Improved Mode I fracture resistance of CFRP composites by reinforcing epoxy matrix with recycled short milled carbon fibre

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HIGHLIGHTS

- Recycled short milled carbon fibres are proved advantageous to increase $G_{IC}$ of epoxy resin.
- Higher energy absorption through individual debonding and pull-out mechanisms is observed.
- Correlation between fracture toughness of matrix and composite is discussed.

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ABSTRACT

This paper proves that incorporation of recycled short milled carbon fibre (SMCF) in epoxy resin can lead to the generation of significantly tougher carbon fibre reinforced polymer (CFRP) systems in a cost effective manner for infrastructural applications. Structural epoxy resin is modified by adding 5 and 10 wt.% of SMCF particles and the ‘fracture toughness’ of the modified matrix ($G_{IC}$) is observed to be increased by 300% and 700% respectively. Subsequently, the SMCF modified epoxy resins were used to fabricate uni-directional carbon fibre reinforced laminates and tested under Mode I crack opening. The SMCF reinforcement showed 50% and 64% improvement in the laminates fracture toughness ($G_C$) after adding 5% and 10% SMCF by wt., respectively. Scanning electron microscope images of the fracture surface highlight improved debonding and pull-out mechanisms contributing to the additional fracture toughness, and at the same time there was no evidence of fibre clustering.

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1. Introduction

Laminated composites are immensely used in civil engineering applications [1,2]. This is because laminated composites offer very high strength to weight ratio when compared with other materials like metals and ceramics. At the same time, the laminated structure makes the system susceptible to delamination initiation from pre-existing cracks [3] possibly because of weak bonding between fabric and resin (well known as the ‘weak link’ [4]). This crack propagation continues through the major component of the laminated system i.e. the polymer matrix which holds the strong fibres together [5]. Epoxy resin is the most commonly used matrix phase in fibre-reinforced polymer (FRP), which is normally brittle. Room temperature cured epoxy has Mode I fracture energy of about less than 100–200 J/m² [6,7]. This limits the full potential of the weight reduction advantage offered by the composite. Therefore the matrix fracture property of epoxy matrix is the key feature that controls crack initiation and growth in the laminated systems, especially through the thickness properties.

The knowledge from strengthening of epoxy in other applications, for example aerospace cannot be directly applied in civil infrastructure applications. One of the most common methods is incorporation of elastomeric/rubbery phase into epoxy resin, which is universally accepted, for improving the fracture energy of epoxy as well as other thermosets. But addition of a rubbery phase has the detrimental effect of reducing the thermal and stiffness properties of the toughened epoxy [8] hence this is not acceptable in many civil engineering applications. Another way is to add a thermoplastic/rigid phase to epoxy such as nano-alumina [9] or silica [10]. In recent times, carbon nano tubes...
(CNTs) are attracting attention as it is shown that CNT either alone [11–13] or with other toughening agents [14] can improve fracture toughness significantly at very low additions of the CNT. CNT in epoxy matrix shows several toughening mechanisms such as crack pinning, CNT bridging and crack deflection [15] and it can also improves elastic, electrical and thermal properties [16]. However, apart from the high cost of CNT, its processing cost is also high due to the challenges reported in processing, including that CNT increases the viscosity of the base polymer [17] and uneven CNT dispersion issues [12] which lead to extra fabrication processes being required such as CNT functionalization [18,19] and alignment [4,20,21].

This discussion led to consideration of recycled short milled carbon fibre (SMCF) as an alternative toughening agent for carbon fibre reinforced polymers for civil infrastructure, that can be introduced in an efficient way. Previous studies [22,23] have proved SMCF to be an advantageous epoxy modifier as it shows uniform dispersion and distribution in the matrix material, resulting in 250% increase in critical stress intensity factor ($K_{IC}$) after adding 10 wt.% of fibre.

In this study, neat epoxy and modified epoxy with 5 and 10 wt. % of SMCF added were used to fabricate

(I) Single Edge Notch Bending samples (SENB), to determine ASTM 5045 standard mode I fracture toughness of epoxy resin matrix ($G_{IMC}$) and

(II) 40% volume fraction CFRP laminates in Double Cantilever Beams (DCB) form, to determine ASTM D5528 standard mode I interlaminar fracture toughness ($G_{IC}$).

Following the conclusions of other researchers [3], only fracture toughness for crack initiation ($G_{IC-initiation}$), and not crack propagation, is studied in this paper, since $G_{IC-initiation}$ (expressed as $G_{IC}$ in later discussion) more accurately reflects the maximum contribution to energy absorption during onset of fracture.

Furthermore, to study the ability of the resin to transfer the fracture properties to the composite, the fracture toughness of neat resin ($G_{IMC}$) is compared with the fracture toughness of the composite ($G_{IC}$) and various possible reasons behind the different $G_{IC}$s are discussed.

2. Materials and methods

2.1. Materials

A general purpose low shrinkage laminating epoxy system (EL-M) consisting of diglycidal ether of Bisphenol A (DGEBA) and curing agent (hardener) cyclo-aliphatic polyamine were obtained from Barnes Pvt. Ltd, Sydney, Australia. The resin to hardener ratio was 2:1 by weight. The toughening agent used for the two component epoxy system was recycled SMCF as received from ELG Carbon Fibre Ltd. The SMCF had average diameter 7.5 $\mu$m, length 100 to 300 $\mu$m, and density 1.8 g/cc as per information provided by the supplier.

Long continuous carbon fibre (CF) was obtained from Colan Products Pty. Ltd, Australia, which was unidirectional woven fabric. Three formulations were pre-
pared in this study to produce the matrix: (a) ESMCF 00, (b) ESMCF 05 and (c) ESMCF 10 representing neat epoxy, 5 and 10 wt.% SMCF doped epoxy matrix respectively. Selection of these weight percentages of SMCF was decided based on the superior results obtained by the authors in previous studies, where ESMCF 05 and ESMCF 10 showed optimum dispersion and distribution [23].

2.2. Fabrication

Samples in this study were fabricated at room temperature with a manual lay-up procedure. Fracture toughness of the base matrix formulation was determined by single edge notch bending samples (SENB) [24]. The SMCF at 5 and 10 wt.% was added to pure epoxy resin then mixed mechanically, followed by ultrasonication for 45 min in a Unisonic ultrasonic bath at a frequency of 40 kHz. After this, the hardener was added and further ultrasonication was carried out for 15 min. Resin-to-hardener ratio was selected as 2:1 by weight, as suggested by the supplier. For making neat epoxy samples, DGEBA was directly added to hardener. The mixture was then transferred to silicone rubber moulds to produce the samples in the form of SENB test samples. Curing was carried out at ambient laboratory temperature (21 ± 4 °C), with optimum curing time of 9 days.

2.2.1. Laminate preparation

After homogeneous mixing of resin and resin/SMCF systems, 10 layers of CF were stacked in epoxy resin/SMCF modified epoxy resin, as shown in Fig. 1A. Each CF sheet was sandwiched between two layers of epoxy resin. This stacking method was preferred over a frequently used Vacuum Assisted Resin Transfer Molding (VARTM) in order to avoid the filtration of the SMCF particles [14]. A 10 μm thick Teflon sheet (see Fig. 1B) was placed at half of the thickness of the laminate i.e. after 5 layers of CF stacking. This Teflon sheet acts as a crack initiator in the Mode I testing of the laminates. Each panel was then vacuum-degassed as per the sequence shown in Fig. 2 and the system was then allowed to cure for 9 days at room temperature.

2.2.2. Sample cutting and preparation

Evaluation of interlaminar fracture toughness of the CFRP laminates was carried out using DCB samples under Mode I failure according to [25,26]. For this, the samples were cut from the cured panel of dimension 190 × 135 × 4.6 mm (L × W × B) (see Fig. 1B). For Mode I failure, 5 specimens of rectangular double cantilever beam (DCB) shape having dimensions of 140 × 23 × 4.6 mm (L × W × B) were cut and edges were polished to accurately locate the ends of the Teflon sheets. After cutting the DCB specimen, the length of the Teflon sheet was 60 mm. To apply the opening forces, piano hinges were glued using commercial two component epoxy which was cured at room temperature. For making neat epoxy samples, DGEBA was directly added to hardener. The mixture was then transferred to silicone rubber moulds to produce the samples in the form of SENB test samples. Curing was carried out at ambient laboratory temperature (21 ± 4 °C), with optimum curing time of 9 days.

2.2.3. Evaluation of Mode I fracture toughness of matrix (GIC)

Mode I fracture toughness (GIC) of matrix was calculated using the SENB test, at the Instron crosshead speed of 2.8 mm/min. and applying Eqs. (1) [24] and (2) [27].

\[ GIC = \frac{(1 - \nu^2)KIC^2}{E} \]  
\[ KIC = \frac{P_{S}}{B_{eff}^{3/2}} \left[ \frac{2.9}{\alpha_{eff}} \left( \frac{a}{W} \right)^{1/2} - 4.6 \left( \frac{a}{W} \right)^{5/2} + 21.8 \left( \frac{a}{W} \right)^{7/2} - 37.6 \left( \frac{a}{W} \right)^{9/2} + 38.7 \left( \frac{a}{W} \right)^{11/2} \right] \]  

In Eq. (1), \( \nu \) is Poisson’s ratio, which for epoxy varies from 0.40 to 0.45 depending upon various factors [28,29]. \( KIC \) is the fracture toughness intensity factor, which is the crack driving force calculated using Eq. (2) where \( P_{S}, a \) and \( W \) are maximum load, crack depth and width of the sample respectively. A sharp crack was created by sliding the sharp razor blade over the notch tip making smooth continuous contact with the sample surface and keeping approximately constant force [30], the value of \( \alpha \) of after sharp crack (+ sharp crack) was measured by a traveling microscope as 2.8 mm. \( E \), elastic modulus, was calculated according to the 3-point bending test [31] on the broken samples from the SENB test. \( E \) can be calculated using Eq. (3),

\[ E = \frac{S^{3}m}{4B^{2}W^{2}} \]  

where \( m \) is slope of the load-extension graph, and \( B \) is thickness of the sample with width \( W \). The average thickness of the 3-point bend sample was 3.9 ± 0.1 mm whereas its width was 12.57 ± 0.5 mm, thereby maintaining the W/B ratio greater than 2 as a requirement for the plane–strain condition.

2.4. Evaluation of Mode I fracture toughness of composite (GICM)

Mode I fracture testing of laminate was performed using an Instron 5982 at a loading rate of 5 mm/min and unloading at 25 mm/min [26]. The crosshead displacement and corresponding reaction force exerted by the specimen were captured at an interval of 0.1 s with the help of Bluehill 3 mechanical testing software from Instron. The record of delamination growth was done after every 100 s by taking high magnification images using a Canon DSLR camera and was related to the load and displacement determined from the Bluehill software.

Delamination was taken to begin where the initial portion of the load displacement curve deviated from linearity. Loading was kept continuing and the point was recorded on the load displacement curve at which the visual onset of delamination movement was observed on the edge of the specimen (by the digital camera). This point was marked as VIS. Initiation fracture toughness \( GICM \) i.e. the critical value of G for delamination initiation as a result of an opening load, was calculated from the initial load curve using Modified Beam Theory (MBT) method [26,32] using Eq. (4),

\[ GICM = \frac{3P_{S}}{2B(a + 1)l_{1}} \]  

where \( P \) is load, \( a \) is load point displacement, \( b \) is width, \( a \) is delamination and \( l_{1} \) is the correction factor determined by the procedure given in [26]. Also, according to the standards, three values of \( GICM \) were calculated using three different P values corresponding to the point on the load displacement curve where

Fig. 3. Schematic diagram of (A) SENB sample for resin fracture toughness and (B) DCB sample for laminate fracture toughness.

Fig. 4. Fracture toughness of matrix (GIC) with and without SMCF addition.
Initial load-displacement curve deviated from linearity (Non-linearity (NL)), Visual delamination was observed (Visual (VIS)), and Intersection with a line drawn from the origin and offset by a 5% increase in compliance occurred i.e. ratio of displacement and load (5% offset).

2.5. Scanning electron microscope

A Hitachi TM 3000 scanning electron microscope (SEM) was used to study the delaminated surfaces of the samples at different magnifications after the samples were gold coated using a Leica EM SCD050 coater. The samples were targeted at 60 mA current for 45 s that produced 15 nm thick gold coating.

3. Results and discussion

3.1. Matrix (SENB sample)

3.1.1. Facture toughness

Fig. 4 shows the improvement achieved in $G_M$ after addition of 5% and 10% of SMCF to epoxy resin. Lower and upper limits of $G_M$ in Fig. 4 were calculated using $\varphi = 0.40$ and $\varphi = 0.45$ in Eq. (1) and the average value is indicated by the red bar in Fig. 4. Average $G_M$ increased nearly 4 and 8-fold relative to that of the neat epoxy.

![SEM images of fractured surfaces of all samples in slow crack growth (left) and fast crack growth (right). (A) and (B) ESMCF 00, (C) and (D) ESMCF 05, and (E) and (F) ESMCF 10.](image)
resin, after addition of 5% and 10% of SMCF respectively. This is because of the combined effect of fibre stereology and individual debonding/pull-out mechanisms as observed in SEM images shown in Fig. 5.

3.1.2. Fractography

Fig. 5 shows fractography of the fractured surfaces of SENB samples in slow and fast crack growth regions. The slow crack growth region is mainly responsible for $G_{IC}$ and as can be seen in Fig. 5, where the neat epoxy has relatively smoother fracture surface (only a few river markings are seen in slow crack growth) compared to that in ESMCF 05 and ESMCF 10 systems. By contrast, ESMCF 05 and ESMCF 10 show rough surfaces indicating ductile failure due to crack pinning and stopping mechanisms offered by SMCF particles. SEM images in Fig. 5C–E reveal good dispersion of SMCF in the matrix which results in individual debonding and pull out mechanisms, which apparently lead to more newly created surface area after debonding (rather than bundle debonding which is observed due to fibre agglomeration), hence absorbing more energy [33].

Most of the fibres on the fracture surface were observed to be nearly perpendicular (mostly 45–90°) to the surface, which is the optimal direction to improve the fracture toughness. This alignment was obtained without any extra provision in fabrication.

3.2. Laminate properties (DCB sample)

3.2.1. Mode I fracture properties

Fig. 6 shows the typical load-extension curves comparing the initial loading behaviour of neat epoxy and modified epoxy laminates. The crack was monitored carefully and corresponding load
and displacement are noted on the graph. Both neat and SMCF modified samples demonstrated a linear load displacement up to crack initiation point. However, the SMCF modified laminates sustained a higher initiation load than neat epoxy laminate and hence showed improved fracture toughness. Examples of crack initiation for three laminate samples are shown in Fig. 7. Fig. 8 shows $G_{IC}$ values calculated by three different methods as explained in Section 2.4 and non-linear $G_{IC}$ was considered for further comparison [4]. Addition of 5% and 10% of SMCF to epoxy has improved $G_{IC}$ (NL) by 50% and 64% respectively. This is somewhat better than other recycled modifiers, e.g. fly ash, which succeeded in improving $G_{IC}$ of epoxy resin laminate by up to 48% after addition of 10 wt.% modifier [34].

3.2.2. Fractography

The SEM images of delaminated fracture surfaces are shown in Figs. 9–11. In all images delamination is growing from top to bottom. Fig. 9 shows the crack initiation surface in neat epoxy laminate (Fig. 9A and C) which was comparatively less rough and more shiny with few river lines on the epoxy rich phase, confirming brittle fracture. This fracture surface also represents the shear out failure mainly dominated by the resin region [4]. By contrast,

![Image](image1.png)

Fig. 9. SEM analysis of delamination initiation i.e. near the end of the Teflon insert of (A and C) ESMCF 00, (B) ESMCF 05, (D) ESMCF 10 laminate systems.

![Image](image2.png)

Fig. 10. Matrix rich and carbon fibre rich phases on delaminated surface. (A) ESMCF 00, (B) ESMCF 10. In figure MR shows matrix rich region where as CR shows CF rich region.
in modified CFRP laminate (Fig. 9B and D), a large number of SMCF particles are taking part in crack initiation resulting in debonding and pull-out, in order to absorb more energy for crack initiation by transforming shear failure to tensile failure (SMCF dominated). This supports the increment observed in $G_C$ after addition of SMCF.

Examination of fracture surfaces of ESMCF 00, ESMCF05 and ESMCF10 indicates similar microscopic fracture surface morphology following the unidirectional pattern of CF. Furthermore, delaminated fractures at low magnification (Fig. 10) are observed to consist of alternate layers of matrix rich (MR) and CF rich region (CR). MR surface is a result of crack propagation through the matrix region whereas CR is due to delamination (separation of matrix and CF). In Fig. 10B, debonding and pull out on MR indicates that SMCF particles act as crack stopper during crack propagation, whereas Fig. 10A shows free propagation of crack in the case of ESMCF00.

The CR region in Fig. 11 shows the smooth propagation of the crack without any hindrance in ESMCF 00 whereas ESMCF 05 and ESMCF10 fracture surfaces show a few SMCF particles (shown by the circles in Fig. 11B and C) on the carbon fibre rich phase acting as obstacles for crack propagation in this region. These SMCF particles, stuck in CF alignment, give interlocking (intralaminar) feature to enhance fracture toughness of the composites.

The best possible alignment of short fibres to get optimum delamination properties is perpendicular to the long carbon fibres. In this study SMCF are observed to take the direction of flow and align at an angle between 0° and 90° to fibres. The fibres that are at lower angle possess crack growth through delamination from epoxy and higher angle fibres act as crack stoppers before undergoing debonding and pull out, hence showing ductile fracture.

### 3.3. Correlation of $G_M$ and $G_C$

Fig. 12 shows the improvement effect of SMCF on $G_M$ and $G_C$, and reveals that addition of 5 and 10 wt.% of SMCF enhances $G_M$ by 261% and 692% respectively whereas the same SMCF wt.% addition show only 50% and 64% increase in $G_C$. The possible reason for this is that two different standard tests were used to determine the fracture toughness which give different loading rates and crack tip geometries that apparently affect the results [35,36]. The SENB specimen contains a sharp, pre-crack where as DCB specimen contains a Teflon insert which may have blunting effect which could in
turn results in higher $G_{IC}$ for crack initiation. According to this mechanism $G_{IC}$ must be greater than $G_{M}^{IC}$, which the authors observed in the case of ESMCF 00 and not the other samples. Contradictory results detected in the case of ESMCF 05 and ESMCF 10 could be because of the higher gain in $G_{IC}$ of the matrix than the composite after addition of SMCF, which counterbalanced the effect of blunting the notch.

The results obtained in this study are in accordance with the model proposed by Kim et al. [37] as shown in Fig. 13. According to Kim’s model [37], in the case of a matrix system having $G_{M}^{IC} \leq 0.5$ kJ/m², the resultant laminate composite shows $G_{C}^{IC} \geq G_{M}^{IC}$ and shows approximately linear relationship between both toughness values up to $G_{M}^{IC} = 0.5$ kJ/m². This is because brittle matrix (ESMCF00 composite, in this study) toughness gets completely transferred to the composite toughness for crack initiation [36]. However, as matrix toughness increases ($G_{M}^{IC}$), only partial $G_{M}^{IC}$ could get transferred to $G_{C}^{IC}$ and hence leading to a smaller increment in $G_{C}^{IC}$ [36,37].

Apart from this theory, the nature of the interaction between SMCF particles and epoxy resin plays a role in fracture toughness, which is different in SENB and DCB samples. SEM images in Figs. 5, 9 and 10 convey the information that SMCF particles in SENB samples are aligned at optimum angles ($45\textdegree$–$90\textdegree$) to give maximum results [21] whereas in DCB samples they follow flow direction and most of the SMCF particles get aligned parallel to crack growth and give smaller increments in $G_{C}^{IC}$ [38].

4. Conclusions

In this study epoxy resin was modified using recycled SMCF and subsequently used for making CFRP laminates. Fracture properties of base epoxy resin (both neat and modified) and laminated CFRPs were determined according to ASTM D5045 and ASTM D 5528 respectively and conclusions are drawn as below:

1. Addition of 5 and 10 wt.% of SMCF improved the $G_{IC}$ of epoxy matrix by 261% and 692%, respectively. Subsequent use of these SMCF modified epoxy resins in CFRP laminates improved laminate $G_{IC}$ by 50% and 64%.

2. This was obtained at very low cost. Compared to other modifiers of its type (i.e. recycled), the increment in $G_{IC}$ of laminate is much higher with the same wt.% addition.

3. Increase in $G_{M}$ of matrix and composite was studied on the basis of SEM images which show intensive individual debonding and pull-out mechanisms, providing evidence of high energy absorption. This is achieved because SMCF particles were well separated from each other, which allows more surface area.

4. The correlation between fracture toughness of matrix ($G_{M}^{IC}$) and composite ($G_{C}^{IC}$) was also discussed.

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