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An investigation of Mode I and Mode II fracture toughness enhancement using aligned carbon nanotubes forests at the crack interface

Brian G. Falzon*

Queen's University Belfast, School of Mechanical and Aerospace Engineering, Belfast, BT9 5AH, UK.

Stephen C. Hawkins, Chi P. Huynh

CSIRO Materials Science and Engineering, Clayton, VIC, 3168, Australia

Racim Radjef & Callum Brown

Monash University, Department of Mechanical and Aerospace Engineering, Clayton, VIC, 3800, Australia

Abstract

A novel approach for introducing aligned multi-walled carbon nanotubes (MWCNTs) in a carbon-fibre composite pre-impregnated (prepreg) laminate, to improve the through-thickness fracture toughness, is presented. Carbon nanotube (CNT) 'forests' were grown on a silicon substrate with a thermal oxide layer, using a chemical vapour deposition (CVD) process. The forests were then transferred to a pre-cured laminate interface, using a combination of pressure and heat, while maintaining through-thickness CNT alignment. Standard Mode I and four-point bend end-notched flexure Mode II tests were undertaken on a set of specimens and compared with pristine specimens. Mode I fracture toughness for T700/M21 laminates was improved by an average of 31% while for T700/SE84LV specimens, an improvement of 61% was observed. Only T700/M21 specimens were tested in Mode II which yielded an average fracture toughness improvement of 161%. Scanning Electron Microscopy (SEM) showed good wetting of the CNT forest as well as evidence of penetration of the forest into the adjacent plies.

Keywords: Carbon nanotubes, Composite materials, Structural failure, Mode I testing, Mode II testing, fracture toughness.

* Corresponding author: Tel: +44-28-9097-5640; e-mail: b.falzon@qub.ac.uk;

1 Introduction

The relatively poor through-thickness strength and toughness of laminated carbon fibre composites makes them particularly susceptible to delamination [1]. Consequently a substantial body of research exists on different approaches to improving through-thickness fracture toughness. These include stitching the plies together using Kevlar or similar fibres [2, 3], 'z-pinning' where carbon-fibre pins are ultrasonically inserted through the thickness of an uncured laminate [4, 5], and 'tufting', a process similar to stitching but utilising only one fibre thread [6]. Stitching requires access to both sides of the part where the sophistication of the machinery increases with increasing complexity in part geometry. Whilst z-pinning and tufting only require single-side access, they are also mostly suited to relatively simple geometries. These mechanical processes are known to induce fibre damage during insertion. Moreover, stitching fibres and z-pins have a diameter of approximately 0.3 mm and their presence forces fibres to deviate around them, potentially decreasing their compression strength by virtue of the increased fibre waviness. The unavoidable presence of resin-rich regions around the reinforcement has also been shown to act as damage initiation sites [7].

The introduction of nanoparticles in the matrix of a carbon or glass fibre reinforced polymer (C/GFRP), to enhance structural properties, has received considerable attention in recent years [8]. Studies have included the use of nanoclays [9], carbon nanotubes (CNTs) [10] and carbon nanofibres (CNFs) [11] dispersed in an epoxy resin. CNTs are typically comprised of single or concentric double, triple or multiple cylinders (also termed walls or shells and abbreviated S/D/T MWCNT respectively) of graphene, a single-atom-thick hexagonal carbon structure. Whereas CNTs have walls that are parallel to the fibre axis, CNFs, which also consist of graphene, have walls at an angle to the fibre axis, giving them a 'cup-stacked' (hence 'CSCNF') appearance for low angles, through to 'herringbone' and 'plate stacked' appearance for angles approaching 90°. Interest in CNT reinforcement stems from the phenomenal physical properties reported in the literature, with Young's Modulus for MWCNTs

ranging from 0.8 TPa [12] to 1.8 TPa [13] and strength from 10 GPa [14] to 150 GPa [12]. Although CSCNFs are similarly stiff, they achieve only a fraction of this strength because tensile failure only entails the sliding of the graphene cups (truncated cones) rather than the breaking of any chemical bonds [15]. Attempts have also been made to grow CNTs directly onto alumina fibres which were subsequently soaked in an epoxy resin and cured. While the approach has yielded promising results in improving interlaminar shear strength and electrical conductivity [16], the high temperatures (~ 750 ºC) required for producing CNTs by chemical vapour deposition (CVD), makes their growth directly onto carbon fibre somewhat problematic since catalyst iron particles deposited on the carbon fibre surface at these high temperatures are known to induce defects [17].

Improvements in fracture toughness, stiffness and strength, reported in the literature, have been variable and are shown to be highly dependent on dispersion, interfacial strength between the nanotubes and the epoxy resin, and alignment of the CNTs within the matrix. Inadequate dispersion may yield little or no structural benefit [8] and a reduction in fracture propagation toughness, resulting from the addition of CNTs in the polymer matrix, has consequently been reported [18]. CNTs may be grown as a random mass of fibres collected continuously from the reactor atmosphere, (hence requiring dispersion for most purposes) or as adjacent/aligned 'carpets' or 'forests' on smooth inert substrates [19].

A high level of CNT dispersion in an epoxy resin, prior to fibre impregnation, may be achieved using high-speed mixing, rolling mills, sonication or, indeed, a combination of these. Sonication is also known to rupture the CNTs, reducing their aspect ratio and their effectiveness as a reinforcement [20] . Dispersion may also be improved by oxidation, chemical functionalization of the CNT surface or the use of surfactants [21]. In all cases, the CNTs are likely to be randomly orientated and may align in the direction of resin flow in a resin infusion process [22] or bridge across narrow channels due to the very

high CNT aspect ratio. If through-thickness reinforcement is sought, it is highly unlikely that conventional processing approaches for producing prepreg or CNT-enhanced resin-infused structures will yield a biased orientation in this direction. Moreover, the increased viscosity, resulting from the addition of CNTs, also presents considerable difficulties in the processing of resin-infused structures [22, 23]. While this can be somewhat mitigated by the use of additives to reduce viscosity, such as acetone [21], it facilitates re-aggregation and tangling of the CNTs and introduces additional processing steps.

This paper explores the approach of placing highly-aligned CNT forests, grown on silicon, between carbon-fibre prepreg plies to improve fracture toughness. This produces a hierarchical composite with through-thickness reinforcement, analogous to stitching or z-pinning without the drawbacks associated with these techniques. Garcia et al. [24] were the first, and to the authors' knowledge, the only group to explore this approach using a 'transfer printing' method. A prepreg ply was mounted onto a roller and rolled over the CNT forest attached to a silicon substrate, using a constant speed and pressure. A different approach is used in this paper to promote better penetration of the CNT forest into the ply, and to maintain the structure and orientation of the forest. The silicon substrate bearing the CNT forest is inverted onto the prepreg ply and heat and pressure applied to the forest through the substrate. This slightly warms the resin in contact with the forest, thereby reducing the viscosity as the CNTs penetrate the prepreg and resin flows through the forest through capillary action. Evidence of this penetration was observed using scanning electron microscopy. Two prepreg systems, sharing the same fibre (T700) but with different epoxy resins, were considered; (i) a low-temperature cure epoxy resin mainly used in the marine industry, GURIT SE84LV and (ii) a high performance epoxy resin used in primary aircraft structures, HexPly M21. Mode I tests were performed on T700/SE84LV specimens and both Mode I and Mode II were conducted on T700/M21 specimens.

2   Experimental procedure

a.   CNT forest fabrication

The CNT forests for this study were grown on silicon wafers (100 mm diameter) bearing a layer of silicon oxide (500 nm) and an iron catalyst film (2.5 nm) deposited by electron beam evaporation [19]. Coated substrate pieces were placed in a quartz reactor (with a 44 mm internal diameter) within a three-zone furnace, heated to 670° C under helium (650 sccm) and acetylene (34 sccm) added (Figure 1). The growth rate of the forest was approximately 15 μm per minute. Figure 2a shows a forest with a height of 100 μm. The resulting CNTs were multi-walled with an average diameter of 10 nm (± 3 nm) and 7 walls (± 3). The density of the forest was approximately 1% by volume fraction. A high resolution transmission electron microscope image of these MWCNTs is shown in Figure 2b.

b.   CNT forest transplantation

In developing a protocol for the transfer of the CNT forest onto the prepreg laminate, it was necessary to ensure that the forest was completely transplanted from the substrate onto the composite and that it was not damaged in the process. The CNTs were also expected to maintain their vertical alignment and partially penetrate into the adjoining plies to increase their effectiveness as nano-scale stitches across a crack propagating along the interface of these plies. Initial transplantation tests on CNT forests with dimensions of between 20 mm and 30 mm in length, 8 mm in width and with a height of between 100 and 200 μm were conducted by inverting the silicon wafer, so that the top of the CNT forest was in direct contact with the prepreg, and applying load through a set of laboratory weights at room temperature (20˚C). The weights were kept relatively low, under 500g, applied over the area of the CNT forests to ensure that the alignment of the CNTs was not significantly affected.

Figure 3 is a schematic of the process adopted where initial tests were performed with no external heat applied.

The use of pressure only, for both T700/SE84LV and T700/M21 composites, failed to completely transplant the CNT forest onto the prepreg. This may be seen in the upper right quadrant of Figure 4 for tests on T700/SE84LV laminates where 200g and 500g weights were applied for five minutes. Most of the CNT forests remained attached to the silicon wafer when it was pulled away from the prepreg. The next step was to increase the tack of the prepreg by local heating. This was accomplished by investigating the heating of different weights in an oven, to a specified temperature, and then placing them on the inverted silicon wafer for specific periods of time. It is acknowledged that as the heating of the prepreg, by thermal conduction through the silicon wafer and the CNT forest, was performed at ambient lab conditions, the temperature would have decreased slightly over the treatment period. This was not of particular concern for the current exploration and there is scope for an investigation into the optimization of these particular transplantation parameters as part of a future research programme. A number of combinations of heat and pressure were investigated, a selection of which are shown in Figure 4.

At 60˚C some of the CNT forests often remained attached to the substrate at various weights and times. By contrast, when the applied weights were heated to 90˚C all weights and times resulted in complete transplantation and the wafer was generally easily removed. There was also clear visual evidence of penetration of the CNT forest into the prepreg. This was particularly noticeable for the 500 g weight when applied for a five minutes interval. The forest seemed to have penetrated into the prepreg almost completely and, as a result, the silicon wafer came into contact with the prepreg resin which made it difficult to remove. This is shown in the upper left quadrant of Figure 4. For this reason, a weight of 200 g at a temperature of 90˚C was chosen for this sized CNT forest and scaled for CNT

forests with greater widths, used later in the preparation of Mode I and Mode II specimens, to approximately maintain the same pressure. Again, it should be stressed that more research would be required to select optimum parameters but was not within the scope of this initial study. A similar exercise was undertaken for the T700/M21 prepreg where a temperature of 90˚C, applied through a heated 200 g weight for five minutes, was found to yield complete forest transplantation. At 60˚C, problems were also encountered when attempting complete transplantation, with some specimens failing to transfer almost 50% of the CNT forest. The complete wetting of the CNT forest, through the capillary action of resin available from a single ply, is shown in the SEM images of Figure 5 (arrows indicating the CNT-direction in Figure 5a and the z-axis in Figure 5b.)

c. Specimen preparation

Four sets of fracture toughness specimens comprising two resin systems (GURIT SE84LV and HEXCEL M21) each with and without CNT forests at the crack tip were prepared. Mode I and II specimens were produced in accordance with the guidelines for the manufacture of test specimens outlined in ASTM D5528-01 [25]. To achieve the required specimen thickness of 3-5 mm, specimens produced from Gurit T700/SE84LV consisted of 14 plies (0.281 mm nominal cured ply thickness) with a 13 μm thick polytetrafluoroethylene (PTFE/Teflon) insert located between the 7th and 8th ply to form the starter crack. As detailed later, CNT forests were also introduced at this point for the CNT-enhanced specimens. The specimens produced from T700/M21 consisted of 28 plies (0.13 mm nominal cured ply thickness) with a PTFE insert between the 14th and 15th ply. The difference in the nominal ply thickness reflects the difference in the prepreg thickness as produced by the respective manufacturers.

Each set of specimens was produced from a single laminate and cut using a water-jet cutter. In preparing the laminates, a 10mm thick aluminium plate was sand blasted and polished before being thoroughly cleansed with acetone, after which a non-porous PTFE sheet was laid on the plate instead of the application of a release agent. A debulking process was undertaken after the placement of every two or three plies (at a vacuum of -1 bar for five minutes). When the lay-up was complete, a peel ply, perforated release film, resin-bleed cloth and a Teflon release film were placed over the stack. A second aluminium caul plate, of 3mm thickness, was positioned on top of this assembly for improved pressure distribution and surface quality. A breather cloth, in direct contact with the vacuum port, was placed over the caul plate. The edges of the breather and bleeder cloth extended beyond the edges of the laminate and placed in contact to provide a path for the extraction of volatiles. The entire laminate was enclosed in a vacuum bag and sealed with tape. Different cure cycles were implemented for the respective resin systems. For T700/M21, a heat-up rate of 2 °C/minute to a final cure temperature of 180 °C, was held at a constant autoclave pressure of 450 kPa and constant vacuum pressure of -98 kPa for 120 minutes and cooled to room temperature at a rate of 2 °C/minute. The T700/SE84LV specimens were subjected to a heat-up rate of 2 °C/minute to a final cure temperature of 110 °C, held at a constant autoclave pressure of 150 kPa and constant vacuum pressure of -98 kPa for 120 minutes. It should be noted that the inclusion of 150 kPa autoclave pressure is not specifically requested in the supplier's specifications, but was included to reduce the presence of voids observed in previous cure cycles which utilised a vacuum only.

For sample specimens containing the CNT forest, the transplantation procedure outlined in Section 2b was used. When half the thickness of the laminate was reached, CNT forests were placed at the edge of the Teflon film. Forests of dimensions 20 mm x 20 mm were positioned to form a continuous band across the width of the laminate and weights of 500 g heated to 90 °C, applied for five minutes, applied to each. The silicon substrates were removed and the remaining plies assembled as

for the first group. Due to slight fluctuations in the CNT growth conditions, forest heights varied between 80 µm and 100 µm however this was not anticipated to significantly affect the test results. In total, 25 specimens were tested: six pristine and three CNT-enhanced T700/SE84LV specimens were tested in Mode I; five pristine and two CNT-enhanced T700/M21 specimens were also tested in Mode I and four pristine and five CNT-enhanced T700/M21 specimens were tested in Mode II.

d. Mode I Tests

All Mode I specimens were water-jet cut to a length, L, of 160 mm and a width , b, of 20 mm with the crack tip at 60 mm from the split edge of the specimen. Piano hinges were attached to the two arms of the specimen, as shown in Figure 6a, using a two-part epoxy resin. The contact surfaces were roughened using fine-grade sand paper to promote better adhesion. The hinges were positioned such that the distance of the loading points to the initial crack tip location, was 50 mm (a_0). With reference to Figure 6a, h=1.97 mm for the T700/SE84LV specimens and h=1.82 mm for the T700/M21 specimens.

The tests were performed on an Instron 5848 MicroTester with a calibrated 2 kN load cell under displacement control, at a loading rate of 0.5 mm/min as outlined in the ASTM standard [25]. To enable the visual location of the crack front, each side of each specimen was painted with white correction fluid and marked at 1 mm intervals. Digital cameras were placed at both sides of the specimen, to ensure a uniform crack front across the width of the specimen, and positioned on moveable platforms to track the crack propagation. No significant variation in the location of the crack position on either side of the specimen could be discerned, confirming the uniformity of the crack front. The location of the crack tip was tracked at regular intervals and recorded along with the applied loading and opening displacement at each measured crack extension. Modified beam theory, which accounts for crack tip rotation [25], was used for the data reduction. This approach was chosen because

it is known to give a slightly more conservative estimate for G_{IC}, compared to the compliance calibration methods and is also consistent with the data reduction approach adopted for Mode II for the type of fixture used.

e. Mode II Tests

Mode II test specimens prepared from T700/M21 were water-jet cut to the same dimensions as the Mode I specimens and a four point bend, end notched flexure test rig, proposed by Martin and Davidson [26], was used (Figure 6b). The outer rollers were situated 100 mm apart and the inner rollers were 65 mm apart. With reference to Figure 6b, 2L=100 mm, S_L=17.5 mm, S_R=82.5 mm, b=20 mm, h=1.82 mm and a=35 mm. The fixture available for this study was fixed, not pinned, to the load cell. As a consequence, G_{IIC} could only be determined using beam theory and following the approach presented in [26].

As the loads recorded for these tests were estimated to approach the capacity of the 2 kN load cell on the Instron 5848 MicroTester used for the Mode I tests, the next available option was an Instron 5982 testing machine, with a 100 kN load cell. While this load cell had a maximum capacity which was significantly higher than the maximum loads required for the Mode II specimens, its accuracy, which was quoted as $\pm$ 0.5% at 1/1000 of the load cell capacity, was deemed sufficient. A loading rate of 0.5 mm/min was applied and as for the Mode I specimens, the sides were painted with white correction fluid, marked at 1 mm intervals, and the crack front tracked by observing the crack tip on each side of the specimen using the two digital cameras.

3   Results

This investigation focused on the determination of the fracture toughness associated with crack *propagation*. The variability in the conditions at the initial crack tip, and the difficulty in controlling these, made the initiation fracture toughness values uncertain. The option of pre-cracking the specimens, to achieve better initial crack tip uniformity, was not pursued as this would have reduced the effective length of the CNT forest available for the crack propagation toughness evaluations. Multiple specimens were used for each test to ensure statistical significance although only two specimens were available for the T700/M21 Mode I tests containing CNT forests. Nonetheless, the results obtained from these two specimens were in good agreement. Figures 7 to 9 show representative R-curve values taken from the full complement of tests conducted. An average fracture toughness, associated with crack propagation, was determined for each tested specimen and an overall average taken for each set of tests. The statistical spread of these results is presented in Table 1 by one standard deviation for each set of tests.

Figure 7 shows representative Mode I R-curves for the T700/SE84LV samples. The results for specimens with the CNT forest at the crack interface show an increase in Mode I fracture toughness. The fracture toughness values resulting from the crack propagation through the CNT forest were averaged and compared to the corresponding average for the pristine specimens. The average fracture toughness of the pristine specimens was $G_{IC} = 210$ J/m^2 with a standard deviation, SD, of 17.8 J/m^2 and for the CNT forest specimens $G_{IC} = 338$ J/m^2 (SD = 96.2 J/m^2). This yielded an average increase in fracture toughness of 61%. Ideally, a 'plateau' region of the R-curves would be expected, supporting the hypothesis that fracture toughness is a material property and hence independent of crack length. The CNT results show a positive slope which may have been the result of fibre bridging, a known artifact of Mode I testing [27] and possibly reflecting a CNT failure mechanism where the inner shells

are pulled out of the outer shells and hence continue to provide some resistance. However the CNT result has a high standard deviation with more scatter observed in the early stages of crack propagation which may not reflect true steady-state propagation values.

The Mode I results obtained for the T700/M21 specimens, Figure 8, show a modest average increase in G_{IC} of 31% but on a somewhat higher base value and with much lower standard deviation. Thus the average G_{IC} for the pristine T700/M21 specimens was 331 J/m^2 (SD=19.4 J/ m^2) and 435 J/m^2 (SD=12.0 J/m^2) for the specimens with the CNT forests. The R-curve for the CNT forest specimens shows a negative slope, similar to that reported by Garcia et al. [24]. They attributed this phenomenon to the side-by-side placement of the CNT forest patches in their specimens but do not explain why such an arrangement should lead to the observed negative slope. Moreover, in this present study a single forest was placed at the interface.

The Mode II tests on the T700/M21 displayed a much larger scatter in the results for both the pristine and the CNT specimens as well as a significant improvement in fracture toughness of 161%. The pristine samples yielded an average fracture toughness of G_{IIC} = 443 J/m^2 (SD = 283 J/m^2) and the CNT forest samples had an average fracture toughness of G_{IIC} = 1155 J/m^2 (SD = 479 J/m^2). The R-curve for the CNT-enhanced specimen shows an initial increase in G_{IIC} followed by a negative slope after the crack had propagated nearly halfway through the CNT forest. This pattern was seen in most of the specimens tested in this configuration.

4   Discussion

The results in this initial study strongly suggest that the insertion of a CNT forest at the relatively weak ply interfaces offers the prospect of substantially improving the fracture toughness at critical locations. Nonetheless, there are many factors which need further investigation, first to

establish a reliable protocol for consistent outcomes and second to identify the optimum CNT and assembly parameters. One dominant feature of the CNT forest specimens is the presence of a CNT-enriched interlayer between adjoining plies (Figure 10a). Ideally what is sought is a forest that is fully embedded within these adjoining plies and does not hold them apart. The CNT forests used in this study had a height of 80-100 μm, which is either longer than necessary to penetrate the carbon fibre plies as far as possible (and hence the excess length remains as an interlayer), or which requires different parameters such as reduced resin viscosity, higher pressure or longer time, to accomplish full penetration without buckling the individual CNTs. In addition to the CNT forest height, a number of other CNT parameters remain to be explored and optimised. Figure 10b is a highly magnified SEM image which clearly shows the manner in which the CNT forest penetrates into the ply and impinges and wraps around the carbon-fibres. Figure 10a also shows that the forest appears to have maintained its through-thickness alignment.

To extract the full benefit of the CNT forest, the crack has to propagate through this region where the additional energy required to fracture the aligned CNTs yields a higher fracture toughness. An examination of the fracture surfaces of the tested specimens revealed a number of different crack paths which would account for the variability in the results. While some specimens indicated fracture through the forest, other fractures were characterized by partial propagation through the CNT forest followed by crack migration to the CNT forest/ply interface while others seemed to crack along this interface from the onset of crack propagation. If adequate penetration of the CNT forest into the ply is achieved, the fracture toughness would not be expected to vary significantly with these differing crack paths although the local orientation of the forest around the carbon fibres may give rise to transient variations. The high roughness of the fracture surface observed on most specimens was a further indication of improvements in fracture toughness. Figure 11 shows a detailed SEM image of a Mode I fracture surface where a number of CNT strands are shown to protrude from the fracture surface.

These CNT strands also seem to be tapered and this is consistent with a tensile failure mechanism of MWCNTs reported by Yu et al. [14]. It is postulated that the outer walls of the MWCNTs are strongly bonded to the epoxy resin and the inner walls, which are held together by comparatively weaker van der Waal forces, slide over each other in a 'sword-and-sheath' or 'telescopic' manner giving rise to the observed taper.

While the optimisation of the various processing parameters should yield consistently high fracture toughness values, these improvements will need to be weighed against the added cost associated with the introduction of these aligned CNT forests within a production process. To this end, this technology would be best utilized at strategic locations where the need for added through-thickness fracture toughness is required. Examples may include bonded joints [28], skin-stiffener interfaces in co-cured stiffened composite panels [29-32] or regions which are particularly susceptible to impact damage [1]. The production of the CNT forests is a readily scalable process and the placement of these, at strategic locations, could be automated to yield a high deposition rate.

5   Concluding Remarks

The CNTs produced on a silicon substrate, using a chemical vapour deposition process and an iron catalyst, were shown to be highly aligned with an areal density of approximately 1%. The transplantation of these CNT forests to the interface of two adjoining plies within a laminate was achieved using a combination of applied pressure and local heating. SEM imaging showed that overall CNT alignment, through the thickness, was maintained with evidence of the CNT forest penetrating into the adjoining plies with the ends of the forest impinging and wrapping around the adjacent carbon fibres. Mode I tests on two composite material systems with a common fibre (T700) but with low and high temperature cure epoxy resins, SE84LV and M21 respectively, showed an increase in the average fracture toughness of 61% for the T700/SE84LV specimens and 31% for the T700/M21 specimens.

Mode II tests were performed on T700/M21 specimens only and while the average fracture toughness was shown to be 161% higher than the pristine specimens, there was a large scatter in these results. The use of a test fixture which was fixed (not pinned) to the load cell required further data manipulation which may have contributed to the observed scatter. Nonetheless, this scatter requires further investigation. The height of the CNT forests, of between 80 μm and 100 μm, used in this study also meant that the ideal of full embedding of the CNTs into the adjoining plies using a range of transplantation parameters could not be achieved, resulting in a CNT-enriched interlayer between the plies. Separate tests showed that even with incomplete embedding of the CNT forest into the ply, full wetting of the forest was still achieved through capillary action of the resin available from this ply. Future work will aim to produce shorter forests and to optimize the transplantation and penetration parameters.

Acknowledgement

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