The use of tapered double cantilever beam (TDCB) in investigating fracture properties of particles modified epoxy

Wing Lam Tsang

Abstract
This study compares fracture energy of an epoxy polymer from the addition of different wt% of nanoparticles, for both experimental and FEA modelling studies. Silica and core–shell rubber (CSR) particles, and the hybrid of both (from 0.5 wt% to the maximum concentration of 25.4 wt%) are used. An increase in fracture energy was found in the CSR and hybrid specimens, but clustering of particles caused a reduction in the mechanical properties when the concentration of particles was high. As there was interfacial failure found with some tapered double cantilever beam (TDCB) specimens. Therefore, the fracture energies measured with TDCB specimens are also compared with simulation results using the finite element analysis software ‘Abaqus’. These results provided further information for the next stage of investigations in fracture properties of particles modified epoxy.

Keywords Fracture · Polymer · Mechanical properties · Particle-reinforced epoxy

1 Introduction
There is a long history in the use of adhesives in industry. There are many advantages in using adhesives in industry; one big advantage is the reduction in cost. There is also an improvement in product appearance, and an improvement in stress distribution and corrosion resistance; these factors enhance the design possibilities [1]. However, due to the brittleness of adhesives, they are often modified by particles to improve their fracture toughness without changing their glass transition temperature, \( T_g \) [2]. However, some of the toughening mechanisms—particle bridging, crack pinning and deflection are not applicable for nanoscale particles, as the particles are smaller than the crack opening displacement [2, 3]. Therefore, the size of the particles used is one of the most important parameters in toughening epoxy. There is a higher critical stress for debonding for smaller particles; hence, a reduced amount of debonding would be expected. The toughness of the modified epoxy depends on the amount of crosslinking of the epoxy, the type of particles used, the particles’ size and their concentration [4].

There are different theories in the study of fracture mechanics; the two main approaches to quantity toughness are by the consideration of the energy approach and stress intensity approach [5, 6]. Linear elastic fracture mechanics (LEFM) is used in considering the fracture circumstances in epoxy polymers. The tapered double cantilever beam (TDCB) test and the double cantilever beam (DCB) test are in the LEFM methods that are commonly used in determining the fracture energy, \( G_C \), of epoxy adhesive joints, because these methods can determine the fracture resistance of crack to initiation, propagation and arrest. Moreover, the R-curve (resistance curve) of the...
adhesive fracture energy against crack length can also be found from the data obtained in the test, as the toughness may increase with crack length due to additional toughening mechanisms. Therefore, they are very useful in providing information about the fracture performance of the adhesive [7, 8].

The TDCB specimen is designed such that the fracture energy, calculated using Eq. (1), is not dependent on the value of crack length, so the rate of change of compliance with crack length is constant. The value of $G_c$ can be calculated using Eq. (2). The relationship between compliance and crack length is kept constant by varying the height of the specimen with the equation [7, 8]:

$$\frac{dC}{da} = \frac{3a^2}{h^3} + \frac{1}{h} = m$$  \hspace{1cm} (1)

where $a$ = crack length, $h$ = height of substrate beam at a crack length $a$, and $m$ = specimen geometry factor (constant).

For bulk linear elastic behaviour away from the crack tip, $G_c$ is given by:

$$G_c = \frac{P^2}{2B \frac{dC}{da}}$$  \hspace{1cm} (2)

Both TDCB and DCB specimens use the same principles in the test method (mode I, in-plane tensile), but TDCB is more stable as its shape reduces the stress concentration at the start of the crack, hence improving the accuracy of the results [8]. The TDCB is more suited to high rate tests as the failure load does not depend on the crack length, and hence the crack length does not need to be measured.

There are two main categories of failure types (1) cohesive and (2) adhesive/interfacial failure. Cohesive failure is when failure happens within the adhesive layer. This occurs when the interface strength is high [9]. Adnan et al. [9] showed that cohesive failure can occur under tensile loading or shear loading, where adhesive deformed through cavitation and bulk shear [9].

Adhesive or interfacial failure is when failure is in-between the adhesive and substrate [6], due to the presence of low interfacial strength [9]. Therefore, the fracture energy measured would be that of the adhesive/substrate interface, but not of the adhesive itself. Aluminium alloy has a relatively high yield stress, so a plastic zone cannot be formed there, and the measured fracture energy will be much lower than the cohesive value.

When the test rate is increased, there is less crack tip blunting [10]. Less load is required to propagate the crack than to initiate it, and hence stick–slip failure occurs. When the temperature is low and the loading rate is high, crack initiation only needs a minimum yielding at the crack tip; therefore, the crack is sharp and results in a low stress intensity factor. It is the same when there is a very high crack tip strain rate with very short deceleration times at arrest points [11].

The failure mechanisms of the related low wt% of particles modified reinforced epoxy have not been clearly studied, especially for the use of hybrid particles. The wt% in-between low and high wt% of particles are only expected to provide a steady increase in their fracture properties, but it is not confirmed as the mechanisms and behaviour are not clearly known. Therefore, this study would provide further information for the understanding of the related fracture properties and their mechanisms.

2 Materials

There were three materials used in mixing of the adhesive (epoxy, nanoparticles and hardener):

Epoxide resin Araldite LY 556 (Huntsman Advanced Materials, Belgium), which is a diglycidyl ether of bisphenol A (DGEBA) with an epoxy equivalent weight (EEW) of 185 g/mol and density of 1.175 g/ml. As some of the nanoparticles are supplied in epoxy resin, the stoichiometric amount of the epoxy for the silica, CSR, epoxy and hardener were found by using their equivalent weight [11].

Hardener Albidur HE-600 (Nanoresins, Germany), which is an accelerated methylhexahydrophthalic acid anhydride with a density of 1.08 g/ml. This was used at a stoichiometric ratio of 1:1.09 to the resin.

Particles:

1. Silica Nanopox F400 (Nanoresins, Germany). It is a DGEBA master batch with 40 wt% of silica particles in DGEBA and a density of 1.4 g/ml. These silica particles have a mean diameter of 20 nm, and they are in the form of a colloidal silica sol. The silica has been surface-treated by the manufacturer to prevent agglomeration.

2. CSR Paraloid EXL-2300G (Rohm and Haas, UK). They are powder form core–shell rubber particles sieved into three sizes: > 106 µm, in-between 106 µm and 38 µm and < 38 µm. Size of in-between 106 µm and 38 µm was used in this work.

3. Hybrid The same % of silica nanoparticles and CSR were mixed into the epoxy, e.g. 5 wt% of silica plus 5 wt% of CSR.

3 Experimental procedure

3.1 TDCB specimen preparation

Aluminium alloy substrates (grade EN AW 2014A) were used in preparing the TDCB specimens. The substrates were first cleaned with acetone, and grit-blasted with...
180/220 mesh alumina grit. The surface was then cleaned with acetone again before chromic acid etch treatment. The substrates were placed in a 70 °C chromic-sulphuric acid bath for 10 min (composition of bath is 0.1 kg of copper sulphate, 3.87 kg of sodium dichromate, 0.06 kg of powdered aluminium, 7.2 litres of sulphuric acid (s.g. 1.84) and 40 litres of distilled water) [12]. They were then rinsed with tap water and placed in a tap water bath for 15 min. They were rinsed with distilled water and then dried in an oven for 5 min.

3.1 Epoxy preparation

1. **Mixing the particles in unmodified epoxy** Epoxy was first preheated to 60 °C until the viscosity was reduced and the solution was warm. Particles were added and mixed in using a mechanical stirrer at 60 °C for 15 min at 90 rpm and degassed in a vacuum oven. Each type of particles were mixed separately, as in, there was only one type of particles needed mixing in the epoxy using the stirrer at one time.

2. **Mixing the modified epoxy with hardener** Hardener was added in only after the particles and epoxy were mixed properly. The epoxy resin and hardener were poured into a breaker, mixed using a mechanical stirrer at 60 °C for 15 min at 90 rpm. The epoxy and hardener were mixed and degassed in a vacuum oven. The mixture was spread on the substrate using a spatula, ensuring that it covers the whole surface. A piece of polytetrafluoroethylene (PTFE) film (Aerovac, UK) of 60-mm long was placed at one end for creating a pre-crack, and a stainless steel wire of 0.4 mm diameter was placed at each end of the substrate to provide a constant thickness of adhesive layer of 0.4 mm.

A bonding jig was used to clamp the substrates together, see supporting information. Three specimens are prepared each time; this can provide a higher consistency of the specimen’s conditions (as they would be prepared with the same jig). The jig was coated with release-agent Frekote 700-NC (Loctite, UK) to prevent the adhesive sticking to the jig and allowing removal of the specimens. The jig was placed in a fan oven, and the adhesive was cured.

After curing, the excess adhesive was removed using sandpaper. The joint was coloured by white correction fluid and a paper ruler marked in millimetres was secured under the bonding line to allow the crack length to be measured, see supporting information.

3.2 Differential scanning calorimetry (DSC) tests

The completeness of curing was confirmed by measuring glass transition temperature, $T_g$, of the specimens using differential scanning calorimetry (DSC) [13]. There were two different curing cycles used in the first and second sets of control specimens to compare the $T_g$ of the specimens.

The two curing cycles used were:

- **Control first three specimens** Preheat at 60 °C, ramp at 1 °C/min to 95 °C, dwell for 1 h, ramp at 1 °C/min to 165 °C, and dwell for 2 h, ramp at 2 °C/min to room temperature (20 °C).

- **Control second three specimens** Ramp at 1 °C/min to 95 °C, dwell for 3 h, ramp at 1 °C/min to 155 °C and dwell for 5 h, ramp at 2 °C/min to room temperature (20 °C).

DSC works by measuring the amount of heat energy needed for increasing temperature of the sample.

For the DSC measurements, 10 mg samples were used. Samples were taken from the TDCB joints and weighed. The samples were heated from 30 to 180 °C, at a rate of 10 °C/min. The $T_g$ was obtained from the second heating cycle. The glass transition temperature, $T_g$, measured was 133.2 °C for both curing cycles, which was in the expected range (expected value is 148.0 °C measured from DMA). It is found by Mohammed et al. [11] that $T_g$ of the same unmodified epoxy was 153 °C, the value was not affected by the addition of silica particles. The $T_g$ value can be slightly different when there is a different curing cycle used, as well as different specimen size. Therefore, no adjustment is needed for the curing cycle use in all the other specimens. The curing cycle for all the rest of specimens was the first one: Preheat at 60 °C, ramp at 1 °C/min to 95 °C, dwell for 1 h, ramp at 1 °C/min to 165 °C, and dwell for 2 h, ramp at 2 °C/min to room temperature (20 °C).

3.3 Quasi-static rate tests

The TDCB tests were performed using a tensile testing machine with a cross-head displacement rate of 0.1 mm/min, see Fig. 1. The specimen is fixed with a load cell of 5 kN, and the load and displacement were recorded by the testing machine. The experiment was set up with a traveling microscope for measuring the crack length. The crack length was measured to a precision of ± 0.5 mm.

3.3.1 Initial loading and reloading

There were two loadings performed in each quasi-static TDCB test: 1. Initial loading (precracking) and 2. Reloading (actual loading) [8].

1. During the initial loading, the test was stopped when the crack travelled to the end of the starter film and
started to propagate into the adhesive, which would be the insert length ($a_0$).

The specimen was then unloaded and crack would be closed up, specimen was unloaded slowly at a constant cross-head rate of 1 mm/min, and readings were taken at about every 0.1 mm of change of extension. The unloading curves should be able to go back to original, a slightly negative force when the extension was zero was acceptable, as there might be slight inaccuracy from reading, but a large negative load value would be an indication of permanent deformation of the substrate and test would not be valid.

2. Reloading rate was the same as the initial loading (0.1 mm/min). The first crack propagation would be the precrack value (NL, Visual and Max/5%). The crack length readings were taken until specimen was opened up completely or until there were enough data points. At least 15 readings are recommended by the protocol from Blackman et al. [14].

3.3.2 Initiation and propagation values

There were three types of initiation values, and visual observation was used in this study [15]:

- **Nonlinear (NL)** There is a linear region at the beginning of the graph where material can go back to original shape with linear elastic deformation. NL is the point at which the elastic behaviour ends.
- **Visual observation (Vis)** It is the first visible crack propagation.
- **5% or Max** It is the maximum point from the curve, or where a line of initial compliance +5% cuts the graph. The value which occurs at the smaller displacement should be used.

The thickness of the substrate was measured at 3 points (near both ends and at the middle) of the beam before and after bonding, in order to monitor the thickness of the adhesive layer.

The height of specimen is tapered such that a constant specimen geometry factor, $m$, is used

$$m = \frac{3a^2 \cdot h^3 + 1}{h}$$  \hspace{1cm} (3)

where $a =$ crack length, $m = 2 \text{ mm}^{-1}$, $h =$ thickness of substrate beam at a crack length of $a$ [15].

3.3.3 Determination of $G_c$ in TDCB

There are three methods in determining the value of $G_c$: experimental compliance method (ECM), simple beam theory (SBT) and corrected beam theory (CBT) [16]. Their equations are shown below. The use of ECM and CBT can provide more accurate results [8] than SBT.

- Experimental compliance method (ECM):

$$G_c = \frac{nP\delta}{2B a N}$$  \hspace{1cm} (4)

where $P =$ critical load, $\delta =$ displacement, $a =$ crack length, $B =$ width of specimen, $F =$ displacement correction and $N =$ load-block correction.

- Simple beam theory (SBT)

$$G_c = \frac{P^2}{2Bm}$$  \hspace{1cm} (5)

- Corrected beam theory (CBT)

$$G_c = \frac{4P^2m}{E_s s B^2} \left[ 1 + 0.43 \left( \frac{3}{ma} \right)^{\frac{1}{2}} \right]$$  \hspace{1cm} (6)

4 Finite element analysis (FEA)

4.1 Finite element analysis introduction

The experimental results found would be compared with the results of a modelling study using Abaqus. The amount of debonding of particles would be calculated with the use of 2D plane-strain cohesive surface elements, where only mode I would be considered. The boundary conditions would be at the front of the beams, and Fig. 2 shows the movements in the beams. For the lower beam, as there would be a small rotation in the beam during the mode I test, rotation would be allowed. No movement in any direction other than $y$ would be allowed. For the front of the upper beam, only the mode I opening ($y$-direction) would be allowed to move.
Table 1 shows the material properties information in the study. The properties of the epoxy were obtained from calibration of the stress–strain data from other studies in the group.

The initial values of the fracture energies used were taken from the average initial value from experimental results. Cohesive traction–separation would be used as parameters in the simulation. When only mode I is under consideration, the parameters for describing cohesive law are stiffness $K_i$, the separation at damage initiation, $\delta_{n0}$ and critical energy release rate (fracture energy), $G_c$ [18].

The values for the traction–separation curve are calculated using [18]

$$K_i = \frac{E}{t_a} \delta_{n0} = \frac{\sigma_y}{E} t_a \sigma_{nc} = \delta_{n0} K_i$$

(7)

where $t_a$ is the thickness of the adhesive layer.

- Properties of Cohesive layer used
- *Quades Damage* Nominal Stress to Normal-only mode, First Direction and Second Direction were 60
- Damage Evolution conditions used were energy type with linear softening, mode-independent mixed mode behaviour that allowed maximum degradation. Initial Fracture energy $= 20$ (according to initial value from the control specimens)
- *Traction behaviour* $E/Enn$, $G1/Ess$ and $G2/Ett = 1E + 06$

The zero-thickness cohesive layer was tied in-between the top and lower the adhesive layers (see Fig. 3).

Element size of $0.5 \times 0.25$ mm is used.

5 Results

5.1 Fracture energies

Results of quasi-static rate TDCB were compared using simple beam theory (SBT). Stable crack propagations were compared separately to stick–slip. The amount of stick–slips was found different with different formulae. The results then act as initial values in FE model predictions.

The three methods used to calculate the fracture energy values were expected to give similar values, and they did. Table 2 compares the $G_c$ values for the control (unmodified) epoxy for the three methods. Simple beam theory (SBT) usually gives a slightly lower value according to previous experience [8], and these data fit this observation.

There are two types of crack propagation–stable propagation and stick–slip. These values cannot be averaged, and need to be considered separately, such as comparing averaged initiation values, etc. [8]. This is expected to show increase in the amount of stick–slip when test rate is increased [19].

Similar fracture energies values of the control specimens were found when compared to studies from Hsieh et al. [4], and more comparison of results is shown in the next section.

5.1.1 Control

Table 2 and Fig. 4 show the control TDCB fracture energies from the SBT, CBT and ECM methods. Figure 7 shows standard epoxy SEM image showing microstructure of epoxy. The fracture energies from the control specimens were at the lowest end of results when compared to studies in the past, but these results were realistic [20]. The lower fracture energy values might be due to the thin layer of adhesive applied on the joint, and with relatively small standard deviations, the control results were considered to be reliable.

5.1.2 Silica-modified epoxy

See supporting information for SEM images showing the morphological structure of low and high wt% of silica-modified epoxy. The addition of silica generally increased the toughness, see Table 3. There was an increasing trend in mean $G_c$ from control to the addition of 2 wt% of silica, but when there was a higher amount of silica added; no pattern was formed, and values were a lot lower than expected. There was interfacial failure, and no stick–slips, in specimens with 10 and 15 wt% of silica. All the results found were lower than the values from Hsieh et al. [4]. More about the interfacial fracture surfaces is discussed in the next section.

According to the propagation curve, see Fig. 5, there is a peak shown in $G_c$ value with the addition of 2 wt% of silica, and the $G_c$ value dropped after this point. This could be due to the presence of greater than 15% of debonding when a lower % of silica is added. The % of debonding reduces when there is a higher % of silica added, because when particles are more concentrated, they would become too close to each other, so the energy needed for voiding would be higher [13]; therefore, these results are according to predictions. It is also found by Mohammed et al. [13] that there was a high increase in fracture energy when 13% of silica nanoparticles were added in [13]. However, there were two lower values when 3% and 15% of silica particles were used, these drops were not expected, and these were believed to be due to uneven distribution of particles in some of the specimens. A plateau is expected after the peak, and the relatively high wt% of silica particles would not show significant effects in toughening. At very high wt% of
silica particles, the toughness will decrease due to there being too little epoxy between the particles to absorb the maximum energy, and this occurred to some of the specimens.

5.1.3 CSR

It is shown that the fracture energy of the CSR-modified epoxy was about one time higher than the silica-modified epoxy for all wt%. As seen in supporting information, SEM images show the morphological structure of low and high wt% CSR-modified epoxy. There is a general increase in toughness when the % of particles increase, and the small drop in fracture toughness at 2% of CSR might be caused by clustering of particles that could not be mixed properly. Most regions of the CSR-modified TDCB beams showed cohesive failure, while some of the silica-modified beams had interfacial failure, which explains why there were remarkably larger $G_c$ values for the CSR specimens. This indicated that the fracture energies of the silica-modified joints were not measured accurately due to the effect of interfacial failure; see Tables 3 and Fig. 6.

The cause of inaccuracy in the silica-modified TDCB specimens can also be due to the viscosity of the resin. Silica-modified epoxy had a low viscosity and some of the resin dropped down from the beams during making of the joints. It caused uneven thickness of the bondline. Hybrid mixture would have a higher viscosity and would be expected to improve accuracy of the measurements.

Table 1 Properties of aluminium alloy (EN AW 2014-A) [17] and epoxy [18] for the FE model

| Property | Al alloy | Epoxy |
|----------|----------|-------|
| $E$ (GPa) | 72.4 | 2.9 |
| $\sigma_y$ (MPa) | 430 | – |
| UTS (MPa) | 485 | – |
| $\rho_s$ (kg/m$^3$) | 2700 | 1200 |
| $v_s$ | 0.33 | 0.35 |

Fig. 2 Forces in TDCB

Table 2 Summary of fracture energies for control from TDCB specimens

| Point (J/m$^2$) | $G_c$ (SBT) | $G_c$ (CBT) | $G_c$ (ECM) |
|----------------|-------------|-------------|-------------|
| Mean propagation | 73 | 80 | 111 |
| SD of propagation | 7 | 7 | 9 |
| Mean initiation | 81 | 89 | 123 |
| SD of initiation | 5 | 6 | 10 |
| Mean arrest | 56 | 62 | 83 |
| SD of arrest | 3 | 3 | 4 |

Fig. 3 Cohesive layer was tied in-between the top and bottom adhesive layer

5.2 Fracture surfaces

There was an increasing amount of interfacial failure found when there is 1 and 2 wt% of silica added in. The amount of interfacial failure was reduced by changing the acid tank for refining the quality of the acid etch treatment. This showed that the surface treatment of the aluminium alloy highly affects the adhesive bonding and its failure. However, specimens with higher wt% of silica (from 3 wt% onwards) showed mainly interfacial failure with propagation only. It could be due to the differences on the surface of beams used (new and recycled beams), and this could cause variations in bonding of joints. Most of the regions in CSR specimens were cohesive failure, so the toughness values were reliable. Figure 7 shows the two failure types (interfacial and cohesive) and indicates the stick–slip region in the specimens.
In terms of the two particles, the silica nanoparticles have a size smaller than the plastic zone size and the crack opening displacement; therefore, there would be debonding and void growth. A higher % of void growth expected when a small % of them is added [6].

The micro-size rubber particles toughen the epoxy by shear yielding, and this caused larger deformation zones and absorbed strain energy [21]. Rubber particles that cavitated at a relatively lower stress caused localised shear yielding (cavitation will occur before shear banding), followed by plastic void growth [6].

5.3. Finite element analysis results

As initial values from experimental results were used, the failure predictions were assumed to have the same failure pattern as experimental ones, so when there were only stick-slips were found from experimental results, there would only be initiation and arrest points predicted in the model. Most of the prediction of fracture energy values were found to be similar to the experimental values; however, there was no very clear trend shown regarding relationship between fracture type and % of particles used.

Boundary conditions were used instead of load, because this provides a better convention of results data and it is the control factor in this experiment.

For all specimens

Crack openings are stable within the whole simulation (see Fig. 8). The complete opening of joint is shown in supporting information. Complete fail of joint at BC = 50 mm

5.2.1 Silica‑modified epoxy

The FEA prediction results for the silica-modified epoxy are shown in Table 4 and Fig. 9. The FEA model predictions had a very similar pattern of curves in silica; most of the results agree with the experimental data, but predicted model had slightly higher values than experimental data. The shape of the prediction curve for propagations was exactly the same as the experimental one, while some of the stick-slips values were predicted to an about 1 time higher values. There had been interfacial failure for the silica-modified epoxy TDCB specimens, which would reduce the fracture energy measurements; it is therefore expected to have higher predicted values. There were no stick-slips
5.2.2 CSR-modified epoxy

FEA predictions results of CSR-modified epoxy are shown in Table 5 and Fig. 10. The predicted results were very similar to the experimental data with slightly lower values, and the predicted results agreed well with the experimental findings. There was mostly cohesive failure in the CSR-modified epoxy TDCB specimens, and hence results were reliable.

All the predictions are according to experimental data, except arrest data. This proof that arrest at very brittle condition is not predictable (Table 6).

6 Conclusions

This work aimed to provide insight to the fracture mechanics profile of modified epoxies using the established fracture mechanics approach. The use of TDCB geometry helped in understanding crack growth, and with the use of high rate testing, and further brittle behaviour is studied. The fracture study included both experimental and FEA modelling; these results provided further insights in the fracture properties of particles reinforced epoxy. However, FEA simulation predictions are not applicable for unstable
cracks, as the model can assume propagations only. Other details of the failure mechanisms can be revealed in their fracture surfaces; they provided evidence of the brittleness recorded. This information can be used in modifying the model properties for future studies.

### Compliance with ethical standards

**Conflict of interest** On behalf of all authors, the corresponding author states that there is no conflict of interest.

**Open Access** This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing,
adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit http://creativecommons.org/licenses/by/4.0/.

References

1. Kinloch AJ (1997) Adhesives in engineering. Proceedings of the Institution of Mechanical Engineers Part G-Journal of Aerospace Engineering 211(G5):307–335
2. Dittanet P, Pearson RA (2012) Effect of silica nanoparticle size on toughening mechanisms of filled epoxy. Polymer 53(9):1890–1905
3. Imanaka M et al (2001) Fracture toughness of spherical silica-filled epoxy adhesives. Int J Adhes Adhes 21(5):389–396
4. Hsieh TH et al (2010) The toughness of epoxy polymers and fibre composites modified with rubber microparticles and silica nanoparticles. Journal of Materials Science 45(5):1193–1210
5. Bandopadhyay S (1990) Review of the microscopic and macroscopic aspects of fracture of unmodified and modified epoxy-resins. Materials Science and Engineering A-Structural Materials Properties Microstructure and Processing 125(2):157–184
6. Tsang WL, Taylor AC (2019) Fracture and toughening mechanisms of silica- and core–shell rubber-toughened epoxy at ambient and low temperature. J Mater Sci 54(22):13938–13958
7. Blackman BRK, Kinloch AJ (2008) Protocol for the determination of the mode I adhesive fracture energy, GIC, of structural adhesives using the double cantilever beam (DCB) and tapered double cantilever beam. ESIS
8. BS7991, Determination of the mode I adhesive fracture energy, GIC, of structural adhesives using the double cantilever beam (DCB) and tapered double cantilever beam (TDCB) specimens. BS 7991:2001, BSI
9. Adnan A, Sun CT (2008) Effect of adhesive thickness on joint strength: a molecular dynamics perspective. J Adhes 84(5):401–420
10. Kinloch AJ (1990) Adhesion and adhesives science and technology. Chapman and Hall, London
11. Kinloch AJ, Shaw SJ, Hunston DL (1983) Deformation and fracture behaviour of a rubber-toughened epoxy: 2. Failure criteria. Polymer 24(10):1355–1363
12. Feito DA (2012) Ph.D. thesis, Fracture mechanics of carbon fibre reinforced plastic to Ti-alloy adhesive joints. Mechanical Engineering Department 2012, Imperial College London
13. Mohammed RD et al (2008) Toughening mechanisms of nanoparticle-modified epoxy polymers. In: Laudon M, Romanowicz B (eds) NSTI Nanotech 2008, vol 1. technical proceedings. CRC Press-Taylor & Francis Group, Boca Raton, pp 798–801
14. Blackman BRK et al (2009) The fracture behaviour of structural adhesives under high rates of testing. Eng Fract Mech 76(18):2868–2889
15. DS5023 A (2007) standard test method for plastics: dynamic mechanical properties: In Flexure (three-point bending), ASTM
16. Blackman BRK et al (2003) The calculation of adhesive fracture energies in mode I: revisiting the tapered double cantilever beam (TDCB) test. Eng Fract Mech 70(2):233–248
17. Karac A et al (2011) Modelling the fracture behaviour of adhesively-bonded joints as a function of test rate. Eng Fract Mech 78(6):973–989
18. Brett M (2011) Ph.D. thesis, Prediction of the performance of adhesively-bonded composite joints. Mechanical Engineering Department, Imperial College London
19. Blackman BRK et al (2012) The fracture behaviour of adhesively-bonded composite joints: effects of rate of test and mode of loading. Int J Solids Struct 49(13):1434–1452
20. Mohammed RD et al (2008) Toughening mechanisms of nanoparticle-modified epoxy polymers. In: Laudon M, Romanowicz B (eds) NSTI Nanotech 2008, vol 1, technical proceedings
21. Masania K (2010) Ph.D. thesis, Toughening mechanisms of silica nanoparticle-modified epoxy polymers. Mechanical Engineering Department, Imperial College London

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.