THE FRACTURE BEHAVIOUR OF BEAD-FILLED EPOXIES AND ASSOCIATED HYBRID COMPOSITES

JUNG JU LEE

A thesis submitted for the degree of Doctor of Philosophy
Materials Science and Engineering Department
University of Surrey
December 1992
SUMMARY

The plane strain fracture toughness of seven different particle-filled epoxies has been measured using compact tension specimens. These toughened epoxies were based on 828 epoxy resin filled with three types of phenolic beads and four types of carbon beads. Significant increases in toughness were observed (up to about 50% with 30% volume fraction of bead) and the mechanisms of toughening have been studied using scanning electron microscopy. The suggested major toughening mechanisms are crack pinning, localized plastic deformation associated with particle-matrix debonding and transparticle fracture. The shape of the load-displacement records obtained during the compact tension tests have been correlated with the failure mechanisms and compared with other studies in the literature. Based on the results obtained from the fracture toughness testing of bead filled epoxies, a carbon bead filled epoxy was selected as the matrix material for a hybrid composite.

A method of preparing glass fibre laminates using bead filled epoxy as matrix has been developed which results in the beads concentrating at the inter-ply regions. The interlaminar fracture behaviour of the hybrid composite has been investigated using DCB (double cantilever beam) and ENF (end notch flexure) specimens for Mode 1 and Mode 2 tests respectively. The hybrid composite shows an increase in both $G_{IC}$ initiation and $G_{IIC}$ values as compared to a GFRP laminate with pure epoxy matrix. The optimum bead volume fraction for
the hybrid composite is between 15 and 20 %. However, the pure epoxy glass fibre composite shows a higher $G_{IC}$ propagation value than that of the hybrid composites due to fibre bridging which is less pronounced in the hybrids as the presence of the beads results in a matrix rich interply region. The relationship between the Mode 1 interlaminar fracture mechanics parameters (i.e. $G_{IC}$ and $K_{IC}$ values), obtained from DCB specimens, has been reviewed using orthotropic fracture mechanics. It has been shown that $K_{IC}$ values calculated using an isotropic analysis of the DCB specimen are an overestimate and that they can be corrected by a factor derived from orthotropic fracture mechanics.
ACKNOWLEDGEMENTS

Important contributions have been made by a number of individuals in the M.S.E. department during the course of this work. The author would like to acknowledge these efforts.

First and foremost I would like to express profound gratitude to my supervisors Dr. Paul Smith and Dr. Steve Ogin. Their energy, enthusiasm and commitment have been invaluable. Again I would like to thank them for their great efforts in helping me to carry on this project. It is a pleasure to acknowledge the enthusiastic help and guidance of Dr. Lynn Boniface, Dr. Amir Rezaifard and Mr. Conrad Doran during this work as well as the technical assistance of Mr. Reg Whattingham. I would like to acknowledge Kobe Steel Europe Ltd for provision of materials and financial support.

Finally, I would like to thank my parents and family (Jung-Hee Lim, Jong-Min and Jong-Young Lee) for their encouragement and endurance.
CONTENTS

SUMMARY i
ACKNOWLEDGEMENT iii
CONTENTS iv

1. INTRODUCTION 1

2. LITERATURE REVIEW 6
  2.1 INTRODUCTION 6
  2.2 APPLICATION OF FRACTURE MECHANICS TO COMPOSITE MATERIALS 7
    2.2.1 Introduction 7
    2.2.2 Basic concept of fracture mechanics 8
    2.2.3 Anisotropic fracture mechanics 11
  2.3 MECHANICAL PROPERTIES AND FRACTURE BEHAVIOUR OF TOUGHENED EPOXY 17
    2.3.1 Introduction 17
    2.3.2 Mechanical properties of pure and toughened epoxy resins 18
    2.3.3 Fracture behaviour of toughened epoxy 22
  2.4 INTERLAMINAR FRACTURE TOUGHNESS OF COMPOSITE MATERIAL 28
    2.4.1 Introduction 28
    2.4.2 Previous study of interlaminar fracture in standard and toughened matrix composites 30
    2.4.3 Measurement of Mode 1 and Mode 2 interlaminar fracture toughness 34
  2.5 CONCLUSION OF LITERATURE REVIEW 41

3. MATERIAL PROCESSING AND EXPERIMENTAL METHOD 55
  3.1 MATERIAL PROCESSING 55
    3.1.1 Base materials 55
    3.1.2 Plaque fabrication for compact tension specimens 56
    3.1.3 Laminate fabrication 59
    3.1.4 Fibre volume fraction measurement 60
  3.2 PREPARATION OF TEST SPECIMENS 61
    3.2.1 Compact tension specimens 61
    3.2.2 Tension and bend specimens 62
    3.2.3 Plain strain compression test specimens 62
    3.2.4 DCB and ENF specimens 62
  3.3 EXPERIMENTAL TEST METHODS 63
    3.3.1 Compact tension test 63
    3.3.2 Young's modulus measurement 63
    3.3.3 Yield stress measurement 64
    3.3.4 Mode 1 interlaminar fracture toughness test 65
    3.3.5 Mode 2 interlaminar fracture toughness test 65
  3.4 FRACTURE SURFACE OBSERVATION 66
4. FRACTURE BEHAVIOUR OF EPOXY RESIN TOUGHENED WITH CARBON AND PHENOLIC BEADS

4.1 INTRODUCTION

4.2 CRACK GROWTH BEHAVIOUR AND LOAD-DISPLACEMENT RECORDS
4.2.1 Crack growth behaviour
4.2.2 Load-displacement records

4.3 FRACTURE TOUGHNESS, $K_{IC}$, OF PURE AND TOUGHENED EPOXIES
4.3.1 Pure epoxy
4.3.2 Effect of phenolic and carbon beads on the $K_{IC}$ value as function of bead volume fraction
4.3.3 Comparison of $K_{IC}$ values of toughened epoxies containing the same volume fraction of seven different types of beads
4.3.4 Effect of bead size on the $K_{IC}$ value

4.4 YOUNG'S MODULUS OF PURE AND TOUGHENED EPOXY
4.4.1 Pure epoxy
4.4.2 Toughened epoxy

4.5 FRACTURE ENERGY, $G_{IC}$, OF TOUGHENED EPOXY
4.5.1 Calculation of $G_{IC}$ from $K_{IC}$
4.5.2 $G_{IC}$ values for phenolic and carbon bead filled epoxy

4.6 FRACTOGRAPHIC ANALYSIS
4.6.1 Neat resin
4.6.2 Epoxies containing beads

4.7 HYBRID PARTICLE FILLED EPOXY
4.7.1 Fracture toughness of hybrid particle filled epoxy
4.7.2 Fracture surface

4.8 DISCUSSION
4.8.1 Effect of pre-cracking process
4.8.2 Load-displacement behaviour
4.8.3 Qualitative discussion of toughening mechanism
4.8.3.1 Overview
4.8.3.2 Crack pinning
4.8.3.3 Multi-level cracking, plastic deformation, debonding, particle cracking
4.8.3.4 Transparticle fracture
4.8.3.5 Summary
4.8.4 Quantitative aspect of toughening mechanism
4.8.4.1 Crack pinning
4.8.4.2 Localized plastic deformation
4.8.4.3 Summary
4.8.5 Selection of bead type for hybrid composite

4.9 CONCLUSIONS

5. MODE 1 INTERLAMINAR FRACTURE BEHAVIOUR OF HYBRID COMPOSITE MATERIAL FABRICATED WITH A TOUGHENED MATRIX

5.1 INTRODUCTION

5.2 DATA REDUCTION METHODS FOR DCB TESTS
5.2.1 Compliance methods to determine $G_{IC}$
5.2.2 Area method to determine $G_{IC}$
5.2.3 Calculation of $K_{IC}$ values
5.3 EXPERIMENTAL RESULTS

5.3.1 The compliance variance as a function of crack length 201
5.3.2 GIC values from DCB tests 202
5.3.3 Effect of bead volume fraction on the fracture toughness (KIC) of the hybrid composite 204

5.4 FRACTOGRAPHIC ANALYSIS AND FRACTURE MECHANISMS 204

5.4.1 Fractographic analysis 204
5.4.2 Fracture mechanisms 206

5.5 DISCUSSION 207

5.5.1 Load-displacement behaviour, GIC and KIC values 207
5.5.2 Optimum bead volume fraction 208
5.5.3 Translation of resin toughness into composite interlaminar toughness 212

5.6 CONCLUSIONS 215

6. MODE 2 INTERLAMINAR FRACTURE BEHAVIOUR OF HYBRID COMPOSITE MATERIAL FABRICATED WITH A TOUGHENED MATRIX 256

6.1 INTRODUCTION 256
6.2 ANALYSIS OF END NOTCH FLEXURE (ENF) TEST DATA 257
6.3 EXPERIMENTAL RESULTS 258
6.4 FRACTOGRAPHIC ANALYSIS AND FRACTURE MECHANISMS 260

6.4.1 Fractographic analysis 260
6.4.2 Fracture mechanisms 260

6.5 DISCUSSION 261
6.6 CONCLUSIONS 263

7. THE APPLICATION OF ORTHOTROPIC FRACTURE MECHANICS TO HYBRID COMPOSITE MATERIALS 279

7.1 INTRODUCTION 279
7.2 APPLICATION OF FRACTURE MECHANICS TO COMPOSITE MATERIAL 281

7.2.1 The orthotropic fracture model 281
7.2.2 Limitations 284

7.3 INPUT DATA FOR ORTHOTROPIC FRACTURE MODEL 286
7.3.1 Measured fracture parameters 286
7.3.2 Determination of elastic constants 286

7.4 DATA ANALYSIS AND DISCUSSION 287

7.4.1 Deviation of GIC and KIC values 287
7.4.2 Calculation of orthotropic KIC values 292
7.4.3 Relation between measured GIC values and isotropic KIC values 293

7.5 CONCLUSION 295

8. CONCLUSIONS AND FURTHER WORK 311
8.1 CONCLUSIONS 311
8.2 FURTHER WORKER 314

REFERENCES
CHAPTER 1. INTRODUCTION
1. INTRODUCTION

Constructional materials for use in aircraft, in high speed marine craft and in rapidly moving pieces of machinery need to have high specific modulus and strength. The high specific modulus and strength of continuous fibre reinforced composites, combined with their excellent corrosion and fatigue resistance makes them prime candidate materials for aerospace, marine and other structural applications.

During the past decade a large growth in the use of composite materials in aircraft applications has been reported. In particular, some advanced military fighters are fabricated with much of the wing and fuselage structures made from composite materials. Currently, this trend towards designing with composites is moving into large cargo/transport and new military cargo airplanes in order to reduce structural weight. Studies show that by the mid 1990s, as much as 40% of the structural weight could be composite materials and, by the year 2000, composites could account for more than half the structural weight, see Fig.1.1 (Kam and Walker, 1987).

However, one of the limiting features of composite materials in service is their tendency for matrix cracking either within a ply (e.g. transverse ply cracking) or between plies (i.e. delamination or interlaminar cracking). Delamination is the most common and life-limiting damage mechanism in composite structures. The growth of a
Delamination initiated from matrix cracking is of major concern to designers of composite structures, because it redistributes the stress in the plies of laminates and may influence residual stiffness, residual strength and fatigue life. Consequently, correct characterization of delamination resistance, leading to more damage tolerant composite structures, has been a major goal of composite material research and development activities (Johnston, 1987, Kim et al., 1992).

Delamination in composites is strongly dependent on the properties of the matrix. One factor thought to contribute to delamination in composites is brittleness (low toughness) of the matrix material. Currently, epoxy resin is one of the most important materials being used as a matrix in fibre reinforced composites for structural applications. Materials with epoxy matrices, and in particular continuous fibre reinforced composites, are notch sensitive and lose their structural integrity when damaged. Damage can occur either during processing or under service loading. Generally it initiates from pre-existing defects or stress concentrations. The most important damage modes in laminated composites are matrix cracking, delamination and fibre fracture. Matrix cracking and delamination depend highly on matrix dominated-properties. To improve the resistance to delamination, much attention has been concentrated on improving the fracture toughness of epoxy resins (Evans and Master, 1987, Jordan et al., 1989).
According to previous research, there are two basic approaches to improve the mechanical performance of current resin matrices. One is to use an alternative type of polymer, for example high toughness thermoplastics such as poly-ether-etherketone, PEEK, (Cogswell and Hopprich, 1983) and the other is to modify existing epoxies (Scott and Phillips, 1975). This second approach is attractive because epoxy matrices possess many advantageous properties except for their lack of toughness. In addition, a drawback with the thermoplastic approach is the high fabrication cost (Garg and Mai, 1988).

To toughen epoxies by a particulate route, we can consider two methods. Firstly, there are rubber-toughened epoxies. Secondly, there are systems based on particle reinforcement where the particle could be inorganic or organic in nature. Many results have been reported in the literature for systems based on rubber toughening and inorganic particle reinforcement. However, few results associated with the addition of organic particles (such as carbon or phenolic beads) are available, and there appear to be no results available for hybrid composites fabricated with such matrices.

This thesis has the following objectives:

(1) To evaluate the effect of the addition of phenolic and carbon beads on the mechanical properties of epoxy resin and to review the toughening mechanisms in such particle-filled epoxy systems.
(2) To evaluate the interlaminar fracture toughness of hybrid composites fabricated using an epoxy matrix toughened with carbon beads and to observe the associated fracture mechanisms.

(3) To use fracture mechanics to investigate the relationships between the toughness parameters that can be measured for the bead-filled epoxies and the hybrid composites.
Fig. 1.1 Projected increase in use of composite material in primary aircraft structure (taken from Kam and Walker, 1987)
CHAPTER 2. LITERATURE REVIEW
CHAPTER 2. LITERATURE REVIEW

2.1 INTRODUCTION

2.2 APPLICATION OF FRACTURE MECHANICS TO COMPOSITE MATERIALS
   2.2.1 Introduction
   2.2.2 Basic concept of fracture mechanics
   2.2.3 Anisotropic fracture mechanics

2.3 MECHANICAL PROPERTIES AND FRACTURE BEHAVIOUR OF TOUGHENED EPOXY
   2.3.1 Introduction
   2.3.2 Mechanical properties of pure and toughened epoxy resins
      2.3.2.1 Pure epoxy resin
      2.3.2.2 Rubber toughened epoxy
      2.3.2.3 Particle-filled epoxy
   2.3.3 Fracture behaviour of toughened epoxy
      2.3.3.1 Fracture criteria
      2.3.3.2 Stability of crack growth
      2.3.3.3 Failure mode in toughened epoxy resin
      2.3.3.4 Toughening mechanisms

2.4 INTERLAMINAR FRACTURE TOUGHNESS OF COMPOSITE MATERIAL
   2.4.1 Introduction
   2.4.2 Previous study of interlaminar fracture in standard and toughened matrix composites
2.4.2.1 Interlaminar fracture toughness of composites based on toughened thermoset matrices

2.4.2.2 Interlaminar fracture toughness of composites based on thermoplastic matrices

2.4.3 Measurement of Mode 1 and Mode 2 interlaminar fracture toughness

2.4.3.1 Test method standardization

2.4.3.2 DCB Mode 1 test ($G_{IC}$ value)

2.4.3.3 ENF Mode 2 test ($G_{IIIC}$ value)

2.5 CONCLUSION OF LITERATURE REVIEW
2. LITERATURE REVIEW

2.1 Introduction

As indicated in chapter 1, methods of improving the matrix dominated properties of composite materials are receiving significant attention in order to improve key properties (such as damage tolerance and the design allowable strain) of fibre reinforced composites for aerospace, marine and other structural applications. As matrix materials in fibre reinforced composites for engineering application (and also as structural adhesives), epoxies are some of the best polymeric materials and extensive use of epoxies is being made in aviation engineering.

Since their initial development in the 1960's, epoxy-based composite materials have generated an extensive volume of literature. It is not the purpose of this review to cover the whole field, but to identify papers relevant to the work to be carried out in the present study. Hence the main topics of interest are the fracture behaviour of epoxies and the interlaminar fracture behaviour of composite material fabricated with epoxy-based matrices.

The structure of the review is as follows, Firstly, in section 2.2, the basic concepts of fracture mechanics and its applicability to composite materials are described, since experimental methods used in this study will be based on
fracture mechanics techniques. Then a brief survey of fracture toughness and toughening mechanisms in unmodified and modified epoxies is given in section 2.3. Finally, a survey of the interlaminar fracture behaviour of composite materials is given in section 2.4, with particular reference to test methods.

2.2 APPLICATION OF FRACTURE MECHANICS TO COMPOSITE MATERIALS

2.2.1 Introduction

Linear elastic fracture mechanics (LEFM) evolved from Griffith's theory of fracture for brittle materials, such as glass, which states that an existing crack will propagate if the elastic strain energy release rate exceeds the energy required to increase the surface area of the crack faces (Griffith, 1920). Such a global energy balance approach does not consider the details of fracture at the crack tip.

In the middle of the 1950s, Irwin (1957) contributed another major advance by showing that the energy approach is equivalent to a stress intensity factor (K) approach, according to which fracture occurs when a critical stress distribution ahead of the crack tip is reached. The material property governing fracture may therefore be stated either as a critical stress intensity factor, $K_{IC}$, or from the energy approach as a critical value of strain energy release rate,
G_{IC}. These properties are introduced formally in section 2.2.2.

In the 1960s, the concept of fracture mechanics was well established and was expanded by many researchers (Irwin, 1960, Paris and Sih, 1965, Rice, 1968). In particular, Sih, Paris and Irwin (1965) have shown that the basic concepts of isotropic fracture mechanics can be extended to anisotropic materials such as orthotropic fibre reinforced composite materials. In the remainder of this section, the principles of fracture mechanics and its applications to composite materials will be reviewed.

2.2.2 Basic concepts of fracture mechanics

Linear elastic fracture mechanics has been developed to deal with crack-like defects by relating defect geometry and design stress to a material response, normally the fracture toughness or critical strain energy release rate. According to Irwin's (1948) modification to the Griffith theory, the crack extension criterion can be expressed as:

\[ \left[ \frac{dW}{da} - \frac{dU}{da} \right] = G \leq \left[ \frac{dU'}{da} + \gamma \right] = G_c \]  \hspace{1cm} (1)

where \( W \) is the work done by the external force, \( U \) is the global elastic strain energy, \( U' \) is the local irreversible strain energy dissipated at the crack tip, \( G \) is strain energy release rate and \( \gamma \) is the energy required per unit area to
form the crack surface. Equation (1) states that for a linear elastic body, crack growth occurs when the energy release rate (G) in the body is at least equal to the energy dissipated at the crack tip. Equation (1) can be rewritten in such a way as to allow G to be determined experimentally from compliance measurements for a given load condition and geometry of the body.

The strain energy release rate can also be calculated analytically by knowing the stress and strain field around the crack tip. For a large, linear elastic isotropic plate containing a through-thickness crack of length 2a, the distribution (Fig. 2.1) of the component of stress normal to the crack is given by (Irwin, 1957, Paris and Sih 1965).

\[
\sigma_y = \frac{K_1}{\sqrt{2\pi r}} \cos \frac{\theta}{2} [1 + \sin \frac{\theta}{2} \sin \frac{3\theta}{2}] \tag{2}
\]

Under plane stress conditions, the displacement in the y direction is

\[
u_y = \frac{K_1}{E} \sqrt{\frac{r}{2\pi}} \sin \frac{\theta}{2} (2 - 2v - \cos^2 \frac{\theta}{2}) \tag{3}
\]

where \(K_1\) is the stress intensity factor \((=\sigma\sqrt{a})\), \(E\) is Young's modulus and \(v\) is Poisson's ratio. The principle of the stress intensity factor approach is that at onset of crack
propagation the stress field near a crack tip reaches a critical level. In other words, whatever the geometry and loading configuration of a specimen, the stress field near the crack tip is always the same at fracture. If equation (2) is examined in the light of above statement, it is clear that at the onset of fracture, stress intensity factor $K$ reaches a unique value for a given material. This value of the stress intensity factor is defined as the critical stress intensity factor, $K_{IC}$ and is often called the fracture toughness. The stress intensity factor is a function of the applied loads, the crack length and the geometry of the specimen. Stress intensity factors have been calculated analytically for a variety of crack problems in linear elastic materials (Sih and Liebowitz, 1969).

From equations (2) and (3), the strain energy release rate is then

$$G = \frac{2}{\Delta a} \int_0^{\Delta a} \frac{1}{2} \sigma y u y dx$$  \hspace{1cm} (4)

and on integrating it can be shown that,

$$G_1 = \frac{K_1^2}{E} (1-v^2) \hspace{1cm} \text{plane strain}$$
The inter-relation between the global energy balance parameter, $G$, and the crack tip parameter, the stress intensity factor, $K$, is an essential feature of LEFM.

2.2.3 Anisotropic fracture mechanics

The applicability of LEFM to conventional isotropic materials has been well documented. LEFM has thus become a standard technique for characterizing the fracture resistance of engineering materials, more specially for materials of high strength and moderate toughness.

Fracture behaviour in laminated composite materials is more complicated than in isotropic materials and will depend on additional parameters such as applied loading, fibre orientation, ply stacking sequence in a laminate and the constitutive relations which describe the mechanical response of fibre, the matrix and the interface. This behaviour is characteristic of composite materials and can be a restrictive factor in the application of linear elastic fracture mechanics derived for homogeneous isotropic materials. The applicability of linear elastic fracture mechanics to composite materials has been examined by many investigators and in the absence of more adequate theory, it has been used widely to interpret experimental test results for the

For multi-ply laminates containing through-thickness cracks the suitability of fracture mechanics to describe macroscopic crack propagation is questionable because of the tendency for blunting by intralaminar crack growth and delamination. We restrict the present review to geometries of unidirectional laminates where the crack is constrained to grow in its own plane.

Sih, Paris and Irwin (1965) reported that it is possible to extend conventional fracture mechanics methods to represent the fracture condition for anisotropic bodies with crack-like imperfections. The main theoretical results from their studies are outlined below.

In a unidirectional fibre reinforced laminate (Fig. 2.2) there are three mutually perpendicular planes of material symmetry and the properties at any points may be different in the three mutually perpendicular directions. Such a material system is termed orthotropic (Hull, 1980). In practice, the 2 and 3 directions are generally assumed to be equivalent. For a homogeneous orthotropic linear elastic plate, the stress and displacement field near the crack tip can be obtained in a similar way to the isotropic case. Sih,
Paris and Irwin (1965) showed how the normal Irwin-Westergaard expressions for the stress about a crack tip has to be modified for a crack in a homogeneous orthotropic solid. The stress field in the vicinity of a mode 1 crack (Fig. 2.3), loaded such that a principal material direction and the loading direction are coincident, is expressed as:

\[ \sigma_{ij} = \frac{K_1}{\sqrt{2\pi r}} \text{Re}[F_{ij}(\theta, s_1, s_2)] \quad (i,j=1,2) \]  

(6)

where \( K_1 \) is the stress intensity factor, \( F_{ij} \) is a complex function of \( \theta \) and the complex parameters \( s_1, s_2 \) which are the roots determined from the characteristic equation and depend on the material elastic constants (Sih and Liebowitz, 1968).

Sih et al. (1965) reported that for a through-thickness crack of length 2a in a large plate, the expression for the stress intensity factor for the orthotropic material is theoretically identical to that obtained for the isotropic case. Konish (1975) investigated the stress intensity factor in composite materials for other crack geometries, the double edge notch and finite width centre-crack tension specimen, using numerical methods. He reported that, generally, the stress intensity factor for a composite material is identical to that of an isotropic material except for small modifications to the finite geometry isotropic correction factors. These modifications account for the influence of material anisotropy which introduces a different degree of
interaction between the crack-tip and the external boundaries of the specimen. However, the anisotropic effect depends on the specimen geometry and material properties. Thus it was suggested that careful checking is needed, for example by numerical analysis, for any particular material.

On the other hand, the alternative LEFM parameter, energy release rate, $G$, can be evaluated experimentally from the compliance method for orthotropic composite materials.

$$G = \frac{P^2}{2B} \frac{dC}{da} \quad (7)$$

where $C$ is compliance, $P$ is the load and $B$ is the specimen thickness. Equation (7) is valid for all linear elastic materials regardless of whether the material is isotropic or anisotropic, homogeneous or heterogenous. The only precondition is that the derivative of the compliance must be evaluated for crack growth along the direction of the crack propagation. In isotropic homogeneous materials the crack growth is always self-similar and normal to the uniaxial tension. In other types of material, the crack may propagate in a different direction.

An interrelationship between energy release rate ($G$) and stress intensity factor ($K$) can be determined for anisotropic material. Sih, Paris and Irwin (1965) showed that while the expression for the stress intensity factor in the
opening mode, $K_I$, remained the same, the relationship between energy release rate, and the stress intensity factor becomes for plain strain:

\[
G_I = K_I^2 \left( \frac{b_{11} b_{22}}{2} \right)^{\frac{1}{2}} \left[ \left( \frac{b_{22}}{b_{11}} \right)^{\frac{1}{2}} + \frac{2b_{12} b_{66}}{2b_{11}} \right]^{\frac{1}{2}} 
\]

(8)

where the $b_{ij}$ terms are elastic coefficients which are derived from the elastic constants. The validity of equation (8) has been investigated by Sih et al., (1973, 1979), Phillips (1974), Newaz (1988), and their results are not consistent, as described below.

Sih et al. (1973) measured fracture toughness using compact tension specimens of unidirectional material (loaded perpendicular to the fibre direction so that crack propagation is parallel to the fibre direction) fabricated with two different fibres (glass and graphite) of various fibre volume fractions (glass fibre : 0, 10, 20, 50, 60 %, graphite: 0, 50 (a), 50 (b) %). They obtained four different fracture parameters ($K_{IC}^{(1)}$, a measured value; $G_{IC}^{(1)}$, a value calculated using equation (8) with $K_{IC}^{(1)}$; $G_{IC}^{(2)}$, a measured value; $K_{IC}^{(2)}$, a value calculated using equation (8) with $G_{IC}^{(2)}$). They compared the measured values with calculated values to check accuracy. To do this they defined the percentage deviation as:

\[
G_{IC} (% \text{ deviation}) = \left( \frac{G_{IC}^{(2)} - G_{IC}^{(1)}}{G_{IC}^{(2)}} \right) \times 100
\]
The results are shown in Table 2.1. The orthotropic fracture model was in close agreement with the experimental results in the glass fibre composite at 50% and 60% volume fraction. However, in graphite composite, the accuracy was not so good.

Philips (1974) measured $K_{IC}$ values from centre notched tension (CNT) specimens and $G_{IC}$ values from tapered compact tension (TCT) specimens. These values were then converted to respective $K_{IC}$ and $G_{IC}$ values by means of the effective modulus, based on the orthotropic fracture model. He reported excellent agreement between the CNT and TCT specimen.

Newaz (1988) also investigated the validity of the orthotropic fracture model for an advanced thermoplastic composite (graphite/PEEK, APC-2) using DCB specimens. He reported that the orthotropic model does not accurately represent the fracture behaviour of graphite/PEEK composites due to complex damage modes such as fibre bridging and isolated delaminations.

The application of LEFM to fibre reinforced materials apparently involves more than just a simple extension of the techniques used for isotropic, homogeneous material for which LEFM was developed. The precise relationship between the strain energy release rate $G$ and the stress intensity factor $K$ for a heterogeneous system such as a fibre reinforced
composite is not known and cannot be easily obtained analytically. This issue was discussed by Sih and co-workers (1979). Further work is required to resolve some of the existing apparent contradictions in the literature.

2.3 MECHANICAL PROPERTIES AND FRACTURE BEHAVIOUR OF TOUGHENED EPOXY

2.3.1 Introduction

Epoxy resins are some of the most important polymers used as matrix materials for fibre reinforced composites. However, these highly cross linked matrices are inherently brittle (Hibbs et al., 1987) and so have poor resistance to crack propagation. Consequently, they have limited utility in applications requiring high impact and fracture strength. We can consider the three most important damage mechanisms in a laminated composite to be delamination, matrix cracking and fibre fracture. The first two modes depend highly on the properties of the matrix so that brittle matrices will impose limitations on the composite.

Because the growth of delaminations has such a significant effect on fibre reinforced composites, many studies have been carried out to improve delamination fracture resistance (e.g. Johnston, 1987). Most commonly, toughened epoxies are used as matrix material in fibre reinforced

To understand how the improved interlaminar fracture toughness of composites fabricated with toughened epoxy originates, it is necessary to review the nature of epoxy resins, the fracture behaviour and the toughening mechanisms. In the remainder of this section, the characteristics of epoxy, these points are reviewed briefly.

2.3.2 Mechanical properties of pure and toughened epoxy resins

2.3.2.1 Pure epoxy resin

Epoxy resins are characterized by the presence in their structure of the epoxy group which is made up two carbon atoms and one oxygen atom.

\[ \text{- C - C - : EPOXY GROUP} \]

The essential feature of epoxy resin technology is the conversion of the resin into a hard composition, infusible three-dimensional network in which the resin molecules are linked together by means of strong covalent bonds. This process is termed polymerisation, but is more commonly called curing or hardening of resin. The epoxy composition is made up
of at least two constituents, the resin and the hardener or curing agent. Curing is an irreversible change so that once the resin has been cured, it cannot be returned to its original form. The curing process can be slowed down, stopped or speeded up, but it cannot be reversed. Hence epoxy resins fall into the category of polymers known as thermosets which, once polymerised, cannot be re-used by melting and reprocessing in the way that thermoplastic polymers can. The properties of cured epoxies depend upon the epoxy, the curing agent and the curing process (e.g. Potter 1975, Morgan, 1980).

Epoxy resins are amongst the most brittle types of polymer and this is reflected in their stress/strain behaviour. A series of stress/strain curves for an epoxy tested in tension over a range of temperatures is shown in Fig. 2.4 (Pink and Campbell, 1974). There is a trend of increasing ductility (strain to failure) with increasing temperature. Although thermosetting polymers are generally thought to be rather brittle, especially at low temperature this brittle type of behaviour is suppressed under certain stress/strain condition. Fig. 2.5 show a series of stress/strain curves for an epoxy resin deformed under different states of stress. In simple uniaxial tension the system is brittle, failing at very low strain. However the epoxy will yield and undergo considerable plastic deformation in uniaxial compression or in pure shear (Kinloch and Young, 1983).
2.3.2.2 Rubber toughened epoxy

Rubber toughened thermoplastic polymers have been in existence for over 40 years, but rubber toughened epoxies are more recent about 20 years old (Bucknall, 1977). Amongst the earliest studies, Sultan and McGarry (1973) reported rubber toughened epoxy systems containing the carboxyl-terminated butadiene-acrylonitrile (CTBN) elastomer. In these systems, the CTBN co-polymerizes with the epoxy prior to gelation to form a dispersed phase of particles having diameters of a few micrometers or less. Since then many research results for rubber toughened epoxies have been reported in the literature.

The addition of rubber to a brittle resin modifies many of its properties. It reduces the stiffness and yield strength, and increases the thermal expansion coefficient. In particular, it also increases the fracture resistance significantly (e.g. Bascom et al., 1975, 1981, Kinloch et al., 1983). Dispersed rubber particles enhance the toughness of the unmodified epoxy by mechanisms that involve plastic flow of the epoxy matrix and elongation of the particles (e.g. Bascom et al. 1977, Beaumont et al., 1980, Kinloch et al., 1983 and see section 2.3.3.3). The changes in properties of a toughened epoxy resin depend upon various parameters, such as size and volume fraction of dispersed rubber, temperature and other factors. Table 2.2 shows the variation of a range of properties with elastomer concentration for CTBN toughened DGEBA epoxy resin (Bascom et al., 1975).
2.3.2.3 Particle-filled epoxy

There are two main reasons for using filler materials in epoxy resin systems: firstly, to reduce the overall cost of a component by incorporating a low-cost material and secondly, to impart some particular property to the system. For example, in certain cases mechanical, thermal, and electrical properties may be improved (Moloney et al., 1983). Young and Beaumont (1975) reported that incorporating silica particles into an epoxy resin reduced the cost, degree of shrinkage, exothermic temperature rise and coefficient of thermal expansion while increasing the thermal conductivity and fracture toughness.

Various studies (Lange, 1974, Young and Beaumont, 1977, Spanoudakis and Young, 1984, Moloney and Kausch, 1984, 1987) of the effect of filler material (glass bead, silica, alumina) on the fracture toughness (in terms of the critical stress intensity factor, $K_{IC}$) of particle-filled epoxy systems have shown that $K_{IC}$ increases with particle volume fraction, $V_p$. In addition, Young and Beaumont (1977), Moloney and Kausch (1983) have also reported increases in Young's modulus ($E$) and yield stress ($\sigma_y$) for silica particle-filled epoxy.

As indicated briefly in the previous paragraphs, the effect of inorganic filler material on the mechanical properties of particle-filled epoxies is well documented in the literature for a wide range of epoxy resins and filler
materials. Moloney (1987) has conducted an extensive literature review and summarized the parameters (such as volume fraction of filler, particle size, modulus and strength of particles, aspect ratio, resin-filler adhesion) which determine the strength and toughness of particle-filled epoxy resins. However, it seems that few research results have been reported for epoxies toughened with organic filler materials. In the next section, we consider the fracture behaviour of toughened epoxies in more detail.

2.3.3 Fracture behaviour of toughened epoxy resins

2.3.3.1 Fracture criteria

The type of fracture (whether it is brittle or ductile) seen in polymer materials depends not only on the material type but also on other factors such as loading rate, temperature and environment (Kinloch et al., 1983, Spanoudakis and Young, 1984). At low temperature and high loading rates, materials usually behave in a brittle manner with a correspondingly low fracture toughness. In contrast, with temperature increase or loading rate decrease, the materials tend to behave in a more ductile manner with associated toughness increases. Such effects of temperature and loading rate on the fracture toughness of pure epoxies and rubber toughened epoxies are shown in Fig. 2.6 (Kinloch et al., 1983). The factors which increase the toughness tend to reduce the yield stress and hence increase the size of the plastic
zone near the crack tip.

The significant plastic deformation of toughened epoxies may invalidate the use of LEFM, especially for rubber toughened epoxy resin at high temperature. For such cases, several alternative models have been proposed which are based on a critical plastic zone size \( r_y \) (Bascom et al. 1975, 1980) or critical opening displacement at the crack tip \( \delta_c \) (Marshall et al., 1974, Gledhill et al., 1976) or a crack tip blunting model (Kinloch and Williams, 1980).

2.3.3.2 Stability of crack growth

Kinloch et al. (1983) reported three basic types of crack growth in unmodified and rubber modified epoxies, namely:

**type A**: ductile stable crack growth in which cracking is continuous and is dominated by plastic deformation in the specimen;

**type B**: brittle unstable crack growth during which the crack proceeds in a stick-slip manner;

**type C**: brittle stable crack growth in which crack growth is continuous.

Type A crack growth was observed only at high test
temperatures (above 40°C). In the transition regions between one basic type of crack growth and another it was observed that combinations of the above types could occur. Typical load-displacement records corresponding to the main types of crack growth behaviour and their combinations, as seen in compact tension specimens, are shown in Fig. 2.7. Type C behaviour through to type A behaviour occurred with increasing testing temperature and decreasing loading rate. The addition of other fillers to epoxies can modify the type of load-displacement behaviour in a similar way. A transition from stable continuous crack growth behaviour in unmodified epoxies to unstable stick-slip crack growth in filled epoxies has been reported by Young and co-workers (Young and Beaumount, 1975, Spanoudakis and Young, 1984)

2.3.3.3 Failure mode in toughened epoxy resin

The fracture behaviour of an epoxy polymer toughened by rubber or inorganic fillers may involve several mechanisms which contribute towards improving the fracture toughness. Such possible mechanisms are shown schematically in Fig. 2.8 and 2.9. These are:

(1) shear band formation near rubber particles;
(2) fracture of rubber particles;
(3) stretching of rubber particles;
(4) debonding of rubber particles;
(5) tearing of rubber particles;
Several of the above failure modes may occur simultaneously in a toughened polymer.

2.3.3.4 Toughening mechanisms

As indicated in the previous section, many investigators have reported on the possible toughening mechanisms for rubber toughened epoxies and particle-filled epoxies. Such toughening mechanisms depend on the matrix material and toughening agent. Based on these studies, the major contributors to the enhancement of toughness in the two main types of toughened epoxy are summarized below:

(a) Toughening mechanisms in rubber modified epoxy

The enhancement of fracture toughness of rubber toughened epoxies is due mainly to the large energy dissipating deformations occurring in the vicinity of the crack tip. The main deformation process is plastic shear
yielding in the epoxy matrix and this is considered as the major source of energy dissipation. Due to the interaction between the stress field ahead of the crack tip and the rubber particles, plastic shear yielding is larger for rubber toughened epoxies than for unmodified epoxies. The plastic deformation causes crack tip blunting, leading to a reduction of local stress concentration which consequently improves the fracture toughness and arrests crack propagation (Sultan, 1971, 1973; Bascom et al., 1975, 1981; Bucknall, 1977; Kunz-douglass et al., 1980; Kinloch et al. 1983, 1984, 1985).

(b) Toughening mechanisms in particle-filled epoxy resin

A second phase dispersion of particles in a matrix has been reported to lead to three main mechanisms which affect the fracture toughness of a brittle matrix: plastic deformation, crack pinning and increase in crack surface area (Lange, 1974).

Plastic deformation of the matrix around the particle is associated with the high stress at the crack front and stress concentration around the particle. This deformation consequently produces crack tip blunting which absorbs energy as the crack propagates.

The interaction of a crack front with impenetrable obstacles (i.e. crack pinning) has been reported by many
investigators. It has been shown that second phase inhomogeneities can act as obstacles which impede the moving crack front (i.e. momentary pinning of the crack front takes place at the position of an inhomogeneity). When the crack front begins to move between each pair of pinning positions, new fracture surface area is formed and the crack front increases in length. Work must be done by the applied forces both to form the new fractured surface and to create the increased crack front length. These events lead to an enhancement of the crack propagation resistance of a matrix which has second phase inhomogeneities (Fig. 2.9).

Roughness of the fracture surface is a result of the crack being deflected by the particles. This surface roughness leads to an additional increase in the fracture toughness of the particle-filled material.

Various studies on toughening mechanisms in toughened epoxies have been reported (Lange and Ladford, 1971; Evans, 1972; Green et al., 1979; Moloney et al., 1983, 1984, 1987; Kinloch et al., 1983, 1985; Spanoudakis and Young, 1984; Garg and Mai, 1988). From a review of such literature for particle-reinforced epoxies, it emerges that most studies have used inorganic filler material such as glass beads, alumina, and silica and, in addition, many workers have considered the crack pinning mechanism as the major source of toughness enhancement. However, Spanoudakis and Young (1984), in their work on glass bead-filled epoxy resin, reported that crack
propagation in particle-filled epoxy resin is complex with both crack tip blunting and crack pinning taking place simultaneously. This suggests that mechanisms of fracture need to be examined closely and that both crack tip blunting (by plastic yielding of the matrix) and crack pinning may be important as toughening mechanisms.

2.4 INTERLAMINAR FRACTURE TOUGHNESS OF COMPOSITE MATERIALS

2.4.1 Introduction

A demand in the use of high performance composite materials has generated extensive research results which are concerned with improving the interlaminar fracture properties of composites and developing methods for precise measurement of the interlaminar fracture resistance (Johnston, 1987). The driving force for such research is that delamination or interlaminar fracture is seen commonly in practice and is considered one of the predominant types of damage in composite materials. The initiation and growth of delamination may result in progressive stiffness degradation and lead eventually to failure of a composite structure.

Delamination may initiate and grow at free edges or at stress raisers in laminates under tensile and compressive loading (Pagano, 1973; O'Brien, 1982) applied quasi-statically or cyclically. It can also be caused by low energy impact
damage (Rhodes and Williams, 1981).

The improvement of structural damage tolerance (especially resistance to delamination) can be achieved somewhat by design optimization using current epoxy systems. In particular the laminate stacking sequence can be chosen so as to minimize out of plane stresses (Ratwani and Kan, 1982; Heyliper and Reddy, 1985). However the development of toughened composites would provide a far greater potential for extending the use of composite material structures.

It has been found that delamination resistance is increased through the use of matrices with higher toughness. To develop a high performance composite with a much tougher matrix phase, recent research has proceeded in two different directions. The first approach is the modification of conventional thermoset matrix systems. Methods include the incorporation of rubber elastomers such as CTBN (Penn et al., 1977; Scott and Phillips, 1975) and blending an epoxy resin with a thermoplastic polymer (Bucknall and Partridge, 1984). The second direction of research has been to develop a new range of composite systems employing tougher and more ductile thermoplastic matrices such as PEEK (polyether etherketone, Hoggat, 1975; Carlile and Leach, 1983; Cogswell and Hopprich, 1983). Other areas of research include the production of interleaved composites and selective toughening in the region of free edges or stepped parts of structures (Evans and Master, 1987).
Several test methods have been developed to evaluate delamination behaviour. The most commonly used specimens currently are the double cantilever beam (DCB) specimen for measurement of mode 1 fracture toughness and end notch flexure (ENF) specimens for measurement of mode 2 fracture toughness (Whitney et al., 1982; Carlsson et al., 1986; Smiley and Pipes, 1987; O'Brien et al., 1989; Davies et al., 1992). Within the sections that follow, we review first (section 2.4.2) the study of interlaminar fracture in general. In section 2.4.3 we consider test methods in more detail.

2.4.2 Previous studies of interlaminar fracture in standard and toughened matrix composites

2.4.2.1 Interlaminar fracture toughness of composites based on toughened thermoset matrices

First generation epoxy resins developed for use in fibre reinforced composite materials maximized the stiffness and the glass transition temperature ($T_g$) by using a very high cross-link density. Such matrix resins have good hot/wet performance, but are inherently quite brittle and hence notch sensitive (Hibbs et al., 1987; Evans and Master, 1987). The fracture toughness of the bulk resin is about 0.08 kJ/m$^2$ (this value is slightly dependent on the specific resin, but is generally less then 0.1 kJ/m$^2$) and the average interlaminar fracture toughness of composites fabricated with the matrix of
such a resin is about 0.15 kJ/m$^2$ (generally less than 0.2 kJ/m$^2$) see Fig. 2.10, (Sela and Ishai, 1988).

Attempts have been made to improve the fracture toughness of neat resin by the addition of a toughener. By adding liquid rubber (Bascom et al., 1975, Kinloch et al., 1983) or a thermoplastic polymer (Bucknall and Partridge, 1984) to the uncured neat epoxy, a phase separation occurs during cure. The cured elastomer-modified epoxy resin consists of finely dispersed rubber or thermoplastic rich domains (0.1 - 5 μm in size) chemically bonded to the epoxy matrix. This modification improves the fracture toughness of the neat epoxy significantly. However the percentage increase in fracture toughness for the composite is not as high as the corresponding increase for the bulk resin. For example, Bascom et al., (1980) reported that improving the fracture toughness of the resin itself by eighteen-fold led to an increase in interlaminar fracture toughness of glass and graphite woven composites, based on the same resin, of four- to seven-fold. Similar results on different systems were found by Bradley and Cohen (1983).

Table 2.3 compares $G_{IC}$ values of four different base epoxy resins with the Mode 1 and Mode 2 interlaminar fracture toughness values of composite materials fabricated from the same epoxies. The characteristics of the four matrices shown in Table 2.3 are: high crosslink density and brittle (3502); low crosslink density and ductile (HX205); low crosslink
density and toughened with rubber at 6% by volume (F155); low crosslink density and toughened with rubber at 8% by volume (F185).

Hunston et al., (1987) have also investigated the relationship between neat resin fracture toughness and Mode 1 and Mode 2 delamination interlaminar fracture toughness. They reported that initial increases in neat resin fracture toughness from the first generation value of 70 J/m² result in significant increases in the Mode 1 delamination fracture toughness. However, at values of $G_{IC}$ for the matrix of greater than 400 J/m², further increases in neat resin fracture toughness lead to smaller corresponding incremental increases in the respective composite delamination fracture toughness, as shown in Fig.2.11. Bradley (1989) suggested that the low efficiency of translation of resin fracture toughness into delamination fracture toughness for a very ductile resin is the result of constraint by the fibres in the adjacent plies restricting the development of a large plastic zone in the resin rich region between plies.

If we emphasize only the improvements in the fracture toughness, it seems that the rubber toughening of epoxy is one of the most successful ways of improving the composite interlaminar properties. However, when using the rubber-modified epoxies there is a trade-off between a reduction in some mechanical strength properties and the increase in fracture toughness. The rubber additives degrade the
environmental stability of the composite due to the substantial increase in water pick-up. Hence the hot/wet performance of a toughened system is seriously reduced, making them of little advantage compared to unmodified epoxy resins as structural materials. Improvements in matrix toughness by the rubber modifying route are limited, therefore, because of the requirement to minimize the sacrifice in hot/wet performance (Evans and Master, 1987).

2.4.2.2 Interlaminar fracture toughness of composites based on thermoplastic matrices

The potential advantages of thermoplastic matrices as compared to thermosetting matrices include shelf-life, toughness and rapidity of fabrication as noted by Hoggat (1975). However, until the last ten years, thermoplastic composite materials have not been considered for use in aircraft structures. There appear to be two main reasons for this (Cogswell and Hopprich, 1983). Firstly, existing thermoplastic resins were unable to combine an adequate stiffness at high temperature with sufficient resistance to chemical attack. Secondly, due to the high viscosity of thermoplastic polymer melts, thermoplastic composites could only be fabricated by laborious, high pressure, film stacking technology.

In 1981, polyether etherketone (PEEK) resin under the trade name of Victrex was introduced onto the market by ICI. A
composite material, Aromatic Polymer Composite APC-1, containing 52% by volume of collimated, high strength, carbon fibre in PEEK resin was introduced in 1982. Since the introduction of APC, many research results concerned with fracture behaviour and toughening mechanism of the resin (Carlile and Leach, 1983; Leach and Moore, 1985; Cebe et al., 1987; Gillespie et al., 1987; Hine et al., 1988; Friedrich et al., 1989) and evaluation of delamination resistance in the composite (Hartness, 1984; Donaldson, 1985; Smiley and Pipes, 1987; Leach et al., 1987; Hashemi et al., 1990; Davis et al., 1992) have been reported.

Thermoplastic matrices gave an order of magnitude increase in interlaminar fracture toughness compared to contemporary epoxy resin composites (thermoplastic composite about 1.8 kJ/m², compared to the epoxy resin composite value of about 0.18 kJ/m², see Fig.2.11). However fabrication costs of thermoplastic composites are high due to the high pressure and temperature (10 atm and 400°C) and fabrication technology is not yet fully mature. There are also problems with maintaining fibre alignment during processing and some mechanical properties, notably compression, are poor. However development effort is being continued.

2.4.3 Measurement of Mode 1 and Mode 2 interlaminar fracture toughness

2.4.3.1 Test method standardization
A delamination can grow under pure Mode 1, pure Mode 2 or mixed mode loadings. The most common tests used for interlaminar fracture toughness characterization in the various modes are illustrated schematically in Fig. 2.12 (Johnson and Mangalgiri, 1987). However, so far, no widely accepted standard test method exists for the determination of interlaminar fracture toughness properties, even though these types of test have been performed on composites for around 20 years.

In order to develop a testing standard, an ASTM task group and an EGF, European Group on Fracture, (Davies et al., 1990, 1992), have started round robin tests on interlaminar fracture toughness and three material systems are being tested within this programme: a thermoplastic system AS4/PEEK, a toughened epoxy system AS4/BP907 and a first generation epoxy system AS4/3501-6. There are a number of reasons for the difficulty in establishing standards which relate to the interpretation of the results, as well as to the test methods themselves. Until a few years ago, the consensus of opinion was in favour of the use of the propagation value of $G_{IC}$ to characterise the delamination resistance of unidirectional composites under Mode 1 loading, although delamination resistance was sometimes observed to increase during propagation (the so-called R-curve effect: Hashemi et al., 1987). This R-curve behaviour could be explained in terms of fibre bridging and multiple matrix cracking. However Chai (1986) and Davies et al., (1989), amongst others, argued
strongly for the adoption of the initiation toughness value, because for a number of materials, the R-curve obtained has been shown to be specimen dependent. Unfortunately few data are available to show whether the initiation value can be defined unambiguously or measured reliably (Davies et al., 1990).

As indicated earlier, the most commonly used tests for interlaminar fracture toughness characterization in Mode 1 and Mode 2 are DCB (Double Cantilever Beam) and ENF (End Notch Flexure) tests, respectively. These two test methods are being used in the round robin interlaminar fracture test program organized by ASTM and EGF (Davies et al., 1992). They are described in more detail in the sections below.

2.4.3.2 DCB mode 1 test ($G_{IC}$ value)

An extensive investigation has been performed by NASA, ASTM, EGF and others in order to establish the DCB test as a standard test for the measurement of composite material resistance to interlaminar crack growth. There are two basic types of DCB specimen, the constant width DCB and the width-tapered DCB (WTDCB). The tapered specimen is designed so that $a/b$ (where $a$ is crack length and $b$ is specimen width) is constant. The strain energy release rate derived from the analysis of a WTDCB specimen is therefore independent of crack length. Hence the need to monitor the crack length during the test is eliminated (Whitney et al., 1982; Bascom et al., 1980;
Daniel et al., 1987). The interlaminar fracture toughness \( G_{IC} \) can be determined from the DCB test using a number of different methods (including compliance, area, load and displacement methods). These will be discussed further in chapter 5.

Table 2.4 show some of the reported data for \( G_{IC} \) of different materials. There are several factors which may affect fracture toughness values for a given material, including loading rate, temperature, specimen lay-up and thickness. Relevant studies are discussed briefly in the reminder of this section.

Smiley and Pipes (1987) investigated the effect of crosshead speed on the Mode 1 interlaminar fracture toughness in graphite/PEEK (APC-2) and graphite/epoxy (AS4/3501-6) using DCB specimens. The crosshead speed range was \( 4.2 \times 10^{-6} - 6.7 \times 10^{-1} \) m/s. The toughness of both material systems was rate sensitive. The mode 1 interlaminar toughness of APC-2 decreased from 1.5 to 0.35 kJ/m² over five decades of loading rate and the fracture toughness of AS4/3501-6 decreased from 0.18 to 0.04 kJ/m², as shown in Fig. 2.13. Gillespie et al. (1987) also examined the effect of loading rate on \( G_{IC} \) in brittle graphite/epoxy (AS4/3501-6) and in ductile graphite/PEEK (APC-2). The tests were performed over a range of crosshead speed from 0.0042 to 4.2 mm/s. The toughness of AS4/3501-6 was insensitive to rate over the test range (\( G_{IC} = 190 \) J/m²). The toughness of APC-2 for the onset of subcritical
crack growth decreased somewhat with increased loading rate, while the toughness for critical crack growth $G_{IC}$ peaked at an intermediate displacement rate (for loading rates of 0.0042, 0.042, 0.42, 4.2 mm/s, $G_{IC} = 1560, 1750, 1980, \text{ and } 1710 \text{ J/m}^2$ respectively). Even though Similey and Pipes and Gillespie et al. have used the same material and the same specimen geometry (DCB), it is difficult to compare their results directly due to the different loading rate ranges. However, there appears to be a strain rate effect at high strain rate.

Hunston and Bascom (1983) reported that the fracture toughness of rubber modified epoxy increased sharply with temperature and decreased with loading rate. However they found that the $G_{IC}$ of composites fabricated with rubber toughened epoxy had no significant variation between $-25^\circ \text{ C}$ and $40^\circ \text{ C}$ at cross head speeds from 0.0008 - 0.8 mm/s.

A DCB specimen of unidirectional lay-up with the fibre direction parallel to the length of the specimen is the simplest specimen to fabricate and test. Unidirectional DCB specimens have maximum stiffness compared to any other lay-up. When the DCB specimen has low stiffness the deformation is large and nonlinear condition may occur. However, Ramkumar and Whitcomb (1985) compared interlaminar fracture toughness of T300/5208 using two different lay-ups of DCB specimen and found no significant difference in the result: $G_{IC} = 102 \text{ J/m}^2$ for $0_{24}$ specimen and $G_{IC} = 100 \text{ J/m}^2$ for $(0_2/\pm45/0)_s$ specimens.
Hunston and Bascom (1983) examined the lay-up effect on interlaminar fracture toughness using DCB specimens. They reported that if there are no $0^\circ$ plies in the midplane where the crack propagates, then there is a tendency for the crack to wander from ply to ply. They suggested, thus, that at least one or more $0^\circ$ plies should be placed midplane to control the crack propagation.

When fibre bridging occurs, the measured fracture toughness values are higher than for delamination through the matrix alone and an increase in $G_{IC}$ with increasing crack length is observed (R-curve). Fibre bridging is attributed to nesting of the fibre and the weak fibre/matrix interface. When two plies of the same orientation are adjacent to each other in the laminate, cure pressure forces the plies to merge together and remove the characteristic resin rich interface. This nesting is thus maximized between unidirectional laminates ($0/0$ interface) and minimized at $0/90$ interfaces (Wilkins et al., 1982; Johnson and Mangalgiri, 1987).

Wilkins et al. (1982) examined two types of interface in DCB specimens, $0/0$ interface and $0/90$ interface. A $G_{IC}$ of 88 J/m$^2$ was obtained from the $0/0$ interface of T300/5208 specimen, and a much higher value of 298 J/m$^2$ was measured from the $0/90$ interface. However, the $G_{IC}$ value of the $0/90$ interface was reported as invalid because of crack branching through the $90^\circ$ degree ply. Johnson and Mangalgiri (1987) used unidirectional specimens. However the plies above and below
the midplane were laid at a small angle to each other. Three angles were chosen for testing: 0°, 1.5° and 3°. The angles of 1.5° and 3° were intended to avoid nesting of fibres along the midplane but perhaps surprisingly there was no significant effect on mode 1 behaviour.

Prel et al. (1989) examined the delamination behaviour of glass/epoxy (E glass/DGEBA), graphite/epoxy (T300/914) and graphite/PEEK (APC-2) using DCB specimens of two thicknesses (4.5 and 20 mm). They found little difference between $G_{IC}$ value of thick and thin epoxy/composite specimens (initiation $G_{IC}$ was 264 J/m² for thick (20 mm), 228 J/m² for thin (4.5 mm) in glass/epoxy composite; initiation $G_{IC}$ was 185 J/m² for both (5mm, 20mm) in graphite/epoxy composites). For thick graphite/PEEK specimens, the initiation $G_{IC}$ value tended towards thin specimen values only when long starter cracks were used (initiation $G_{IC}$ value of graphite/PEEK, 1460 J/m² for thin and 1500 to 3500 J/m² for thick).

2.4.3.3 ENF Mode 2 test ($G_{IIc}$ value)

Interlaminar fracture toughness in Mode 2 was initially derived from mixed mode tests (Willkins, 1982) since this was the only way to evaluate $G_{IIc}$ until a pure mode 2 test was developed. The crack lap shear (CLS), see Fig 2.12, was used mainly for such tests (Wilkins, 1982; Ramkumar et al., 1985; Russell et al., 1985). However this has been largely replaced by the ENF test which is used in existing round robin
test programmes (Davis et al., 1992). The other specimen type which is used is the end loaded split (ELS) specimens (Carleto and Bradley, 1989; Hasehimi et al., 1990).

Russell and Street (1985) introduced the end-notched flexure (ENF) specimen for pure mode 2 testing. The validity of the ENF test was examined and demonstrated by Gillespie et al. (1985) and O'Brien et al. (1987). In the ENF test, mode 2 crack propagation causes relative sliding of the crack surfaces. Friction between the crack surfaces may oppose the sliding and consequently increase the $G_{IIc}$ value. Carlsson et al. (1986) investigated the effect of friction on $G_{IIc}$ values using the finite element method and found that ENF $G_{IIc}$ values can be overestimated as a result of friction by 2 to 4%.

A protocol for interlaminar fracture testing (Davis, 1989: EGF task group on polymers and composites) suggested that the optimum thickness of unidirectional carbon fibre/epoxy composite ENF specimens is 3 mm. Table 2.5 shows some reported for $G_{IIc}$ values for different materials.

2.5 CONCLUSION

As a consequence of recognizing the importance of the interlaminar fracture toughness for the safety of composite structures, extensive studies have been carried out to develop more damage tolerant composite materials but further work is
required. These relevant areas for research are:

- development of toughened matrix resin;
- fabrication of high performance composite materials using toughened resins;
- evaluation of interlaminar fracture toughness using various test methods.

The use of rubber-toughened or particle-filled epoxies have been reported as two major ways of improving the fracture toughness of pure epoxy resin. Several toughening mechanisms have been identified but plastic deformation and crack pinning appear to be the two most important.

To evaluate the interlaminar fracture toughness of composite materials, several testing methods have been reported. However, it can be concluded that DCB and ENF tests are preferred for measurement of $G_{IC}$ and $G_{IIC}$ respectively.

LEFM has been used widely to interpret the experimental results for the fracture toughness of fibre reinforced composite materials. However orthotropic fracture models may be invalid because of the complex fracture behaviour associated with the heterogeneities of composite materials. Therefore, the applicability of LEFM for composite materials requires further investigation.

Even though considerable information is available on
inorganic particle-filled epoxies, little information is available about organic particle-filled epoxies (such as carbon and phenolic beads) and the use of such particle-filled epoxies as matrices in fibre reinforced composites. Such information is produced in this thesis.
<table>
<thead>
<tr>
<th>fibre volume (% E glass)</th>
<th>calculated value</th>
<th>measured value</th>
<th>deviation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K_{IC}^{(2)}$</td>
<td>$G_{IC}^{(1)}$</td>
<td>$K_{IC}^{(1)}$</td>
</tr>
<tr>
<td>0</td>
<td>380</td>
<td>0.75</td>
<td>373</td>
</tr>
<tr>
<td>10</td>
<td>865</td>
<td>4.05</td>
<td>1020</td>
</tr>
<tr>
<td>20</td>
<td>800</td>
<td>3.63</td>
<td>965</td>
</tr>
<tr>
<td>50</td>
<td>1090</td>
<td>2.32</td>
<td>1090</td>
</tr>
<tr>
<td>60</td>
<td>1060</td>
<td>1.97</td>
<td>1100</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>fibre volume (%) graphite</th>
<th>calculated value</th>
<th>measured value</th>
<th>deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K_{IC}^{(2)}$</td>
<td>$G_{IC}^{(1)}$</td>
<td>$K_{IC}^{(1)}$</td>
</tr>
<tr>
<td>0</td>
<td>380</td>
<td>0.75</td>
<td>373</td>
</tr>
<tr>
<td>50 (A)</td>
<td>600</td>
<td>1.37</td>
<td>765</td>
</tr>
<tr>
<td>50 (B)</td>
<td>322</td>
<td>0.40</td>
<td>413</td>
</tr>
</tbody>
</table>

Table 2.1 Orthotropic fracture data (taken from Sih, 1979)
<table>
<thead>
<tr>
<th>CTBN concentration (%)</th>
<th>Fracture energy ( G_{JC} ) (kJ/m(^2))</th>
<th>Tensile strength ( \sigma^1 ) (MPa)</th>
<th>Tensile modulus ( E ) (GPa)</th>
<th>Thermal coefficient of expansion ( \alpha ) (per ( ^\circ)C x 10(^{-5}))</th>
<th>Glass transition temperature ( T_g ) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.12</td>
<td>72</td>
<td>3.3</td>
<td>7.8</td>
<td>80</td>
</tr>
<tr>
<td>4.5</td>
<td>1.05</td>
<td>70</td>
<td>2.3</td>
<td>8.0</td>
<td>70</td>
</tr>
<tr>
<td>10</td>
<td>2.72</td>
<td>56</td>
<td>2.2</td>
<td>8.7</td>
<td>65</td>
</tr>
<tr>
<td>15</td>
<td>3.43</td>
<td>45</td>
<td>2.0</td>
<td>9.6</td>
<td>62</td>
</tr>
<tr>
<td>20</td>
<td>3.59</td>
<td>20</td>
<td>1.0</td>
<td>10.2</td>
<td>60</td>
</tr>
<tr>
<td>30</td>
<td>2.00</td>
<td>17</td>
<td>0.1</td>
<td>14.2</td>
<td>67</td>
</tr>
</tbody>
</table>

Table 2.2 Some properties of a rubber modified epoxy system (CTBN toughened DGEBA, taken from Bascom, 1975)

<table>
<thead>
<tr>
<th>Material</th>
<th>AS4/3502</th>
<th>T6T145/F155</th>
<th>T6T145/HX205</th>
<th>T6T145/F185</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mode I (neat resin)</td>
<td>70</td>
<td>730</td>
<td>460</td>
<td>8100</td>
</tr>
<tr>
<td>Mode I (composite)</td>
<td>189</td>
<td>520</td>
<td>455</td>
<td>2205</td>
</tr>
<tr>
<td>Mode II</td>
<td>570</td>
<td>1270</td>
<td>1050</td>
<td>2440</td>
</tr>
</tbody>
</table>

Table 2.3 Critical energy release rate \( G_{IC} \) values (J m\(^{-2}\)) of neat resin and composite interlaminar toughness parameters for four different systems (taken from Jordan and Bradley, 1987)
<table>
<thead>
<tr>
<th>No</th>
<th>Material</th>
<th>Specimen</th>
<th>$G_{IC}$ (J m$^{-2}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>neat 3502 resin</td>
<td></td>
<td>69</td>
<td>Bradley et al. (1985)</td>
</tr>
<tr>
<td>2</td>
<td>neat 205 resin</td>
<td></td>
<td>270</td>
<td>Bascom et al. (1980)</td>
</tr>
<tr>
<td>3</td>
<td>neat F155 resin</td>
<td></td>
<td>730</td>
<td>Bradley et al. (1985)</td>
</tr>
<tr>
<td>4</td>
<td>neat F185 resin</td>
<td></td>
<td>5100</td>
<td>Bascom et al. (1980)</td>
</tr>
<tr>
<td>5</td>
<td>neat F185</td>
<td></td>
<td>6000</td>
<td>Bradley et al. (1985)</td>
</tr>
<tr>
<td>6</td>
<td>T300/5208 DCB 0$_{24}$</td>
<td></td>
<td>102.6</td>
<td>Ramkumar &amp; Whitcomb (1985)</td>
</tr>
<tr>
<td>7</td>
<td>T300/5208 DCB (02/±45/0)$_{S}$</td>
<td></td>
<td>100</td>
<td>Ramkumar &amp; Whitcomb (1985)</td>
</tr>
<tr>
<td>8</td>
<td>AS4/3501-6 DCB</td>
<td></td>
<td>198</td>
<td>Aliyu &amp; Daniel (1985)</td>
</tr>
<tr>
<td>9</td>
<td>AS4/3501-6 DCB 0$_{24}$</td>
<td></td>
<td>190</td>
<td>Gillespie et al. (1987)</td>
</tr>
<tr>
<td>10</td>
<td>AS1/3502 DCB</td>
<td></td>
<td>155</td>
<td>Bradley et al. (1985)</td>
</tr>
<tr>
<td>11</td>
<td>AS1/3502 DCB</td>
<td></td>
<td>148.7</td>
<td>Browning &amp; Schwarz (1986)</td>
</tr>
<tr>
<td>12</td>
<td>AS4/3502 DCB</td>
<td></td>
<td>225</td>
<td>Bradley et al. (1985)</td>
</tr>
<tr>
<td>13</td>
<td>AS4/3502 DCB</td>
<td></td>
<td>169.8</td>
<td>Browning &amp; Schwarz (1986)</td>
</tr>
<tr>
<td>14</td>
<td>T145/F-185 DCB</td>
<td></td>
<td>2700</td>
<td>Bradley et al. (1985)</td>
</tr>
<tr>
<td>15</td>
<td>Grcloth/F-185 WTDCB</td>
<td></td>
<td>4600</td>
<td>Bascom &amp; Bitner (1980)</td>
</tr>
<tr>
<td>16</td>
<td>AS4/PEEK (APC-2) DCB</td>
<td></td>
<td>2890</td>
<td>Leach (1985)</td>
</tr>
<tr>
<td>17</td>
<td>AS4/PEEK (APC-2) DCB</td>
<td></td>
<td>1750</td>
<td>Gillespie &amp; Carlsson (1987)</td>
</tr>
</tbody>
</table>

Table 2.4 $G_{IC}$ values of a range of resins and their composites (taken from Sela and Ishai, 1988)
<table>
<thead>
<tr>
<th>No</th>
<th>Material</th>
<th>Specimen</th>
<th>$G_{IIC}$ ($J \ m^2$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>T300/5208</td>
<td>CLS</td>
<td>433</td>
<td>Ramkumar &amp; Whitcomb (1985)</td>
</tr>
<tr>
<td>2</td>
<td>T300/914</td>
<td>ENF</td>
<td>518</td>
<td>Prel et al. (1987)</td>
</tr>
<tr>
<td>3</td>
<td>CYCOM982</td>
<td>ENF</td>
<td>982</td>
<td>Gillespie &amp; Carlsson (1985)</td>
</tr>
<tr>
<td>4</td>
<td>APC-2</td>
<td>ENF</td>
<td>1930</td>
<td>Gillespie &amp; Carlsson (1985)</td>
</tr>
<tr>
<td>5</td>
<td>AS4/PEEK</td>
<td>ENF</td>
<td>1765</td>
<td>Russell &amp; Street (1985)</td>
</tr>
<tr>
<td>6</td>
<td>AS4/PEEK</td>
<td>ENF</td>
<td>1109</td>
<td>Prel et al. (1987)</td>
</tr>
<tr>
<td>7</td>
<td>AS4/3502</td>
<td>ENF</td>
<td>2050</td>
<td>Sela &amp; Ishai (1898)</td>
</tr>
</tbody>
</table>

Table 2.5 $G_{IIC}$ values for a range of composites (taken from Sela and Ishai, 1988)
Fig. 2.1 Definition of co-ordinate system and stress field near a crack tip
Fig. 2.2 Three mutually perpendicular planes of material symmetry in a unidirectional lamina (taken from Hull, 1980)

Fig. 2.3 Stress field near a crack tip in an orthotropic solid showing definition of principal material directions, 1 and 2
Fig. 2.4  Stress/strain curves for an epoxy resin deformed in tension at various temperatures (taken from Pink and Campbell, 1980)

Fig. 2.5  Stress/strain curves for an epoxy deformed at 20°C under different states of stress (taken from Kinloch and Young, 1980)
Fig. 2.6 Stress intensity factor, $K_{IC}$, at the onset of crack growth as a function of test temperature and loading rate for unmodified and rubber modified epoxies. Loading rates of, (i) $R=8.33 \times 10^{-1} \text{ m s}^{-1}$ (ii) $R=1.67 \times 10^{-5} \text{ m s}^{-1}$ (iii) $R=1.67 \times 10^{-4} \text{ m s}^{-1}$. The types of crack growth are: type A-ductile stable crack growth, type B-brittle unstable crack growth, type C-brittle stable crack growth (taken from Kinloch et al., 1983).

Fig. 2.7 Load, $P$, versus displacement, $\Delta$, curves for the rubber modified epoxy associated with the different types of crack growth in the compact tension specimen. Type C through to type A occurs with increasing temperature of test (taken from Kinloch et al., 1983).
Fig. 2.8 Toughening mechanisms in rubber modified polymer:
(1) shear band formation near rubber particles,
(2) fracture of rubber particles after cavitation
(3) stretching (4) debonding (5) tearing of rubber particles (6) transparticle fracture (7) debonding of hard particle (8) crack deflection by hard particles
(9) void cavitated rubber particles (10) crazing
(11) plastic zone at craze tip (12) diffuse shear yielding (13) shear band/craze interaction (taken from Garg and Mai, 1988)

Fig. 2.9 Schematic diagram of crack pinning mechanism (taken from Lange, 1974)
Fig. 2.10 Comparison of interlaminar fracture toughnesses of a range of composite materials (taken from Sela and Ishai, 1988)

Fig. 2.11 Composite interlaminar fracture toughness as a function of neat resin fracture energy (taken from Hunston et al., 1987)
- Double cantilever beam flexure test (tension)
- Edge delamination tensile test (mixed tension/shear)
- Cracked lap shear test (mixed tension/shear)
- End-notched flexure test (shear)

Fig. 2.12 Four specimen types used for determination of interlaminar fracture toughness (taken from John and Mangalgiri, 1987)

Fig. 2.13 Rate sensitivity of Mode 1 interlaminar fracture toughness (taken from Smiley and Pipes, 1987)
CHAPTER 3. MATERIAL PROCESSING AND EXPERIMENTAL METHOD
CHAPTER 3. MATERIAL PROCESSING AND EXPERIMENTAL METHOD

3.1 MATERIAL PROCESSING

3.1.1 Base materials
3.1.2 Plaque fabrication for compact tension specimens
3.1.3 Laminate fabrication
3.1.4 Fibre volume fraction measurement

3.2 PREPARATION OF TEST SPECIMENS

3.2.1 Compact tension specimens
3.2.2 Tension and bend specimens
3.2.3 Plain strain compression test specimens
3.2.4 DCB and ENF specimens

3.3 EXPERIMENTAL TEST METHODS

3.3.1 Compact tension test
3.3.2 Young's modulus measurement
3.3.3 Yield stress measurement
3.3.4 Mode 1 interlaminar fracture toughness test
3.3.5 Mode 2 interlaminar fracture toughness test

3.4 FRACTURE SURFACE OBSERVATION
3. MATERIAL PROCESSING AND EXPERIMENTAL METHODS

3.1 MATERIAL PROCESSING

3.1.1 Base materials

(a) Epoxy resin

The epoxy system is based on EPIKOTE 828 resin because of its suitable mechanical properties and the continuity of this project to previous related work in-house.

The basic formulation is:

Resin type - SHELL EPIKOTE 828 epoxy
Cure agent - SHELL EPICURE : Methyl Endomethylene tetrahydrophthalic Anhydride (NMA)
Accelerator - SHELL Benzyl Dimethyl Amide (BDMA)

(b) Toughening agent

Three types of phenolic beads and four types of carbon beads as indicated in Table 3.1, have been used for the present investigation and these materials were supplied by KOBE steel. They were assigned the reference codes S1, S2, S3, S4, S5, S6, S7 as shown in Table 3.1.

Carbon beads (mesocarbon micro beads) are
microspherical beads obtained from the heat treatment (350°C - 500°C) of coal tar or coal tar pitch. These carbon beads were not graphitized. Thus carbon bead is quite different from carbon fibre in nature. Phenolic beads are a powder-like phenolic resin (technical data of manufacturer, 1990).

(c) Glass fibre

The glass fibre was 600-tex 'Silenka' E-glass roving finished with an epoxy-compatible size.

3.1.2 Plaque fabrication for compact tension specimens

To characterise the effect of beads at varying volume fractions on the fracture toughness of epoxy resin filled with beads, plaques of two types were prepared:

- neat epoxy resin
- epoxy resin filled with beads

Preparation of the plaques is detailed below:

a) Neat epoxy resin

This formulation was produced to compare the $K_{IC}$ value of neat resin with that of particle filled epoxies and contained the following proportions:
resin 100g + NMA 80g + BDMA 1.5g

Upon thorough mixing, the above formulation was degassed at 50°C for 20 minutes before curing for 3 hours at a temperature of 100°C using an aluminum mould, coated with a release agent, of dimensions 130 x 130 x 10 mm.

b) Epoxy resin filled with beads

A standard technique, which had been developed in a previous project (Doran et.al. 1990) was used for the production of resin plaques containing the seven different types of bead, as follows:

1) Epoxy resin was heated at a temperature of 40°C for 15 minutes in order to make mixing and stirring easy.

2) The relevant mass of bead is added, together with NMA, to the 828 epoxy resin.

3) These components are then magnetically stirred at a temperature of 40°C for 15 minutes in order to make even distribution of beads

4) 1.5 cc of BDMA are then added

5) The formulation is degassed at a temperature of 50°C
for 20 minutes under vacuum in order to remove entrapped air bubbles.

6) The formulation is then cured in an oven at a temperature of 100°C for 3 hours using an aluminum mould, coated with a release agent, of dimensions 130 x 130 x 10 mm.

(c) pre-cracking procedure

In this study, over two hundred compact tension specimens were tested to evaluate and compare the fracture toughness of each toughened epoxy system. To minimize problems associated with crack tip sharpness and in particular to maintain the same sharpness of crack in each specimen (see section 4.8.1), we have developed a method of moulding a crack around an insert outlined below:

- Thin pink melinex was put vertically on the bottom of the assembled mould using tape

- A support is put on the top of the mould, the aim being to keep the insert straight when the formulation is poured in and also if there is ventilation air flow during curing (Fig.3.1).

- The mixed formulation was then poured into the mould and cured at a temperature of 100°C for 3 hours
3.1.3 Laminate fabrication

In preparation, two glass plates (270 x 270 mm) and one large steel plate were placed in the oven at 100°C for one hour before fabrication. Glass rovings were wound through a tension device onto a 410 mm square steel frame revolving at a constant speed as shown in Fig. 3.2. The speed of traverse of the roving relative to the frame was variable to allow variable density of fibre tows in each unidirectional winding. The total thickness of fibre was increased by repeated traverses of the frame.

The epoxy resin, NMA and BDMA and beads (carbon or phenolic) were first mixed thoroughly and then transferred to a vacuum oven at 50°C for 20 minutes to remove entrapped air (as explained in 3.1.2). The laminate was then fabricated by the following process (Fig. 3.3).

a) The heated hot steel plate was placed on the bottom of the large vacuum chamber.

b) The heated thick (10 mm) glass plate was placed on the hot steel plate and covered with silicon-coated 'Melinex' release film on which resin/bead mixture was poured and distributed evenly.

c) The wound steel frames were placed on the resin/bead mixture layer distributed on the release film inside a large
d) The resin/bead mixture was then introduced at top and bottom of the stack of frames and at each interface. The resin has to be applied at each interface since there is a tendency for the glass fibres to filter out the beads.

e) A thin (13 μm) layer of PTFE material was located at the midplane to provide a starter crack in the DCB and ENF specimens.

f) The chamber was then evacuated and wetting of the fibres occurred as the resin warmed up and was drawn through the rovings under vacuum. When the resin had fully impregnated the fibres (after 25 minutes), the frame stack was removed from the chamber and excess resin and air bubbles were expelled from the laminate before placing in an air-circulating oven between thick glass plates.

g) Finally the laminate was cured for 3 hours at 100°C under 64 kg weight.

3.1.4 Fibre volume fraction measurement

The fibre volume fraction of GFRP laminates was determined using a matrix burn-off technique. A sample weighing approximately 6-7 g was cut from the laminate and weighed accurately. The sample was placed in a furnace at
450°C in a crucible of known weight with a lid to prevent the loss of fibres from the crucible during heating. The minimum time for burning off the matrix was about one hour but this varied with the thickness of the laminate and was determined by experience. After heating, the crucible with the residual fibres was re-weighed and the fibre volume fraction of the sample was calculated as follows.

before heating : mass of crucible + sample = a
mass of crucible = b

after heating : mass of crucible + fibres = c
mass of fibres = c - b
mass of matrix = a - c

$$V_f = \frac{[(c-b)/\rho_f]}{[(a-c)/\rho_m] + [(c-b)/\rho_f]}$$

where $\rho_f$ is the fibre density and $\rho_m$ is the matrix density.

3.2 PREPARATION OF TEST SPECIMENS

3.2.1 Compact tension specimens

Compact tension specimens (40 x 40 x 8 mm, Fig. 3.5)
were cut from the plaque using a water-lubricated diamond saw. Nine specimens can be made from each plaque (130 x 130 x 8 mm). Each specimen cut from the plaque was machined as shown in Fig. 3.6. The machined specimens were then post-cured for 3 hours at 150°C.

3.2.2 Tension and bend specimens

To measure Young's modulus of pure and bead filled epoxy, tension specimens (120 x 15 x 4 mm) were cut from the plaque which was fabricated with same process as CT specimen plaque. Different size specimens (80 x 10 x 4 mm) were cut from the same plaque to measure Young's modulus using three point bending method according to British Standard (Fig.3.5 and 3.6).

3.2.3 Plane strain compression test specimens

Uniaxial compression test specimens were cut from the halves of broken compact tension specimen to establish relationship between material's properties obtained from same specimen. The specimen size used (10 x 30 x 3 mm) was such as to satisfy plane strain condition (Williams, 1964) see Figs. 3.5 and 3.6.

3.2.4 DCB and ENF specimens

DCB (200 x 25 x 4 mm) and ENF (110 x 25 x 4 mm)
specimens (Fig. 3.6 and 3.7) were cut from unidirectional laminates using a water-lubricated diamond saw. These were post-cured for 3 hours at 150°C. For DCB specimens, aluminum alloy end blocks were bonded to the cracked end of the specimens. Adhesion was promoted by lightly abrading the surface of specimen. The end blocks were cleaned using acetone and bonded with a thin layer of adhesive. The specimens were then placed in the jig whilst the adhesive cured. Load was applied via pins through holes in the blocks.

3.3 EXPERIMENTAL TEST METHODS

3.3.1 Compact tension test

Fracture toughness tests to determine the value of plain strain fracture toughness were carried out in accordance with ASTM E399 using an Instron 1175 testing machine. The specimens were tested using a compact tension test jig compatible with existing 1175 INSTRON tensile testing equipment at constant displacement rate and at room temperature. An extensometer was attached onto each specimen to obtain the load-displacement record which was recorded on an X-Y recorder. The testing equipment is shown in Fig. 3.8.

3.3.2 Young's modulus measurement

The strain during tensile test was measured using an
electrical resistance strain gauge. A single 10 mm - length wire strain gauge was bonded to the surface of the specimen with rapid-setting adhesive. The connection between the strain gauge and a 'Vishay' strain indicator was made by leads soldered onto copper tabs bonded on an electrically insulating backing to the surface of the specimen. These tabs relieved the weight of the leads and prevented damage to the fine wires attached to the strain gauge. The change in resistance of the gauge element with increasing tensile load was processed by the strain indicator. The corresponding analogue voltage was then input to the X-axis of an X-Y chart recorder, where the Y- input was the signal from the Instron load cell. Young's modulus, E, can be obtained from the load - strain graph on the X-Y recorder. The testing equipment is shown in Fig. 3.9.

Young's modulus, E, was also determined during three point bending tests in an Instron 1195 testing machine (British Standard : BS2782) from the load and corresponding crosshead displacement. The testing procedure is shown in Fig. 3.9.

3.3.3 Yield stress measurement

The plane strain compression test specimen was placed between two parallel, flat, highly polished lubricated compression dies which are installed in the Instron 1195 and forced into the plate by compression load as shown in Fig.3.10. The yield stress was calculated from the onset of
non-linearity in load-displacement graph and the contacting area. The testing equipment is shown in Fig. 3.10.

3.3.4 Mode 1 interlaminar fracture toughness test

All DCB specimens were tested using an Instron 1195 in displacement control. Test were performed in ambient laboratory condition and at a constant crosshead displacement rate of 2 mm/min. To monitor the position of the crack front, one edge of the specimen was coated with a white brittle fluid (typewriter correction fluid) to assist in visually locating the crack tip. Fine marks were put on this edge at 5 mm intervals to aid measuring the crack length.

An initial load was applied to all DCB specimens until the crack extended for 2 mm from the tip of the teflon insert. The crosshead was stopped and the specimens were unloaded and then loaded again. This pre-cracking procedure is a means of avoiding problems arising from the resin rich region usually associated with the presence of the insert. Specimens were then loaded in a continuous monotonic fashion with load, \( P \), and displacement, \( \delta \), for crack initiation and the subsequent crack extension being marked at the corresponding points on the chart record for later identification and calculation. The testing process is shown in Fig. 3.11.

3.3.5 Mode 2 interlaminar fracture toughness test
ENF specimen (Fig.3.7) was placed on the three point bending testing jig installed in Instron 1195. Test was performed at constant displacement rate (0.5mm/min) and load-displacement graph was recorded on the Instron chart record. The testing process is shown in Fig. 3.12.

3.4 FRACTURE SURFACE OBSERVATION

The fracture surfaces of a large number of specimens were examined using a scanning electron microscope (STEREOSCAN 100, Cambridge Instrument). The specimens were coated with a thin layer of gold to make the surface conductive and reduce charging. Specimens were prepared from compact tension specimen, DCB and ENF specimens.
<table>
<thead>
<tr>
<th></th>
<th>phenolic bead</th>
<th></th>
<th></th>
<th>carbon bead</th>
<th>Green powder</th>
<th>Carbon powder</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>R-800</td>
<td>H-300</td>
<td>C-800</td>
<td>ICB</td>
<td></td>
<td></td>
</tr>
<tr>
<td>specific gravity</td>
<td>1.18</td>
<td>1.25</td>
<td>1.55</td>
<td>1.37</td>
<td>1.85</td>
<td>1.85</td>
</tr>
<tr>
<td>mean particle size μm</td>
<td>15</td>
<td>15</td>
<td>15</td>
<td>20</td>
<td>20</td>
<td>6</td>
</tr>
<tr>
<td>mark</td>
<td>S7</td>
<td>S6</td>
<td>S5</td>
<td>S4</td>
<td>S3</td>
<td>S2</td>
</tr>
</tbody>
</table>

Table 3.1 Technical data for the seven different types of bead used during the present work
Fig. 3.1 Photograph of moulded plaque with insert
Fig. 3.2 Photograph of fibre winding apparatus
Fig. 3.3 Schematic diagram of steps in laminate fabrication process
Fig. 3.4 Photograph of vacuum chamber used in laminate processing
Fig. 3.5 Dimensions of specimens (a) compact tension, (b) tension and bend, (c) compression
Fig. 3.6 Photographs of each specimen type (a) compact tension, (b) tension, bend and compression, (c) DCB and ENF specimens
Fig. 3.7 Dimension of DCB and ENF specimens
Fig. 3.8 Testing of compact tension specimen
Fig. 3.9 Testing to measure tensile and flexural moduli
(a) tensile (b) flexure
Fig. 3.10 Plane strain compression test
Fig. 3.11 DCB testing
Fig. 3.12 ENF testing
CHAPTER 4. FRACTURE BEHAVIOUR OF EPOXY RESIN TOUGHENED WITH CARBON AND PHENOLIC BEADS
CHAPTER 4. FRACTURE BEHAVIOUR OF EPOXY RESIN TOUGHENED WITH CARBON AND PHENOLIC BEADS

4.1 INTRODUCTION

4.2 CRACK GROWTH BEHAVIOUR AND LOAD-DISPLACEMENT RECORDS
4.2.1 Crack growth behaviour
4.2.2 Load-displacement records

4.3 FRACTURE TOUGHNESS, $K_{IC}$, OF PURE AND TOUGHENED EPOXIES
4.3.1 Pure epoxy
4.3.2 Effect of phenolic and carbon bead on the $K_{IC}$ value as function of bead volume fraction
4.3.3 Comparison of $K_{IC}$ values of toughened epoxies containing the same volume fraction of seven different types of beads
4.3.4 Effect of bead size on the $K_{IC}$ value

4.4 YOUNG'S MODULUS OF PURE AND TOUGHENED EPOXY
4.4.1 Pure epoxy
4.4.2 Toughened epoxy

4.5 FRACTURE ENERGY, $G_{IC}$, OF TOUGHENED EPOXY
4.5.1 Calculation of $G_{IC}$ from $K_{IC}$
4.5.2 $G_{IC}$ values for phenolic and carbon bead filled epoxy

4.6 FRACTOGRAPHIC ANALYSIS
4.6.1 Neat resin
4.6.2 Epoxies containing beads
4.7 HYBRID PARTICLE FILLED EPOXY

4.7.1 Fracture toughness of hybrid particle filled epoxy
4.7.2 Fracture surface

4.8 DISCUSSION

4.8.1 Effect of pre-cracking process
4.8.2 Load-displacement behaviour
4.8.3 Qualitative discussion of toughening mechanism
  4.8.3.1 Overview
  4.8.3.2 Crack pinning
  4.8.3.3 Multi-level cracking, plastic deformation, debonding and particle cracking
  4.8.3.4 Transparticle fracture
  4.8.3.5 Summary
4.8.4 Quantitative aspects of toughening mechanisms
  4.8.4.1 Crack pinning
  4.8.4.2 Localized plastic deformation
  4.8.4.3 Summary
4.8.5 Selection of bead type for hybrid composite

4.9 CONCLUSIONS
Fracture toughness, the resistance of materials to crack growth, is one of the most important properties for materials used for load bearing structures. Hence, improving the toughness of materials which are very stiff and strong but brittle (such as epoxy-based composite materials fabricated with a brittle matrix) is a major requirement for widening the range of usage of these materials.

Since the late 1960's, many investigators have reported that improvements in epoxy toughness can be obtained by adding rigid inorganic filler materials (such as glass beads, silica, alumina and silicon carbide etc) without loss of the inherent stiffness and strength of the resin, provided that the filler is surface treated appropriately. In these systems, generally, the rigid filler materials have much higher modulus and strength than the matrix resin. However, there is a material processing problem in that it is difficult to get uniform mixing and dispersion of filler material due to the higher density of the filler material compared to that of the matrix polymer.

On the other hand, research since the early 1970's
(Siebert et al., 1971) has reported that crack resistance of epoxies can be improved by the addition of rubber. If we are concerned only with improving the toughness of pure epoxy, then the rubber modified epoxies can be regarded as the most successful method. However rubber toughened epoxies possess lower stiffness and strength than pure epoxies because of the low stiffness and strength of the rubber elastomer. In addition, the elastomeric phase increases the melt viscosity of the mixture, thus reducing processability.

More recently, as an alternative to rubber toughening, organic filler materials such as polyethersulphone, polyether ether ketone, polybutylene terephthalate, nylon 6 and polyvinylidene fluoride have been used for toughening epoxy resin (Bucknall and Patridge 1983, 1986, Jang et al., 1990, Kim and Robertson, 1992)

Adding polymeric filler materials (or rigid polymer) as second phases into the resin is relatively new compared to the addition of inorganic fillers or rubber and there is not so much literature in this area. In this chapter, within the category of epoxy toughened with polymeric filler material, the effects of three different phenolic beads and four different carbon beads on the crack growth behaviour and fracture toughness value of epoxy resin are studied as a function of bead volume fraction. The $K_{IC}$ values of toughened epoxies containing the same volume fraction of seven different types of beads are presented. The various fracture
surface morphologies are examined and the toughening mechanisms and associated theories are reviewed.

4.2 CRACK GROWTH BEHAVIOUR AND LOAD-DISPLACEMENT RECORDS

The fracture behaviour of neat resin and seven different particle filled epoxies has been examined. Each material system has been given a reference letter, S0 for neat resin and S1 through to S7 for each bead-filled system as explained in Chapter 3 and summarised in Table 4.1. The load-displacement curves for the different materials are shown in Figure 4.1 where different materials showing similar crack growth and load-displacement behaviour have been grouped together.

4.2.1 Crack growth behaviour

The crack propagation behaviour of pure epoxy and toughened epoxies depends on the loading rate, temperature and the presence of filler material (Kinloch et al., 1983, Spanoudakis and Young, 1984, Garg and Mai, 1988). Stable continuous type of crack growth tends to occur in compact tension specimens at low temperature and high strain rates; stick-slip type unstable crack growth is promoted by high temperature, low strain rates and by adding filler material.

In this study, the crack growth behaviour has been controlled only by the type of filler material since all
experiments were performed at constant strain rate and room temperature. The different types of crack propagation behaviour obtained in this study are grouped together in Fig. 4.1. The typical brittle stable crack growth behaviour was observed in pure epoxy S0 and S2 (Fig. 4.1 (a)). Brittle unstable crack growth was observed in S4, S6 and S7 (Fig. 4.1 (b)). A somewhat ductile trend of crack propagation (caused as will be shown later by debonding, transparticle fracture and localized plastic deformation) was observed in S1, S3 and S5 (Fig. 4.1 (c)).

The unstable stick-slip mode of fracture (S4, S6, S7) caused several crack arrest/initiation bands (thumbnail line trace) to appear on the fracture surface. A schematic diagram of a compact tension specimen fracture surface showing this type of behaviour is shown in Fig 4.2.

4.2.2 Load-displacement records

The different shapes of the load-displacement curves for the various materials are associated with different types of crack growth behaviour. In the remainder of this section we relate the load-displacement curves of the present study to those reported by Kinloch and co-workers (1983).

Kinloch et al. (1983) observed three basic types of crack growth behaviour in experiments on unmodified and rubber-modified epoxies, namely (the notation follows
Type C : Brittle-stable crack growth in which cracking is continuous. This type of crack propagation may be thought of as a classic example of brittle fracture.

Type B : Brittle-unstable crack growth during which the crack proceeds in a slip/stick manner. This type of crack propagation is still essentially brittle in nature, but the crack propagates intermittently in a stick/slip manner (showing unstable crack growth behaviour).

Type A : Ductile-stable crack growth in which cracking is continuous but is dominated by gross plastic deformation in the specimen. Unlike the stable brittle propagation (Type C), a relatively high value of $K_{IC}$ is associated with this behaviour and the fracture surfaces are far rougher in appearance, indicating a more ductile fracture process.

Typical load-displacement records for these types of crack growth behaviour in a compact tension specimen geometry are shown in Fig.4.3 (taken from Kinloch et al., 1983). Sometimes transitional crack growth behaviour is seen, where a combination of the above types occurs in a specimen. Type C
through to type A occur with increasing temperature and decreasing loading rate. Kinloch et al. (1983) reported that type A crack growth behaviour was generally observed at high temperature (above 40°C). Under such conditions, it is questionable whether valid $K_{IC}$ values can be obtained.

In the present study, we obtained the load-displacement records of neat resin and seven different toughened epoxies at room temperature and the same loading rate. These records are shown in Fig. 4.1. In Fig 4.1(a) we can see typical brittle-stable crack growth (Kinloch et al., 1983, type C) and these materials (S0, S2) display the lowest fracture toughness values of all the materials tested. In Fig. 4.1(b) (material S4, S6, S7) we can see the load-displacement records which are similar to type B corresponding to brittle-unstable crack growth. The other load-displacement records in the present study differ from those reported by Kinloch and his co-workers. These records, Fig. 4.1(c), are combinations either of type B/type A or of type C/type A. Both these combinations can be termed "quasi-ductile" in that the load-displacement records show rounded peaks, but they are not sufficiently exaggerated for the curves to be considered pure Type A (following Kinloch et al., 1983). Instead it is suggested that these types of combinations can be termed "quasi-ductile unstable crack growth" (type B/type A) and "quasi-ductile stable crack growth" (type C/type A). The various types of load-displacement records observed in our experiments are summarised schematically in Fig. 4.4.

87
4.3 FRACTURE TOUGHNESS, $K_{IC}$, OF PURE AND TOUGHENED EPOXIES

Plane strain fracture toughness values, $K_{IC}$, at the onset of crack propagation were obtained from the load-displacement curves using the following relationship (ASTM E399):

$$K_{IC} = \left(\frac{P_f}{BW^{1/2}}\right) F(\frac{a}{w})$$

where $P_f$, $B$, $W$, and $a$ are the maximum load, specimen thickness, specimen width and crack length respectively.

Fracture toughness data for the neat epoxy resin are shown in Figs 4.5 (plaque 1), Fig. 4.6 (plaque 2) and Fig. 4.7 (data from both plaques). Data for each of the seven different bead types at the same volume fraction (30%) are shown in Figs 4.8 to Fig. 4.14. In each plot of fracture toughness data, all nine individual data points are shown together with the minimum (MI), mean (ME) and maximum (MX) values. Fig. 4.15 compares the mean data from each material.
4.3.1 Pure epoxy

Spanoudakis and Young (1984) have reported unstable crack growth in neat resin at low strain rates using DT (double torsion) specimens and they have thus derived two values of $K_{IC}$ appropriate to crack initiation ($K_{II}$) and to crack arrest ($K_{IIa}$). In our experiments using the CT (compact tension) specimen (cross head speed 0.5mm/min), typical brittle stable crack growth behaviour was observed. Because we have carried out our experiments at a higher cross head speed than that which gives rise to unstable crack growth, such an unstable behaviour was not observed. The mean value of fracture toughness of eighteen specimens was 0.64 MPa $\sqrt{m}$. All the results from individual tests are shown in Fig. 4.5 - 4.7. The data from the two different plaques were felt to be acceptably close to each other. Although the mean from plaque 1 was lower, this is really a consequence of one particularly low value.

4.3.2 Effect of phenolic and carbon beads on the $K_{IC}$ value as a function of bead volume fraction

It can be seen from Figs.4.16 and 4.17 for S7 and S3 material that the volume fraction of particles ($V_p$) has a significant effect on the $K_{IC}$ value. Such a trend has been well documented in the related literature for a wide range of epoxide resins and filler materials. Moloney et al. (1983, 1984, 1987), for example, have reported that the relationship
between $K_{IC}$ value and volume fraction of silica, alumina or glass beads was linear. Spanoudakis and Young (1984a,b) have reported also that increasing volume fractions of glass beads led to a significant increase in the $K_{IC}$ value.

From our experiments we find that the relationship between $K_{IC}$ value and volume fraction of S7 type phenolic beads (Fig.4.16) is reasonably linear within experimental error. The fracture toughness of carbon beads-filled epoxies (S3) increased with increase of bead volume fraction up to 40 % and then decreased sharply as shown in Fig. 4.17. It seems that the reduction of the $K_{IC}$ value after 40 % was caused by material processing problems, in particular voids. The individual fracture toughness values at each volume fraction are shown in Figs.4.18-22 (S7), Fig. 4.23-27 (S3).

4.3.3 Comparison of $K_{IC}$ values of toughened epoxies containing the same volume fraction of seven different types of beads

The results from all the phenolic and carbon bead-filled epoxies showed significant toughness enhancement, as compared to the neat resin, at a bead volume fraction of 30 % (Fig. 4.15). At lower volume fractions (up to 30 %) it was found that sedimentation, leading to non-uniform bead distribution, is a potential problem and at high volume fractions (over 40-50 %) voids can be caused as a result of material processing problems. Thus, for most practical
systems, the maximum volume fraction of filler material which may be incorporated is around 40% to avoid the presence of voids (this was also found by Moloney et al. 1987). Hence a volume fraction of 30% is a realistic one at which to compare the toughness benefit of each of the seven different beads.

From Fig. 4.15, it can be seen that the highest toughness value for filled epoxy is 1.06 MPa\sqrt{m} (S5) and the lowest is 0.71 MPa\sqrt{m} (S2). The highest value is 60% larger than the $K_{IC}$ value for the neat epoxy (0.64 MPa\sqrt{m}) while the lowest value is 10% larger. If we exclude these two materials, there is really no significant difference in the $K_{IC}$ values of the other five toughened epoxies.

4.3.4 Effect of bead size on the $K_{IC}$ value

Some observations may be made with regard to the effect of bead size since S1 and S2 are nominally the same material but the mean particle size of S2 (6 μm) is much smaller than S1 (20 μm). S2 has a significantly lower fracture toughness than that of S1 and has, in fact, the lowest fracture toughness of all the bead-filled materials. Also, while the fracture surface and load-displacement record of S2 are very similar to those of neat resin (Fig. 4.1 (a) and see 4.6.2), the load-displacement behaviour of S1 does show some degree of ductility. Consistent with a rounding of the load-displacement curve, the fracture surface of S1 has a rough appearance (compared to S2) suggesting some degree of matrix plasticity. It is possible that the large particle size
(S1) leads to a greater surface roughness (if the crack avoids the particle) or to more effective crack tip blunting. Both these effects could lead to a greater toughness in the material with larger particles compared to that with smaller particles.

Interestingly, the results found that the large beads (S1) produces a higher fracture toughness than the smaller beads (S2) are slightly in disagreement with those of other works. Moloney et al. (1987) have reported that particle size had little effect on the $K_{IC}$ value for the same volume fractions in their silica particle-filled epoxies. In addition, Spanoudakis and Young (1984) reported that the particle size has a secondary effect on the $K_{IC}$ value in their glass bead-filled epoxies. The reason for the discrepancy with these other workers is not clear. To assess the effect of bead size on the $K_{IC}$ value more clearly, additional experiments with more variation of particle size would be necessary.

4.4 YOUNG’S MODULUS OF PURE AND TOUGHENED EPOXY

Although this research is concerned principally with the fracture behaviour and toughening mechanism of particle filled epoxy, it was necessary to measure the Young’s modulus, $E$, for the toughened epoxy in order to calculate $G_{IC}$ values from the measured $K_{IC}$ values. In the present section these results are presented together with some analysis.

92
4.4.1 Pure epoxy

As described in Chapter 3, the Young's modulus was measured by two different methods: a tensile test and a three-point bending test. The test results are shown in Fig.4.28. Two different types of epoxy sample were tested: EP-A which, after curing, had been aged in the laboratory for one year, and EP-B which was tested within seven days of curing. The Young's modulus of specimens EP-A and EP-B are 3.69 and 3.48 GPa (flexure modulus) and 4.07 and 3.88 GPa (tension modulus) respectively.

There are two points to note:

a) The Young's modulus of specimen EP-A (cured a year before testing) is higher than that of specimen EP-B (cured within seven days of testing). This means that further stiffening has taken place in specimen EP-A, presumably as a result of additional cross-linking.

b) The tension moduli of both specimens are higher than the flexure moduli. This is probably a consequence of the combined tension and compression present in the bend test. The response of a polymer in tension and compression may be different. This means that the simple bending analysis is not strictly applicable. Hence the calculated flexural modulus may be lower than the tensile modulus - a discrepancy which increases with increasing deformation.
4.4.2 Toughened epoxy

It is well known that the addition of particles (such as silica, glass bead, alumina and silicon carbide) to epoxies, modifies the modulus in a way which depends upon the volume fraction of particle and Fig. 4.29 shows results by Spanoudakis and Young (1984) and Moloney et al. (1987). This behaviour has been well documented in the literature and many theories have been developed to quantify the observed behaviour.

Ishai and Cohen (1967) modelled the composite as cubic particles surrounded by a shell of matrix. If the boundary of the cube is subjected to a uniform displacement then for a particle volume fraction \( V_p \)

\[
E_c = E_m \left[ 1 + \frac{V_p}{[m/(m-1) - V_p^{1/3}]} \right]
\]  

(2)

where \( E_c \) and \( E_m \) are the composite and matrix moduli and \( m \) is the modulus ratio, \( m = E_p/E_m \), where \( E_p \) and \( E_m \) are the moduli of the particle and matrix respectively. If the boundary of the cube is subjected to a uniform stress then it follows that

\[
E_c = E_m \left[ \frac{1+(m-1)V_p^{2/3}}{1+(m-1)(V_p^{2/3}-V_p)} \right]
\]  

(3)
Equations (2) and (3) have been plotted as lower and upper bounds in Fig. 4.30 and 4.31 for the work here on carbon and phenolic beads, assuming that $E_p = 3.12$ GPa for carbon beads and 5.8 GPa for phenolic beads. These moduli values were calculated from the data as the best fits to the experimental results for 15% by volume fraction of carbon bead and 40% by volume fraction of phenolic bead.

In both systems, there is not as dramatic an effect of particle addition on the Young's modulus when compared to the inorganic-particle filled epoxy systems shown in Fig. 4.29. This is obviously because there is not a large difference between the modulus of the carbon or phenolic beads and the matrix resin compared to the inorganic particle filled epoxy systems (alumina etc). In our systems, the differences of modulus between the calculated values for the phenolic and carbon beads, 5.80 GPa and 3.12 GPa respectively, and epoxy resin (3.88 GPa) is small.

4.5 FRACTURE ENERGY, $G_{IC}$, OF TOUGHENED EPOXY

4.5.1 Calculation of $G_{IC}$ from $K_{IC}$ values

The fracture energy (or critical energy release rate) has been determined from the plane stress relationship
$$G_{IC} = \frac{K_{IC}^2}{E} \quad (4)$$

where $K_{IC}$ has been measured experimentally. The value of $E$ is determined from the mean values of equation (2) and (3) as plotted in Figs 4.30 and 4.31.

4.5.2 $G_{IC}$ value for phenolic and carbon bead filled epoxy

The critical strain energy release rate as a function of bead volume fraction for the carbon (S3) and phenolic (S7) bead-filled systems, are shown in Figs 4.32 and 4.33. Because the effect of the bead on the composite modulus is small, the trend in $G_{IC}$ is broadly similar to that of $K_{IC}$. The dependence of $G_{IC}$ on $K_{IC}^2$ means that for both systems the percentage change of $G_{IC}$ with bead volume fraction is larger than the corresponding change in $K_{IC}$. This effect is slightly larger in the carbon system where the decrease in modulus with bead volume fraction, although a small effect, adds to the large increase in $G_{IC}$ caused by the increase in $K_{IC}$. In systems based on inorganic fillers quite different behaviour is seen. In Fig.4.34 (Moloney et al., 1983), the mechanical properties of some inorganic particle filled epoxies are shown. In these systems, the trends of variation of the energy release rate, $G_{IC}$, (Fig. 4.34d) are quite different from that of fracture toughness $K_{IC}$ (Fig. 4.34a). These differences are caused by the large increase of modulus of the particle filled epoxies with increase of particle volume fraction. This can lead to the
modulus rising at a faster rate than $K_{IC}^2$ with increasing volume fraction of filler so that the value of $G_{IC}$ will go through a maximum and then fall.

4.6 FRACTOGRAPHIC ANALYSIS

The fracture surfaces of a large number of specimens were examined in the scanning electron microscope. Some typical examples from each material are shown in Fig. 4.35 to 4.44. In Fig. 4.35, we can compare the fracture surfaces of the seven different particle-filled epoxies at similar magnifications. There are three main types of fracture surface:

a) Fracture surfaces showing very irregular crack paths due to multi-level cracking, transparticle fracture and localized yielding deformation (S1, S3, S5) – Fig. 4.36

b) Fracture surfaces showing crack pinning (S4, S6, S7) – Fig. 4.37

c) Typical brittle fracture surfaces (S0, S2) – Fig. 4.38

These three groups correspond to the quasi-ductile stable and unstable crack growth (Fig. 4.36), brittle unstable crack growth (Fig. 4.37), and typical brittle crack growth
4.6.1 Neat resin

Looking at the neat resin fracture surface (Fig. 4.38 (a)) we see that it is mainly smooth and featureless which is representative of brittle fracture. At high magnification, fine river markings are discernible which emanate mainly from the crack initiation region. The river markings are steps in the fracture surface extending approximately in the crack propagation direction and they arise from adjacent sections of the crack front following paths at slightly different levels. The river markings are shown clearly in Fig. 4.39.

SEM micrographs did not reveal any plastic flow except for the limited plastic shear yielding occurring along the river markings as shown in Fig. 4.39.

4.6.2 Epoxies containing beads

A typical SEM photograph of the fracture surface of specimens of type S1 (Fig. 4.40(a)) shows that the dominant event is particle-matrix debonding accompanied by localized plastic deformation of the matrix. Fig. 4.40(b) shows the fracture surface of S2 (at high magnification) which has the lowest fracture toughness of the seven toughened systems tested. The visual appearance of the fracture surface of S2
(at low magnification) is similar to that of the neat resin.

Comparing the fracture surface of S2 and S1 further, figs 4.40(b) and 4.35(b) the roughness of the fracture surface of S2 (at 1000 x) looks similar to that of S1 (at 100x). However, consistent with the load-displacement records in Fig. 4.1 (a),(c) (S1-round peak type and quasi-ductile, S2-sharp peak type and brittle fracture), in absolute terms there is more irregular crack path and associated localized yielding deformation at interface (between particle and matrix) in the fracture surface of S1 compared to that of S2. These observations are consistent with the higher toughness value being achieved in S2 compared to S1 as discussed in section 4.3.4.

In the photographs of S6, S7 (Fig.4.37) we can see many tails and steps behind the beads in the direction of crack propagation. These may be considered as typical characteristics of crack pinning dominated fracture surface (Lange, 1971, Spanoudakis and Young, 1983). Material S4 (Fig. 4.37) also shows these features but the number of tails is less than for materials S6, S7 (Fig. 4.37) and consistent with this, system S4 shows the lowest toughness value of the three materials (S4, S6, S7) showing the crack pinning mechanism.

In contrast to the S4, S6 and S7 systems where crack pinning dominates fracture surface, we can see far rougher
fracture surfaces for materials S1, S3, S5 (Fig. 4.36) due to more widespread severe irregularities in the crack path (multi-level cracking) and localized plastic deformation caused by debonding. Material S3 (Fig. 4.41) shows additionally transparticle fracture (the only system to show this). The main features of the fracture behaviour of each of the seven different materials and the characteristics of the fracture surface are summarized in Table 4.2.

Finally, Figs. 4.42, 4.43 and 4.44 are a polished section and fracture surfaces showing the material processing problems at low volume fraction (sedimentation) and high volume fraction (porosity) respectively.

4.7 HYBRID PARTICLE FILLED EPOXY

4.7.1 Fracture toughness of hybrid particle filled epoxy

We have investigated the possibility of increasing the toughness using a mixture of bead types, by evaluating the fracture toughness of hybrid particulate epoxy containing two bead types (S3 and S7) in three different mixing ratios. Since S3 (carbon bead) and S7 (phenolic bead) show distinctively different toughening behaviour (in one case typical crack pinning mechanism (S7) and in the other transparticle fracture accompanied by localized deformation around the particle during the crack propagation (S3)) it was felt that they were
an appropriate combination for a hybrid material. The mixing ratios were as follows (total bead volume fraction was 30%):

(a) S7 : S3 = 2 : 1 (20% : 10%)
(b) S7 : S3 = 1 : 1 (15% : 15%)
(c) S7 : S3 = 1 : 2 (10% : 20%)

The material processing used was the same as with all the other materials. The mean fracture toughness values of the three hybrid materials were 0.98 MPa√m, 1.01 MPa√m and 1.1 MPa√m respectively and the results are shown in Fig. 4.45. The highest value (S3:S7 = 2:1; 1.1 MPa√m) is over 20% larger than both S3 (carbon bead) and S7 (phenolic bead) at the same bead volume fraction (30%), as shown in Fig. 4.46. There is strong evidence of a synergy between the toughening mechanisms as indicated in the next section.

4.7.2 Fracture surface

The fracture surfaces of hybrid particulate epoxy specimens were examined in the scanning electron microscope. A typical example of these specimens is shown in Fig. 4.47. In this photograph, tails and steps, debonded particles, transparticle fracture and a severely irregular crack path have been observed together. The basic appearance of the fracture surfaces of all three types of hybrid specimen was similar.
One possible toughening mechanism in hybrid system is secondary crack tip blunting. Localized plastic deformation around the carbon bead blunts the crack tip which was pinned by the phenolic beads. In hybrid system, it appears that the crack pinning and crack tip blunting effects are not simply additive.

4.8 DISCUSSION

4.8.1 The effect of the pre-cracking process

In the present study, twenty two different systems (different particles or different volume fractions of particles) have been prepared and over two hundred fracture toughness specimens have been tested. Table 4.3 summarises the various systems used in this work. One of the main purposes of the fracture toughness experiments was to rank the toughness of all the bead systems under the same conditions (pre-crack sharpness, loading rate, temperature) rather than to make an absolute measurement of the toughness. Hence, an important factor was to introduce the same pre-crack sharpness in all specimens since it is well known that fracture toughness values from compact tension specimens can be highly dependent on the pre-crack sharpness.

Generally, the razor tapping method has been used by many previous researchers. This can be an ideal method for the
pure epoxy case, since the pre-cracking process can be checked visually using fluorescent light. However, for the phenolic and carbon bead filled systems, visual checking is impossible, because the system is opaque (the pure epoxy system is quite transparent). Hence to make the same pre-crack sharpness in all specimens, the specimens were moulded around an insert as explained in Chapter 3.

To check the validity of this insert method, the measured fracture toughness ($K_{IC}$) values of pure epoxy and phenolic filled (S7) epoxy system from specimens which were moulded with inserts were compared with those obtained using specimens pre-cracked with the razor tapping method. The results may be compared in Figs. 4.48 and 4.49. For the pure epoxy case, the mean fracture toughness value of the specimens which were prepared with the two different pre-crack methods are almost the same (insert method: $0.64 \text{ MPa } \sqrt{\text{m}}$, tapping method: $0.65 \text{ MPa } \sqrt{\text{m}}$), with the razor tapping method giving a more even data distribution. Fig. 4.50 shows the difference of the crack tip shape between the two methods schematically. The crack tip shape due to the insert was quite straight, while that due to the razor tapping shows some uneven micro-cracking ahead of the starter crack.

For the phenolic bead-filled system (Fig. 4.49), the fracture toughness of specimens pre-cracked using the razor tapping is almost 40% higher than that with the insert method. The problem with these opaque systems during the pre-cracking
process was controlling the degree of tapping. Overcautious tapping, to avoid breaking or damaging the specimens can blunt the crack tip, while careless tapping may also cause damage rather than lead to a sharp crack tip. The only way to overcome the problem was trial and error which was very time consuming.

In the light of these problems, it is felt that the use of the insert method is justified in that uniformity of pre-cracking is assured and hence comparative toughness values can be obtained for both the pure epoxy and the bead-filled systems.

4.8.2 Load-displacement behaviour

A record of the load-displacement behaviour of the material is very useful as it gives information which complements the $K_{IC}$ values and the fracture surface observations. We have distinguished here between "brittle" and "ductile" behaviour on the basis of the behaviour near the peak load - a sharp peak indicates brittle behaviour and a round peak indicates ductile behaviour. Brittle behaviour was observed in S0, S2, S4, S6 and S7. In contrast, somewhat ductile behaviour was observed in S1, S3 and S5. These load-displacement records showed good correlation with subsequent fractographic analysis:

brittle stable crack growth-S0, S2 (Figs. 4.38)
brittle unstable crack growth-S4, S6, S7 (Figs. 4.37)
quasi-ductile stable crack growth-S1 (Fig. 4.36)
quasi-ductile unstable crack growth-S3, S5 (Fig. 4.36)

In addition, while investigating the effect of the volume fraction of carbon beads on fracture behaviour, we obtained different types of load-displacement record for the five bead volume fractions of 10, 20, 30, 40, 50%, as shown in Fig. 4.51. The load-displacement records show increasingly ductile behaviour with increasing bead volume fraction. This suggests that transparticle bridging and particle fracture increasingly encourage crack tip blunting, causing an improvement in the fracture toughness. This is discussed further in section 4.8.3.4.

4.8.3 Qualitative discussion of toughening mechanisms

4.8.3.1 Overview

In considering the toughening of epoxies by the addition of a second phase, it is convenient to consider two classes: namely rubber-toughened epoxies and other particle-filled epoxies (organic or inorganic particle). In rubber-toughened epoxies, toughening mechanisms include plastic deformation mechanisms involving crazing, shear yielding and interaction of crazes with shear bands. The toughened systems in the present work belong to the latter category of particle filled epoxies.
Much previous research suggests that there are several possible toughening mechanisms for particle-filled epoxies. These are summarised below together with the systems of the present study which showed such behaviour:

a) An increase in fracture energy as a result of increased fracture surface area due to the irregular path of the crack (multi-level cracking) : S1, S3, S5

b) Localized shear yielding of the matrix around the particle (localized plastic deformation) : S3, S5

c) Debonding of internal boundaries which also causes an increase of fracture surface area and localized shear yielding : S1

d) Transparticle fracture of filler materials : S3

e) The interaction between a crack front and the reinforcing particle (crack pinning) : S4, S6, S7

Lange and Radford (1971), Green et al. (1979), Moloney et al. (1985) reported that fracture surface roughness, mechanism (a) above, may give rise to a relatively small increase in toughness compared to crack pinning in rigid particle filled epoxies. They suggested that mechanism (c), crack pinning, was the most significant source of toughening in their inorganic particle (alumina trihydrate, silica,
alumina, glass bead, silicon carbide) epoxy systems. Crack pinning has been the subject of extensive research (Lange 1970, Evans 1972, Green et al. 1979, Moloney et al. 1983, Spanoudakis and Young 1984 a, b, Kinloch et al., 1985).

Mechanisms (b) and (c) arise from the particles acting as stress concentrators and inducing the formation of localized yielding around the particle leading to crack tip blunting. In mechanism (d), transparticle fracture, much energy must be absorbed during the crack propagation, if filler material is an elastomer. However it was reported (Moloney et al., 1983) that transparticle fracture is detrimental to crack pinning. The relative contribution of the mechanism to the fracture toughness depends on the test temperature and various factors such as size and type of particle, volume fraction, and particle/matrix adhesion.

In rubber-modified epoxies or for high temperature testing conditions, the second mechanism (localized plastic deformation) is the predominant toughening mechanism and much information is available concerning this phenomenon. Some information is available about the localized plastic deformation for particle-filled epoxies. In the following paragraphs, the individual fracture mechanisms are examined in more detail.
4.8.3.2 Crack pinning

The proposed mechanism of crack pinning (Lange, 1972) is that a crack can be obstructed by rigid impenetrable, well-bonded particles. When a crack meets such an array of impenetrable obstacles, the crack front is pinned and tends to bow out between the particles, forming secondary cracks (Fig. 4.52). Thus new fracture surface is formed and the length of the crack front is increased due to the change of shape of crack front between the pinning positions. In order to create an increase in crack front length, an increase in strain energy is required which in turn leads to an increase in the fracture energy of the material.

Spanoudakis and Young (1984 a,b) and Kinloch et al. (1985) reported strong evidence of crack pinning phenomena in their fractographic studies of glass-particle-filled epoxies. When the secondary cracks eventually break away from the pinning positions, then this frequently leads to characteristic tails and steps on the fracture surface at the rear of the particle. This is due to the meeting of the two arms of the crack front from two slightly different planes. In our fractographic studies, typical characteristic tails and steps were observed in S4, S6, S7. These are shown in Figs. 4.35 (g) and (h).
4.8.3.3 Multi-level cracking, plastic deformation, debonding and particle cracking

As described earlier in the review of the fracture surfaces of materials S1, S3 and S5, only a few tails and steps were observed in these systems. Instead of evidence of the crack pinning mechanism, a far rougher fracture surface was observed here which is indicative of multilevel cracking, caused by an irregular crack path, and of localized shear yielding, caused by stress concentrations around the particle, transparticle fracture or debonding.

Spanoudakis and Young (1984) suggested that the absence of tails does not necessarily mean that no pinning occurs, since at high volume fractions (over 30%) of particles there may be considerable overlap of secondary crack. However, it seems clear that the fracture toughness behaviour of the specimens used in this study falls broadly into two groups, and the major differences between the two groups are described below:

(a) the load-displacement behaviour near the maximum load of specimens S1, S3, S5 is a round peak, but that of S4, S6, S7 is a sharp peak (Fig. 4.1). It can be deduced that the round peak of S1, S3, S5 indicates ductile behaviour, perhaps caused by localized yielding of matrix around particle, debonding or transparticle fracture.
(b) the fracture surfaces of S1, S3, S5 are much rougher than those of S4, S6, S7. The general appearance of debonded interface between particles and matrix in S4, S6, S7 are smooth and featureless and no characteristic appearance is evident. On the contrary, the particle/matrix interface in each of S1, S3, S5 shows particular features:

S1 : Many remnants of the matrix may be observed in the gaps between matrix and particle and the fracture surface has a rough and irregular shape (Fig. 4.40(a)). The deformation of the matrix to produce these features may cause crack tip blunting.

S3 : In this system transparticle fracture was observed and severe irregularity of the interface is shown. It may be said that significant localized yielding deformation has taken place within the matrix around the particle during the transparticle fracture (Fig. 4.41)

S5 : In this system the debonded interface is similar to S4, S6, S7, but the whole fracture surface is rougher than that of S4, S6, S7. S5 showed the highest toughness value but the "lubricity" specified by the manufacturer probably produced the material processing problem which led to porosity in the material (Fig. 4.44).

It is clear that macroscopic plastic deformation has not taken place during crack propagation in the material.
However it can be said that significant localized yielding has occurred in the matrix surrounding the particles. This localized plastic deformation causes the crack tip blunting which leads to an increase in the fracture toughness. Based on this discussion it can be concluded that the increase in fracture toughness for the S1, S3, S5 materials can be explained by localized deformation causing crack tip blunting, rather than by crack pinning.

4.8.3.4 Transparticle fracture

In material S3, transparticle fracture was observed (Fig 4.41). The phenomenon of particle fracture has been reported in the literature of rubber toughened epoxies (Kunz-douglass et al., 1980). Lange and Ladford (1971), Moloney et al. (1983) also reported transparticle fracture in their inorganic particle (alumina trihydrate, dolomite) filled epoxies. In the latter case, transparticle fracture was detrimental to the toughness.

For the better understanding of the behaviour of system S3, we need to consider the competing toughness mechanisms in more detail. The crack pinning mechanism is based on the assumption that the filler material is rigid and impenetrable. Moloney et al. (1983) noted that this assumption, proposed by Lange (1970) and Evans (1972), is clearly invalid in the case of weak particles. For example, in their dolomite-filled epoxy resins, it was found that above a certain critical volume
fraction (20%), a plateau is reached and the fracture
toughness no longer increases (as shown in Fig. 4.53). They
explained that this plateau was associated with transparticle
fracture. They reported that for volume fraction of up to 20%,
crack pinning was the major source of toughening and above
20%, crack pinning was no longer so important because
transparticle fracture dominates. The transition can be
understood by noting that as the particles become closer with
increasing volume fraction the stress needed to propagate
secondary cracks between the particles increase. Hence
fracture may start to dominate.

In material S3, microscopic observations have shown
that transparticle fracture takes place from low volume
fraction (10%) to high volume fraction (50%) and that fracture
toughness increases steadily with increasing bead volume
fraction up to 40%. These results suggest that in system S3,
the crack pinning mechanism is not the major toughening source
even at low bead volume fractions and that the increase in
toughness in S3 can be attributed to the transparticle
fracture and localized yielding deformation around the
particle. Fig. 4.51 shows schematic load-displacement records
and the corresponding crack growth behaviour at each volume
fraction of S3 (0-50%). Typical brittle crack growth behaviour
is shown at 10% and the corresponding load-displacement curve
at 10% is quite similar to that of pure epoxy resin (Type C,
section 4.2.2). Unstable brittle crack growth behaviour is
shown at 20% and the load-displacement record is similar to
Type B. After 30%, more ductile behaviour is shown and the load-displacement record is approaching that of ductile crack growth behaviour (Type A). From the above result, it can be said that increasing the bead volume fraction increases the degree of crack tip blunting (due to more localized yielding deformation) leading to an increase in fracture toughness for S3. Fig.4.51 shows the crack path behaviour schematically at each volume fraction (0-50%). The crack path becomes more irregular with increasing bead volume fraction.

An additional important factor in toughening which is associated with localized plastic deformation mechanisms is the variation in yield stress of the particle-filled system with increasing bead volume fraction. The yield stress of the S3 system decreases with increasing bead volume fraction, as shown Fig. 4.54. A decrease in the yield stress will lead to an increase in the degree of crack tip blunting, which is consistent with the increase in the $K_{IC}$ value.

4.8.3.5 Summary

Spanoudakis and Young (1984), Kinloch et al. (1985) have pointed out that the toughening mechanisms in particle filled epoxies are quite complex with various toughening mechanisms (such as crack tip blunting and pinning) taking place simultaneously. It may be said that crack pinning and crack tip blunting are two major mechanisms which are responsible for the enhancement of toughness in the particle filled
epoxies tested in this work. Because these two toughening mechanism can take place simultaneously during the crack propagation, it is difficult to separate these two mechanisms completely to explain toughness source. Only as major and minor sources of toughness improvement can the two mechanisms be classified.

4.8.4 Quantitative aspects of toughening mechanisms

The main toughening theories concerned with particle filled epoxy have been reviewed in the previous section in the context of the results of this work. The two most generally accepted and commonly quoted toughening mechanisms are crack pinning and localized deformation around the particle causing crack tip blunting. In this section, these two mechanisms will be considered quantitatively. Experimental results for the fracture toughness of S7 (which showed typical crack pinning characteristics) are compared with a theoretical prediction (Green et al., 1979). Crack tip blunting of S3 is quantified in terms of the crack tip opening displacement (CTOD).

4.8.4.1 The crack pinning mechanism

This mechanism was modelled theoretically by Lange (1970) and his work was modified by Evans (1972) and Green et al. (1979). The theory (suggested by Lange, 1970) is based on the concept of a crack "line tension". Evans (1972) carried out detailed calculation of the line tension (T) and
Green et al. (1979) modified and extended Evans' calculation. In the present section this modelling is outlined and then compared with experimental data.

(A) Lange's model

This model assumes that as an initially straight crack front propagates, the crack front bows out between the rigid pinning second phase particles. During this initial stage of crack propagation, new fracture surface is formed and the length of crack front is increased due to the change in shape of the crack front between the pinning positions. Energy is required not only to create the new fracture surface, but also to increase the line length of the crack front, which is assumed to possess line energy. This was analyzed by Lange (1970) as outlined below.

When the crack propagates in a particle filled matrix under the applied load, the increment of fracture energy ($\Delta U$) absorbed due to the increment of crack extension ($\Delta c$) can be divided into two parts. One is associated with the energy to create new fracture surface area ($\Delta U_s$) and the other is associated with the energy to form the increased length of the crack front ($\Delta U_1$). If the shape of the crack front is known (as it propagates between the pairs of particles), both $\Delta U_s$ and $\Delta U_1$ can be calculated. Lange (1970) assumed that the shape of the crack front is an arc of a circle. The interaction of the crack front with a linear array of equally spaced...
inhomogeneities is illustrated in Fig. 4.52. It is assumed that breaking away from the pinning position take place when the radius of the curvature of the crack front reaches $R$, where $2R$ is the distance between the particles. In Fig. 4.52 a unit of the crack front between a pair of particles and the variables $r$ and $\theta$ which define its shape are illustrated. The hatched area represents one of the two newly formed fracture surfaces which are bounded by the line of the particles and the crack front. The amount of energy required to form these surfaces, per unit length of crack front, is given by:

$$\Delta U_s = \frac{\gamma_0}{2R} r^2 (\theta - \sin \theta)$$  \hspace{1cm} (5)

where $\gamma_0$ is the fracture surface energy of the matrix. The amount of energy per unit length of crack front required to increase the line length of the crack front is given by:

$$\Delta U_l = T \left( \frac{r\theta}{2R} - 1 \right)$$  \hspace{1cm} (6)

where $T$ is the line tension energy per unit length of the crack front. The total amount of absorbed energy ($\Delta U$) for a crack extension of $\Delta c$ can be expressed as:
\[ \Delta U = \Delta U_s + \Delta U_1 \]  

Following Lange (1970), \( G_{IC} \) is given by the following expression:

\[ G_{IC} = 2(y_0 + \frac{T}{d}) \]

where \( d(=2R)=2d_p\left[(1-V_f)/3V_f\right] \)

Here \( G_{IC} \), \( d_p \), \( V_f \) and \( d \) are the critical strain energy release rate, mean particle size, particle volume fraction and interparticle spacing (Fullman, 1953, Lange and Radford, 1971) respectively.

The Lange model was examined by Evans (1972) who carried out detailed calculations of the line tension (T) and demonstrated that the line energy contribution to the fracture energy depends on the particle size and spacing.

Subsequently, Green et al., (1979) modified and expanded Evans' analysis (which was based on impenetrable obstacles) to account for penetrable obstacles, obstacle shape and secondary crack interactions. Crack interaction (between adjacent cracks separated by the particles) lowers the predicted fracture toughness because the stress field of the cracks in the array will tend to interact to reduce the stress needed to propagate each individual flaw (Paris and Sih,
1965). In addition, Green et al. (1979) compared their experimental results on a glass-nickel system with their theoretical predictions (Figs. 4.55, 4.56). They concluded that poorly bonded nickel spheres in a glass matrices acted as relatively weak obstacles. Due to the poor bonding, the measured $K_{IC}$ value of nickel particle system is lower than that predicted, but if crack interaction is considered, then the agreement is improved.

(B) Comparison of the fracture toughness of phenolic-bead-filled epoxies with theoretical predictions.

The predicted ratio of the fracture toughness of particle reinforced epoxy to the fracture toughness of the pure epoxy is given simply by the ratio of the stress needed to propagate the secondary cracks between the spherical particles in the epoxy resin matrix, $\sigma_a$, to the stress needed to propagate the primary crack in their absence, $\sigma_0$, i.e. (Green et al., 1979, Spanoudakis and Young, 1984):

$$\frac{\sigma_a}{\sigma_0} = \frac{K_{ICC}}{K_{IC0}} \quad (9)$$

where the suffixes c, 0 indicate the composite and the matrix respectively. The model of Green et al. enables $\sigma_a/\sigma_0$ to be predicted based only upon geometry considerations namely the particle size and spacing (Fig. 4.55). Hence data for different composites should fall on the same predicted curve.
The theory of Green et al. may be compared with experimental results obtained in this work. Figure 4.57 shows measured values of $K_{ICC}/K_{IC0}$ for different volume fractions of phenolic bead plotted against $r_0/C$ (Fig. 4.55). The solid lines represent the theoretical values predicted by Green et al. (1979). The measured values of $K_{ICC}$ are lower than the theoretically predicted values. In Fig. 4.58, direct comparison of our results with those of Green et al. (1979) is shown. The trend of our results is similar with that of Green and his co-workers.

It is useful, therefore, to review the fracture of phenolic bead filled epoxy in the light of the crack-pinning theories. Firstly, it is clear that the fracture surface of the phenolic bead-filled-epoxy shows that particle-matrix adhesion is poor (Fig. 4.35(h) and 4.37(c)). This does not match the assumption of well-bonded impenetrable obstacles required in the crack pinning theory. The phenolic beads act as weak obstacles (similar to the nickel particles of Fig. 4.56) due to the poor bonding.

Secondly, the analysis of neighbouring secondary crack interaction considered in the model assumes that the neighbouring cracks are co-planar. However, the fracture surfaces show many steps indicating that in general this was not the case.
4.8.4.2 Localized plastic deformation

The toughening mechanism in the systems S1, S3, S5 were discussed earlier (section 4.8.3) in terms of the qualitative evidence such as load-displacement records and photographs of the fracture surfaces in the SEM. In this section, a more quantitative discussion is presented using the crack tip opening displacement (CTOD) criterion. To explain at a fundamental level a toughening mechanism which involves plastic deformation, it is necessary to examine the yield behaviour of the particle-filled epoxy and to ascertain the effect of plastic deformation on the extent of crack-tip blunting.

Various models such as those of Irwin (1964) and Dugdale (1960), have been proposed to describe the extent and shape of the localized plastic deformation zone at a crack tip. From these models we may define a parameter known as the crack tip opening displacement at onset of crack growth $\delta_c$ (Fig. 4.59). The value of, $\delta_c$, reflects the degree of crack-tip blunting and can be calculated using the following relationship (Knott, 1973, Marshall et al., 1974, Gledhill et al., 1978, Kinloch et al., 1983)

$$\delta_c = \frac{K_{IC}^2}{E\sigma_{yt}} \quad (10)$$

where $K_{IC}$ is the stress intensity factor at the onset of crack
growth, $\sigma_{yt}$ is the tensile yield stress and $E$ is the Young's modulus. The tensile yield stresses ($\sigma_{yt}$) in this work were obtained from plain strain compression test values, $\sigma_{yc}$, for the yield stress assuming that $\sigma_{yt} = 0.75 \sigma_{yc}$ (Kinloch et al., 1983). In the carbon bead filled epoxy system (S3), the yield stress of S3 decreases with increasing bead volume fraction (Fig. 4.54). The yield stress measured in this study is somewhat higher than that reported by Kinloch et al. (1983) perhaps due to the differences of crosshead speed (this work: 2mm/min, Kinloch et al.: 0.5mm/min).

An example of the behaviour of the crack opening displacement at the onset of crack growth as a function of test temperature at three different strain rates is shown in Fig 4.60(a) and (b) for unmodified and rubber-modified epoxies respectively (Kinloch et al., 1983). The result show that the value of $\delta_c$ increases with increasing temperature and decreasing strain rate. This means that the extent of localized plastic deformation and associated crack tip blunting increase steadily as the temperature is increased or the strain rate is decreased, i.e. as the yield stress falls.

In Fig. 4.61, the calculated CTOD at fracture (from equation 10) is plotted against bead volume fraction for the carbon-bead-filled system, S3. In this system the yield stress falls with increasing bead volume fraction and the fracture toughness increases. The value of $\delta_c$ goes through a peak at a volume fraction of 40% because $K_{IC}$ value drop sharply at a
volume fraction of 50% possibly due to material processing problems as discussed earlier. This emphasizes the importance of localized plastic deformation in increasing the toughness.

One final question which might arise is the comparison of the CTOD values shown in Fig. 4.61 with the thickness of the polymer insert (45μm) used for moulding the pre-crack. We might suppose that the CTOD of these specimens is equal to the thickness of the insert. A CTOD of 45 μm is large compared to the value of the CTOD of pure epoxy (around 2 μm, Young and Beaumont, 1977; Moloney and Kausch, 1985) and it might be expected that the fracture toughness of these specimens should be very high. In fact, the measured fracture toughness of these specimens was almost the same as that of specimens which were pre-cracked using the razor tapping method (described in section 4.8.1) and the calculated CTOD values are reasonable. This suggests that the inserts are in fact acting as sharp cracks. Moreover, if the CTOD of these specimens was indeed 45 μm, we would expect to see plastic deformation at the crack tip due to the blunted crack tip and no such evidence was observed on SEM photographs. The explanation appears to be as follows. Prior to placing the melinex inserts into the mould, they were cut using a very sharp blade. The shape of the tip of the melinex insert is close to 90°. It has been observed on SEM photographs and confirmed by checking of broken specimens that the crack starts at one corner of the insert as shown schematically in Fig. 4.62. Hence the CTOD will be much less than the thickness of the inserts.
4.8.4.3 Summary

In this section (4.8.4), a quantitative discussion for the crack pinning mechanism in system S7 has been provided together with a description of the crack tip blunting mechanism of system S3. It is suggested that system S7 does not satisfy the basic assumptions of crack pinning theories (Evans, 1972) due to poor bonding of the particle to the matrix leading to a \( K_{IC} \) value which is lower than that predicted. Based on qualitative and quantitative evidence, it can be concluded that in system S3, crack tip blunting is the dominant toughening mechanism due to transparticle fracture and localized plastic deformation.

4.8.5 Selection of bead type for hybrid composites

Based on the experimental results, described above, we selected one filler material out of the seven possible materials for the next phase of the study in accordance with the following criteria:

a) the fracture toughness value and its reproducibility

b) the ease of material processing

The highest fracture toughness value was given by material S5, with S3 and S6 having the second highest values. Material S5 however had a serious problem with regard to
processing because fractography revealed voids on the fracture surface (Fig. 4.44). Materials S3 and S6 have the next highest \( K_{IC} \) values, but S3 shows a lower scatter in the experimental results suggesting that it has a more even distribution of particle.

Hence, material S3 (carbon bead) was chosen for incorporation into the matrix of glass fibre/epoxy resin laminates. The following two chapters describe the effect of the beads on the interlaminar fracture properties of the composites.

4.9 CONCLUSION

The toughness of particle-filled epoxies containing seven different filler materials has been evaluated. Based on the results one filler material was selected (carbon bead, S3) for the next part of the study and the following additional results were obtained:

- Fractography has shown that the particle-filled materials display the most important toughening mechanisms, namely crack pinning (in systems S4, S6, S7) and localized plastic deformation causing crack tip blunting in systems (S1, S3, S5).

- Of all the materials, only the material containing the
carbon bead (S3) showed transparticle fracture, which can be considered as an additional mechanism of toughening.

- Load-displacement records are generally in agreement with fractographic results with regard to toughening mechanisms and related values of fracture toughness.

- Following from the studies of Kinloch and co-workers, two new categories of fracture are proposed as a result of this work, namely quasi-ductile stable and quasi-ductile unstable crack growth behaviour.

- Hybridization, that is a mixture of more than one bead type, can give an additional enhancement of toughness compared to using one bead on its own.
<table>
<thead>
<tr>
<th>Material</th>
<th>phenolic beads</th>
<th>carbon beads</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>R-800</td>
<td>H-300</td>
</tr>
<tr>
<td>mark</td>
<td>S7</td>
<td>S6</td>
</tr>
</tbody>
</table>

Table 4.1 Filler material list
<table>
<thead>
<tr>
<th>Load - Displacement</th>
<th>Fracture surface</th>
<th>Debonded surface</th>
<th>K&lt;sub&gt;IC&lt;/sub&gt;</th>
<th>Particle size</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO</td>
<td>Typical brittle fracture, Sharp peak</td>
<td>Smooth and featureless</td>
<td>0.64</td>
<td></td>
</tr>
<tr>
<td>S1</td>
<td>Quasi ductile stable, Round peak</td>
<td>Rough fracture surface, A few steps and tails</td>
<td>Coarse, tearing of matrix</td>
<td>0.88</td>
</tr>
<tr>
<td>S2</td>
<td>Typical brittle fracture, Sharp peak</td>
<td>Relatively smooth and featureless, slightly rougher than SO</td>
<td>0.71</td>
<td>6</td>
</tr>
<tr>
<td>S3</td>
<td>Quasi ductile unstable, Round peak</td>
<td>Very rough fracture surface</td>
<td>Transparticle fracture surface</td>
<td>0.91</td>
</tr>
<tr>
<td>S4</td>
<td>Brittle unstable, Sharp peak</td>
<td>Smooth compared to S1, S3, S5, Steps and tails</td>
<td>Smooth and featureless</td>
<td>0.82</td>
</tr>
<tr>
<td>S5</td>
<td>Quasi ductile unstable, Round peak</td>
<td>Very rough surface</td>
<td>Irregular boundary shape</td>
<td>1.06</td>
</tr>
<tr>
<td>S6</td>
<td>Brittle unstable, Sharp peak</td>
<td>Smooth compared to S1, S3, S5, Steps and tails</td>
<td>Smooth and featureless</td>
<td>0.91</td>
</tr>
<tr>
<td>S7</td>
<td>Brittle unstable, Sharp peak</td>
<td>Smooth compared to S1, S3, S5, Steps and tails</td>
<td>Smooth and featureless</td>
<td>0.88</td>
</tr>
</tbody>
</table>

units: K<sub>IC</sub> (MPa \(\sqrt{m}\)), particle size (\(\mu\)m)
<table>
<thead>
<tr>
<th>bead</th>
<th>$V_f$</th>
<th>pre-cracking method</th>
</tr>
</thead>
<tbody>
<tr>
<td>pure epoxy (S0)</td>
<td>0</td>
<td>insert</td>
</tr>
<tr>
<td>&quot;</td>
<td>0</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>0</td>
<td>razor</td>
</tr>
<tr>
<td>phenolic (S7)</td>
<td>7</td>
<td>insert</td>
</tr>
<tr>
<td>&quot;</td>
<td>13</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>26</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>30</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>37</td>
<td>&quot;</td>
</tr>
<tr>
<td>carbon (S3)</td>
<td>10</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>20</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>30</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>40</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>50</td>
<td>&quot;</td>
</tr>
<tr>
<td>S1</td>
<td>30</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S7</td>
<td></td>
<td>razor</td>
</tr>
<tr>
<td>hybrid (S3:S7=1:2)</td>
<td></td>
<td>insert</td>
</tr>
<tr>
<td>&quot; (S3:S7=1:1)</td>
<td></td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot; (S3:S7=2:1)</td>
<td></td>
<td>&quot;</td>
</tr>
</tbody>
</table>

Table 4.3 Particle-filled epoxy systems used in this study
Table 4.4 The variation of $\sigma_y$, $K_{IC}$, $E$ and $G_{IC}$ with volume fraction of carbon bead filled (S3) epoxies

<table>
<thead>
<tr>
<th>$V_f$</th>
<th>$\sigma_y$ (MPa)</th>
<th>$K_{IC}$ (MPa $\sqrt{m}$)</th>
<th>$E$ (GPa)</th>
<th>$G_{IC}$ (J/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>96</td>
<td>0.64</td>
<td>3.88</td>
<td>106</td>
</tr>
<tr>
<td>10</td>
<td>89</td>
<td>0.74</td>
<td>3.79</td>
<td>144</td>
</tr>
<tr>
<td>20</td>
<td>83</td>
<td>0.76</td>
<td>3.71</td>
<td>156</td>
</tr>
<tr>
<td>30</td>
<td>80</td>
<td>0.91</td>
<td>3.61</td>
<td>229</td>
</tr>
<tr>
<td>40</td>
<td>77</td>
<td>1.08</td>
<td>3.55</td>
<td>328</td>
</tr>
<tr>
<td>50</td>
<td>70</td>
<td>0.88</td>
<td>3.48</td>
<td>222</td>
</tr>
</tbody>
</table>
Fig. 4.1(a) S0, S2
Fig. 4.1(b) S4, S6, S7
Fig. 4.1(c) S1, S3, S5

Fig 4.1 Load-displacement record of pure epoxy and seven different bead filled epoxy systems
(a) S0, S2 : brittle-stable crack growth
(b) S4, S6, S7 : brittle-unstable crack growth behaviour
(c) S1, S3, S5 : Quasi ductile-crack growth behaviour
Fig. 4.2 Schematic diagram of the fracture surface arising from unstable stick-slip crack growth in compact tension specimen
Fig. 4.3 Load-displacement record of rubber modified epoxy compact tension specimens (taken from Kinloch et al., 1983)
Fig. 4.4 Types of load-displacement behaviour identified in the present study for materials S0 - S7
Fig. 4.5 $K_{IC}$ value of neat resin (plaque 1), S0
(MI=minimum, ME=mean value, MX=maximum)

Fig. 4.6 $K_{IC}$ value of neat resin (plaque 2), S0
Fig. 4.7 $K_{IC}$ value of neat resin (plaque 1 + 2), S0
Fig. 4.8 $K_{IC}$ value of S1 (carbon bead, 20 μm)

Fig. 4.9 $K_{IC}$ value of S2 (carbon bead, 6 μm)
Fig. 4.10 $K_{IC}$ value of S3 (carbon bead : green powder)

Fig. 4.11 $K_{IC}$ value of S4 (carbon bead:ICB)
Fig. 4.12 $K_{IC}$ value of S5 (Phenolic bead:C-800)

Fig. 4.13 $K_{IC}$ value of S6 (Phenolic bead:H-800)
Fig. 4.14 $K_{IC}$ value of S7 (Phenolic bead: R-800)
Fig. 4.15 Comparison of mean $K_{IC}$ value for neat epoxy and all bead filled epoxy system at a volume fraction of 30%
Fig. 4.16 Variations of fracture toughness $K_{IC}$ with volume fraction for S7 type phenolic bead filled epoxy
Fig. 4.17 Variation of fracture toughness $K_{IC}$ with volume fraction for carbon bead (S3) filled epoxy
Fig. 4.18 $K_{IC}$ data for phenolic beads (S7) at a volume fraction of 7%.

Fig. 4.19 $K_{IC}$ data for phenolic beads (S7) at a volume fraction of 13.5%.
Fig. 4.20  $K_{IC}$ data as for Figure 4.19 but material magnetically stirred for 30 minutes during processing

Fig. 4.21  $K_{IC}$ data for phenolic beads (S7) at a volume fraction of 26 %
Fig. 4.22 $K_{IC}$ data for phenolic beads (S7) at a volume fraction of 37%
Fig. 4.23 $K_{IC}$ data for carbon bead (S3) at a volume fraction of 10%.

Fig. 4.24 $K_{IC}$ data for carbon bead (S3) at a volume fraction of 20%.

148
Fig. 4.25 $K_{IC}$ data for carbon bead (S3) at a volume fraction of 30%.

Fig. 4.26 $K_{IC}$ data for carbon bead (S3) at a volume fraction of 40%.
Fig. 4.27 $K_{IC}$ data for carbon bead (S3) at a volume fraction of 50%
Fig. 4.28 Comparison of moduli of base epoxy (EP-A, tested about one year after curing; EP-B, tested within seven days of curing), cb15 (carbon bead 15%), ph10 (phenolic bead 10%) and ph40 (phenolic bead 40%)
Fig. 4.29 Flexural modulus $E$ as a function of volume fraction of filler: (a)x:silica, Δ:alumina, o:silicon carbide (taken from Moloney et al., 1987); (b) glass bead with different particle size (taken from Spanoudakis and Young, 1984)
Fig. 4.30 Young's modulus variation of carbon bead (S3) filled epoxy as a function of volume fraction.

- eq.1
- eq.2
- measured value
Fig. 4.31 Young's modulus variation of phenolic bead (S7) filled epoxy, as a function of volume fraction
Fig. 4.32 Fracture energy variation with phenolic bead (S7) volume fraction
critical strain energy release rate $G_{IC}$ (J/m$^2$)

carbon bead volume fraction (%)

Fig. 4.33 Fracture energy variation with carbon bead volume fraction (S3)
Fig. 4.34 The variation of (a) critical stress intensity factor, (b) Young's modulus, (c) yield stress and (d) fracture energy with volume fraction of particle (o: alumina, •: silica, taken from Moloney et al., 1983)
Fig. 4.35(c) S2

Fig. 4.35(d) S3

159
Fig. 4.35(e) S4

Fig. 4.35(f) S5

160
Fig. 4.35 Comparison of fracture surface of various bead filled epoxies (a) S0, (b) S1, (c) S2, (d) S3, (e) S4, (f) S5, (g) S6, (h) S7
Fig. 4.36(a) S1

Fig. 4.36(b) S3
Fig. 4.36 Fracture surface of S1, S3, S5 (debonding, transparticle fracture, multi-level cracking)
(a) S1, (b) S3, (c) S5
Fig.4.37(a) S4

Fig.4.37(b) S6
Fig. 4.37 Fracture surface of S4, S6, S7 (crack pinning)
(a) S4, (b) S6, (c) S7
Fig. 4.38 Fracture surface of S0, S2 (typical brittle fracture surface)
Fig. 4.39 River markings of neat resin fracture surface
Fig. 4.40 Fracture surface of (a) S1, (b) S2 at high magnification (around 1000x)
Fig. 4.41 Fracture surface of S3 (transparticle fracture surface)
Fig. 4.42 Fracture surface of bead-filled epoxy (S7) showing material processing problem (sedimentation)

Fig. 4.43 Polished section through the thickness of a plaque of phenolic bead (S7) filled epoxy showing uneven bead distribution
Fig. 4.44 Fracture surface of S5 (porosity)
Fig. 4.45 (a) $K_{IC}$ values of hybrid particulate epoxy ($S3: S7 = 2:1$)

Fig. 4.45 (b) $K_{IC}$ values of hybrid particulate epoxy ($S3: S7 = 1:1$)
Fig. 4.45 (c) $K_{IC}$ values of hybrid particulate epoxy ($S3: S7 = 1:2$)
Fig. 4.46 Comparison of mean $K_{IC}$ value for hybrid particulate epoxies
Fig. 4.47 Fracture surface of hybrid particulate reinforced epoxy
(a-1)

(a-2)

176
Fig. 4.48 Comparison of pre-cracking process effect for pure epoxy (a-1) insert, plaque 1, (a-2) insert plaque 2, (b) razor tapping
Fig. 4.49 Comparison of pre-cracking process effect for system S7 (a) insert (b) razor tapping
Fig. 4.50 Comparison of pre-crack tip shape (a) insert (b) razor tapping
Fig. 4.51 Schematic diagram of the load-displacement traces and crack path of pure and carbon bead-filled epoxy (S3) with different bead volume fractions
Schematic representation of the pinning process and the interaction of the crack front with second phase particles.

Fig. 4.52 Schematic diagram of crack pinning process
Fig. 4.53  The variation of fracture energy with volume fraction of dolomite particle (taken from Moloney et al., 1983)
Fig. 4.54 The variation of calculated tensile yield stress with volume fraction for carbon bead (S3) filled epoxy
Fig. 4.55 Definition of $r_0$ (particle size) and $C$ (interparticle spacing)
Fig. 4.56 Comparison of measured toughness of glass-nickel system with predicted value (taken from Green et al., 1979)
Fig. 4.57 Comparison of measured toughness ratio, $K_{ICc}/K_{IC0}$ (phenolic bead filled epoxy) with predicted value, $\Delta$: measured value, solid line: predicted value
Fig. 4.58 Comparison of the theoretical predictions of Green et al. with results of this study: a phenolic-bead filled epoxy, Δ and a glass-nickel system, o
Fig. 4.59 Schematic diagram of crack tip opening displacement: CTOD (6) (taken from Gledhill and Kinloch, 1976)
Fig. 4.60 Crack opening displacement $\delta$ as function of test temperature (a) pure epoxy, (b) rubber modified epoxy (taken from Kinloch et al., 1983)
Fig. 4.61 Calculated variation of CTOD with the bead volume fraction for carbon bead (S3) filled epoxies.
Fig. 4.62 Schematic diagram of melinex insert (45 μm) and the initiation of a crack from one side of the insert
CHAPTER 5. MODE 1 INTERLAMINAR FRACTURE BEHAVIOUR OF HYBRID COMPOSITE MATERIAL FABRICATED WITH A TOUGHENED MATRIX
Chapter 5. Mode 1 interlaminar fracture behaviour of hybrid composite material fabricated with a toughened matrix

5.1 Introduction

5.2 Data reduction method for DCB tests
   5.2.1 Compliance method to determine $G_{IC}$
   5.2.2 Area method to determine $G_{IC}$
   5.2.3 Calculation of $K_{IC}$ values

5.3 Experimental results
   5.3.1 The compliance variation as a function of crack
   5.3.2 $G_{IC}$ values from DCB tests
   5.3.3 Effect of bead volume fraction on the fracture toughness ($K_{IC}$) of the hybrid composite

5.4 Fractographic analysis and fracture mechanisms
   5.4.1 Fractographic analysis
   5.4.2 Fracture mechanisms

5.5 Discussion
   5.5.1 Load-displacement behaviour, $G_{IC}$ and $K_{IC}$ values
   5.5.2 Optimum bead volume fraction
   5.5.3 Translation of resin toughness into composite interlaminar toughness

5.6 Conclusions
5. Mode 1 interlamonar fracture behaviour of hybrid composite material fabricated with a toughened matrix

5.1 Introduction

One of the limiting features of composite materials in service is their tendency for matrix cracking either within a ply (e.g. transverse ply cracking) or between plies (delamination). Over the years a number of methods have been considered for improving matrix toughness and hence delaying the occurrence of these potentially critical events. Amongst these methods are the use of thermosetting matrices with a two-phase microstructure (Jordan and Bradley, 1987, Jang et al., 1990), use of thermoplastic matrices (Cogswell, 1992) and addition of secondary reinforcement such as SiC whisker (Doran et al., 1990). While this last method has been shown to be successful in increasing matrix cracking thresholds there are safety hazards in processing the whisker, the whisker reduces the volume fraction of glass fibre that can be incorporated into the resin and it also appears to degrade the strength of the composite (Doran et al., 1990).

The present study is concerned with using a different type of secondary reinforcement - carbon and phenolic beads. In chapter 4, the effect of varying
volume fractions of different types of carbon and phenolic beads on the plain strain fracture toughness of pure epoxy resin has been investigated. Based on these results, the effect of introducing beads as a secondary reinforcement of the matrix in a continuous glass fibre composite has been investigated by studying the interlaminar fracture behaviour.

Over the last decade a range of tests have been developed for measurement of the interlaminar toughness properties of fibre reinforced composite. These tests are generally identified by the type of loading applied (Mode 1, Mode 2 and Mixed Mode). In this chapter, the Mode 1 interlaminar fracture toughness of hybrid composites fabricated with a bead-reinforced matrix is examined using DCB specimens. The DCB specimen is now the most widely accepted testing method for determining the Mode 1 interlaminar fracture toughness of a continuous fibre composite.

First, DCB test data reduction methods are described. Then the experimental results obtained in the present study are presented. Finally the fracture mechanisms are examined using the SEM.
5.2 Data reduction methods for DCB tests

The data reduction methods for calculating $G_{IC}$ from Mode 1 fracture tests are the compliance method and the direct energy method (also known as area method). Both the compliance and the area method are based on the energy balance concept of linear elastic fracture mechanics (LEFM). These are reviewed below as well as a method of determining the fracture toughness $K_{IC}$.

5.2.1 Compliance method to determine $G_{IC}$

5.2.1.1 The basic analysis

The double cantilever beam specimen geometry is illustrated in Fig. 5.1. The analysis of the double cantilever beam test for an elastic body is based on a change in compliance as illustrated in Fig. 5.2. A crack extension from $a$ to $a + da$ causes a change in compliance which results in a loss of strain energy, $dU$. The Mode 1 strain energy release rate, $G$, is defined as (Irwin and Kies, 1954)

$$G = -\frac{1}{B} \left( \frac{dU}{da} \right)$$  \hspace{1cm} (1)
where $U$ is the total strain energy in the elastic body and $B$ and $a$ are the beam width and crack length respectively. From Fig. 5.2, it can be seen that strain energy lost due to the crack extending from $a$ to $a+da$ for a linear elastic body is simply the area, $dA$, between the loading and unloading curves.

\[-dU = dA = \frac{1}{2} (Pd\delta - \delta dP) \quad (2)\]

where $P$ and $\delta$ are the applied load and resulting deflection, respectively. Combining (1) and (2), the following expression can be obtained:

\[G = \frac{1}{B} \frac{dA}{da} = \frac{1}{2B} (P \frac{d\delta}{da} - \delta \frac{dP}{da}) \quad (3)\]

The value of compliance, $C$, is given by

\[C = \frac{\delta}{P} \quad (4)\]

Substitution for $\delta$ from equation (4) into equation (3) yields

\[G = \frac{1}{2B} (P \frac{d(PC)}{da} - PC \frac{dP}{da}) = \frac{P^2}{2B} \frac{dC}{da} \quad (5)\]
To evaluate $G_{IC}$ via equation (5), a plot of $C$ versus $a$ is
determined experimentally and then a curve fitted so
that $dC/da$ can be found for a given value of $a$. Hence
from the crack propagation load, $P$, a point value of $G_{IC}$
can be found (Wilkins et al., 1982). A typical plot of $C$
versus $a$ for a hybrid composite in Mode 1 DCB specimen
can be seen in Fig. 5.4. Equation (5) is the basis of the
compliance method.

5.2.1.2 Beam theory analysis and the compliance method

(a) Load method

From simple beam theory, the value of the
compliance $C$ is given by

$$C = \frac{\delta}{P} = \frac{2a^3}{3EI} \quad (6)$$

and because $I = Bh^3 / 12$

$$C = \frac{8a^3}{BEh^3} \quad (7)$$

where $E$ is the longitudinal modulus of laminate, $I$ is
second moment of area, and $2h$ is the total thickness of
the DCB specimen. Hence from equations (5) and (7)
The displacement method is based on substitution for $P$ from equation (6) into equation (8) to give

$$G_{IC} = \frac{P^2a^2}{BEI}$$

(8)

The raw form of the experimental fracture data normally consist of a load-displacement record for a cracked specimen. Using equation (9), we can calculate the fracture energy directly from the load-displacement record of a cracked specimen. As mentioned in chapter 2, there is no widely accepted standard test procedure for Mode 1 and 2 tests - protocols are still under development. The terminology of "load and displacement method" was used by Hashemi, Kinloch and Williams (1989).

5.2.2 Area method to determine $G_{IC}$

Another LEFM approach for determining $G_{IC}$ is called the area method. This method is also based on the definition of $G$ of equation (1). Consider a typical
loading and unloading curve (i.e. before and after crack propagation) for a DCB specimen, as shown in Fig. 5.3. When load versus displacement curves for cracked specimens exhibit a linear elastic response, the change in elastic energy $U$ due to the crack extension from $a$ to $a+da$ is simply the area between the loading and unloading curves shown as the shaded area in Fig. 5.3 and the value of $G_{IC}$ can be determined from

$$G_{IC} = \frac{1}{B} \frac{\Delta A}{\Delta a} = \frac{1}{2B(\Delta a)} (P_1 \delta_2 - P_2 \delta_1)$$

(10)

where $P_1$, $P_2$ and $\delta_1$, $\delta_2$ are the load and displacements corresponding to the crack extension from $a$ to $a+\Delta a$ as shown in Fig.5.3.

5.2.3 Calculation of $K_{IC}$ values

As an alternative to the $G_{IC}$ analysis described in the previous sections, it is possible to obtain $K_{IC}$ values. Two limiting solutions for the stress intensity factor for a DCB specimen loaded by point loads valid for large and small $a/h$ ratios (Fig.5.1) are available in literature.

For very small values of $a/h$ the stress intensity
factor approaches Irwin's solution (1957) for a crack in an infinite plate.

\[ K = \frac{P}{b} \left( \frac{2}{\pi a} \right)^{1/2} \quad (11) \]

where \( b \) is the specimen width, \( a \) is the distance from the crack tip to the loading points and \( h \) is the height of cantilever beam (Fig. 5.1).

For large values of \( a/h \), the stress intensity factor can be extracted from an analysis by Gilman (1959) based on elementary beam theory:

\[ K = \frac{P}{b} \left( \frac{12}{h} \right)^{1/2} \left( \frac{a}{h} \right) \quad (12) \]

For intermediate values of \( a/h \), \( 2 < a/h < 10 \), two different expressions for \( K \) are available. Gross and Srawley (1966) obtained the following expression by boundary collocation methods:

\[ K = \frac{P}{b} \left( \frac{12}{h} \right)^{1/2} \left[ \left( \frac{a}{h} \right)^{2} + 0.687 \right] \quad (13) \]

Fichter (1983) has reported an approximate solution for DCB specimen using Fourier transforms and the Wiener-Hopt
technique (which is a method for solving partial differential equation).

\[ K = \frac{P}{B} \left( \frac{12}{h} \right)^{1/2} \left[ \frac{a}{h} + 0.6728 + 0.0377 \left( \frac{h}{a} \right)^2 \right] \]  \hspace{1cm} (14)

More recently, Foote and Buchwald (1985) have reported an exact solution for the stress intensity factor for the DCB specimen which is valid for all values of \( a/h \), provided that \( C/h > 2 \) where \( C \) is the uncracked ligament size.

\[ K = \frac{P}{b\sqrt{h}} \left[ \sqrt{12} (a/h + 0.673) + \sqrt{(2h/\pi a)} - \left[ 0.815(a/h)^{0.619} + 0.429 \right]^{-1} \right] \]  \hspace{1cm} (15)

In our study, the values of \( a/h \) for the DCB specimens lie in the range, \( 10 < a/h < 40 \), with \( C/h > 2 \). Equation (15) is thus valid for the DCB specimens used in this study.

Note: All the equations introduced in this section have been established for homogeneous isotropic materials. This limitation will be discussed in Chapter 7. In the next section we present experimental data for hybrid composite materials based on carbon-bead-reinforced glass fibre epoxy.
5.3 Experimental results

5.3.1 The compliance variation as a function of crack length

Figs. 5.4 a-e show the compliance variation with crack length for specimens with different amounts of carbon beads in the epoxy resin matrices. To check the power law dependence of the compliance on crack length, the data were plotted on log-log scales, Figs 5.4 a'-e'. The results show data from five tests, together with the mean values from the test data. In Fig.5.4 (f and f'), a comparison of the compliance-crack length data for all the hybrid composites is shown. The plots show that, at any particular value of crack length, the compliance increases with increasing bead volume fraction due to the associated decrease in glass fibre volume fraction.

It can be seen from the log-log plots (Fig. 5.4 a'-f') that the slope is very close to 3 which is necessary to justify using the displacement method to determine \( G_{IC} \) (as discussed in the next section). The slope for the 15% hybrid composite material is almost exactly three. A very slight deviation from three can be observed for the pure epoxy glass fibre composite and for the 30% hybrid composite material. However, it can be said that the slopes observed are all acceptably close to
the theoretical value (equation 6 and 7).

5.3.2 $G_{IC}$ values from DCB tests

The $G_{IC}$ values obtained in this study were calculated by displacement method using equation (9):

$$G_{IC} = \frac{3P\delta}{2Ba}$$

where $P$, $\delta$, $B$ and $a$ are load, displacement, specimen width and crack length respectively. The results from the DCB tests carried out on four bead reinforced epoxy resin based GFRP laminates (at bead fractions of 10, 15, 20, and 30 % by volume of matrix) and the baseline pure epoxy matrix laminates are shown in Figs.5.5 to 5.9 as plots of $G_{IC}$ versus crack length $a$ (R-curve). For each material five specimens were tested. In every case, the $G_{IC}$ values associated with the onset of crack growth ($G_{IC, init}$) are different from those of the subsequent $G_{IC}$ growth values i.e. the materials show a rising R-curve.

Based on the R-curves, Figs 5.5 to 5.9, the value of $G_{IC, init}$ at the onset of crack growth was evaluated in two ways. The first value was calculated based simply on the load at which initial crack propagation from the
insert occurs. After about 2 mm increment of crack growth, the specimens were unloaded and then loaded again to obtain a second $G_{IC \text{ init}}$ value corresponding to a 2 mm increment of crack growth ahead of the insert (Hashemi et al., 1990). This latter method is a means of avoiding problems arising from the fibre disturbance and the resin rich region usually associated with the presence of the insert. Both methods of determining $G_{IC \text{ init}}$ gave higher values for the hybrid composites than for the pure epoxy glass fibre composite as shown in Fig. 5.10 (b). However, after crack extension to a crack length of greater than about 60 mm the subsequent $G_{IC}$ propagation value of the GFRP laminates based on unmodified epoxy is higher than that of any of the hybrid composites.

Figs. 5.10 (a) and (b) enable the $G_{IC}$ behaviour of the five different composite materials to be compared. Fig. 5.10 (a) shows the full R-curves for each material (obtained from the average of figs 5.5-5.9) while Figs. 5.10 (b) enables values for the initiation and early stage of crack propagation to be compared more clearly. The effect of bead volume fraction on the $G_{IC \text{ init}}$ value is not consistent with that on the subsequent $G_{IC}$ propagation value. The $G_{IC}$ initiation value at 20 % bead by volume shows the highest value of the five different composites. However, the subsequent $G_{IC}$ propagation values of the 20% hybrid composite are lower
than those of both the pure epoxy and the 10% hybrid composite. These results were associated with the fracture mechanisms in these materials and will be explained with the aid of fractographic analysis (section 5.4).

5.3.3 Effect of bead volume fraction on the fracture toughness ($K_{IC}$) of the hybrid composite

The crack growth resistance calculated in terms of the critical stress intensity factor ($K_{IC}$) of the composites with pure epoxy and bead reinforced matrices are shown in Figs. 5.11-5.15 as plots of $K_{IC}$ versus crack length $a$. Again, each plot shows the results for five specimens and the mean value. The mean values from each material are summarised in Fig.5.16(a). The general trend of the $K_{IC}$ curves is similar to the $G_{IC}$ curves except that the hybrid composite fabricated with a reinforced matrix with 15% by volume of bead shows the highest $K_{IC}$ initiation value, Fig.5.16(b).

5.4 Fractographic analysis and fracture mechanisms

5.4.1 Fractographic analysis

SEM photographs of the fracture surfaces of the
unmodified epoxy and hybrid composites from the Mode 1 DCB test specimens are shown in Figs. 5.17-5.19. A large amount of fibre bridging can be seen on the fracture surface of the pure epoxy glass fibre composite, Fig. 5.17. Increasing bead volume fraction decreases the degree of fibre bridging as shown in Fig. 5.18 (15% bead reinforced matrix) and Fig. 5.19 (30% bead reinforced matrix).

The resin rich region associated with the presence of the insert is shown in fig. 5.20, fig. 5.20(a) for pure epoxy matrix and fig. 5.20 (b) for a bead reinforced matrix. This resin rich area has an irregular width (as shown schematically in Fig. 5.21) and with the average value being around 1 to 2 mm.

General views of the fracture surfaces of carbon bead filled DCB composite specimens and similar phenolic-bead filled composite specimens (same bead volume fraction) are shown in Fig. 5.22 and Fig. 5.23 for comparison. The fracture surface of carbon bead (S3) reinforced hybrid composite is characterised by fibre bridging (as well as fibre debonding and pullout) and transparticle fracture of the carbon beads and associated plastic deformation. The fracture surface of phenolic bead (S7) reinforced hybrid composite shows similar fibre related fracture surface but the tails characteristic of
crack pinning (which were observed clearly in phenolic bead reinforced epoxy without the fibre) are not now observed.

5.4.2 Fracture mechanisms

The detailed observations made on the carbon-bead filled composites may be summarized as follows:

(a) Interlaminar crack propagation occurs largely at the fibre-matrix interface, rather than in the resin in the pure epoxy/glass fibre composite. With increasing bead volume fraction, there is a trend away from this, with the crack path increasingly following resin rich regions.

(b) Interlaminar crack growth leads to fibre bridging, debonding, breakage and pullout behind the crack tip. A large number of fibres link across the Mode 1 crack from one half of the beam to the other, so forming a bridge as shown schematically in Fig.5.24. The degree of fibre bridging depends on the bead volume fraction (with higher volume fractions leading to less bridging).

(c) The presence of carbon bead (S3) in neat resin samples was shown in chapter 4 to localize plastic deformation (leading to crack tip blunting) prior to fracture of the particle. A similar mechanism seems to
operate when the bead is incorporated into the matrix of the composite DCB specimen since fractured beads are seen on the fracture surface.

5.5 Discussion

5.5.1 Load - displacement behaviour, $G_{IC}$ and $K_{IC}$ values

Figs. 5.25 and 5.26 show the real and idealized load-displacement behaviour of pure epoxy glass fibre composite (a) and hybrid composite (b). The loads at which subcritical cracking (point $A'$) and macroscopic crack growth (point $B'$) start in the hybrid composite are higher than the corresponding points (points $A$, $B$) in the pure epoxy glass fibre composite. This is a consequence of the matrix toughening effect - the carbon bead reinforced matrix has a higher toughness than the pure epoxy matrix, as described in chapter 4.

The pure epoxy glass composite has a higher fibre volume fraction (66%) than that of hybrid composite (54 % at bead volume fraction 15 %) and the same thickness (4 mm). As a result of this, for a given load the displacement of the hybrid composite is higher than that of pure epoxy glass fibre composite, i.e. the hybrid composite has a higher compliance, see Figs.5.4 and 5.25.
Consequently all hybrid composites show a higher $G_{IC}$ initiation value, calculated from equation (9), than the pure epoxy glass fibre composite.

After the early stage of crack growth, the load for further crack extension in the pure epoxy glass fibre continues to increase and is higher than that of hybrid composite due to the large amount of fibre bridging. In contrast, the load for further crack extension in the hybrid composite drops fairly sharply after a short initial rise close to the onset of crack growth. Therefore, the $G_{IC}$ propagation value in the pure epoxy glass fibre composite is higher than that in the hybrid composite. These relationships between $G_{IC}$ and $K_{IC}$ initiation and propagation values are shown in Figs. 5.10 and 5.16.

5.5.2 Optimum bead volume fraction

In Figs. 5.10 and 5.16, $G_{IC}$ and $K_{IC}$ values of five different composite laminates (pure epoxy glass fibre and four different hybrid composites fabricated with 10, 15, 20, 30% bead reinforced matrix) have been compared and each composite system shows a slightly different $G_{IC}$ and $K_{IC}$ behaviour. Before we comment on the optimum bead volume fraction, we have to comment on the relevance of the initiation and the propagation values.
As mentioned in chapter 3, DCB specimens used in this study were not fabricated from prepreg but using a filament winding technique which is useful for laboratory level fabrication of specimens. Fig. 5.27 shows a schematic comparison of the interface between plies in laminates fabricated with prepreg and by the filament winding method. The interface between plies of a laminate fabricated using the filament winding method is considerably rougher due to the nature of the winding process.

Fibre bridging is generally attributed to the nesting of fibre and weak fibre-matrix interfaces. When two plies of the same orientation are adjacent to each other in the laminate, the cure pressure forces the plies to merge together and removes the characteristic thin layer of resin between plies. In our fabrication method, merging of fibres can take place more easily compared to the prepreg method (Fig. 5.27) leading to more fibre bridging. However, if we introduce bead into the matrix, the extent of the thin layer of bead-rich resin between the plies of the laminate increases with increasing bead volume fraction because the fibre prevents the beads from evenly distributing within the plies. The beads tend to inhibit fibre bridging and, consequently, the amount of fibre bridging decreases with increasing bead volume.
fraction in the matrix material. Therefore the $G_{IC}$ propagation value of the hybrid composites decreases with increasing bead volume fraction and pure epoxy glass fibre composite shows the highest value of the five different composites.

Close to the insert in the DCB specimen (around the area from which the $G_{IC}$ initiation value is obtained), plies can be prevented from fibre nesting as a result of the presence of the insert. Hence, the condition of the interface between the plies becomes similar to that if the laminate had been fabricated from prepreg. To summarise, it might be said that the $G_{IC}$ initiation value obtained from the filament winding method using an insert would therefore be close to that of a laminate manufactured using the prepreg method. On the other hand, the $G_{IC}$ propagation value of pure epoxy glass fibre was considerably higher because of the additional fibre bridging.

From an engineering design viewpoint, it might be said that the $G_{IC}$ initiation value is more important than the $G_{IC}$ propagation value of an established crack. In the light of this argument, the optimum bead volume fraction for maximizing the $G_{IC}$ and $K_{IC}$ initiation values is discussed below.
As indicated earlier, from examining Fig. 5.10 and 5.16 it is clear that the presence of the bead results in an increase in the initiation value of interlaminar toughness and fracture toughness $G_{IC}$ and $K_{IC}$, compared to the standard epoxy laminate. The materials containing nominally 15% and 20% by volume of bead (S3) in the matrix showed higher toughness than the 30% material even though, the 30% material was tougher when tested as a bead-filled epoxy without the fibres (Fig. 4.17). One possible explanation for this is that the nominal bead volume fractions will certainly be underestimates of the actual bead volume fraction present in the plane of propagation of the interlaminar crack, due to the fibres preventing the beads from being distributed uniformly within the matrix. Hence the interlaminar toughness will not correspond to those of bead-filled epoxies where the distribution of beads is much more uniform.

A comparison of Fig. 5.10 and Fig. 5.16 shows that the highest $K_{IC}$ and $G_{IC}$ initiation values occur at different volume fractions of bead. The highest $G_{IC}$ value occurs at a volume fraction of 20%, whilst the highest $K_{IC}$ value occurs at 15%. This can be explained by considering equations (8) and (14), from which $G_{IC}$ and $K_{IC}$ respectively, were calculated. In equation (9), the important variables are load ($P$) and displacement ($\delta$), but in equation (14) only the load ($P$) appears.
The 15% hybrid composite shows the highest crack initiation load \((P)\). The \(K_{IC}\) value, which is independent of the displacement of the laminate is thus the highest value of all five materials from the 15% hybrid composite. But the 20% hybrid composite shows a higher displacement (Fig.5.2 (f) and (f')) compared to 15% hybrid composite, although the crack initiation load is slightly lower than that of 15% hybrid composite in the load - displacement record. Consequently, the 20% hybrid composite shows the highest \(G_{IC}\) value, which depends on the product of load \((P)\) and displacement \((\delta)\).

5.5.3 Translation of resin toughness into composite interlaminar toughness

In Fig.5.28 (a),(b) (Hunston and Dehl, 1987, Bradley, 1989) a plot of Mode 1 interlaminar toughness against neat resin toughness is shown. It is clear that an increase in neat resin toughness from that of the first generation epoxy (around 70 - 100 J/m\(^2\)) results in a significant increase in Mode 1 toughness. However, at values of neat resin \(G_{IC} > 400\) J/m\(^2\), further increases in toughness are met with smaller corresponding incremental increases in the respective composite interlaminar toughness.

The reason why the interlaminar toughness value of...
the composite is higher than the value of $G_{IC}$ of the neat matrix at values of matrix epoxy $G_{IC} < 400$ J/m$^2$ can be explained by the following factors (Bradley, 1989):

(a) Increase in fracture surface area: Generally, the interlaminar crack propagation occurs largely through the fibre-matrix interface, rather than through the resin. The delamination fracture surface of the composite has the morphology of a corrugated roof, giving an actual surface that may be better modelled by a group of cylinders (as shown in Fig. 5.17) than the largely flat fracture surface observed in the fracture of a brittle resin without fibre reinforcement.

(b) Interfacial fracture gives rise to some fibre bridging behind the crack tip. The fibre pullout and breakage that accompanies crack growth would also dissipate additional energy.

It has also been reported (Jordan and Bradley, 1987) that the low efficiency of translation of resin fracture toughness into delamination fracture toughness $G_{IC}$, for neat resin with $G_{IC} > 400$ J/m$^2$ is the result of the constraint in the development of a large plastic zone in the resin rich region between plies due to the fibres in the adjacent plies.
In Fig. 5.29, the results of our study are presented as a plot of interlaminar toughness $G_{IC}$ at crack initiation against $G_{IC}$ of matrix resin at the same nominal bead volume fraction. The fracture energies of the unfilled matrix materials used in this study are well below $400 \text{ J/m}^2$ and hence the increase in neat resin toughness due to the carbon bead reinforcement results in a significant increase in Mode 1 interlaminar toughness of the composite. The general trends of these results are similar to those shown in Fig. 5.28 for values of neat resin $G_{IC} < 400 \text{ J/m}^2$.

In Fig. 5.30, the R-curve behaviour of a hybrid composite fabricated with carbon bead (S3) reinforced matrix is compared with that of a hybrid composite reinforced by phenolic bead (S7) at the same bead volume fraction (15%). The $G_{IC}$ initiation and propagation values of carbon bead reinforced hybrid composite are both higher than those for the phenolic bead reinforced hybrid composite. It can, therefore, be concluded that the toughening mechanism of localised plastic deformation leading to crack tip blunting, together with the associated transparticle fracture (which are the major toughening mechanisms of the carbon bead (S3) reinforced epoxy) are more effective in enhancing interlaminar toughness than the crack pinning mechanism (which is the major toughening mechanism of the phenolic bead (S7))
reinforced epoxy).

Transparticle fracture mechanism was also observed in the fracture surface of the hybrid composite. However, the characteristic tail and step of the crack pinning mechanism was not observed in the fracture surface of the phenolic bead reinforced composite. It seems that crack pinning by the beads does not occur in the hybrid composite material. In addition, since material toughness is generally linked to plastic deformation, the plastic deformation linked with the crack growth in the carbon bead (S3) material is more effective in improving the interlaminar toughness of the hybrid composite than the phenolic bead (S7).

5.6 Conclusions

Based on the results of chapter 4, six different composites (pure epoxy glass fibre composite, 10, 15, 20, 30% by volume of matrix carbon-bead reinforced hybrid composite and a 15% by volume of matrix phenolic bead reinforced hybrid composite) were fabricated and evaluated to determine the optimum bead volume fraction for enhancing the Mode 1 interlaminar toughness of hybrid composites.
The pure epoxy glass fibre composite showed the greatest R-curve behaviour due to the large amount of fibre bridging resulting from the filament winding method of laminate fabrication. The carbon bead reinforced hybrid composite material showed an increase in Mode 1 interlaminar toughness at crack growth initiation compared to the standard epoxy laminate. The optimum volume fraction for $G_{IC}$ and $K_{IC}$ initiation values is between 15% and 20% (the 15% and 20% hybrid composites showed the highest $K_{IC}$ and $G_{IC}$ initiation values, respectively).

The carbon bead reinforced hybrid composites showed higher toughness than the phenolic bead reinforced hybrid composites at 15% bead volume fraction. This suggests that transparticle fracture and associated crack tip blunting is more effective than crack pinning in the improvement of the interlaminar toughness of hybrid composites.
Fig. 5.1 Double cantilever beam specimen
Fig. 5.2 Change of compliance due to the crack extension

Fig. 5.3 The loading and unloading curve for determining $G_{IC}$ using the area method
Fig. 5.4 (a) A plot of $C$ versus $a$ for pure epoxy glass fibre composite
Fig. 5.4 (a') A plot of $C$ versus $a$ for pure epoxy glass fibre composite (log-log scale)
Fig. 5.4(b) A plot of $C$ versus $a$ for 10% hybrid composite
Fig. 5.4 (b') A plot of $C$ versus $a$ for 10 % hybrid composite (log-log scale)
Fig. 5.4 (c) A plot of $C$ versus $a$ for 15 % hybrid composite
Fig. 5.4 (c') A plot of C versus a for 15 % hybrid composite (log-log scale)
Fig. 5.4 (d) A plot of $C$ versus $a$ for 20% hybrid composite
Fig. 5.4 (d') A plot of C versus a for 20 % hybrid composite (log-log scale)
Fig. 5.4 (e) A plot of $C$ versus $a$ for 30% hybrid composite
Fig. 5.4 (e') A plot of C versus a for 30 % hybrid composite (log-log scale)
Fig. 5.4 (f) Comparison of compliance of hybrid composite of different bead volume fraction
Fig. 5.4 (f') Comparison of compliance of hybrid composite of different bead volume fraction (log-log scale)
Fig. 5.5 Plot of interlaminar toughness, $G_{IC}$, as a function of a crack length, $a$, for DCB specimen of pure epoxy glass fibre composite.
Fig. 5.6 Plot of interlaminar toughness, $G_{IC}$, as a function of crack length, $a$, for DCB specimen of hybrid composite (10 % bead)
Fig. 5.7 Plot of interlaminar toughness, $G_{IC}$, as a function of crack length, $a$, for DCB specimen of hybrid composite (15 % bead)
Fig. 5.8 Plot of interlaminar toughness, $G_{IC}$, as a function of crack length, $a$, for DCB specimens of hybrid composite (20% bead)
Fig. 5.9 Plot of interlaminar toughness, $G_{IC}$, as a function of crack length, $a$, for DCB specimens of hybrid composite (30% bead)
Fig. 5.10 (a) Plot of interlaminar toughness, $G_{IC}$, as a function of crack length, $a$, for DCB specimens of hybrid composite laminates with bead fractions in the range 0 to 30 % by volume of matrix
Fig. 5.10 (b) Comparison of $G_{IC}$ initiation values of hybrid composites (cb 0 to cb 30) in the range 0 to 30% (carbon bead) by volume of matrix.
Fig. 5.11 Plot of fracture toughness, $K_{IC}$, as function of crack length, $a$, for DCB specimens of pure epoxy glass fibre composite
Fig. 5.12 Plot of fracture toughness, $K_{IC}$, as a function of crack length, $a$, for DCB specimen of hybrid composite (10% bead)
Fig. 5.13 Plot of fracture toughness, $K_{IC}$, as a function of crack length, $a$, for DCB specimens of hybrid composite (15 % bead)
Fig. 5.14 Plot of fracture toughness, $K_{IC}$, as a function of crack length, $a$, for DCB specimens of hybrid composite (20% bead)
Fig. 5. 15 Plot of fracture toughness, $K_{IC}$, as a function of crack length, $a$, for DCB specimens of hybrid composite (30 % bead)
Fig. 5.16 (a) Plot of fracture toughness, $K_{IC}$, as a function of crack length, $a$, for DCB specimens of hybrid composite laminates with bead fractions in the range 0 to 30% by volume of matrix.
Fig. 5.16 (b) Comparison of $K_{IC}$ initiation value of hybrid composite with bead fractions in the range 0 to 30% by volume fraction of matrix.
Fig. 5.17 SEM micrograph of the fracture surface of pure epoxy glass fibre composite

Fig. 5.18 SEM micrograph of the fracture surface of hybrid composite (15% bead by volume)
Fig. 5.19 SEM micrograph of the fracture surface of hybrid composite (30% bead by volume)
Fig. 5.20 (a) SEM micrograph of resin rich region due to the insert (pure epoxy glass fibre composite)

Fig. 5.20 (b) SEM micrograph of resin rich region due to the insert (hybrid composite)
average width: 1-2 mm

Fig. 5. Schematic diagram of resin rich area of fracture surface of DCB specimens
Fig. 5.22 SEM micrograph of fracture surface of carbon bead reinforced hybrid composite

Fig. 5.23 SEM micrograph of fracture surface of phenolic bead reinforced hybrid composite
fibre bridging behind the crack tip in Mode 1 test

Fig. 5.24 Schematic diagram of fibre bridging in composite material
Fig. 5.25 The real load-displacement record of pure epoxy glass fibre composite and hybrid composite

Fig. 5.26 Idealized load-displacement record of pure epoxy glass fibre composite and hybrid composite
Fig. 5.27 A schematic diagram of the interface between plies manufactured with a different fabrication method: (a) filament winding technique; (b) prepreg method
Fig. 5.28 (a) Composite interlaminar fracture toughness as function of neat resin $G_{IC}$ (taken from Hunston et al., 1987)

Fig. 5.28 (b) Composite interlaminar fracture toughness as function of neat resin $G_{IC}$ (taken from Bradley, 1989)
Fig. 5.29 A plot of $G_{IC}$ of hybrid composite versus $G_{IC}$ of matrix for carbon-bead filled hybrid composites (0, 10, 15, 20, 30% by volume of matrix) and one phenolic-bead filled hybrid composite (15% by volume of matrix)
Fig. 5.30 Comparison of $G_{IC}$ value of carbon and phenolic bead reinforced hybrid composite
CHAPTER 6. MODE 2 INTERLAMINAR FRACTURE BEHAVIOUR OF HYBRID COMPOSITE MATERIAL FABRICATED WITH A TOUGHENED MATRIX
Chapter 6. Mode 2 interlaminar fracture behaviour of hybrid composite material fabricated with a toughened matrix

6.1 Introduction

6.2 Analysis of end notch flexure (ENF) test data

6.3 Experimental results

6.4 Fractographic analysis and fracture mechanisms
   6.4.1 Fractographic analysis
   6.4.2 Fracture mechanisms

6.5 Discussion

6.6 Conclusions
6.1 Introduction

In many situations, initiation and growth of delaminations is caused by interlaminar normal stresses. Historically, much attention has been given to Mode 1 interlaminar fracture toughness. However, interlaminar shear stresses may also cause delamination (Mode 2) (see e.g. early work by Pipes et al., 1973). Attention is now being directed increasingly towards understanding the relationship between interlaminar shear Mode 2 and damage tolerance.

To evaluate Mode 2 interlaminar fracture toughness, Russell and Street (1985) introduced the ENF (end notch flexure) specimen. The ENF specimen is now the most widely accepted, and frequently used, test method and is viewed as a potential standard (Davies, 1989).

In this chapter, the interlaminar Mode 2 fracture toughness of hybrid composites has been evaluated using the ENF specimen. First, the data analysis method for the ENF specimen is presented. Test results and fractographic analysis then follow.
6.2 Analysis of end notch flexure (ENF) test data

The derivation of the strain energy release rate (G_{IIC}) for the ENF specimen is, like the DCB specimen analysis, based on the change in compliance with crack extension. The compliance of the ENF specimen (Fig. 6.1) is defined as the displacement, \( \delta \), at the central loading pin divided by the applied load, \( P \). The displacement may be calculated from (Fig. 6.2):

\[
\delta = \frac{\Delta_{AB} + \Delta_{BC} + \Delta_{CD}}{2}
\]  
(1)

From beam theory, the compliance (\( C = \delta/P \)) of the specimen can be expressed as (Russell and Street, 1985, Carlsson et al., 1986):

\[
C_{ENF} = \frac{2L^3 + 3a^3}{8E_1Wh^3}
\]  
(2)

From equation (5) of chapter 5

\[
G = \frac{P^2}{2W} \frac{dC}{da}
\]

The energy release rate of ENF specimen (\( G_{IIC} \)) can then be
obtained as:

\[ G_{IIc} = \frac{9a^2P^2}{16E_1W^2h^3} = \frac{9P^2Ca^2}{2W(2L^3+3a^3)} \]

\[ = \frac{9P\delta a^2}{2W(2L^3+3a^3)} \]  \hspace{1cm} (3)

6.3 Experimental results

A typical load-displacement trace in an ENF test is shown in Fig. 6.3. The load increases linearly until subcritical crack initiation (point A in Fig. 6.3) after which the load-displacement response is non-linear (from point A to B in Fig. 6.3). In the transparent pure epoxy glass fibre composite, subcritical crack initiation could be observed directly by looking closely at the precrack front. Unstable crack growth took place after the maximum load (point B in Fig. 6.3). Since crack growth is unstable, only one value of \( G_{IIc} \) can be obtained from each specimen.

Results of ENF tests (for three different bead volume fractions of hybrid composite and for the pure epoxy glass fibre composite) are shown individually in
Figs. 6.4-6.7 and the mean values are compared in Fig. 6.8. Fig. 6.8 shows that there is a peak toughness at a bead volume fraction of around 15%. There is a decrease thereafter and at higher volume fractions the toughness is less than that of the laminate based on the unmodified epoxy.

An interesting feature of these results is that the Mode 2 interlaminar fracture toughness \( (G_{IIc}) \) is high compared to the Mode 1 interlaminar fracture toughness as shown in Table 6.1 and Fig. 6.9. Bradley (1989) also observed similar behaviour in his study. These results were attributed to the unique nature of the fracture process of the Mode 2 test: namely the formation of sigmoidal shaped microcracks over a considerable distance ahead of the crack tip, causing significant load redistribution.

In Fig. 6.10, it is shown that the ratio \( (G_{IIc}/G_{IC}) \) of Mode 2 to 1 fracture toughness decreases with increasing bead volume fraction. It has been reported that the ratio of \( G_{IIc} \) to \( G_{IC} \) of brittle matrix composites is generally higher than that of ductile matrix composites and that the ratio \( (G_{IIc}/G_{IC}) \) of very tough matrix composites approaches unity (Bradley, 1989). The data of Fig. 6.10 follow this general trend; they show a reducing \( G_{IIc}/G_{IC} \) ratio with increasing bead,
consistent with tougher behaviour.

6.4 Fractographic analysis and fracture mechanisms

6.4.1 Fractographic analysis

SEM photographs of the fracture surfaces of ENF specimens are shown in Figs. 6.11 - 6.14. Compared with the DCB specimens there is little fibre bridging in the ENF specimens. This can be seen by comparing Fig. 6.11 (ENF) with Fig. 5.17 (DCB).

In fractographs of pure epoxy glass fibre composite (Fig. 6.11) many uneven looking facets (called hackles, Bradley, 1989) can be seen. The distinctive nature of these features decreases with increasing bead volume fraction in the matrix as shown in Figs. 6.11 - 6.14.

6.4.2 Fracture mechanisms

In Fig. 6.11 (a), the fracture surface of both Mode 1 and Mode 2 crack growth is seen simultaneously. The contrast between Mode 1 and Mode 2 fracture surfaces is due to different fracture mechanisms. Bradley (1989) has described in detail the fracture mechanisms of Mode 1
and 2 interlaminar crack growth using "in situ" observations in the SEM. Fig. 6.15 shows two SEM photographs reproduced from his work. Mode 1 failure occurs with the development of a small deformation zone ahead of the crack tip, as evidenced by the considerable microcracking in Fig 6.15. On the other hand, Mode 2 delamination crack growth begins with the formation of a series of sigmoidal shaped matrix microcracks ahead of the crack tip with an orientation of approximately 45° to the fibre direction (which for Mode 2 loading is the principal tensile stress plane).

Similar features have been observed in this work. The fracture surfaces of Mode 1 DCB specimens (chapter 5) suggest that the crack growth in Mode 1 occurs principally along the resin/fibre interface. By contrast, discontinuous crack growth by microcrack coalescence leaves the Mode 2 delamination fracture surface with many "hackles", as shown in the fractographs of the hybrid composites (Figs. 6.11 - 14).

6.5 Discussion

With regard to the Mode 2 fracture toughness data (Fig. 6.8), it can be seen that at low bead volume fractions an increase in toughness is obtained while at
high volume fractions (20%) there is a fairly dramatic drop-off. It seems that this decrease is associated with a change in the Mode 2 interlaminar fracture mechanism of the hybrid composite at high bead volume fractions.

As mentioned previously (section 6.4.2), the reason why the Mode 2 interlaminar fracture toughness of a brittle matrix composite is high compared to the Mode 1 toughness is due to the fracture mechanism of the Mode 2 crack propagation (namely sigmoidal shaped microcracks which cause hackles). In Fig. 6.14, the fracture surface of the high bead volume fraction hybrid composite (20%) is shown. In this SEM photograph of the fracture surface, two different aspects of fracture in this material, compared to the materials with lower bead volume fractions, can be seen.

(a) hackles were not present in the fracture surface of the 20% hybrid composite;

(b) the amount of bare debonded fibres seen in the fracture surface of the 20% hybrid composite is much less than in the other materials.

From these differences, it is clear that the 20% hybrid composite has a somewhat different fracture mechanism from the hybrid composites of lower bead volume...
fractions. The differences can be partly explained by the absence of hackles which suggests that the characteristic sigmoidal shaped microcracking did not take place due to the high bead volume fraction in the matrix. This is presumably related to the relatively thick bead filled interlayer, which is present at the high bead volume fraction of 20%. It is likely that the thick interlayer fails in shear comparatively easily because it is not constrained effectively by the fibre and hence the sigmoidal shaped hackles are not formed.

6.6 Conclusion

The Mode 2 interlaminar fracture toughness of ENF specimens (machined from the same composite panels as the DCB specimens) shows high toughness compared to the Mode 1 interlaminar fracture toughness. This is believed to be due to a different fracture mechanism, related to the formation of sigmoidal shaped microcracks as evidenced by hackles in the fracture surface.

Carbon bead reinforced hybrid composites show an optimum Mode 2 interlaminar fracture toughness at a bead volume fraction of about 15%. However, at a higher bead volume fraction (20%) a sharp drop occurs. This is suggested to be a consequence of a different fracture
mechanism occurring within a thicker bead-filled interlayer.
### Table 6.1 Comparison of $G_{IC}$ and $G_{IIC}$ values of hybrid composites

<table>
<thead>
<tr>
<th>$V_f$</th>
<th>$G_{IC}$ (J/m²)</th>
<th>$G_{IIC}$ (J/m²)</th>
<th>$G_{IIC} / G_{IC}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>204</td>
<td>1560</td>
<td>7.7</td>
</tr>
<tr>
<td>10</td>
<td>296</td>
<td>1930</td>
<td>6.5</td>
</tr>
<tr>
<td>15</td>
<td>342</td>
<td>1970</td>
<td>5.8</td>
</tr>
<tr>
<td>20</td>
<td>384</td>
<td>1210</td>
<td>3.2</td>
</tr>
</tbody>
</table>
Fig. 6.1 End notch flexure (ENF) specimen

Definition of vertical displacements for the ENF specimen.

Fig. 6.2 Method used in calculation of the displacement, $\delta$, of the loading point C of the ENF specimen (Displacements are calculated relative to point C.)
Fig. 6.3 Typical load - displacement record of an ENF test
Fig. 6.4 $G_{IIc}$ values of pure epoxy glass fibre composite.
Fig. 6.5 $G_{IIc}$ values of hybrid composite (10 % bead)
Fig. 6.6 $G_{IIIC}$ values of hybrid composite (15% bead)
Fig. 6.7 $G_{IIc}$ values of hybrid composite (20% bead)
Fig. 6.8 Comparison of $G_{IIc}$ values of hybrid composite
Fig. 6.9 Comparison of $G_{IC}$ and $G_{IIC}$ values of hybrid composites
Fig. 6.10 Ratio of $G_{IC}$ to $G_{IIC}$ values for hybrid composites (carbon beads)
Fig. 6.11 (a) Fracture surface of ENF specimen of pure epoxy glass fibre composite in SEM showing differences between Mode 1 right side and Mode 2 left side crack path

Fig. 6.11 (b) Fracture surface of Mode 2 ENF specimen of pure epoxy glass fibre composite
Fig. 6.12 Fracture surface of ENF specimen of hybrid composite (10% bead)

Fig. 6.13 Fracture surface of ENF specimen of hybrid composite (15% bead)
Fig. 6.14 Fracture surface of ENF specimen of hybrid composite (20% bead)
In situ observation in SEM of mode-I (top, 1500x) and mode-II (bottom, 600x) delamination in AS4/3501-6.

Fig. 6.15 Comparison of Mode 1 with Mode 2 delamination using in situ observation (taken from Bradley, 1989)
CHAPTER 7. THE APPLICATION OF ORTHOTROPIC FRACTURE MECHANICS TO HYBRID COMPOSITE MATERIALS
Chapter 7. The application of orthotropic fracture mechanics to hybrid composite materials

7.1 Introduction

7.2 Application of fracture mechanics to composite materials
  7.2.1 The orthotropic fracture model
  7.2.2 Limitations

7.3 Input data for the orthotropic fracture model
  7.3.1 Measured fracture parameters
  7.3.2 Determination of elastic constants

7.4 Data analysis and discussion
  7.4.1 Deviation of $G_{IC}$ and $K_{IC}$ values
  7.4.2 Calculation of orthotropic $K_{IC}$ values
  7.4.3 Relation between measured $G_{IC}$ values and isotropic $K_{IC}$ values

7.5 Conclusion
7. The application of orthotropic fracture mechanics to hybrid composite materials

7.1 Introduction

Fracture mechanics is now widely accepted, and has frequently been used, to characterise the toughness of engineering materials which are isotropic and homogeneous on the macroscopic scale, for example metallic alloys. With the development of high performance composites, the application of fracture mechanics to composite materials has received attention. The fundamental issue, whether the complexity of the heterogeneity and anisotropy of composites may preclude practical application of fracture mechanics, has been introduced by Sih (1979) and others.

A popular approach for the characterization of the delamination crack growth resistance of composite materials has been the application of linear elastic fracture mechanics, using the critical energy release rate parameter, $G_{IC}$. On the other hand, another important parameter in fracture mechanics, namely the critical stress intensity factor or fracture toughness, $K_{IC}$, is also used frequently. Both parameters are used to evaluate fracture resistance in engineering materials. In linear elastic fracture mechanics for homogeneous and isotropic materials, the strain energy release rate, $G$, and the stress intensity factor, $K$, can be related.
Application of fracture mechanics to delamination crack growth in unidirectional composites with the crack front moving parallel to the fibre direction seems to be possible. It is generally the case that interlaminar crack growth is self-similar and crack surfaces are planar. Thus, many researchers believe that the strain energy release rate, $G$, and the stress intensity factor, $K$, could be related in composite material much as they are in metals or homogeneous materials. This means that if $K$ or $G$ is known, the other parameter can be calculated. However the precise relationship between the energy release rate, $G$, and stress intensity factor, $K$, for heterogeneous and anisotropic material such as a fibre-reinforced composite material is not known and cannot be easily obtained analytically (Sih, 1979). However, composite materials can be treated generally as macroscopically orthotropic, which allows some simplification.

Sih and Liebowitz (1968) formulated the orthotropic fracture model for homogeneous and anisotropic material in which the direction of crack propagation is co-linear with the original crack. Sih (1979) and Newas (1988) have investigated the possibility of using an orthotropic fracture model for unidirectional composite material using compact tension and DCB specimens.
In this chapter, data from DCB specimens of three different composite materials (pure epoxy glass fibre, 15% and 30% hybrid composite, carbon beads) have been used to investigate the relationship between $G$ and $K$.

7.2 Application of fracture mechanics to composite materials

7.2.1 The orthotropic fracture model

In examining the stability of cracks, it is customary to determine the stress condition around the crack tip so that the relationship between the elastic stresses and the input energy rates in crack extension may be established. Sih, Paris and Irwin (1965) have shown that the basic concepts of isotropic fracture mechanics can be extended to the anisotropic case. They reported that if the applied loads on the crack surface are self-equilibrating, the stress intensity factor of isotropic and anisotropic materials are theoretically identical. With careful interpretation, the analysis obtained for isotropic crack systems may be transferred to crack systems in anisotropic materials.

The orthotropic fracture model in which the direction of crack propagation is coplanar with the original crack was formulated by Sih et al. (1965, 1968).
The stress field in the vicinity of a Mode 1 crack tip (see Fig.2.3) is expressed using complex functions as (Sih and Liebowitz, 1968):

\[
\sigma_x = \frac{K_I}{(2\pi r)^{1/2}} \text{Re} \left[ -\frac{s_1 s_2}{s_1 - s_2} \left( \frac{s_2}{(\cos \theta + s_2 \sin \theta)^{1/2}} s_1 \frac{s_1}{(\cos \theta + s_1 \sin \theta)^{1/2}} \right) \right] \quad (1)
\]

\[
\sigma_y = \frac{K_I}{(2\pi r)^{1/2}} \text{Re} \left[ \frac{1}{s_1 - s_2} \left( \frac{s_1}{(\cos \theta + s_2 \sin \theta)^{1/2}} s_2 \frac{s_2}{(\cos \theta + s_1 \sin \theta)^{1/2}} \right) \right] \quad (2)
\]

where \( s_1, s_2 \) are the roots determined from the characteristic equation (Sih and Liebowitz, 1968). The displacements can be expressed as:

\[
u_x = K_I \sqrt{\frac{r}{2\pi}} \text{Re} \left[ \frac{1}{s_1 - s_2} \left( s_1 p_2 (\cos \theta + s_2 \sin \theta)^{1/2} - s_2 p_1 (\cos \theta + s_1 \sin \theta)^{1/2} \right) \right] \quad (3)
\]
\[ u_y = K_I \sqrt{\frac{r}{2\pi}} \text{Re} \left[ \frac{1}{s_1 - s_2} \left( s_1 q_2 (\cos \theta + s_2 \sin \theta) \right)^{1/2} \right. \]

\[ - s_2 q_1 (\cos \theta + s_1 \sin \theta) \left. \right)^{1/2} \] \quad (4)

where \( p_1 = a_{11} s_1^2 + a_{12} - a_{16} s_1 \), \( p_2 = a_{11} s_2^2 + a_{12} + a_{16} s_2 \)

\[ q_1 = (a_{12} s_1^2 + a_{22} - a_{26} s_1) / s_1 \quad \text{and} \quad q_2 = (a_{12} s_2^2 + a_{22} - a_{26} s_2) / s_2 \]

and \( a_{11} = 1/E_{11} \), \( a_{22} = 1/E_{22} \), \( a_{12} = - \nu_{12}/E_{11} \), \( a_{23} = - \nu_{23}/E_{22} \), \( a_{66} = 1/G_{12} \)

The work associated with the crack is then:

\[ W = \frac{1}{2} \int_{-a}^{a} \sigma_y u_y dx \]

\[ = \frac{\pi a^2 p^2}{2} a_{22} \text{Re} \left[ i \left( \frac{s_1 + s_2}{s_1 s_2} \right) \right] \quad (5) \]

Taking the derivative of \( W \) with respect to the crack length \( a \) gives

\[ G = \frac{\partial W}{\partial a} = \pi K_I^2 a_{22} \text{Re} \left[ i \left( \frac{s_1 + s_2}{s_1 s_2} \right) \right] \quad (6) \]

From further mathematical manipulation, the
interrelationship between the energy release rate, $G_{IC}$, and the stress intensity factor, $K_{IC}$, for the plain strain condition can be expressed as:

$$G_{IC} = K_{IC}^2 \left( \frac{b_{11}b_{22}}{2} \right)^{1/2} \left[ \left( \frac{b_{22}}{b_{11}} \right)^{1/2} + \frac{2b_{12} + b_{66}}{2b_{11}} \right]^{1/2}$$  \hspace{1cm} (7)

Where the elastic coefficients $b_{ij}$ are related to the principal material constants as follows:

$$b_{11} = a_{11} - a_{12}^2 / a_{22} \ ; \ b_{22} = a_{22} - a_{23}^2 / a_{22} \ ;$$
$$b_{12} = a_{12} - (a_{12} a_{23}) / a_{22} \ ; \ b_{66} = a_{66}$$

7.2.2 Limitations

The fracture model of section 7.2.1 is for homogeneous and anisotropic material. Composite materials can be treated as macroscopically homogeneous but, strictly speaking, fibre reinforced composite materials are heterogeneous locally. A more sophisticated model, which can show the precise relationship between $G$ and $K$ for a heterogeneous system such as a fibre reinforced hybrid composite, is not available. It can be said that such a model could not be obtained easily analytically.
The classical concept of fracture toughness is restricted to a single phase material containing a single dominant crack. Equation (7) is established with the assumption that the crack has to coincide with one of the principal axes of material symmetry and that the crack propagates co-linearly. In composite materials, this precondition can be violated often by an isolated and deflected microcrack in front of the main crack.

Another precondition of equation (7) is that the fracture surfaces of material should have a smooth appearance (e.g. the fracture surface of compact tension specimen of pure epoxy) as opposed to the somewhat fibrous, brushy appearance (due to the fibre bridging) which is often encountered in the fracture of fibre reinforced composites.

With regard to the strain energy release rate, a $G_{IC}$ value obtained from the compliance method is valid for all elastic materials regardless of whether the specimen is isotropic or anisotropic, homogeneous or heterogeneous. To evaluate $K_{IC}$ accurately, we need to know the correct stress state around the crack tip. The stress state at the crack tip in composite materials is rather complex due to the crack tip geometry, fibre debonding, pullout and breakage, and so on. Thus, it can be said that in a DCB specimen the energy release rate,
7.3 Input data for the orthotropic fracture model

7.3.1 Measured fracture parameters

In this chapter, we attempt to relate four different toughness related parameters. \( G_{IC\text{-me}} \) and \( K_{IC\text{-me}} \) are the fracture parameters measured as described in chapter 5. The \( G_{IC} \) value was obtained based on the compliance method with load, \( P \), crack length, \( a \), and displacement, \( \delta \), measured directly from the load-displacement record. The \( K_{IC} \) values of chapter 5 were obtained based on an equation which was established originally for an isotropic and homogeneous material. Two additional parameters will be introduced in this chapter, \( G_{IC\text{-ca}} \) and \( K_{IC\text{-ca}} \), (section 7.4.1).

7.3.2 Determination of elastic constants

Table 7.1 shows the elastic properties of the pure epoxy glass fibre composite and two different bead volume fraction hybrid composites (carbon bead). These data were determined from a combination of direct measurement and the open literature. Fig.7.1 (a) shows the variations of \( E_{11} \), \( E_{22} \) and \( G_{12} \) with fibre volume
fraction for epoxy-glass fibre composites (Sih, 1979). Fig. 7.1 (b) shows $v_{12}$ and $v_{23}$ variations with fibre volume fraction (Sih, 1979). In Fig. 7.2, data from the present study for $E_{11}$ and $E_{22}$ are compared with Sih's data and good agreement is shown. On the basis of this comparison, $G_{12}$ and Poisson's ratios (which were not measured in the present study) are taken from Fig. 7.1. This may introduce some error. However, the basic purpose of this chapter is not to evaluate absolute values but to discuss the general trends observed in the relationship between $G_{IC}$ and $K_{IC}$ values for hybrid composites. In any case the calculations carried out in the following section are most sensitive to the $E_{11}$ and $E_{22}$ values. Thus, it seems that these elastic constant data are acceptable.

7.4 Data analysis and discussion

7.4.1 Deviation of $G_{IC}$ and $K_{IC}$ values

$G_{IC-me}$ is the value determined from direct measurement. We now introduce another parameter, $G_{IC-ca}$, which is a value calculated from equation (7) using the $K_{IC-me}$ value. A fourth parameter, the $K_{IC-ca}$ value was determined from the $G_{IC-me}$ value in the same manner. The $G_{IC}$ and $K_{IC}$ deviations are calculated from the following relationships (Sih, 1979).
\[ G_{IC} \text{ deviation (\%)} = \left( \frac{G_{IC-me} - G_{IC-ca}}{G_{IC-me}} \right) \times 100 \]

\[ K_{IC} \text{ deviation (\%)} = \left( \frac{K_{IC-me} - K_{IC-ca}}{K_{IC-me}} \right) \times 100 \]

Fig. 7.3 (a) shows the extent of deviation of the \( G_{IC} \) values. The calculated \( G_{IC-ca} \) value is much higher than the measured value \( G_{IC-me} \) and the deviation percentage is over 270\%.

Fig.7.3 (b) shows the extent of deviation of \( K_{IC} \) value. The calculated \( K_{IC-ca} \) value is much lower than the measured \( K_{IC-me} \) value and the resulting deviation is around 50\%.

Table 7.2 shows results by Sih (1979) and Newas (1988) using CT (machined from E glass - epoxy and carbon fibre - epoxy composite panels) and DCB (machined from graphite-PEEK, APC-2, panel) specimens respectively. In Table 7.2(a) which shows the data of Sih, relatively good agreement between measured and calculated values is shown (i.e. low deviation value), especially for glass fibre composites of 50 and 60\% fibre volume fraction. On the other hand in Table 7.2 (b), which shows the data from Newas, very poor agreement and high percentage deviation is found (\( G_{IC} \) deviations over 1400\%).

The fundamental reason for this discrepancy is as
follows:

(a) Sih (1979) measured both $G_{IC}$ and $K_{IC}$ using the compact tension specimen in which the anisotropic stress intensity factor can be closely approximated by its isotropic counterpart (Bowie, 1973), while Newas (1988) and the present work used DCB specimens and assumed the isotropic formula to determine $K_{IC}$. Furthermore, Newas used a PEEK matrix which shows significant plastic deformation.

(b) It has been said that the stress intensity factor, $K_{IC}$, is more well defined in the compact tension specimen than the DCB specimen. Thus, the interlaminar crack resistance of DCB specimen is generally expressed in terms of $G_{IC}$ (Sela and Ishai, 1989). These points are discussed further in the following pages.

From the two previous studies and the present work, we can make the following observations.

(a) In all three studies, it is found that the measured $K_{IC-me}$ value is higher than the calculated $K_{IC-ca}$ value.

(b) The result of the compact tension specimens of Sih (1979) shows much better agreement than that of DCB specimens.
To analyze and find out the major error source of equation (7), it is necessary to check the input data used in each study. According to orthotropic linear elastic fracture mechanics theory, the ratio $G_{IC}E_0/K_{IC}^2$ in equation (7) should be identical to unity where $E_0$ is effective modulus, i.e.

$$\frac{1}{E_0} = \left( \frac{b_{11} b_{22}}{2} \right)^{1/2} \left( \left( \frac{b_{22}}{b_{11}} \right)^{1/2} + \frac{2b_{12} + b_{66}}{2b_{11}} \right)^{1/2}$$  \hspace{1cm} (8)

The value of $G_{IC-me}E_0 / K_{IC-me}^2$ for the pure epoxy-glass fibre, the 15 % hybrid and the 30 % hybrid composites are 0.311, 0.268 and 0.296 respectively. All of these value are far from unity. This means that either there is some error in the values of $G_{IC-me}$, $E_0$ or $K_{IC-me}$ or that the assumption of LEFM is in error.

Accepting for the moment the validity of LEFM, we consider the terms in the ratio $G_{IC}E_0/K_{IC}^2$. $E_0$ is determined without any limitation or preconditions and all the elastic constants used are reliable. Thus, we need to check carefully the $G_{IC-me}$ and $K_{IC-me}$ values.

The compliance method from which the $G_{IC-me}$ values were determined is valid for all elastic materials regardless of whether the specimen is isotropic or
anisotropic, homogeneous or heterogeneous. Hence the
\( G_{\text{IC-me}} \) value obtained is acceptable.

On the other hand, the \( K_{\text{IC-me}} \) value was obtained
from equation (9), which was reported to be the exact
solution for a DCB specimen of linear elastic homogenous
and isotropic material by Foote and Buchwald (1985):

\[
K_{\text{IC}} = \frac{P}{B^2h} \left[ \sqrt{12} \left( \frac{a}{h} + 0.673 \right) + \left( \frac{\sqrt{2h}}{\pi a} \right) \right]
- [0.815(a/h)^{0.619} + 0.429]^{-1} \tag{9}
\]

Based on the compliance method (and assuming "\( K^2 = E'G' \)"
the alternative homogeneous isotropic expression can be
derived (Broek, 1986) which is

\[
K_{\text{IC}} = 2\sqrt{3} \frac{Pa}{Bh^{3/2}} \tag{10}
\]

Plotting this expression and equation (9) together shows
that they are very close (Fig. 7.4).

To summarize, if we accept that the composite
material can be regarded as macroscopically orthotropic
so that LEFM may be applied, we need to concentrate on a
careful check of the fracture toughness $K_{IC-me}$ obtained from equation (9). As long as $E_0$ and $G_{IC-me}$ are acceptable, for $G_{IC-me} E_0/K_{IC-me}^2$ to approach unity, the $K_{IC-me}$ value should be decreased.

7.4.2 Calculation of orthotropic $K_{IC}$ values

In chapter 5 and section 7.4.1, the isotropic stress intensity factor $K_{IC-me}$, obtained from equation (9), was used. The true orthotropic fracture toughness values may be found from these values, however, as follows. Equation (7) establishes the relation for an orthotropic material i.e. $G_{IC-ortho} = K_{IC-ortho}^2/E_0$ (where $E_0 = f(b_{11}, b_{12}$ etc)). The equivalent isotropic relation, which equation (9) should satisfy is $G_{IC-isol} = K_{IC-isol}^2/E_{11}$ (where $E_{11}$ is the longitudinal modulus of the DCB specimen). Now since the measured values of $G_{IC}$ are independent of the orthotropic or isotropic nature of the material, we may equate $G_{IC-ortho} = G_{IC-isol}$ to obtain a relationship between the measured fracture toughness value and the true orthotropic value, i.e.

$$K_{IC-ortho} = K_{IC-isol} \cdot C \quad (11)$$

where $C = (E_0/E_{11})^{1/2}$ and $K_{IC-isol}$ is the measured toughness, i.e. $K_{IC-me}$. The values of the correction
factor C for DCB specimens of pure epoxy/glass fibre, 15% and 30% hybrid composite material in this study were 0.53, 0.51 and 0.50 respectively. Fig. 7.5(a), (b) and (c) shows the orthotropic fracture toughness, calculated from equation (11) and the isotropic (measured) value, $K_{IC-m_e}$.

Ye (1992) carried out a similar analysis to that described here and reported correction factors for T300/634DDS carbon fibre/epoxy composite as low as 0.277. This difference is a consequence of the different material elastic constants of the carbon system of Ye to the glass systems of the present study.

7.4.3 Relation between measured $G_{IC-m_e}$ values and isotropic $K_{IC-m_e}$ values

In section 7.4.2, it is suggested that the isotropic fracture toughness value, $K_{IC-m_e}$, obtained using equation (9) can be corrected to an equivalent orthotropic value by multiplying this value by $(E_0/E_{11})^{1/2}$. We can now define a parameter $I'$ which relates the experimental $G_{IC-m_e}$ values, the longitudinal modulus, $E_{11}$, and the $K_{IC-m_e}$ values (obtained using equation (9) or (10)) such that

293
It is expected that $I'$ should have a constant value of unity and this is found to be so for most crack lengths plotted in Figs 7.6(a), (b) and (c).

In Fig. 7.6 (a), quite a large deviation of $I'$ (up to 30%) is shown at an early stage of crack propagation. Of the three figures, Fig. 7.6(b), for 15% hybrid composite, shows the closest approximation to unity. The general trend of the $I'$ value will be influenced strongly by the slope of the compliance-crack length plot. The reason why the 15% hybrid composite, Fig. 7.6(b), shows the most constant value of $I'$ is that the slope of the compliance plot for the 15% hybrid composite is closest to the ideal slope, namely three, as shown in Fig. 5.3(c'). The importance of this can be seen theoretically by combining equations (10) and (9) in chapter 5 to give the relation:

$$I' = \frac{G_{IC} E_{11}}{K_{IC}^{2}} = \text{Const.} \frac{\text{compliance}(c)}{a^3}$$

In this equation, crack length, $a$, is well defined. Thus the trend of the $I'$ values depends highly on the measured
value of the compliance. Of course, in composite materials, the stiffness of specimens can be different locally at each crack length due to material heterogeneity. Thus, a real variation in the compliance of a composite material can give a local deviation from the average slope at each crack length.

7.5 Conclusion

In this chapter, a quantitative discussion of the fracture data of chapter 5 has been presented, based on fracture mechanics principles.

According to orthotropic fracture mechanics theory, the $K_{IC}$ values determined using expressions derived for isotropic materials are overestimates, and the true anisotropic $K_{IC}$ values can be obtained using the correction factor $C$, where $C = (E_0/E_{11})^{1/2}$.

It also has been shown that the ratio $G_{IC}E_{11}/K_{IC}^2$ should be equal to unity, theoretically. However, in practice the value approximates to unity. It is suggested that this is due to a combination of experimental measurement errors and real variations in the local stiffness of the material as a result of heterogeneity.
<table>
<thead>
<tr>
<th>elastic constant</th>
<th>E₁₁ (GPa)</th>
<th>E₂₂ (GPa)</th>
<th>G₁₂ (GPa)</th>
<th>ν₁₂</th>
<th>ν₂₃</th>
<th>Vᵢ</th>
</tr>
</thead>
<tbody>
<tr>
<td>pure epoxy</td>
<td>51.5</td>
<td>11.7</td>
<td>5.2</td>
<td>0.25</td>
<td>0.28</td>
<td>66</td>
</tr>
<tr>
<td>glass fibre</td>
<td>42.3</td>
<td>9.0</td>
<td>4.2</td>
<td>0.27</td>
<td>0.29</td>
<td>54</td>
</tr>
<tr>
<td>15 % hybrid</td>
<td>36.2</td>
<td>7.4</td>
<td>3.6</td>
<td>0.29</td>
<td>0.31</td>
<td>46</td>
</tr>
<tr>
<td>30 % hybrid</td>
<td>36.2</td>
<td>7.4</td>
<td>3.6</td>
<td>0.29</td>
<td>0.31</td>
<td>46</td>
</tr>
</tbody>
</table>

Table 7.1 Elastic constants of composite materials used in this study
<table>
<thead>
<tr>
<th>fibre volume (%)</th>
<th>calculated value</th>
<th>measured value</th>
<th>deviation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K_{IC}^{(2)}$</td>
<td>$G_{IC}^{(1)}$</td>
<td>$K_{IC}^{(1)}$</td>
</tr>
<tr>
<td>E glass (a)</td>
<td>lb/in$^{3/2}$</td>
<td>lb/in</td>
<td>lb/in</td>
</tr>
<tr>
<td>0</td>
<td>380</td>
<td>0.75</td>
<td>373</td>
</tr>
<tr>
<td>10</td>
<td>865</td>
<td>4.05</td>
<td>1020</td>
</tr>
<tr>
<td>20</td>
<td>800</td>
<td>3.63</td>
<td>965</td>
</tr>
<tr>
<td>50</td>
<td>1090</td>
<td>2.32</td>
<td>1090</td>
</tr>
<tr>
<td>60</td>
<td>1060</td>
<td>1.97</td>
<td>1100</td>
</tr>
<tr>
<td>graphite (b)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>380</td>
<td>0.75</td>
<td>373</td>
</tr>
<tr>
<td>50A</td>
<td>600</td>
<td>1.3↑</td>
<td>765</td>
</tr>
<tr>
<td>50B</td>
<td>322</td>
<td>0.40</td>
<td>413</td>
</tr>
<tr>
<td>APC-2 (b)</td>
<td>30000</td>
<td>4.83</td>
<td>1900</td>
</tr>
</tbody>
</table>

Table 7.2 Fracture toughness data showing percentage deviation. (a) taken from Sih, 1979; (b) taken from Newas, 1988
Fig. 7.1(a) Plot of $E_{11}$ and $E_{22}$ versus fibre volume fraction (after Sih, 1979)

Fig. 7.1(b) Plot of $v_{12}$ and $v_{23}$ versus fibre volume fraction (after Sih, 1979)
Fig. 7.2 Comparison of data from the present study with that of Sih (E_{11} and E_{22})
mean deviation of $GIC$
- pure epoxy-glass: 278% 
- hybrid (15%): 298% 
- hybrid (30%): 274%

Fig. 7.3(a) The extent of $GIC$ deviation

mean deviation of $KIC$
- pure epoxy-glass fibre: 49% 
- hybrid (15%): 50% 
- hybrid (30%): 48%

Fig. 7.3(b) The extent of $KIC$ deviation
Fig. 7.4 (a) Comparison of $K_{IC}$ values obtained from different equations for the glass/pure epoxy composite.
Fig. 7.4 (b) Comparison of $K_{IC}$ values obtained from different equations for the 15% hybrid composite
Fig. 7.4 (c) Comparison of $K_{IC}$ values obtained from different equations for the 30% hybrid composite

- equation (9) + equation (10)
Fig. 7.5(a) Comparison of $K_{IC-ca}$ (i.e. $K_{IC-orth}$) value with measured $K_{IC-me}$ value for pure epoxy glass fibre composite
Fig. 7.5(b) Comparison of $K_{IC-ca}$ (i.e. $K_{IC-orth}$) value with measured $K_{IC-me}$ value for 15% hybrid composite
Fig. 7.5(c) Comparison of $K_{IC-ca}$ (i.e. $K_{IC-orth}$) value with measured $K_{IC-me}$ value for 30 % hybrid composite
Fig. 7.6 (a) A plot of $I'$ values as a function of crack length for pure epoxy/glass fibre composite.
Fig. 7.6 (b) A plot of $I'$ values as a function of crack length for 15% hybrid composite
Fig. 7.6 (c) A plot of $I'$ values as a function of crack length for 30% hybrid composite.
Fig. 7.6 (d) Comparison of $I'$ values of three different bead volume fraction hybrid composites.
CHAPTER 8. CONCLUSIONS AND FURTHER WORK
8 CONCLUSIONS AND FURTHER WORK

8.1 Conclusions

In this study, the fracture behaviour of particle filled epoxies containing seven different filler materials has been evaluated using compact tension specimens. Based on the results obtained, one filler material (S3: carbon bead) was used to fabricate hybrid composite laminates consisting of continuous glass fibres in a bead-reinforced epoxy matrix. The conclusions which may be drawn from the work are summarised below.

(a) For the particle-filled epoxies:

- Fractography has shown that the particle-filled epoxies display a range of toughening mechanisms namely: crack pinning (in systems S4, S6, S7), localized plastic deformation causing crack tip blunting (in systems S1, S3, S5) and transparticle fracture (system S3).

- Load-displacement records from the compact tension tests may be correlated with fractographic results.

- Two new categories of fracture are proposed as a result of this work (in addition to the categories proposed by Kinloch and co-workers) namely quasi-ductile stable and quasi-ductile unstable crack growth behaviour.
- The fracture toughness shown by the bead-filled systems at a bead volume fraction of 30% is between 10 and 50% greater than that for the neat epoxy.

- The relation between the fracture toughness and volume fraction of bead type is approximately linear (this was shown for bead type S7). The carbon bead filled epoxy system (S3) also shows a more or less linear increase in toughness with bead volume fraction up to 40%. After this there was a drop attributed to processing problems.

- Hybridization, that is a mixture of more than one bead type, can give an additional enhancement of toughness compared to using one bead on its own.

(b) For the hybrid composite laminates

Based on the results of fracture toughness tests of bead-filled epoxies, six different composites (pure epoxy glass fibre composite, 10, 15, 20, 30% carbon bead reinforced hybrid composite and 15% phenolic bead reinforced hybrid composite) were fabricated. The Mode 1 and Mode 2 interlaminar toughness of the hybrid composites were evaluated and the following results were obtained:

- The carbon bead reinforced hybrid composite material shows an increase in Mode 1 interlaminar toughness at crack growth onset compared to the standard epoxy laminate. The
optimum bead volume fraction for $G_{IC}$ and $K_{IC}$ initiation values is between 15 and 20% by volume of the matrix. The 15 and 20% hybrid composites show the highest $K_{IC}$ and $G_{IC}$ initiation values, an increase of about 20% and 90% respectively, compared to the laminate based on unmodified epoxy.

- The pure epoxy glass fibre composite shows the most severe R-curve behaviour due to the large amount of fibre bridging resulting from the filament winding method of laminate fabrication.

- The carbon bead reinforced hybrid composites show higher interlaminar toughness than the phenolic bead reinforced hybrid composite at 15% bead volume fraction. This suggests that crack tip blunting and associated transparticle fracture in the carbon bead system are more effective than the crack pinning mechanism of phenolic bead in improving the interlaminar toughness.

- The mode 2 interlaminar fracture toughness values measured from ENF specimens (machined from the same composite panel as the DCB specimen) are higher than the mode 1 interlaminar fracture toughness values due to the different fracture mechanism (namely sigmoidal shaped microcracks forming ahead of the crack tip).

- Carbon bead reinforced hybrid composites show an
improvement in mode 2 interlaminar fracture toughness as compared to the base epoxy system at 15% bead volume fraction. However, at higher bead volume fractions a sharp drop-off was shown. This is believed to be a consequence of change in fracture mechanism associated with the relatively thick bead-filled interlayer.

- According to orthotropic fracture mechanics theory, the $K_{IC}$ values based on analyses developed for isotropic materials, are overestimates and the true anisotropic $K_{IC}$ values can be obtained using the correction factor $C$, where $C = (E_0/E_{11})^{1/2}$ ($E_0$ is the effective modulus of the orthotropic material and $E_{11}$ is the longitudinal modulus).

- From fracture mechanics considerations of the DCB test it is shown that the toughness $G_{IC}$ and the fracture toughness $K_{IC}$ (calculated from the isotropic relation) should be related by $G_{IC} E_{11}/K_{IC}^2 = 1$. The available data approximates to unity. Deviations from unity are due to a combination of experimental measurement errors and real variations in the local stiffness of the material.

8.2 Further work

The following pieces of work follow naturally from the results presented in this thesis.

Firstly, having established that using two bead types
can enhance the toughness, it would be interesting to investigate the hybrid toughening effect using different combinations of particles.

Secondly, having established in this work that beads can improve the interlaminar fracture toughness, it would be worthwhile investigating the effect on intralaminar cracking (e.g. matrix cracking in cross-ply laminates).

Thirdly, it would be interesting to see whether all bead-filled epoxies, where the toughening mechanism is by plastic deformation, show good interlaminar fracture toughness behaviour when used as composite matrices and whether those that show crack pinning are all poor.

Finally, on the theoretical side, it is clear that the modelling of crack pinning requires further work with the inclusion of such parameters as the particle modulus and the coefficient of thermal expansion of particles and matrix.
REFERENCES

ASTM, D30.02, Round Robin, "Test procedure for the double cantilever beam (DCB)".


British Standard: BS2782.


320


G.R. Irwin, "Fracture dynamics", fracturing of metals: a seminar on the fracturing of metals, ASM publ. p147, 1948


