Multi-scale reinforcement of composites using coated fabrics; epoxy - carbon nanotube (CNT) - carbon fibre (CF) composites with improved inter-laminar fracture toughness.

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Abstract

Multiwall carbon nanotubes (MWCNT) were dispersed in an epoxy binder of low molar mass and the resulting mixture was used to coat a woven carbon fibre (CF) fabric reinforcement prior to moulding of composites by resin infusion to produce multi-scale composite. The effects of this reinforcement on the CF-epoxy interface with MWCNT was studied using mode I and mode II inter-laminar fracture toughness (ILFT) using double-cantilever beam (DCB) and 4 point end-notch flexure (4ENF) tests, respectively. It was found that, relative to an equivalent composite reinforced with non-coated CF reinforcement, the binder/MWCNT treatment significantly enhanced the ILFT of CF-epoxy composite; mode I by 110% and mode II by 60%. This increase in ILFT was attributed to two main reasons: Firstly, the binder (without MWCNT), which has a much lower Tg than that the matrix (45 vs. 140 °C), hindered crack propagation and increased the ILFT of the epoxy matrix by 35% for mode I and 25% for mode II; Secondly, the contributions of MWCNT during fracture (pull-out and crack bridging).

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1. Introduction

Laminar CF – epoxy composites combine excellent in-plane mechanical properties with low density[1]. However, the inter-laminar toughness of these composites can be problematic, particularly under low-energy impact conditions where significant delamination can occur with only barely-visible-impact-damage (BVID) on the laminate surface[2]. Recently, attempts have been made to mitigate this problem by hybridising CF-epoxy composite with carbon nanotubes (CNT); thus providing nano-scale reinforcement along with micro-scale reinforcement to produce a multi-scale reinforced composite. Up until now, most research has been focused on two main methods; a) dispersion of CNT into epoxy resin using techniques such as, calendering, milling, grinding, high speed shear mixing, high-pressure homogenization, and sonication and b) growing CNT on to the surface of reinforcement substrates, e.g. carbon fibre/fabric using techniques such as chemical vapour deposition (CVD)[3]. Due to the large surface area of the nano-scale MWCNT and their tendency to aggregate it is very difficult to efficiently disperse and distribute CNT into epoxy resin[4]. In addition, the viscosity of the epoxy resin system used in this study increased by 3 orders of magnitude on addition of only 0.33 wt.% of MWCNT, creating significant problems for processing. The main aim of this research is to develop functional multi-scale composite by modifying fibrous reinforcement with MWCNT.

2. Materials and Methods

2.1 Preparation of multi-scale composite

The epoxy resin system used in this research is a mixture of resin Araldite LY 564, a DGEBA based resin and curing agent Aradur 2954 [2, 2'-dimethyl-4.4'-methylenebis (cyclohexylamine)] obtained from Huntsman Advanced Materials. The CNT are Nanocyl NC7000, an industrial grade MWCNT obtained from Nanocyl, with average diameter and length of 9.5nm and 1.5µm respectively. The size (binder) used to bind the CNT to the carbon fibre (CF) is an aqueous dispersion of DGEBA epoxy resin (EPI-REZ 3522-W-60) obtained from Momentive Performance Materials. The reinforcement - CF fabric is supplied by Sigmatex UK (code R100026), which is a 5- harness satin weave (5HS) with an areal density of 380 g/m^2 (gsm).

CF fabric was cut into the rectangle pieces of 30 cm x 30 cm, as-received CF fabric, CF fabric treated with binder and CF fabric coated with the MWCNT-binder mixture were the three different types of reinforcements used in initial study. MWCNT were mixed with the binder using mechanical stirrer for 1 hour, weight % of MWCNT in the mixture was kept at 2.5%. Either binder or mixture of MWCNT-binder was applied to the CF fabrics by using metered metal bar which provides wet coating thickness of 12µm. Fabrics were subsequently dried overnight in an oven at 50 ˚C. Weight % of binder and mixture of MWCNT-binder obtained after drying were 13.5 ± 0.4 % and 14.2 ± 0.5 % respectively.

Flat panels of CF – epoxy composites were prepared with three different CF fabric mentioned above using resin infusion (RI) process. During preparation of the composites CF fabrics were vacuum bagged on a flat aluminium plates followed by RI, where resin flows from the inlet to the exit which is connected to a vacuum pump. After completion of the RI, samples were cure at 80 ˚C for 1 hour followed by the post curing at 140 ˚C for 8 hours.

2.2 Mode I ILFT

Mode I ILTF is a test to measure the critical strain energy release rate, G_{IC}, from the resistance to the initiation and propagation of a delamination crack in continuous fibre-reinforced composite laminates under mode I opening load. Testing was carried out according to ASTM standard D5528, in which, mode I crack opening occurs due to a load applied perpendicular to the plane of delamination using a

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double cantilever beam (DCB) specimen. The side faces of the specimens were polished and painted white. The specimens were then marked from the edge of the insert film with vertical lines every 1 mm up to 50 mm to facilitated accurate measurement of crack length by direct visual observation with the help of a magnifying glass.

Tests were carried out on an Instron universal testing machine (model 5969) equipped with 10 kN load cell. A crack-opening load was applied at a rate of 3 mm/min to the DCB specimen, perpendicular to the plane of delamination, through the piano hinges under displacement control as shown in figure 1. The Mode I critical strain energy release rate G_{IC} was calculated by modified beam theory using equation 1.

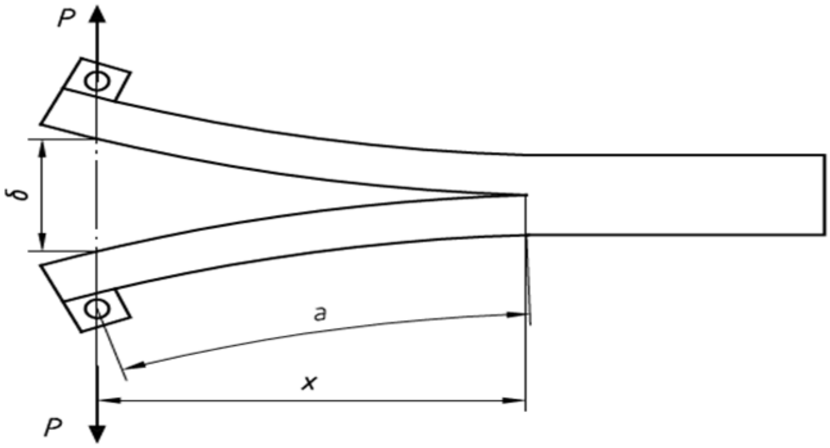

Figure 1. DCB specimens upon the application of load[5]. Where x is delamination length measured along the horizontal direction, a is crack length, P is applied load and δ is displacement.

$$G_{IC} = \frac{3P\delta}{2b(a + I\Delta I)} \quad (1)$$

Where, P is load, δ is displacement, b is specimen width, a is crack length and IΔI is calculated using the compliance calibration method.

2.3 Mode II ILFT

Mode II testing is a technique to measure the interlaminar shear strength in terms of the critical strain energy release rate, G_{IIC}. It can be measured using several test geometries, and in this study four point end-notched flexure (4ENF) test was used. The specimens for the 4ENF test were 140 mm in length and 20 mm in width and were prepared using the method described by Hogg et.al.[6]. The side faces of the specimens were polished, painted white and then marked from the edge of the insert film with vertical lines every 1 mm up to 40 mm to facilitate accurate measurement of crack length by direct visual observation with the help of a magnifying glass.

Tests were carried out using the same Instron test machine described in section 2.2. The diameter of the support beam rollers and loading noses was 10 mm and their lengths were 100 mm and 60 mm, respectively. The speed of the cross-head was fixed for all tests at 0.3 mm/min. Pre-cracking was performed by applying the load until the delamination grew to 2 mm, the load was then removed at

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the same rate of 0.3 mm/min to zero. The main reason for pre-cracking is to avoid false readings from the resin-rich area at the tip of the predefined crack. Following pre-cracking, specimens were loaded again at 0.3 mm/min and the load and displacement were recorded up to 40 mm, ideally every 1 mm. From the data obtained G_{IIC} was calculated using equation 2. A schematic representation of the 4ENF test is given in figure 2.

$$G_{IIC} = \frac{P^2 m}{2b} \qquad (2)$$

Where, P is the applied load, m is the gradient from a compliance curve according to modified beam theory and, b is the width of the specimen.

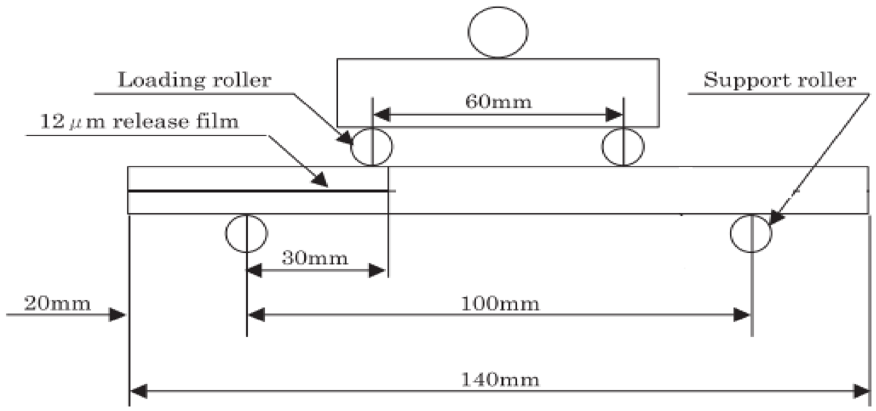

Figure 2. Test configuration for the four point end-notched flexural (4ENF) ILFT test[6].

3. Results and discussion

3.1 Mode I ILFT

Typical load extension curves from the DCB tests are shown in figure 3.

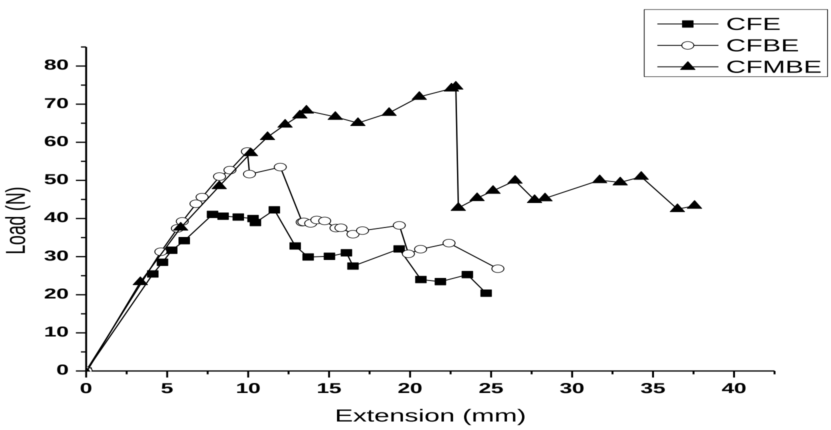

Figure 3. Load extension curves from the mode I DBC test for epoxy composites containing as-received CF, CF treated with binder and CF treated with MWCNT dispersed in binder.

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The curves in figure 3 all show an initial steep, stable rise in load followed by a region of unstable decline. This behaviour is a result of the fabric reinforcement used for the composites as described by Hogg et. al.[7]

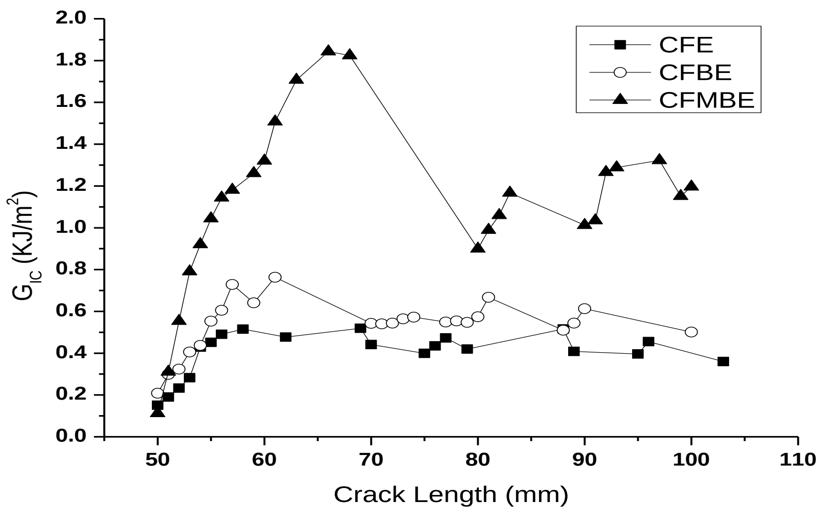

Figure 4. GIC versus crack length curves (R curves) of the mode I DCB tests for epoxy composites containing **a)** as-received CF, **b)** CF treated with binder and **c)** CF treated with MWCNT dispersed in binder.

Table 1. Average values for mode I ILFT G_{IC} for epoxy composites containing as-received CF, CF treated with binder and CF treated with MWCNT dispersed in binder.

Epoxy Composite Containing	G_{IC} kJ/m^2
As-received CF	0.47 ± 0.04
CF treated with binder	0.63 ± 0.04
CF treated with MWCNT dispersed in binder	0.99 ± 0.12

The results in figure 4 and table 1 show increased G_{IC} values for the CF-epoxy composites with binder and mixture of MWCNT-binder compared to the composite containing as-received CF-epoxy composite. In particular, the average G_{IC} value for the composite containing CF with MWCNT-binder mixture was 0.99±0.12 kJ/m^2 compare to 0.47±0.04 kJ/m^2 for the as-received CF composite which is an increase of approximately 110%. This increase in ILFT can be attributed to the action of CNT within the epoxy matrix, namely CNT pull-out and crack bridging[8]. In addition, from the results it was clear that a composite with CF and binder on its own also increases the ILFT of the composite. It is believed that the binder material may act as a thermoplastic toughener and hinder the crack propagation.

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3.2 Mode II ILFT

Results obtained from the 4ENF tests are given in figure 5 and table2.

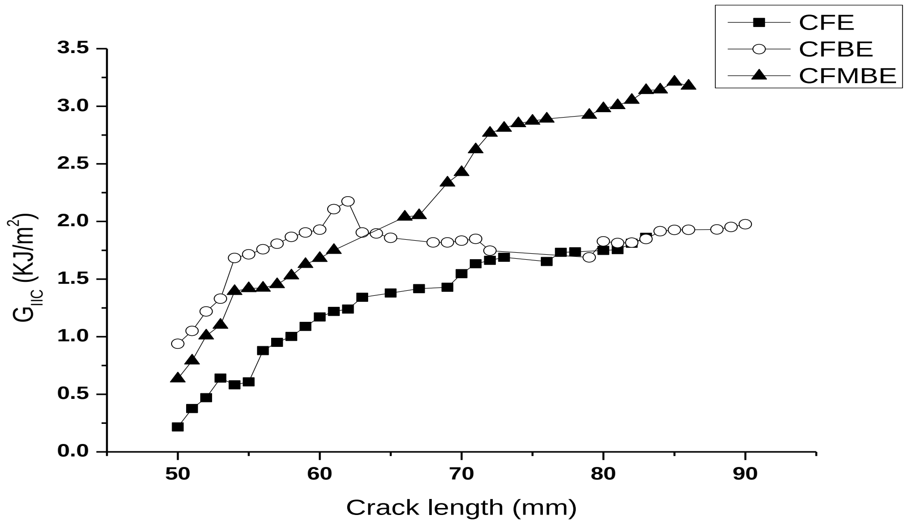

Figure 5. G_{IIC} versus crack length curves (R curves) of the mode II 4ENF tests for epoxy composites containing as-received CF, CF treated with binder and CF treated with MWCNT dispersed in binder.

Table 2. Average values for mode II ILFT, G_{IIC} for epoxy composites containing as-received CF, CF treated with binder and CF treated with MWCNT dispersed in binder.

Composite	**G_{IIC} KJ/m^2**
CFE	1.48 ± 0.22
CFBE	1.84 ± 0.01
CFMBE	2.40 ± 0.27

During mode II ILFT testing crack propagation did not occur from the initial pre-crack for two out of five specimens of the composite containing CF with binder and CF with MWCNT- binder mixture. Instead, a new crack initiation above the precrack in the middle of the specimen was observed leading to the compressive failure of the specimens rather than crack propagation. This might be a good indication of toughening of epoxy matrix by the binder and MWCNT. Results from specimens exhibited compressive failure were not considered in the calculation of the G_{IIC} values of the composites. In addition to the compressive failure of some of the specimens, the increased values of G_{IIC} also suggest that the binder and the MWCNT enhance the ILFT of the composites.

4 Conclusions

Multi-scale composites were prepared by coating CF with MWCNT with the help of binder prior to resin infusion. To investigate the effect of MWCNT as well as binder, composites were fabricated using as received CF, CF coated with binder and CF coated with MWCNT dispersed in binder.

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Mode I ILFT testing of the composite with binder and MWCNT showed an increase of 110 % in G_{IC}. It is also clear from the results that binder itself also enhances the fracture toughness of the composites. Mode II ILFT of the multi-scale composite showed G_{IIC} was also increased by 60 % compared to the as-received CF-epoxy composite. It was very difficult to monitor the crack propagation during the 4ENF test of the multi-scale composites as for some of the specimens crack propagation did not occur from the pre-crack, instead compressive failure was observed. This might be an indication of improved fracture toughness.

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