Abstract

Fibre reinforced prepreg systems due to the properties of the polymer matrix can suffer from premature failure by through thickness forces, such as impacts or out of plane loading. This research investigates the use of plasma treated carbon nanotube fillers as a way of modifying the matrix to improve the delamination resistance. The method involves adding carbon nanotubes (CNTs) between the prepreg plies using a simple drawdown coating procedure. The mode I results show that with a low loaded coating the fracture toughness can be increased, however at higher loaded concentrations the fracture toughness decreases. Mode II testing by end notch flexure demonstrated that the crack initiation energy increased in all cases, but propagation testing by end load split showed a reduction in toughness in all cases. This research demonstrates a simple coating method to incorporate a nano interlayer on to a prepreg system, which would also be applicable to other filler materials.

1 Introduction

Due to the specific strength and stiffness properties of fibre reinforced composites they are being used in increasing quantities in aerospace and automotive industries. However fibre reinforced composites are prone to matrix damage and are weak in their through thickness direction. The lack of toughness can result in parts failing by delamination in service, either from external loads or impact events. The presence of a delamination can seriously reduce the strength and stiffness of a laminate especially under compressive loads, potentially leading to catastrophic failure [1]. Fig. 1 Shows the types of crack modes that exists, many reinforcing strategies try to address these modes, the most common ones being Z-pinning, 3D-Weaving, particulate toughening, short fibres and interleaving tough layers between the plies. These methods work on the macro scale and each method has its own advantages and disadvantages compared to the nanoscale reinforcement presented in this study. For example Z-pinning [2-6] is known to give large improvements in delamination resistance, but at the cost of in-plane properties as the pins acting like nails can damage fibres and add to fibre waviness. 3D woven composites [7-8] as well as interleaving tough layers [9-15] can improve the delamination resistance, at the cost of reduced in plane properties.

Carbon nanotubes have been shown individually to be extremely strong, stiff and tough [16-18] and should make excellent candidates as reinforcements for a polymer. However commercial grades of carbon nanotubes are produced as an agglomerated powder of highly entangled nanotubes, added to this their large surface areas [19] and low surface energy makes them difficult to disperse evenly within a solvent or polymer [20]. To counter this, some pre-treatment to the CNTs is needed such as acid [21-23] or dispersants [24-25] to improve compatibility with the host matrix.

Plasma treatment of carbon nanotubes [26-29] offers an alternative to wet chemistry methods and has the advantages of being dry, single step, controllable, quick and highly flexible in terms of the variety of gases available which can give different functionalities. The carbon nanotube as a reinforcement has previously been shown as an effective method for reinforcing an epoxy polymer [20] and further developments have been made incorporating CNTs into fibre reinforced composites with varying success [30-34].
This study uses a drawdown process on aerospace grade prepreg as an alternative manufacturing technique which is simpler than previously presented methods for incorporating a nano filler into a composite system. The process is quick, single step, potentially scalable and negates CNT filtering problems and increased viscosity associated with resin transfer moulding methods [35].

This report investigates the use of this coating technique with previously developed plasma treated carbon nanotubes [29] and its effect on mode I and mode II fracture toughness.

2 Experimental

2.1 Materials:

Bayer Materials Science Baytubes C150P, carbon nanotubes have been used for this study. The C150P nanotubes are a commercial grade of multiwalled carbon nanotubes and come in an agglomerated powder form. To improve their stability in common solvents, they have been oxygen plasma treated by Haydale Ltd (UK).

E-Glass 913 unidirectional prepreg from Hexcel was used to create double cantilever beam (DCB), end notch flexure (ENF) and end load split (ELS) specimens for testing.

2.2 Manufacture:

To modify the crack plane region a drawdown coating procedure of the CNTs on to the glass fibre prepreg was used. The method is as follows; oxygen plasma treated carbon nanotubes were dispersed in 30ml of ethanol at 0.5g and 1.5g concentrations. These solutions were then vortex mixed using an IKA MS 3 Basic for 60 seconds. The solutions were then dispensed onto the top edge of the prepreg (Hexcel E-Glass 913) using a pipette. Using a drawdown bar (wire gauge 0.5mm) the solution was drawn down the prepreg resulting in a coating of carbon nanotubes. An illustration of the drawdown coating equipment is shown in Fig.2 and an example of a coated prepreg in Fig.3. The ethanol is allowed to evaporate for approximately 2-3 minutes before another ply is placed on top and the process is repeated. The stacking process is repeated in parallel until two stacks of five plies are complete, only one of the stacks is then given a top coating. The next procedure is to lay release film on this stack forming an artificial crack. The other stack is then laid on top, locking in the release film creating a stack of ten plies, nine of which are coated. Another seven uncoated plies are then added either side of the stack to produce a 24 ply laminate all at zero degrees. The laminate is then bagged and cured in an autoclave in accordance with the manufacturers curing schedule (125°C for 1 Hour at 7 Bar) with an added dwell to reduce any exotherm. Once the laminate is cured DCB, ENF and ELS specimens are cut to size using a diamond cutting disc to the geometry recommended in the relevant standards ASTM D5528-01, JIS K7086 and ESIS-TC4 respectfully. A schematic of these test specimens is shown in Fig.4. For the DCB specimen piano hinges and for the ELS specimens aluminium T sections were attached to facilitate loading, bonding was achieved using Redux 810 two part epoxy adhesive.

2.4 Zeta Potential CNT stability

Zeta potential measurements were performed using a Malvern Zetasizer Nano Z system with folded capillary cells. The system directly measures electrophoretic mobility the velocity of the suspended particles in solution within an electric field, achieved by laser Doppler velocimetry. Using the solvent properties of ethanol (Table1) the electrophoretic mobility and the Henry equation [36] (equation 1) the zeta potential can be calculated. This was all done automatically by the Zetasizer software. All measurements were conducted at 25°C.

$$U_E = \frac{2\varepsilon f(ka)}{3\eta}$$  \hspace{1cm} (1)

Where $U_E$ is the electrophoretic mobility, $\varepsilon$ the solution dielectric constant, $\zeta$ zeta potential, $\eta$ viscosity and $f(ka)$ Henry’s function taken as 1.5 as used by a similar study [37]
2.3 Mechanical Testing.

Three types of mechanical testing were carried out to evaluate the CNTs affect on laminate toughness. DCB testing for mode 1 \((G_{IC})\), ENF for mode 2 initiation \((G_{IIC})\) and ELS for mode 2 propagation \((G_{IIc})\).

DCB testing was executed according to ASTM D5528-01 using an Instron 3343 testing machine and a 1kN load cell. The crosshead displacement speed was set at 2mm/min. The crack growth was monitored using a digital video recorder. The energy release rate \(G_{IC}\) was calculated using the modified beam theory method, equation (2).

\[
G_{IC} = \frac{3P\delta}{2b(a + |\Delta|)}
\]

Where: \(P\) = load, \(\delta\) = displacement, \(b\) = width, \(a\) = crack length and \(|\Delta|\) = correction factor. (see ASTM D5528-01)

The ENF testing was carried out in accordance with JIS K7086 again using an Instron 3343 testing machine with a 1kN load cell. As per the standard the testing rate was set to 0.5 mm/min. As this test method does not produce stable crack growth only a \(G_{IIC}\) initiation value can be taken [38], which has been taken at the maximum load at the point of failure, using equations 3 and 4.

\[
G_{IIC} = \frac{9aI_{c}^{2}C_{1}}{4 B^{2} E h^{3}} \left[ 1 - \theta_{1} \left( \frac{\delta}{L} \right)^{2} - \theta_{2} \left( \frac{\delta}{L} \right)^{2} \right]
\]

(5)

\[
\theta_{1} = \frac{3}{20} \left[ 15 + 50 \left( \frac{a}{L} \right)^{4} + 63 \left( \frac{a}{L} \right)^{4} \right] \left[ 1 + 3 \left( \frac{a}{L} \right)^{3} \right]
\]

(6)

\[
\theta_{2} = -3 \frac{a}{L} \left[ 1 + 3 \left( \frac{a}{L} \right)^{4} \right] \left[ 1 + 3 \left( \frac{a}{L} \right)^{3} \right]
\]

(7)

Where: \(G_{IIC}\) = Mode 2 corrected energy release rate, \(a\) = delamination length, \(P\) = load, \(\Delta_{H}\) = delamination correction factor from mode 1 tests, \(\delta\) = displacement, \(I_{c}\) = loading point to mid plane, \(E\) = flexural modulus, \(B\) = width of specimen, \(h\) = half thickness of specimen, \(L\) = free length of specimen, \(\theta\) = correction factors.

2.3 Optical and SEM Analysis

To understand the failure of the specimens optical and electron microscopy techniques have been used. Optical micrographs were made using a Zeiss Axio Imager 2. Scanning electron microscopy (SEM) images were taken by a JEOL JSM 6330F ultra high vacuum scanning electron microscope at an acceleration voltage of 15KV. SEM samples for the fracture surface images were silver sputtered to remove charging effects and allow imaging.
3 Results and Discussion

3.4 Zeta Potential.

The zeta potential results are shown in Table 2. The increased magnitude shows that the treated CNTs are much more stable compared to the as received CNTs and that once treated have a negative charge in the ethanol solution. Fig. 5 shows a visual representation of the zeta potential results.

3.1 DCB Results

The DCB ‘R’ curve results are shown in Fig 6. In general the results show that at the lower coating concentration the mode I fracture toughness increases significantly during crack propagation, whilst this is not present in the glass control or the 1.5g coated specimens. It is also important to note the exceptionally large error bars present on the 1.5g coated experiments representing one standard deviation. This is due to the almost random nature of the crack sticking and slipping during these tests which results in large peaks and troughs in the load displacement response, unique to this specimen.

The increase in the mode I fracture toughness during propagation can be attributed largely to an increase in the quantity of glass fibres bridging. A steady state of glass fibre bridging occurs after about 80mm of crack growth for the 0.5g coated specimen.

3.2 DCB Fracture response

The micrographs in Fig. 7 are of the DCB specimens held open during an epoxy casting process. The samples are ground, polished and submerged in an ultrasound water bath to remove any glass chips. The images shown are the bright field images with regions highlighted such as the crack and the CNT interlayers which are only visible in the dark field observations. For the glass control the crack has propagated very repeatedly and uniformly between the prepreg plies. In stark contrast the 0.5g coating crack has propagated away from the CNT mid plane layer and propagates within the ply. This causes fibre bridging to occur, and hence increase the fracture toughness.

The main difference between the fracture surfaces observed by the SEM images in Fig. 8 is the quantity of exposed glass fibres. The increased exposure of the glass fibres in the 0.5g coating, Fig. 8(b) compared to the control Fig. 8(a) and 1.5g coating Fig. 8(c) indicate more bridging has occurred, the primary reinforcement mechanism seen in this study.

3.2 ENF Results

A summary of the ENF results is given in Table 3. There is a notable improvement in the initiation fracture toughness with the addition of the CNT filler of upto 16% for the most highly loaded specimen using the 1.5g CNT solution. The 0.5g solution has also shown improve the initiation energy but to a slightly lower extent.

3.3 ENF Fracture response

SEM images in Fig. 9 shows the fracture planes at the crack initiation site. The specimens were wrapped in sticky tape to protect the inside from debris and carefully cut in this area using a diamond cutting wheel. Then opened up, mounted on an SEM stub and silver coated. The SEM images appear fairly similar between the control and the CNT loaded specimens. In both cases the epoxy has been sheared fairly cleanly off the fibre surfaces indicating an adhesive failure between the fibre and matrix, and that the modified CNT matrix had little influence upon this. On the opposite half the trenches are smooth in both cases, and for the CNT coated laminates there is no evidence of exposed CNTs within the trenches, showing the coating method has not penetrated through to the fibre matrix interface, however there is a presence of patches of carbon nanotubes in Fig. 9(b) on the fracture planes which have been highlighted.

3.4 ELS Results

The ELS results are shown in Table 4. The results indicate that for small additions of carbon nanotubes there was little affect upon the mode 2 propagation results, but at higher concentrations a negative influence was found.
3.5 ELS Fracture Response

A noticeable increase in crack stick and slip was found for the CNT coated specimens, especially for the 1.5g coating. The microscope cross section images in Fig.10 show a strong difference in the crack line across the width of the specimen. The images show that in the case of the 0.5g coatings the crack has propagated sporadically cutting through CNT regions indicating the interlayer has had a profound affect on the crack path compared to the fairly linear glass control and for the 1.5g coated sample the crack appears to run along the top of the CNT interlayer.

SEM Fracture images are shown in Fig.11 and appear fairly similar except for the increase in glass fibre debris along the fracture plane, which can incidentally also be seen from bright reflections with the naked eye. The lighter patches seen in Fig.11 (a), the glass control is due to surface charging and represents no significant features. It was found difficult to locate any CNTs on the fracture surfaces of the coated specimens, unlike the DCB specimens indicating the CNTs have locally altered the plastic zone properties and diverting the crack around, above or below them and not through them.

It appears a contradiction exists in the mode 2 results as initiation was found to be higher for the CNT coated laminates whilst the propagation is lower than the control. However considering stick and slip response this can be explained. During the propagation testing the crack sticks and slips, propagation is not steady and when crack sticks the load increases substantially and for a that instance the toughness appears to have increased, as seen during the mode 2 initiation testing. But as the crack then quickly propagates / slips the average fracture toughness value is decreased until it sticks again.

4 Conclusions

The work presented shows a simple and effective method to add carbon nanotubes onto a prepreg surface which would be suitable as a coating method with other filler materials. This coating method is an inexpensive alternative to preparing nano material infused prepgres.

Plasma treatment of CNTs was essential to improve dispersion in a solvent allowing an ink like solution to be made.

By coating pre-pregs in this way it is possible improve the fracture properties of the system for mode I and mode II initiation, but not mode 2 propagation. Care must be taken as at higher filler quantity the properties can reduced below the baseline.

References


[31] D.C. Davis and B.D. Whelan, An experimental study of interlaminar shear fracture toughness of nanotube


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<th>Table 1 Ethanol Constants [39]</th>
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<th>Table 2 Zeta potential results</th>
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<td>Material</td>
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<td>C150P As received</td>
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Fig. 1. Crack modes
Fig. 2. Draw down coating equipment.

Fig. 3. Prepreg after coating with the carbon nanotube solution.

Fig. 4. Schematic of the double cantilever beam, end notch flexural test and end load split specimens, width 20mm.
Fig. 5. CNT ethanol solutions. (a) As received, (b) Oxygen plasma treated.

Fig. 6. Delamination resistance results from embedded carbon nanotubes between pre-preg plies. (Error bars represent one standard deviation)
**Fig. 7.** Optical Micrographs showing the variation of the crack paths through the DCB specimens.

**Fig. 8.** SEM images showing the variation of the fracture and quantity of exposed fibres through the DCB specimens.
Fig. 9(a) Glass Control

Fig. 9(b) 0.5g coating

Fig. 9. SEM images of the end notch flexure specimens at the crack initiation site.
Fig. 10. Optical micrograph images of the end load split specimens, looking at half a specimen down the fibre length. Bright field images with colour added for clarity, Red: Crack line, Blue: CNT interlayer.

Fig. 11. SEM images of the end load split specimens, looking at the fracture plane after testing.