Aligning carbon nanofibres in glass-fibre/epoxy composites to improve interlaminar toughness and crack-detection capability

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Abstract

An electric field is used to align carbon nanofibres (CNFs) in the matrix of a glass-fibre reinforced-polymer (GFRP) composite to simultaneously improve the (a) delamination toughness, (b) electrical conductivity and (c) damage-sensing capability. The CNFs are added to the epoxy resin prior to the manufacture of the GFRP composites. To align the CNFs, an alternating current (AC) electric field of 30 V/mm at 10 kHz is applied across the GFRP sheet throughout the matrix-curing process. The electromechanical force induced by the electric field, applied in the through-thickness direction of the composite sheet, rotates and aligns the CNFs in the direction of the applied electric field prior to the gelation of the epoxy matrix. After curing, the resultant aligned, 'chain-like', microstructure of the CNFs in the epoxy matrix significantly enhances both the interlaminar fracture toughness and the through-thickness electrical conductivity of the GFRP composite. Specifically, the addition of 0.7 vol% of randomly-orientated CNFs in the GFRP composite yielded an ~50% and 25% increase in the values of the mode I fracture toughness pertinent to the initiation, G_{Ici} , and steady-state growth, G_{Icss} , of delamination crack, respectively, compared to the control GFRP composite. The alignment of the CNFs, in the transverse direction to the direction of the crack growth, increases the mode I toughness values of G_{Ici} and G_{Icss} by ~100% and ~80%, respectively, compared to the control GFRP composite. These significant increases are attributable to multiple toughening mechanisms, including debonding of the CNFs from the matrix, void growth of the epoxy matrix, pull-out and rupture of the CNFs. Further the electric-field induced alignment of the CNFs, in the through-thickness direction, increases the out-of-plane electrical conductivity of the GFRP by about twenty-six times, compared to the GFRP composite containing randomly-orientated CNFs. Of

particular interest, the damage-sensing capacity is enhanced for the GFRP composite with aligned CNFs in the epoxy matrix, which stems from the greatly increased out-of-plane electrical conductivity, as confirmed by a modelling study. Therefore, this present work has identified a new strategy to develop GFRP composites with greatly improved delamination toughness, electrical conductivity, and higher crack-detection sensitivity.

Keywords: A: Functional composites; B: Delamination; B: Electrical properties; Carbon nanofibres.

1. Introduction

Fibre-reinforced polymer (FRP) composites, which are increasingly used in aerospace, automotive, and renewable energy industries due to their excellent mass-specific mechanical properties, typically show a relatively low interlaminar strength and fracture toughness. The poor out-of-plane properties of FRPs make them susceptible to microscale damage, such as interfacial debonding and delamination [1-2], parallel to the structural fibres. To overcome these weaknesses, considerable attention has been focused on improving the through-thickness properties of the laminates by various techniques, including z-pinning [3], stitching [4], and 3D weaving [5]. These techniques greatly enhance the interlaminar fracture resistance to large cracks by introducing microscale pins or fibres in the out-of-plane direction. However, microscale reinforcement by these techniques is not very effective in preventing the initiation and growth of relatively small matrix or interlaminar cracks and can degrade the in-plane properties of the composites due to misalignment, crimp, or fracture of the load-carrying in-plane fibres [6].

An appealing alternative approach to improve the delamination resistance, without damaging the structural fibres, is to add various toughening agents, including nanoclays [7], thermoplastic polymers [8], nanoparticles (e.g. nanosilica) [9], carbon black [10], block copolymers [11-12], etc., into the polymer matrix. In particular, carbon nanomaterials with outstanding mechanical properties, including graphene nanoplatelets (GNPs) [13], carbon nanotubes (CNTs) [1], and carbon nanofibres (CNFs) [14], have been intensively investigated as fillers for fibre-reinforced polymer composites. These carbon nanomaterials offer the prospect of improving the interlaminar fracture toughness at a low content by introducing multiple toughening mechanisms, such as crack-bridging, crack pinning, void growth of the matrix, and crack deflection [15-19]. More importantly, adding carbon nanomaterials confers multifunctional properties to the composites, such as enhanced thermal and electrical conductivities as well as better mechanical properties. However, the property improvements achieved

so far by adding carbon nanomaterials as fillers to polymer materials remain much lower than theoretical predictions, which is probably due to the fact that the dispersion, and particularly the orientation, of such nanofillers have not yet been optimized [20]. Theoretical modelling suggests that aligning the nanofillers can result in much larger property improvements compared with randomly-oriented nanofillers [21]. More recently, we have demonstrated experimentally that by aligning CNFs and GNPs using an external electric- or magnetic-field the electrical conductivity, thermal conductivity, and fracture toughness of epoxy polymers can be greatly enhanced, compared to those containing randomly-oriented nanofillers [16-17, 19, 22].

To better utilize the potential of aligned carbon nanofillers to improve the properties of fibre-reinforced composites, some recent investigations have focused on growing nanofillers, mostly CNTs, on the surface of fibres which were subsequently impregnated with a thermosetting resin matrix [23-27]. This technique can control precisely the organization and alignment of the nanofiller around the fibres, leading to significant improvements in both the interlaminar and intralaminar regions of the laminates. However, considerable care must be taken to avoid possible damage to the fibres during the growing process [26-27]. Furthermore, the growing of CNTs on the surface of fibres is relatively expensive and time-consuming. Therefore, in contrast, the concept of using an electric field to alter the distribution of carbon nanofillers, such as carbon black [28] and CNTs [29] in glass-fibre reinforced-plastic (GFRP) composites has been investigated. The results showed that the electrical conductivity was increased by about one order of magnitude in the through-thickness direction by applying an electric field, compared to GFRP composites prepared without the application of the electric field. However, only marginal improvements in the delamination toughness have been reported so far [28-29]. Furthermore, there is a lack of understanding of the effect of alignment on the damage detection sensitivity.

The increase in electrical conductivity brought about by the use of conductive nanofillers, e.g. CNTs and CNFs, has prompted interests in damage sensing [30-32]. CNFs with a high-aspect-ratio are used due to their relatively low cost compared to CNTs [33] while offering good electrical conductivity (i.e. $\sim 10^3$ S/cm). Apart from improving the out-of-plane mechanical properties of the CNF/GFRP composites, the presence of a percolated-CNF network is expected to generate significant improvements in the crack-detection capability for these CNF/GFRPs, arising from their expected greatly increased electrical conductivity in the through-thickness direction. However, it remains unclear how the application of an external electric field during the curing process of the composites would affect their damage-sensing capability. Building on the recent findings that CNFs can

be aligned by external electrical field in polymers to simultaneously enhance fracture toughness, fatigue resistance, and electrical conductivity [15, 18, 34], we present herein an investigation of the electric-field induced alignment of CNFs in glass-fibre composites and its effects on the fracture toughness, electrical conductivity, and the crack detection sensitivity. The electrical responses of the CNF/GFRP composites are measured *in-situ* during the mode I interlaminar fracture tests. A model is then proposed to relate the growth of a delamination crack to the change in electrical resistance. Hence, the crack-detection capability of the CNF/GFRP composites can be assessed.

2. Experimental Section

2.1 Materials

The carbon nanofibres used in the present work are vapour grown carbon nanofibres (VGCNFs) (Pyrograf®-III, grade PR-24-XT-HHT), sourced from Applied Sciences Inc., USA. The CNFs had an average diameter of ~100 nm and a length of between 50 and 200 μm . The epoxy resin used was a liquid blend of bisphenol A and bisphenol F ('105' from West System, Australia) together with a slow-curing hardener ('206' from West System, Australia), being mixed at a weight ratio of 5:1. The glass fibre reinforcement used was a plain-weave E-glass fabric with an areal density of 830 g/m^2 , supplied by Colan, Australia.

2.2 Preparation of the CNF/glass fibre reinforced composites

The procedure for preparing sheets of the CNF/GFRP composites involved three steps. Firstly, the CNFs were dispersed in the liquid epoxy resin using a three-roll milling process, followed by the addition of the hardener. Further details of the CNFs dispersion process can be found in our previous studies [15, 18]. Secondly, a hand lay-up process (as shown in **Fig.1**) was used by applying the CNF/epoxy/hardener dispersion (with 0.70 vol% of CNFs) into eight plies of glass fabric. It should be noted that the selection of 0.70 vol% for this study is based on our previous finding that the epoxy nanocomposites containing 0.70 vol% CNFs show the excellent combination of electrical conductivity and viscosity which are needed for an efficient alignment process [15, 18]. A 25 μm thick Teflon film was inserted at the mid-plane of the composite laminate to act as the pre-crack for mode I double-cantilever beam (DCB) tests. The application of an electric field is expected to align CNFs in the composites as illustrated in **Fig.1a**. To this aim, two thin aluminum plates were placed on the top and bottom of the glass fabric and connected to an AC power source (as shown in **Fig.1b**). A thin plastic (Teflon) film was inserted between the aluminium electrode and the glass fabric stack so that the electrodes were not in

direct contact with CNFs in the matrix, to avoid any Joule heating by electric current. Thirdly, this assembly was wrapped with bleeders and release films inside a vacuum bag, which was evacuated for ~ 30 minutes. The epoxy matrix was then cured at room temperature for 24 h. An AC electric field of 30 V/mm at 10 kHz was applied throughout the matrix-curing process. This level of field strength and frequency were based on our previous studies [15, 17, 22] and were selected to achieve alignment before the resin reaches gelation. Control specimens of GFRP and CNF/GFRP composites were also prepared but without applying an electric field. The glass-fibre volume fraction of the unmodified GFRP composites was ~ 39-44 vol%, which was not significantly different compared to the GFRP composites modified with either randomly-oriented or aligned CNFs (~36-43 vol%). (Here the fibre volume fraction was calculated from $V_f = nA_w/(\rho_f t)$, where A_w , ρ_f , n , and t are the areal weight and density of the fabrics, the number of plies, and the thickness of the cured composites.)

Fig. 1. Schematic illustration of (a) orientation of CNFs in the CNF/GFRP composites and (b) the experimental setup for preparing the composites.

2.3 Mechanical and electrical tests

The mode I interlaminar fracture toughness, G_{Ic} , was measured using an Instron tensile testing machine and DCB specimens with geometry and dimensions as shown in **Fig.2**. The crack-opening load was applied to the specimens at a crosshead speed of 1 mm/minute, in accordance with ASTM Standard D5528. At least three duplicate DCB specimens were tested for each composite type. The load versus displacement curves were recorded, and the crack growth was monitored using a travelling microscope. For the *in-situ* crack-growth sensing tests, two conductive silver-paint electrodes were positioned directly above and below the initial crack tip, respectively. Before applying the silver paint, the resin-rich surface layer of the laminates was gently sanded

to reduce the contact resistance. Thin copper wires were attached to the electrodes and were connected to a digital multimeter (34465A, Keysight Technologies) to record the resistance continuously as the delamination crack propagated.

Fig. 2. Schematic illustration for the specimen used for the mode I interlaminar fracture toughness and the *in-situ* resistance measurement.

2.4 Alignment, electrical conductivity and fractographic studies

The angular distribution of the CNFs after they were dispersed in the liquid epoxy-resin was measured using a Leica optical microscope. The liquid CNFs/epoxy resin mixture was placed on a glass slide. Two parallel aluminum tapes were used as the electrodes for the application of the electric field and time-lapse images were acquired. The DC and AC electrical conductivities in the out-of-plane and in-plane directions were measured using a resistance meter and impedance analyser (HP4192A), respectively. After DCB testing, the fracture surfaces and side-views of the crack tip regions were sectioned and sputter-coated with a thin layer of gold for examination using a FEI Nova NanoSEM scanning-electron microscope (SEM) operated at 15 kV with a 5 mm working distance.

3. Results and Discussion

3.1 Morphological characterization

When subjected to an external electric field, a non-spherical solid particle in a dielectric liquid medium will rotate to align itself in the direction of the applied electric field, via a dielectrophoresis process [15, 17, 22]. This has been demonstrated in our previous work using nanomaterials such as CNFs [15, 22] and graphene

nanoplatelets [17] in epoxy resin. Briefly, without application of the electric field, the CNFs are evenly dispersed in an liquid epoxy resin. This is shown in **Fig.3a**, where it can be seen that the CNFs show no preferential orientation and very little aggregation. The application of the electric field results in rotation and alignment of the CNFs along the field direction, followed by a ‘chain formation’, termed ‘chaining’, of the CNFs. This can be clearly seen in **Fig.3b** which is an optical micrograph of the mixture of the CNFs and liquid epoxy resin after applying an electric field of 30 V/mm for 10 minutes. Any possible effects of the glass fibres interfering with such an alignment of the CNFs under electric field were investigated by placing glass fibres in the liquid epoxy-resin/CNF mixture. **Figs.3c-d** reveal that the glass fibres do not hinder the alignment of CNFs, suggesting that the CNFs will indeed align in the GFRP composite. The alignment of the CNFs will, of course, be preserved upon curing of the epoxy resin, as was demonstrated in our previous work [15, 17, 22].

Fig. 3. Optical micrographs of the *in-situ* alignment of 0.05 vol% CNFs in the liquid epoxy resin: (a-b) without and (c-d) with the presence of glass fibres. In (a) and (c) no electric field was applied; and in (b) and (d) the time period for the application of the AC electric field was $t=10$ minutes. (In (b) and (d) the direction of the applied AC electric field is indicated as EF, i.e. from bottom to top of the micrographs. Note that the concentration of CNFs has been reduced to 0.05 vol% to facilitate the imaging.)

The alignment and distribution of the CNFs in the cured composites were examined by using the SEM and optical microscopy. **Fig.4** shows the fracture surface of a DCB test specimen, clearly indicating that the CNFs are present in both the resin-rich areas as well as in the narrow resin channels between fibres in a ply. To further investigate the distribution and alignment of CNFs within the composites, cross-sections of the composites were examined using optical microscopy. **Figs.5a-c** indicate that the CNFs are aligned in the resin regions between plies. In contrast, no alignment is observed for the CNF/GFRP composite manufactured without applying an electric field, see **Fig.5d**, i.e. where the CNFs were randomly orientated in the epoxy matrix.

Fig. 4. SEM micrographs of the delamination fracture surfaces of the 0.70 vol% CNF/GFRP composite cured under the electric field: (a) low magnification view; (b) the relatively narrow resin microchannel between the glass fibres (from the region marked by the rectangle in (a)); (c) the relatively wide resin microchannel between the glass fibres (from the region marked by the oval in (a)).

Fig. 5. Optical micrographs of the cured CNF/GFRP composites: (a-c) with the application of the AC electric field and (d) without the application of the AC electric field. Note that (b) and (c) are from the regions marked by the rectangle and oval in (a), respectively. The arrows indicate the orientation of the CNFs. (In (a-c) the direction of the applied AC electric field (EF) is indicated (i.e. from top to bottom of the micrograph).)

3.2 Mode I interlaminar fracture toughness of the composites

Fig.6a shows the typical mode I crack-growth resistance (i.e. R-curve) behaviour of the various types of the GFRP composites under quasi-static loading, as measured using the DCB test specimens. The value of the interlaminar fracture toughness, G_{Ic} , for all the composites increased over the initial 10 to 15 mm of delamination growth and then reached a steady-state propagation (i.e. plateau), G_{Icss} , value. The R-curve behaviour was attributable to the bridging by cross-over fibres in the wake of the advancing delamination crack. **Fig.6b** summarizes the average values of the crack initiation, G_{Ici} , and steady-state, G_{Icss} , interlaminar fracture toughnesses of the composites. The presence of randomly-orientated CNFs in the GFRP composite results in 50% and 25% increases in G_{Ici} and G_{Icss} , respectively, compared to the GFRP composites without CNFs. Of greater note, it is found that the application of the electric field further increases the values of G_{Ici} and G_{Icss} by about

100% and 80% respectively for the GFRP composite containing aligned CNFs, compared to the GFRP composite without CNFs. The improvements in the values of the interlaminar fracture toughness, G_{Ic} , caused by the introduction of the CNFs (randomly-orientated and aligned) from the present study are compared in **Table 1** to values measured using other fillers, such as CNTs, silica nanoparticles, nanoclay and rubber mircoparticles, as reported in the literature [35-36]. As may be seen, the improvements in the values of G_{Ic} from the introduction of the CNFs is relatively moderate. However, for most of the fillers, a significantly higher content is needed to achieve similar levels of improvements, except for some CNT-epoxy matrix systems. Also, it should be noted that the toughening efficiency induced by adding such fillers is highly dependent on the degree of crosslinking of the epoxy matrix, as demonstrated by Kinloch et al. [37]. Therefore, it is important to take into consideration the glass transition temperature, T_g , of the epoxy matrix when making such comparisons.

Fig. 6. The quasi-static (a) crack growth resistance-curves (i.e. R-curves) and (b) Mode I interlaminar fracture toughness values for crack initiation, G_{Ici} , and steady-state (i.e. plateau) propagation, G_{Icss} , for the GFRP composites which contain no CNFs (i.e. the control GFRP composite) and for the GFRP composites containing 0.70 vol% of randomly-oriented or aligned CNFs. (The error bars indicate the measured standard deviations.)

Table 1 Examples of improvements in the fracture toughness, G_{Ic} , of hierarchical-filled composites

Fibre	T_g of the epoxy matrix ($^{\circ}\text{C}$)	Toughening agent/filler	Content	G_{Ic}^1 improvement	Ref.
Glass fibre	60	CNFs	1 wt%	25% (Random) 80% (Aligned)	Present work
Glass fibre	144	CTBN ² microparticles	15 wt%	1145%	[38]
Glass fibre	153	CTBN microparticles	9 wt%	168%	[39]
		Nanosilica particles	10 wt%	207%	
Glass fibre		CTBN microparticles	9 wt%	44%	
		Nanosilica particles	10 wt%	-13%	
Carbon fibre		CTBN microparticles	9 wt%	137%	
		Nanosilica particles	12 wt%	11%	
Carbon fibre	90	CNTs	0.5 wt%	Up to 80%	[40]
Carbon fibre	Not provided	MWCNTs	0.1-1 wt%	Up to 33%	[41]
Carbon fibre	Not provided	Cup-stacked CNTs	5 wt%	98%	[42]
Carbon fibre	Not provided	Montmorillonite nanoclays particulates	4 wt%	85%	[7]
Carbon fibre	154	Triblock copolymers ³	5-15 wt%	Up to 290%	[43]

¹ G_{Ic} values listed in the Table are equivalent to the steady-state interlaminar fracture toughness, G_{Icss} ;

²Carboxyl-terminated butadiene-acrylonitrile rubber;

³Poly(styrene)-poly(butadiene)-poly(methyl methacrylate) triblock copolymers.

SEM micrographs of the fracture surfaces of DCB specimens of the control GFRP composite and GFRP composites containing 0.70 vol% of CNFs are shown in **Figs. 7a-d**. For the control GFRP composite shown in **Fig. 7a**, the fracture surface shows clean, debonded fibres, with little or no epoxy matrix on the fibre surfaces. This indicates a predominantly adhesion failure at the fibre/matrix interface which is often associated with a low resistance to crack propagation. Also, the typical featureless and smooth fracture surface indicates brittle fracture of the epoxy matrix within the plies. In contrast, the fracture surfaces of the CNF/GFRP composites (**Figs. 7b-d**) show that the crack tends to propagate more within the epoxy rich regions. **Fig. 7b** is a typical

SEM image of the fracture surface and shows a much rougher fracture surface compared to that of the control GFRP composite, with features such as tear marks which indicate that plastic deformation of the epoxy matrix has accompanied crack growth. Further, as shown in **Figs. 7c-d**, some CNFs have been (a) debonded from the matrix which has initiated significant void growth of the epoxy matrix surrounding the disbonded CNFs, and (b) pulled-out from the opposing fracture surfaces and then fractured. These various features account for the large increase observed in the delamination toughness due to the CNFs initiating multiple toughening mechanisms.

Fig. 7. SEM micrographs of the mode I interlaminar fracture surface of (a) the control GFRP composite and (b)-(d) the GFRP composite containing aligned CNFs. Micrographs (c) and (d) are taken from the regions marked by the blue oval and rectangle in (b), respectively. (Note that the arrows in yellow indicate CNF pull-out and rupture, while arrows in blue indicate void-growth of the epoxy matrix).

Further studies on the crack growth behaviour were conducted by observing the side-view of the DCB specimens of the CNF/GFRP composites (**Fig. 8**). It was observed that the crack propagated along the interfaces between adjacent glass-woven fabrics (**Fig. 8a**). However, frequently the crack-front deflects and propagates

within an epoxy rich-region (marked by the dashed yellow oval in **Fig. 8b**). Behind the crack tip, the extrinsic toughening mechanisms of CNF pull-out, crack-bridging and fracture are clearly visible (**Fig. 8c**). During these processes a relatively large amount of stored strain-energy is dissipated due to (a) the interfacial frictional sliding between the CNFs as they bridge behind the crack tip and the matrix and (b) the fracture of the CNFs. Furthermore, the alignment of the CNFs perpendicular to the crack path results in a higher fraction of CNFs participating in these toughening mechanisms. Therefore, when the CNFs are aligned, they are far more likely to be pulled-out, and hence bridge the interlaminar crack, and then be fractured; as has also been seen for aligned CNTs grown on the surfaces of the fibres in a woven-fabric ply [27]. Therefore, a higher delamination fracture toughness is observed for the GFRP composite manufactured under the application of an electric field that aligns the CNFs in the epoxy polymer matrix.

Fig. 8. Side-view of the crack tip of the GFRP composite containing aligned CNFs from the DCB tests: (a) and (b) low-magnification views; (c) is taken from the region marked by the blue rectangle in (b). Note that in (b) the region marked by the yellow oval indicates where the crack front has deflected. In (c) the yellow arrows indicate CNF pull-out while the white arrows indicate CNF bridging.

3.3 Electrical conductivity studies

The electrical properties of the control GFRP composite and the GFRP composites containing either randomly-orientated CNFs or aligned CNFs were measured. The DC conductivities along the fibre direction, denoted as σ_{11} , and the through-thickness direction, denoted as σ_{33} , are given in **Fig. 9a**. Significant increases of approximately four and seven orders of magnitude in the out-of-plane and in-plane conductivities, respectively, have been achieved by adding 0.70 vol% of randomly-orientated CNFs, compared to the control GFRP composite. The anisotropy is undoubtedly due to the architecture of the composites, whereby the insulating glass-fibre layers are laid-up with the conductive CNF/epoxy-matrix regions being continuous in the in-plane direction between the glass-fabric plies. In contrast, in the through-thickness direction, the conductive epoxy/CNFs regions are interrupted by the glass fibres. Therefore, the conductivities of the CNF/GFRP composites in the through-thickness direction are much lower than that for the in-plane direction.

The alignment of the CNFs in the GFRP composite using the externally applied electric field greatly increases the electrical conductivity in the through-thickness direction. As shown in **Fig. 9a**, the electrical conductivity in the through-thickness direction increases by as much as about twenty-six times, when compared to that of the GFRP composite containing the randomly-orientated CNFs. Such increases in the electrical conductivities in epoxy nanocomposites with a carbon nanofiller aligned using an electric field or magnetic field has also been demonstrated in our previous work [15-17, 19, 22]. These results are due to the preferential orientation and aggregation, i.e. ‘chain formation’, of the CNFs or graphene nanofillers when aligned in the through-thickness direction. However, in contrast, the in-plane conductivities of the CNF/GFRP composites remain almost unaffected by the application of the electric field; with a value of about 5.8×10^{-3} S/m being measured for the aligned-CNF/GFRP composite, compared to a value of $\sim 7.2 \times 10^{-3}$ S/m for the randomly-orientated CNF/GFRP composite which have not been exposed to the electric field.

Fig. 9b shows logarithmic plots of the AC conductivity as a function of the frequency in the through-thickness direction for the control GFRP composite and the GFRP composites containing randomly-orientated CNFs or aligned CNFs. The control GFRP composite exhibit the behaviour typical of an insulator, with the AC conductivity increasing linearly on a logarithmic versus logarithmic plot. In contrast, the GFRP composites containing CNFs show a plateau (i.e. a frequency-independent conductivity) up to a critical frequency, which can be explained by a resistance-capacitance model as discussed in our previous work [15]. This low-frequency

plateau corresponds to the behaviour of a finite conductor. A linear dependency is observed above the critical frequency, which corresponds to a capacitive response. Upon the application of the electric field to CNF/GFRP composites, the low-frequency plateau conductivity increases from $\sim 3.2 \times 10^{-6}$ to $\sim 8.7 \times 10^{-5}$ S/m, in agreement with the DC conductivity results measured using a resistance meter.

Fig. 9. (a) In-plane (σ_{11}) and out-of-plane (σ_{33}) DC conductivities and (b) out-of-plane AC conductivities (σ_{33}) for the control GFRP composite and the GFRP composites containing 0.70 vol% of randomly-oriented and aligned CNFs in the epoxy matrix.

3.4 In-situ resistance measurements during the DCB fracture test (i.e. in-situ damage-sensing)

The technique of determining the crack length, a , by measuring the change in the electrical resistance was reported by Fischer and Arendts [44] for a carbon-fibre reinforced-plastic (CFRP) composite. To extend this approach to GFRP composites, which are insulators, it is necessary to add conductive fillers such as carbon black or CNTs [45-46]. The present work for the first time investigates the effects of alignment of the nanofillers on the crack-detection sensitivity. To this end, we have measured the electrical resistance *in-situ* during the mode I interlaminar DCB fracture tests (a) to investigate the damage-sensing capability of the CNF/GFRP composites and (b) to study the effects of the alignment of the CNFs on the mechanical, electrical, and damage detection properties of the GFRP composites.

Figs.10a and **10b** show the typical applied load versus displacement curves and the *in-situ* electrical resistance changes across the GFRP composites containing randomly-orientated and aligned CNFs, respectively. During

the DCB tests, for both types of CNF/GFRP composites, a series of unstable, stick-slip crack growth steps occurred which, as may be seen, were reflected in the measured applied load versus displacement traces. Each stick-slip point in the load versus displacement curve was accompanied by an increment of crack growth. The conductive area of the DCB specimen therefore decreased, leading to the through-thickness electrical resistance increasing in a stepwise manner. The normalized changes in the electrical resistance that occurred over the incremental growth of the crack up to ~ 60 mm (i.e. 50% of the total length of the DCB test specimen) are presented in **Fig.11a**. It is interesting to note that the GFRP composite containing the aligned CNFs show a significantly larger resistance change for the same increment of crack growth, indicating a higher crack-detection sensitivity than the GFRP composite with randomly-orientated CNFs in the epoxy matrix. The present GFRP composites containing CNFs show a relatively large resistance change for the same crack increment (i.e. $\Delta a/(L-a_0)$) compared to the recently reported carbon fibre/epoxy composites containing graphene/epoxy interleaves by Du et al. [47]. However, it should be noted that the change in electrical resistivity depends on the fibre type (e.g. conductive carbon fibres or insulating glass fibres), the content and dispersion/orientation state of the conductive nanofillers, the testing methods which may introduce different failure and damage mechanisms (e.g. delamination, microcracking, fibre breakage, etc.) and the way that the nanofillers are incorporated into the composite (e.g. whether the nanofillers are dispersed in the epoxy matrix or spray-coated onto the surfaces of the fibres) [48].

To better understand the measured crack-sensing performance of the CNF/GFRP composites, the relationship is presented below for the change in the electrical resistance relative to the increment of crack growth. **Fig. 11b** shows a schematic of the expected current path and the dimensions of the DCB test specimen. In the special case of strong orthotropy, i.e., $\sigma_{33} \ll \sigma_{11}$, the total electrical resistance, R , measured between the electrodes positioned at the initial crack tip location is the sum of the resistances of the composite ahead of the crack tip, denoted as R_1 , and of the delaminated half-laminates behind the crack tip (between the electrodes and the crack tip), denoted as R_2 [31]. As the crack propagates (i.e. the incremental increase in crack length, $\Delta a > 0$), the uncracked area decreases, leading to an increase in the out-of-plane (i.e. through-thickness) resistance. The resistance is inversely proportional to the uncracked area which may be expressed as $b * (L - a_0 - \Delta a)$. Therefore, the total resistance, R , between the electrodes at the crack tip is:

$$R = R_1 + 2R_2 \quad (1)$$

In the limiting case of σ_{11} being much greater than σ_{33} , which is the true for GFRP with either random or aligned CNFs, the respective resistance values, R_1 and R_2 , can be approximated by [31]:

$$R_1 = \frac{t}{\sigma_{33}b(L-a_0-\Delta a)} \quad (2a)$$

$$R_2 = \frac{2\Delta a}{\sigma_{11}b(t/2)} = \frac{4\Delta a}{\sigma_{11}bt} \quad (2b)$$

The parameters b , L , and t are the width, length, and thickness of the specimen, respectively. The initial resistance, R_0 , (at $\Delta a = 0$) is given by:

$$R_0 = \frac{t}{\sigma_{33}b(L-a_0)} \quad (3)$$

The normalized resistance change, $\Delta R/R_0$, hence becomes:

$$\frac{\Delta R}{R_0} = \frac{R-R_0}{R_0} = \left(\frac{4(L-a_0)^2\sigma_{33}}{t^2\sigma_{11}} + \frac{1}{1-\frac{\Delta a}{L-a_0}} \right) \frac{\Delta a}{L-a_0} \quad (4)$$

From Eqn. (4) the predicted changes in electrical resistance as a function of the normalized crack growth may be calculated. The values of σ_{33} and σ_{11} for the CNF/GFRP composite containing the randomly-orientated or the aligned CNFs were taken from the data presented in **Fig. 9a**. The results from the model are given in **Fig. 11a**, where the predictions are compared to the experimental results for two duplicate DCB test specimens. An excellent agreement is seen between the model predictions and the experimental results. Thus, these modelling studies reveal that the greatly increased electrical resistance changes observed for the aligned-CNF/GFRP composite can be attributed to the remarkable increase in the out-of-plane conductivity of these materials, leading to the increase in the ratio of σ_{33}/σ_{11} to 1.5×10^{-2} for the GFRP composite containing the aligned CNFs, from 4.4×10^{-4} for the GFRP composite containing the randomly-orientated CNFs.

Further tests were conducted to identify the effect of unloading on the measured resistance change of the DCB test specimen. The electrical resistances for ‘closed cracks’ were recorded after completely unloading the DCB specimens with varying crack lengths. **Fig. 11c** gives the typical results and shows the difference in the measured changes in resistance between ‘open cracks’ and ‘closed cracks’ in the DCB test. It is found that the

resistance is somewhat reduced upon crack closure, which may be attributed to the re-formation of the conductive pathways between pulled-out CNFs on the fracture surfaces of the composite. Moreover, the piezoresistivity of the composites may also contribute to this difference, i.e. the resistance increases when the specimen is loaded which recovers when the load is released [49]. The estimated crack lengths, using Eqn. (4) and based on the resistance that was recorded when the crack was closed, are thus smaller in value when compared to those measured experimentally.

Fig. 10. Typical load versus displacement curves and the *in-situ* electrical resistance change for the GFRP composites containing (a) randomly-oriented or (b) aligned CNFs, respectively.

Fig. 11. (a) The normalized electrical resistance change as a function of the normalized crack growth from the experimental measurements, for duplicate test specimens, and from the modelling studies; (b) schematic showing the expected current path; (c) comparison of the changes in electrical resistance measured while the DCB test specimen was loaded or completely unloaded.

4. Conclusions

An electric field has been used to align carbon nanofibres (CNFs) in the matrix of a glass-fibre reinforced-polymer (GFRP) composite to simultaneously improve the (a) delamination toughness, (b) electrical conductivity and (c) damage-sensing capability.

- Improvements of 50% and 25% in the initiation and steady-state interlaminar fracture toughness have been measured for the GFRP composite containing randomly-orientated CNFs in the epoxy matrix, compared to the GFRP composite without CNFs. The alignment of the CNFs in the direction transverse to the crack

growth direction further enhanced the interlaminar fracture resistance. That is, the initiation and steady-state fracture toughness were about 100% and 80% higher when compared to the unmodified GFRP composite. These increases are attributable to several toughening mechanisms, including debonding and pull-out of CNFs, void growth around CNFs in the matrix, and rupture of the CNFs. When the CNFs were aligned in the GFRP composite, as opposed to being randomly-orientated, they were far more likely to be pulled-out and be effective in bridging an interlaminar crack, leading to the higher interlaminar fracture toughness.

- Adding CNFs to the epoxy matrix of the GFRP composites also improved the electrical conductivities of the composite in both the in-plane and out-of-plane (i.e. through-thickness) directions. By aligning the CNFs in the through-thickness direction, the out-of-plane electrical conductivity of the composite was further increased by around twenty-six times compared to that of the GFRP composite containing randomly-orientated CNFs. However, the in-plane conductivities of the GFRP composites remain similar.
- The crack-detection capability of the CNF/GFRP composites has been investigated. It is interesting to note that the GFRP composite containing the aligned CNFs displayed a greater change in their electrical resistance with an advancing crack in the fracture toughness test, i.e. they exhibited a greater damage-detection sensitivity. A model for the relationship between the change in the electrical resistance and the extent of crack growth has been developed, which correlates very well with the experimental results from ‘open-crack’ measurements. Based on this model, the higher sensitivity of the aligned-CNF/GFRP composite has been attributed to the greatly increased out-of-plane conductivity for the GFRP composite containing the aligned CNFs in the epoxy matrix.

This research has demonstrated that the use of an applied electric field to align CNFs in the matrix of a GFRP composite is a very promising technique for developing multi-functional GFRP composites which possess a greatly improved delamination toughness, electrical conductivity and crack-detection sensitivity.

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