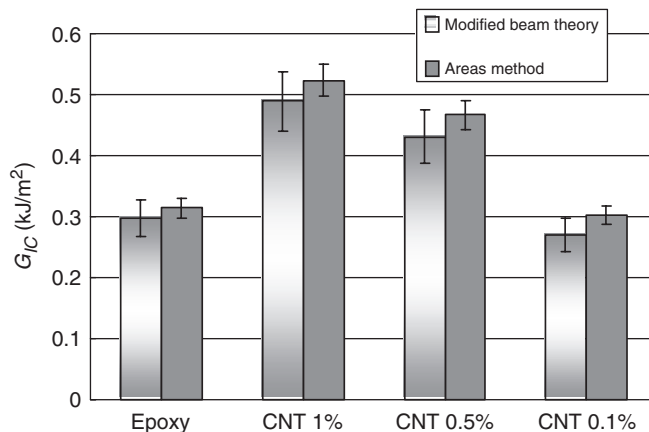
$$G_{IC} = \frac{3P_c \delta_c}{2Ba_c} \quad (1)$$

where,  $P_c$ ,  $\delta_c$ , and  $a_c$  are the critical applied load, displacement, and crack length, respectively [14,15]. Additionally the Areas method was used for determining the fracture energy using:

$$G_{IC} = \frac{\Delta A}{B\Delta a} \quad (2)$$

where,  $\Delta A$  is the area enclosed under the load–displacement curve [14,15]. The calculated values are compared in Figure 2.

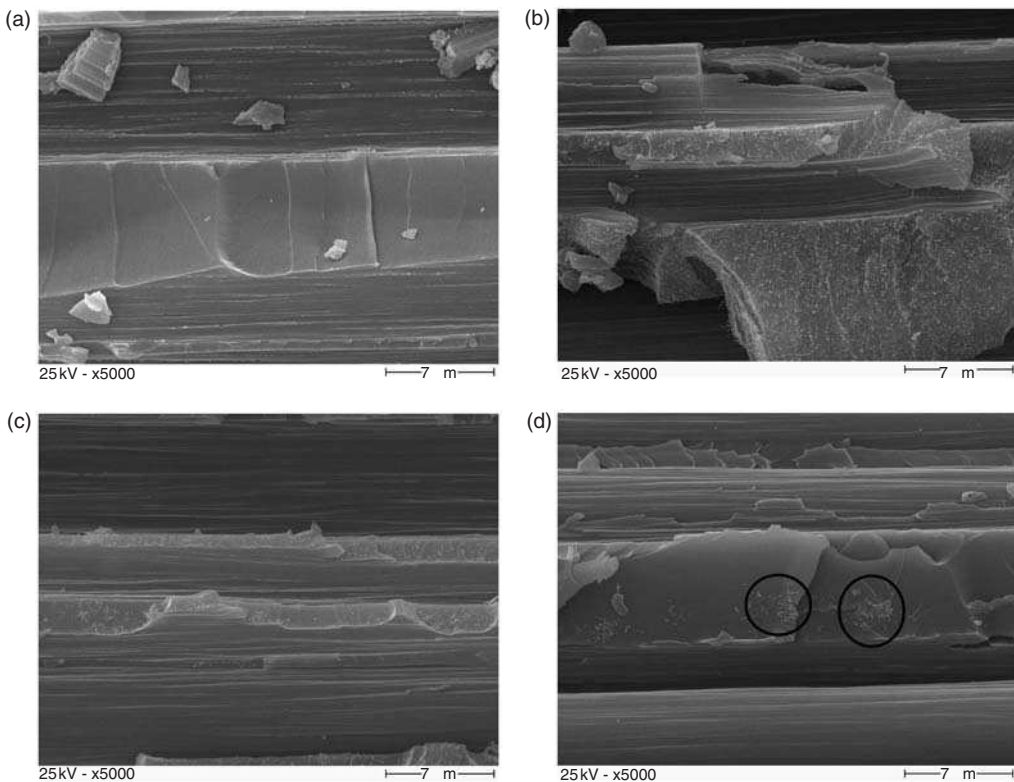
The doped CFRPs not only showed an increase in the load bear but also a significant increase in the fracture energy,  $G_{IC}$ , compared to the reference neat epoxy matrix. More specifically the increase in  $G_{IC}$  was of a magnitude of 60% for the specimens containing 1% MWCNT., The above behavior may be explained due to significantly large aspect ratio of CNTs which allows them to act as nano-bridges between the notch edges. Extra energy is needed in order to pull them out from the matrix or break them and then initiate the crack propagation [16]. Scanning electron micrographs (SEM) of the fractured surfaces of neat epoxy and 1% MWCNT can be seen in Figure 3(a–c), respectively. In the latter figure the distinctive pull-out of the CNTs during the fracture phenomenon is obvious. As it is known from the literature [14] Mode I delamination resistance is clearly a matrix-dominated parameter. For this reason one area of great research interest is to produce tougher or more ductile matrix resins. It is anticipated that the enhancement in the matrix fracture toughness can lead to an overall advanced fracture behavior. The degree of interfacial adhesion between nanotubes and polymers is a key parameter in both the production and physical properties of carbon nanotube



**Figure 2.** Mode I fracture energy of the different panels (calculated with two different methods).

composites, and is vital in understanding the surface behavior of nano-composites. Adequate interfacial stress transfer from the matrix to the reinforcement is only possible when the interface has not failed during composite loading. Failure of the interface effectively neutralizes the efficiency of the reinforcement.

On the other hand the incorporation of 0.1% CNTs led to a slight reduction of the  $G_{IC}$  value (Figure 3d). A similar tendency was also observed for the composite modulus as shown in Table 2. Tensile tests were performed on specimens cut from each of the manufactured panel according to the ASTM D-3039 standard and were performed for consistency. Moreover the value  $E$  of Young's modulus was needed for the Mode II calculations. The above can be explained due to the small amount of MWCNTs. For small addition of nanotubes the viscosity of the resin remains to very low levels leading successively to low shear during stirring. As a consequence, the CNT agglomerations were not subject to high shear forces and therefore it was not possible to break them and achieve an even CNT dispersion, resulting in a material with agglomerations (acting as defects in the matrix) and thus low mechanical properties.



**Figure 3.** (a) SEM picture of neat epoxy sample fractured under Mode I loading, (b) SEM picture of 1% MWCNT fractured sample under Mode I loading. Evidence of good dispersion can be seen. The intensive carbon nanotube pull-out and breakage, which contributed to higher  $G_{IC}$  values, is apparent, (c) SEM picture of 0.5% MWCNT sample fractured under Mode I loading. Evidence of no agglomerations present can be seen. The difference of the amount of CNTs being pulled-out is more than obvious, (d) SEM picture of 0.1% MWCNT sample fractured under Mode I loading. Agglomerations are present and indicated with the black circles. The lack of dispersion can be seen if directly compared with (b) and (c).

**Table 2. Summary of the Young's Modulus of the tested CFRPs according to ASTM D-3039 standard.**

Composite	Young's modulus (GPa)
Epoxy	121.85
1% CNT	128.85
0.5% CNT	127.6
0.1% CNT	121.15

## Mode II Results

Figure 4 shows the Mode II fracture energy for each CFRP calculated with two methods. By using the elastic beam theory an expression for the strain energy release rate can be derived [14,15]:

$$G_{IIC} = \frac{9P^2 C \alpha^2}{2B(2L^3 + 3\alpha^3)} \quad (3)$$

where  $P$  is the applied load at the midspan,  $C$  is the compliance,  $\alpha$  is the crack length,  $B$  is the specimen width, and  $L$  is the span length (length between central loading pin and the outer support pins).

The compliance may be calculated from the following formula, based on the beam theory [14,15]:

$$C = \frac{2L^3 + 3\alpha^3}{8EBh^3} \quad (4)$$

where  $E = E_{11}$  the modulus in the fiber direction,  $\alpha$  is the crack length,  $B$  is the specimen width and,  $L$  is the span length. Additionally the Areas method was used for determining the fracture energy using Equation (2).

It can be seen that the panels doped with 0.5% and 1% CNT exhibit higher  $G_{IIC}$  when compared to the panel with neat epoxy matrix. The increase is of about 75 and 45%, respectively. The above can be attributed to the various energy absorbing mechanisms involved by the presence of CNTs during the fracture tests. The CNTs need extra energy in order to be broken and to be pulled-out and, that extra energy contributes to the higher  $G_{IIC}$  values [17]. It has been noted that the influence of such fillers has also been extended to the reinforcing fibers by making more CFs to be involved during the delamination process and thus increasing the fracture toughness [18]. Another interesting observation is that a higher increase in  $G_{IIC}$  is achieved with 0.5% CNT compared to the laminate doped with 1% CNT., It is speculated that the higher amount of CNTs may affect the interface between the EP matrix and the CFs, which according to the literature controls the Mode II failure. The short CNTs also tend to move away the stress concentration from the crack tip helping in this manner the CFRP to withstand higher loading before fracture [19]. Similar results have been observed by Barber et al. [20] who performed nano-scaled pull-out tests on MWCNTs/PE polymer using atomic force microscope and concluded that tougher composites may result from the increased interfacial fracture energies observed when nanotubes are used as a reinforcing phase. In the case of Mode II fracture the

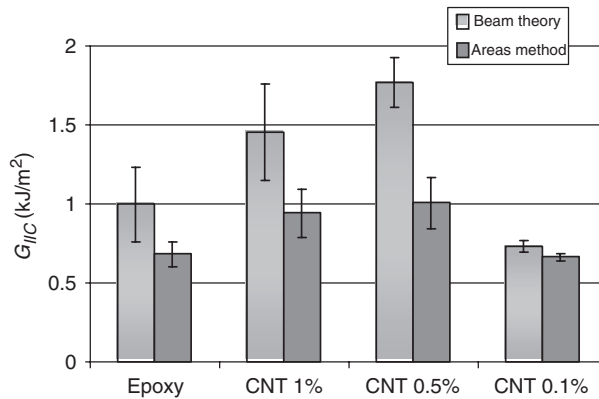


Figure 4. Mode II fracture energy of the different CFRP panels.

incorporation of 0.1% CNTs led to a reduction of the  $G_{IIC}$  value. The above can be explained in the same manner as in the interpretation of the Mode I results.

## CONCLUSIONS

Carbon nanotubes are envisaged to be ideal reinforcements for polymers due to their high aspect ratios and exceptionally superior mechanical properties. As a result, CNT–polymer composites possess the potential to be the next generation structural materials. The aim of the authors was to investigate the reinforcing effect of the CNTs into an actual carbon reinforced composite panel. The present study dealt with the use of MWCNTs as dopants for the epoxy matrix of unidirectional CFRP laminates. Three different CNT contents were used (0.1, 0.5, and 1 wt%) and compared to the neat epoxy. The matrix mixtures were prepared with the aid of a high shear mixing device (torus-mill). The effect of these nano-fillers on the fracture behavior was thoroughly investigated. In Mode I the presence of CNTs, even at low contents of 1 wt%, led to a significant increase in the fracture energy of the laminates (about 60%). This trend is closely connected to fiber bridging and fiber pull-out phenomena, confirmed by SEM investigation, which require extra energy, additional to that needed for crack initiation and propagation within the material. Additionally, the Mode II fracture behavior of the laminates was examined and an increase was noted in fracture energy of the CFRPs doped with 0.5% and 1% CNTs (about 45% and 75%, respectively). Nevertheless, the incorporation of 0.1% CNTs led to a slight decrease in the fracture properties due to the low viscosities of these mixtures (non suitable for high shear methods) and thus, the presence of agglomerations (clusters).

Wichmann et al. [21] investigated the effect of MWCNTs on the interlaminar shear strength of nano-modified glass fiber composites manufactured by RTM. A significant improvement (+16%) was noted by adding only 0.3 wt% of CNTs. On the other hand the fracture toughness tests showed no significant improvement on the interlaminar toughness  $G_{IC}$  and  $G_{IIC}$  compared with the reference material leading to the conclusion that the influence of nanoparticles on the fiber/matrix interface has to be thoroughly studied since is the key property. A further enhancement of the compatibility to the composite material could be achieved by chemical functionalization of the carbon nanotube surface, through covalent or ionic bonds to the polymeric matrix. These bonds enable a stress transfer

between the polymer and the CNTs that leads to improved interfacial interactions as qualitatively determined previously [22]. Moreover functionalized CNTs may achieve better dispersion and higher interfacial properties, e.g., Ganguli et al. [23] achieved an increase of 80% in the fracture toughness has been achieved at 0.15 wt% loading in the acid-treated MWCNT nano-composites. Another issue with processing of the composites is the inability to align the nanotubes in the epoxy. Ideally, the nanotube should be aligned along the direction of maximum loading, where the probability of failure is maximum. In case of random alignment of the tubes, most of the nanotubes are not in the direction of loading and act as defects in the composite instead of enhancing the mechanical strength; this results in degradation of the composite performance [24]. Zhu et al. [25] along the same lines exploited the possibility of over-coating glass fiber weaves with SWCNTs during a VARTM process of glass fiber vinyl ester composite. A maximum of 45% increase in shear strength over control sample was observed on several types of nanotubes with a very small amount of nanotubes (0.015 wt%) coated in the middle plane only. Similar investigation was done by Zhou et al. [26] investigating the effect of 0.3 wt% MWCNTs on the flexural properties of carbon/epoxy composites. An improvement was observed for the flexural modulus. The experimental data were then compared with Weibull models and showed a good agreement.

More to the point is that most of the recent literature has investigated various resin infusion or transfer molding techniques in order to incorporate CNTs into a fiber reinforced composite panel and usually the flexure properties are studied. The current work has proved that it is feasible to pass the reinforcing effect of the CNTs from a polymer into a carbon fiber reinforced panel using typical hand lay-up and autoclave manufacturing techniques. As a consequence it is expected that the improvements on the fracture toughness will also have a positive side effect on the fatigue and impact properties and therefore further investigation on the aforementioned properties will be conducted.

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