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Development of Sizing-free Multi-Functional Carbon Fibre Nanocomposites

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Abstract

High quality multi-walled carbon nanotubes (CNTs) grown at high density using a low temperature growth method are used as an alternative material to polymer sizing and is utilised in a series of epoxy composites reinforced with carbon fibres to provide improved physical and electrical properties. We report improvements for sizing-sensitive mechanical and physical properties, such as the interfacial adhesion, shear properties and handling of the fibres, whilst retaining resin-infusion capability. Following fibre volume fraction normalisation, the carbon nanotube-modified carbon fibre composite offers improvements of 146 % increase in Young's modulus; 20% increase in ultimate shear stress; 74 % increase in shear chord modulus and an 83 % improvement in the initial fracture toughness. The addition of CNTs imparts electrical functionalisation to the composite, enhancements in the surface direction are 400%, demonstrating a suitable route to sizing-free composites with enhanced mechanical and electrical functionality.

Keywords: A multifunctional composites, A nanocomposite, A carbon nanotubes and nanofibers, polymer sizing.

1. Introduction

Carbon fibre reinforced polymers (CFRP) are key carbon-based materials to industries, such as the aerospace industry, that require mechanically strong materials with high degrees of dimensional stability, whilst minimising the weight of the components [1-3]. The reinforcing carbon fibres (CFs) provide the high strength and elastic modulus necessary for critical components, whilst the polymer matrix (typically thermoset, but also thermoplastic) allows the load to be exerted evenly

to the fibres. It also, protects them from impact and environmental degradation, abrasion [4], inhibits crack propagation and enhances the transverse and out-of-plane properties of the laminate [4, 5].

Currently, the manufacturing value of aerospace composites accounts for around \$10 billion *per annum* and it has been estimated that the aerospace composites market is on track to reach \$50 billion annually by 2018. Thermosetting polymers are by far the most widely used matrices in this application and account for about 60% of the total CFRP market (*ca.* 7 Mt *per annum* worldwide) [3]. Epoxy resins, which are the subject of this study, are one of the most important families of cross-linked, thermosetting polymers [6], which offer a suitable balance of properties for the neat resin, such as strength and fracture toughness, coupled with a high glass transition temperature. Consequently, they account for ~ 90 % of advanced composite matrices and form the basis for the fuselage of the Boeing 787 Dreamliner, and various other components, including the centre wing box of the Airbus A380-800 [3].

The interface links the matrix and the reinforcing CFs to form a region of chemical heterogeneity, making it more susceptible to thermal or chemical degradation than either of the bulk phases. This region is responsible for facilitating stress transfer from the moderately low strength polymer matrix to the high strength CFs. However, as a result of the inherently low surface energy (poor wettability of polymer matrix on the CF) and the small active specific area of the CFs, this stress transfer is poor [7]. Therefore, the interface is improved by applying a polymer ‘sizing’ to the CFs. The polymer sizing (typically a low molecular weight epoxy resin [8, 9]), is applied to the CFs to aid handling by reducing billowing [8] and increasing the surface energy of the CF surface by introducing polar molecules (improving the wettability). This increases the shear stress transfer to the fibre and toughness of the composite by encouraging crack propagation away from the interface [8, 10]. The sizing is designed so that a particular group of the molecule (in this case the aromatic rings of the bisphenol-based epoxy) associate with the sp^2 -hybridised CF surface whilst a different group (e.g. a short alkylene chain bearing a hydroxyl group) associates with the polymer matrix *via* the formation of hydrogen bonds [8, 11] to couple the two materials together.

Composite performance arises from the synergistic effect of its constituent materials. This has been the motivation for incorporating nanomaterials with tensile strengths and moduli beyond current reinforcements in order to impart these impressive properties. For example, incorporating a nano-phase within the CFRP improves matrix dominated processes such as the delamination resistance and through-thickness strength [12, 13]. Adding carbon nanotubes (CNTs), with their highly crystalline structure [14] and large specific surface area into the polymer matrix leads to significant (and rapid) increases in melt viscosity due to agglomeration of the CNTs and complications with processing. Consequently, interest has shifted towards the growth of CNTs directly on the CF (known as ‘fuzzy’ fibres – FFs) by means of chemical vapour deposition (CVD) processes [15]. However, whilst this overcomes the problem of high melt viscosity, the high growth

temperatures typically associated with CNT growth (typically 600 - 1200 °C) [16,17] result in thermal degradation to the CFs [16] and removes the polymer sizing. Subsequently, a low-temperature approach for growing the CNTs and metallic architecture on the carbon fibre that circumvents this limitation is used, showing an industrially-viable way of implementing this in large-scale.

An alternative to the polymer sizing currently used in CFRP manufacture is presented, by growing high quality CNTs at a high density on CFs. The modification offers the additional advantage of entangling the CNTs with each other, improving the handleability of the CF cross ply even without the presence of polymer sizing. Once infused using an industrially relevant process, the fuzzy carbon fibre composite (F-CFRP) featured no voids and as a consequence of the presence of the CNTs, the modified composite displayed improvements in mechanical performance. Subsequently, comprehensive mechanical tests are presented using a range of intermediate materials (sized removed fibre composites and, for the tensile test, sized removed at growth temperature), allowing for accurate determination of the contribution to the mechanical properties from the CNTs. The sp^2 hybridisation of the carbon atoms in CNTs leads to the formation of pi-electrons (high mobility electrons), resulting in high electrical conductivity. This property has been demonstrated by performing electrical measurements in the surface direction for standard and CNT-modified composites. To summarise, an alternative material to the polymer sizing currently employed in fibre composites, that enhances mechanical properties as well as imparts electrical functionality, is presented.

2. Experimental Section

The CFs (Pyrofil TR30S 3K PAN (Grafil Inc.) were woven in a 2/2 twill weave pattern, with a proprietary polymer sizing applied (epoxy resin of 2 wt %) [17]. The typical properties are given in the Supplementary Data, Table S1. The polymer matrix used was a formulated low viscosity, room temperature-curing, bisphenol A/bisphenol F based epoxy resin, 'IN2 Epoxy Infusion Resin' (EasyComposites)¹, see Supplementary Data, Table S2. The infusion of the epoxy resin was carried out using an industrially-relevant vacuum-assisted resin transfer moulding (VARTM) process [17].

2.1 Fuzzy Fibre Fabrication

An aluminium thin-film barrier layer (35 nm) was deposited on the CFs using DC magnetron sputtering (JLS MPS 5000) on both sides of CF cross ply followed by a thermal treatment at 800 °C under a flow of H₂ (100 sccm) for 15 minutes at pressure of 2 Torr. The CF temperature was measured using a K-type thermocouple placed in contact with the CF cross ply. The catalyst for CNT growth (thin-film iron, (6 nm)) was then sputter-deposited using DC magnetron sputtering from

¹ Bisphenol-A- (epichlorhydrin (30 – 50 %), Bisphenol F (30 – 50 %), 1,6-bis(2,3-epoxyproxy)hexane (20-30 %), propylene carbonate (5 %).

a pure Fe target, on one side of the CF cross ply. The CNT growth was performed using a photo-thermal chemical vapour deposition (PT-CVD) system (Surrey Nanosystems (1000N), Supplementary Figure S1), which is a (substrate table and chamber-wall) water-cooled system (cooling to 10 °C via a closed-circuit). Thermal heating is provided via top-down from an array of light-sources (halogen tungsten bulbs, maximum output of 8 kW) which efficiently delivers thermal energy to the top of the fibres whilst the bulk of the fibres remain in contact with the cooled substrate holder [18]. This method of heating has demonstrated to deliver low degradation to CFs under CNT growth conditions [17]. Iron oxide was reduced by flowing hydrogen, at a flow of 200 sccm and pressure of 10 Torr, for a duration of 10 minutes at 750 °C. The CNT growth process was performed using acetylene (50 sccm) for 15 minutes. After this period had elapsed and the temperature of the CF had equilibrated at 800 °C, the acetylene was switched off. The chamber was cooled with the hydrogen flowing, prior to sample removal. After this step, iron catalyst was sputter-deposited on the remaining side of the cross ply, and the growth sequence was repeated.

2.2 Scanning Electron Microscopy

Scanning electron microscopy (SEM) was performed on the dry cross ply and on the CFRP cross-section using a FEI Quanta 200 operating under high vacuum with a secondary electron detector employed. Typical voltages were between 20 - 20 kV, spot sizes of 2 - 4 nm with a working distance of 10 mm.

2.3 Scanning Transmission Electron Microscopy

To prepare the CNTs for STEM analysis, a FF tow was placed in a vial containing isopropyl alcohol (IPA) (5 ml) and ultrasonicated (10 minutes). The CNT and IPA were drop cast on a carbon grid for imaging.

2.4 Fibre Volume Fraction Normalisation

Fibre volume fraction (V_f) was determined using thermogravimetric analysis (TGA) on pure epoxy resin, (confirming complete decomposition and determining the residue) followed by TGA on CFs (to confirm thermal stability). From this, the values of the V_f for the CFRP, size-removed CFRP (SR-CFRP) and F-CFRP composites were subsequently determined. The composites were placed in a platinum pan and subjected to a flow of nitrogen (60 cm³/min), undergoing a temperature ramp of 20 °C to 600 °C with a variable heating rate. The complete methodology and calculations for the determination of fibre volume fraction can be found elsewhere [19]. V_f normalisation of the tensile and in-plane shear test were carried out using the rule of mixtures, of the form:

$$A = A_f V_f + A_m V_m \quad (1)$$

where A_f and A_m are the fibre and matrix contributions to the arbitrary property, A , and V_m is the polymer matrix volume ($V_m = 1 - V_f$).

Given that only two of the 18 plies were modified with CNTs (negligible thickness increase), V_f normalisation was not carried out for the mode-I interlaminar fracture toughness test. In addition, Compston *et al.* [23] determined that crack initiation values are independent of V_f . Similarly, V_f normalisation was not necessary for the electrical characterisation as only surface electrical measurements were determined.

2.5 Pull-Out Test

Interfacial shear testing was performed on tows and tested in a pull-out configuration. This was preferred over testing on a single fibre, as it results in a more realistic measurement of the interfacial adhesion and reduces the errors associated with handling single fibres, which typically require more manipulation due to their small size. This manipulation also increases the probability of CNTs departing from the CF. Furthermore, CFs in the composite are bundled in tows within the composite which is important when one considers that the interphase between the polymer matrix and CF could potentially be greater than the fibre-to-fibre distance within the tows. In addition, the deposition of the interlayer, catalyst and growth of CNTs occurs with the CFs bundled in tows, therefore the quality of the deposition and growth of CNTs are captured in the pull-out test.

For the test, a single tow of CFs was removed from the dry cross ply by gluing a small section of paper to the end of the tow. All samples were suspended by clamping the paper holder and submerging the ends to a depth of 1-3 mm in a vessel (1 μm^3 volume) completely filled with the infusion polymer matrix. A diagram of the experimental set-up can be seen in the Supplementary Data, Figure S2. Care was taken to ensure the CNT coated section was submerged into the epoxy resin. The volume of epoxy resin was substantially greater than the embedded tow to maximise the possibility of a successful pull-out (as opposed to fibre or matrix failure). After a 24 hour cure time, the samples were placed in an Instron 1175 universal testing rig with a 1 kN load cell running the Bluehill 2 software. An adjustable clamp was used to hold the paper holder at the top, whilst a two-piece metal cylinder held the epoxy resin-filled vessel (Supplementary Figure S3). The test was complete once the tow had fractured from the polymer matrix. The interfacial shear stress (σ_{IFSS}) was calculated using [20]:

$$\sigma_{IFSS} = \frac{F_{max}}{\pi d_f l} \quad (2)$$

where F_{max} is the maximum load prior to the carbon fibre tow fracturing, d_f is the diameter of the carbon fibre tow and l is the embedded length (including the meniscus), as determined by SEM.

In conjunction to the standard CF and FF, a sized-removed (SR-CF) sample was tested. This improved the determination of the effects of the CNTs as the polymer sizing is removed during the CNT growth procedure. The polymer sizing was removed by placing part of the tow in acetone for 12 hours [25,26]. The use of a solvent provides control as to where the sizing is removed which means the cross ply retains the majority of its handleability but the submerged section is devoid of sizing.

2.6 Ultrasound Testing

Ultrasound testing was performed using an Olympus Omniscan phased array ultrasonic testing instrument with a MX 5 MHz probe in a water filled immersion tank. The sample tested was a FF ply consolidated into a composite with a stack of unmodified carbon fibre plies.

2.7 Cross-sectional Analysis

Cross-sections were obtained by cutting a 4 ply-thick sample using a guillotine, followed by an 8 stage polishing process, concluding with a 0.05 μm particle-fine abrasive size (see Table S3 in supplementary data for complete procedure). A 7.5 nm gold layer was deposited using DC magnetron sputtering system to allow imaging by SEM.

2.8 Contact Angle Measurements

Contact angle measurements were carried out using a Kruss EasyDrop instrument, DSA1 and ImageJ software. A water droplet was carefully placed on the samples for the measurement of the contact angle. The measurements were carried out using the algorithms of the DSA1 and ImageJ software.

2.9 Tensile Test

The ply lay-up for the tensile tests was $[0/90]_4$ and samples were cut to the dimensions of (100 x 15) mm with tabs of dimensions (15 x 25) mm attached on both ends (25 mm) of the specimens, on each side (see Supplementary Data, Figure S4). Tabs were attached to the test specimens using Scotch-Weld EPX Epoxy Adhesive DP490 (3M) and measurements of load and strain of the sample to failure were carried out using an Instron 1175 universal testing instrument equipped with a 100 kN load cell and Bluehill 2 software, from which the load, time and extension information was recorded. The strain data were measured using a dynamic extensometer (Instron 2620-602) with a gauge length of 12.5 mm. The cross-head speed was 1 mm/min with a data collection rate of 10 Hz.

For the composite tensile test, CFRP, F-CFRP and a sized-removed CFRP (SR-CFRP) and SR-CFRP at growth temperature (SR-CFRP at GT) were tested. The SR-CFRP was fabricated by placing the dry carbon fibre cross ply in an oven at 450 °C (air atmosphere), whilst the SR-CFRP at GT was fabricated by subjecting the dry carbon fibre cross ply to the same growth conditions as those used in the PTCVD system for CNT growth. Alternatively, the difference in methodology between the F-CFRP and SR-CFRP at GT is the metallic interlayer and catalysts for the F-CFRP that enabled the growth of CNTs. The SR-CFRP informs how the removal of the polymer sizing influences the tensile test, whilst in conjunction, the SR-CFRP at GT informs how the temperature of growing CNTs on the CF affects the tensile performance

2.10 In-Plane Shear Test

For the in-plane shear (IPS) test, samples containing 4 plies with the lay-up [$\pm 45^\circ$] were cut to the dimensions of (100 x 15) mm, with tabs of dimensions (50 x 25) mm attached on the initial and final 25 mm of the sample, on both sides. A schematic diagram of a sample for IPS testing is shown in Supplementary Data, Figure S5.

Samples were analysed in accordance with the ASTM D3518 (2007) standard [21]. The shear stress and shear strain were measured using an Instron 1175 equipped with Bluehill 2 software and a 5 kN load cell with a cross-head speed of 1 mm/min and a data collection rate of 10 Hz (a Vishay StrainSmart 7000 data logger). A strain gauge (EA-06-250BF-350/P strain gauge by Vishay Precision Group, Inc. with dimensions of 13.2 mm x 5.6 mm and grid dimensions of 6.35 mm x 3.18 mm) was chosen to measure the transverse strain (perpendicular to the uniaxial load) and an extensometer to measure the longitudinal strain as shown in Supplementary Data, Figure. S5.

The ultimate in-plane shear stress (τ_{IPS}) was calculated using [21]:

$$\tau_{IPS} = \frac{F_{max}}{2A} \quad (3)$$

where F_{max} is the maximum load and A is the cross-sectional area. The shear chord modulus (G_{SC}) was calculated using [21]:

$$G_{SC} = \frac{\Delta\tau}{\Delta\gamma} \quad (4)$$

where $\Delta\tau$ is the difference in applied shear stress between two shear strain points and $\Delta\gamma$ is the difference between the two respective shear strain points.

The shear strain (γ) was calculated using [21]:

$$\gamma = \varepsilon_y - \varepsilon_x \quad (5)$$

where ε_y is the longitudinal strain and ε_x is the lateral strain. A shear strain range of 1500 to 5500 $\mu\varepsilon$ is recommended by the ASTM standard [21].

2.11 Interlaminar Fracture Toughness

The procedure described in this work followed the ASTM D 5528-01 (2007) [22] standard, using samples (85 x 15) mm in a cross ply $[0/90]_{16}$. A schematic diagram of the double beam cantilever sample used for the test is shown in the Supplementary Data, Figure S6. The initial crack was created by laying a 25 μm PTFE film 10 mm from the end of the samples in the middle of the lay-up (after the 8th ply), with the remaining 8 placed on top. Aluminium ‘T’ loading blocks were adhered to the sample using an epoxy adhesive (3M DP490). An Instron 1175 testing instrument was modified to accept the ‘T’ loading blocks and a pip counter. The measurement was carried out at a constant cross-head speed of 1 mm/min with the pip counter activated as the crack delaminated passed each marker. Data were collected at a rate of 10 Hz, whilst data recorded as the crack was between the PTFE film were removed. To understand the effects of CNTs, the SR-CFRP was tested alongside the CFRP and F-CFRP. In the same manner for the sample fabrication as Wicks *et al.* [23], only the adjacent plies (to the progressing crack) were modified. The purpose of the remaining 14 plies was to stiffen the sample and prevent bending failure.

The Modified Beam Theory (MBT) was chosen for the data reduction method, as recommended by the ASTM D 5528 – 01 standard [22]. In this method, the strain energy release rate (G_I), is corrected for the rotation at the delamination point as follows:

$$G_1 = \frac{3P\delta}{2b(a + |\Delta|)} \quad (6)$$

where P is the load; δ is the load point displacement; b is the sample width, and a is the crack length from the load point. By creating a least squares plot of the cube root of compliance as a function of the delamination length, Δ can be determined by the value of the x-intercept.

2.12 Electrical Conductivity Measurements

Standard CFRP was tested alongside the F-CFRP composite samples with lay-up $[0/90]_4$ cut to the dimensions of (40 x 20) mm with conductive paint (silver DAG) applied over an area of (10 x 20) mm on each side, top and underside. Current-voltage (I-V) measurements were obtained from a Keithley 4200-SCS with tungsten tips for a two-probe measurement on the surface of the composite as shown in Supplementary Data, Figure S7.

3. Results and Discussion

3.1 Analysis of Growth of CNTs

Comparing the CF against the FF plies (Figure 1), shows that the addition of the CNTs has retained the integrity of the cross ply, even after the polymer sizing had been removed. The FF cross ply displayed greater mechanical integrity than the sized CF cross ply, which can be observed in Figure 1(a) with the tows parting from the sample and the retained rectilinear form of FF cross ply (Figure 1(b)). This enabled easy manipulation of the FF samples for testing and also demonstrated the possibility of the CNTs being an adequate replacement for the polymer sizing.

Figure 1. (a) Standard carbon fibre (CFRP) and (b) the fuzzy fibre (FF) cross ply.

The SEM and STEM images of the fuzzy fibres are displayed in Figure 2. The density of the growth was observed to be significantly greater than that reported in previous work [17] and is such that the CF (the growth substrate) is not visible apart from the regions where the catalyst has not been able to deposit (see Figure 2b). The lengths of the CNTs varied from 10 μm to 300 μm . The average density of growth, $\sim 2 \times 10^{10} \text{ cm}^{-2}$ was obtained by SEM imaging. This compares

well with Sonoyama *et al.* [24], who reported a density of $2 - 6 \times 10^9 / \text{cm}^2$ and Zhang *et al.* [9] who reported $8 \times 10^9 / \text{cm}^2$. STEM images of the CNT from the cross ply revealed that the CNTs were multiwall with typical diameters of 12.5 nm (Figure 2c).

Figure 2. Electron microscope images of the fuzzy fibres. (a) Warp and weft tows coated with CNTs, (b) higher magnification image of the fuzzy fibres from the dashed area in (a), (c) STEM image of the multi-wall CNT. Lines beyond the image have been added to clarify the walls of the CNTs.

3.2 Wettability and infusion

The removal of the polymer sizing leads to CFs of low wettability for infusing the polymer matrix due to their inherent low surface energy. Contact angle measurements were conducted on samples of CF, SR-CF and on the FF to monitor the changes in hydrophobicity before and after the sizing was removed and after the growth of CNTs. For the polymer sizing on the CF with its high wettability, a water droplet could not be formed. This high wettability is a result of the polymer sizing increasing the number of polar molecules (in this case low molecular weight, oligomeric epoxy) on the surface of the CF. The SR-CF (4 droplets analysed) and FF (4 droplets analysed) samples, however, were capable of sustaining a droplet, as shown in Figure 3.

Figure 3. Water droplet on (a) SR-CF and (b) FF using DSA1 software.

Figure 3 suggests similar wettability for both materials (high hydrophobicity) as a result of predominantly non-polar surfaces. The averaged results from the DSA1 and ImageJ software (Table 1) state that the contact angle for the FF specimen (combined average of 134.6°) is greater than that of the sized removed specimen (combined average of 125.8°).

Table 1. Averaged results from contact angle measurements using DSA1 and ImageJ software

<i>Sample</i>	<i>DSA1 ($^\circ$)</i>	<i>ImageJ ($^\circ$)</i>
<i>SR-CF</i>	(122.6 ± 3.9)	(129.0 ± 1.3)
<i>FF</i>	(136.6 ± 2.6)	(132.6 ± 2.4)

Thus, the CNTs have reduced the wettability (increased hydrophobicity) from the sized removed sample. This could be attributed to the following possibilities: the growth process has removed impurities from the CF and added highly graphitic (less defective structures), increasing the number of non-polar molecules. However, the primary reason is expected to be from an increase in surface roughness, as a result of the tall forests of CNTs on the fibre surface. Surface roughness is known to influence the wettability in a non-linear manner [25]. Lau *et al.* [26] found that this hydrophobicity is typically not seen for shorter CNTs where the water was observed to penetrate into the forest, presumably as a result of capillary action, which has also been observed by Qian *et al.* [27] and Garcia *et al.* [28]. Lau *et al.* [26] fabricated taller CNTs (10 – 15 μm) and achieved a contact angle of 161° , but the droplet was not stable and dissipated after a few minutes. This phenomenon was not seen for the SR and the FF cross ply in this project, nor in other studies [29]. Instead, the CNTs on the surfaces resulted in ‘superhydrophobicity’, likely as a consequence of the growth of CNTs in this work

featuring a higher density, thereby minimising free space for water to deform the CNT forest and seep into the available space.

However, the ultrasound results show that once infused in a composite, the FFs led to a well infused composite with no observable voids during ultrasound testing. This can be noted in Figure 4 by the absence of red areas in the ply stack.

Figure 4. Ultrasound image of the composite with a single ply of fuzzy fibre. The side and end profiles are the complete cross-section.

Further confirmation of the complete infusion of the FF was obtained from SEM images taken of the cross-section of the composite (Figure 5). The presence of CNTs (highlighted in Figure 5c) is evident, when compared to the standard CFRP (5a), and the SR-CFRP (5b). The figure reveals the coverage of CNTs on the CFs of ~ 40 % of the circumference of the fibres, with the fibres on the outside of the tow being coated. There is evidence of fibres having undergone degradation in Figure 5c, but this was also observed while scanning the surface of the conventional CFRP and SR-CFRP.

Figure 5. SEM of the cross-section of (a) the standard CFRP and (b) SR-CFRP and (c) F-CFRP.

Following infusion, V_f values were determined for CFRP ($n = 3$), SR-CFRP ($n = 3$) and F-CFRP ($n = 6$), including different samples and different configurations ($[0/90]$ and $[\pm 45]$). The addition of the CNTs reduces the V_f (confirmed using TGA, see Supplementary Data, Figure S8) compared to the CFRP (48.5 ± 0.5 %) and SR-CFRP (48.2 ± 0.7 %) to (20 ± 2.0 %) for the F-CFRP. This is likely to be a consequence of the long and dense CNTs displacing fibres in the material and creating resin rich regions. This difference highlights the need to perform V_f normalisation.

3.3 Single Tow Pull-Out Tests

Tow pull out test on the standard CF ($n = 28$), SR-CF ($n = 31$) and the FF ($n = 41$) showed three distinct failure modes (Figure 6): fibre pulling through the polymer matrix cleanly ($F \rightarrow M$ – fracture at the fibre-matrix interface); the fibre pulling through the matrix with a portion of the matrix adhering to the fibre ($F/M \rightarrow M$ – combination of fracturing at the interface and fracturing within the polymer matrix) and matrix-to-matrix fracturing ($M \rightarrow M$ – fracture within the polymer matrix). Any epoxy matrix remaining on the tow is typically found when ductile behaviour is observed, as opposed to a clean, brittle fracture [30].

Figure 6. SEM images showing the different failure modes observed for the pull-out test.

When the loads required for fracture at a particular tow depth are plotted by failure mode (Figure 7), a positive correlation between load and immersion depth for CF and SR-CF and FF is observed. There is a comparatively large scatter in the data for each sample, most notably for FF, and to a lesser extent, for SR-CF, which could be a result of the removal of the polymer sizing creating a more consistent surface for testing. On the other hand, a possible reason for the poor correlation that is observed for the FF samples could be due to the variable area of contact between the CNTs and the polymer matrix. Increasing the contact area (*via* the immersion depth) could reduce the data distribution, but would risk encouraging other failure modes.

Figure 7. Graphs of the load to failure at particular depths and the modes of failure for (a) CF (b) SR-CF and (c) FF.

The most prominent failure mode for CF is $F \rightarrow M$; for SR-CF it is $F/M \rightarrow M$ and for FF it is $M \rightarrow M$. The $F \rightarrow M$ failure is expected to be one of the most dominant failure mechanisms in the composite, but whilst it accounts for 61% in CF samples, it is less prevalent in the other samples: SR-CF (24 %) and FF (20 %). This result is surprising given the fact that the experiment was designed to encourage $F \rightarrow M$ failure, with minimal contact with the polymer matrix. It might have been expected that the CF samples (containing the polymer sizing), would have displayed a greater number of failures *via* $F/M \rightarrow M$ or $M \rightarrow M$, but this was not the case. Alternatively, in the absence of polymer sizing, the SR-CF and FF might have been expected to fail predominately *via* $F \rightarrow M$, but this was also not observed. This observation

suggests that the polymer sizing does not aid the interfacial strength of the fibres. This is consistent with the findings of Lu *et al.* [31], who used molecular modelling techniques to demonstrate the comparatively poor compatibility of epoxy oligomers for mildly oxidised PAN fibres, compared with *e.g.* an epoxy-diamine copolymer. This in turn supported empirical observations that suggested the epoxy matrix tends to migrate from the fibre surface during cure leading to domains of low epoxy concentration in close proximity to the fibre surface.

For FF samples, the F/M $\rightarrow$ M and M $\rightarrow$ M failure modes display better correlations (between load and immersion depth) than the F $\rightarrow$ M mode, which might be a result of inconsistent density of CNTs interacting with the polymer matrix from sample to sample. The F $\rightarrow$ M mode shows a positive correlation between load and immersion depth for CF and SR-CF, whereas the quality of linearity becomes poorer for the F/M $\rightarrow$ M failure mode and, most noticeably, the M $\rightarrow$ M failure mode. This is likely a result of the number of variants within the two latter failure modes.

Plots of the observed η_{FSS} against the embedded depth of the tow (Figure 8) show little correlation with failure mechanism. Typically, for ductile matrices there should be no dependence of η_{FSS} on the depth and a decreasing force with increasing depth attributed to a brittle failure [30] - the SEM images from the pull-out test (Figure 6) suggest brittle fracture. Arguably, the SR-CF samples (Figure 8b) and to a lesser degree, CF samples (Figure 8a) display positive correlations, but it is unknown how this relates to the fracture mode (brittle, ductile, *etc.*) [30]. The F $\rightarrow$ M failure mode for the F-CFRP is negative (brittle fracture), however the correlation is relatively poor. All the failure modes (apart from the F $\rightarrow$ M and F/M $\rightarrow$ M of the F-CFRP and M $\rightarrow$ M of the SR-CFRP) display positive correlations, however, as mentioned the SEM images suggest brittle fracture.

Figure 8. Interfacial shear strengths (τ_{IFSS}) of each material against the depth categorised by the failure mode.

The interfacial shear strength (τ_{IFSS}) data for $F \rightarrow M$ failure mode are displayed in Figure 9. The FF (3.18×10^1 MPa) samples displayed the greatest average (11 %), followed by CF (2.87×10^1 MPa) and then SR-CF (2.75×10^1 MPa, reduction of 14 % compared to FF and 4 % reduction compared to the CF). Under similar error consideration, the error bar percentages are ± 10 % (CF), ± 23 % (SR-CF) and ± 16 % (FF); both the upper limits of CF and SR-CF overlap the average of FF. A one-way ANOVA test was carried out on the data for the ' $F \rightarrow M$ only' failure mode of the pull-out samples and no statistical significance was observed, including comparisons made between each material using the Tukey

– Kramer *post-hoc* test. It is expected that removing the polymer sizing (without any further modification) reduces the interfacial adhesion between the carbon fibre and polymer matrix [32, 33].

Improvements are typically expected for τ_{IFSS} after CNT modification (compared to sized removed carbon fibres).

Thostenson *et al.* [34] attributed the enhancement to local stiffening of the polymer matrix near the interface, while Guo *et al.* [35] observed fibre surface structure changes and polarity matching with the polymer matrix. Zhang *et al.* [36] suggested the origin of the improvements is related to improvements in the chemical bonding, van der Waals binding and mechanical interlocking. These improvements in τ_{IFSS} go beyond those typically observed by roughening the surface of the fibres [37], as this usually only result in surface area enhancements by one order of magnitude, compared with typical enhancements of 300 [38] to 750 [9] for fuzzy fibres.

Figure 9. Interfacial shear strengths (τ_{IFSS}) for CF, SR-CF and FF as a function of failure mode.

3.4 Tensile Tests

The V_f -normalised results of the measurement of ultimate tensile stress (σ_{UTS}) and the Young's modulus (E_M) for the CFRP ($n = 10$), SR-CFRP ($n = 10$), sized removed CFRP at growth temperature (SR-CFRP at GT) ($n = 10$) and F-CFRP ($n = 5$) are displayed in (Figure 10). The CFRP and SR-CFRP display similar results, but the SR-CFRP at GT has an average σ_{UTS} and E_M that is markedly lower than that of the SR-CFRP and CFRP by 11 % and 7 %, respectively. As the tensile load is transmitted in the outer skins of the carbon fibre, the tensile performance of the composite will be sensitive to any modifications to the outer layer of the carbon fibre [39]. It is well documented that growing CNTs *via* CVD

reduces the tensile performance of the fibres and given the composite tensile test is fibre dominated, the SR-CFRP at GT will state this reduction [15].

Figure 10. V_f -normalised ultimate tensile stress (σ_{UTS}) and Young's modulus (E_M) results for CFRP, SR-CFRP, SR-CFRP at GT and F-CFRP.

The F-CFRP displayed a 33 % reduction in the σ_{UTS} compared to the CFRP, suggesting additional degradation from the CNTs (as the SR-CFRP at GT displayed an 11% degradation). The degradation for the F-CFRP is in contrast with the 9.7 % degradation in single fibre tensile test observed in a previous publication [17]. This additional degradation has been observed before, and has been attributed to catalyst interacting with the fibre (pitting). Vogel *et al.* [40] stated that an aluminium interlayer removes this interaction and reduces the thermal degradation to the fibre. Improvements have been reported by Suraya *et al.* [41] who observed maximum improvements of 52 % in σ_{UTS} and 133 % in E_M for their FF (chopped) composites in comparison to un-sized fibre composites.

The F-CFRP displayed the largest improvement in E_M with a 146 % increase over the CFRP. This is likely due to the CNTs improving interfacial properties, preventing fibre-matrix slip and reducing the elongation to break. The SR-CFRP exhibited similar E_M values, whilst the SR-CFRP at GT exhibited a 7 % reduction in comparison to the CFRP.

The V_f normalised results (Figure 10) suggest that the polymer sizing does not affect the tensile properties of the composite material: both CFRP and SR-CFRP have similar σ_{UTS} and E_M values. The low V_f of the F-CFRP should lead to improvements in the tensile properties once normalised for V_f , although these could yield an underestimate, as composites with low V_f tend to have a random distribution of fibre orientation [42]. Further work should be carried out to assess the theoretical prediction of V_f normalising nano-modified composites for the low V_f quoted. Regardless of the limitations of the rule of mixtures, the raw data of the F-CFRP presents a 2 % increase in E_M for a V_f that is 60 % less than the CFRP.

3.5 In-Plane Shear Test

The plotted data for stress against extension (*via* the extensometer) obtained from the in-plane shear (IPS) test are shown in Figure 11a (for all three materials tested: CFRP ($n = 5$), SR-CFRP ($n = 4$) and F-CFRP ($n = 5$)) and it is apparent that the IPS loading of composites induces ductile behaviour. A description of the various mechanical characteristics are shown in Figure 11b. Strain hardening is expected to be a consequence of fibre rotation (the scissoring action of the fibres, aligning themselves to the stress field) [43], whereas the necking phase is expected to be the result of the fibre scissoring (rotation), inducing stress inwards, contributing to a Poisson contraction. In addition to the fibre rotation, the orientation of the fibres hinders transverse crack propagation, allowing for progressive failure (as opposed to the tensile tested specimens). Interfacial de-bonding of the fibre from the matrix does not occur until a high shear strain is reached [43] with the ultimate failure of the $\pm 45^\circ$ woven fibre composites occurring due to the fibre breakage and pull-out [21].

Figure 11. (a) Typical stress curves of the non- V_f -normalised results displaying calibrated shear stress *versus* the calibrated extension for the samples of CFRP (black), SR-CFRP (blue) and F-CFRP (red). During testing, the C-FRP and SR-CFRP displayed progressive failure, whereas the F-CFRP failure was instantaneous. (b) Description of behaviour of the in-plane shear samples.

The SR-CFRP displayed a large extension of the strain-hardening regime, resulting in an overall larger extension to failure compared to the other materials. This could be the matrix not effectively transferring stress to the fibres (poor fibre-matrix interface) leading to fibre-matrix slippage.

Unlike the tensile test, no expression exists to describe the fibre contribution to shear stress testing of bi-directional fibre composites oriented in a symmetric lay-up [44]. Totry *et al.* [43] carried out simulations and experiments on IPS properties of CFRP and attributed the initial elastic region and the strain hardening to be dependent on the V_f with greater

G_{SC} accompanying higher V_f [43, 45]. Barbero *et al.* [46] stated increased τ_{IPS} values with increasing V_f for E-glass composites. Evidently, the τ_{IPS} and G_{SC} are expected to increase with V_f , but the exact relationship is not known. Thus, although a crude estimate, the rule of mixtures was applied.

By calculating the shear strain from the transverse and longitudinal strains and the stress applied, the G_{SC} was determined. In accordance with ASTM D3518-94 standard [21] the G_{SC} of elasticity was calculated over a linear portion of the stress curve (1500 – 5500 $\mu\epsilon$).

Figure 12. The V_f -normalised ultimate shear stress (τ_{IPS}) and shear chord modulus (G_{SC}) for the CFRP, SR-CFRP and F-CFRP samples.

The normalised results for τ_{IPS} and G_{SC} are displayed in Figure 12. The F-CFRP samples have shown remarkable improvements in both τ_{IPS} and G_{SC} with improvements (in comparison to the CFRP) of 20 % and 74 %, respectively. Alternatively, SR-CFRP displayed reductions of 8 % and 9 %, respectively. Misalignment of the fibres for the SR-CFRP samples could be a possibility (sizing reduces integrity of the cross ply), however, this would typically result in a large distribution of results, which was not observed. Therefore, it is expected that the degradation is due to the removal of the sizing, as the IPS test is sensitive to surface modifications. Hence the improvement in τ_{IPS} and G_{SC} for F-CFRP, could potentially be alluded to the CNTs improving the interface between fibre and matrix, even more so than that of the polymer sizing.

Kim *et al.* [45] reported improvements of 54 % and 29 % in τ_{IPS} and G_{SC} respectively for their ($\pm 45^\circ$) IPS test for CNT modified samples. They also reported that additional thickness from CNT mat layer decreases in-plane shear strength [45]. Using a double notched compressive IPS test (as per the ASTM D3846 guide [47]), An *et al.* [13] noted a ~70 % increase in τ_{IPS} over the baseline material for their ozone-PEI treated MWCNTs that were attached to the CFs *via*

electrophoretic deposition. After spraying a pre-preg with a SWCNT solution, Kim *et al.* [48] reported a 7 % increase in the τ_{IPS} .

3.6 Interlaminar Fracture Toughness

CFRP (n = 13), SR-CFRP (n = 13), and F-CFRP (n = 13) were tested for the interlaminar fracture toughness (G_I) by progressing a mode-I fracture in a double cantilever beam assembly. A cross ply was used in the form of a $[0/90]_{16}$ configuration, which is not consistent with the ASTM D 5528-01 (2007) [22] standard and which also specifies a larger test sample (125 x 20) mm than that employed in the present work. However, owing to the difficulty of growing CNTs on unidirectional fibres, which commonly relies on a polymer binder that would decompose at CNT growth temperatures, the cross ply was chosen. A bi-directional weave configuration had previously been successfully carried out by Kepple *et al.* [49], who also reported satisfactory data using the same dimensions as in this work. In that study, it was reported that the load applied to drive crack propagation decreased smoothly with increasing crack length.

Analysis of the load vs. displacement data revealed decreasing load in a ‘step-like’ fashion (Figure 13a) and was attributed to the material delaminating in a ‘Velcro-like’ fashion. In other words, the crack front ceased to propagate until enough energy could be transferred to the material to increase the additional fracture surface, leading to crack propagation. However, this load can be beyond the critical toughness value beyond the initial point, hence the material is unable to resist the crack growth in these sections and the result is rapid crack growth.

Figure 13. (a) Typical raw data of the load with increasing displacement, (b) a least squares fit of the compliance ($C^{1/3}$) as a function of the crack length. The inset describes the measurement to determine Δ , which is used to apply the rotation correction.

Sager *et al.* [50] observed similar behaviour to that seen in this work, but in contrast, Kepple *et al.* [49] reported a smooth drop in load with increasing crack length for samples of a similar fibres carbon cross ply and dimensions. However, it should be noted that the data presented to support this claim involved far fewer data points compared with the present work. It is proposed that the trend observed in the work is influenced from the local fluctuations in toughness throughout the interlaminar region, which is expected to result from the bi-directional weave. In addition to the observed step-like load behaviour, bi-directional cross-ply have higher fracture toughness than UD due to the 90° fibres acting as built-in crack arrestors [51], but, they do not display fibre bridging. Thus, comparisons with UD interlaminar fracture toughness testing should be avoided, as fibre bridging is an effective artificial fracture toughness enhancer [52, 53]. During the experiment, any rapid crack growth was difficult to measure with the pip counter, but fortunately, these were easily identified and removed during the rotation correction stage. In common with the results reported by Kepple *et al.* [49], a linear relationship between the cube root of compliance and crack length was observed (Figure 13b), verifying the use of linear elastic fracture mechanics.

The fracture mechanism of the F-CFRP involved a delamination of one of the FF plies from the adjacent CF ply (as opposed to the intended FF-to-FF delamination). This typically occurred after the crack had propagated a significant distance along the sample (Figure 14), but the cause of this phenomenon is not known. Evidently, delamination is favoured between the CF-FF in comparison to the FF-FF ply in this case suggesting increased interlaminar toughness between the two FF plies. As this form of delamination violates the test's criteria, all points that recorded this delamination were removed.

Figure 14. (a) Image of a F-CFRP undergoing interlaminar testing. The FF ply has evidently delaminated from a CF ply
(Inset: for clarity, the red markings indicate the location of the FF plies).

After the pip count data were translated to the crack length, these were plotted against the energy release rate (Figure 15a). Few definitive conclusions can be obtained from the data, given the close proximity of the data points and significant error values from all three materials (especially beyond a crack length of 15 mm, where the data points converge). The large errors are the result of data scatter which is typical of cross ply composites [50], but the initial points ($G_{1c, i}$) can easily be distinguished. The addition of CNTs leads to significant improvements in the initial fracture toughness, even when compared with the sized CFRP. Despite the significant errors in all sets of data, a trend can clearly be seen - the data points reach a critical fracture toughness after the crack has extended to ~15 mm. Following data smoothing (Figure 15b) the F-CFRP (1480 J/m^2) displays greater initial toughness (83%) with respect to the CFRP (810 J/m^2). The SR-CFRP (700 J/m^2) displays a 14% reduction compared to the standard CFRP, suggesting that the polymer sizing plays a role. The F-CFRP and, to a lesser degree, the CFRP displays decreasing fracture toughness with respect to crack length, whereas the SR-CFRP data displays stable behaviour

Figure 15. (a) Graph displaying the energy release rate of the CFRP, SR-CFRP and F-CFRP as a function of crack length. The absence of error bars indicate that only a single measurement contributed to the average, (b) The data has been smoothed for clarity. The initiation fracture toughness value for each type of sample has been identified and labelled.

Typically, for fracture toughness testing, the initial values and propagation values at steady state are compared. Veedu *et al.* [54] opted to compare only the initial fracture toughness values of their SiC fibres (plain weave) modified with CNTs, stating that these initiation values represent the generic fracture toughness and Prel *et al.* [55] suggested that initiation values for fracture toughness are independent of sample thickness. Garcia *et al.* [56] also observed reduction in fracture toughness with crack length for their CNT-modified samples and attributed this to the discontinuous placement of CNTs on the cross ply (although this is not the case in the present work, see Figure 2). Crucially, Composton *et al.* [57] determined that crack initiation values are independent of V_f . It has been previously stated that an increase in the interlayer reduces fibre bridging [55], but unlike UD composites this was not observed for any of the materials [53]. An *et al.* [13] suggested that different V_f fractions may not significantly affect the fracture toughness, but this theory has only been applied to composites with only slight variations in V_f .

An *et al.* [13] reported a 80 % increase in the fracture energy between the ozone- and PEI-treated MWCNTs that were deposited electrophoretically on CFs and CFRP. They observed that the scatter in fracture initiation data obscured clear correlations with treatment times. Elsewhere, Kepple *et al.* [49] reported a 50 % improvement in the fracture toughness for their F-CFRP (plain weave) in comparison to their standard CFRP but they also observed a small increase (~ 6 %) in the fracture toughness for their SR-CFRP (removed through solvent rinsing). Wicks *et al.* [23] observed 67 % and 76 % improvements in the initiation and steady-state fracture toughness respectively, for their F-CFRP. Improvements by CNTs are expected to be the result of additional pull-out fracturing mechanism of the CNTs [56] and due to the crack having to propagate amongst microstructures. However, reduction in the fracture toughness with crack length is not

understood, but is a feature observed in other studies [56] and has also been demonstrated in this work to affect standard materials.

3.7 Electrical Measurements

Electrical measurements were performed in the surface direction for both CFRP ($n = 2, 36$ measurements) and F-CFRP ($n = 2, 36$ measurements) and the results are presented in Table 2. The addition of the CNTs has led to enhancements in electrical conductivity of 400 %. This is a remarkable result when considering that the conductive CFs are aligned in the direction of the measurements. Therefore, CNTs are expected to be bridging the insulating region from the CF ply and the electrical probe as well as increasing electrical percolation pathways in the surface direction.

Table 2. Electrical conductivity results from CFRP and F-CFRP in the surface direction.

<i>Measurement</i>	<i>CFRP</i>	<i>F-CFRP</i>
<i>Electrical Conductivity (S/cm)</i>	(0.23 ± 0.01)	(0.93 ± 0.097)

4. Conclusions

An alternative to the polymer sizing applied to CFs has been demonstrated using a diverse range of mechanical tests for the standard and CNT-modified composite as well as testing an intermediate, sized-removed carbon fibre composite. The testing of the sized-removed samples has provided an accurate insight to the benefits of incorporating CNTs. MWCNTs (dia. 12.5 nm) grown on the carbon fibre (2×10^{10} tubes/cm²) retained integrity of the cross ply and their infusion capability even after the polymer sizing has been removed. The mean interfacial shear strength for a fibre tow pull out test was 32 MPa for the FF compared with 28.5 MPa for the unmodified fibre tow. For the tensile test, the SR-CFRP at GT and F-CFRP displayed an 11 % and 33 % degradation for the σ_{UTS} , respectively - the addition of the CNTs have provided additional degradation beyond the thermal degradation from growing the CNTs. However, the F-CFRP displayed the largest improvement in E_M , with a 146 % increase above the CFRP. For the IPS test, the F-CFRP samples have shown improvements of (in comparison to the CFRP) of 20 % and 74 %, for the τ_{IPS} and G_{SC} , respectively. Alternatively, the SR-CFRP displayed reductions of 8 % and 9 %, respectively. An improvement of 83% in the initial fracture toughness for the F-CFRP (compared to standard, unmodified CFRP) was also observed, whereas the SR-CFRP displayed a 14 % reduction. The addition of CNTs imparted electrical functionalisation to the composite, with remarkable improvements of 400% in the surface direction.

The outcome of the present study is the demonstration of the ability to omit the use of a polymer sizing agent from the production of advanced composites, whilst significantly improving the nature of the polymer matrix/fibre interface and imparting electrical functionalisation. For the mechanical test that were sensitive to the polymer sizing (where degradation was observed for the sized removed samples), improvements were observed for the CNT-modified samples. Alternatively, the CNTs were more effective than the polymer sizing for particular mechanical characteristics associated with the polymer sizing. This methodology has not been optimised and offers further scope for tailoring the interphase region by reducing the concentration of CNTs and increasing their polarity. One of the acknowledged benefits of employing of this technology in advanced composites is the significant enhancement in electrical properties that can be achieved for application as lightning strike protection solution for the aerospace industry.

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