TOUGHENING EPOXY SYNTACTIC FOAMS WITH MILLED CARBON FIBRES: MECHANICAL PROPERTIES AND TOUGHENING MECHANISMS

Sammy He\(^1\), Declan Carolan\(^2\), Alexander Fergusson\(^2\) and Ambrose C. Taylor\(^1\)

\(^1\) Department of Mechanical Engineering, Imperial College London, London SW7 2AZ, UK
Email: sammy.he12@imperial.ac.uk (S. He), a.c.taylor@imperial.ac.uk (A. C. Taylor)
Webpage: http://www.imperial.ac.uk/people/a.c.taylor (A. C. Taylor)

\(^2\) FAC Technology, 53 Lydden Grove, Wandsworth, London SW18 4LW, UK
Email: declan@factechnology.com (D. Carolan), alex@factechnology.com (A. Fergusson)

**Keywords:** syntactic foam, milled carbon fibre, tension, fracture, toughening mechanisms

**ABSTRACT**

Syntactic foams comprising hollow glass microspheres (GMS) in an epoxy matrix are critical for lightweight structures, being extensively used in marine and aerospace as cores for composite sandwich panels. They are buoyant and crush resistant, but their use is limited by their brittleness. Milled carbon fibres (MCF) were used to increase toughness, by introducing energy absorption mechanisms, to foams comprising \(\sim 60\) vol\% GMS. Weight ratios of up to 40% MCF:GMS were used. The tensile modulus of the foams increased from 3.36 GPa to 5.41 GPa with the addition of 40% weight ratio of MCF. The tensile strength of the syntactic foam decreased then increase when more MCF particles are added, and the mechanisms responsible are explained for the first time. The fracture energy of the syntactic foam increased by 183%, from 182 J/m\(^2\) to 516 J/m\(^2\), due to the addition of 40% weight ratio of MCF. Toughening mechanisms were identified as crack deflection, debonding and subsequent plastic void growth, and fibre pull-out. Thus, the simple and cheap addition of MCF greatly increases the toughness of the syntactic foams, enabling lighter or more damage-resistant structures.

**1. INTRODUCTION**

Syntactic foams are composite materials comprising of hollow particles in a matrix material. The present work prepared densely packed syntactic foams (i.e. with a high volume fraction of particles) using hollow glass microspheres (GMS) in a thermosetting polymer matrix. These materials exhibit low density, high specific strength, low moisture absorption, and low thermal and electrical conductivity, making them attractive for structural, weight-sensitive applications in the aerospace and marine industries, such as the core in composite sandwich structures [1]. Sandwich structures are used in aircraft interiors and cargo pallets to reduce weight and thus improve fuel efficiency [2]. However, the applications of syntactic foams are limited due to their brittle nature. Defects reduce their stiffness and strength, and cracks can propagate with little energy absorption to cause catastrophic failure. One method to improve the fracture toughness is to reduce the GMS volume fraction [3], but at a cost of increasing the density. Alternative attempts to improve the mechanical and fracture properties include the addition of nanoclay [4], graphene [5], and high aspect ratio fibres [6, 7]. However, processing becomes difficult at high particle loadings, leading to very modest improvements in toughness (from 25-90%). Studies of fibre-reinforced syntactic foams with densely-packed GMS to achieve minimal density are therefore rare. This study investigates the effect of milled carbon fibre (MCF) particles on the tensile and fracture properties of a syntactic foam. MCF was used to introduce fibrous toughening mechanisms. The GMS and MCF particles will be randomly packed, such that the volume fraction of the particles is kept at the maximum for all of the syntactic foam formulations, at around 60%, to minimise density. The tensile modulus, tensile strength, fracture toughness and fracture energy are measured. The toughening mechanisms are then identified using scanning electron microscopy. Various models to predict the tensile
modulus, tensile failure strength, and fracture energy are discussed and applied.

2. EXPERIMENTAL

2.1. Materials and manufacturing

The matrix used a standard diglycidyl ether of bisphenol-A (DGEBA), ‘Araldite LY556’, with an epoxide equivalent weight (EEW) of 185 g/eq, cured using a methyltetrahydrophthalic anhydride, ‘Aradur HY917’, with an anhydride equivalent weight (AEW) of 166 g/eq. This was accelerated by a heterocyclic amine catalyst, 1-methylimidazole, ‘Accelerator DY070’ (all supplied by Huntsman, UK). A stoichiometric ratio of 90 parts per hundred resin (phr) of HY917 and 1 phr of DY070 was used.

Borosilicate glass microspheres of type ‘S38’ from 3M, UK, were used. These have a mean diameter of 40 µm, a mean wall thickness of 1.28 µm with no porosity, a crush strength of 27.6 MPa (90% survival), a true density of 380 kg/m³, and no surface treatment [8]. The milled carbon fibres were ‘Carbiso Mil 100µ’ from easycomposites, UK. The MCF have a mean length of 100 µm and a mean diameter of 7.5 µm, with a true density of 1800 kg/m³ [9].

The syntactic foams were manufactured so that the volume fraction of GMS in the unmodified syntactic foams should be around 60% [8]. The MCF was added at weight ratios up to 40% MCF:GMS. The MCF and GMS were weighed into a beaker and stirred until a uniform grey-coloured powder was achieved. This was then passed through a sieve with holes approximately 1.5 mm square several times to remove any large agglomerations. The plates of foam were manufactured in a mould and were cured at 80 °C for 4 hours, followed by a post-cure at 140 °C for 8 hours. The plates produced were then milled to thicknesses of 3 mm and 8 mm using a TM-2 CNC machine from Haas, UK.

2.2. Mechanical testing

Uniaxial tensile tests were performed in accordance with ISO 527-1 [10]. Specimens of type 1BA with a thickness of 3 mm and a gauge length of 25 mm were machined from the plates using a router. At least eight specimens of each formulation were tested at room temperature at a loading rate of 1 mm/min using an Instron 3366 universal testing machine fitted with a 10 kN load cell. The strain was measured using an Instron 2620-601 clip-on extensometer with a 25 mm gauge length. The tensile modulus was calculated over the strain interval of 0.0005-0.0025.

The fracture energy, $G_{IC}$, was determined using single edge notch bending (SENB) tests in accordance with ISO 13586 [11] using specimens of dimensions 80 × 16 × 8 mm³. A V-notch was machined at the mid-length using a horizontal mill to a depth of 5.3 mm. A liquid nitrogen cooled razor blade was then carefully tapped into the V-notch to produce a sharp pre-crack before testing. The specimens were tested at room temperature at a displacement rate of 1 mm/min using an Instron 3366 universal testing machine fitted with a 10 kN load cell. At least ten valid tests were performed for each formulation.

2.3. Image analysis

A Hitachi S-3400N scanning electron microscope (SEM) was used to observe the fracture surfaces of the SENB samples to identify the toughening mechanisms. The samples were mounted on aluminium stubs and sputter-coated with a 10 nm thick layer of gold to minimise charging. An accelerating voltage of 10 kV was used.

Optical microscopy was used to observe the microstructure. Cross-sections were cold-mounted using an acrylic resin (VARI-SET 10), and were polished to a 0.25 µm finish using a Saphir 330 polishing machine from ATM, Germany. The optical micrographs were obtained using an AxioScope.A1 optical microscope from Carl Zeiss, Germany, in reflection mode. Image analysis was performed using ImageJ.

3. RESULTS & DISCUSSION

In this section, results from microscopy, tensile, and fracture tests are described. These are followed by the application of analytical models to explain and predict the tensile strength and fracture energy.
3.1. Microstructure

The optical micrographs confirmed that the glass microspheres were densely packed within the epoxy matrix, see Figure 1. Milled carbon fibres can be seen as bright spots due to their reflective nature, see Figure 1b.

![Figure 1: Optical micrographs of (a) unmodified syntactic foam and (b) 40% MCF:GMS weight ratio modified syntactic foam](image)

According to the Delesse principle [12], the area fraction of the particles in a cross-section is exactly equal to the volume fraction. Image analysis showed that the microspheres in the unmodified syntactic foam have a volume fraction of 60.7%, as expected in a randomly packed structure, and agrees well with the data sheet [8]. The volume fraction of the GMS reduces as the weight ratio of MCF increases, down to 49.3% at 40% weight ratio MCF:GMS, so the overall volume of epoxy matrix has therefore also increased.

The method of ellipses [13] was applied to the optical micrographs to determine the orientation of the milled carbon fibres. The analysis gives a second order orientation tensor, \( A_{ij} \), with each diagonal component describing the probability of the fibre aligning in the corresponding direction, ranging in value from 0 to 1, and off-diagonal components describing the tilt of orientation in the corresponding plane, varying from -0.5 to 0.5, with 0 representing no tilt. The resulting tensor is:

\[
A_{ij} = \begin{bmatrix}
0.427 & -0.044 & 0.011 \\
-0.044 & 0.415 & 0.016 \\
0.011 & 0.016 & 0.158
\end{bmatrix}
\]

This shows that the fibres favour towards a 2D random planar orientation in the 1-2 plane, despite the random mixing method of the MCF and GMS particles before the manufacturing process.

3.2. Tension

3.2.1. Tensile modulus

This tensile modulus of the unmodified syntactic foam was measured to be \( 3.36 \pm 0.08 \) GPa, and increases to \( 5.42 \pm 0.45 \) GPa with the addition of 40% weight ratio MCF, see Figure 2a, which is expected due to the high modulus of the carbon fibres (\( E_p = 200 \) GPa [9]).

The Halpin-Tsai model [14] predicts the tensile modulus of the composite in a given direction, \( E_{ii} \), by:

\[
E_{ii} = \frac{1 + \zeta_{ii} \eta V_f}{1 - \eta V_f} E_m \tag{1}
\]

\[
\eta = \frac{E_p}{E_m} \frac{1}{\frac{E_p}{E_m} + \zeta_{ii}} \quad \text{where } i = 1, 2 \tag{2}
\]
where $E_m$ is the modulus of the matrix, $E_p$ is the modulus of the particle, and $V_f$ is the volume fraction of the MCF particles. The geometry factor, $\zeta$, depends on the particle orientation [14]. For particles aligned in the loading direction, $\zeta_{11} = 2(l/d)$, where $l$ and $d$ are the length and diameter of the particle respectively. This will give the parallel composite modulus, $E_{11}$. For particles aligned in the perpendicular direction, $\zeta_{22} = 2$, giving the perpendicular composite modulus, $E_{22}$.

The MCF are rod-like (cylindrical) particles where $l = 100 \text{ µm}$ and $d = 7.5 \text{ µm}$. The modulus in the loading direction uses $\zeta_{11} = 26.6$ to determine $E_{11}$. The perpendicular modulus, $E_{22}$, uses $\zeta_{22} = 2$. The tensile modulus of the composite, $E_t$, will have contributions from both the parallel and perpendicular moduli components. Work by van Es [15] described the tensile modulus for composites with 3D randomly orientated fibres as:

$$E_{t, 3D\text{random}} = 0.184 E_{11} + 0.816 E_{22} \quad (3)$$

The tensile modulus for composites with 2D planar orientated fibres was described [15] using laminate theory as:

$$E_{t, 2D\text{planar}} = 0.375 E_{11} + 0.625 E_{22} \quad (4)$$

The modulus values predicted by the Halpin-Tsai model and the van Es equations for MCF particles are shown in Figure 2a for 3D random and 2D planar fibre orientations. The agreement between the predictions for 2D planar orientated fibres and the measured values is excellent, and validates the orientation found by the method of ellipses in Section 3.1, which implies 2D planar orientation of MCF in the syntactic foam.

### 3.2.2. Tensile failure strength

The tensile failure strength of the bulk epoxy polymer was measured to be $88 \pm 1 \text{ MPa}$. This decreased to $21 \pm 2 \text{ MPa}$ when $\sim60\%$ vol GMS was added to create the syntactic foam. This was expected since particles impart a stress concentration on thermoset polymers. A decrease in tensile failure strength was observed in syntactic foams modified with up to 8% weight ratio of MCF. The tensile failure strength then recovers when the weight ratio is further increased, see Figure 2b, to a maximum value of 32 MPa at a weight ratio of 40%.

### 3.3. Prediction of tensile failure strength

To model the tensile strength of the MCF modified syntactic foams, models for fibre and spherical particle modified composites were used individually and then combined.

#### 3.3.1. Milled carbon fibre modified epoxy

Firstly, the conditional tensile strength of the epoxy polymer modified with MCF only, $\sigma_Q$, was predicted using the model developed by Baxter [16] for composites with randomly oriented discontinuous fibres.
This model utilizes the equations for the three failure mechanisms in fibre reinforced composites postulated by Jackson and Cratchley [17]. These mechanisms are longitudinal, shear, and transverse failure, and are dependent on the loading angle, $\theta$, between the stress axis and the fibre axis. These equations are combined with the Tsai-Hill failure criterion [18], and is then integrated for all angles of $\theta$, giving:

$$\sigma_Q = \frac{1}{\pi} \int_0^\pi \left[ \cos^4 \theta \frac{\sigma^2}{\sigma^2_L} + \left( \frac{1}{\tau^2} - \frac{1}{\sigma^2_L} \right) \sin^2 \theta \cos^2 \theta + \frac{\sin^4 \theta}{\sigma^2_T} \right]^{-\frac{1}{2}} d\theta$$  \hfill (5)

where $\sigma_L$ is the longitudinal stress calculated using the shear-lag model developed from Kelly and Tyson [19], $\tau$ is the shear stress of the epoxy matrix, and $\sigma_T$ is the transverse stress of the composite. The transverse stress has lower and upper limits, and depends on the strength of the interfacial bond between the matrix and fibre. If the interfacial bond is weaker than the matrix, the lower limit of $\sigma_T$ can be modelled by considering the fibres as purely defective cylindrical holes, thus reducing the cross-sectional area of the composite. For a square array of fibres, the transverse stress is given by Hull and Clyne [20]:

$$\sigma_T\text{(min)} = \sigma_m \left[ 1 - 2 \left( \frac{V_f}{\pi} \right)^{\frac{1}{2}} \right]$$  \hfill (6)

where $\sigma_m$ is the tensile strength of the matrix. If the interfacial bond is stronger than the matrix, the transverse stress of the composite is equal to the strength of the matrix:

$$\sigma_T\text{(max)} = \sigma_m$$  \hfill (7)

The predicted tensile strengths of the MCF modified epoxies using the Baxter model with $\sigma_T\text{(min)}$ and $\sigma_T\text{(max)}$ are shown in Figure 3. A line showing a constant tensile strength of the matrix, $\sigma_m$, is also shown. There is little change in the tensile strength due to the length of the MCF being smaller than the critical length, such that little stress transfer occurs between the matrix and the fibre. The minimum transverse stress from Equation 6 from Hull and Clyne is also shown in Figure 3, which models the tensile stress of the MCF modified epoxy if the MCF was treated as purely defects.

Figure 3: Predicted tensile strength of MCF modified epoxy using the Baxter and Hull and Clyne models

3.3.2. Glass microsphere and milled carbon fibre modified epoxy

The conditional tensile strengths, $\sigma_Q$, can be used to predict the tensile strength when GMS is added to the MCF modified epoxy to create the syntactic foam. The tensile strength will show a particulate response to the GMS, with the model developed by Nicolais and Narkis [21] and modified by Zare [22].

Consider a unit cell filled with $n^3$ uniformly distributed spherical particles, where at a particular plane perpendicular to the loading direction, the particles occupy a maximum cross-sectional area fraction, $A$. The model states that the tensile strength of the composite, $\sigma_t$, is dependent on the remaining
cross-sectional area fraction of the matrix, $A_m$, and the interfacial strength between the particles and the matrix, $\sigma_i$, such that:

$$\sigma_t = \sigma_Q A_m + \sigma_i A$$

(8)

Zare included an interphase thickness, $t$, into the area fraction of the particles. For a cubic array of $n^3$ spherical particles with an interphase thickness, $t$, which will model the glass microspheres, the maximum cross-sectional area they can occupy on a particular plane is:

$$A = n^2 \pi (r + t)^2$$

(9)

where $r$ is the radius of the spheres. The volume of $n^3$ spherical particles is:

$$V_s = n^\frac{4}{3} \pi r^3$$

(10)

Substituting Equation 10 into Equation 9 gives:

$$A = \pi \left( \frac{3V_s}{4\pi r^3} \right)^\frac{2}{3} (r + t)^2$$

(11)

Substituting Equation 11 into Equation 8 gives:

$$\sigma_t = \sigma_Q \left[ 1 - \pi \left( \frac{3V_s}{4\pi r^3} \right)^\frac{2}{3} (r + t)^2 \left( 1 - \frac{\sigma_i}{\sigma_m} \right) \right]$$

(12)

The interfacial strength and interphase thickness between the matrix and the microspheres cannot easily be determined. Fitted values of $\sigma_i = 18$ MPa and $t = 1$ µm were chosen, and these values agree well with those found in the literature investigating glass fibre/epoxy composites [23]. As for the bulk epoxy discussed above, four cases are considered. Equation 12 is used for when $\sigma_Q$ is equal to the constant matrix stress $\sigma_m$, or the stresses of the MCF modified epoxy from the Baxter model with $\sigma_T (\text{min})$ or $\sigma_T (\text{max})$. The predictions show good agreement to the experimental results at higher MCF:GMS weight ratios, see Figure 4. The predictions from using different $\sigma_Q$ are not significantly different, since the length of the fibres is below the critical length. The tensile failure strength is more severely affected by the reduction of the volume fraction of the glass microspheres than by the addition of the MCF. The volume fraction of the GMS reduces as the weight ratio increases, increasing the matrix cross-sectional area and thus increasing the tensile strength.

To model the reduction of tensile strength at the lower MCF:GMS weight ratios, the Zare model is added onto the Hull and Clyne equation (Equation 6), giving:

$$\sigma_t = \sigma_m \left[ 1 - 2 \left( \frac{V_f}{\pi} \right)^\frac{1}{2} - \pi \left( \frac{3V_s}{4\pi r^3} \right)^\frac{2}{3} (r + t)^2 \left( 1 - \frac{\sigma_i}{\sigma_m} \right) \right]$$

(13)

The predictions from the modified Hull and Clyne model are shown in Figure 4, and there is excellent agreement between the predictions and the experimental data up to 8% MCF:GMS weight ratio.

3.3.3. Transition in tensile failure strength

There is a transition region where the tensile failure strength of the MCF modified syntactic foam goes from where the MCF acts as defects, as in the modified Hull and Clyne model, to where they do not act as defects, as in the constant $\sigma_m$ or the Baxter model. This transitional behaviour has been reported in studies of discontinuous fibre reinforced composites [24, 25], but an explanation for this behaviour is currently unclear in the literature.

For this study, the transition region begins at around 10% MCF:GMS weight ratio, which corresponds to a volume fraction of MCF of about 1.3% in the syntactic foam. The end of the transition region occurs
at around 20% MCF:GMS weight ratio, which corresponds to a volume fraction of MCF of about 2.8%, see Figure 4. These volume fractions are reminiscent of those for electrical percolation and steady state conductivity respectively, for short carbon fibre reinforced composites [26, 27]. Electrical percolation and steady state conductivity also occur over a transition region, much like the tensile failure strength.

Below electrical percolation, the fibres are individual particles and can therefore act as defects, reducing the tensile failure strength. However, above percolation, the fibres form an interconnecting network which allow a flow of electrons from one fibre to another. Since the fibres are interacting, they do not have a detrimental effect on the tensile strength. It is concluded that there is a similarity between electrical properties (percolation threshold and steady state conductivity) and tensile failure strength, and this mechanism can explain the observed trend in the strength values.

3.4. Fracture

The fracture energy, $G_{IC}$, was determined using SENB tests. The fracture energy for the bulk epoxy polymer is $102 \pm 11$ J/m$^2$. This increased to $183 \pm 15$ J/m$^2$ when \sim 60 vol\% of GMS was added to create the syntactic foam, and further increased with increasing MCF content, with a fracture energy of $517 \pm 34$ J/m$^2$ being measured for syntactic foam modified with 40% weight ratio of MCF in the syntactic foam, see Figure 5a. This impressive 182\% increase in fracture energy shows good promise for MCF as a toughener for syntactic foams. This study achieved a percentage increase in fracture energy much higher than in the literature [4–7], while maintaining the maximum possible packing factor to minimise density.

![Figure 4: Predicted tensile failure strength of MCF modified syntactic foams using the Zare model](image)

![Figure 5: (a) Fracture energy of MCF modified syntactic foams and (b) SEM image of fracture surface with toughening mechanisms](image)
3.5. Fractography

The fracture surfaces of the bulk epoxy polymer were found to be smooth and featureless, as is typical for brittle thermoset polymers. When GMS is added to create the syntactic foam, the fracture surfaces show crack deflection, debonding and plastic void growth toughening mechanisms. Crack deflection is evident from the step structures in the epoxy matrix and the characteristic ‘tails’ behind the rigid particles. When the syntactic foams were modified with MCF, fibre pull-out can be seen from the exposed fibres and cavities left by the fibres. The fibres also exhibit debonding and plastic void growth. The toughening mechanisms are identified on the scanning electron micrograph shown in Figure 5b.

3.6. Prediction of fracture energy

The fracture energy of the modified syntactic foam can be predicted analytically using [28]:

\[ G_{IC} = G_{ICU} + \Psi \]  

(14)

where \( G_{ICU} \) is the fracture energy of the unmodified epoxy and \( \Psi \) is the sum of the fracture energy contributions from the toughening mechanisms provided by the GMS and MCF particles. A fracture energy of \( G_{ICU} = 102 \pm 11 \text{ J/m}^2 \) was measured for the bulk unmodified epoxy [29]. Each of the toughening mechanisms identified from the fractography will be discussed and modelled. The identified toughening mechanisms were crack deflection from the GMS, debonding and plastic void growth from both the GMS and MCF, and fibre pull-out from the MCF.

3.6.1. Crack deflection

The fracture energy contribution from crack deflection by the GMS, \( \Delta G_{cd} \), can be predicted using the Faber and Evans [30] model, which takes into account the tilt and twist of the crack front when it approaches a rigid particle. The nominally mode I crack is deflected so is subjected to local mixed-mode loading, thus imparting an increase in fracture toughness. This mechanism is applicable provided that the diameter of the particles is larger than the crack tip opening displacement [31]. The crack opening displacement under plane strain conditions, \( \delta_o \), can be calculated using [28]:

\[ \delta_o = \frac{G_{IC}}{\sigma_y} \]  

(15)

Using \( \sigma_y = 88 \text{ MPa} \), and \( G_{IC} = 517 \text{ J/m}^2 \) for the 40% MCF:GMS weight ratio syntactic foam, a crack opening displacement of 5.9 \( \mu \text{m} \) was calculated, which is much smaller than the diameter of the glass microspheres of 40 \( \mu \text{m} \). Application of the Faber and Evans model is therefore readily justified.

3.6.2. Debonding

The GMS and the MCF were observed to debond from the epoxy matrix. Hull and Clyne [20] derived an expression to predict the fracture energy contribution from particle debonding, \( G_{db} \):

\[ \Delta G_{db} = \int_0^L \frac{V_p}{\pi r^2 L} \left( \frac{2 \pi r x_o G_{i}}{x_o} \right) \text{d}x_o \]  

(16)

where \( x_o \) is the embedded length of the particle, \( L \) is half the length of the particle, \( r \) is the radius of the particle and \( G_i \) is the interfacial fracture energy between the particle and the matrix. Integrating leads to the expressions for debonding energy for spheres and fibres respectively:

\[ \Delta G_{db,s} = \frac{V_p}{\pi r} \ln(4) G_{i,s} \]  

(17)

\[ \Delta G_{db,f} = \frac{V_f L}{r} G_{i,f} \]  

(18)
The interfacial fracture energy of carbon fibre in epoxy was determined by Wang et al. [32] as $G_{i,f} = 10 \text{ J/m}^2$. For GMS, the interfacial fracture energy, $G_{i,s}$, can be estimated using [33]:

$$G_{i,s} = \frac{3\sigma_m^2 r}{4\pi E_m} \quad (19)$$

Substituting the parameters for the epoxy polymer gives a value of $G_{i,s} = 10 \text{ J/m}^2$, which is similar to values for glass/epoxy interfaces [34].

### 3.6.3. Fibre pull-out

The MCF undergo pull-out, and the fracture energy contribution, $\Delta G_{po}$, was derived from Hull and Clyne [20]:

$$\Delta G_{po} = \frac{V_f L^2}{3r} \tau_u \quad (20)$$

The value of $\tau_u$ is taken as 51 MPa from Section 3.3.1. This equation assumes unidirectional fibre alignment. Since the MCF particles are 2D planar randomly orientated, the fracture energy contribution from particle pull-out will be overestimated. Therefore an fibre orientation efficiency factor, $\eta_o$, is used:

$$\Delta G_{po,2D} = \eta_o \frac{V_f L^2}{3r} \tau_u \quad (21)$$

For 2D planar randomly orientated fibres, it can be shown that the fibre orientation factor is [35]:

$$\eta_o = \frac{1}{\pi} \int_0^\pi \cos^4 \theta \, d\theta \quad (22)$$

where $\theta$ is the angle between the fibre axis and the loading axis. This gives a value of $\eta_o = 0.375$.

### 3.6.4. Plastic void growth

When the GMS or the MCF debond, the void created can grow by plastic deformation of the epoxy matrix. The plastic void growth contribution to the fracture energy was calculated using [36]:

$$\Delta G_v = \left( 1 - \frac{\mu_m^2}{3} \right) \left( V_v - V_p \right) \sigma_{yc} r_{yu} K_{vm}^2 \quad (23)$$

where $V_v$ is the volume fraction of the voids created by debonding. The uniaxial compressive yield stress of the matrix, $\sigma_{yc}$, is related to the uniaxial tensile yield stress by the following [36]:

$$\sigma_{yc} = \sigma_{yt} \left( \frac{3^{3/2} + \mu_m}{3^{3/2} - \mu_m} \right) \quad (24)$$

The radius of the plastic zone, $r_{yu}$, can be calculated using the equation proposed by Irwin [37]:

$$r_{yu} = \frac{1}{6\pi} \left( \frac{K_{ICU}^2}{\sigma_{yt}^2} \right) \quad (25)$$

where $K_{ICU}$ is the fracture toughness of the unmodified epoxy, which was measured to be $0.61 \pm 0.05 \text{ MPa m}^{1/2}$ [29]. The von Mises stress concentration factor, $K_{vm}$, varies linearly with the volume fraction of the particles [38]:

$$K_{vm} = 0.59 V_p + 1.65 \quad (26)$$

From the SEM micrographs, the voids left by the GMS particles showed an average 8% increase in volume, while voids left by MCF showed an average 32% increase in volume. The fracture energy contribution from plastic void growth can therefore be calculated for GMS and MCF by applying the volume fraction of particles ($V_p = V_i$ or $V_f$) and voids in Equations (23) and (26).
3.6.5. Predicted fracture energies

The predicted fracture energy contributions from each of the toughening mechanisms are shown in Figure 6a. The contribution from fibre pull-out becomes dominant at higher MCF weight ratios. The contributions from the other toughening mechanisms remain approximately constant, as they depend on the particle volume fraction which does not change significantly. The void growth, crack deflection, and debonding mechanisms give contributions of around 55 J/m$^2$, 39 J/m$^2$, and 11 J/m$^2$ respectively. The GMS particles provided the majority of the fracture energy contributions from debonding and void growth due to the much higher volume fractions of GMS compared to MCF. When all of the above models are applied, the fracture energy contributions are summed and added to the fracture energy of the bulk epoxy polymer to give a prediction in the fracture energy of the syntactic foams. Note that the fracture energy of the unmodified syntactic foam is predicted, so does not need to be measured. The predictions in fracture energy shows excellent agreement with the experimental values, see Figure 6b. Note that these predictions require no fitting to the data, but are derived solely from material properties and observation of the fracture surfaces.

![Figure 6: (a) Fracture energy contributions from identified toughening mechanisms (b) Analytical and experimental fracture energy of MCF modified syntactic foams](image)

4. CONCLUSIONS

Syntactic foams comprising hollow glass microspheres in an epoxy matrix are extensively used in lightweight structures, but their use is limited by their brittleness. Foams comprising 60% volume fraction of hollow glass microspheres (GMS) embedded in an epoxy matrix were modified with milled carbon fibre (MCF) with the aim to increase toughness and strength. Milled carbon fibre was added to the glass microspheres (GMS) at different weight ratios.

At 40% weight ratio, the tensile modulus of the syntactic foam increased to 5.41 GPa from 3.36 GPa for the unmodified syntactic foam. The Halpin-Tsai model for tensile modulus shows very good agreement to the experimental data. The tensile strength of the syntactic foam decreased when low volume fractions of MCF were added, but increased at higher volume fractions. Although this behaviour has been observed previously, an explanation for this transition in tensile strength is lacking. By comparing the tensile strengths with the electrical properties of short carbon fibre reinforced polymers, the mechanisms involved in the transition in tensile strength have been proposed. The experimental results showed excellent agreement to analytical models which treat the MCF as defects at low volume fractions, and uses a constant matrix strength at higher volume fractions. The transition occurs at approximately the percolation threshold for MCF. The fracture energy also increased to 517 J/m$^2$ at 40% MCF:GMS weight ratio from 183 J/m$^2$ for the unmodified, showing good promise for MCF as a toughener in syntactic foams. Scanning electron microscopy identified the toughening mechanisms as crack deflection, fibre pull-out, and debonding with subsequent plastic void growth. Analytical modelling of these toughening mechanisms showed excellent agreement to the experimental data, and showed that
fibre pull-out is the main contributor to fracture toughness at higher loadings of MCF. The significant increases in tensile strength (of over 50%) and fracture energy (of almost 200%) achieved in this study can increase the overall usefulness of syntactic foams in structural applications in the aerospace and marine industries, enabling the design of stronger, lighter, and more fuel-efficient vehicles.

ACKNOWLEDGEMENTS

This work was supported by the EPSRC [grant number EP/N509486/1].

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