DAMAGE SENSING IN FIBRE-REINFORCED COMPOSITES USING CARBON NANOTUBE NETWORKS BY SPRAY COATING

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Keywords: Damage sensing, Airbrushing, Hybrid composites, Carbon nanotubes

Abstract

An innovative route to deliver carbon nanotubes (CNTs) into fibre-reinforced composites with homogeneous dispersion and localization at damage prone zones is introduced, which has also overcome the high viscosity issue associated with the introduction of CNTs in composites resin for liquid moulding manufacturing routes. Spraying of CNTs gives leads to good dispersion on fibre preforms and percolated networks at extremely low nanotube concentrations (0.012 wt.%). These networks were used as a sensing tool to detect internal damage and micro-cracking in composites laminates. The use of sprayed CNTs networks for in-situ damage sensing was set-up and characterized. The measured change in electrical resistivity was correlated with the change in mechanical deformation, providing the possibility to monitor damage. The effect of the addition of CNTs at the fibre/matrix interface on interlaminar properties has also been characterized and analysed.

1 Introduction

The demand of using fibre-reinforced composites has significantly increased in recent years, which raises concern on their health monitoring and in-service damage detection, especially for structural components. Various failure modes can be found in fibre-reinforced composites such as matrix cracking, delamination, and fibre breakage [1-3]. Many studies had been addressing the issue of real time damage sensing in fibre-reinforced composites [4-6], by measuring electrical resistance in composites and then correlating these with mechanical deformation to estimate the internal damage state in composites. For carbon fibre reinforced plastics (CFRPs), the use of electrical resistance measurement to detect damage is widely used, although mainly focused on fibre breakage rather than matrix dominated failure [6-8]. In the case of glass fibre reinforced plastics (GFRPs), due to the insulating nature of glass fibre and epoxy resin, conductive fillers such as metal particles and carbon black have been added in order to perform damage sensing [5, 6]. The addition of conductive fillers to polymer resins has the added advantage that this will allow for the monitoring of early damage modes such as matrix cracking and delamination, rather than fibre breakage which happens typically near the end of a components life time.

Carbon nanotubes (CNTs) are the ideal multi-functional filler for composites, not only because of their extraordinary electrical, mechanical, and thermal properties, but also because of their extremely high aspect ratio (length to diameter) which significantly lowers the percolation threshold of electrical conductivity [9-11]. The dimensions of CNTs which are at least three orders lower than that of glass or carbon fibres, provides opportunities to localize them in between fibres and at fibre/matrix interfaces, which is the most desirable position for both damage sensing properties and mechanical reinforcement. Nevertheless, the nanoscale dimensions of CNTs also make them prone to form agglomerates, making the dispersion of CNTs in polymer resins a challenge.

Although great efforts on CNT dispersion in various polymeric matrices have been made [7, 12], homogeneous dispersions remain challenging, especially in liquid moulding processes based on thermosetting resins. Traditionally, CNTs are introduced by mixing them into a resin such as epoxy before subsequent composites manufacturing procedures, leading to an increase in viscosity of the resin which interferes with composite manufacturing processes such as resin transfer moulding (RTM). In addition, spatial control of the CNTs in the epoxy matrix is not feasible, using conventional mixing strategies.

Spraying or airbrushing techniques are one of the simplest methods to deposit and disperse materials onto a substrate, using strong airflows to generate very fine droplets from liquids drawn in the nozzle, creating a spray which can be directly delivered onto collecting substrates such as films, fabrics or fibres. Apart from its simplicity and versatility, airbrushing techniques are also easy to scale-up which is very important for automated production in industries. After sonication, which breaks down most of the CNTs agglomerates in the spraying solution, the strong air-flow within the airbrush chamber can further break down the weak entanglements within CNT bundles, enhancing the dispersion of CNTs.

It is well known that fibre-reinforced composites possess great mechanical properties such as high specific stiffness and strength, which allows them to be used in various engineering applications. Unfortunately, due to the brittle nature of thermosetting resins such as epoxies, laminated composites are suffering from low toughness, especially in out-of-plane loadings, which greatly limits their potential [13, 14]. The deposition of CNTs on reinforcing fibre surfaces is also expected to enhance mechanical properties at the interfacial region, improving the resistance to delamination and other matrix dominated properties such as transverse matrix cracking and delaminations, making the CNTs act as truly multi-functional nanofillers.

In this work, CNTs were deposited by airbrushing techniques onto glass fibre fabrics, where they formed conductive percolated networks for in-situ damage sensing detection in GFRPs. Concentrations were as low as 0.012 wt.% CNTs, and composite laminates were fabricated using a vacuum assisted resin transfer moulding (VARTM) processes. In-situ damage sensing during mode-I interlaminar testing was set up and changes in electrical resistance were recorded and correlated with the force applied during the test. It was shown that airbrushing is an effective technique to disperse and deliver CNTs onto fabrics, providing very good levels of dispersion of CNTs at low concentrations, with the potential to use this for damage sensing in GFRPs. Mechanical reinforcement in the interlaminar region due to the presence of CNTs at the fibre/epoxy interface was evaluated in terms of interlaminar fracture toughness tests.

2 Materials and experimental procedures

2.1 Materials

The composites system employed in this work is based on a 2x2 twill glass fibre woven fabric, which is supplied by SIGMATEX (UK) Ltd., with an areal weight of 876 g/m^2, and a two component epoxy resin system RTM6-2 from HexFlow®. Release film used is A6000 supplied by Aerovac. The non-functionalized high aspect ratio multi-walled carbon nanotubes are supplied from Nanocyl (Belgium) (Product No. C7000), and methanol is from VWR.

2.2 Airbrushing

Measured amounts of CNTs were dispersed into methanol, using an ultra-sonication probe to break down the CNTs agglomerates, with 20% of maximum amplitude and 5000 joules energy. After sonication, the solution was placed into an airbrush container for spraying deposition. Two stages airbrushing using an Iwata Performance plus model H4001 HP-CPLUS, connected to an Iwata studio series air compressor, with parameters: 30 psi (2.07 bar) for air pressure and 10 cm for the distance between spraying nozzle and fibre substrate. These parameters were optimized after various trials. A heating stage was also applied underneath the glass fibre fabric during airbrushing in order to aid evaporation of solvent. All these parameters were optimized in order to achieve a homogeneous CNT dispersion on the glass fibre fabrics.

2.3 Resin infusion

Vacuum assisted resin transfer moulding (VARTM) was used to manufacture composite laminates based on six plies of glass fibre fabric and five interlayers of CNT deposited by airbrushing. The epoxy resin and mould was preheated to 80 °C, and 110 °C, respectively. After degassing of epoxy resin for 30 min in a vacuum oven, the infusion process was carried out under a vacuum of 1 bar. The impregnated sample and mould was then heated in an oven at the rate of 3 °C/min up to a temperature of 140 °C for 1.5 hrs. Post curing was then carried out at a temperature of 180 °C for another 2 hrs using the same heating rate. For the mode-I fracture toughness tests, release film was placed in the middle layer of the glass woven composite laminates, acting as a starting point of interlaminar failure.

2.4Mode-I interlaminar toughness testing

The cured woven composite panels were cut by a diamond blade into specimens with dimensions of 135 mm (in length) by 20 mm (in width). Double cantilever bending (DCB) testing was performed to examine the Mode-I interlaminar fracture toughness of the CNT coated fabric composites, with test conditions being in accordance with ASTM D5528 [15]. An Instron 5566 universal testing machine equipped with a 1 kN load cell was used for the DCB test, with the test speed being 1 mm/min. The load-displacement data and delamination crack propagation length was recorded, respectively.

2.5 In-situ damage sensing

The edges of the pre-opened specimen ends were cut open to expose some of the composites laminate, and thin copper wire was positioned along the width of the exposed edge by silver paint. After the silver paint dried, a layer of epoxy was placed on top to completely cover it, in order to not only anchor and ensure the connection, but also prevent the surface resistance affect the tested volume resistance results. The electrodes were directly connected with copper wire on both tabs to measure the volume resistance of the specimen, equipped by Agilent 34401A digit multi-metre with four-wire direct current measurement throughout the test.

3 Results and Discussion

3.1 CNTs coated glass fibre fabric and fracture surface morphology

The dispersion of CNTs on glass fibre fabric after airbrushing (Fig. 1a and 1b), and fracture surface of the tested specimen (Fig. 1c and 1d) was examined by SEM. A very good and homogeneous CNT dispersion is clearly observed, as shown in Fig.1 below. No obvious CNT agglomeration is apparent in both the matrix and the interfacial region. As expected, localization of CNTs in the damage prone matrix and interfacial zone in between fibres has been achieved. The CNTs deposited by airbrushing are not only positioned near the surface of the glass fibre, but also in the matrix region in between glass fibres. This is attributed to two main factors: first, the strong airflow during the airbrushing deposition which directly positions CNTs within the gaps between glass fibres; secondly, the infusion process during the VARTM, which aids to some of the CNTs to migrate into the infused epoxy resin, especially as a result of through thickness resin flow.

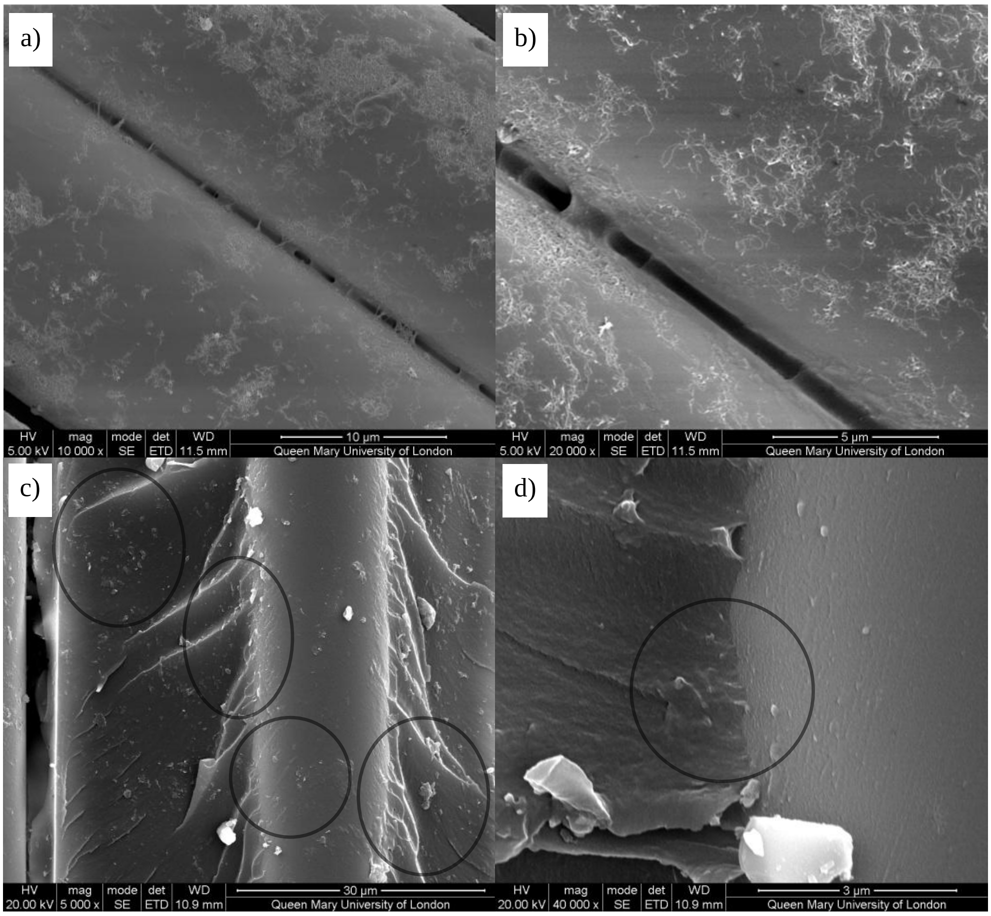

Figure 1. SEM images of 0.012 wt.% CNTs coated glass fibre fabrics: a) relatively low magnification for CNTs dispersion on glass fibre fabrics, b) higher magnification view for interfacial region, c) relatively low magnification for larger area view of CNT dispersion, d) relatively high magnification view for CNTs near the interfacial region.

From the SEM fracture surface images, it can be seen that the glass fibres were well covered by epoxy, indicating good adhesion between fibres and resin with the presence of CNTs.

CNTs could also be found in the connected interfacial regions between fibres and matrix (see Fig. 1d), which also can contribute to better stress transfer compared to composites without CNTs. The well dispersed CNT network within these GFRPs can now be used for damage sensing through the monitoring of resistivity changes with progressive cracking.

3.2 In-situ damage sensing

Using spraying technology a percolation threshold as low as 0.012 wt.% could be achieved, indicating excellent dispersion and network formation of CNTs within the composites. The obtained electrical conductivity is believed to be not only attributed to an initial dispersion of CNTs onto the fibres, but also due to a "dynamic percolation" process [16, 17] to take place after the infusion process, but before complete cross-linking of the epoxy resin as this will block all possible movements of CNTs.

As mentioned before, the in-situ damage sensing test is established on the basis of the existence of a conductive percolated CNT network. Simultaneously with the load-displacement data read out from the DCB test, the volumetric electrical resistance of the specimen was measured and recorded, as plotted in Fig. 2.

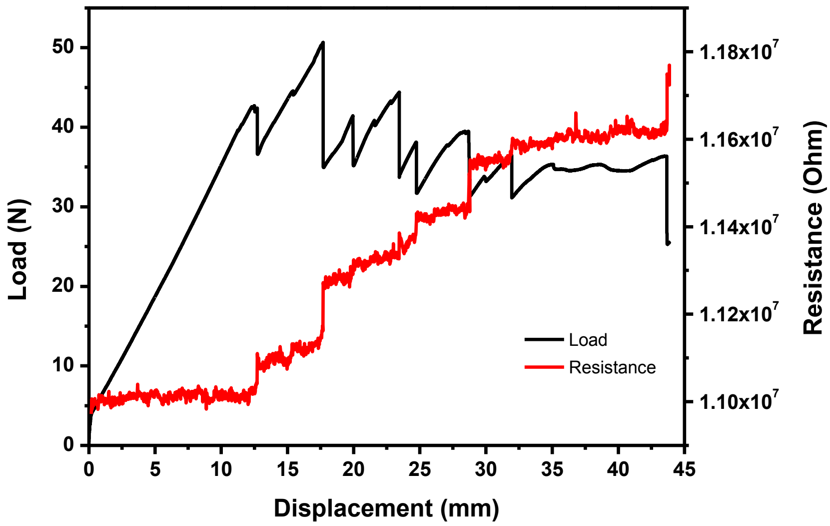

Figure 2. The in-situ damage sensing results: measured volume resistance of the specimen during the DCB test, accompanying with load-displacement curve

A typical applied load and corresponding displacement curve for the DCB specimens is shown in Fig. 2. The applied load increased linearly to a maximum, followed by a sudden load drop as the crack propagated in a rather unstable manner. This unstable fracture is typical for glass fabric/epoxy laminates, exhibiting fibre rich and resin rich regions, leading to differences in local toughness and consequently unstable crack propagation. After crack initiation, the force builds up again, until causing the crack to propagate which results in a load drop. This process is carried out until the crack length of the specimen reaches a certain value. The load-displacement curves can also been analysed to obtain the exact displacement value for each load drop, to be used for the further analysis of the damage sensing study. As the crack opens, the overall trend of electrical resistance is increasing, which is due to the longer distance for the electrons to pass-through the testing samples. Each load drop is associated with a resistance jump and indicates a breakdown of the CNT conductive network due to crack propagation.

It can be clearly seen that with each load drop, the electrical resistance increases from a starting level to a higher level, which is maintained until the next load drop. The increment of electrical resistance which can be attributed to crack initiation and propagation can be correlated to each associated load drop. This correlation confirms that the spray-coated conductive CNT network on the glass fibre fabrics can be used as a sensitive tool to detect micro-cracking within the composite specimens during mechanical deformation.

To develop a further understand of the relationship between measured electrical resistance and internal damage of the specimen, the derivative of the force curves was plotted. According to each negative value on these derivative curves, the exact point of cracking point can be found and with this the resistance change and force change at those cracking points can be calculated. Only data points with a force change above 0.15N were collected in order to obtain an obvious comparison and minimize instrumentation error. Apart from the correlation of change in force and resistance, the relative change of those two parameters was also plotted.

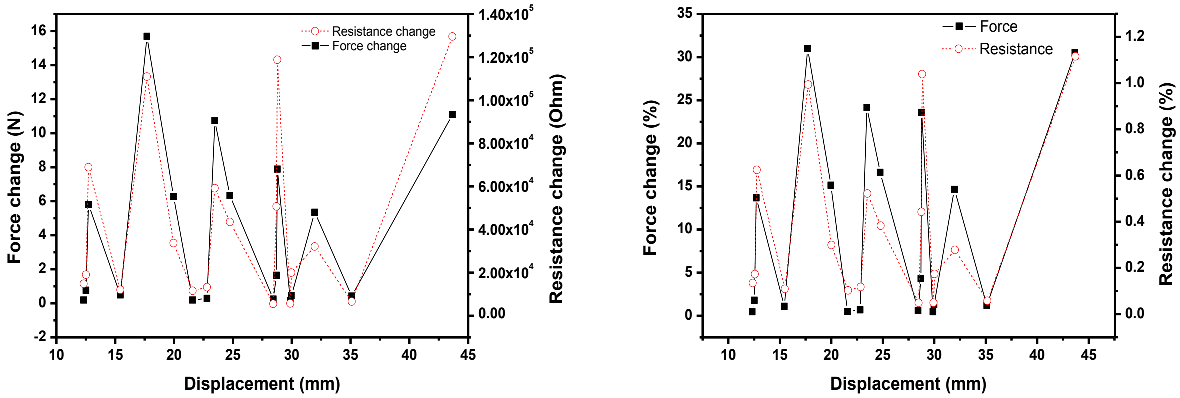

Figure 3. Correlation between resistance change and force change (left: actual changed value, right: changed percentage), indicating large changes in resistance with large load drops and small changes in resistance with small load drops.

Fig. 3 shows the relationship between force change and resistance change at the same cracking point throughout the experiment. The trend of these two parameters matches exactly, especially for the percentage graph (right), confirming a correlation between the change in force and the change in electrical resistance as a result of damage. Most of the internal damage can be quantified through the measured resistance change, as shown from the graph where for the same point, the resistance change is often slightly higher than that of the force. Although some data points are not completely consistent with the general trend, this is probably due to the complex CNTs network within the composites. For instance, certain connected pathways in a CNT network are weaker than most others, which leads to a significant resistance change at relatively small changes in external load. In fact, even more diluted networks could lead here to even more sensitive networks able to detect even smaller internal damage such as microscopic matrix cracks and/or interfacial de-bonding.

3.3 Interlaminar toughening by CNTs

The mechanical reinforcement of the GFRP/CNT hybrid micro-nano composites is evaluated in terms of interlaminar fracture toughness, as delamination is one of the most critical failure modes for structural composites. DCB tests were performed with crack length visually observed from the marked side. The energy release rate under Mode-I (G_I) conditions was calculated according to ASTM D 5528-94D standard test method, based on modified beam theory [18]. The equation is shown below:

$$G_I = \frac{3P\delta}{2b(a+|\Delta|)} \quad (1)$$

Where δ is the load point displacement, P is the applied load, a is the delamination length, b is the width of the specimen, and Δ is determined experimentally by generating a least square plot of the cubic root of compliance, $C^{1/3}$, as a function of delamination length.

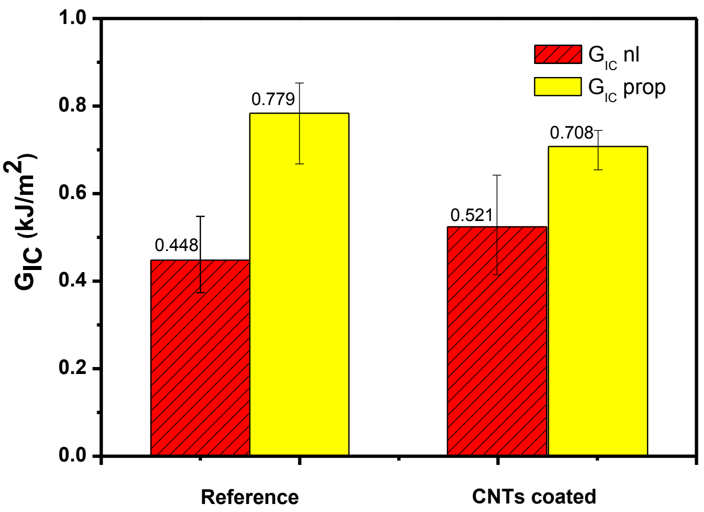

Figure 4. Influence of spray coated CNTs on the interlaminar toughness of woven fabric GFRP. Results show G_{IC} value from DCB tests, for both reference and CNT coated glass fibre fabrics.

Fig. 4 shows the G_{IC} values for both non-linear initiation (G_{IC} nl) and propagation (G_{IC} prop) obtained from the DCB test. The higher the G_{IC} value, the more energy is required to start or propagate the crack, which results in a better resistance to delaminations. A slight increment of non-linear G_{IC} value is obtained for CNT coated glass fabrics, improving the resistance for the onset of cracking, although the value of G_{IC} prop is almost the same as for the reference specimen. This relative indifference in toughness with CNT coating is due to the extremely small amount of CNTs introduced into the composites for the reported damage sensing application (0.012 wt.%). However, the developed airbrushing technique should also allow for well dispersed higher CNT loadings, which could significantly improve their mechanical reinforcement effect.

4 Conclusions

An in-situ damage sensing concept for fibre composite laminates using spray coated conductive CNT network was established. The use of an airbrushing technique has proven to be an effective route to deliver CNTs to fibre performs such as woven fabrics, with homogeneous dispersion and localization near damage prone zones. Measured electrical resistance changes during testing of DCB specimen was analysed and correlated with mechanical load changes and crack propagation, showing the potential of this integrated damage detection concept by providing the possibility to quantify internal damage by measured electrical resistance.

The established damage sensing concept is extremely useful to detect real-time micro-crack initiation and propagation in fibre reinforced composites, especially for internal micro-cracks which cannot be visually observed. Furthermore, in-situ damage detection can be utilized for in-service health monitoring of structural composite components, without the need of down-time as a result of regular inspection, solving a critical issue related to the use of advanced composites.

5 Acknowledgements

This research work is carried out under the framework of the European Research Programme "IMS & CPS" in the Seventh Framework Programme.

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