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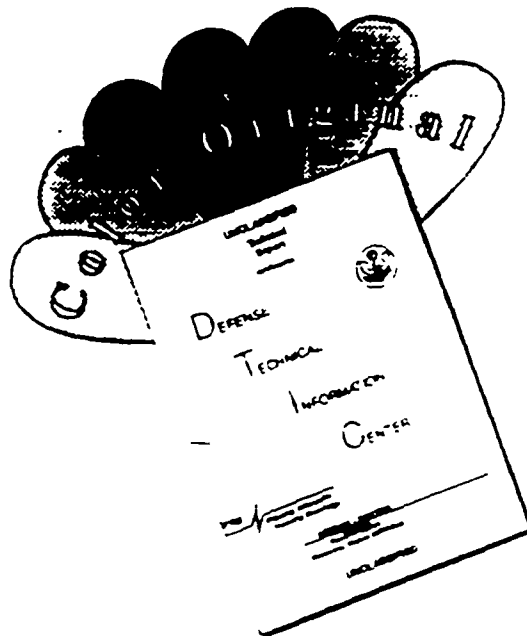
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) This Final Report presents and discusses the results obtained in the following areas (i) Mode I and mixed mode testing of bonded joints (ii) the use of an oxygen plasma surface treatment to pretreat thermoplastic fibre composites before bonding (iii) the effect of test rate on the fracture behaviour of bonded joints and finally (iv) the effects of test environment on the fracture behaviour of bonded joints.		

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ABSTRACT

This thesis discusses an investigation into the fracture behaviour of adhesively bonded fibre-composite joints. Three fibre-composite substrates have been employed. Two of these were based upon carbon fibre reinforced thermoplastic matrices i.e. U/C PEEK and U/C PPS and the third was a carbon fibre reinforced thermoset, U/C epoxy. The adhesives employed were two rubber modified structural epoxy adhesives, one a single part epoxy-film adhesive and the other, a two part epoxy-paste adhesive.

Firstly, a beam theory analysis has been applied to the study of crack growth in adhesive joints, using a linear elastic fracture mechanics approach and the double cantilever beam test specimen. It was demonstrated that if the simple beam theory analysis was corrected for the effects of shear rotation, large beam displacements and end-block stiffening, then excellent agreement was obtained between values of the adhesive fracture energy, G_c , calculated via three different "corrected beam theory" analyses and via the traditional "compliance method". One version of the "uncorrected beam theory" analysis showed that the various substrate moduli were dependent upon crack length, and that all the joint systems exhibited an 'R-curve', i.e. increasing crack resistance with crack length. However, the "corrected methods" clearly showed that the substrate moduli were independent of crack length, and that really none of these joint systems exhibited an 'R-curve' effect. For joints bonded with the epoxy-film adhesive, a modified mixed-mode bending test apparatus was employed to deduce the mixed-mode failure locus for this joint system. All failure at slow rates was cohesive.

Secondly, it was shown that an oxygen plasma treatment was a very effective procedure by which to improve the level of intrinsic adhesion of either of the two thermoplastic based fibre-composites. Indeed, when this treatment was applied to the U/C PEEK substrates, then high fracture energy, in adhesive failures were observed. However, when this treatment was applied to the U/C PPS substrates, then the dominant failure mechanism was by interlaminar crack growth through the composite. Scanning electron microscopy and X-Ray photoelectron spectroscopy have been employed to correlate the observed fracture behaviour following a plasma treatment to the physical and chemical characteristics of the treated substrate surfaces.

Thirdly, the effect of test rate on the joint fracture behaviour has been investigated. A high-speed servo-hydraulic test machine has been used in conjunction with high-speed photography to determine the dependence of the adhesive fracture energy, G_c , on increasing test rate up to a rate of 10m/s. It was shown that misleading results were obtained if versions of the analysis requiring values of the load to be measured were employed. This problem was overcome by using a version of the "corrected beam theory" analysis which did not require values of the load to be measured. Using this analysis, it was shown that, for joints prepared with the epoxy-film adhesive, then no rate dependence existed, but for joints prepared with the epoxy-paste adhesive, the value of G_c decreased at higher test rates, accounting for a 40% reduction in G_c at 10m/s. The locus of failure remained cohesive at all test rates.

Finally, the effect of ageing joints in a hostile environment (water at 50°C) for periods of up to one year was investigated. It was shown that all the joint systems were adversely affected by this exposure. When the U/C epoxy composite was bonded with either adhesive, then the effect of ageing in the environment was to decrease the adhesive fracture energy by almost 50%, but not to change the locus of joint failure, which remained cohesive. However, when the U/C PEEK substrates were employed, then the locus of joint failure and the calculated values of G_c depended upon the adhesive employed and upon the test rate. A series of additional bulk adhesive tests and interfacial thermodynamic calculations were conducted in order to better understand this complex behaviour.

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LIST OF SYMBOLS

English Alphabet

A	Cross sectional area
B	Substrate width
C	Compliance
C_{∞}	Equilibrium water concentration
C_t	Water concentration at time t.
D	Diffusion coefficient
E_B	Binding energy
E_k	Kinetic energy
E_s	Axial substrate modulus
E_{11}	Axial substrate modulus
E_{22}	Out of plane substrate modulus
E_a	Adhesive modulus
F	Large displacement correction factor
F_1	Large displacement correction factor for MMB test
F_2	Large displacement correction factor for MMB test
G	Energy release rate
G_I	Energy release rate in mode I
G_{II}	Energy release rate in mode II
G_c	Adhesive fracture energy in mode I
G_{Ic}	Fracture energy in mode I
G_{IIc}	Fracture energy in mode II
$G_{I/IIc}$	Fracture energy in mixed mode when $\psi=45^\circ$
G_{12}	Shear modulus
G_0	Intrinsic energy term
G_0	Critical mode I component to cause failure in the mixed-mode failure criterion
I	Second moment of area
K	Stress intensity factor
L	Length of beam
M	Bending moment
M_{∞}	Mass of water absorbed at equilibrium
M_t	Mass of water absorbed after time t
N	Correction factor for end-block effects
P	Load
P_c	Critical load
T	Temperature

List of Symbols

T_g	Glass transition temperature
U_e	External energy
U_s	Strain energy
W_A	Thermodynamic work of adhesion in an inert environment
W_{AL}	Thermodynamic work of adhesion in a liquid environment
W_d	Work done

a	Crack length
$\dot{a}$	crack speed
h	substrate thickness
l_1, l_2	End-block dimensions
r	Plastic zone radius
t	time

Greek Alphabet

Ω	Weighted % dipole moment
Ω_c	Critical weighted % dipole moment
Ψ	Visco-elastic and plastic energy term
Γ	Ratio of elastic constants
θ	Correction factor functions
ω	Slope of the fracture surface roughness
ϵ	Strain
ρ	Density
τ	Shear stress
ψ	Phase angle of applied loading
Ψ_0	Phase angle which arises due to elastic mismatch
σ	Stress
σ_y	Yield stress
σ_{yy}	Transverse tensile stress (out of plane)
σ_{yyc}	Critical transverse fracture stress in composite substrates
σ_{yyci}	Critical transverse stress required to cause interfacial debonding
δ	Displacement
γ	Surface free energy
γ^D	Dispersion component of the surface free energy
γ^P	Polar component of the surface free energy
ξ	Ratio of substrate thicknesses
χ	Shear correction term in mode I
χ_{II}	Shear correction term in mode II

ABBREVIATIONS

ASTM	American Society for Testing Materials
BE	Backscattered electrons
CAA	Contact angle analysis
CFRP	Carbon fibre reinforced plastic
CT	Compact tension specimen
DCB	Double cantilever beam specimen
DGEBA	Diglycidyl ether of bisphenol A
DMTA	Dynamic mechanical thermal analysis
ELS	End-loaded split specimen
ESCA	Electron spectroscopy for chemical analysis
EWC	Equilibrium water concentration
fps	frames per second
FRMM	Fixed-ratio mixed mode
HF	High frequency
IR-RAS	Infra-Red reflection-absorption spectroscopy
LEFM	Linear elastic fracture mechanics
LEWC	Limiting equilibrium water concentration
LMD	Lost motion device
LVDT	Linear velocity displacement transducer
MMB	Mixed-mode bending test
PEEK	Poly(ether-ether) ketone
PPS	Poly(phenylene sulphide)
pps	pictures per second
RH	Relative humidity
RF	Radio frequency
SEM	Scanning electron microscopy
SENB	Single edge notched bend specimen
WDM	Weighted % dipole moment
WLF	Williams-Landel-Ferry Eqn.
TDCB	Tapered double cantilever beam specimen
U/C	Reinforced with unidirectional carbon fibre
VUV	Vacuum ultraviolet
XPS	X-Ray photoelectron spectroscopy

Chapter One

Introduction

1.1 An Introduction to the Bonding of Polymeric Fibre-composites

The use of adhesives to join components in engineering structures is becoming increasingly common as designers and engineers capitalize on the many advantages which adhesives offer over more traditional methods of joining. The avoidance of stress concentrations, associated with riveting, and internal stresses, induced by welding, coupled with weight and potential cost savings, have all contributed to the rapid increase in the use of adhesives by industry. Furthermore, as new grades of adhesives have been developed and their engineering properties improved, so has confidence in their performance grown. Formerly used to secure only secondary, non-critical components, adhesives are now employed to secure primary structures. The British Aerospace BAe146 and the European Airbus AE320 aircraft are examples of structures in which critical components are adhesively bonded.

One of the more significant advances in recent years in the engineering materials sector has been the development of polymeric fibre-composites based upon thermoplastic matrices, rather than the traditionally-favoured thermosetting resins. This development has, however, posed a novel challenge. Although thermoplastics may be inherently tougher than thermosets, due to the absence of cross-linking in thermoplastics, and are more readily moulded into complex shapes, they are by contrast inherently difficult to bond.

Modern structural adhesives, typically based on epoxy, phenolic or acrylic resins are able to bond thermosetting based polymeric materials with much success [1]. Clearly, if the problems associated with bonding could be overcome, then the advantages offered by thermoplastic fibre-composites would be significant. This problem was successfully overcome by the implementation of a corona-discharge surface pretreatment technique [2]. Indeed, it is now possible to bond fibre reinforced thermoplastics and thermosets with equal success. However, before bonded thermoplastic fibre-composites can be used in engineering structures, it is important that their mechanical performance under various service conditions is ascertained.

1.2 The Aims of this Project

The principal aim of this project is to address the lack of basic engineering data on the properties of bonded polymeric fibre-composites under various service conditions. Two thermoplastic fibre-composites, and for comparative purposes, a thermoset fibre-composite will be studied. The principal aims are:

- (i) To use a fracture mechanics approach to assess the behaviour of bonded fibre-composite joints under different loading regimes, i.e. under pure mode I and mixed-mode loadings.
- (ii) To ascertain whether this fracture behaviour in the most important of the above regimes i.e. tensile loading, is dependent upon the test rate.
- (iii) To determine whether the fracture behaviour of these joints is adversely affected by ageing in a hot-wet environment for periods of up to one year.
- (iv) To combine the effects of high test rate and long term environmental exposure to investigate how the bonded joints would perform under these most hostile service conditions.
- (v) In addition, to establish whether another surface pretreatment technique, namely oxygen plasma, may be employed as an alternative to the corona-discharge treatment with equal success. This would be potentially valuable in circumstances where it is impossible, or difficult, to use a corona treatment.

1.3 An Introduction to the Main Experimental Sections

1.3.1 The Corona-discharge and Oxygen Plasma Surface Treatments

Essentially the corona-discharge and oxygen plasma surface pretreatment techniques are similar in that they both utilize electrically activated gas molecules to modify the physical and chemical nature of a polymer surface. Kinloch and Kodokian [3] showed that, by the application of a corona-discharge treatment, difficult-to-bond thermoplastic fibre-composites could be bonded with much success. Without this treatment, the joints failed at the adhesive-substrate interface with a correspondingly low value of the adhesive fracture energy, G_c . However, after a corona treatment, the locus of joint failure became cohesive, i.e. within the adhesive, and the value of G_c was greatly increased. The corona-discharge surface pretreatment technique will be discussed in Chapters Two and Three.

However, as will be discussed in Chapter Five, there are situations in which it is difficult to use the corona-discharge, e.g. in complex mouldings where the surfaces to be bonded are not readily accessible. Therefore, in order to investigate whether another technique may be employed with equal success, a surface preparation using an oxygen plasma technique has been carried out. The results of this study are presented in Chapter Five, together with a detailed surface analysis of the treated surfaces. It should be noted that in all other Chapters, when the thermoplastic substrates were employed, then the corona-discharge surface pretreatment technique has been followed.

1.3.2 The Application of Fracture Mechanics to Adhesive Joints

The concepts of continuum fracture mechanics have been widely employed in studies concerned with crack growth in adhesive joints [1]. The basic tenet of this approach is that the strength of most real solids is governed by the presence of flaws. Adhesive joints usually fail by the initiation and propagation of flaws. Flaws are often naturally occurring, termed intrinsic flaws, and may take the form of dirt particles, voids, cracks or other inhomogeneities in the adhesive which may be initially present at a critical size or develop during a fracture test. Of the various test geometries that have been used to measure the adhesive fracture energy, G_c of bonded joints, the double cantilever beam (DCB) specimen has been one of the most widely used and is employed in the present work. Various linear elastic fracture mechanics (LEFM) methods for analysing mode I test data have been employed. It will be shown in Chapter Four that the adhesive fracture energy may be accurately deduced from a "corrected beam theory analysis". It will be shown that these "corrected methods" for calculating the value of G_c show excellent agreement with the traditional "compliance method". The corrected beam theory approach has also been followed to analyse mixed-mode fracture of bonded joints.

1.3.3 Effects of Test Rate

It can be said with reasonable confidence that at some stage during the service life of an adhesive joint it will be subjected to impact conditions. This is certainly true when the adhesive joint is to be incorporated into vehicle structures [4]. For this reason it is necessary to investigate whether the fracture resistance of the adhesive joint is rate sensitive. Clearly it is important to investigate to what extent the energy dissipating mechanisms operating in the plastic zone ahead of the crack tip still do so under impact conditions. Further, above a particular impact speed the locus of joint failure may switch from cohesive to adhesive or even to within the composite substrate (i.e. interlaminar fracture may occur). A series of tests will be described in Chapter Six in which the DCB adhesive joints are subjected to a wide range of

crack opening displacement rates. A high-speed servo-hydraulic testing machine has been employed, together with high-speed photography and electronic data acquisition facilities to monitor the test parameters required for the calculation of the adhesive fracture energy, G_c . Different versions of the "corrected beam theory analysis" have been employed to ensure that accurate and valid values of G_c were deduced.

1.3.4 Effects of Test Environment

Developing adhesive joint systems which can retain a sufficient proportion of their mechanical performance after extended exposure to hostile environments represents a major challenge to those working in the adhesives sector. It has been shown [5, 100] that moisture represents one of the most deleterious environments in which an adhesive joint can serve. This is of particular concern as it is the one which is most commonly encountered in service. If the joint is exposed to water, either in the liquid or vapour state, it may suffer environmental attack. Water can attack the adhesive-substrate interface, undermining the intrinsic forces of adhesion and it also can modify the bulk properties of an adhesive, e.g. yield strength and modulus, and it can also cause a degradation of the substrate materials.

A series of long term environmental tests have been conducted in order to investigate the effect of water on the fracture behaviour of bonded fibre-composite joints. This will be discussed in Chapter Seven. The variation in adhesive fracture energy, G_c , has been determined as a function of joint system and length of exposure. Particular care has been taken to accurately determine the locus of joint failure in each case, and the effects of water on the bulk adhesives has been studied in a series of separate tests. Water diffusion coefficients and solubility parameters have been deduced for each adhesive and the variation in tensile properties has been measured for adhesives containing various concentrations of water. Finally, the effects of high rate testing and environmental exposure have been combined in order to investigate the behaviour of a bonded joint under these most hostile service conditions. This is discussed in Chapter Seven.

It is clear from the foregoing discussion that, before bonded thermoplastic fibre-composites can be adopted into a wide range of engineering structures, then their mechanical performance over a wide range of service conditions needs to be evaluated. However, before presenting the major experimental Chapters, a review of the literature will be undertaken in order that some of the many complexities associated with the behaviour of adhesive joints may be more fully understood.

Chapter Two

Literature Survey

2.1 Introduction to the Literature Survey

The study of the fracture behaviour of adhesive joints is a complex task. In order to better understand this behaviour it is necessary to appreciate that a joint is best considered as a system. The behaviour of this system will depend, not only on the test conditions, but also on the adhesive employed, on the substrate materials and also on the properties of the adhesive-substrate interface. The importance of obtaining and then maintaining adequate adhesion between the adhesive and the substrate cannot be over emphasized. It is for this reason that the mechanisms of adhesion are reviewed first in Section 2.2, followed by a discussion of the forces acting across an interface in Section 2.3, and then the surface pretreatment techniques which are known to greatly enhance the intrinsic adhesion of polymeric fibre-composites are discussed in Section 2.4.

The concepts of fracture mechanics have been widely employed in studies concerned with crack growth in adhesive joints and these are discussed in Section 2.5. The Griffith energy balance and Irwin's stress intensity factor approach to fracture have been reviewed. It will be shown that the energy balance approach is the more appropriate method to use when studying fracture in adhesive joints. The application of beam theory to the study of interlaminar fracture in fibre-composites is reviewed, since an analogous approach can be followed for fracture in adhesive joints.

If sufficient adhesion has been achieved at the adhesive-substrate interface, then a propagating crack will either run within the adhesive or within the substrate. The substrates employed in this work are all polymeric fibre-composites, and the interlaminar fracture behaviour of these materials has been extensively studied elsewhere [34,77]. However, the energy absorbed by a crack propagating cohesively, within the adhesive, will be very sensitive to the adhesive formulation. Modern, rubber toughened, epoxy adhesives possess multiple energy absorbing mechanisms, and these mechanisms are discussed in Section 2.6. In Section 2.7, the effects of test rate will be reviewed. This section includes a discussion of the different types of impact test which may be followed and also the commonly observed types of crack

propagation. Finally, the factors concerned with the environmental durability of adhesive joints are reviewed in Section 2.8.

2.2 Theories of the Mechanisms of Adhesion

2.2.1 Introduction

An adhesive may be defined as a material which, when applied to the surfaces of materials can join them together and resist separation [1]. In engineering structures this will often require the transmission of considerable loads. In this section the nature of the intrinsic forces which act across the interfaces to resist such loads will be discussed. It is these intrinsic forces which account for the level of intrinsic adhesion across an interface. There is no universally accepted theory of adhesion, and many mechanisms have been proposed to describe the effect. The four main theories which have been proposed are: mechanical interlocking, the diffusion theory, the electronic theory and the adsorption theory. These will now be discussed in turn.

2.2.2 Mechanical Interlocking Theory

This theory proposes that the adhesive locks into irregularities on the substrate surface. If 'ink-bottle' type pits are present on the substrate surface, then this may contribute to the intrinsic adhesion between adhesive and the substrate. In the case of porous substrates e.g. paper, this mechanism may be significant, but when this is not so, the relative contribution to the intrinsic adhesion by this mechanism is not thought to be very significant [1, 6]. This is because roughened surfaces do not tend to possess this type of irregularity. In addition, it is known that good adhesion can be obtained between smooth substrates such as glass, so roughness cannot be a general requirement. The benefits obtained by roughening the surface of a substrate prior to bonding may usually be explained in terms of an increased surface area, an improvement in the surface wetting and the removal of weak surface layers. This will be discussed further in Section 2.2.6.

2.2.3 Diffusion Theory

This theory proposes that the intrinsic adhesion of high polymers to themselves (autoadhesion), is due to the diffusion of polymer molecules across their mutual interface [7]. For this diffusion to occur, the polymer chains must be sufficiently mobile and mutually soluble. However, where the solubility parameters are not similar, or where the polymer is highly crosslinked, crystalline, or above its glass transition temperature, T_g , then

interdiffusion is an unlikely mechanism [1]. This mechanism is therefore not likely to explain the adhesion between epoxy adhesives and other polymeric materials.

2.2.4. Electronic Theory

This theory proposes that adhesion is due to the formation of an electrical double layer which is created when the two substrates are brought together. Then, interfacial forces arising from the electrical double layer contributes to the intrinsic adhesion. Thus, the forces of adhesion in a joint can be explained in the same manner as the electrical forces across a capacitor. The main proponents of this theory were Deryaguin and co-workers [8]. A major criticism of their argument is the fact that the electrical phenomena, which are the basis of this theory, only occur when the joint is broken. Thus a fracture process was used to explain a joining process. As the chemical and rheological states of the the adhesive are different in the two cases, it is difficult to see how they can be directly related. In addition, when they calculated the electrical energy stored in the capacitor by correlating to the work of adhesion, they included the energy dissipated by visco-elastic and plastic processes. Clearly, this should not have been equated with electrical energy. Finally, this theory would suggest that conductive materials should not form joints and, of course, they do.

2.2.5 Adsorption Theory

According to the adsorption theory, adhesion is achieved as a result of the intimate contact between the adhesive and the substrate. This intimate contact is achieved if the adhesive can fully spread over, or wet, the substrate. As a result of this contact, short range interatomic and intermolecular forces come into play across the bimaterial interface and, the adhesive macromolecules are attracted to the substrate by these forces. The most common of these forces are the van der Waals forces, which can be described as secondary bonds. Another secondary bond which may form is the hydrogen bond and this may form between molecules containing a hydrogen atom and an electronegative atom, e.g. oxygen or nitrogen. In some circumstances, chemical reactions may occur resulting in chemical bonds forming across the interface. These bonds may be ionic or covalent in nature and are known as primary bonds due to their greater strength. In addition to these, a further bond of intermediate strength has been proposed, [9,108] resulting from various possible acid-base interactions occurring at the interface.

The adsorption theory is the most widely accepted of the various theories of adhesion. A recent criticism of this theory however, has stemmed from the question of whether the interfacial forces of attraction really occur across a two dimensional interface, or whether they

occur within a three dimensional volume, or interphase. It has been further questioned whether a theory which relies strictly on interfacial interactions can be expected to describe the response of a system in which volume deformations are occurring. Indeed there is currently a great deal of debate regarding the significance of the interphase, and it has been the subject of a recent conference on adhesion [110]. However, due to the importance ascribed to the adsorption theory in the literature, the nature of these interfacial interactions will now be discussed.

2.3 The Adhesive-Substrate Interface

2.3.1 Introduction

Of the various theories of adhesion proposed, the adsorption theory has proved to be the most widely accepted. In this section the nature of the interatomic and intermolecular forces proposed by this theory to be responsible for adhesion will be discussed. The significance of weak boundary layers to the attainment of interfacial adhesion is then discussed.

2.3.2 Interfacial Secondary Forces

2.3.2.1 Introduction

Huntsberger [10] and others [11, 12] showed that dispersion forces alone, which are one of three types of van der Waals interactions, were sufficient to account for joints of even the highest strength. They showed that these forces could impart a tensile strength of 100MPa to a joint. It was argued that these levels of strength are not commonly attained due to the imperfections in the bond, e.g. the existence of air-filled voids and other stress concentrations. However, their calculation showed that, at least in theory, dispersion forces acting across the interface may indeed account solely for the adhesion between an adhesive and substrate. There has been a wealth of experimental evidence, e.g. [5, 13] to support the notion that that secondary forces are indeed sufficient to account for commonly measured joint strengths.

A further secondary interaction which may take place across the interface is the formation of hydrogen bonds. These are formed between molecules containing the hydrogen atom covalently bonded with an electronegative atom. The resulting electrostatic attractions may be exploited by the adhesives technologist by promoting their existence across the interface, enhancing the intrinsic adhesion of the joint.

2.3.2.2 The thermodynamic work of adhesion

If it is assumed that only secondary forces are acting across an interface then the thermodynamic work of adhesion, W_A , required to separate a unit area of solid and liquid phase may be related to surface and interfacial free energies by the dupre equation. Thus, the reversible work of adhesion, W_A , in an inert environment may be expressed as:

$$W_A = \gamma_s + \gamma_{lv} - \gamma_{sl} \quad (2.1)$$

where γ is the surface free energy and subscripts 's', 'lv' and 'sl' denote solid, liquid-vapour and solid-liquid interfaces respectively. By relating these free energies to the equilibrium contact angle, θ , measured by contact angle analysis, then eqn.2.1 may be rewritten as:

$$W_A = 2(\gamma_s^D \gamma_s^P)^{\frac{1}{2}} + 2(\gamma_s^P \gamma_s^D)^{\frac{1}{2}} \quad (2.2)$$

where subscripts 'a' and 's' now denote adhesive and substrate respectively. The superscripts 'D' and 'P' denote the dispersion and polar components of the surface free energy respectively and these components are discussed further in Section 2.4.3. The terms on the right hand side of eqn.2.2 may be experimentally determined from contact angle measurements and hence W_A can be deduced.

Several workers have attempted to find a correlation between W_A and adhesive joint strength with conflicting results. Clearly, a correlation would only be expected if a joint failed at the interface, because the term W_A does not include energy dissipation from either viscoelastic or plastic processes, i.e. it is concerned only with the contribution to the intrinsic adhesion arising from secondary forces. By adopting a fracture mechanics approach, Andrews and Kinloch [13] and Gent and Kinloch [14] defined a geometry-independent measure of joint strength, G_a , which for a joint system comprising of a crosslinked, rubbery adhesive and a rigid plastic substrate could be divided into two major components, as given in eqn. 2.3:

$$G_a = G_0 + \Psi \quad (2.3)$$

where G_0 is the energy required to propagate a crack through unit area of interface in the absence of viscoelastic or plastic energy losses and Ψ is the energy dissipated within the adhesive per unit area of fracture surface created. Thus, if only secondary forces are acting across the interface then W_A may be correlated directly with G_0 . If the crack is purely interfacial, then:

$$W_A = G_0 \quad (2.4)$$

However, purely interfacial cracks are rare and the viscoelastic-plastic energy term Ψ usually dominates in toughened adhesives. The value of Ψ can be expressed as:

$$\Psi = G_0 f(\dot{a}, T, \epsilon) \quad (2.5)$$

where f is a function, the value of which depends on the crack growth rate $\dot{a}$, the temperature T and the strain ϵ . It is intriguing to notice that the value of Ψ also depends on G_0 . The reason for this is that, when the crack is propagating away from the interface e.g. within the adhesive, energy can only be absorbed in the plastic zone ahead of the crack tip while the adhesive-substrate interface is able to transmit the load. If the interfacial forces of adhesion are exceeded, then the Ψ term in eqn 2.3 may become zero.

2.3.2.3 Thermodynamic work of adhesion in a liquid environment.

The stability of an interface in the presence of a liquid environment can be assessed by the thermodynamic arguments advanced by Gledhill and Kinloch [5]. Writing eqn. 2.1 in terms of the adhesive and substrate, we have:

$$W_A = \gamma_a + \gamma_s - \gamma_{as} \quad (2.6)$$

Now, if only secondary forces are acting across the interface, then the thermodynamic work of adhesion in the liquid environment may be expressed as:

$$W_{AL} = \gamma_{al} + \gamma_{sl} - \gamma_{as} \quad (2.7)$$

where the subscript 'l' now denotes the liquid environment, and γ_{al} and γ_{sl} are the interfacial free energies between the adhesive-liquid and substrate-liquid interfaces respectively. By again relating this term to the equilibrium contact angle, eqn. 2.6 may be recast as:

$$W_A = 2(\gamma_a^D \gamma_s^D)^{\frac{1}{2}} + 2(\gamma_a^F \gamma_s^F)^{\frac{1}{2}} \quad (2.8)$$

and eqn. 2.7 may be expressed as:

$$W_{AL} = 2 \left[\gamma_{lv} - (\gamma_s^D \gamma_{lv}^D)^{\frac{1}{2}} - (\gamma_s^P \gamma_{lv}^P)^{\frac{1}{2}} - (\gamma_s^D \gamma_{lv}^P)^{\frac{1}{2}} - (\gamma_s^P \gamma_{lv}^D)^{\frac{1}{2}} + (\gamma_s^D \gamma_s^D)^{\frac{1}{2}} + (\gamma_s^P \gamma_s^P)^{\frac{1}{2}} \right] \tag{2.9}$$

where γ^D and γ^P are the dispersion and polar components of the surface free energy respectively, and γ_{lv} is the surface free energy of the liquid. Now, in an inert medium, the work of adhesion, W_A , for an adhesive-substrate interface is usually positive, indicating that the interface is thermodynamically stable. However, in the presence of a liquid environment, W_{AL} may become negative, indicating that the interface is now unstable. If the presence of the liquid causes the work of adhesion to change from positive to negative, then this will provide the driving force for the displacement of the adhesive from the substrate surface by the liquid. This will in due course, lead to the progressive weakening of the joint and also change the locus of failure from cohesive to interfacial. In some cases where the value of W_{AL} is not negative, but $W_A > W_{AL} > 0$, it has been shown [15] that the adhesive fracture energy is reduced by the presence of the liquid.

TABLE 2.1 Values of W_A and W_{AL} for various interfaces and environments.

Interface	W_A (mJ/m ²) Inert Medium	Liquid Environment	W_{AL} In Liquid	Evidence of Interfacial failure
Epoxy adhesive Ferric oxide	291	Ethanol	22	No
		Formamide	-166	Yes
		Water	-255	Yes
Epoxy adhesive Al oxide	232	Water	-137	Yes
Epoxy adhesive CFRP (Epoxy)	88-99	Water	22-44	No

Table 2.1 shows the calculated values for W_A and W_{AL} for some common joint systems in various environments. It can be seen that high surface energy substrates e.g. metal oxides represent the greatest difficulty in terms of ensuring the durability of the bond in a liquid environment, i.e. W_{AL} is negative. It can be seen that carbon fibre reinforced plastics (CFRP) substrates do not appear to exhibit thermodynamic instability in a water environment when bonded with epoxy adhesives. However, this data refers to CFRP substrates based on an epoxy matrix and not on a thermoplastic matrix. Values of W_A and W_{AL} for both U/C

epoxy and U/C PEEK substrates, bonded with various epoxy adhesives and exposed to a water environment, have been calculated in Chapter Seven.

The thermodynamic arguments put forward in this section consider only secondary forces acting across an interface i.e. van der Waals and hydrogen bonds and it will be shown later in Chapter Seven that they may not always accurately predict the behaviour of a joint system in a liquid environment.

2.3.3 Interfacial Primary Bonds

The existence of interfacial primary bonds was reported in the work of Andrews and Kinloch [13] and Gent and co-workers [16] when bonding and crosslinking elastomers against reactive substrates. Klein et al. [17], using an infrared analysis, found evidence for covalent primary bonds between a polyurethane adhesive and epoxy-based primers. Such bonds gave high joint strengths and were partly ionic in nature due to the different electronegativities of the atoms of the covalent bond. Webster and Wightman [18] reported the formation of a covalent interphase region between a plasma modified thermoplastic and an epoxy adhesive using infrared reflection-absorption spectroscopy (IR-RAS) analysis.

2.3.4 Acid-Base Interactions

Fowkes and co-workers [19] argued that the formation of acid-base interactions between an adhesive and a substrate may represent a major source of intrinsic adhesion across the interface. The acid may be defined as an electron acceptor, in the Lewis sense, and similarly the base as an electron donor. They included hydrogen bonds in this classification. Essentially, a material may have one of three types of acid-base capability. It may:

- (i) Act as an electron acceptor e.g. poly(vinyl chloride) and chlorinated polyethylene.
- (ii) Act as an electron donor e.g. polymethyl-methacrylate and polyimide.
- (iii) Act as both electron acceptor and electron donor e.g. amides and polyamides.

The significance of these interactions to the intrinsic adhesion of polymeric materials is not fully understood and is currently the subject of much research.

2.3.6 Weak Boundary Layers

In the preceding sections it was assumed that the adhesive comes directly into contact with the bulk substrate to form an interface, across which the intrinsic adhesion forces act. This is an idealized situation, and Figure 2.1 shows that, in reality a boundary layer is likely to exist.

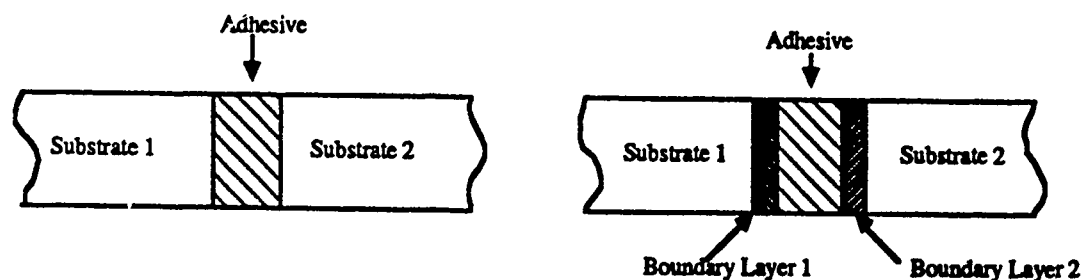


FIGURE 2.1 Idealized and Real Adhesive Joints

Boundary layers may have physical and chemical properties different from the parent bulk material. Therefore, since they are part of the joint system, they will modify its behaviour. Bikerman [20] discussed the various sources of weak boundary layers. These include oils, grease, dust and oxides of relatively low strength. Others might include mould release agents, various additives in formulated polymeric systems or low molecular weight fragments. Often the poor performance of an adhesive joint is attributed to the existence of a weak boundary layer. But, as observed by Sharp [21] this can be a circular argument - we reason that a weak boundary layer exists because the joint is weak. The existence, or possible existence of weak boundary layers has increased the necessity to undertake some form of surface pretreatment of the substrate materials prior to bonding. Clearly, if this weak surface layer could be removed, then a more consistent adhesive joint could be formed.

From the preceeding discussions it is clear that, in order to achieve an adhesive joint system with high strength and with consistent mechanical properties, then careful consideration should be paid to the interface or interphase region between adhesive and substrate. In order to enhance the sources of intrinsic adhesion and remove any weak boundary layers which may be present, it is necessary to employ various surface pretreatment techniques. Some of the most sophisticated techniques currently available involve the use of activated gases or 'plasmas'. The application of various plasma techniques has extended the applicability of adhesive bonding to new classes of materials previously difficult to bond e.g. thermoplastics. Some of these techniques will now be reviewed.

2.4 High Frequency and Radio Frequency Plasmas

2.4.1 Introduction

From the preceeding discussion it can be seen that adhesion between materials involves complex interactions occurring across the interface or within the interphase between adhesive

and substrate. The aim of a surface pretreatment is to alter the physiochemical nature of the substrates in order to promote the surface interactions which enhance adhesion. It has been known for about 25 years that plasmas can significantly improve the intrinsic adhesion of difficult-to-bond materials. Indeed, the use of plasmas have made a very significant impact on widening the applications of adhesive bonding. From the treatment of polyethylene film prior to printing, to the preparation of semiconductor materials, the applications are indeed wide.

The plasma may be generated in air, termed a 'corona discharge' or under reduced pressure, termed a 'glow discharge' or 'low-pressure gas plasma'. An essential feature of these techniques is that the resulting modification is restricted to the uppermost layers of the substrate, leaving its overall bulk properties unaffected. The nature of the plasma responsible for these effects will now be considered.

2.4.2 The Nature of Plasma

In his excellent review article, Liston [22] defined a plasma as, an ionized gas with an equal number of positive and negative charges within its volume. Plasma is a naturally occurring phenomena. Examples include the solar corona and lightening bolts. Man made examples include neon signs and fluorescent lighting. Within a gas plasma the positive charges occur as positive ions, and the negative charges as electrons. Because the positive ions are very much more massive than the electrons, the positive ions tend to remain almost stationary within the plasma, while the electrons carry the current. However, the ions very close to the electrodes, or material surfaces can be accelerated by the sheath voltage. These accelerated ions can potentially break chemical bonds on a substrate surface. If bond breaking occurs, unpaired atoms or groups of atoms will be temporarily created on the surface. These are known as 'free radicals' and are chemically unstable or metastable. In addition to the creation of free radicals on the material surface, the plasma gas itself will contain a significant quantity of free radicals. The glow discharge associated with the plasma has the effect of dissociating gas molecules through electron bombardment and photochemical processes, creating gas phase free radicals. These may exist either in the ground state, or they may be electronically excited and possess a significant amount of energy. For example, the lowest excited state for the oxygen radical is 220 kcal/mole above its ground state, which is sufficient energy to break any organic bond [22]. Thus the constituents of gas plasma are ions, free radicals and a large amount of extremely energetic vacuum ultraviolet (VUV) light. Therefore, these gas phase free radicals, in addition to the accelerated positive ions and ultraviolet photochemical processes, may induce physiochemical changes in a substrate exposed to the plasma. The nature of these physiochemical changes will now be considered.

2.4.3 The Effects of Plasma on Polymeric Surfaces

2.4.3.1 Surface cleaning

Firstly, a plasma treatment can clean a polymer surface. The excited gas species may have sufficient energy to displace contaminant fragments of low molecular weight from the material surface. Kodokian [2] used an X-ray photoelectron spectroscopy (XPS) technique to show that a corona-discharge treatment was an effective way to remove surface contamination resulting from the use of mould release agents. In addition, it was reported by Liston [22] that plasma can very effectively remove organic contamination deposited during a solvent rinse, which is usually undertaken to clean the substrates. Liston showed that as little as a single molecular layer of organic contamination on a substrate surface can interfere with bonding. Plasma is able to remove this layer of surface contamination, resulting in a polymer surface which is significantly cleaner than one which has received a solvent wipe.

2.4.3.2 Surface ablation

Secondly, a plasma treatment can cause the ablation, or removal of material from the polymer surface which may be important for three reasons. Firstly, if the surface is heavily contaminated, the plasma may remove much or all of the contaminant as described above. Secondly, as amorphous polymer is removed many times more quickly than crystalline polymer, a surface topography may form with the amorphous regions being preferentially ablated. Thus the surface area may be increased, providing a greater area for an adhesive to interact with. Finally, a complex surface topography increases the possibility of mechanical interlocking between the surface and the adhesive. However, Kinloch et. al. [23] found no evidence that the degree of surface roughness had any major effect on the intrinsic adhesion at the adhesive-substrate interface. Liston [22] on the other hand, concluded that surface ablation did result in improved bonding to graphite yarn, though this may have been due to the associated mechanisms mentioned in Section 2.2.2.

2.4.3.3 Surface crosslinking

Thirdly, excited gas atoms in the very energetic environment of the plasma together with vacuum ultra-violet (VUV) light tend to attack a polymer surface and break some of the primary C-C and C-H bonds. This process generates free radicals on the surface as previously described. If the free radicals are generated in the presence of a noble gas and in the absence of oxygen, then they are stable, as they cannot combine to form stable moieties. In this case, crosslinking is possible if the radical can migrate along, or if there is flexibility

in, the polymer chain. In this way crosslinking can occur, strengthening potentially weak surface layers and improving the material's heat resistance.

2.4.3.4 Surface chemical modification

Finally and most importantly, a plasma treatment can modify the surface chemistry of a substrate. A review of the literature reveals that these surface chemical effects induced by plasma have received the most attention. Indeed, it is the surface chemical modification, where the surface layer of the polymer is altered to create chemical groups capable of interacting with the adhesive, that represents the most dramatic and widely-used effect of plasma. Many workers have reported the surface chemical effects of plasma on polymeric materials. Evans et. al. [24] used XPS to detect the enhanced oxygen concentration on the plasma treated surfaces of PEEK and used CAA to show that this corresponded to a high polar surface energy. Webster and Wightman [18] used oxygen and ammonia plasmas to treat the thermoplastic polymer, polyphenylene sulphide (PPS), and Chin and Wightman [25] also employed an argon plasma to treat an aromatic thermoplastic polyimide. They used XPS and IR-RAS to identify specific surface functionalities induced by the treatment.

Kinloch and co-workers [2, 3, 23, 107] identified using XPS that a corona-discharge treatment led to a dramatic increase in the concentration of oxygenated species on several thermoplastic fibre-composites. In particular, they noticed an increase in the concentration of carbonyl (C=O) groups and the introduction of carboxy (O-C=O) groups. Using CAA, they showed a good correlation between the concentration of these polar groups and the surface free energy of the fibre-composite substrate. This leads to an increase in both the extent of wetting by the adhesive on the substrate and in the intrinsic adhesion across the adhesive-substrate interface. These effects will result from enhanced interfacial interactions arising from the polar secondary bonds i.e. dipole-induced dipole, dipole-dipole, hydrogen bonds and also from possible primary and acid-base forces.

2.4.4 The Corona-discharge Technique

In the corona-discharge treatment, atmospheric air is ionized in the gap beneath a high voltage electrode, operating at high frequency (15-20 kHz). A substrate beneath the electrode is exposed to the corona-discharge and treated. The technique has been used for many years for treating polyethylene film. The effect of the corona-discharge treatment on polyethylene film was studied by Carley and Kitze [26]. They related the improved intrinsic adhesion of corona treated polyethylene to the increased polar component of the surface free energy, γ_s^p .

More recently, Kodokian and Kinloch [2, 3] used the corona-discharge technique to pretreat various thermoplastic fibre-composites prior to bonding with toughened epoxy adhesives. They used contact angle analysis to measure the increase in the surface free energy of various thermoplastic substrate materials corona treated to different levels. Figure 2.2 shows the variation in the values of both the polar component, γ_s^P , and the dispersion component, γ_s^D , of the surface free energy after corona treating a U/C PEEK substrate to various treatment levels.

Figure 2.2 shows several interesting features. Firstly, the dispersion energy component of the surface free energy, γ_s^D , remained constant despite increased levels of corona treatment. Secondly however, the polar component of the surface free energy, γ_s^P , dramatically increased after a corona treatment, indicating that the corona treatment had increased the concentration of the active polar species on the substrate surface. This increase in the value of γ_s^P was correlated to the improvement in the measured adhesive fracture energy obtained after bonding corona treated U/C PEEK with an epoxy adhesive. A typical variation in the adhesive fracture energy, G_c , of joints prepared with corona treated U/C PEEK and bonded with a toughened epoxy-film adhesive is shown in Figure 2.3.

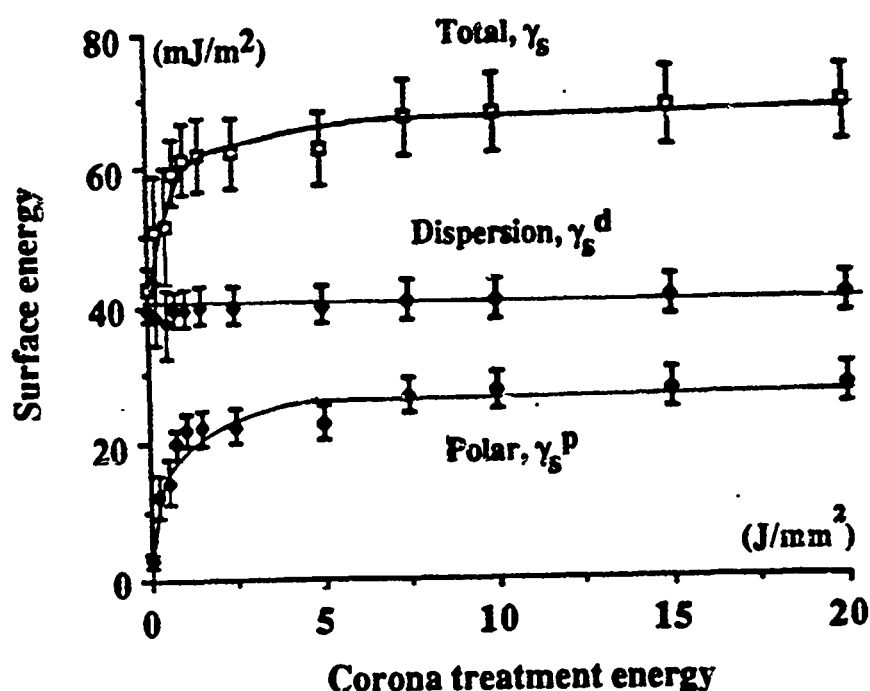


FIGURE 2.2 Surface energy versus corona pretreatment energy for U/C PEEK substrates. After Kodokian [2]

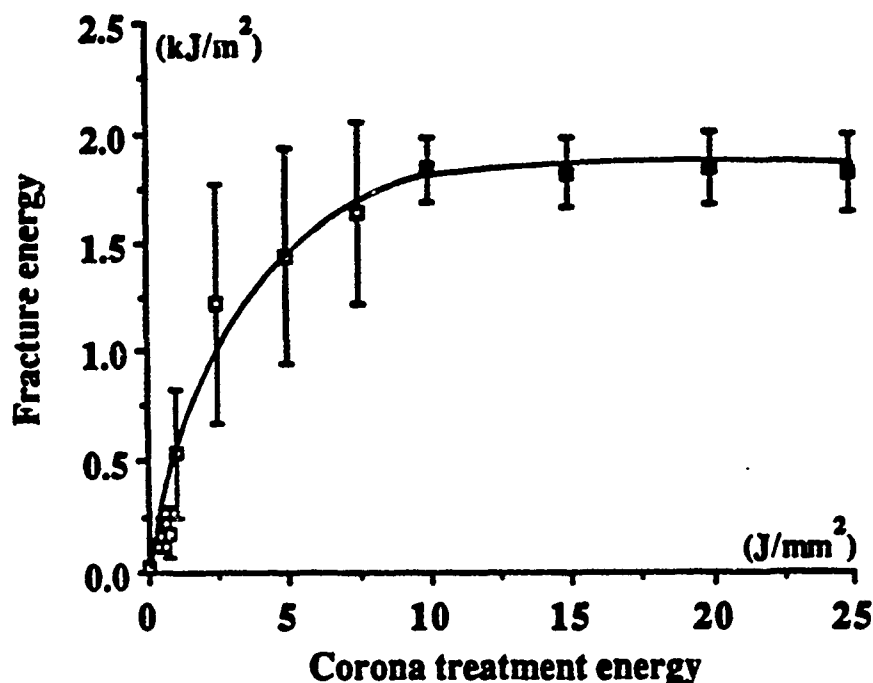


FIGURE 2.3 The adhesive fracture energy for a U/C PEEK composite, corona treated to various levels and bonded with an epoxy-film adhesive. Open points indicate interfacial failure; Closed points indicate cohesive failure. After Kodokian [2]

Figure 2.3 shows that as the level of corona treatment was increased, then the locus of joint failure switched from interfacial, associated with low values of G_c , to cohesive, associated with higher G_c values. Thus, the corona treatment had increased the intrinsic adhesion across the adhesive-substrate interface by inducing interfacial forces which had not previously been present in sufficient quantity to maintain interfacial integrity. The direction of crack propagation was no longer along the interface, but within the adhesive, resulting in visco-elastic and plastic energy absorption mechanisms within the adhesive which increased the fracture resistance and thus increased the value of G_c .

2.4.5 Gas Plasma Technique

In this technique, the substrate surface is exposed to the operating gas at reduced pressure (typically 0.1-1 Torr), within a reactor chamber. Radio frequency (RF) power is generated, which is then matched, such that the impedance of the plasma conforms to the required output impedance of the generator. The gas within the chamber is then ionized by the RF field, producing the gas plasma. Perhaps one of the most valuable features of this technique is the ability to employ different gases to achieve different effects. Some of the earliest work in this field was done by Schonhorn and Hansen [27]. They treated low surface energy polymers e.g. polyethylene with an RF plasma employing an inert operating gas and observed

improved adhesive properties. They concluded that perhaps the most significant mechanism responsible for this was the enhancement in the cohesive strength of a weak surface region on the polymer i.e. that the treatment had strengthened a weak interface. However, it is more likely that the improved adhesion was largely the result of a modification in the surface chemistry of the polymer, as noted by Kodokian and Kinloch in their work with the corona-discharge technique [23, 28]. The relative significance of the different mechanisms responsible for enhanced adhesion after exposure to plasma will now be discussed.

2.4.6 The Use of Plasma Treatment for Bonding Thermoplastic Fibre-composites

Kodokian and Kinloch [2, 3] showed that a corona-discharge surface pretreatment could successfully be employed to overcome problems associated with the lack of intrinsic adhesion of difficult-to-bond thermoplastic fibre-composites. It was shown in Section 2.4.4 that before corona treatment, U/C PEEK substrates which had received a standard abrasion-solvent wipe pretreatment and bonded with a toughened epoxy adhesive, failed in an interfacial manner with low values of G_c . However, after a corona treatment (the intensity of which was a function of the substrate and adhesive), the locus of joint failure moved away from the interface.

Davies and co-workers [29] and Moyer and Wightman [30] reported the effectiveness of employing an oxygen plasma surface pretreatment technique on various thermoplastic substrates prior to bonding. Davies et al tested lap shear joints manufactured from plasma treated U/C PEEK, bonded with a commercial modified epoxy adhesive ('AV118' from Ciba-Geigy). They reported that the lap shear strength increased from 17MPa in the untreated condition to 35MPa after a 30 minute oxygen plasma treatment. Moyer and Wightman employed a single lap shear test and a wedge test to evaluate the effect of surface pretreatment on the strength and durability of bonded joints. Of the various treatments which they employed, oxygen plasma was the most effective.

In the present work, a corona-discharge and also, an oxygen plasma surface pretreatment techniques have been employed. The joints containing the U/C PEEK substrates which were prepared for slow rate, high rate and environmental testing were corona-treated. The details of this treatment are described in Chapter Three. In Chapter Five, a series of tests will be described which were conducted on joints which had received an oxygen plasma treatment. Details of the fracture results and surface analysis from plasma-treated substrates will be presented in Chapter Five.

Of the various techniques which have been employed to study the fracture performance of adhesive joints, fracture mechanics has been one of the most successful. Extensive use has been made of the concepts of fracture mechanics in this work. In the next Section, the use of fracture mechanics to describe crack growth in engineering materials will be reviewed. In addition, the application of beam theory to the study of this important subject has been considered.

2.5 Fracture Mechanics

2.5.1 Introduction

The study of fracture in engineering materials is a complex task. Many workers have attempted to gain an understanding of the phenomena of fracture and many theories have been presented in an attempt to describe this process. In recent years the concept of Fracture Mechanics has been widely employed in what has been an attempt to provide a logical framework inside which the study of fracture can proceed. The basic tenet of fracture mechanics is that the strength of most real solids is governed by the presence of flaws. In the case of adhesive joints, these flaws are often naturally occurring and referred to as intrinsic flaws. Examples of intrinsic flaws include air bubbles, dirt particles, additive particles or cracks. These may have been present since manufacture, or may develop during a fracture test. There are various fracture mechanics approaches and all are concerned with analysing mathematically the way in which cracks propagate.

2.5.2 Modes of Failure

A crack may be loaded in three different modes, denoted I, II, and III, as depicted in Figure 2.4. and superposition of the three modes constitutes the general case of crack loading. The cleavage or tensile opening mode, mode I, is technically the most important because it is the one most commonly encountered and that most frequently causes failure [1]. However, it is not uncommon for an adhesive joint to be subjected to mixed-mode loading. This is because crack propagation in adhesive joints is often constrained to the adhesive layer, regardless of the orientation of the joint to the applied loads. Most frequently this results in a mixture of mode I and mode II loading. Mode II loading is the 'in plane shear' mode and mode III is the 'antiplane shear' or tearing mode of loading.

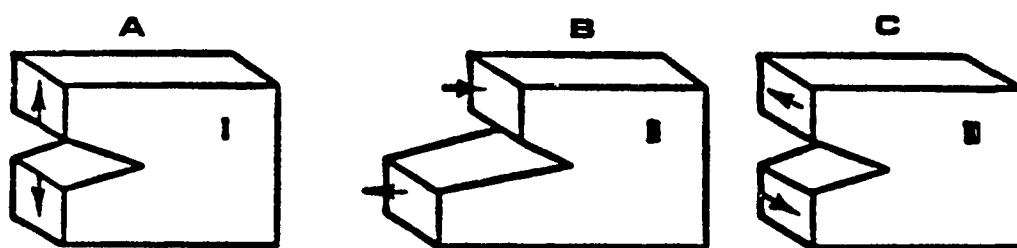


FIGURE 2.4 Modes of crack loading: (a) mode I (b) mode II (c) mode III

2.5.3 Energy Balance Approach

AA Griffith [31] was the first to employ the concept of fracture mechanics when attempting to explain why small glass objects generally exhibited higher strengths than larger ones. He proposed that fracture initiated from flaws in the material and that although all materials contained flaws, a larger object would be likely to contain bigger flaws than a smaller one, and hence failure would occur at a lower load in the larger object than in the smaller one. As a result of Griffith's and later Orowan's [32] work, a fracture criterion was developed. It was proposed that fracture occurs when sufficient energy is released (from the stress field) by growth of the crack to supply the energy requirements of the new fracture surfaces. The energy released comes from the stored elastic or potential energy of the loading system and can, in principle, be calculated for any type of test specimen.

Griffith described quasi-static crack propagation as the conversion of work done, W_d , by the external force and the available elastic energy stored in the bulk of the specimen, U , into surface free energy γ_m , which may be written:

$$\frac{\partial(W_d - U)}{\partial a} \geq \gamma_m \cdot \frac{\partial A}{\partial a} \quad (2.10)$$

where ∂A is the increase in surface area associated with an increment of crack growth ∂a . For a crack propagating through a section of thickness, B , the criterion becomes:

$$\left(\frac{1}{B}\right) \frac{\partial(W_d - U)}{\partial a} \geq 2\gamma_m \quad (2.11)$$

Griffith's work had focussed on a perfectly brittle material and when Orowan [32] and Rivlin and Thomas [33] examined this criterion with respect to metals and cross linked rubbers respectively and found that the energy required to cause crack growth was far greater than twice the surface free energy. There are two main reasons for this difference. Firstly, as discussed in Section 2.3.2, the value of $2\gamma_m$ (equivalent to W_A in the case of interfacial crack growth) only takes into account the energy required to break secondary bonds such as van der Waals forces. Indeed, as previously described, crack growth often requires the rupture of stronger forces such as primary bonds. The energy required to rupture these intrinsic bonding forces (secondary and primary) was termed G_0 . Therefore, if the material was perfectly elastic, G_0 could replace $2\gamma_m$, in Eq. 2.11. Secondly however, fracture in real materials invariably involves localized visco-elastic and, or plastic energy dissipative processes and such micromechanisms usually represent the main source of energy absorption. Hence, if $2\gamma_m$ is replaced by G_c (after Griffith), and this term encompasses all the energy losses incurred around the crack tip, then the fracture criterion becomes:

$$\left(\frac{1}{B}\right) \frac{\partial(W_d - U)}{\partial a} \geq G_c \quad (2.12)$$

where G_c is the total energy required to increase the crack by unit length in a specimen of unit width. Now, for a crack of width B and length a , the fracture condition may be expressed as [34]:

$$G_c = \frac{1}{B} \left\{ \left(\frac{\Delta U_e}{\Delta a} \right) - \left(\frac{\Delta U_s}{\Delta a} \right) \right\} \quad (2.13)$$

where U_e is the external work done, U_s is the strain energy and Δa is the associated increment of crack length. This definition is true for any elastic behaviour, linear or not and is illustrated in Figure 2.5.

Now, when the load, P is plotted against the displacement, δ as in Figure 2.5, then the change in external energy, ΔU_e , and internal strain energy, ΔU_s , may be represented by the areas: $\Delta U_e = \text{ADD}'A'$ and $\Delta U_s = \text{OA}'D' - \text{OAD}$, so that the total change in energy of the system, shown shaded, is OAA' and G_c may be determined from this value and the change in the crack area $B\Delta a$. Thus, G_c may be expressed by:

$$G_c = \frac{\text{area OAA}'}{B \times \text{crack growth}} = \frac{\Delta U}{B\Delta a} \quad (2.14)$$

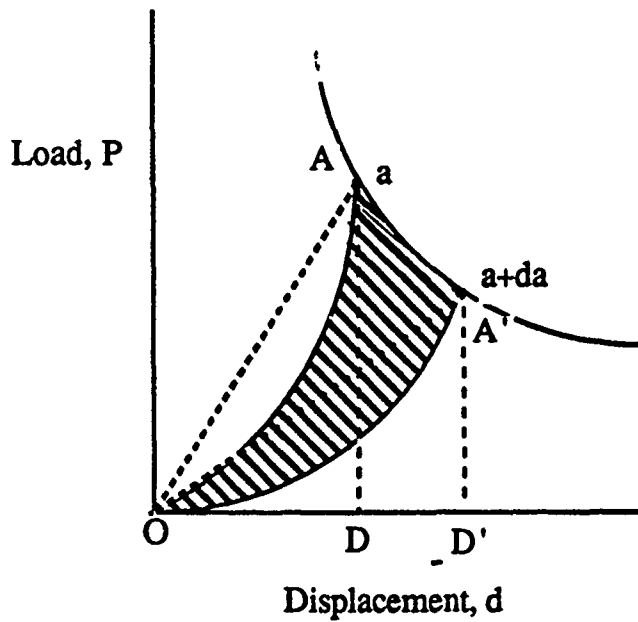


FIGURE 2.5 The definition of G and the 'Area Method'.

If the deformation behaviour is assumed to be linear then the straight lines shown in Figure 2.5 may be used. If A is given the coordinates P_1 and δ_1 and A' given by P_2 and δ_2 then it may be shown that:

$$\Delta U = \frac{1}{2}(P_1\delta_2 - P_2\delta_1) \quad (2.15)$$

This will be referred to as the "area method" in the present work. However, this expression for the change in system energy is imprecise because a derivative is estimated from two finite measurements i.e. an average value of G_c is obtained over an increment of crack growth, Δa . By invoking a function for the specimen compliance, which can be measured as a function of crack length, i.e.

$$C(a) = \frac{\delta}{P} \quad (2.16)$$

and noting in eqn. (2.15) that $P_2 = P_1 + \Delta P$ and $\delta_2 = \delta_1 + \Delta \delta$, then it can be shown that for test specimens exhibiting bulk linear-elastic behaviour i.e. obeying Hooke's Law away from the crack tip, then eqn. 2.13 becomes:

$$G_c = \frac{P^2}{2B} \frac{dC}{da} \quad (2.17)$$

Therefore if $C(a)$ is determined experimentally and curve fitted so that dC/da can be found for a given value of crack length, then a point value of G_c can be determined. This method for calculating G_c will be referred to as the "compliance method" in the present work.

2.5.4 Stress Intensity Approach

A different approach was followed by Westergaard [35] who developed certain stress function solutions which define the state of stress at the crack tip. Figure 2.6 shows a sharp crack in a uniformly stressed, infinite and homogeneous lamina. Assuming Hookean behaviour and infinitesimal strains (LEFM) Westergaard proposed the stress function solution:

$$\sigma_{ij} = \sigma_0 \left(\frac{a}{2r} \right)^{\frac{1}{2}} f_{ij}(\theta) \quad (2.18)$$

Where σ_{ij} are the components of the stress tensor at a point, taking the crack tip as the origin, and $2a$ as the length of the crack.

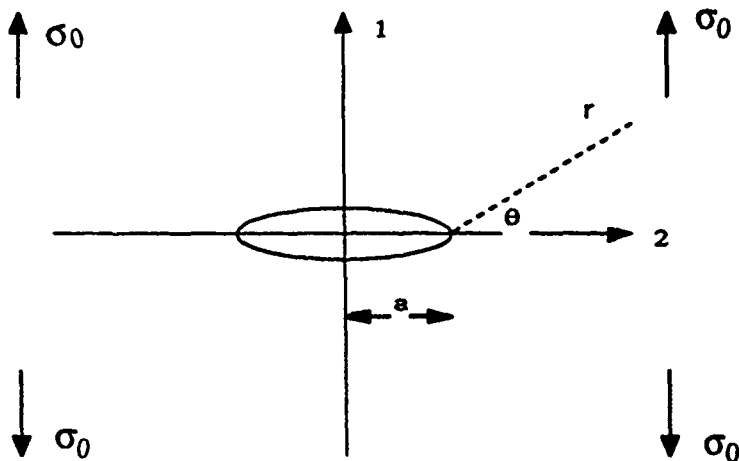


FIGURE 2.6 Sharp crack in a uniformly stressed, infinite lamina.

This stress solution was later modified by Irwin [36] to a solution of the form :

$$\sigma_{ij} = \frac{K}{\sqrt{2\pi r}} f_{ij}(\theta) \quad (2.19)$$

where the parameter K is the stress intensity factor relating the magnitude of the stress intensity local to the crack in terms of the applied load and the geometry of the structure in which the crack is located. For a crack loaded in mode I (tensile opening) Irwin postulated that :

$$K_I \geq K_{Ic} \quad (2.20)$$

represented a fracture criterion where K_I uniquely defines the stress field around the crack tip and K_{Ic} represents a critical value of this stress parameter and is a material property.

The stress intensity approach so far described has concentrated on a crack in a bulk material far away from an interface. However, the presence of a nearby interface as is the case in an adhesive joint, very much complicates the analysis because an applied tensile stress will also induce shear stresses at or near the interface. Thus both K_{II} and K_{III} are required to describe the behaviour of the crack near the interface, (i), but in this region these quantities lose the precise physical significance which they possessed in the bulk material. Mathematical models have been developed to attempt to describe the behaviour of a crack at or near an interface but so far no completely satisfactory model exists. For this reason when applying fracture mechanics to adhesive joint systems, the energy balance approach is the one most frequently followed.

2.5.5 Beam Theory Methods of Analysis

2.5.5.1 Introduction

Eqns. (2.14 and 2.17) require that the load P , the displacement δ and the crack length a be ascertained during crack growth. This can present problems if unstable crack propagation occurs, i.e. if the crack rapidly jumps. However, Williams [37] derived a general analysis for the determination of G for a delamination as shown in Figure 2.7. By applying beam theory to a section just behind the crack tip, where M_1 and M_2 are the bending moments applied to the upper and lower sections respectively and the uncracked portion has a bending moment (M_1+M_2) , then the total energy release rate may be written as:

$$G = \frac{3}{4B^2h^3E_s} \left\{ \frac{M_1^2}{\xi^3} + \frac{M_2^2}{(1-\xi)^3} - (M_1 + M_2)^2 \right\} \quad (2.21)$$

where $\xi=h_1/h_2$, and E_s is the axial modulus of the beam. This result may be partitioned into mode I and mode II components [37] such that:

$$G_I = \frac{6h_1^3}{B^2 E_s h_2^3 (h_1^3 + h_2^3)} \left\{ M_2 - \left(\frac{h_2}{h_1} \right)^2 M_1 \right\} \quad (2.22)$$

$$G_{II} = \frac{18h_1 h_2}{B^2 E_s (h_1 + h_2)^2 (h_1^3 + h_2^3)} [M_2 + M_1]^2 \quad (2.23)$$

which enables an analysis of mixed-mode fracture to be undertaken.

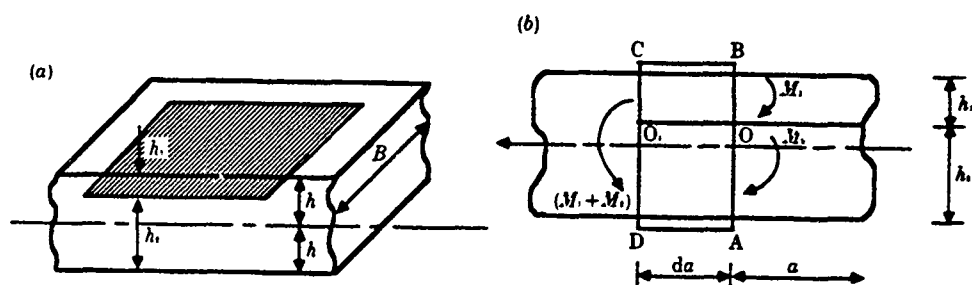


FIGURE 2.7 (a) Delamination and (b) loading on a delamination. After Hashemi et al.

2.5.5.2 Analysis of mode I fracture

Now, for the mode I case, $M_2 = -M_1 = Pa$, so $G_{II} = 0$ and $h_1 = h_2 = h$, so G_c may be expressed as:

$$G_c = \frac{12P^2 a^2}{B^2 h^3 E_s} \quad (2.24)$$

which is referred to as the "load method" in the present work. The specimen compliance, C , may be expressed as:

$$C = \frac{\delta}{P} = \frac{8a^3}{BE_s h^3} \quad (2.25)$$

hence, substituting for E_s from eqn. 2.25 into eqn. 2.24, G_c may be expressed as :

$$G_c = \frac{3P\delta}{2Ba} \quad (2.26)$$

which will be referred to as the "displacement method" in the present work. Hashemi et al [34] showed that it is necessary to correct eqns. 2.24 and 2.26 for the effects of shear rotation, large deflections and end-block stiffening. Indeed, it will be shown in Chapter Four that when the correction factors are employed for adhesive joints, excellent agreement is observed between the values of G_c calculated for adhesively-bonded DCB specimens via equation eqn. 2.17 and via the "corrected" versions of eqns. 2.24 and 2.26. This will be discussed in Chapter Four.

2.5.5.3 Analysis of mixed-mode fracture

In engineering structures, the loading on a component is often a combination of mode I and mode II. This is particularly common in fibre-composites or adhesive joints because crack propagation is often confined to within the interlaminar or adhesive region regardless of the orientation of the applied loads. Various test geometries have been used to measure the fracture energy within these materials when subjected to different ratios of mode I to mode II loading. Two of these geometries will now be discussed.

2.5.5.4 Fixed-ratio mixed mode test

The Fixed-ratio mixed-mode (FRMM) test geometry was employed by Hashemi et. al. [34] and is shown in Figure 2.8. If the specimen contains a symmetrical crack, the ratio of mode I to mode II loading is approximately constant throughout the test at 4/3, hence the values of G_I / G_{II} is 1.33. The bending moments are $M_1 = 0$ and $M_2 = Pa$ in the lower and upper arms of the specimen respectively. Putting these values into eqns. 2.22 and 2.23, the values of the mode I and mode II energy release rates are:

$$G_I = \frac{3P^2 a^2}{B^2 h^3 E_s} \quad (2.27)$$

$$G_{II} = \frac{9P^2 a^2}{4B^2 h^3 E_s} \quad (2.28)$$

The ratio of G_I to G_{II} can be altered by making test specimens with asymmetrically placed cracks, and then testing the specimens using the FRMM test rig. As with the DCB test geometry which is shown in Figure 3.6, it is necessary to correct eqns 2.27 and 2.28 for the effects of shear rotations, large displacements and end-block stiffening. This will be discussed in Chapter Four.

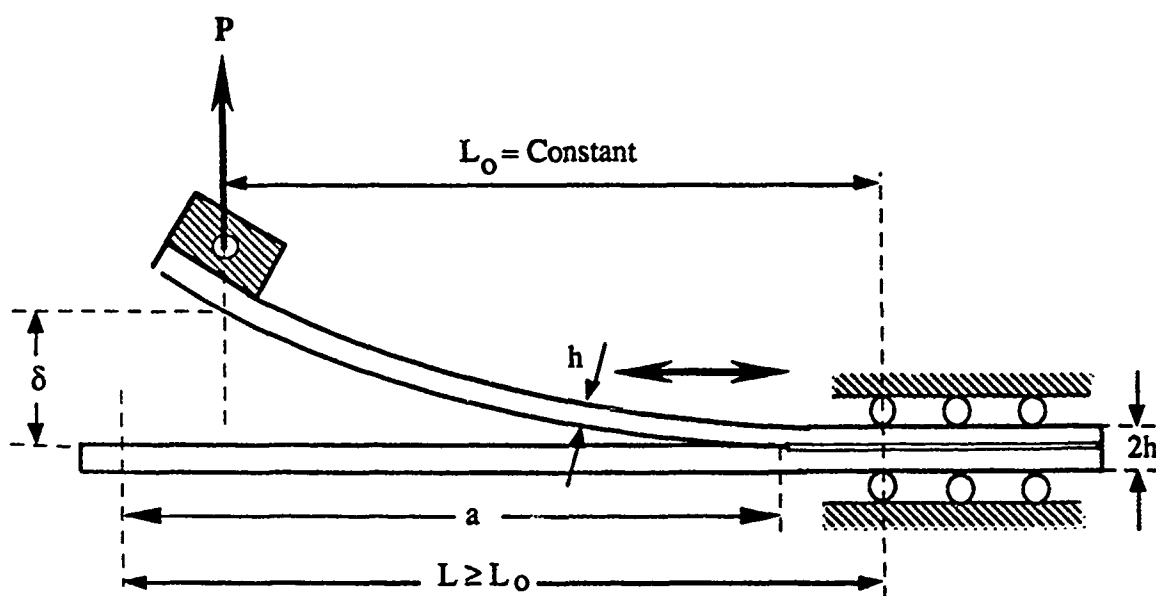


FIGURE 2.8 The fixed-ratio mixed-mode (FRMM) test apparatus. The specimen may slide through the rollers, eliminating any induced axial forces. If symmetrically cracked, then $G_I/G_{II} = 1.33$.

2.5.5.5 The mixed-mode bending test

The mixed-mode bending (MMB) delamination test, designed by Reeder and Crews [38] employs laminates containing symmetrically placed cracks, and can provide a wide range of G_I/G_{II} ratios by the adjustment of the loading lever and lever fulcrum positions. The basic MMB test is shown in Figure 2.9 The bending moments M_1 and M_2 acting on the arms can be calculated by considering the force and moment equilibrium of the specimen, and are given by:

$$M_1 = Pa \left(\frac{c}{b} \right) \quad (2.29)$$

$$M_2 = Pa \left(1 - \frac{c+b}{L} \right) \quad (2.30)$$

Since the specimens used in the MMB test contain symmetrically placed cracks then $\xi = 1/2$. Substituting into the generalized equations (2.22 and 2.23) this yields:

$$G_I = \frac{3P^2 a^2}{B^2 h^3 E_s} \left\{ \left(1 - \frac{c+b}{L} \right) - \frac{c}{b} \right\}^2 \quad (2.31)$$

$$G_{II} = \frac{9P^2 a^2}{4B^2 h^3 E_s} \left\{ \left(1 - \frac{c+b}{L} \right) + \frac{c}{b} \right\}^2 \quad (2.32)$$

and G_I/G_{II} is given by:

$$\frac{G_I}{G_{II}} = \frac{4}{3} \left\{ \frac{\left(1 - \frac{c+b}{L} \right) - \frac{c}{b}}{\left(1 - \frac{c+b}{L} \right) + \frac{c}{b}} \right\}^2 \quad (2.33)$$

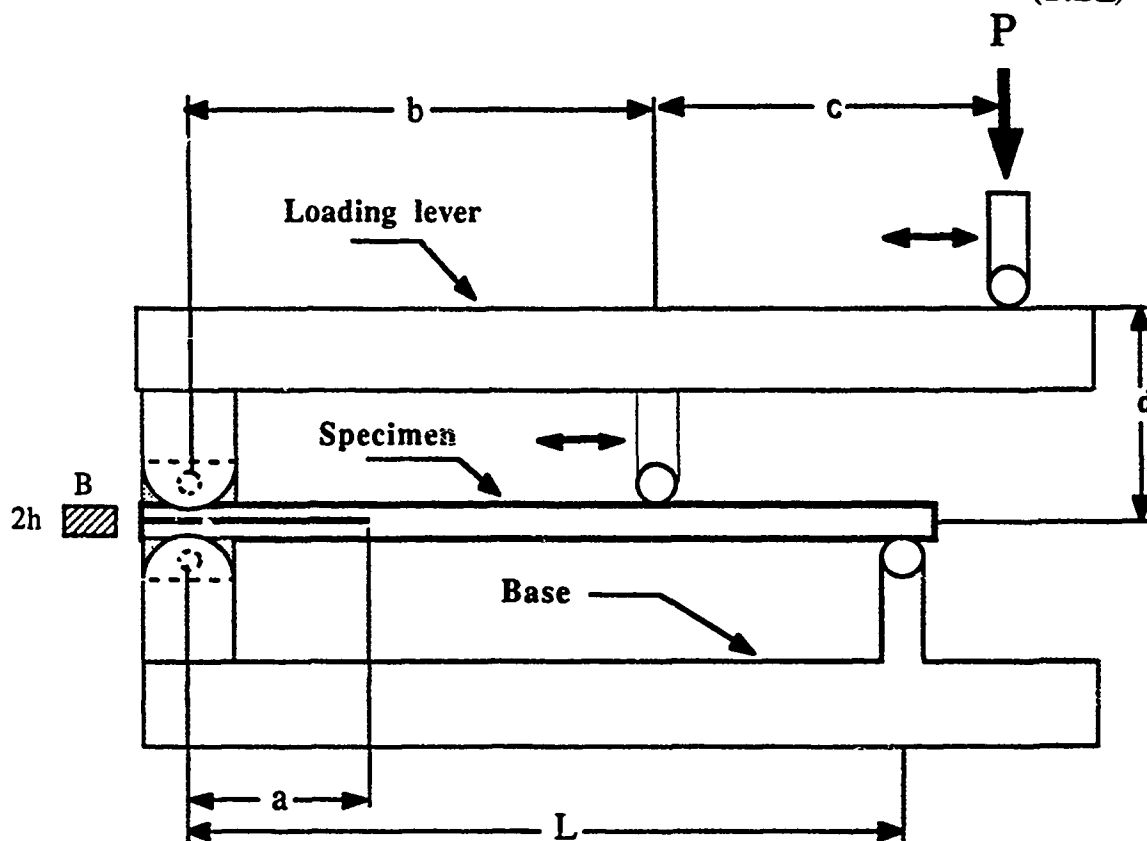


FIGURE 2.9 The basic mixed-mode bending (MMB) test apparatus, designed by Reeder and Crews.

When employing this test apparatus, Reeder and Crews found that the loading lever rotated severely during crack propagation and that the bending moments varied with the crack length, a. However, this geometrically induced nonlinear effect was eliminated in the modified MMB test rig, which is shown in Figure 2.9.

2.5.5.6 The modified mixed-mode bending test

Reeder and Crews [38] found that the non-linear effect in the basic MMB test apparatus shown in Figure 2.9 could be eliminated by making a simple experimental modification. The modification consisted of employing a saddle and bearings through which the load was applied. This eliminated the horizontal force induced in the original MMB test. The modified test apparatus is shown in Figure 3.8. The advantage of the modified MMB test is that it uses symmetrically cracked specimens which are more convenient to study than asymmetrical specimens. In addition, a very wide range of mode I to mode II ratios can be obtained from this test. The correction factors required for the calculation of G_I and G_{II} from this test will be discussed in Chapter Four.

2.5.5.7 A mixed-mode failure criterion

Charalambides et al. [39] proposed that mixed-mode fracture is controlled by the mode I component and that mechanisms exist which convert part of the mode II component to mode I. They then proposed that failure occurs when the total mode I component experienced is equal to a constant, termed G_0 . Thus, failure occurs when G_0 is attained. In pure mode I, G_0 is therefore equivalent to G_c . However, this term should not be confused with the 'intrinsic' G_0 term in eqn. 2.3, as the two are clearly different. Two mechanisms were then proposed whereby G_{II} could be converted to G_I . Firstly, the conversion could be induced by surface roughness, such that the mode I component could be expressed as:

$$G_0 = G_I + \sin^2 \omega \cdot G_{II} \quad (2.34)$$

where ω can be regarded as the slope of the fracture surface roughness. The remaining component of G_{II} i.e. $\cos^2 \omega G_{II}$ is assumed to be lost due to friction and is not converted to mode I. Secondly, the conversion could be induced by a mismatch of elastic properties at an interface. This could be a fibre-matrix interface or an adhesive-substrate interface. This mismatch could be expressed as a change in the applied phase angle of loading ψ , such that the elastic mismatch induces a change ψ_0 in this phase angle. Low values of ψ_0 would

suggest that small amounts of elastic mismatch occurred in the region of the crack tip. These two mechanisms could then be combined into a general criterion for mixed-mode failure given by:

$$G_c = G_c \{ \cos^2(\psi - \psi_0) + \sin^2 \omega \sin^2(\psi - \psi_0) \} \quad (2.35)$$

where G_c is the measured fracture energy, Ψ is the phase angle of the applied loads, Ψ_0 is the phase angle which arises from the elastic mismatch across a bimaterial interface and where ω can be regarded as the slope of the fracture surface roughness.

Using this equation, the failure loci curve, i.e. the curve obtained when the mode I component of G_c is plotted against the mode II component of G_c may be drawn. Figure 2.10 shows a failure locus for the interlaminar fracture of the U/C PEEK composite after Kinloch et al. [40].

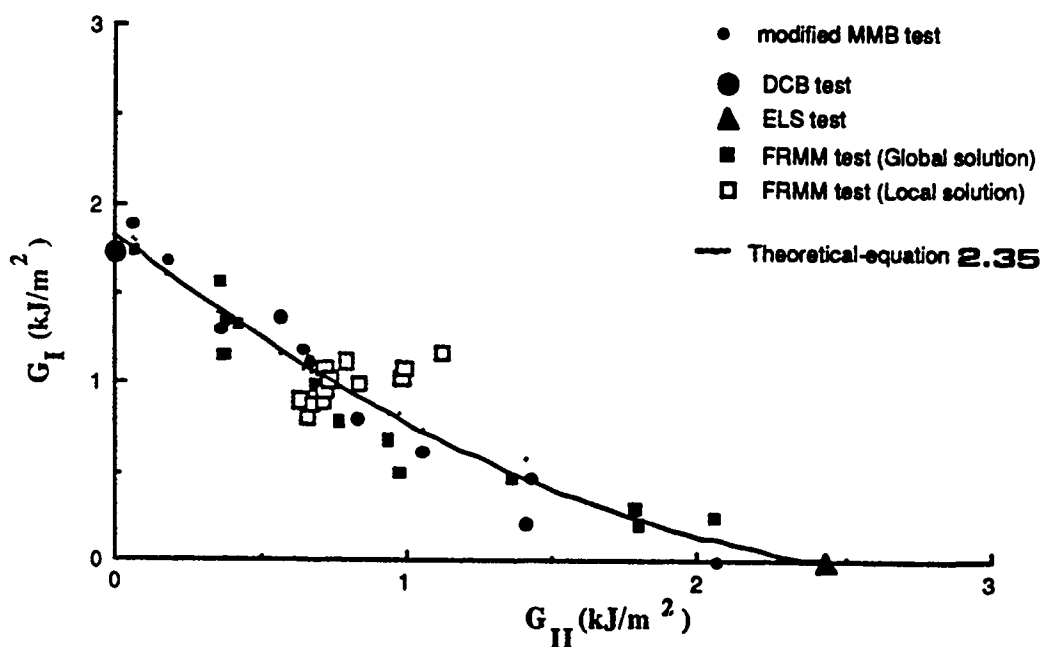


FIGURE 2.10 Failure locus for the U/C PEEK composite at crack initiation. After Kinloch et al [40].

It can be seen that eqn. 2.35 provides a good description of the failure locus. In addition, the pure mode I values of G_c obtained by the DCB test, and the pure mode II values of G_c obtained using an end-loaded split geometry agree well with the theoretical description. In the next section, the mechanisms which contribute to the adhesive fracture energy in modern, toughened structural adhesives will be considered.

2.6 Toughened Structural Adhesives

2.6.1 The Nature of Structural Adhesives

Structural adhesives include epoxy, phenolic or acrylic resins, though epoxies are the most common. They essentially consist of an epoxy resin often based on DEGBA, and harden to give a thermosetting polymer by step-growth or addition polymerization. The term "structural adhesive" is commonly used to indicate that the adhesive possesses relatively high modulus and high strength when hardened, so that the resulting joint can reliably transmit a specified load and hence may be used in 'structural' applications.

Modern structural adhesives are usually toughened by the addition of a second phase material, as are the adhesives employed in the present research. Rubber is commonly added to epoxy adhesives and is designed to react and phase separate before the epoxy hardening reaction has proceeded very far. The resulting microstructure of small, well-bonded rubber particles in a matrix of hardened epoxy may significantly increase the toughness of the adhesive without major losses in important properties such as modulus and creep resistance. Much of the energy which is dissipated during the cohesive failure of a toughened structural adhesive is due to the localized mechanisms operating as a result of the rubber particles within the plastic zone ahead of the crack tip. Given that these mechanisms may be sensitive to test variables e.g. rate and temperature, and that they also may be affected by a hostile environment, they will now be considered in more detail.

2.6.2 Energy Absorbing Mechanisms

2.6.2.1 Shear yielding

According to Huang [41] and Kinloch [42] shear yielding represents the major source of energy dissipation within a toughened adhesive. Shear yielding is the inhomogeneous plastic deformation of a material in the vicinity of the crack tip. Essentially it occurs at constant volume. In a brittle material, e.g. epoxy, shear yielding may be limited to a very small volume ahead of the crack tip. Hence the total amount of energy absorbed by this process is small. However, the inclusion of well bonded and dispersed rubber particles into the epoxy resin may change this behaviour significantly. The inclusion of these particles causes multiple, but localised shear yielding in the matrix. This yielding will be initiated by the stress concentrations which will exist at the rubber particle sites. Shear yield bands form between the rubber particles at 45° to the direction of maximum tensile stress, i.e. in the plane of maximum shear stress. Since about 10% by weight of rubber particles can be added to the

epoxy resin without altering the modulus or T_g of the adhesive, then this is a very effective way to improve its fracture resistance.

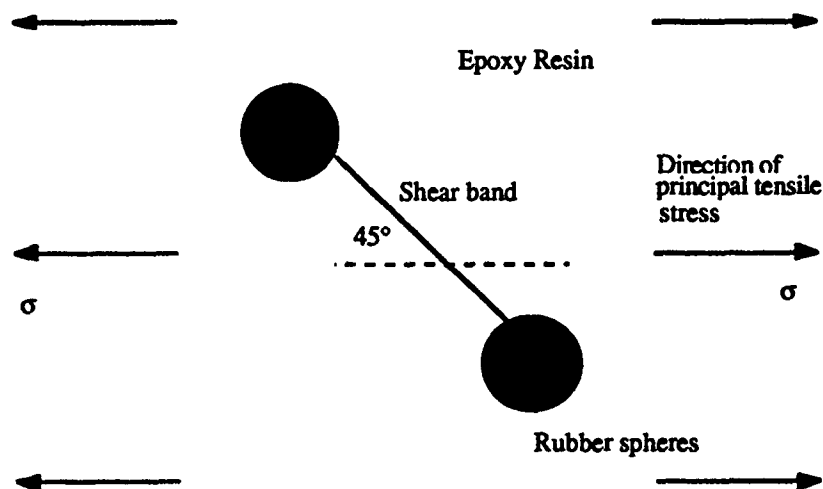


FIGURE 2.11 Shear yielding between rubber particles in an epoxy adhesive.

2.6.2.2 Cavitation and debonding of rubber particles

Heavily crosslinked polymers such as epoxies do not normally possess the chain mobility or extensibility necessary for the formation of crazes [42]. However, the addition of rubber particles introduces stress concentration sites within the epoxy resin. A state of triaxial stress develops at these sites, which may cause the rubber particles to cavitate. This process relieves the stress at the site of concentration and also absorbs energy. In addition, the rubber-epoxy interface may debond and absorb energy, though this mechanism is not thought to be very significant [41].

2.6.2.3 Rubber bridging

It is possible that rubber particles in the crack path may bridge the advancing crack if the rubber-epoxy interface is not sufficiently strong. The deformation and rupture of these particles will also absorb energy in the way that polymer fibrils span a craze.

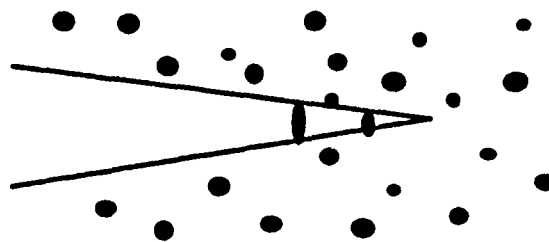


FIGURE 2.12 Rubber particles bridging a crack in a toughened epoxy adhesive.

Having considered the toughening mechanisms which operate within a modified epoxy adhesive, the effects of test rate will now be reviewed.

2.7 Effects of Test Rate on Adhesive Joint Failure

2.7.1 Introduction

In this Section, the effect of test rate on the adhesive fracture energy, G_c , will be reviewed. Clearly, a number of factors should be considered. Firstly, it is possible that the locus of joint failure is sensitive to the rate of applied loading. If so, then a joint system which failed with a high fracture energy, cohesive locus of failure at slow rate, may exhibit an interfacial fracture behaviour at higher rate. Secondly, if the locus of failure remains cohesive, it is possible that the mechanisms responsible for energy absorption, i.e. contributing to the ψ term in eqn (2.3) are rate dependent. Thirdly, the size of the plastic zone ahead of the crack tip, i.e. the volume in which energy absorbing processes are occurring, may be influenced by the rate of loading.

2.7.2 Time Dependent Nature of Polymers

Epoxy adhesives, like all polymeric materials, are visco-elastic, and therefore exhibit time-dependent behaviour. A distinctive feature of their mechanical behaviour is the way in which their response to an applied stress or strain depends on the rate of loading [43]. Elastic materials obey Hooke's Law whereby the stress is proportional to the strain whereas viscous materials, such as liquids, tend to obey Newton's Law whereby the stress is proportional to the strain rate and independent of the strain. The behaviour of polymers is in between these two extremes and is therefore often described as visco-elastic.

At low temperatures and high rates of strain polymers display elastic behaviour whereas at high temperatures and low rates of strain they behave in a viscous manner, flowing like a liquid. Several models have been used to describe linear viscoelastic behaviour. These

models combine elastic springs and viscous dashpots such as the Maxwell model (spring and dashpot in series) or the Voigt model (spring and dashpot in parallel).

A consequence of viscoelastic behaviour is that the strain response of a polymer will lag behind an applied stress. This behaviour is often examined using dynamic mechanical testing [44] where the polymer is subjected to an oscillating sinusoidal stress. Two dynamic moduli may be defined. Firstly, an "in-phase" modulus and secondly, an "out-of-phase" or "loss" modulus. The ratio of the two moduli is known as the loss factor, $\tan \delta_r$. Measuring the dynamic mechanical behaviour of a polymer over a range of temperatures, it is common for the value of $\tan \delta_r$ to show distinct peaks at certain temperatures. These peaks correspond to viscoelastic relaxations or transitions within the material.

The mechanical behaviour of polymers depends on both the testing rate and temperature. A general equivalence was found to exist between these two parameters, such that if a series of mechanical measurements are made over a range of temperatures at different rates the data can be put onto a simple 'master curve' by shifting the data measured at one temperature along the rate axis, by a factor which is a function of the test temperature. Ferry and co-workers [45] proposed an empirical shift factor, a_T , whereby:

$$\log a_T = \frac{-C_1(T - T_r)}{C_2 + (T - T_r)} \quad (2.36)$$

where C_1 and C_2 are constants and T_r is a reference temperature. Eqn. 2.36 is known as the Williams-Landel-Ferry (WLF) equation, and has subsequently been justified theoretically by a consideration of free volumes.

2.7.3 Bulk versus Joint Adhesive Tests

There are two main reasons why the testing of a bulk adhesive may not represent the performance of an adhesive in a real structure. Firstly, the adhesive will typically take the form of a thin bond line within the structure. The proximity of the adhesive, in these circumstances, to the usually higher modulus substrates may well affect the state of stress at the tip of a crack in the adhesive. This in turn will influence the size of the plastic zone ahead of the crack tip and hence the energy absorbed. Secondly, a change in the loading conditions experienced by the real structure may cause a change in the locus of failure. For example, the failure mechanism may change from cohesive to interfacial. A test on a bulk specimen would not be able to indicate this behaviour. It is for these reasons that adhesive joint specimens are preferred to bulk adhesive specimens for the purposes of mechanical testing.

2.7.4 Impact Testing of Adhesive Joints

2.7.4.1 Introduction

Several different approaches have been identified in the literature for impact testing of adhesive joints. Although the different techniques serve to provide useful additional information on what is, a poorly understood area, it should be appreciated that it is difficult to correlate results from one impact test to another. This is because results from an impact test often depend upon the specimen geometry, upon how the load is applied and how the response of the system to the impact is measured and then how this data is analysed. Thus, the desired material property may well be masked by artefacts of the test. Several workers have used an LEFM approach to determine the fracture energy, G_c of adhesive joints. The merit of this approach is that the value of G_c should be a 'material' characterising parameter, independent of the geometry of the specimen and hence extremely useful in the development and selection of adhesives and in engineering design.

2.7.4.2 Instrumented Charpy impact test

An instrumented Charpy impact machine has been previously employed by Kinloch and co-workers [46, 47] to determine the impact resistance of structural adhesive joints. Both bulk adhesive and adhesive joint specimens were tested. The adhesive joint specimens consisted of modified and unmodified epoxy, bonded to aluminium as shown in Figure 2.13. The pendulum striker employed was fitted with a transducer, so that an accurate record of force versus time could be recorded. Since thermosetting polymers are generally brittle and exhibit very little plastic deformation, they readily meet the requirements of LEFM.

By introducing the concept of a dimensionless geometry factor ϕ , [48], such that:

$$\Phi = \frac{C}{\partial C / \partial (a/W)} \quad (2.37)$$

where W is the width of the specimen, C is the compliance and a is the crack length. It may be readily shown that :

$$G_c = \frac{U_c}{BW\phi} \quad (2.38)$$

where U_c is the stored elastic strain energy at the onset of crack growth. The value of ϕ may either be evaluated from measuring the compliance as a function of crack length, or more readily, from published tables.

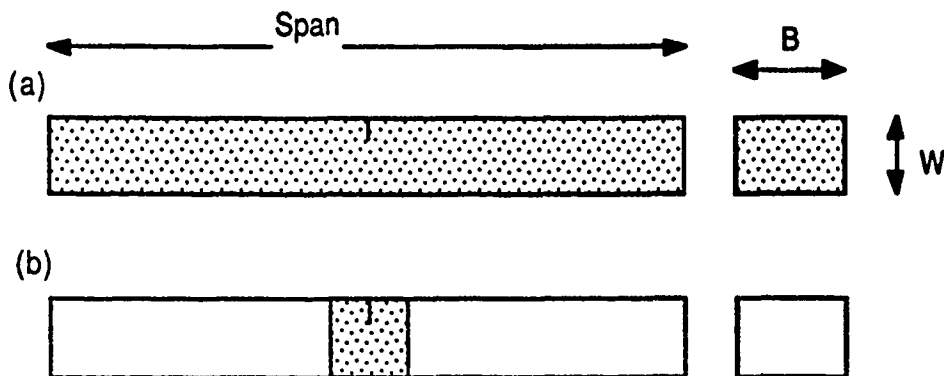


FIGURE 2.13 Charpy impact single edge notched three point bend (SENB) specimens. (a) Bulk adhesive specimen. (b) Epoxy-Aluminium adhesive joint.

Kinloch et al found very good agreement between G_c values for bulk and adhesive joint specimens because crack propagation remained cohesive in the joints, i.e. away from the aluminium-epoxy interface. It was reported [47] that when the rate of loading was increased, the amount of cavitation occurring at the rubber particle sites within the toughened epoxy adhesive decreased, and it was concluded that this might explain the reduction in G_c which was observed at higher rates. The difference between the values of G_c obtained from impact (0.5m/s) and slow rate tests increased with increasing temperature, i.e. as the glass transition temperature, T_g , of the adhesive was approached. Impact speeds of 0.5m/s were not exceeded due to the onset of dynamic effects.

2.7.4.3 Cleavage test

Khalil and Bayoumi [49] employed a cleavage test (ASTM D1062-78) to measure the effect of loading rate on the fracture toughness of adhesively bonded joints. They used compact tension (CT) specimens with aluminium and brass substrates bonded with a two part epoxy adhesive. The specimen geometry is shown in Figure 2.14

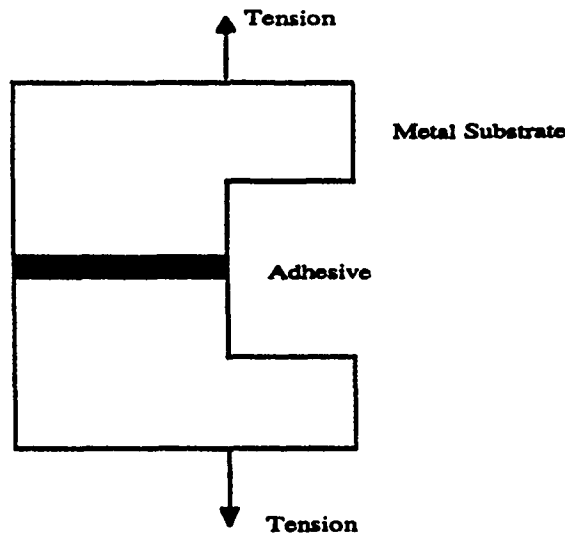


FIGURE 2.14 Compact tension (CT) adhesive joint specimen.

The specimens were tested under tensile loading. Cross-head speeds from 30 to 90 mm/min were employed. G_c was calculated by measuring the area under a load-displacement curve and dividing this figure by the area of the fracture surfaces created. It was found that the effect of increasing the loading rate was to reduce G_c or K_c . A three fold reduction in G_c was recorded over the above range of test speeds.

2.7.4.4 Block shear joint test

The ASTM D 950-82 impact resistance test utilises a block shear joint as shown in Figure 2.15. The fracture energy of the joint is related to the loss of kinetic energy of the impacting pendulum. Clearly, G_c is not obtainable from this test and therefore it does not provide particularly useful engineering data.

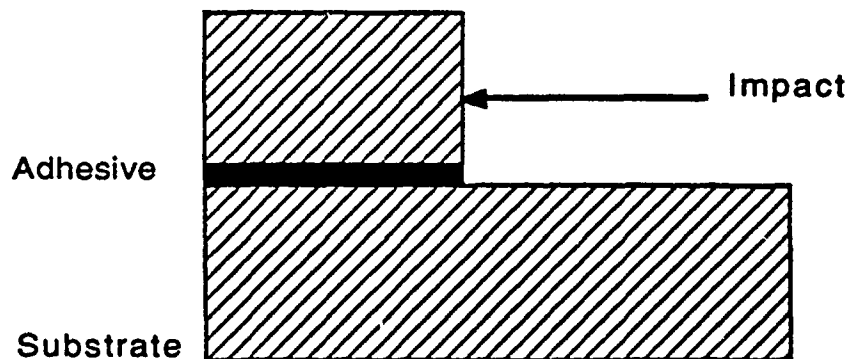


FIGURE 2.15 The ASTM block shear joint test.

2.7.4.5 Tapered double cantilever beam tests.

Gledhill and co-workers [50] and Yamini and Young [51, 52] used a fracture mechanics approach with tapered double cantilever beam (TDCB) specimens to study the effect of resin formulation and conditions of testing on the crack propagation within various adhesive joint systems. Aluminium alloy was employed as the substrate material, which was machined into tapered beams. The epoxy adhesives employed were based upon a DGEBA resin. Starter cracks had been inserted into the adhesive layer, and the joints were loaded at various constant rates of displacement until crack propagation was observed. The adhesive fracture energy, G_c , was determined from the relationship:

$$G_c = \frac{4P_c^2 m}{E_s B^2} \quad (2.39)$$

where P_c is the applied load required to cause crack growth, E_s is the modulus of the substrate, B is the specimen thickness and 'm' is a geometry factor. It was found that both the yield stress and modulus increased with increasing crosshead displacement rate, but over the range of rates employed (10^{-6} - 10^{-3} m/s), there was no significant change in G_c . However, as the rate of test varied, a change in crack propagation behaviour was observed. As the test rate was increased, a change from stick-slip to more continuous crack propagation was observed. This was also observed in bulk adhesive specimens. It was shown that the formulations which had the highest yield stress tended to fail by continuous propagation whereas the materials with lower yield stresses undergo stick-slip propagation. They argued that when crack propagation was continuous, a constant crack opening displacement provided a unique failure criterion. However, this criterion did not predict failure when stick-slip crack propagation occurred, nor did it explain why there was a transition between the two types of propagation behaviour. The different types of crack propagation will be considered in section 2.7.5.

2.7.4.5 Double cantilever beam tests

A review of the literature suggests that the DCB specimen has not been previously used for testing adhesive joints at high rates. However, the DCB test specimen has been widely used for the measurement of interlaminar fracture energies of composites materials at high rates of strain e.g. [53-55]. Smiley tested two fibre-composite materials, a U/C epoxy composite and a U/C PEEK composite. He reported that the fracture toughness in mode I for both composites decreased as the rate of test increased. For the U/C epoxy composite, Smiley

reported that G_c decreased from 0.18 kJ/m^2 to 0.04 kJ/m^2 over four decades of loading rate. For the U/C PEEK composite, he reported that G_c decreased from 1.6 kJ/m^2 to 0.4 kJ/m^2 at crack initiation over five decades of loading rate. However, Kinloch et al. [56] showed that, over the same range of loading rates, there was no reduction in the value of G_c for either the U/C epoxy composite or the U/C PEEK composite. Their results for the U/C PEEK composite can be seen in Figure 2.16. Beguelin [53] used a Fast Fourier transform filtering technique to filter out some of the oscillations in the force-time traces recorded during the mode I testing of U/C PEEK. He employed displacement rates of up to 1.3 m/s and showed that the value of G_c (il) for this composite decreased only slightly over four decades of test rate.

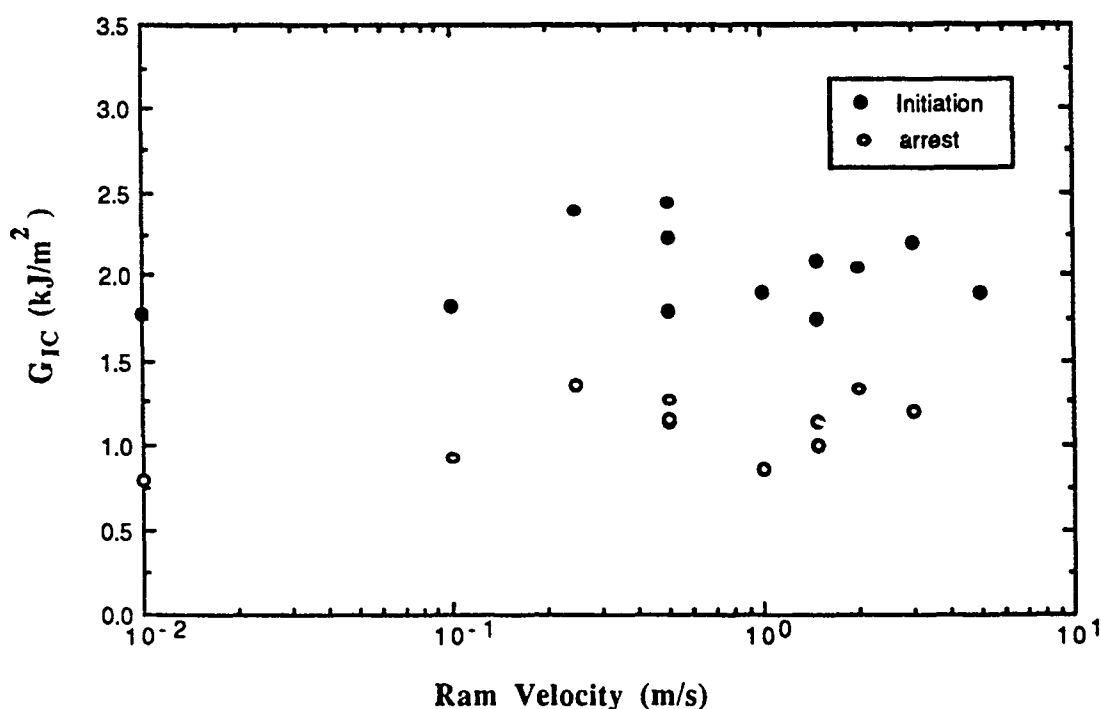


FIGURE 2.16 The variation in the value of the interlaminar fracture energy, G_c , for the U/C PEEK composite versus ram displacement rate. Values of G_c at both crack initiation and crack arrest are shown. After Kinloch et al [56].

The review of the work performed in the area of high rate testing of fibre-composites indicates that the results obtained by different workers differ considerably. It is therefore important that careful attention is paid to correctly interpreting data from a high rate DCB test, to ensure that valid values of G_c are obtained. This will be discussed further in Chapter Six, when it will be shown that the values of G_c obtained from a high rate DCB test depend significantly on how the values of G_c are calculated.

2.7.5 Types of Crack Propagation

It has been reported [1] that there are three distinct types of crack propagation which may occur in rigid substrates. These will now be described in turn. It should be noted that an adhesive may exhibit a combination of these types and the type of propagation will also depend on the temperature and rate of test, as will be discussed later in this Chapter.

2.7.5.1 Stable, ductile propagation (Type A).

Stable, ductile propagation, termed Type A, is characterised by slow, stable growth of the crack through the adhesive. Plasticity in the vicinity of the crack-tip causes blunting of the crack and ductile, but stable crack growth results. The resulting fracture surfaces are rough, showing extensive signs of plasticity and stress whitening. The corresponding value of G_C or K_C is much higher than for Type C fracture.

2.7.5.2 Unstable, brittle propagation (Type B)

Unstable, brittle propagation, termed Type B, is characterised by the stick-slip propagation of the crack. The resulting force-displacement trace has a saw tooth appearance as shown in Figure 2.17. The saw tooth represents repeated crack initiation and arrest. The fracture surface clearly shows the jump and arrest points and it is possible to calculate G_C or K_C at initiation (G_{Ci} , K_{Ci}) or at arrest (G_{Ca} , K_{Ca}). This type of crack growth occurs in adhesives which are more ductile than Type C, as was observed by Yamini and Young [51]. Gledhill and co-workers [50] reported that the transition from Type B to Type A crack propagation behaviour may be induced by a change in test temperature or test rate. A possible explanation for this effect was proposed [51] in terms of dG_C/da' becoming negative and so leading to stick-slip propagation. However, they argued that this was more likely to be a consequence of the transition rather than a reason for it. They concluded that there must be subtle changes in the structure of the material at different testing rates and temperatures which lead to the different types of crack propagation taking place.

2.7.5.3 Stable, brittle propagation (Type C)

Stable, brittle crack propagation, termed Type C, is the third type of crack propagation commonly observed. The resulting fracture surfaces are relatively featureless and failure occurs at a low value of G_C or K_C . The resulting force versus displacement trace for a typical failure of this type is shown in Figure 2.17.

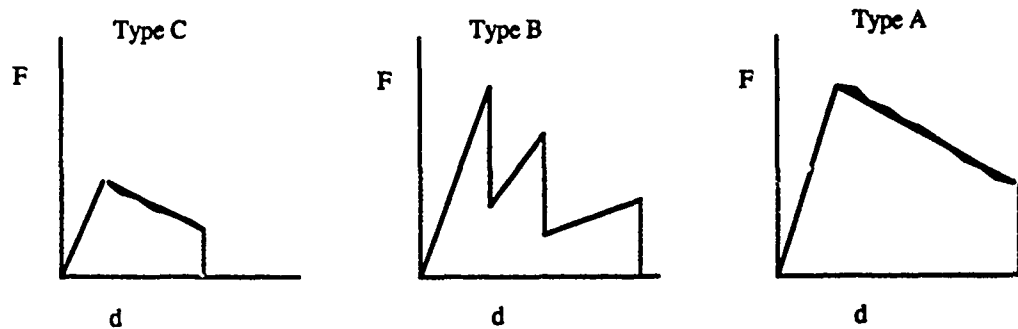


Figure 2.17 Types of crack propagation : (C) stable, brittle; (B) unstable, brittle; (A) stable,

2.7.6 Dynamic Effects

The occurrence of dynamic effects have been widely reported in impact testing [46, 57]. In the instrumented charpy impact test, for example, a pendulum striker impacts upon a supported specimen. Often the force transducer is mounted on the pendulum. It is therefore important to realise that the energy deduced from such measurement is that lost by the stiker. However, for the calculation of the true "material property" values e.g. G_c , the force that is needed is that acting on the specimen and the energy needed is that gained by the specimen. These values may be different for the following reasons:

- (i) High contact stiffnesses of the striker / specimen interface.
- (ii) Repeated reflection of stress waves in the specimen.
- (iii) The repeated loss and regain of contact between striker and specimen during the test.

As the rate of test increases, these effects become more pronounced. Kalthoff [57] observed the loss of contact directly and such effects have been modelled using theories recently advanced by Williams and Adams [58]. They proposed a mass-spring model to describe the behaviour of a charpy impact specimen during a test. In addition, much can be done to minimise the magnitude of dynamic effects. This aspect will be discussed further in Chapter Three.

2.7.7 Concluding Remarks

It can be seen that from a review of the literature, there is some confusion as to the effect of test rate on the fracture behaviour of adhesive joints. Kinloch and co-workers [46] showed a considerable reduction in G_{Ic} at impact speeds of 0.5m/s. Khalil and Bayoumi [49] reported a three fold reduction in K_{Ic} over a narrow range of test rates, whereas Yamini and Young [51]

reported no significant change in G_{Ic} over three decades of displacement rate. In addition, there was little agreement on the results obtained from the high rate DCB testing of composite materials. Smiley [59] reported that the interlaminar fracture energy of both U/C epoxy and U/C PEEK was severely reduced by an increase in the rate of the test. However, over the same speed range, Kinloch et al [56] showed that the value of G_c of these materials were not sensitive to test rate, and Beguelin and co-workers reported only a small strain rate sensitivity.

In Chapter Three, a procedure for for measuring G_c over a wide range of displacement rates for DCB adhesive joints will be described. The results of these tests will be presented and discussed in Chapter Six. The final Section of the literature review will now consider the effect of a hostile environment (water) on the fracture behaviour of adhesive joints.

2.8 Effects of Test Environment on Adhesive Joint Failure

2.8.1 Introduction

In this section the environmental durability of adhesive joints is reviewed. As the vast majority of bonded structures are exposed to moist air, then before the structures can be accepted in to load bearing applications it is necessary to assess their environmental durability. Many studies have shown that water represents one of the most aggressive environments commonly encountered by adhesively bonded structures [1]. This problem is compounded by the polar nature of adhesives, that is they are inherently hydrophilic, and thus they absorb water. The rate at which a humid environment may affect the properties of an adhesive joint depends upon several factors. Firstly, it depends on the concentration of water i.e. the relative humidity if exposed to moist air. Secondly, it depends on the temperature, as a higher temperature will speed up the rate environmental attack. Thirdly it depends on the joint design and whether the joint is under stress. All of these factors influence the rate at which water is able to penetrate into the joint and modify its properties. Several mechanisms for water penetration have been proposed, but it is considered that diffusion represents the most important of these [60]. Now, the reduction in mechanical performance of an adhesive joint system can result from either an alteration of the adhesive properties, from a loss of interfacial adhesion, or possibly by a deterioration of substrate properties.

Traditionally, problems resulting from environmental failure of adhesive joints have mainly stemmed from the use of high surface energy, polar substrates e.g. metals and ceramics. The environmental durability of adhesive joints between these materials has been extensively investigated [5, 61]. By contrast, traditional engineering plastics, e.g. epoxies and phenolics have posed few problems in the area of environmental durability {refer to TABLE 2.1}.

Although adhesives suffer some loss of performance, the interface between CFRP substrates and an adhesive is not generally attacked.

However, the recent rapid increase in the use of thermoplastic materials and the advent of new surface pretreatment techniques e.g. corona discharge and gas plasma, have made adhesively bonded thermoplastics a realistic option for use in engineering structures. A review of the literature reveals however, that little work has been performed in this area. Important questions which should be addressed are firstly, whether the plasma induced interfacial forces between thermoplastic substrates and the structural adhesives are susceptible to environmental attack and if this is the case, then whether this may induce a change in the locus of joint failure as commonly observed with metallic substrates. Secondly, if the interfacial integrity is maintained, it is still possible that a significant loss in the mechanical performance of the joint system may be encountered by exposure to a hot-wet environment. The factors affecting the environmental resistance of adhesive joint systems will now be considered.

2.8.2 Factors Affecting Environmental Resistance

2.8.2.1 Effect Of Water Concentration

A great deal of experimental evidence has been published e.g. [5, 62, 63] showing that the durability of adhesive joints is sensitive to the concentration of water in its environment. Invariably the results show that as the concentration of water, i.e. the relative humidity (RH) is increased, then the rate of loss of mechanical performance of the joint system is accelerated. Joints completely immersed in water have been found to deteriorate most rapidly and hot/wet tropical sites have been shown to be far more damaging than hot/dry desert sites [64].

Gledhill and co-workers [65] proposed a model for predicting joint durability. They proposed that the first stage in the environmental failure process was the accumulation of a critical concentration of water in the interfacial regions of the joint. They reported that when joints, consisting of mild steel bonded with an epoxy adhesive, were kept at 20°C and 55% RH prior to testing they did not appear to suffer from attack by moisture, even when exposed to these conditions for a long duration. The joints suffered no decrease in strength, no change in the locus of failure and it was confirmed that equilibrium conditions did exist, i.e. the concentration of water in the adhesive had reached the equilibrium value, termed C_{∞} . It was therefore proposed that a critical level of water concentration, C_c , might exist in the adhesive layer, below which environmental failure is precluded. This is also referred to as the limiting equilibrium water concentration, (LEWC).

Brewis et al [66] proposed a justification for the existence of a LEWC. They argued that the process may be analogous to the hydration of a salt. Below a certain RH, water is absorbed by the adhesive and held by it i.e. it is not available to attack the interface. However, at higher RH's, the adhesive becomes saturated and hence the surplus water is free to attack the interface. However, Bowditch et al [67] repudiated the claim that a LEWC exists. They argued that the LEWC is really an artefact of the durability test and may be caused by either the adhesive not being in equilibrium with the environment or by a reduction in the internal stresses in the joint due to the presence of moisture. To show this they used a technique in which the normal structure of the joint was reversed and an impermeable substrate was finely divided and surrounded by a permeable adhesive. Their rationale was that they could be sure that the adhesive was in equilibrium with the environment. Measurements of modulus against equilibrium water content (EWC) showed no limiting value and they found that water, even at very low concentrations, caused a reduction in modulus. This was attributed to disruption between the adhesive and 'substrate'. It is matter for debate whether the arguments put forward against the existence of an LEWC are valid. However, it is very possible that there are other complex mechanisms operating simultaneously which account for the existence of the LEWC. Possible mechanisms will be examined later in this Section.

2.8.2.2 Effect of service temperature

Gledhill et al [5] showed that the retention joint strength was sensitive to exposure temperature. Mild steel-epoxy butt joints exposed to water at 20°C for 2500 hours retained 80% of their unaged 'dry' strength, whereas when similar joints were exposed for the same duration at 60°C, the joints retained less than 20% of their dry strength. Increasing the temperature of the environment increases the rate of strength loss. Using a somewhat higher exposure temperature than may be experienced by the actual bonded structure is a typical method of accelerating the rate of attack in a laboratory test [1]. The aim of an accelerated test is to simulate the same mechanism(s) of failure as are seen in normal useage, but cause them to occur more rapidly. However, when some adhesives are heated in water at say, 70°C to 100°C then hydrolysis of the adhesive may occur [60] which would not have occurred in service at moderate temperatures. It is therefore important to avoid introducing mechanisms which would not occur in service and may lead to misleading results being obtained.

2.8.2.3 Effect of the adhesive joint system

If the adhesive possesses a high water solubility parameter, i.e. it is highly hydrophilic, then it will be susceptible to environmental attack if it comes into contact with moisture. In

addition, if the adhesive contains a fibrous carrier, then this may provide an additional path for moisture ingress. This may speed up the passage of water into the adhesive, and accelerate the deterioration of properties. The mechanisms of water ingress will be discussed later in Section (2.8.3).

The type of substrate material employed in an adhesive joint will clearly affect its environmental durability. It is possible that corrosion of the substrate will accelerate the rate of environmental attack. It is also possible that the adhesive-substrate interface will show thermodynamic instability in the presence of an ingressing liquid such as water. In addition, if the substrate is permeable to water, then this may also speed up the rate of environmental attack. Adequate surface pretreatment is a prerequisite for a strong, durable bond. Not only should weak surface layers be removed but, in the case of metallic substrates, it is necessary to form stable oxides to which the adhesive can bond by forming strong, stable intrinsic forces at the interface. Often primers are used to achieve this. In the case of corona or plasma treated thermoplastics, very little experimental data is available concerning their resistance to environmental attack. This will be investigated in detail in Chapter Seven.

2.8.2.4 Effect of applied stress

An applied tensile or shear stress will accelerate the rate of environmental attack. The source of the stress may be external or internal. Internal stresses may be induced as a result of adhesive swelling caused by water uptake, or shrinkage during cure. These stresses may increase the susceptibility of primary and secondary bonds to environmental attack, by lowering the activation energy for bond rupture [60]. Eqn. 2.5 highlighted the adverse effect that premature interfacial bond failure has on the fracture energy, G_c . However, plasticization of the adhesive may induce stress relaxation and crack tip blunting mechanisms which may cause a short term increase in the toughness of the adhesive. In addition, it is possible that, even if an adhesive-substrate interface is thermodynamically stable, the presence of an applied stress will cause interfacial debonding. When the value of W_{AL} is positive, but $W_{AL} \ll W_A$, then the forces of intrinsic adhesion across the interface may have been reduced to a level which is insufficient to prevent instability.

2.8.3 The Mechanisms of Environmental Attack

It has been proposed [68] that water enters an adhesive joint by a combination of one or more of the following processes:

- (a) Diffusion through the adhesive.
- (b) Transport along the interface.

- (c) Capillary action through cracks and crazes in the adhesive.
- (d) Diffusion through the substrate.

The water, having entered the adhesive joint, may then weaken it by a combination of one or more of the following processes.

- (e) Reversible alteration of the adhesive properties e.g. plasticization and depression of T_g .
- (f) Irreversible alteration of the adhesive properties e.g. hydrolysis and cracking.
- (g) Displacement of the adhesive at the adhesive-substrate interface
- (h) Swelling induced stresses in the joint.

Clearly, some or all of the mechanisms proposed for water ingress (a-d) may occur concurrently when a joint is operating in an hostile environment. Taking the example of a joint between metallic substrates (e.g. steel or aluminium), then water transport along the oxide layer at the interface may be significant and represent a mechanism for water ingress into the joint. However, polymeric materials do not form oxide layers, so water transport along a CFRP substrate-adhesive interface is less likely. Capillary action through cracks and crazes is more likely to occur if the joint is under stress, but it is not common for crazes to occur in epoxy adhesives. It is possible that rubber particles cavitation sites may induce a similar effect, particularly if the joint is stressed. Water diffusion through the substrate is clearly a possibility, however the rate of diffusion is likely to be much less than through the adhesive. Of the various mechanisms of water ingress proposed, that of diffusion through the adhesive layer is the one considered to be the most important [60], and to dominate the water ingress process. This will be considered in Section 2.8.6. However, the various effects which water may have on an adhesive is reviewed next.

2.8.4 The Effects of Water on an Adhesive

2.8.4.1 Introduction

Having entered the adhesive, water may alter its properties in either a reversible or an irreversible manner. Plasticization and adhesive swelling are examples of reversible alterations. Their effect will reverse if the adhesive is able to dry out. However, hydrolysis, cracking and crazing are irreversible effects. These cannot be reversed. These effects will now be reviewed.

2.8.4.2 Reversible adhesive effects

The absorption of water causes a reduction in the T_g and may also lower the modulus and yield strength of an adhesive. Thus, its ability to plastically deform may be increased. Plasticization may increase the short term toughness of the adhesive by increasing the size of the plastic zone and thus the energy absorbing micro-processes occurring. In addition, water may cause the adhesive to swell, and therefore introduce undesirable stresses into the joint. The tendency for an adhesive to display reversible alterations appears to depend upon the water concentration within the environment. In addition, the outer adhesive zone in which the critical water concentration is reached may be regarded as a crack of length, a , in the bond line. This has been modelled using a fracture mechanics approach [1].

2.8.4.3 Irreversible adhesive effects

The absorption of water may also cause irreversible changes to occur within the adhesive. Hydrolysis, cracking and crazing are examples of this type of behaviour. Hydrolysis occurs when the adhesive reacts chemically with the ingressing water. This reaction will alter the finely tailored chemical microstructure within the adhesive and may reduce its modulus and yield strength. However, epoxy adhesives are not particularly prone to chemical attack at moderate temperatures, i.e. below 70°C.

The formation of cracks and crazes within the adhesive is potentially more damaging than hydrolysis. They are formed most commonly when the adhesive is subjected to varying climates and particularly, varying temperatures. A craze is essentially a porous region of polymer with a lower density than the surrounding material [69]. It is initially less dangerous than a crack because it transmits some load by the stabilizing polymer fibrils. However, localised yielding, or microvoiding will cause the craze to degenerate into a crack. The voids coalesce and a crack is formed. Clearly the formation of crazes may accelerate the water diffusion process and allow water to ingress into the adhesive by capillary action. This will accelerate the rate of environmental attack and may cause the formation of a crack of critical length to induce catastrophic failure of the joint.

2.8.5 The Effect of Water on the Interface

If a liquid, e.g. water, is able to reach the interfacial region between the adhesive and the substrate, and if W_{AL} becomes negative, then the liquid will displace adhesive. This may result in a change in the locus of failure from cohesive to interfacial. Such a change has a very dramatic effect on the fracture performance of the joint. The major contribution to the

mode I fracture energy, G_c , of a cohesively running crack is from the viscoelastic and plastic energy dissipative processes which occur within the plastic zone ahead of the crack tip. By contrast, the propagation of a purely interfacial crack requires only the rupture of interfacial bonds and the energy absorbed by this process is comparatively small. Thus, the environmental attack of an interface is a serious matter.

The kinetics of the water ingress process, which will be considered in Section 2.8.6, may delay the break down of an interface which is thermodynamically unstable. If the concentration of water needs to reach a critical level at the interface before the adhesive starts to be displaced, then the displacement procedure itself will not be instantaneous. Essentially, if the interface is stable and there are no weak boundary layers present, then interfacial failure will not occur spontaneously. However, if there is an applied stress present, it is possible that there may still be debonding at the interface, despite $W_{AL} > 0$. Thus, an externally applied driving force may overcome the intrinsic forces of adhesion which were weakened by the presence of the environment.

It is generally agreed in the literature that CFRP substrates form stable interfaces with epoxy adhesives. However, most of the data quoted is for fibre-composites based on thermosetting polymers, e.g. epoxy and phenolic resins. Little work has been performed on the environmental stability of joints containing thermoplastic based substrates. This will be investigated in detail in Chapter Seven.

2.8.6 The Kinetics of Water Entry

2.8.6.1 Fick's laws

Steady-state diffusion of water into a polymer operating above its T_g (i.e. in a leathery state), can be described as Fickian, as it obeys Fick's First Law [70, 71]. In general, glassy polymers exhibit non-Fickian behaviour. However, it has been observed that water diffusion in structural adhesives is markedly Fickian, even in the glassy state [60]. Fick's first law states that the amount of substance diffusing in the x -direction across a plane of unit area in unit time is known as the flux, F_x , and is related to the concentration gradient of the substance, $\partial c / \partial x$, by:

$$F_x = -D \frac{\partial c}{\partial x} \quad (2.40)$$

where D is the diffusion coefficient of water in that substance. Eqn. 2.40 may only be applied to steady-state diffusion, i.e. when the concentration of water at any point in the system is not changing with time. Therefore, during uptake and decay of diffusing species, this is not valid.

Non steady-state diffusion can be modelled in terms of Fick's Second Law. This considers the change in concentration of diffusing species with time in an element of the substance. The law proposes that this is controlled by the fluxes crossing the six faces of the element shown in Figure 2.18.

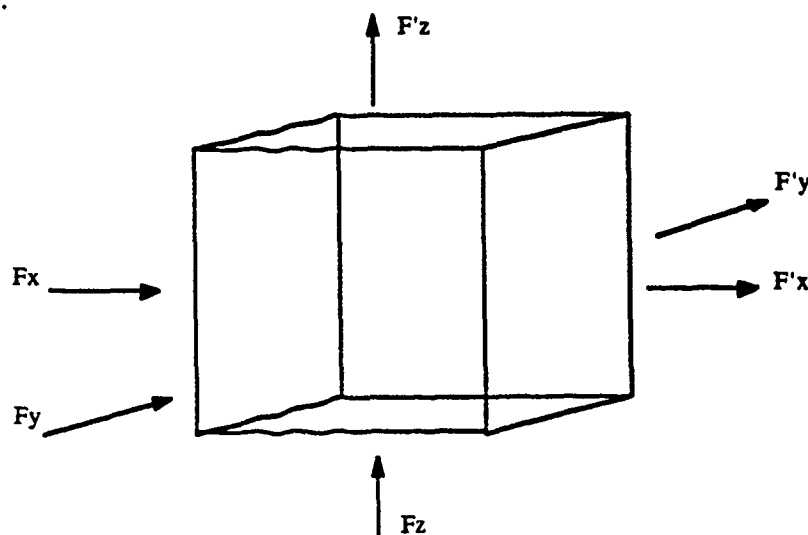


FIGURE 2.18 Fluxes entering and leaving a Cartesian volume element.

Thus, in Cartesian co-ordinates, Fick's second law may be expressed as:

$$\frac{\partial c}{\partial t} = D \left\{ \frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2} \right\} \quad (2.41)$$

This equation may be simplified if it is assumed that diffusion is restricted to only the x -direction. This assumption would be valid for the case of a thin film, where the vast majority of diffusion would occur in one direction. In such a case, eqn. 2.41 may be recast as:

$$\frac{\partial c}{\partial t} = D \left(\frac{\partial^2 c}{\partial x^2} \right) \quad (2.42)$$

Solutions to various forms of the second law appropriate to particular boundary conditions may be determined [70]. A frequently used solution is for the case of a semi-infinite film of thickness $2l$ in an infinite water bath, and is given by:

$$\frac{C_t}{C_\infty} = 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)} \exp\left\{-\frac{D(2n+1)^2 \pi t}{4l^2}\right\} \cos\left\{\frac{(2n+1)\pi x}{2l}\right\} \quad (2.43)$$

where C_t is the concentration of water at time t , at point x and C_∞ is the equilibrium water concentration. It is assumed that the film is initially free from water and that equilibrium between the water bath and the film surface is established instantaneously upon immersion. Eqn. 2.43 may be integrated to give the total water uptake by the film at time t , and may be expressed in terms of the fractional uptake M_t/M_∞ as:

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left\{-\frac{(2n+1)^2 \pi^2 D t}{4l^2}\right\} \quad (2.44)$$

At short times, eqn. (2.44) may be expressed as:

$$\frac{M_t}{M_\infty} = \frac{4}{l} \left(\frac{Dt}{\pi}\right)^{\frac{1}{2}} \quad (2.45)$$

and thus the fractional water uptake is linear with root time. Eqns. 2.40-2.45 require that an accurate value of the diffusion coefficient, D , may be obtained. The measurement of this parameter will now be discussed.

2.8.6.2 The diffusion coefficient, D

The measurement of the water diffusion coefficient for an adhesive material has been well documented by Comyn [60]. Essentially, if a thin film of adhesive is placed in liquid water or liquid vapour at static pressure, then the water diffusion coefficient, D , may be determined. This is achieved by measuring the mass uptake of water by the adhesive, as a function of time.

The adhesive film specimens should be of semi-infinite geometry, so that water uptake from the edges can be ignored. The films are then placed in liquid water, representing an infinite bath, after being accurately weighed. The films are then periodically removed from the bath, carefully wiped dry, and weighed. The fractional mass uptake (M_t/M_∞) may then be plotted against root time. Eqn. 2.45 may then be used to calculate the diffusion coefficient, D , for the linear region of water uptake. Water uptake in this region is termed Fickian and typically extends up to $(M_t/M_\infty) = 0.6$. A graph of this type is known as an uptake or sorption plot.

An example of an uptake plot for an epoxy adhesive, based on DGEBA-DMP epoxide, in water at 45°C is shown in Figure 2.19 [72].

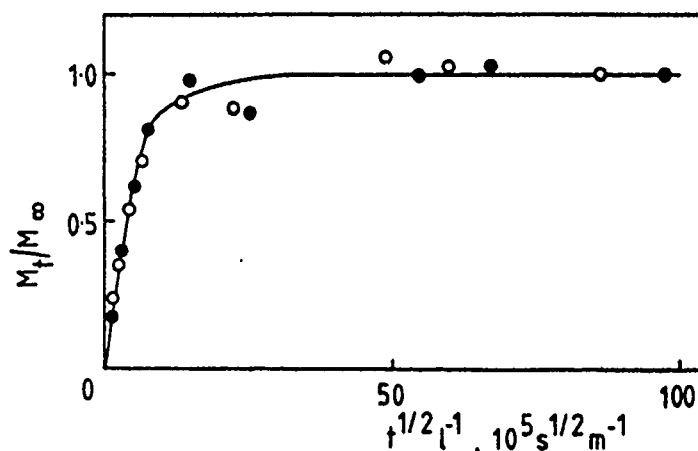


FIGURE 2.19 Uptake of liquid water at 45°C by the DGEBA-DMP epoxides. Adhesives show Fickian behaviour. After Brewis et al. [72]

2.8.6.3 The solubility and permeability coefficients

The solubility coefficient, C_∞ , is defined as the mass of water absorbed in grammes per 100g of adhesive. It thus provides a measure of how soluble a liquid is in a given adhesive. The ability of an adhesive to transmit a liquid is clearly going to depend on the diffusion coefficient, D , and on the solubility coefficient, C_∞ . The permeability coefficient is defined by the product of diffusion and solubility coefficients, i.e. DC_∞ .

2.9 Concluding Remarks

In Chapter Two, the main subject areas which will be extended in the following Chapters have been reviewed. From an understanding of the factors necessary to enhance the intrinsic adhesion of difficult to bond materials, and from a knowledge of fracture mechanics, it is possible to investigate the performance of adhesive joint systems under various test conditions. The materials employed and the major experimental techniques used will now be discussed in Chapter Three.

Chapter Three

Material Characterization

3.1 Introduction

The purpose of this chapter is four-fold. Firstly, a full description of all the materials employed in this project will be given, together with details of the curing cycles involved for both the polymeric fibre-composites and the adhesives. Secondly, the surface pretreatment techniques that have been utilized will be described, including the corona-discharge and gas plasma treatment. Thirdly, the mechanical testing techniques will be described. This includes the experimental techniques employed for the mode I and mixed-mode testing of joints at slow rates, the procedure employed for high rate testing and the details of the various environmental durability tests which were conducted. Finally, the surface analytical techniques of scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS), which have been used to characterize treated surfaces prior to bonding and to characterize the post-failure fracture surfaces will be discussed.

3.2 Materials and Surface Pretreatment Techniques

3.2.1 Materials Employed

3.2.1.1 Polymeric fibre-composites

The polymeric-fibre composites which have been employed in this work were as follows:

(a) **U/C PEEK (APC-2).** APC-2 is a thermoplastic fibre-composite based upon a poly(ether-ether ketone) matrix. PEEK is a semi-crystalline polymer with a glass transition temperature of 140°C and a melting temperature of 343°C. The chemical structure of PEEK is shown in Figure 3.1. The bulky main chain aromatic rings are prone to entanglement and hence impart a high toughness to this material. Indeed, it is the high toughness of this material which explains why it has received so much attention as an engineering thermoplastic. In APC-2 the PEEK matrix is reinforced with unidirectional AS4 carbon fibre with a nominal fibre volume fraction of 61%. The material was supplied by I.C.I Plc.

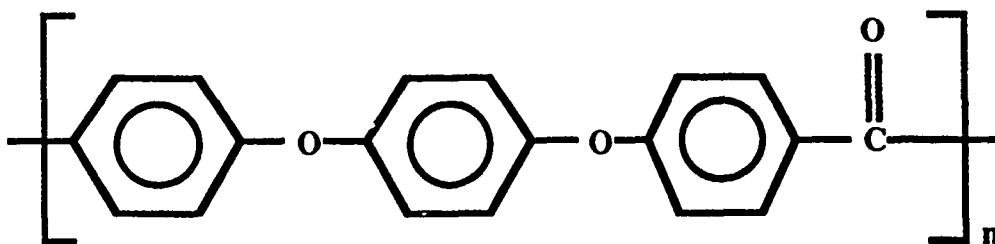


FIGURE 3.1 Chemical structure of poly(ether-ether) ketone (PEEK)

(b) U/C PPS (Avtel Advanced Fibre Composite). A thermoplastic fibre-composite based upon a poly(phenylene sulphide) (PPS) matrix. It is a semi-crystalline polymer with a glass transition temperature of 97°C and a melting temperature of 290°C. The chemical structure of PPS is shown in Figure 3.2. It was reinforced with unidirectional carbon fibre containing a nominal fibre volume fraction of 53% and was supplied by Phillips 66 Company. This material was only used for the plasma treatment work, and thus is only relevant to the tests described in Chapter Five.

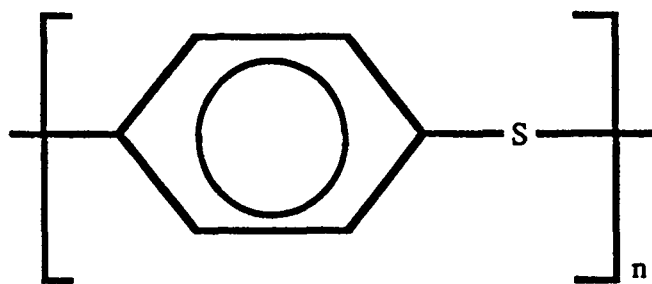


FIGURE 3.2 Chemical structure of polyphenylene sulphide (PPS).

(c) U/C Epoxy (Fibredux XAS913C). This is a thermosetting fibre-composite based upon a polyfunctional epoxy containing modified dicyandiamide. It has a glass transition temperature of 131°C and does not melt due to its crosslinked chemical structure. It was reinforced with unidirectional carbon fibre containing a nominal fibre volume fraction of 60%. This material was supplied by Ciba-Geigy.

3.2.1.2 Structural epoxy adhesives

(a) An epoxy-film adhesive (FM73M), supplied by American Cyanamid. This had been rubber toughened and incorporated a random polyester mat carrier. It was a single part adhesive, curing at 125°C. In the present work, this adhesive will be referred to as the epoxy-film adhesive.

(b) An epoxy-paste adhesive (EA9309.3NA), supplied by Hysol Dexter. This had been rubber toughened , and was a two part formulation, curing at room temperature. In the present work, this adhesive will be referred to as the epoxy-paste adhesive.

3.2.2 Material Cure Cycles

3.2.2.1 Polymeric fibre-composites

The U/C PEEK and U/C Epoxy composites were prepared according the the cure cycles detailed below, using a custom made thermo-mechanical press. This enabled the accurate control of temperature and pressure as well as maintaining a uniform pressure across the platens. The materials were prepared by laying the required number of pre-preg sheets (each typically 125µm thick) into a stack. This was then placed in the mould arrangement, as shown in Figure 3.3. The stacks were sandwiched between clean aluminium sheets, coated with a releasing agent (Frekote 44) supplied by Hysol Dexter, to facilitate the ejection of the composite panel after curing. This particular releasing agent was used because it remains stable at the high temperatures required for the curing of U/C PEEK composite. Two sheets of graphite (each 1mm thick) were also employed in the mould arrangement as shown in Figure 3.3. The graphite, a compliant material, ensured an even pressure distribution through the mould assembly and its use was recommended by the manufacturer when moulding U/C PEEK.

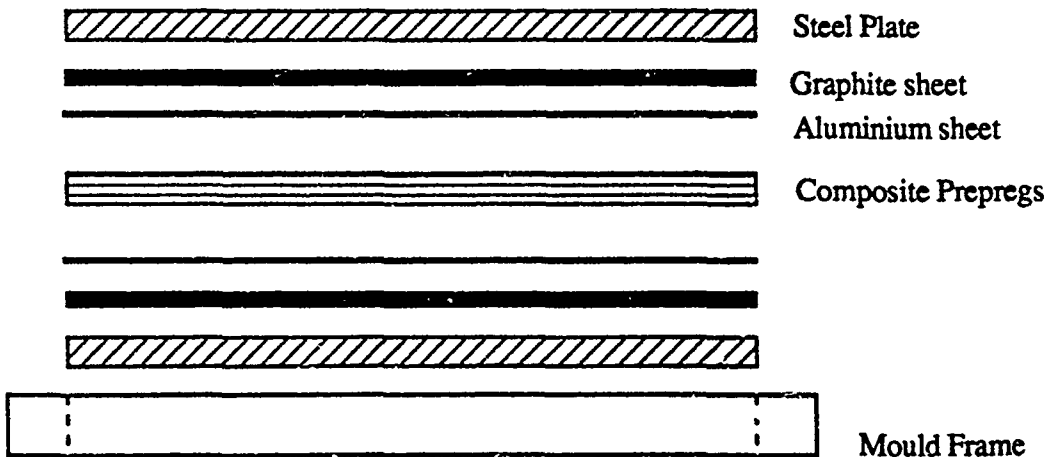


FIGURE 3.3 Exploded diagram of the arrangement used for curing the fibre-composites

(a) U/C PEEK Composite

The cure cycle for this material consisted of three stages. Firstly the 'Heat Conduction' stage: the mould was placed in a preheated press at a temperature of 380°C under a pressure of 100psi. for 30 minutes. Secondly the 'Consolidation' stage: the temperature was held at 380°C while the pressure was increased to 220psi. and held for 5 minutes. Finally the 'Cooling' stage: the platens of the press were rapidly water cooled to below 200°C in 5 minutes, under a pressure of 320psi. Rapid cooling was continued until the mould could be removed from the press. The cured composite sheet was then removed from the mould for cutting and surface preparation prior to bonding.

(b) U/C PPS Composite

This material was supplied by the manufacturer already cured. However, for reference, the cure cycle was: 5 minutes at 360°C, under a pressure of 2MPa and after consolidation, the composite should be cooled down to room temperature rapidly, under pressure.

(c) U/C Epoxy Composite

The cure cycle used for the this material was: 30 minutes at a temperature of 150°C and a pressure of 500psi. An important point to note was that this material had to start off in a cool press (room temperature). It was then heated to 150°C over a period of 30 minutes, which was a heat-up rate of almost 4.5°C/min, and then held at 150°C for 30 minutes. A faster heat-up rate was found to prevent consolidation of the matrix, resulting in a loss of thickness control and the initiation of voids in the material. The mould was then removed from the press hot and cooled naturally to room temperature.

3.2.2.2 Structural epoxy adhesives

Two "state-of-the-art" rubber toughened epoxy adhesives were employed. One was a single part film formulation and the other a two part paste. These types of adhesive are typically employed in engineering structures where structural integrity is essential e.g. the aerospace industry. The cure cycles employed were:

(a) The epoxy-film adhesive (FM73M): Typically, four layers of adhesive film were applied to the joint to achieve a nominal bondline thickness of about 0.35mm. The adhesive

was then cured in the mould arrangement, as shown in Figure 3.4, in an electronically controlled oven. The cure cycle was; 125°C for one hour, under a pressure of 40 kPa.

(b) The epoxy-paste adhesive (EA9309.3NA): The adhesive was carefully mixed in the correct ratio of 100g of resin to 22g of hardener and applied evenly to the composite surfaces. The bondline thickness was controlled by the use of 0.35mm glass beads, finely dispersed throughout the adhesive. The adhesive was then cured at room temperature for five days, under a pressure of 20 kPa.

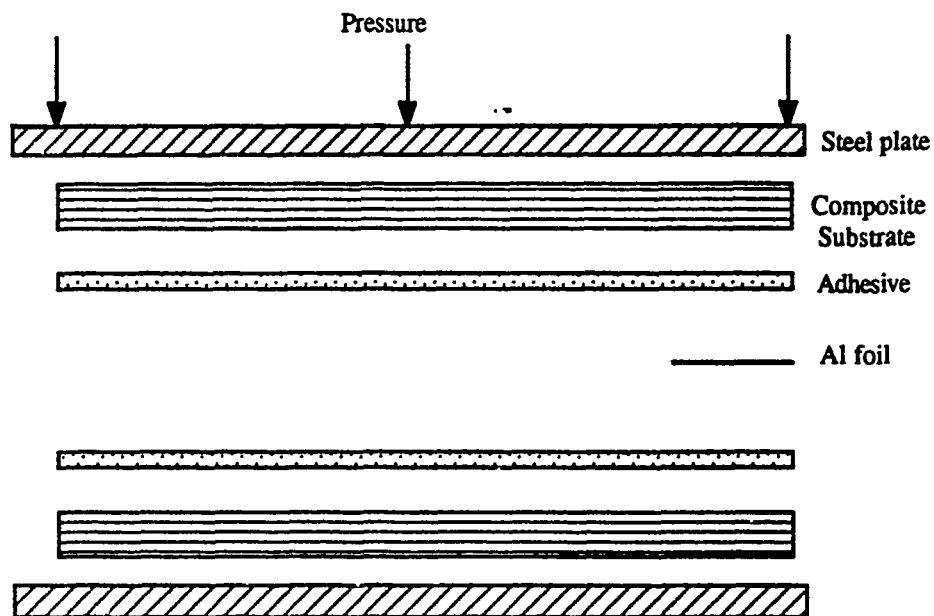


FIGURE 3.4 Exploded diagram of the arrangement used for the curing of the epoxy adhesives in the adhesive joint. Also shown is the aluminium foil insert, at the centre of the glue line. This was inserted to provide a fracture mechanics test specimen.

3.2.3 Standard Surface Pretreatment Techniques

3.2.3.1 Simple abrasion-solvent wipe.

A simple abrasion-solvent wipe surface pretreatment was shown to be sufficient to ensure an adequate level of intrinsic adhesion between the U/C epoxy substrates when either of the two epoxy adhesives were employed [2]. Therefore the epoxy substrates were lightly abraded with alumina grit at a nozzle pressure of 60psi. They were then cleaned thoroughly with acetone prior to bonding.

3.2.3.2 The Corona-discharge surface pretreatment

The simple abrasion-solvent wipe surface pretreatment was found to be insufficient to prevent interfacial failure between the U/C PEEK composite bonded with either of the epoxy adhesives [2, 3]. However, it was shown that interfacial failure can be largely eliminated by pretreating the thermoplastic substrates with a 'corona-discharge' treatment after an abrasion-solvent wipe. The major components of the corona-discharge equipment are: the generator producing high frequency (15-20kHz) power (0.1-0.9kW), the high power (HP) transformer producing the high voltage (15-20kV), the HP cables carrying the high voltage to the electrode and the treater-station. The corona-discharge apparatus is shown in Figure 3.5.

A special feature of this apparatus was that it had been modified so that partially conductive materials, such as CFRP substrates, could be treated. This was achieved by the redesign of the transformer to give good impedance and capacitance matching between the electrode and the somewhat conductive substrates and by the use of a modified electrode. The electrode employed was set inside a silicone rubber covering, as shown in Figure 3.5.



FIGURE 3.5 The corona discharge equipment

The U/C PEEK substrates were placed on an automatically controlled table and passed repeatedly under the high voltage discharge electrode. The velocity of the table was controlled by a stepper motor and pulse generator. The energy output per unit area, E , delivered from the electrode to the substrate surface was determined from:

$$E = \frac{PN}{LV} \quad (3.1)$$

where P is the power of the high frequency generator, N is the number of cycles of the table, L is the length of the treater and V is the velocity of the table. A power of 600W and a table velocity of 14.5mm/s was typically employed. The U/C PEEK substrates were subjected to corona energies ranging from 10 J/mm² prior to bonding with the epoxy-film adhesive to 20J/mm² prior to bonding with the epoxy-paste adhesive. It was described in Chapter Two how the corona-discharge treatment was able to greatly enhance the intrinsic adhesion of thermoplastic fibre-composites. Kodokian and Kinloch [3] showed that the above treatment levels represented the required treatment necessary to obtain high fracture energy, cohesive failure with the U/C PEEK substrates bonded with each of the two adhesives.

3.2.4 Oxygen Plasma Surface Treatment

3.2.4.1 The plasma unit

In order to determine whether an oxygen plasma treatment could also be successfully used, a series of treatments were conducted. Joints which had been prepared from plasma treated substrates were the tested in mode I to deduce the value of G_c and, in addition, these substrates were the subject of a detailed surface analysis. The plasma unit employed was a 'Plasmaprep 100 Plasma Chemistry unit' as shown in Figure 3.5. The principal features of this unit were; the aluminium barrel reactor chamber, the rotary vacuum pump, the 220/240V, 50/60Hz electrical supply, the radio-frequency (RF) power amplifier, the oxygen cylinder, the valve, the high power transformer and the fixed inductor and variable capacitors (60pF, 200pF).

3.2.4.2 Treatment procedure

Substrate beams, 120mm x 20mm ,were cut from cured panels of U/C PEEK and U/C PPS. A simple abrasion-solvent wipe treatment was then applied, followed by a plasma treatment. The plasma reactor chamber was vented to atmospheric pressure and the specimens loaded, two at a time, centrally along its horizontal axis. The chamber was then sealed and the vacuum pump was switched on. When the chamber pressure dropped to below 200 millitorr, oxygen was allowed to flow into the chamber. The gas flow rate was regulated by a venturi meter and was adjusted to give a flow rate of 30cm³ /min. The pressure was again allowed to fall to below 200 millitorr at which point the RF was switched on. The power was slowly

increased and the input-output was tuned to minimise the reflected power. A forward power of 85W was attained and it was noted that the reflected power was 2.5W.

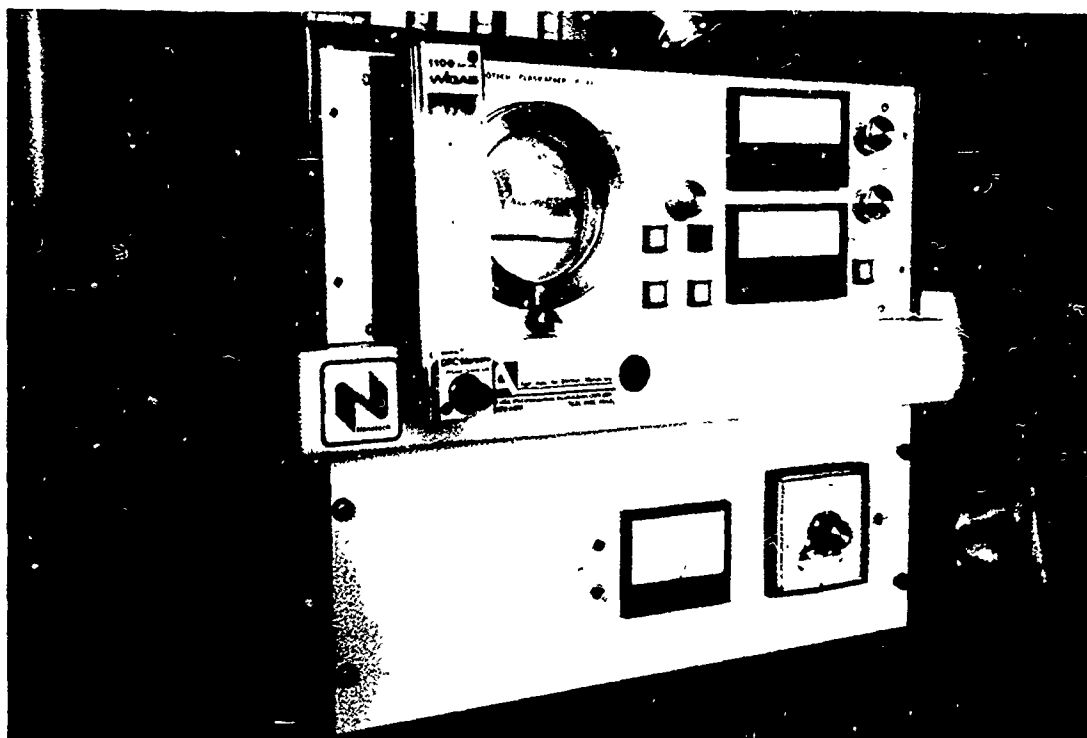


FIGURE 3.5 The Nanotech Plasmaprep 100 chemistry unit

The U/C PEEK substrates were then treated for periods between 2.5 minutes and 20 minutes. The PPS was treated for periods between 2 minutes and 15 minutes. The RF power was then turned off and the chamber again vented to atmospheric pressure. The substrates were then removed from the chamber.

3.2.5 Specimen Storage Prior to Bonding

There have been conflicting reports concerning the degradation of plasma-treated surfaces prior to bonding. Davies et al. [29] reported that lap shear specimens prepared from plasma-treated U/C PEEK suffered a 62% reduction in lap shear strength when the treated substrates were aged in atmospheric air for 10 days prior to bonding. This was correlated to the decrease in surface oxygen species which occurred over this period. The loss of strength was very much reduced if the substrates were stored in a desiccator. However, Nowak et al. [73] reported that polypropylene samples which were stored for five months in air following an oxygen plasma treatment showed no significant change in surface composition measured by XPS. In the present work, all materials were stored in a desiccator before and after surface treatment until bonded. Typically, the substrates were bonded within 24 hours of treatment.

3.2.6 Specimen Preparation

3.2.6.1 The bonded double cantilever beam (DCB) specimen

Bonded double cantilever beam (DCB) test specimens were prepared from the fibre-composite substrates which had received one or more of the above surface treatments. The beams were then bonded with one of the structural epoxy adhesives described in Section 3.2.1 to form the joint. During bonding, an aluminium foil starter crack was inserted at the centre of the adhesive layer. Typically this was 30mm in length and 10 microns in thickness. The starter foil had been coated with release agent to ensure release. When the adhesive had cured, the specimens were removed from the mould and any excess adhesive was removed with a surface grinder. Aluminium end-blocks were then bonded to each specimen with a room temperature curing adhesive (E38 from Permabond). Then, one side of the DCB specimen was whitened with typewriter correction fluid. Finally, marks were scribed onto this side at 5mm intervals to facilitate measurement of the crack length. The DCB specimen is shown in Figure 3.6. Specimens prepared for mixed-mode testing were prepared in exactly the same manner.

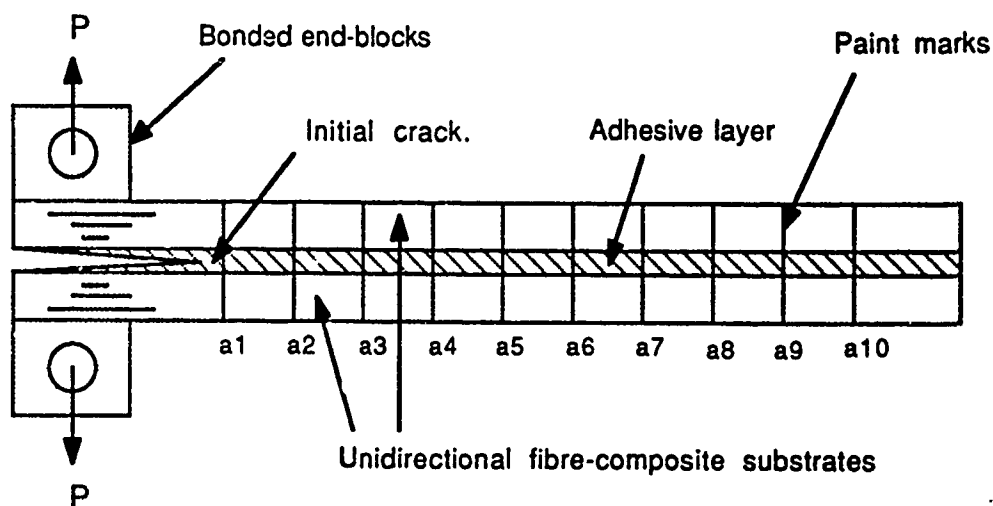


FIGURE 3.6 The Double Cantilever Beam (DCB) Specimen

3.2.6.2 The adhesive joint systems prepared

The following adhesive joint systems were prepared for the purposes of mechanical testing under various test conditions. Joints (5)-(8) apply to the tests conducted in Chapter Five only.

- (1) U/C epoxy substrates¹ bonded with the epoxy-film adhesive.
- (2) U/C epoxy substrates¹ bonded with the epoxy-paste adhesive.
- (3) U/C PEEK substrates² bonded with the epoxy-film adhesive.
- (4) U/C PEEK substrates² bonded with the epoxy-paste adhesive.

- (5) U/C PPS substrates³ bonded with the epoxy-film adhesive.
- (6) U/C PPS substrates³ bonded with the epoxy-paste adhesive.
- (7) U/C PEEK substrates³ bonded with the epoxy-film adhesive.
- (8) U/C PEEK substrates³ bonded with the epoxy-paste adhesive.

Notes: (1) abraded and solvent wiped. (2) abraded and solvent wiped, then corona-treated
(3) abraded and solvent wiped, then plasmatreated.

3.2.6.3 Bulk adhesive specimens

Bulk adhesive specimens were prepared for water diffusion and tensile tests. The adhesive was cured in the usual way, between beams of U/C PEEK having received no surface treatment but simply cleaned with acetone. After cure, the joint could be easily opened up by hand and the adhesive peeled away from the surfaces. For the water diffusion tests, sheets of adhesive 40mm x 20mm x 0.35mm were prepared. For tensile tests, dumbbell specimens were punched from cured sheets of adhesive using a specially designed press. This procedure emphasises just how very poor the level of intrinsic adhesion was between the U/C PEEK substrates and either adhesive prior surface treatment.

3.3 Mechanical Testing At Slow Rates

3.3.1 The Mode I (DCB) Test

The DCB adhesive joint specimens which were prepared as described in Section 3.2 were loaded in the tensile opening mode (mode I) on a screw-driven tensile testing machine {Instron model 1185}. The tests were conducted at a constant crosshead displacement rate of 2mm/min. The temperature of the laboratory was controlled at 21°C. A 1kN load cell was employed. The force and displacement were recorded from the chart recorder during the test. The crack length was monitored using a travelling microscope mounted in front of the specimen. The chart pippier was activated each time the crack passed a 5mm marker on the side of the specimen. In this way, the force and displacement were recorded for each increment of crack length during the test. The specimens were not precracked, i.e. the crack initiated from the foil insert during the test. Typically, about 70mm of crack propagation was

monitored. Data reduction schemes will be discussed in Chapter Four. Figure 3.7 shows a DCB joint during a mode I test.

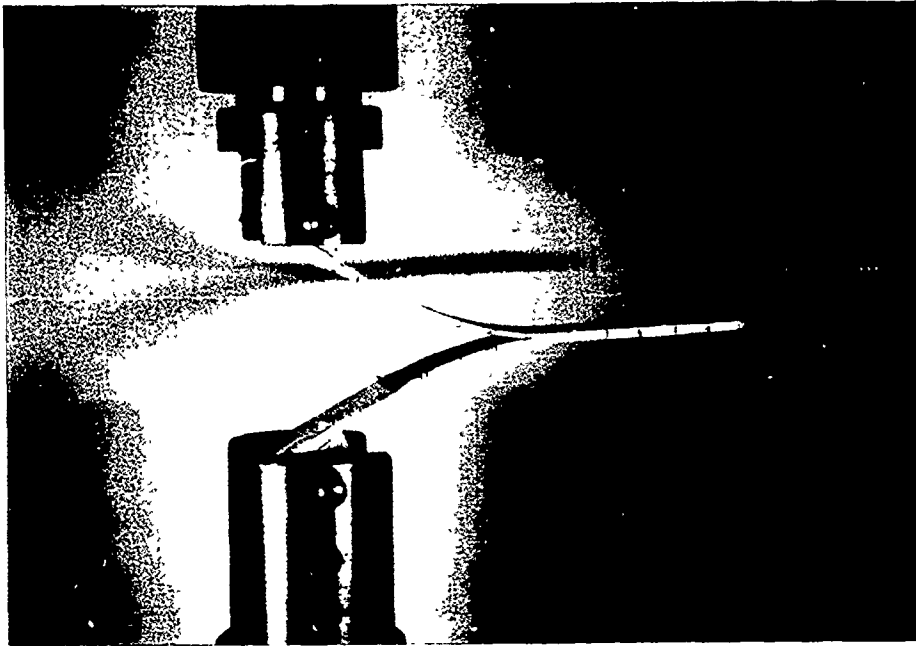


FIGURE 3.7 A DCB adhesive joint specimen during a mode I test at slow rate.

3.3.2 The Modified Mixed-Mode Bending (MMB) Test.

The apparatus employed for the mixed-mode testing of adhesive joints is shown in Figure 3.8(a). The design of the test rig incorporates an additional modification to the one suggested by Reeder and Crews. Firstly, the load is applied through a saddle and bearings which, as Reeder and Crews proposed, successfully eliminated the geometric non-linearity which existed in the original MMB apparatus. Secondly, the position of both the loading lever and the loading saddle could be adjusted so that the distances 'b' and 'c', which are defined on Figure 3.8, could be changed. In this way, the ratio of G_I/G_{II} could be varied over a very wide range, enabling ratios between 35 to 0.002 to be obtained.

A major advantage of this apparatus was that symmetrically cracked DCB test specimens could be employed, which are the most convenient to prepare. The loading of the specimen was again achieved on the screw-driven machine, but this time the force was applied in compression through the loading saddle, as is shown in Figure 3.8(b). Tests were undertaken at a temperature of 21°C and at a constant displacement rate of 1mm/min. The load and displacement values were continuously monitored and the crack length was again observed by using a travelling microscope. Data reduction schemes and test results will be discussed in Chapter Four.

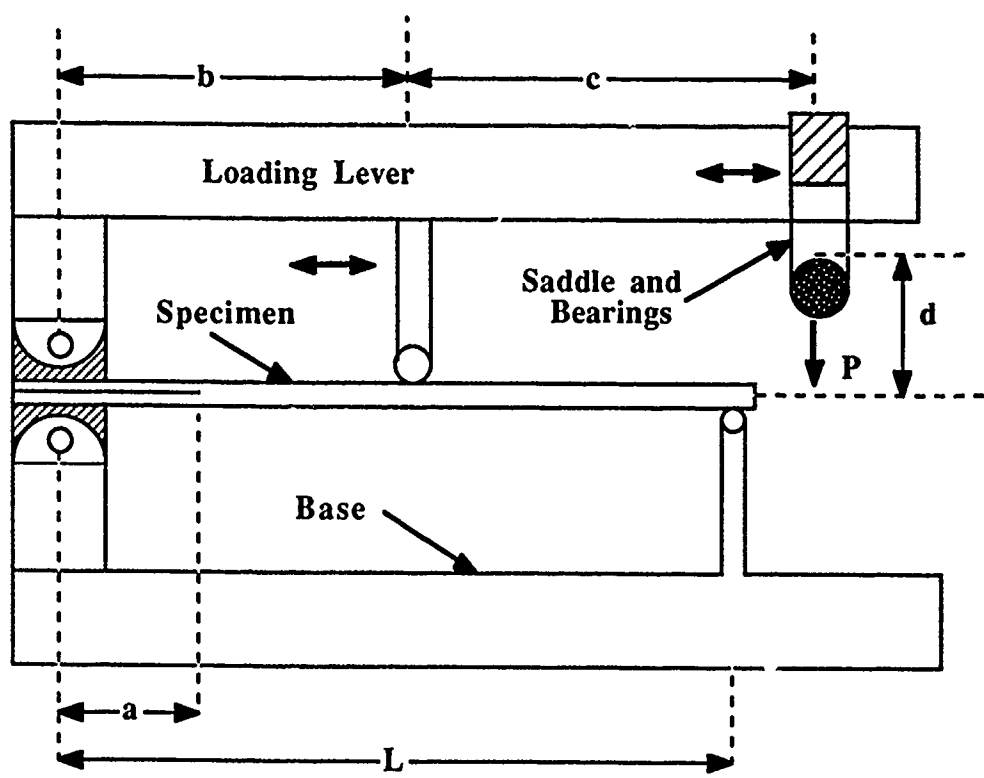


FIGURE 3.8(a) The modified mixed-mode bending (MMB) test apparatus.



Figure 3.8(b) The modified mixed-mode bending (MMB) test apparatus in use during a fracture test.

3.3.3 The Mode II ELS Test

The apparatus employed for mode II testing is shown in Figure 3.9. The test geometry used was the end loaded split (ELS) test geometry. This was a very convenient geometry to use because DCB test specimens could be employed. During the test, the specimen is held at one end between rollers and loaded at the other, as shown in Figure 3.9. Both upper and lower arms of the specimen are subjected to the same bending moments. The purpose of the rollers is to eliminate the horizontal force which is induced during the test if the specimen is clamped rigidly and unable to slide. These tests were again conducted on the screw-driven machine at a rate of 1mm/min and at a temperature of 21°C.

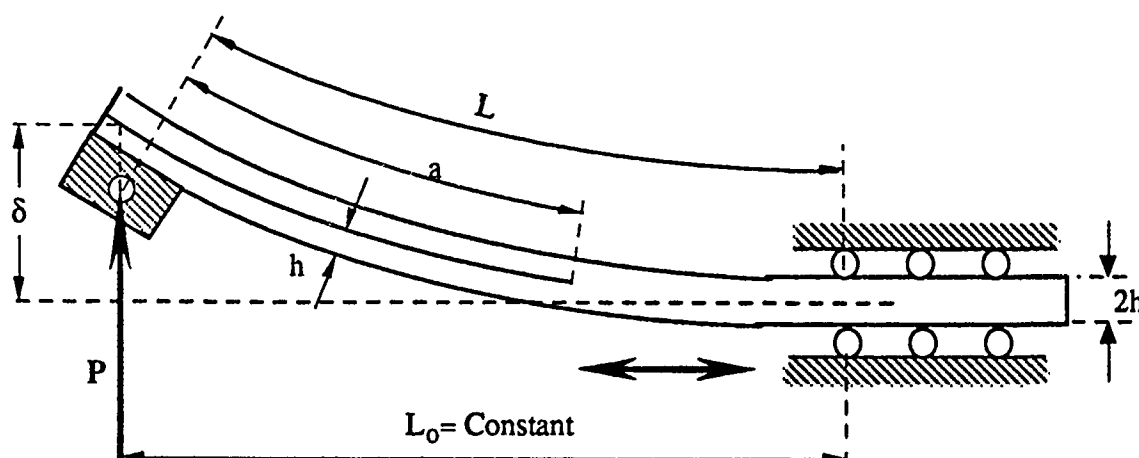


FIGURE 3.9 The mode II end-loaded split (ELS) test specimen.

3.4 Substrate Modulus Measurements

3.4.1 Static Modulus Measurements

In order to obtain an accurate value for the modulus of the fibre-composite substrate beams used to prepare the DCB test specimens, a set of three point bend tests were carried out. Using composite beams with identical geometry and composition to those used in the DCB specimens, the beams were loaded in three point bending at a constant displacement rate of 0.5mm/min. In order to ensure high accuracy, an external transducer was used to record the deflection of the beam during loading. The substrate modulus was also calculated by

corrected beam theory, as will be discussed in Chapter Four, so this procedure served as an independent verification of the beam theory analysis.

3.4.2 Dynamic Modulus Measurements

In order to investigate the dynamic sensitivity of the fibre-composite substrate moduli, a dynamic mechanical thermal analysis (DMTA) was carried out. Specimens of fibre-composite substrate (15mm x 5mm) were prepared and rigidly clamped at one end by the apparatus. The specimen was then excited at frequencies ranging from 0.01Hz to 200Hz on a DMTA apparatus. At each frequency, the specimen was loaded with an oscillatory force ($\pm 4\text{N}$) and the displacement was accurately measured by the apparatus. Using simple beam theory, it was thus possible to calculate the axial modulus of the substrate at each frequency. However, the results obtained from these tests were not very reliable, due to problems encountered with the clamping arrangement, but the results will be discussed in Chapter Six.

3.5 High Rate DCB Testing

3.5.1 Introduction

The DCB test specimen was utilized for the determination of the adhesive fracture energy, G_c , at high test rates. For opening displacement rates of up to 1000mm/min (0.01667m/s) the screw-driven tensile testing machine was employed as described in Section 3.3.1. For faster rates, a servo-hydraulic testing machine has been employed. High rate testing poses several difficulties which are not experienced at lower rates. Firstly, static failure of a joint may take place over a period of several minutes. Impact failure may occur within a few milliseconds. For this reason, high speed data acquisition facilities are necessary. Secondly, high speed impacts may introduce troublesome dynamic effects into the system. These effects may induce resonance in transducers and greatly increase the uncertainty in the measurement of material properties at these rates. The specially designed rig incorporates several features which minimise these effects. The high rate test rig will be described in the following section.

3.5.2 The High Rate Test Rig

The high rate test rig is shown in Figure 3.10. The main features of the test rig include the servo-hydraulic testing machine {Instron model 1343}, the operating control panel, the transient recorder, the computer, the high-speed camera {Hadland Photec IV} and the lighting

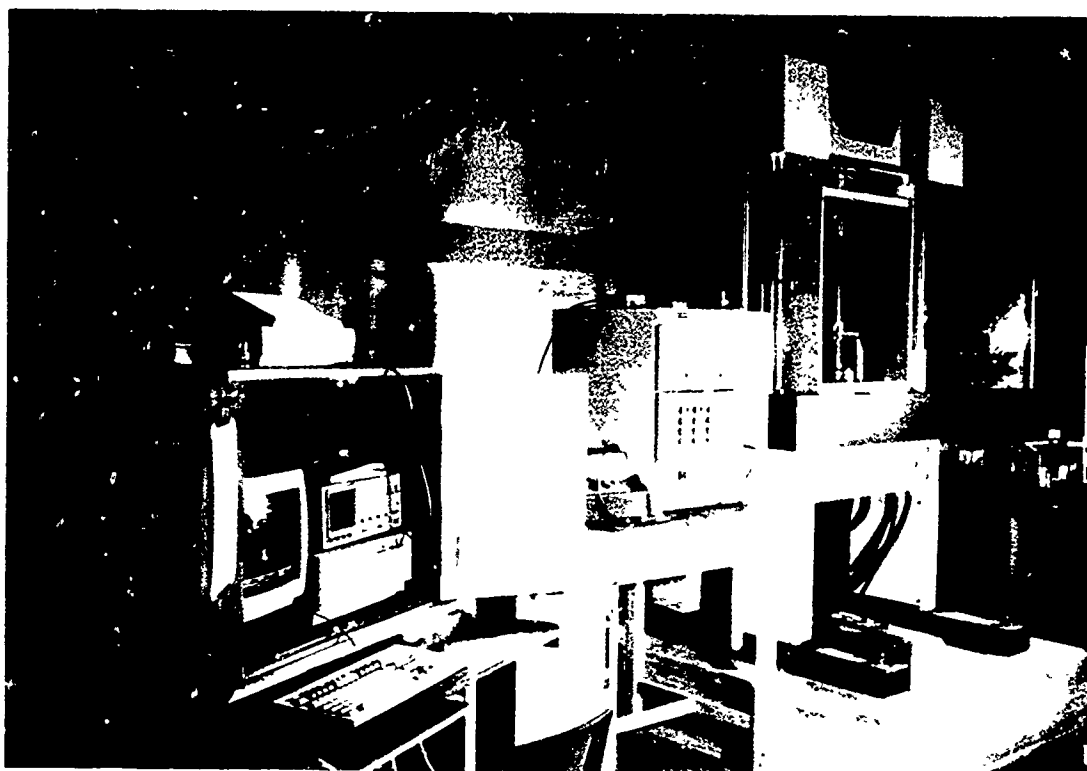


FIGURE 3.10(a) The High Rate Experimental Test Rig.

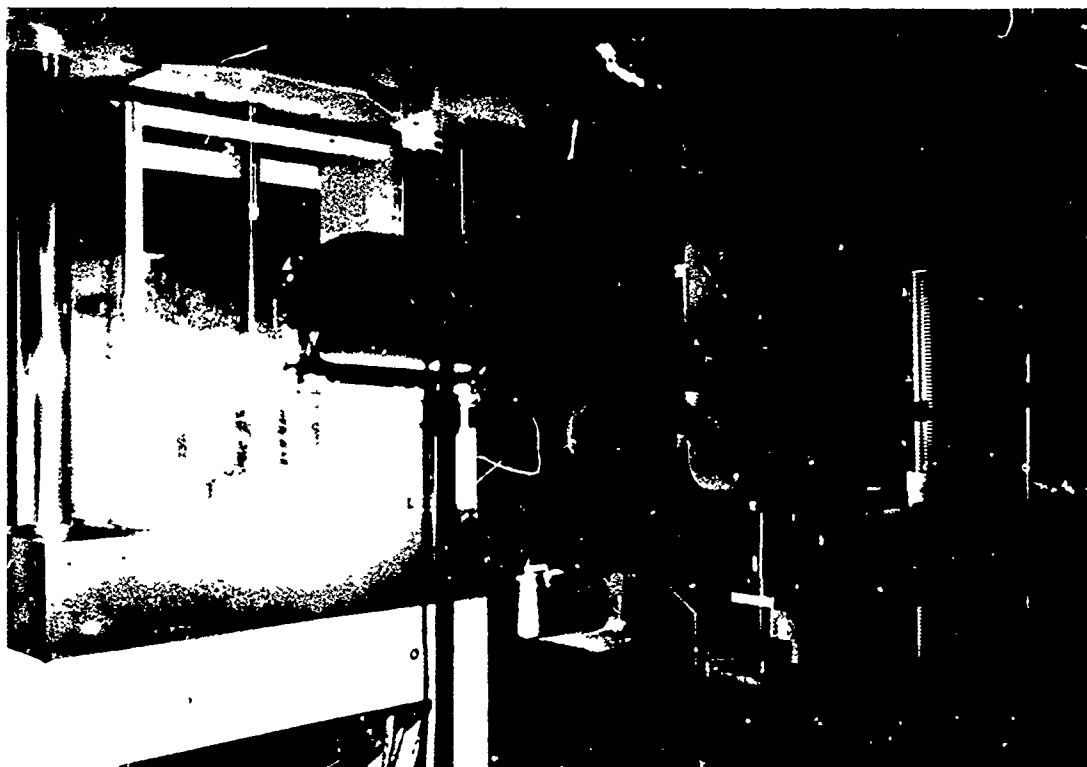


FIGURE 3.10(b) The Hadland High-speed Camera and lighting system employed on the High Rate Test Rig.

system. The servo-hydraulic testing machine can produce displacement rates of up to 25m/s. The machine drives the main ram through either a low or high pressure actuator.

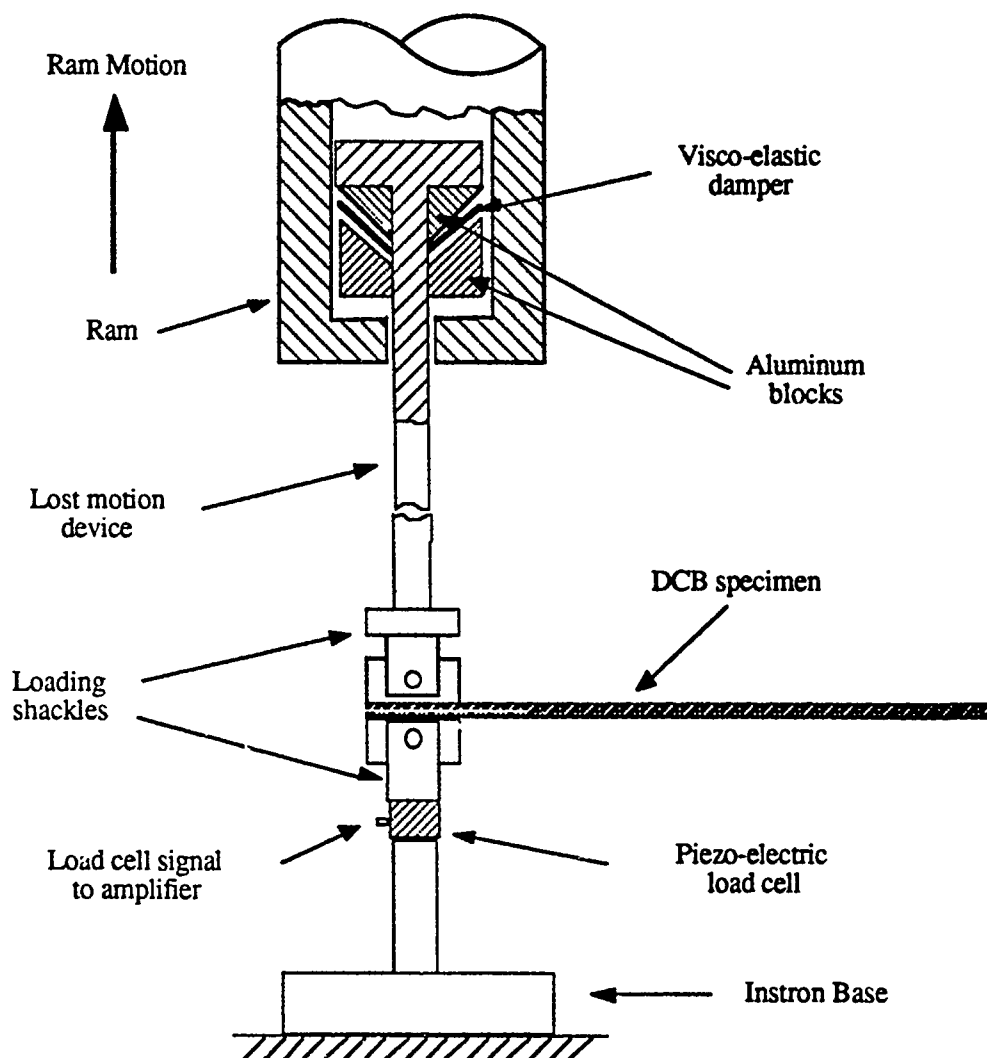


FIGURE 3.11 The arrangement of the DCB test specimen on the high rate experimental test rig.

The arrangement of the DCB on the servo-hydraulic test machine is shown in Figure 3.11. The DCB specimen was positioned onto the rig between two specially designed shackles. These were made of aluminium and titanium with a very low mass (12.1g). The upper shackle was connected to a lost motion device (LMD) which attached to the end of the loading ram. The purpose of the LMD was to allow the ram to attain a steady-state velocity before motion was transferred to the specimen. The lower shackle, on the stationary side of the DCB, was connected to a piezo-electric load cell. The principle features of this load cell were its low mass (24.4g) and its high resonant frequency (70kHz). The load cell possessed an

independent power source, and its output signal was amplified and then passed on to a four channel, Gould 1600 series transient recorder with a frequency of operation of 20MHz. The signal from the internal Instron linear velocity displacement transducer (LVDT) connected to the ram was passed to the control panel and then onto the transient recorder.

It was found that by modifying the contact between the loading ram and the LMD, it was possible to significantly reduce the oscillation induced when motion was transferred to the specimen. Two modifications were made and both are shown in Figure 3.11. Firstly, an aluminium conical contact surface was employed. This has the effect of reducing the vertical component of force by introducing a horizontal component. A reduction of the vertical force component reduces the magnitude of the shock wave travelling down the LMD and thus reduces the amount of oscillation experienced when loading. Secondly, the contact stiffness between the conical surfaces was reduced by the insertion of a visco-elastic damping material. A schematic diagram of the test rig is shown in Figure 3.12

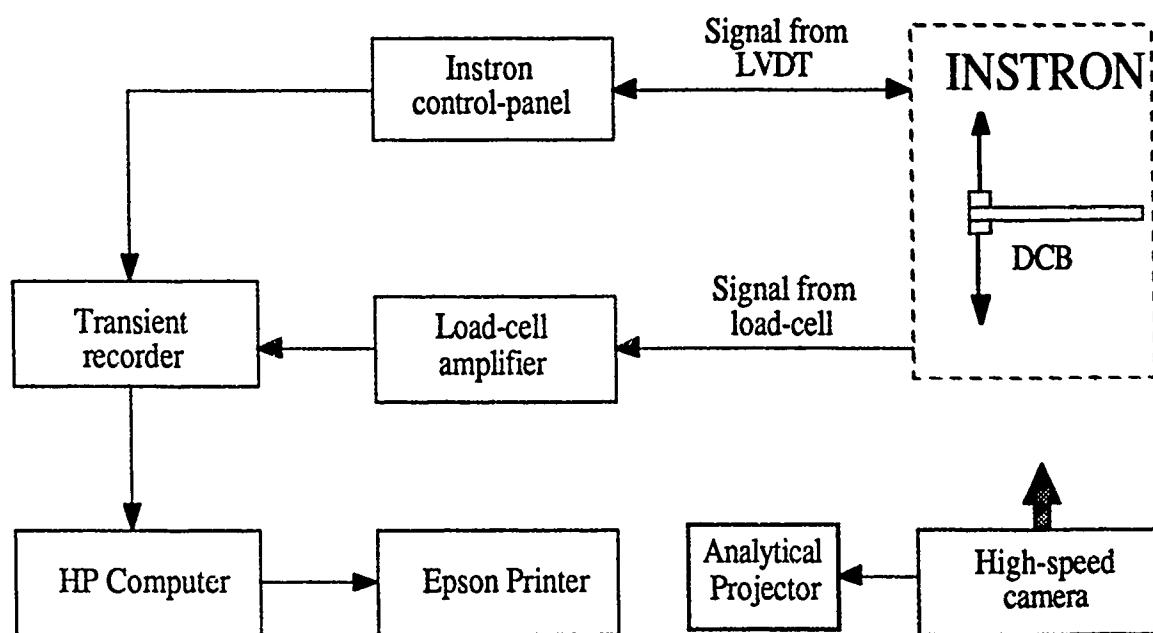


FIGURE 3.12 Schematic diagram of the high rate test rig

3.5.3 High-Speed Photography

The experimental rig incorporated a Hadland Photec (IV), 16mm high-speed camera as was shown in Figure 3.10(b). By photographing the fracture event, it was possible to record accurately the values of the beam opening displacement and the length of the crack during the test. The principal feature of the camera was its rotating prism design, allowing a maximum

framing speed of 40 000 frames per second to be achieved. A choice of lenses was available, but typically a 45mm, f2.8 Mamiya lens was employed. Illumination of the subject was achieved by using two Broadlite 1250W floodlights. A tungsten balanced 7250 Eastman film was used. This provided a high resolution, colour record of the test.

The maximum camera speed employed in the current work was 4000 pictures per second (pps). However, because a half frame converter unit was fitted, this produced a framing rate of 8000 frames per second (fps). An additional feature of this camera was that it incorporated a timing light generator. This was used to mark the film with a timing mark at a frequency of either 100Hz or 1000Hz, depending on the operating speed of the camera. Using this facility, it was possible to check that the camera had reached the required speed during the test. Subsequent analysis of the film was conducted on a Hadland analytical projector, allowing precise frame analysis to be conducted.

3.5.4 Experimental Procedure

DCB adhesive joint specimens were tested on this rig at displacement rates from 0.01m/s up to 10m/s. The Instron signal generator was set to provide the required ram velocity. Depending upon the desired test velocity, either the low or the high pressure actuator was engaged. Sufficient pretravel of the ram, before engaging the LMD, was set to ensure that a steady-state velocity had been achieved at the start of the test. This was verified by checking that the slope of the displacement-time signal was constant at the point of loading. The trigger level, the time base and the output scale of each channel of the transient recorder was set as required. The transient recorder was then armed.

The DCB was inserted between the shackles on the test machine as was shown in Figure 3.11. The camera was focussed on the specimen, and then the film was loaded. The lens aperture and lighting position were set to provide sufficient exposure of the film. The camera speed was then set to provide sufficient detail of the test i.e. faster camera speeds were employed for faster ram speeds. {Further details of the camera speeds employed are shown in Chapter Six}. Then, just before the test, the floodlights were switched on. This was to avoid any heating of the specimens. The camera was activated by remote control just prior to the activation of the Instron ram. After the test the camera was stopped and the force-time and displacement-time signals were transferred from oscilloscope to computer. For the camera speeds employed, constant framing speed was achieved within one second of activating the camera, and therefore constant framing velocity was achieved during the test.

The force-time and displacement-time data was then transferred from the transient recorder to the computer. A signal analysis software package was employed to store and subsequently analyse the data. From an analysis of the high-speed film, values of displacement and crack length were recorded as a function of time. The values of the load at various times could then be obtained from an analysis of the load-time signal. The analysis of this data will be discussed further in Chapter Six.

3.6 Environmental Testing

3.6.1 Introduction

In this Section, a series of tests will be described on both adhesive joint specimens and on bulk adhesive specimens. Adhesively bonded DCB specimens have been aged in a hot-dry and hot-wet chamber in order to determine the extent to which their fracture behaviour is affected by the exposure. Water diffusion and tensile tests on the bulk adhesives were conducted in an attempt to gain a greater understanding of the joint fracture behaviour observed. Slow rate testing was conducted on the screw-driven machine at a displacement rate of 2mm/min. High rate testing was conducted at various speeds on the high rate rig as described in Section 3.5.

3.6.2 Ageing in a Hot-dry Environmental

DCB adhesive joint specimens were prepared employing U/C PEEK substrates. Half of the joints were prepared with the epoxy-film adhesive and the remaining half were prepared with the epoxy-paste adhesive. The substrates had first been corona-treated to 10 and 20 J/mm² respectively, as previously described.

The joints were placed in a preheated chamber at 50°C. The chamber contained a drying agent to remove any moisture present. Two joints of each system were not placed in the chamber, but were fractured in mode I to provide a 'zero-age' control. Joints were exposed to the heated chamber for periods ranging from 1-18 days. On removal, the joints were fractured in mode I. Two joints of each type were tested in each condition. The variation in the adhesive fracture energy, G_c , for each adhesive was plotted against ageing time in the chamber. The results will be discussed in Chapter Seven.

3.6.3 Ageing in a Hot-wet Environment

Four environmental chambers were set up containing de-ionised water held at 50°C. The adhesive joint systems placed into these environments were:

- (1) U/C epoxy substrates¹ bonded with the epoxy-film adhesive.
- (2) U/C epoxy substrates¹ bonded with the epoxy-paste adhesive.
- (3) U/C PEEK substrates² bonded with the epoxy-film adhesive.
- (4) U/C PEEK substrates³ bonded with the epoxy-paste adhesive.

{Notes (1) abraded and solvent wiped; (2) also corona treated to 10J/mm²; (3) also corona treated to 20J/mm²}

Two joints of each system were tested, in the usual way, without being placed in the environmental chambers. These tests acted as the 'zero-age' control. The remaining joints were placed in their respective chambers. Two joints of each system were removed from each chamber at monthly intervals and tested. The maximum exposure period was one year. The mode I fracture energy was deduced as a function of ageing time. In addition, the locus of joint failure was assessed.

When it became clear that the joint system comprising of U/C PEEK bonded with the epoxy-film adhesive suffered interfacial attack during exposure to this environment, a fifth chamber was set up containing U/C PEEK substrates bonded with the epoxy-film adhesive, but this time the substrates were subjected to a more severe corona treatment of 15J/mm² prior to bonding. The reason for this was to determine whether the environmental attack could be avoided or delayed by the application of a more vigorous surface treatment. Thus, the fifth environmental chamber was:

- (5) U/C PEEK substrates⁴ bonded with the epoxy-film adhesive.

{Notes (4) also corona treated to 15J/mm²}

The results of the durability tests will be presented and discussed in Chapter Seven.

3.6.4 Bulk Adhesive Diffusion Tests

Sheet specimens of adhesive 40mm x 20mm x 0.35mm were prepared as described in Section 3.2.6. The specimens were stored in a desiccator for five days to allow them to thoroughly dry out. Each specimen was then carefully weighed using an analytical balance. They were then suspended in de-ionized water at 50°C and removed periodically before being carefully

dried and reweighed on the analytical balance. Water uptake plots were drawn, from which the diffusion parameters were deduced. These tests will be discussed in Chapter Seven.

3.6.5 Bulk Adhesive Tensile Tests

Dumbbell specimens of adhesive were pressed from the adhesive sheets. These dried out in a desiccator before being suspended in a water bath at 50°C for various periods. On removal from the bath, the specimens were weighed and then fixed between the grips of the tensile machine. A clip gauge was attached to a 12mm gauge length on each specimen. The specimens were tested at a constant rate of 0.5mm/min until failure, and the force-extension data was recorded. This data was converted to stress-strain data. The failure stress, failure strain and 1% secant modulus was then calculated for each adhesive as a function of mass uptake of water.

3.7 Scanning Electron Microscopy

3.7.1 Introduction

Scanning electron microscopy (SEM) has been widely used as a surface analytical technique in the area of adhesion science. SEM can provide valuable information on the changes in surface morphology i.e. degree of surface roughness, pitting or fibre exposure as a result of a particular surface treatment. In addition, the technique can be used to analyse post-failure fracture surfaces and such information as the degree of plasticity, evidence of particle cavitation and a more precise indication of the locus of failure may be elucidated. A brief description of the theory of operation will now be given.

3.7.2 Theory of Operation and Equipment

The principal features of the scanning microscope are the electron optical system, the specimen stage and the display and recording system [74]. Essentially, the electron optical system consists of an electron gun, a lens system to form electrons into a fine electron probe, astigmatism correctors and scanning system to control the magnification. The specimen to be analysed is located in the specimen stage, under vacuum on an XYZ coordinate movement mechanism. A finely focussed electron probe is set to scan the specimen surface. This will induce the emission of low energy, secondary electrons (SE), from the specimen surface to a depth of about 10nm. Other signals which may be emitted from the surface include backscattered electrons (BE), which have almost the same energy as the incident electron

beam, X-rays and cathodoluminescence which is light emitted from excited surface atoms. If the specimen is thin, electrons may be transmitted and these transmitted electrons (TE) may be detected. The signals are detected within the display and recording system. These are fed to a synchronously scanned cathode ray tube (CRT) as an intensity modulating signal and thus the image of the specimen is displayed on the screen. The magnification is determined by the ratio of the CRT raster width to the electron probe scanning width. Most microscopes of this type include SE and BE detectors as standard. X-Ray detectors can be fitted as an option and allow a chemical analysis of the surface to be conducted and CL and TE detectors can also be fitted.

3.7.3 Experimental procedure

Sections of composite substrate (50mm x 20mm) were prepared, or cut from post failure fracture surfaces for viewing using an SEM (JOEL-JSM 5300). The specimens were gold-coated in an Edwards S150A sputter coater and then mounted on a carousel. The specimen surfaces were earthed with silver paint to prevent excess charging during analysis. The carousel was mounted in the specimen stage of the microscope, which was then evacuated. The carousel was tilted to 15° to improve surface resolution and an accelerating voltage of 15-25kV was applied. The surfaces were viewed at various magnifications. The microscope was operated in the secondary electron image mode.

3.8 X-Ray Photoelectron Spectroscopy

3.8.1 Introduction

X-ray photoelectron spectroscopy (XPS), also known as electron spectroscopy for chemical analysis (ESCA), has been widely used for the analysis of polymeric surfaces [75]. The technique can provide detailed chemical information on the atoms in the very top surface regions (2-6nm) of a material. This is of importance because, as was discussed in Chapter Two, adhesion is sensitive to the surface chemistry. XPS provides quantitative information on the elements present on the surface and on the species which make up the relevant individual elements. The technique uses X-rays as the incident beam which are less ionizing and hence less disruptive to the surface than an electron beam. Hence XPS is considerably more accurate than X-ray fluorescence, available on most modern scanning electron microscopes. The degree of surface contamination can be quantified. XPS has been used in the present work to quantify the surface chemical changes induced by a plasma treatment.

This will be discussed in Chapter Five. The theoretical basis for this important technique will be discussed.

3.8.2 Theoretical Basis of Technique

Electron spectroscopy is concerned with the emission and energy analysis of low energy electrons, generally in the range of 20-2000 eV. (In electron spectroscopy, energies are expressed in the non-SI unit of the electron volt. $1 \text{ eV} = 1.595 \times 10^{-19} \text{ J}$). In XPS, an X-ray beam is directed onto the material surface. The X-ray contains photons of energy $h\nu$, which can cause photoemission i.e. the ejection of an electron from a core level of a surface atom. The kinetic energy of the emitted photoelectron can then be analysed by a spectrometer. However, this energy is not characteristic of the parent atom because it depends on the X-ray source employed. The binding energy of the electron, E_B , is the parameter which identifies the electron specifically and is given by:

$$E_B = h\nu - E_K - W \quad (3.2)$$

where $h\nu$ is the photon energy, E_K is the kinetic energy of the electron and W is the spectrometer work function. Therefore, by knowing $h\nu$ for the X-ray source and W for the spectrometer, and measuring E_K by use of the spectrometer, it is possible to calculate the binding energy of the electron. Figure 3.13 shows the electron photoemission process. If an electron from the K shell is ejected, it is termed a (1s) photoelectron. If the electron is ejected straight out without collision with another electron, it will contribute to the characteristic peaks in the spectrum. If however, it undergoes collision, termed inelastic scattering, it will lose energy and contribute only to the background of the spectrum. Due to the likelihood of electron collision, only photoelectrons emitted from atoms very close to the material surface are able to escape straight out, so XPS provides information on the top few nanometers of the surface only. Clearly, once the photoelectron has been emitted, the atom is unstable and will either emit an X-ray photon or an Auger electron to return it to the ground state.

The binding energy of a photoelectron peak defines not only the energy level within the atom from which it emerged but also the chemical environment of the atom. Thus not only can surface atoms be identified, but also the valence state can be deduced from the chemical shift phenomenon which was first described by Siegbahn [76]. XPS can therefore provide very useful information on the bonding within chemical species.

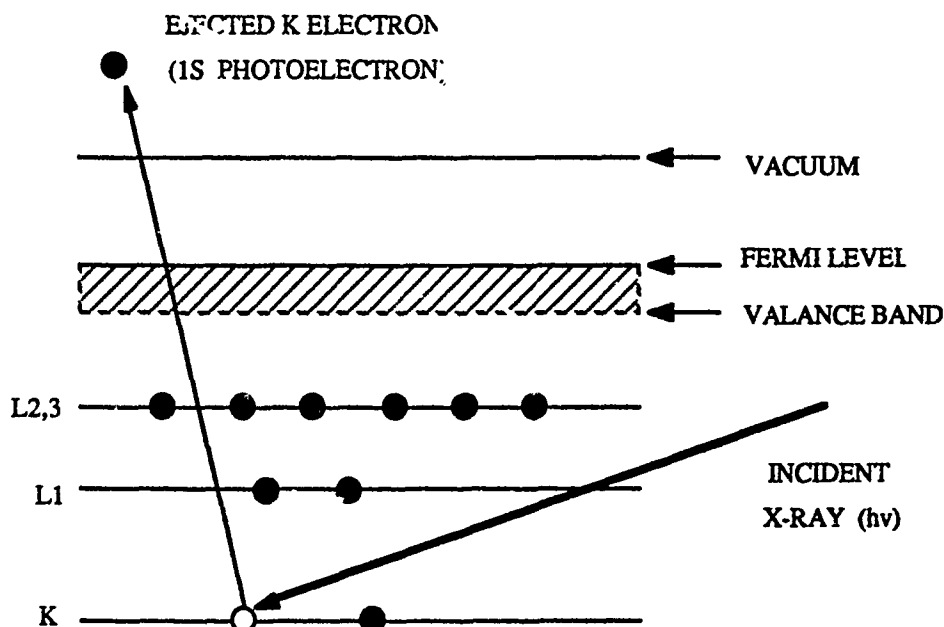


FIGURE 3.13. Schematic of the XPS process, showing the photoemission of an electron after collision with an X-ray photon.

3.8.3 Spectrometer Design

The principal features of the X-ray photoelectron spectrometer are the vacuum system, the X-ray source and the hemispherical sector analyser (HSA). The function of each will now be described. XPS is carried out in the ultra-high vacuum (UHV) range of 10^{-8} to 10^{-10} mbar. There are two reasons why this is so. Firstly, the very low pressure is required to remove possible surface layers of gas which may have adsorbed onto the specimen surface. Due to the surface sensitivity of this technique, this layer should be removed. Secondly, the low energy electrons are easily scattered by the residual gas molecules. Therefore, if these are not removed then the total spectral intensity will decrease, whilst the noise present within the spectrum will increase. Often a series of vacuum chambers of decreasing pressure will be employed to achieve this pressure.

The most popular anode materials are aluminium and magnesium and they are available in a single X-ray gun with twin anode configuration. Thus $AlK\alpha$ and $MgK\alpha$ photons are available with energies of 1486.6 eV and 1253.6 eV respectively. Such twin anode assemblies have a separate filament for each anode so switching from one anode to the other is comparatively simple. Due to the different depths attainable with these anodes ($7 \cos \theta$ nm and $6 \cos \theta$ nm respectively, where θ is the electron take off angle) then a modest depth profiling may be undertaken, without altering the angle θ .

The hemispherical sector analyser (HSA) is the most common form of analyser employed in XPS. The analyser incorporates an electron preretardation stage to achieve adequate resolution. Electron retardation occurs immediately before the electrons enter the hemisphere. The hemisphere may be operated in either constant analyser energy mode (CAE) or in constant retard ratio (CRR). In the CAE mode of operation a constant voltage is applied across the hemispheres allowing only electrons of a particular energy to pass between them. Thus the resolution of the spectrum is constant across the entire energy range. Electrons emitted from the specimen are transferred to the focal point of the analyser by a lens assembly. They are then retarded before entering the hemisphere. Electrons with energy matching the pass energy of the analyser are transmitted, detected and counted by the electron detector. The complete spectrum is recorded by ramping the retarding field potential and plotting the spectrum of electron energy versus electron counts.

3.8.4 Experimental Procedure

Samples of the fibre-composite material (10mm x 10mm) were prepared from freshly treated substrates. They were stored in a desiccator until ready for XPS analysis. They were then analysed using a X-ray photoelectron spectrometer (Model VG Scientific MKIII). The samples were mounted, four at a time, onto a carousel which was placed on rails inside the primary vacuum chamber of the spectrometer. This chamber was partially evacuated, down to a pressure of 10^{-3} mbar. The carousel was then passed into the secondary chamber which was then evacuated to a pressure of 5×10^{-8} mbar. Finally, the carousel was passed into an ultra-high vacuum chamber (10^{-8} - 10^{-10} mbar) for analysis.

The X-ray gun employed possessed a twin anode configuration, with $\text{AlK}\alpha$ or $\text{MgK}\alpha$ radiation available. The $\text{AlK}\alpha$ X-ray source was employed. The X-ray beam was focussed onto the material surface with the aid of a video camera. The beam provided an analysis area of 10mm^2 on the material surface. A take off angle of 45° was employed for all samples. Photoelectrons emitted from the material surface passed through an electrostatic transfer lens before entering the hemispherical sector analyser. A dedicated computer, linked to the analyser enabled the pass energies for the required elements to be inputted. The step sizes used were 1 eV and 0.2-0.1 eV and the analyser energies were 50 eV and 20 eV for the wide and narrow scans respectively. The elements included in the scan were: C (1s), O (1s), N (1s), F (1s) and Si (2p).

3.8.5 Explanation of Output

Typically the spectrometer will produce an output of counts per second (cps) against binding energy (E_B). In the case of wide, survey scans, a complete spectrum of the acquired photoelectron peaks from 0-1000 eV will be produced. In the case of narrow scans a narrower energy range, typically of about 20 eV will be analysed. The purpose of the narrow scan is twofold. Firstly, it allows an elemental quantification to be carried out. Secondly, it enables a peak deconvolution to be conducted, as will be described in Chapter Five. Table 3.1 shows some electron binding energies of elements of interest and species that were frequently encountered with the plasma-treated fibre-composites employed in this work.

TABLE 3.1 Electron binding energies of elements and important species which are accessible during an XPS analysis using the $AlK\alpha$ radiation.

Element / Electron Type	Electron Binding Energy (eV)
Silicon (Si2p)	99
Silicon (Si2s)	149
Sulphur (S2p)	164
C-C, C-H	285.0
C-O	286.5-286.7
C=O	288.0-288.4
O-C=O	289.5-290.1
Nitrogen (N1s)	399-401
Oxygen (O1s)	532-534
Fluorine (F1s)	685

It will be shown in Chapter Five that the use of XPS has enabled a far more detailed understanding of the surface modifications induced by a plasma treatment to be gained than would have otherwise been possible.

3.9 Concluding Remarks

This Chapter has characterized all the materials employed in the present work, their method of manufacture, the specimen manufacture and the experimental techniques. The results obtained from these techniques will be presented in Chapters 4-7, together with a discussion and interpretation of the findings. However, before the beam theory approach to fracture mechanics can be employed in this study, it is necessary correct the analysis for the various assumptions which were described in Chapter Two. These will now be considered.

Chapter Four

Joint Failure: A Fracture Mechanics Approach

4.1 Introduction

In this Chapter, the beam theory analysis which was described in Chapter Two, has been applied to the fracture of the adhesively bonded fibre-composites. When this analysis was previously applied to the study of interlaminar fracture in fibre-composite materials, Hashemi et al [77] reported that there was very poor agreement between the values of the interlaminar fracture energy $G_c(ii)$ calculated via simple beam theory and via the "area" or "compliance" techniques. Further, when the axial modulus of the fibre-composite arms of the DCB specimen was calculated by simple beam theory, it was found that this value increased with increasing crack length. Hashemi et al corrected the beam theory analysis for the effects of shear deflection and large displacements in the composite arms, and for end-block stiffening. When these correction factors were taken into account, excellent agreement was observed between the values of $G_c(ii)$ calculated via the beam theory and by the "area" and "compliance" techniques.

It will be shown that the corrected beam theory analysis can be applied with equal success to the fracture of bonded joints. Excellent agreement has been obtained between the values of the adhesive fracture energy, G_c , calculated via corrected beam theory methods and via the "area" and "compliance" techniques. The use of the uncorrected "load method" indicated that the adhesive joints exhibited a rising 'R-curve' i.e. rising crack resistance with increasing crack length. Further, when the modulus of the substrate arms was calculated by the uncorrected analysis, this value was also observed to increase with increasing crack length. Obviously this is an incorrect conclusion. However, the application of the corrected analysis revealed that these adhesive joints do not exhibit an 'R-curve' and that the modulus of the fibre-composite substrates does not increase with crack length.

The generalised beam theory analysis which was derived by Williams [37] and was discussed in Chapter Two can be used to calculate the fracture energy in situations when a crack is subjected to mode I and mode II loading. Using the mixed-mode bending test apparatus

described in Chapter Three, joints bonded with the epoxy-film adhesive were loaded with different ratios of mode I to mode II loading. The mode I to mode II components were partitioned using the global approach [40]. The pure mode II value of the adhesive fracture energy, G_{IIc} , was measured for joints bonded with the epoxy-film adhesive using the end loaded split (ELS) test geometry. However, joints bonded with the tougher, epoxy-paste adhesive appeared to have a very high resistance to crack growth in mode II and it therefore was not found possible to achieve mode II crack growth in this adhesive without permanent distortion of the composite substrates occurring. For this reason, mode II and mixed-mode loading of joints prepared with this adhesive was not pursued. Finally, the mixed-mode values of the adhesive fracture energy for joints bonded with the epoxy-film adhesive were plotted in the form of the mode I component of the adhesive fracture energy versus the mode II component, to give a failure locus.

4.2 Correction Factors for the Basic Beam Theory Analysis

4.2.1 Correction for Shear Deflection and Crack Tip Rotation

The simple beam theory described in Chapter Two assumed that the fibre-composite substrate arms acted as built in cantilever beams. Thus, only the deflections due to bending were considered, and those due to shear were ignored. However, compared to metallic substrates, polymeric fibre-composites possess a relatively low shear modulus, e.g. {U/C PEEK ~4GPa ; aluminium alloy ~26GPa ; mild steel ~79GPa}. The low shear modulus of the fibre-composite substrates leads to additional rotations and deflections occurring at the crack tip.

In order to account for this effect, Williams [78] conducted a short beam analysis for polymeric fibre-composites. This analysis included shear and distinguished between the angle of rotation of the beam cross-section, ψ , and the slope of the horizontal central axis, dw/dx as is shown in Figure 4.1.

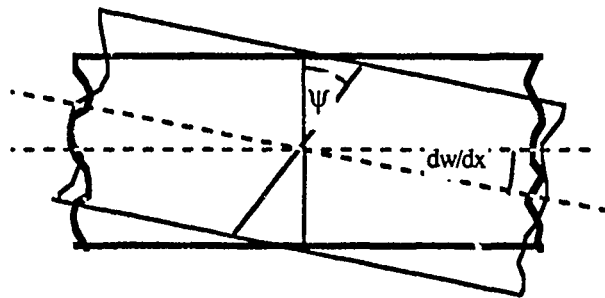


FIGURE 4.1 Distortion of a beam element in the short beam analysis conducted by Williams [78].

Thus the deflection and rotation due to both bending and shear were considered. The shear strain was given by $(dw/dx) - \psi$ and thus the shear force Q , was expressed as:

$$Q = KG_{12}A\left(\frac{dw}{dx} - \psi\right) \quad (4.1)$$

where K is an elastic constant used to correct the distribution of shear stress, G_{12} is the shear modulus of the fibre-composite and A is the cross sectional area of the beam. By applying the equilibrium relationships between the bending moment and the shear force, and applying the necessary boundary conditions, Williams showed theoretically that the value of χ may be given by:

$$\chi = \left(\frac{E_{11}}{12G_{12}}\right)^{\frac{1}{2}} \left[3 - 2\left(\frac{\Gamma}{1+\Gamma}\right)^2\right]^{\frac{1}{2}} \quad (4.2)$$

where E_{11} is equivalent to E_s i.e. the axial modulus of the composite beam, and Γ is given by:

$$\Gamma = 1.18 \frac{(E_{11}E_{22})^{\frac{1}{2}}}{G_{12}} \quad (4.3)$$

where E_{22} is the through thickness modulus of the beam. The shear rotation and deflection at the crack tip was then modelled by adding a length, χh , to the crack length. Hashemi et al. [77] showed that the value of χh could be determined experimentally from the relationship between the measured compliance, C , of the arms of the DCB specimen and the crack length a . The relationship between these parameters is given by equation 4.4

$$C = N \frac{8(a + \chi h)^3}{Bh^3E_{11}} \quad (4.4)$$

where B is the beam width, and N is another correction factor to be discussed in Section 4.2.3. Rearranging equation 4.4:

$$\left(\frac{C}{N}\right)^{\frac{1}{3}} = \left(\frac{8}{Bh^3E_{11}}\right)^{\frac{1}{3}} (a + \chi h) \quad (4.5)$$

Therefore, if the corrected compliance $(C/N)^{1/3}$ measured experimentally, is plotted against the corresponding value of the crack length, a , then the intercept yields the value of χh , from which χ may be deduced. Also, from the gradient of the line, the value of the modulus, E_{11} , may be obtained as, from eqn.4.4 :

$$E_{11} = \frac{P}{\delta} \frac{8N(a + \chi h)^3}{Bh^3} \quad (4.6)$$

where P is the load and δ is the displacement at a given value of crack length, a . Typical values of χ for some fibre-composites are given in Table 4.1 [34].

TABLE 4.1 Typical χ values for some fibre-composites

Composite	mode I (DCB)	mode II (ELS)	mixed-mode ELS
U/C PEEK	2.40 $\pm$ 0.51	2.35 $\pm$ 0.13	2.32 $\pm$ 0.10
U/C PES	2.70 $\pm$ 0.55	2.63 $\pm$ 0.12	2.72 $\pm$ 0.13
U/C Epoxy	3.00 $\pm$ 0.38	2.94 $\pm$ 0.15	2.98 $\pm$ 0.07

4.2.2 Correction for Large Displacements

Substrate arms prepared from fibre-composites tend to be slender beams and often undergo large, albeit linear, displacements during a fracture test. Large displacements in the specimen cause the arm to effectively shorten. In addition, the bonded end-blocks give rise to further changes if the load point is above the beam, since the block tilts as the arm is distorted. The simple beam theory analysis takes no account of this shortening effect and therefore the analysis will over estimate the value of the bending moment at the crack tip.

The large displacements can be reduced by making thicker laminates, but this is expensive and inconvenient. In addition, large displacements could be reduced by reinforcing the beams with metal backing strips, but again this is expensive, time consuming and may introduce errors. Therefore, in order to calculate the effect of finite displacements, Williams [79] derived a general analysis on an element of beam to relate the angle of curvature of the beam to the shortening of the moment arm. The assumption made was that beam deformation was due solely to bending, such that the usual bending moment relations could be applied. The analysis yielded a multiplying factor, F , by which the small displacement values (i.e. the

uncorrected beam theory values of G_c in Chapter Two) should be multiplied in order to correct for the beam shortening effects. Thus:

$$G = FG_s \quad (4.7)$$

Where G is the value of the fracture energy corrected for large displacements and G_s is the small displacement value of G_c . Now, by approximating the exact analytical solution for F by small angle solutions, Williams [80] expressed F as:

$$F = 1 - \theta_1 \left(\frac{\delta}{L} \right)^2 - \theta_2 \left(\frac{\delta l_1}{L^2} \right) \quad (4.8)$$

where δ is the full DCB opening displacement, L is the length of the beam, l_1 is the height of the load point above the axis of the substrate as shown in Figure 4.2 and the values of θ_1 and θ_2 are given in Appendix 1. {For the mode I case, $L=a$ }

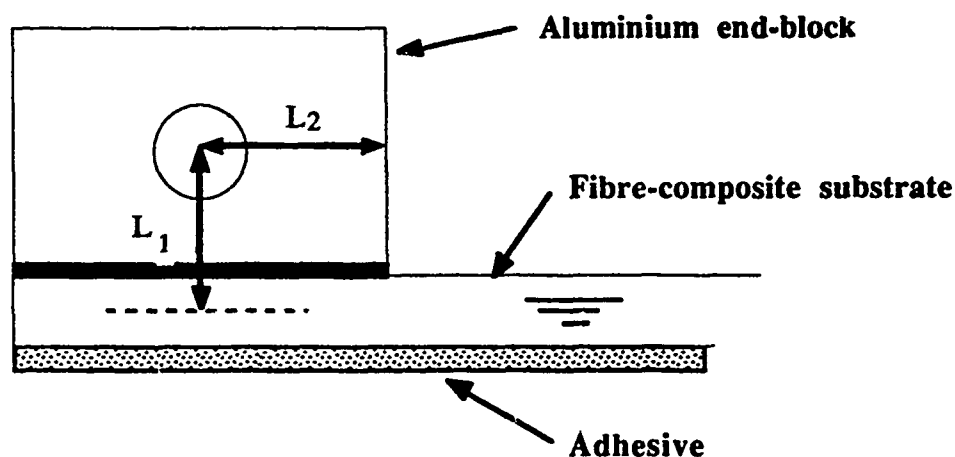


FIGURE 4.2 Arrangement of the bonded end-block on the adhesively bonded DCB specimen. {Dimensions L_1 and L_2 shown}.

4.2.3 Correction for End-Block Effects

Since the test specimens are loaded via end-blocks bonded to the specimen arms, a correction factor is also required to account for the stiffening effect caused by these metal end-blocks. The correction factor was derived by Williams [80] and is most conveniently expressed in the form of the factor N , by which the displacement, δ , should be divided. In this form the correction factor N also includes (in the last two terms) the corrections needed for the end-block tilting and large displacement effects. Thus:

$$N = 1 - \theta_3 (l_2/L)^3 - \theta_4 (\delta l_1/L^2) - \theta_5 (\delta/L)^2 \quad (4.9)$$

where the values of θ_3 , θ_4 , and θ_5 are defined in Appendix 1.

4.2.4 Corrected Beam Theory Equations for Mode I Fracture

By applying the correction factors discussed above to eqn. 2.24 and eqn. 2.26 the corrected beam theory equations for mode I may be expressed as:

The "corrected load method" :

$$G_c = \frac{12FP^2(a + \chi h)^2}{B^2 h^3 E_s} \quad (4.10)$$

The "corrected displacement method":

$$G_c = \frac{F}{N} \frac{3P\delta}{2B(a + \chi h)} \quad (4.11)$$

Substituting for the load from equation 4.6 into 4.11 yields a further expression for the adhesive fracture energy, G_c , which is given in equation 4.12. Thus:

$$G_c = \frac{3}{16} \frac{F}{N^2} \frac{\delta^2 h^3 E_s}{(a + \chi h)^4} \quad (4.12)$$

The significance of this expression is that G_c is now independent of the measured value of the load, P . It will be shown in Chapter Six that at higher test rates, the measurements of the load become less reliable and thus equation 4.12 can be applied with greater confidence than either equations 4.10 or 4.11.

4.3 Mode I Fracture: Results and Discussion

4.3.1 Force-Displacement Behaviour of the Bonded Joints

Bonded DCB test specimens were prepared with either the U/C epoxy or U/C PEEK substrates, bonded with either the epoxy-film or epoxy-paste adhesive. The U/C PEEK was

corona treated to $10\text{J}/\text{mm}^2$ prior to bonding with the epoxy-film adhesive, or to $20\text{J}/\text{mm}^2$ prior to bonding with the epoxy-paste adhesive. Mode I tests were conducted using the screw-driven machine, as was described in Chapter Three. A constant crosshead displacement rate of $2\text{mm}/\text{min}$ was employed. Figures 4.3 and 4.4 show typical force-displacement traces for the U/C epoxy substrates bonded with the epoxy-film and epoxy-paste adhesives respectively.

It can be seen that the loading relations were linear to a point just prior to the instant of visual crack initiation. This effect was also observed by Davies et al [81] during interlaminar fracture testing of fibre-composites. They concluded that the point of deviation from linearity corresponded to the instant when the first microscopic crack tip damage occurred. It was noted that for the adhesive joint specimens, this point of deviation from linearity preceded the onset of visual crack growth by a small, but varying amount. In the present work, crack initiation will be defined as the point when visual crack growth first occurs as observed through the travelling microscope at slow rate, or by the high-speed camera at higher rates. Subsequent unloading and reloading relations were linear for all the joint systems tested.

To determine whether the degree of non-linear behaviour was sufficiently small for LEFM to be applicable, the ASTM [82] standard for testing metals was applied. The method requires that the initial slope of the load-displacement diagram be offset by 5%. If the 5% offset line now intersects the load-displacement diagram at a load $P_{5\%}$, such that the ratio of $P_{\text{max}}/P_{5\%} < 1.1$, then the assumptions of LEFM are valid. This procedure was carried out for each of the four DCB joints systems tested. All of the joint systems obeyed this standard, and typically the ratio of $P_{\text{max}}/P_{5\%} < 1.05$.

The maximum force attained when loading joints bonded with the epoxy-paste adhesive was significantly higher than when loading joints bonded with the epoxy-film adhesive. It is for this reason that it is necessary to corona treat the U/C PEEK to a higher level prior to bonding with the epoxy-paste adhesive. After crack initiation, stable, cohesive crack propagation was observed in both adhesives, when the substrate was the U/C epoxy composite. Similar results were obtained when the substrate material was U/C PEEK, provided that sufficient corona treatment had been applied to this composite before bonding in order to avoid interfacial failure.

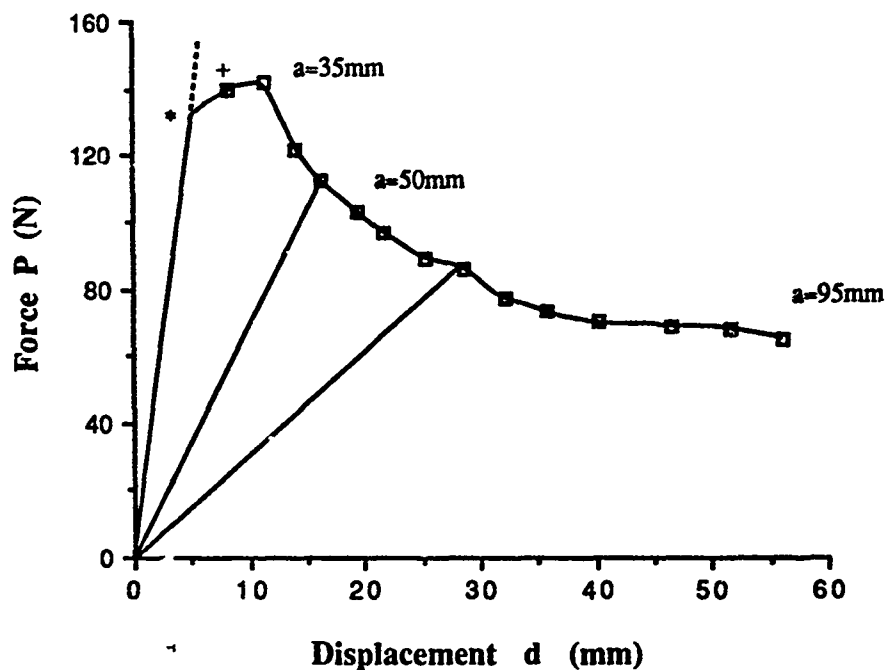


FIGURE 4.3 Force versus displacement trace for the U/C epoxy substrates bonded with the epoxy-film adhesive. {'*' indicates the point of deviation from linearity; '+' indicates the point of visual crack initiation} Some crack length values are also shown.

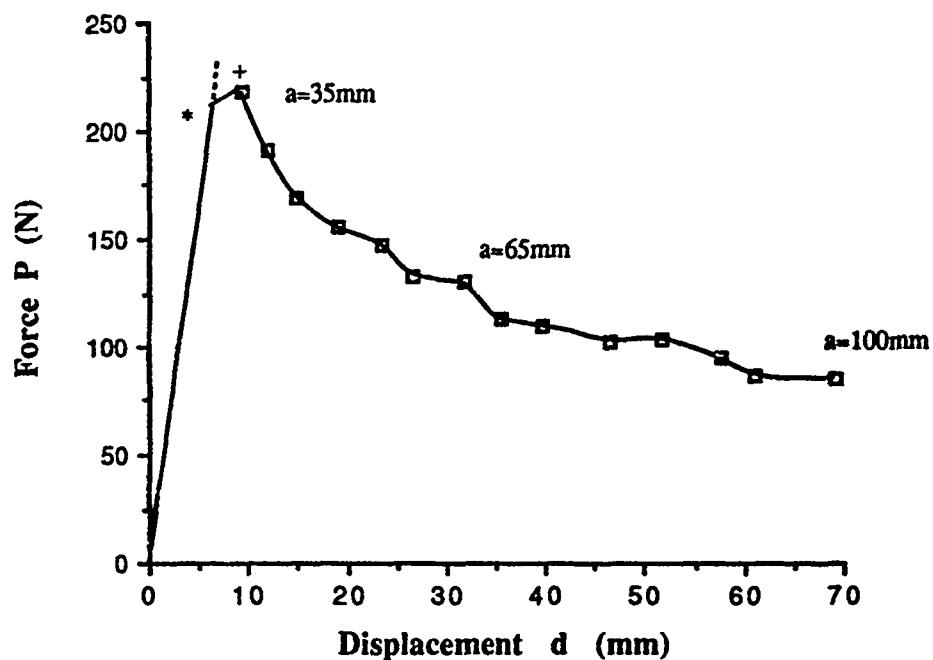


FIGURE 4.4 Force versus displacement trace for the U/C epoxy substrates bonded with the epoxy-paste adhesive. {'*' indicates the point of deviation from linearity; '+' indicates the point of visual crack initiation} Some crack length values are also shown.

4.3.2 Calculation of dC/da and the Shear Correction Term χ

It was described in Chapter Two how the data in Figures 4.3-4.4 could be analysed in a number of different ways. In order to use the "compliance method", the values of dC/da are required at each crack length. This can be achieved if the compliance (δ/P), obtained from the force-displacement traces, is plotted against the crack length. By curve fitting this data to a third order polynomial function, as shown in Figure 4.5, the compliance may be expressed as a function of a . Then, by differentiating this function, the value of dC/da was obtained at each crack length.

In order to use the corrected beam theory expressions discussed in Section 4.2, it was necessary to determine experimentally the value of the shear correction term, χh . This was ascertained by plotting $(C/N)^{1/3}$ versus crack length for each data set. A typical plot of this type is shown in Figure 4.6. It can be seen that an excellent linear fit to the data exists. In this case, the substrate material was U/C epoxy, bonded with the epoxy-film adhesive. The y-axis intercept yielded a value of $\chi h = 5.42$, thus $\chi = 3.28$ for this specimen.

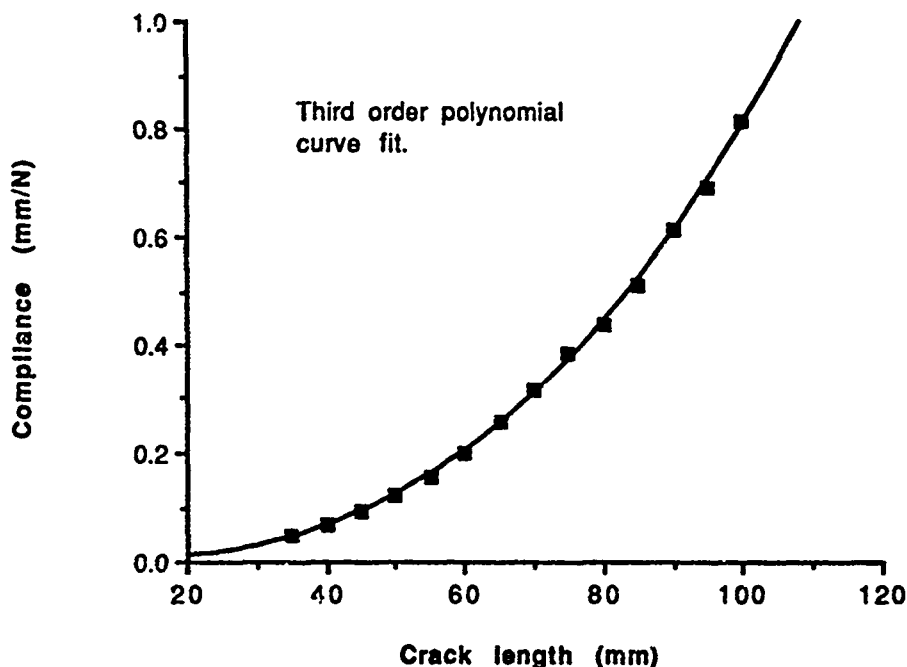


FIGURE 4.5 Third order polynomial curve fit of compliance as a function of crack length for the epoxy composite bonded with the epoxy-film adhesive.

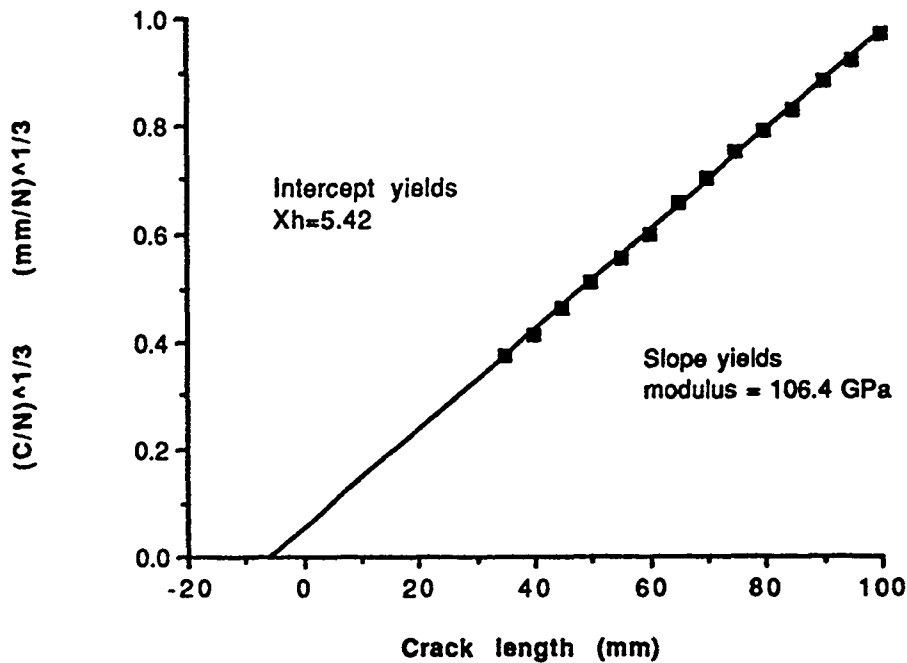


FIGURE 4.6 $(C/N)^{1/3}$ versus the crack length, a for the epoxy composite bonded with the epoxy-film adhesive.

4.3.3 Comparison of the Uncorrected and Corrected G_c Values

As can be seen from Table 4.2, there is reasonable agreement between the values of the adhesive fracture energy, G_c , calculated by the "area" and "compliance" methods. The former method was somewhat less accurate than the latter method due to the fact that a derivative is approximated by two finite measurements when using the "area method". However, there was poor agreement between these values, and the values of G_c calculated by the load and displacement methods, based on the assumptions of simple beam theory i.e. eqns 2.24 and 2.26. Eqn. 2.24 predicts low values of G_c at all crack lengths and this value was seen to rise with increasing crack length, which would suggest that the bonded joint exhibits an "R-curve" effect. These values are shown diagrammatically in Figure 4.7.

TABLE 4.2 Values of G_c and substrate modulus, E_s , calculated from the different methods of analysis

Crack length mm	G_c Area kJ/m ²	G_c Comp. kJ/m ²	G_c Load kJ/m ²	G_c Displ. kJ/m ²	G_c C.Load kJ/m ²	G_c C.Disp kJ/m ²	G_c C.DisE kJ/m ²	E_s GPa	E_s Corr. GPa	F	N
	(2.14)	(2.17)	(2.24)	(2.26)	(4.10)	(4.11)	(4.12)	(2.25)	(4.6)	(4.8)	(4.9)
35		2.51	1.52	2.75	2.49	2.52	2.45	79.4	104.9	0.921	0.922
40	2.50	2.75	1.54	2.86	2.56	2.49	2.42	80.8	109.6	0.913	0.922
45	2.61	2.70	1.58	2.84	2.55	2.50	2.44	83.3	108.7	0.910	0.923
50	2.63	2.66	1.62	2.84	2.55	2.52	2.49	85.4	107.7	0.906	0.922
55	2.49	2.58	1.62	2.76	2.51	2.46	2.42	88.2	108.2	0.905	0.921
60	2.59	2.61	1.70	2.83	2.56	2.54	2.52	90.0	107.4	0.899	0.917
65	3.02	2.44	1.63	2.77	2.41	2.50	2.58	88.4	102.9	0.892	0.913
70	2.42	2.31	1.59	2.63	2.32	2.39	2.45	90.4	103.4	0.891	0.912
75	2.37	2.19	1.54	2.51	2.23	2.29	2.35	91.9	103.5	0.890	0.911
80	1.93	2.44	1.75	2.72	2.48	2.48	2.48	96.7	106.6	0.880	0.903
85	2.20	2.44	1.79	2.68	2.50	2.45	2.40	100.0	108.7	0.877	0.900
90	2.76	2.28	1.70	2.57	2.35	2.36	2.36	99.1	106.2	0.873	0.897
95	2.01	2.50	1.89	2.75	2.57	2.53	2.48	103.1	108.4	0.862	0.888
100	2.83	2.35	1.81	2.65	2.17	2.58	2.44	102.4	89.4	0.857	0.884

Notes: The substrates were prepared from an epoxy matrix, containing unidirectional carbon fibres. The thickness of the composite substrate arms was 1.68mm. The adhesive was the epoxy-film formulation from American Cyanamid.

The value of G_c deduced using the corrected beam theory equations are also shown in Table 4.2. Values from using the "corrected load" (eqn. 4.10) and "corrected displacement" (eqn. 4.11) and "corrected displacement-modulus" (eqn. 4.12) are shown. In these equations, the values of the correction factors F and N and χh were included. It should be noted that F and N become increasingly significant as the crack length increases, i.e. as δ increases. It can be seen in Figure 4.8 that the values of G_c obtained from these corrected beam theory equations are now in excellent agreement with each other, and also with the compliance method of analysis which is unaffected by the correction factors. Further, the corrected load method now shows that there is no increase in G_c with increasing crack length i.e. no "R-curve" actually exists for these joints. It can be seen that the "area method" for calculating G_c shows the most scatter.

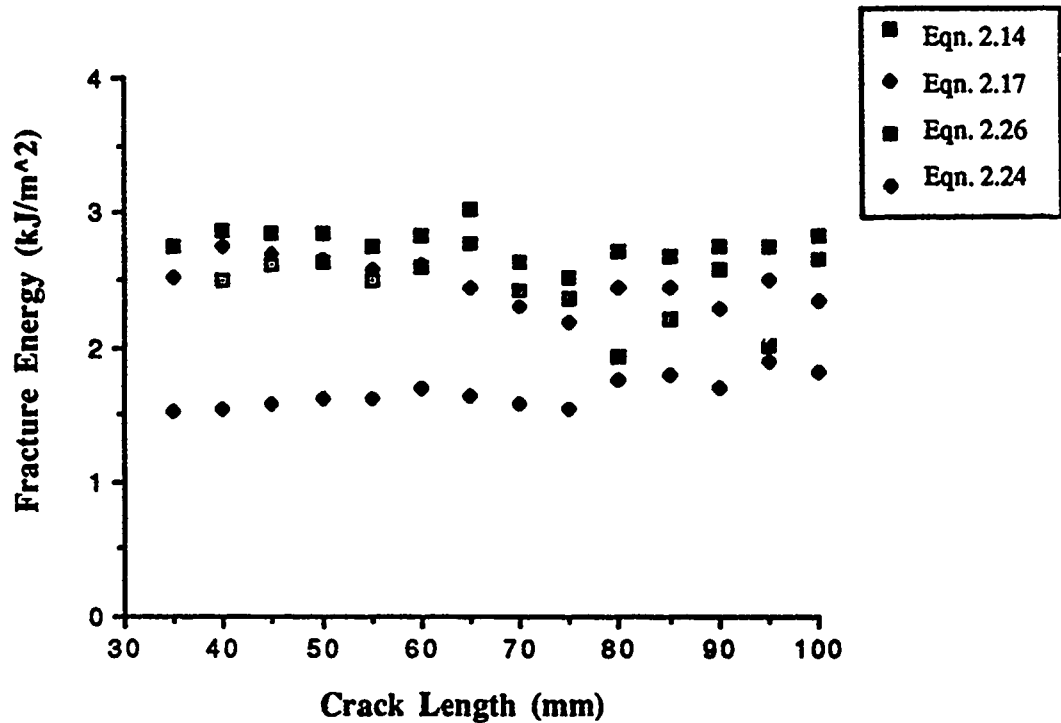


FIGURE 4.7 Comparison of the uncorrected methods for calculating the adhesive fracture energy, G_c , as a function of crack length. The adhesive employed was the epoxy-film adhesive and the substrates were U/C epoxy.

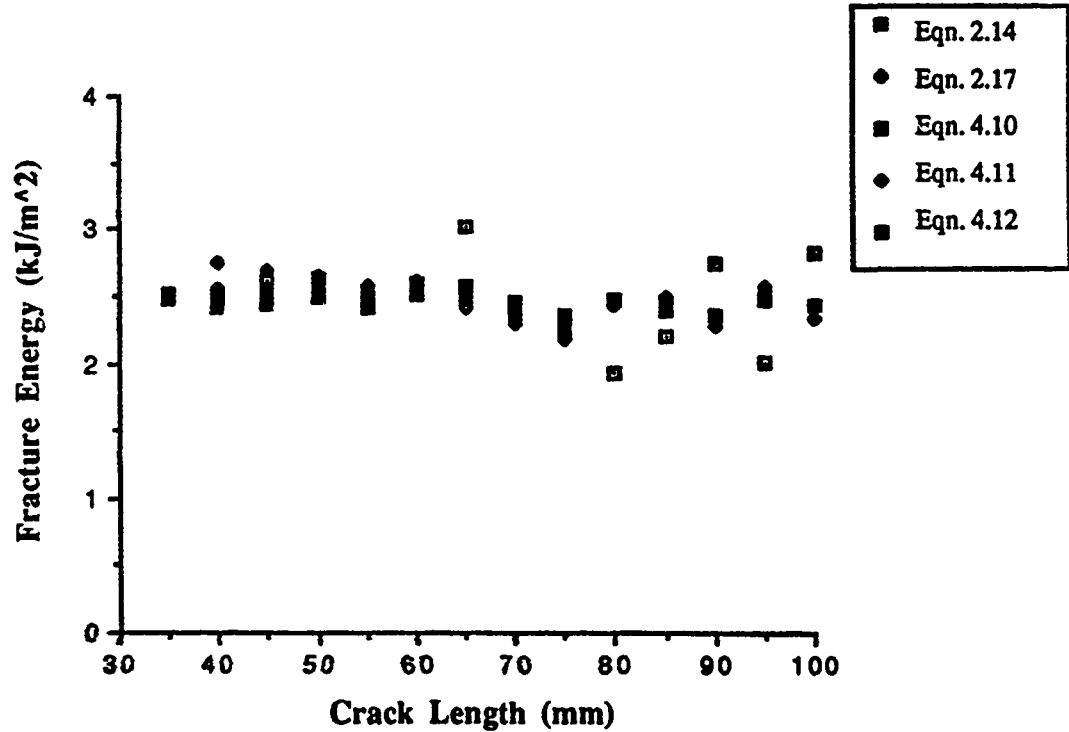


FIGURE 4.8 Comparison of the corrected methods for calculating the adhesive fracture energy, G_c , as a function of crack length. The adhesive employed was the epoxy-film adhesive and the substrates were U/C epoxy.

4.3.4 Comparison of the Uncorrected and Corrected Substrate Modulus Values

Figure 4.9 shows the variation of the uncorrected modulus, obtained by rearranging eqn. 2.25, and the corrected modulus, eqn. 4.6, with crack length for a typical joint prepared with the U/C epoxy composite bonded with the epoxy-film adhesive. It can be seen that when the correction factors are not employed, then the value of E_s was seen to increase with crack length. Obviously, this was an incorrect conclusion. However, when the correction factors were applied, then a constant value of E_s was calculated i.e. E_s was no longer dependent on crack length. A value of 106.4GPa was calculated for this specimen. The same result was obtained from the slope of the $(C/N)^{1/3}$ versus 'a' plot shown in Figure 4.6 for this specimen.

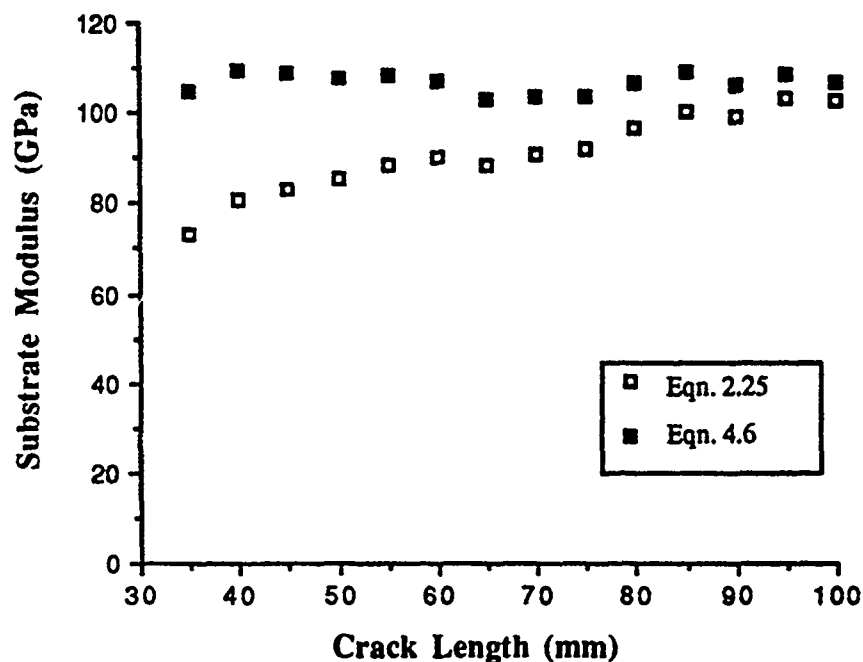


FIGURE 4.9 The variation of the "uncorrected" and "corrected" substrate modulus values versus crack length for the U/C epoxy composite bonded with the epoxy-film adhesive.

The values of E_s obtained for the fibre-composite substrates were in good agreement with the independently measured value obtained using a three-point bend flexure test. This test was described in Section 3.3.4 and it showed that the fibre-composite substrates (both U/C epoxy and U/C PEEK) possessed a uniaxial substrate modulus of approximately 110GPa. This value was somewhat lower than quoted in the manufacturers' data, and this was probably due to the slightly lower fibre-volume fractions obtained during the preparation of the beams. To

achieve beams with exactly the same fibre-volume fraction as quoted in the manufacturers' data sheet, 12 composite pre-preg plies should be compressed to 1.5mm in thickness. However, following the manufacturers' cure cycle, 12 plies compressed to a nominal thickness of 1.65mm. Therefore, the resulting fibre-volume fraction would have been approximately 10% lower than quoted in the data sheet. This would account for the marginally lower E_s values obtained from beam theory and also from the independent measurements [106].

4.3.5 Concluding Remarks on Mode I Fracture

The results in Table 4.2 clearly show that when the corrected beam theory analyses were employed, then excellent agreement was obtained between values of the adhesive fracture energy, G_c , calculated by the compliance methods and by the corrected beam theory methods. Because all crack growth was cohesive, the value of G_c depended only on the adhesive employed, and not the substrate. Typical G_c versus 'a' plots are shown in Figure 4.10 for joints bonded with both adhesives.

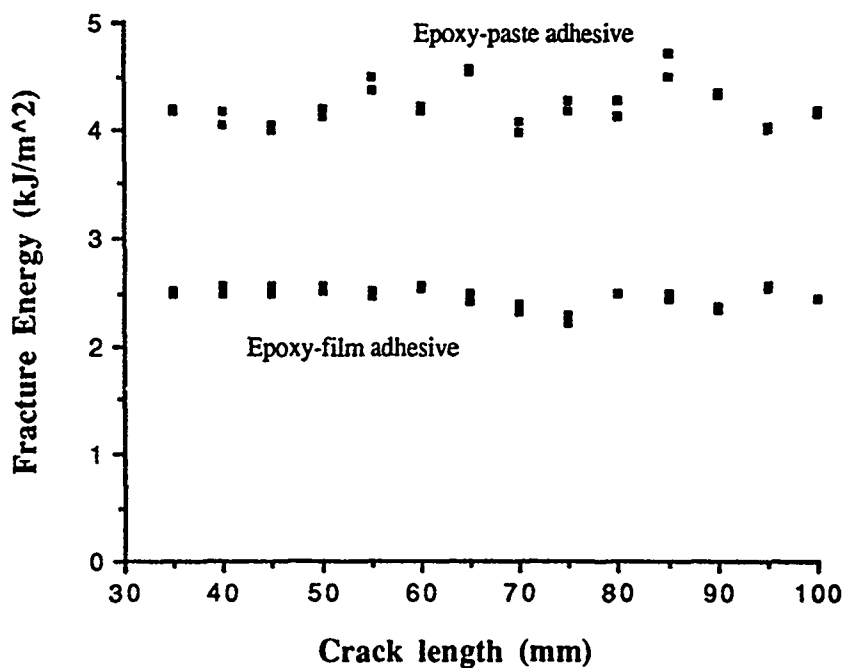


FIGURE 4.10 The variation of the adhesive fracture energy, G_c , versus crack length for the U/C epoxy composite bonded with the epoxy-paste or epoxy-film adhesive. G_c was calculated by the "corrected load" and "corrected displacement" methods. All failure was cohesive

The corrected analysis showed that no "R-curve" existed for these materials. Thus, the adhesive fracture energy at the point of visual crack initiation was equivalent to the propagation value. It can be seen that the epoxy-paste adhesive was significantly tougher than the epoxy-film adhesive.

4.4 Mixed-mode Fracture

4.4.1 Introduction

Although the main emphasis of the current work is to investigate the mode I fracture behaviour of bonded joints under various test conditions, it is of interest to investigate the effect that different ratios of mode I to mode II loading will have on the joint fracture behaviour. Mixed-mode loading is commonly encountered in engineering structures made from bonded fibre-composites because a crack will often propagate through the adhesive layer, irrespective of the applied loading.

The mixed-mode fracture behaviour of bonded joints can be investigated using the mixed-mode bending (MMB) test apparatus designed by Reeder and Crews [38], and which was described in Chapter Three. The apparatus was shown in Figure 3.8. The major advantage of using this apparatus was that a large number of different ratios of mode I to mode II loading could be attained using symmetrically cracked DCB test specimens. The modified version of the test rig has been employed, i.e. the load was applied through a saddle and bearing in order to remove the geometric non-linearity and the lengths 'b' and 'c' could be adjusted.

The bending moments M_I and M_{II} on the upper and lower arms of the test specimen respectively were calculated and then these values were substituted into the generalized beam theory equations (eqn.2.22 and 2.23). Using these equations it is possible to calculate the values of G_I and G_{II} for any loading configuration. However, in order to deduce accurate G values, the simple beam equations must again be corrected for shear rotations and displacements at the crack tip, and for large displacements.

4.4.2 Correction Factors for the Modified MMB Test

The beam theory analysis of mixed-mode fracture assumed that the substrate arms behave as perfectly built in beams with zero deflection and zero rotation of the beam at the crack tip. It was discussed in Section 4.2 that due to the low shear modulus of polymeric fibre-composites, it is necessary to apply the correction factor χ_h to the measured crack length in

order to account for the error in this assumption. The value of χ depends on the mode of loading and hence it was necessary to define the factors, χ_I for the mode I case and χ_{II} for the mode II case. The value of χ_I is equivalent to the previous value of χ calculated for mode I fracture. It was shown by Wang and Williams [83] that the factor χ_{II} may be deduced from:

$$\chi_{II} = 0.42\chi_I \quad (4.13)$$

where χ_{II} is the shear correction term in mode II cases. In addition to shear corrections, the large displacements which can occur during the mixed-mode loading of slender fibre-composite beams effectively shorten the moment arm lengths. This shortening effect was considered by Kinloch et al. [Kinloch, 1992 #86] using the same theoretical approach as was employed for mode I correction. The result was the derivation of the correction factors F_1 and F_2 which should be applied to the bending moments M_1 and M_2 in order to correct for large displacements.

By applying these correction factors to the simple beam theory eqns for G_I and G_{II} , as given in eqns. 2.31 and 2.32, then the corrected equations for G_I and G_{II} may be expressed as:

$$G_I = \frac{3P^2(a + \chi_I h)^2}{B^2 E_{II} h^3} \left\{ \left(1 - \frac{c+b}{L}\right) F_2 - \frac{c}{b} F_1 \right\}^2 \quad (4.14)$$

and:

$$G_{II} = \frac{9P^2(a + \chi_{II} h)^2}{4B^2 E_{II} h^3} \left\{ \left(1 - \frac{c+b}{L}\right) F_2 + \frac{c}{b} F_1 \right\}^2 \quad (4.15)$$

where c , b and L were defined on Figure 3.8 and χ_I , χ_{II} , F_1 and F_2 are the correction factors for shear rotation and large displacements respectively. The values of F_1 and F_2 are given in Appendix 2. It should be noted that the expressions in eqns 4.14 and 4.15 refer to G_I and G_{II} not G_{Ic} {expressed simply as G_c in the present work} and G_{IIc} . Hence, this is not a failure criterion because the crack will grow due to a combination of G_I and G_{II} . A criterion for mixed-mode failure will be discussed in Section 4.4.5.

4.4.3 Mixed-Mode Results

Symmetrically-cracked DCB test specimens were prepared as before and loaded on the modified MMB test apparatus as described in Section 3.3.2. The values of ' c ' and ' b ' were

adjusted in order to achieve seven different ratios of G_I to G_{II} from 0.002 to 35. All crack propagation was cohesive, through the adhesive layer. A typical force-displacement trace is shown in Figure 4.11 for the U/C epoxy substrates bonded with the epoxy-film adhesive. This joint was loaded with a ratio of $G_I/G_{II} = 11$. The trace was linear up to a point just prior to visual crack initiation. The values of G_I and G_{II} were calculated as a function of crack length using eqns. 4.14 and 4.15 respectively. The values of G_I and G_{II} calculated are shown in Figure 4.12. As can be seen, the results show that no "R-curve" exists for this adhesive joint system, as was previously deduced from pure mode I tests and the ratio of G_I to G_{II} is independent of crack length during this test.

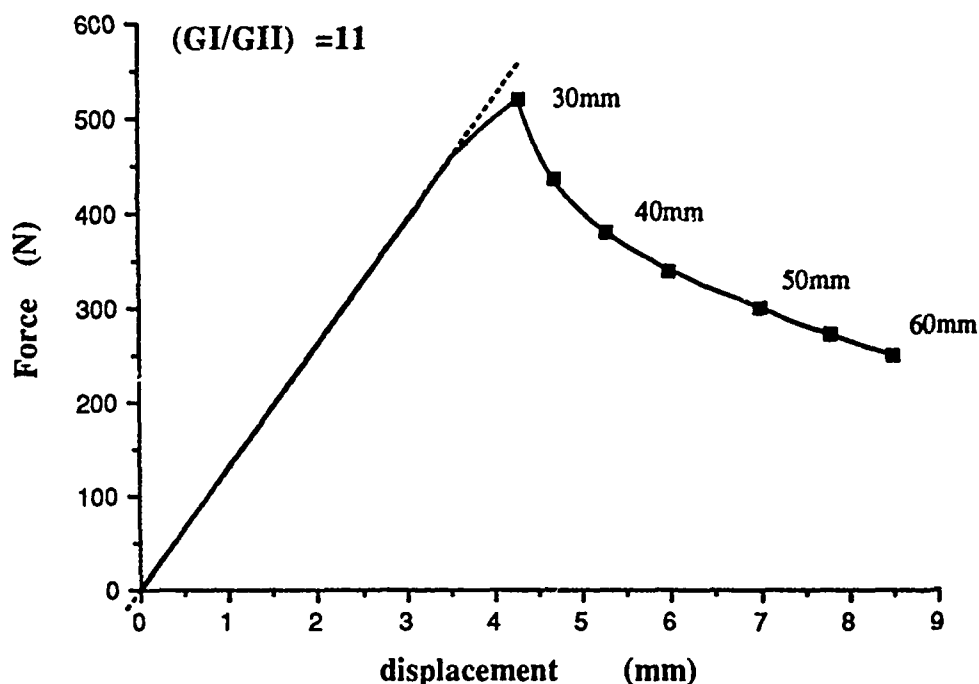


FIGURE 4.11 Force versus load-point displacement, δ_E , for the U/C epoxy composite bonded with the epoxy-film adhesive and tested on the modified MMB test rig with a nominal $(G_I/G_{II})=11$. Locus of failure was cohesive.

Similar tests were performed on joints bonded with the tougher, epoxy-paste adhesive. However, due to the higher toughness of this adhesive, it was not possible to achieve crack growth when the ratio of G_I/G_{II} was less than two. In addition, due to the very large bending moments experienced when testing joints bonded with this adhesive, permanent deformation of the substrate material was observed when crack growth did not occur. Thus, some energy was absorbed plastically deforming the substrates and hence an LEFM approach could not be followed.

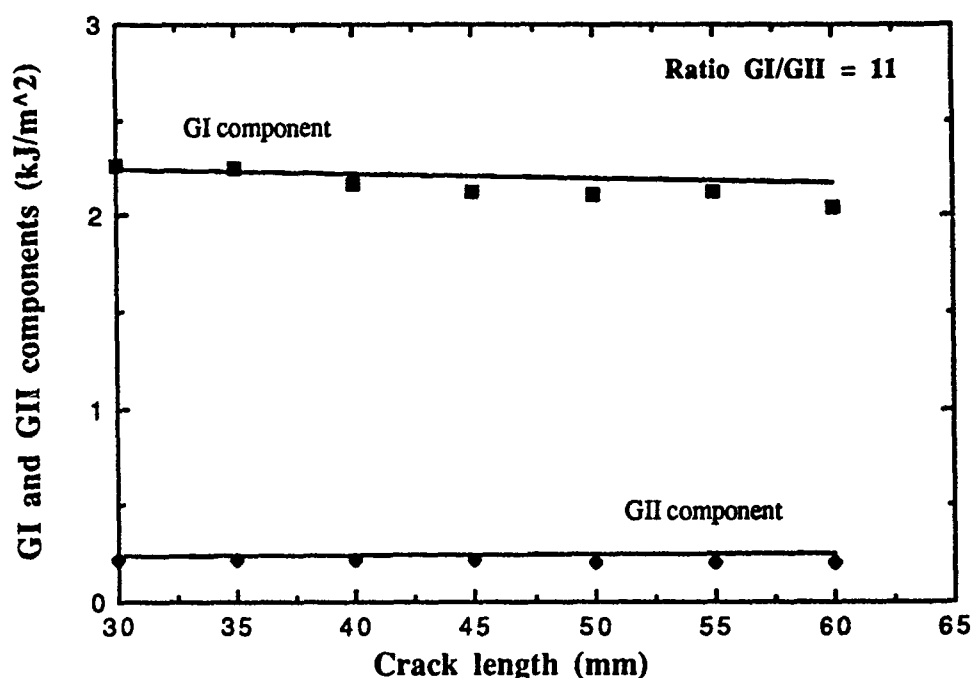


FIGURE 4.12 The mode I and mode II components of G versus crack length from the modified MMB tests for the U/C epoxy substrates bonded with the epoxy-film adhesive. ($G_I/G_{II}=11$).

4.4.4 Mode II ELS Tests

The pure mode II value of the adhesive fracture energy, G_{IIc} , was measured for the U/C epoxy substrates bonded with the epoxy-film adhesive using the end-loaded split (ELS) test, as shown in Figure 3.8. Three similar joints were tested in mode II and, for this adhesive $G_{IIc} = 4.41 \pm 0.3 \text{ kJ/m}^2$. When joints prepared with the tougher, epoxy-paste adhesive were loaded in pure mode II on the ELS rig, no crack propagation was observed. The joints finally failed by the entire beam fracturing in the through thickness direction at the point of roller contact. Attempts to obtain mode II crack growth in this adhesive by employing cracks of different lengths were not successful and it was concluded that the mode II value of the fracture energy of this adhesive was too high to measure using this geometry.

4.4.5 The Mixed-mode Failure Locus

It is clearly of interest to determine the failure locus i.e. the plot of G_I against G_{II} for all ratios, of the adhesive joints systems under investigation. When the loading is pure mode I, then the fracture criterion is that failure occurs when G_I attains the critical value, G_{Ic} . Similarly, when loading is in pure mode II, G_{IIc} must be attained before failure occurs. However, when

G_I and G_{II} are both present the situation is more complex. In order to determine the locus, it is necessary to employ a mixed-mode failure criterion. The mixed-mode failure criterion proposed by Charalambides et al. [39] i.e. eqn 2.35 has been employed and this criterion for mixed-mode failure assumes that a crack globally loaded with G_I and G_{II} will have an induced mode I component equal to the failure value, termed G_0 , such that:

$$G_0 = G_c \{ \cos^2(\psi - \psi_0) + \sin^2 \omega \sin^2(\psi - \psi_0) \} \quad (2.35)$$

where G_c is the measured fracture energy, ψ , is the phase angle of the applied loads, ψ_0 is the phase angle which arises from the elastic mismatch across a bimaterial interface and where ω can be regarded as the fracture surface roughness.

In order to employ the criterion, it is necessary to deduce the experimental values of G_{Ic} , G_{IIc} and $G_{I/IIc}$. The last term is the value of the fracture energy when $G_I = G_{II}$, i.e. when the phase angle of the applied loading $\Psi=45^\circ$. For the epoxy-film adhesive, these values were measured to be 2.5kJ/m², 4.4kJ/m², and 3.3 kJ/m² respectively. The phase angle of the applied loading, which is sometimes referred to as the "mixture" is given by:

$$\Psi = \tan^{-1} \sqrt{\frac{G_{II}}{G_I}} \quad (4.16)$$

The other parameters required by the model are G_0 , Ψ_0 and ω . These terms can be calculated provided that G_{Ic} , G_{IIc} and $G_{I/IIc}$ are known. The procedure for calculating these parameters is given in Appendix 3. These parameters have been determined for the epoxy-film adhesive from DCB, ELS and MMB tests respectively. These basic fracture criterion parameters were calculated to be:

$$G_0 = 2.5 \text{kJ/m}^2, \quad \Psi_0 = 3.5^\circ \quad \text{and} \quad \omega = 48.8^\circ$$

The failure locus for the joints bonded with the epoxy-film adhesive is shown in Figure 4.13. It can be seen that the MMB data agrees well with the data obtained from the DCB and ELS tests for this joint system. The modified MMB test is therefore an accurate method by which to measure the mixed-mode fracture behaviour of joints, provided that the adhesives employed are not too tough. For tougher joint systems, e.g. the joints bonded with the epoxy-paste adhesive in the present work, a non-linear analysis would have to be employed in order to account for the material non-linear effects seen in these tests. Such an analysis has been

conducted by Charalambides [84] for the mode I and mixed-mode fracture of glass reinforced phenolic composites.

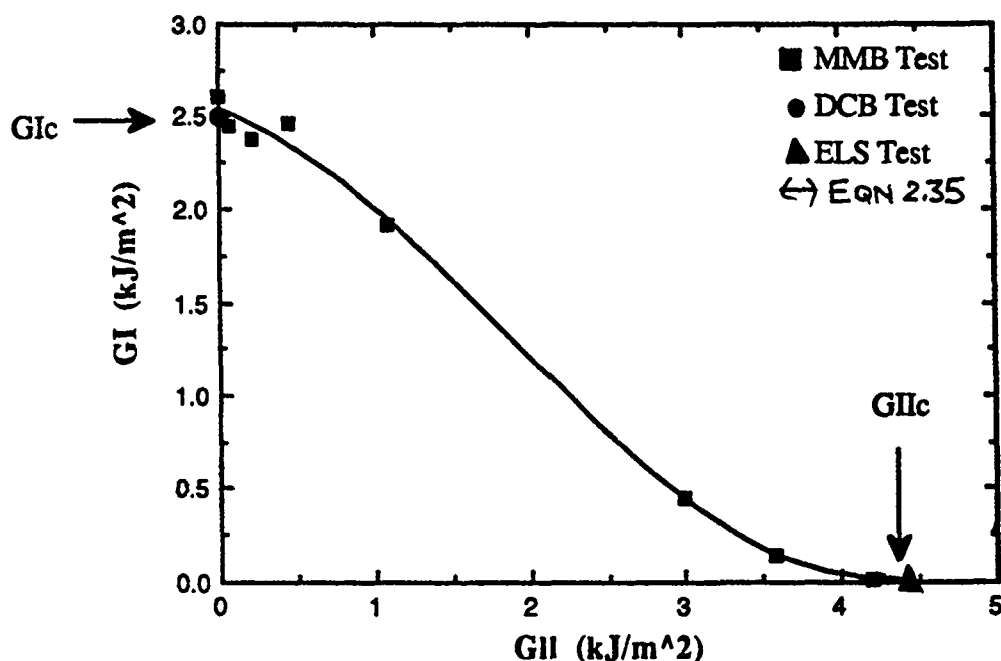


FIGURE 4.13 Failure locus for the U/C epoxy composite bonded with the epoxy-film adhesive.

4.4.6 Discussion of the Mixed-mode Failure Locus

The rather low value of ψ_0 calculated for this joint system implies that the elastic mismatch term is small. This suggests that failure occurred away from the adhesive-substrate interface, and this was confirmed by a visual examination of the fracture surfaces which showed that the locus of failure remained cohesive at all values of ψ . Finally, it was noted that the value of the adhesive fracture energy increased as the proportion of mode II loading increased, i.e. $G_{IIc} > G_{I/IIc} > G_{Ic}$ for this joint system. Although this is a typical result for fibre-composite materials, it is not typical for toughened epoxies. Bascom and Oroshnik [85] found that the value of G_{IIc} was only slightly greater than the value of G_{Ic} for a rubber toughened epoxy. In addition, they showed that the mixed-mode values of $G_{I/IIc}$ were very much less than either G_{Ic} or G_{IIc} . The reasons for this behaviour are not well understood. One possible explanation was suggested by Kinloch [1] for this behaviour. He suggested that the value of $G_{I/IIc}$ may have been suppressed due to the scarf-joint geometry which was employed by Bascom and Oroshnik. This could have been achieved if the locus of failure in a joint of this geometry was

focussed into the interfacial region by the combined stress loading. This in turn may have restrained the development of the plastic zone ahead of the crack tip, and hence restrained the value of $G_{I/IIc}$. However, in the present work, it is clear that $G_{IIc} > G_{I/IIc} > G_{Ic}$ and thus mode I represents the most damaging mode of crack propagation in this joint system.

4.5 Chapter Four Conclusions

The main conclusions from this chapter are:

1. The simple beam theory analyses may be corrected by the use of three correction factors which account for the effects of: (i) shear rotation and deflection of the beams at the crack tip; (ii) large displacements in the arms of the DCB specimen during a fracture test; and finally, (iii) the stiffening of the beams due to the addition of the metallic end-blocks.
2. When the correction factors were employed, then excellent agreement was obtained between values of the adhesive fracture energy calculated via the "compliance method" and by three different "corrected beam theory" equations.
3. The mode I values for the adhesive fracture energy, G_c were found to be $2.5 \pm 0.1 \text{ kJ/m}^2$ and $4.1 \pm 0.3 \text{ kJ/m}^2$ for the epoxy-film and epoxy-paste adhesives respectively. All failure was cohesive, i.e. within the adhesive layer, provided adequate surface preparation was undertaken. Therefore, the values of G_c were independent of which composite substrate was used.
4. When the corrected forms of the analysis were used, it was shown that the adhesive joints did not show an "R-curve" effect when either adhesive was employed. In addition, when the modulus of the composite substrates were calculated via the "corrected-load method", then the value obtained was no longer dependent on crack length, as had been observed when the uncorrected analysis was employed.
5. The value of the substrate modulus was calculated by corrected beam theory to be $110 \pm 5 \text{ GPa}$ for each substrate. This value was confirmed by independent measurements on samples of each composite substrate in a series of three-point bend tests. This value was about 10% lower than quoted by the manufacturer. The discrepancy was most probably caused by the actual fibre-volume fraction achieved during cure being less than the nominally quoted fibre-volume fraction for the two fibre-composites employed.

6. The end-loaded split (ELS) test was successfully used to measure the mode II fracture resistance for the epoxy-film adhesive. It was found that $G_{IIc} = 4.41 \pm 0.35 \text{ kJ/m}^2$ for this adhesive. However, it was not possible to obtain mode II crack growth in the tougher, epoxy-paste adhesive. Specimens fractured in the through thickness direction at the point of roller contact before any crack growth was recorded.

7. The modified mixed-mode bending (MMB) test apparatus was successfully employed to load symmetrically-cracked DCB joint specimens bonded with the epoxy-film adhesive using ratios of G_I/G_{II} from 35 to 0.002. Crack propagation was again cohesive, within the epoxy-film adhesive. For the epoxy-paste adhesive, crack propagation was only observed when the loading was predominantly mode I.

8. For the U/C epoxy composite bonded with the epoxy-film adhesive, the values of G_I and G_{II} calculated by corrected beam theory were successfully fitted to a generalized mixed-mode failure criterion .

Chapter Five

Surface Preparation Using An Oxygen Plasma

5.1 Introduction

Most industrial applications of plasma processing have, until now, been focused towards the preparation of components prior to a printing or painting process. Examples include the treatment of polyethylene film prior to printing and the treatment of moulded polypropylene vehicle bumpers prior to painting. The application of gas plasma processing to the adhesion of difficult-to-bond materials in structural applications is an area in which there is now a growing interest. The significant advantages which thermoplastic materials offer to the engineer and which were described in Chapter One could be more fully exploited if the difficulties relating to their lack of intrinsic adhesion could be overcome.

Several workers [29, 30] have realized the potential advances which might be achieved if a plasma treatment could be successfully employed for the surface pretreatment of thermoplastics prior to bonding. It is clear from their work that this treatment may indeed be successful. The main aim of this Chapter is to assess the fracture behaviour of two plasma-treated thermoplastic fibre-composites and to relate this behaviour to the physical and chemical changes occurring on the material surface during treatment. For this purpose, the results obtained from mode I DCB tests on bonded plasma-treated U/C PEEK and U/C PPS will be presented. The results from a detailed surface analysis will then be discussed. Changes in surface topography and surface chemistry have been considered in an attempt to correlate the measured fracture energy, G_c , and the locus of joint failure, with physical and chemical characteristics of the surface.

Although it was described in Chapter Two how the corona-discharge treatment may be used to overcome the problems associated with the intrinsic lack of adhesion of thermoplastic fibre-composites, it may not always be possible to use this technique. A requirement for using the corona-discharge technique is that the material surface to be treated can be closely accessed by the electrode. As moulding shapes increase in complexity, electrode accessibility may be

restricted and it is possible that the electrode may not be able to access the required surface. In these instances, the alternative gas plasma technique may prove invaluable. In addition, plasma processing is far more versatile than corona-discharge processing. The treatment gas employed in plasma processing may be interchanged to achieve specific surface modifications as was discussed in Section 2.5.4, whereas the corona-discharge operates in atmospheric air. For these reasons, plasma processing is of considerable interest.

In this Chapter, the fracture behaviour of joints prepared from plasma treated U/C PEEK and U/C PPS will be investigated. DCB test specimens have been prepared with these materials bonded with the epoxy-film and epoxy-paste adhesives previously employed. The variation in the adhesive fracture energy, G_c , and the locus of joint failure have been assessed for each joint after having received various durations of treatment. Scanning electron microscopy and X-Ray photoelectron spectroscopy have then been employed in order to determine whether there exists a correlation between the measured fracture results and the physical and chemical characteristics of the treated surfaces.

5.2 Effect of Plasma Treatment on the Fracture Behaviour of Bonded Joints

5.2.1 Effect of Plasma Treatment on the Bonding of the U/C PEEK Composite

U/C PEEK substrates were abraded and solvent cleaned as described in Chapter Three. The substrates were then subjected to an oxygen plasma surface treatment for various periods. The treated substrates were then bonded with either the epoxy-film or the epoxy-paste adhesive as before, to form DCB test specimens. The results obtained from the mode I DCB testing are shown in Figures 5.1-5.2.

Figure 5.1 shows the results obtained when the adhesive fracture energy, G_c , was determined for the joints prepared with the U/C PEEK substrates bonded with the epoxy-film adhesive after various treatment times. It can be seen that when joints were prepared with substrates which had simply received an abrasion-solvent wipe pretreatment, without plasma treatment, then the joints failed in an interfacial manner with a value of $G_c=0.21\text{kJ/m}^2$. However, when the substrates were plasma-treated for 2.5 minutes at a power of 85W, then the subsequent locus of joint failure was cohesive and the value of $G_c=2.55 \pm 0.2 \text{ kJ/m}^2$ was measured for these joints. Increasing the duration of exposure to the plasma had no further effect on either the locus of joint failure or the measured value of G_c . It is therefore clear that a 2.5 minute treatment was sufficient to enhance the level of intrinsic adhesion across the adhesive-substrate to a level which ensured that the crack propagation was within the adhesive.

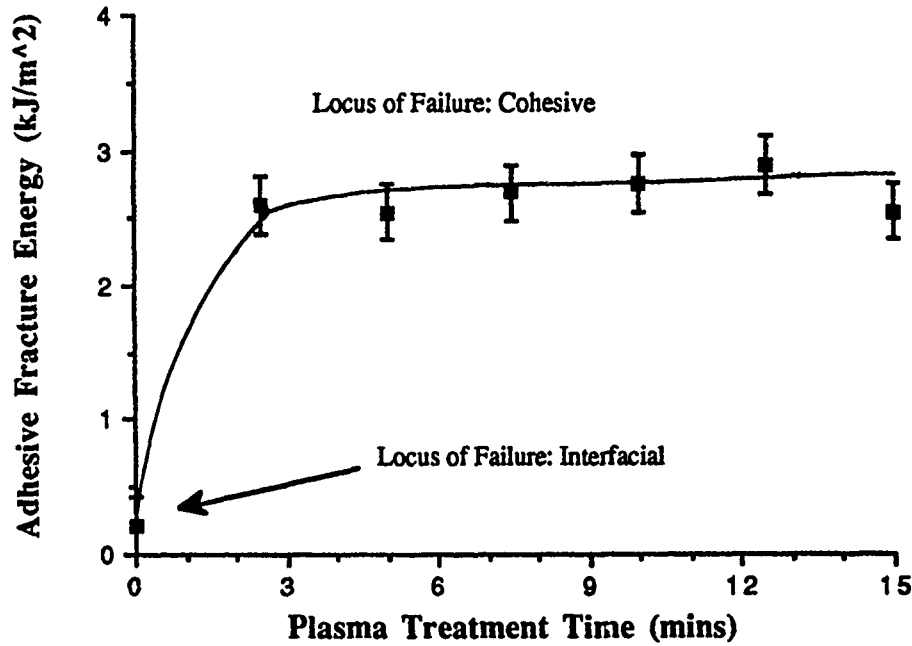


FIGURE 5.1 G_c versus plasma treatment time for the U/C PEEK substrates, bonded with the epoxy-film adhesive after a plasma treatment

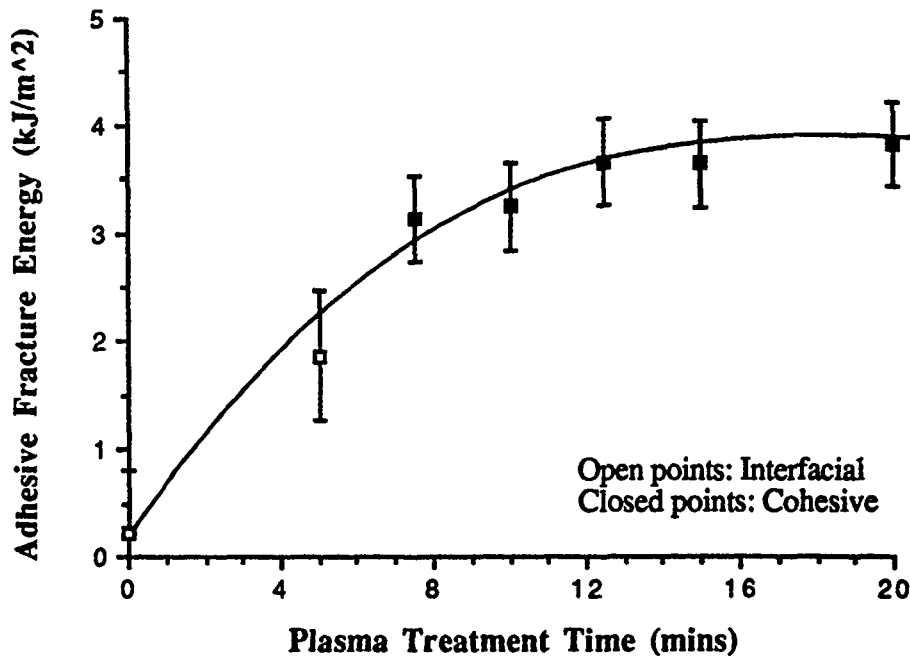


FIGURE 5.2 G_c versus plasma treatment time for the U/C PEEK substrates, bonded with the epoxy-paste adhesive after a plasma treatment

Figure 5.2 shows the results obtained when the adhesive fracture energy, G_c , was determined for the joints prepared with the U/C PEEK substrates bonded with the epoxy-paste adhesive after various treatment times. It can again be seen that when the substrates had received an abrasion-solvent wipe treatment only, prior to bonding, then the joints failed in an interfacial manner with a correspondingly low value of G_c . However, when bonding with this adhesive it can be seen that a plasma treatment of 5 minutes was insufficient to ensure a cohesive locus of failure and high values of G_c . Indeed, a treatment time of ten minutes was necessary to achieve cohesive failure and the high energy plateau for G_c was attained after a treatment lasting 12.5 minutes. The plateau value of the adhesive fracture energy was measured to be $G_c = 3.8 \pm 0.4 \text{ kJ/m}^2$.

These results show the same trend as those obtained by corona treating this material, i.e. when bonding with the tougher, epoxy-paste adhesive, a higher level of surface treatment is required to ensure cohesive failure. It should be remembered from Chapter Four that when the joints were bonded with the epoxy-paste, then the forces attained during the fracture test were considerably higher and thus the forces across the interface more acute, than when bonding with the epoxy-film adhesive. It was noted that cohesive failure was observed before the maximum plateau value of G_c was obtained. A possible explanation for this effect, which was also evident from the results of Kodokian [2] is that the onset of cohesive failure does not coincide with the maximum plastic zone size ahead of the crack tip. As was discussed in Section 2.3.2.2, the fracture energy, G_c , depends largely on the energy dissipative mechanisms occurring within the plastic zone ahead of the crack tip. It is therefore likely that the maximum plateau value of G_c is achieved when this zone is fully developed. As the surface treatment improves the intrinsic adhesion of the surface, then the plane of crack propagation will move away from the interface, allowing the full development of the plastic zone. Hence the maximum plateau value of G_c will be observed after the treatment level at which cohesive crack propagation was first noted.

5.2.2 Effect of Plasma Treatment on the Bonding of U/C PPS Composite

When the U/C PPS substrates were plasma treated and bonded with either the epoxy-film or epoxy-paste adhesives, then a different fracture behaviour was observed than was previously reported for the U/C PEEK composite. Although at short treatment times the locus of failure was interfacial, as previously observed for the joints bonded with the U/C PEEK substrates, at longer treatment times the locus of joint failure became interlaminar, i.e. the crack which was initiated in the adhesive layer jumped to within the fibre-composite substrates. All subsequent crack propagation was then interlaminar in nature. The maximum value of G_c

measured was $1.5 \pm 0.3 \text{ kJ/m}^2$. This is equivalent to the value of the interlaminar fracture energy, $G_c(\text{il})$ for this composite.

The problem of the locus of failure in an adhesive joint switching to within the fibre-composite substrates was investigated by Kodokian [2]. He showed that there is a poor correlation between the value of the interlaminar fracture energy, $G_c(\text{il})$ of the fibre-composite substrates and their propensity to delaminate during a fracture test. This is clearly evident from the data in Table 5.1.

TABLE 5.1 Table showing the values of the interlaminar fracture energy of various fibre-composite substrates together with the locus of joint failure and the value of the transverse tensile fracture stress. After Kodokian [2]

Substrate	Locus of Failure	$G_c(\text{il}) \text{ kJ/m}^2$	$\sigma_{\text{yyc}} \text{ (MPa)}$
U/C PEEK	cohesive	2.30	84.3
U/C PPS	interlaminar	1.45	29.4
U/C PA	cohesive	1.10	83.7
U/C epoxy	cohesive	0.26	58.9

Note: the adhesive employed was the epoxy-film adhesive.

Table 5.1 shows the locus of joint failure which was observed when various fibre-composite substrates were corona treated {except U/C epoxy} and then bonded with the epoxy-film adhesive prior to testing. It can be seen that the U/C PPS substrate failed in an interlaminar manner. However, when the U/C epoxy composite was bonded with this adhesive, then the locus of failure was cohesive, despite the value of the interlaminar fracture energy for this composite being very much less than the equivalent value for the U/C PPS composite. However, it was shown that the property which controlled the tendency for a substrate to delaminate during a joint fracture test was the out-of-plane transverse fracture stress, σ_{yyc} of the composite. Thus, if the value of the transverse tensile stress, σ_{yy} attained this critical value within the composite during the test, then the substrate would delaminate. The values of σ_{yyc} for various composites are shown in Table 5.1. It can be seen that a low value of σ_{yyc} was measured for the U/C PPS composite, and higher values were recorded for other composites including U/C PEEK and U/C epoxy. This is in agreement with the results presented in this Chapter and in Chapter Four, i.e. that joints prepared with either U/C PEEK or U/C epoxy do not delaminate during a fracture test, whereas joints prepared with the U/C PPS substrates do.

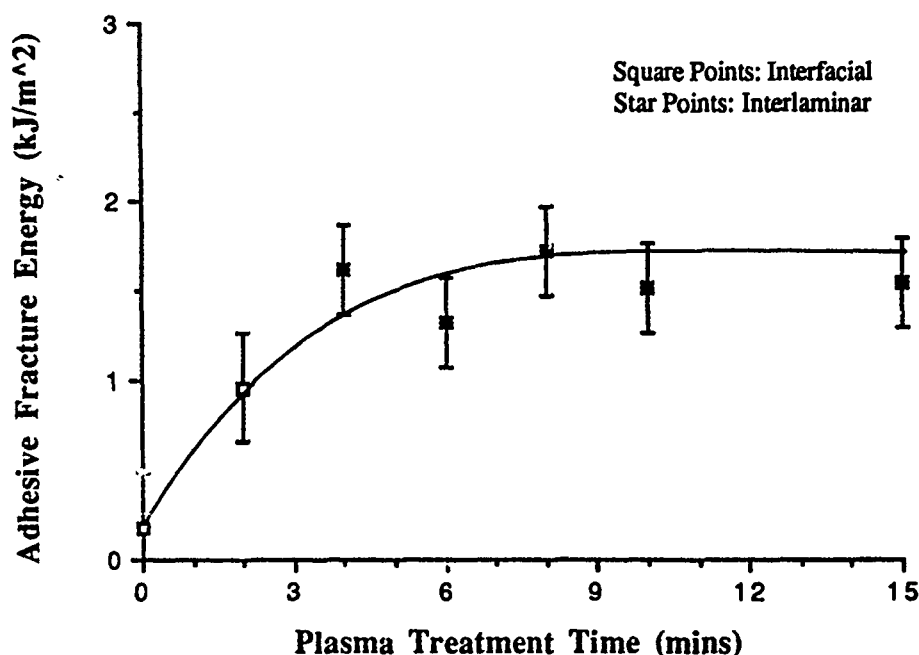


FIGURE 5.3 G_c versus plasma treatment time for the U/C PPS substrates, bonded with either the epoxy-film or epoxy-paste adhesives.

5.2.3 Effect of Not Abrading Composites Prior to Plasma Treatment

A number of joints were prepared from substrates which had not been abraded prior to receiving a plasma treatment. This was undertaken in order to investigate whether surface abrasion was a necessary first requirement, in addition to plasma treatment, in order to achieve a high fracture energy and a cohesive locus of failure from the DCB test. When the U/C PEEK substrates were solvent cleaned and plasma treated for twenty minutes (without first abrading) and then bonded with the epoxy-paste adhesive, the DCB joints subsequently failed in a cohesive manner with a high fracture energy, i.e. $G_c=4.0 \pm 0.4$ kJ/m². However, when similarly treated substrates were bonded with the epoxy-film adhesive, the joints subsequently failed in an interfacial manner, with a fracture energy, $G_c=0.20 \pm 0.05$ kJ/m².

The inconsistency of these results is probably the result of varying degrees of surface contamination on the substrates. If the degree of surface contamination from the mould release agent is low, then it is likely that the abrasion is not required prior to plasma treatment in order to achieve high energy failure. However, if the surface is heavily contaminated, then abrasion is a necessary requirement. These results are consistent with those of Kinloch and Kodokian [3, 107] who reported that abrasion of substrates was not required prior to a corona

treatment and the subsequent attainment of high G_c values, provided the surfaces were not heavily contaminated.

5.3 Scanning Electron Microscopy Studies

5.3.1 Introduction

In order to investigate the effects of the abrasion-solvent wipe pretreatment and the oxygen plasma pretreatment on the surfaces of the fibre-composite substrates, scanning electron microscopy (SEM) was employed. It should be noted that the substrates which received the plasma treatment had also previously received the abrasion-solvent wipe treatment.

5.3.2 Composite Surfaces Before Plasma Treatment

The effect of the simple abrasion-solvent wipe pretreatment on the U/C PEEK and U/C PPS substrates can be seen in Figures 5.4 and 5.5 respectively. In both cases, the abrasion by the alumina grit removed part of the surface polymeric layer. It can be seen that the effect on the U/C PEEK substrates was more pronounced than on the U/C PPS substrates. The former had suffered more matrix removal and fibre damage than the latter. It should be noted that both received the same amount of abrasion. Furthermore, an important feature of this treatment is that it only effects the outermost layers of the composite substrate, and hence the bulk properties of the substrate are not affected.

5.3.3 Composite Surfaces After Plasma Treatment

The effect of abrasion followed by a plasma treatment on the U/C PEEK and U/C PPS substrates can be seen in Figures 5.6 and 5.7 respectively. In both cases it can be seen that the plasma treatment has caused further ablation of the matrix, causing the increased exposure of carbon fibres, previously beneath the surface. The plasma treatment can be seen to have caused a 'pitting' of the surface and hence the development of an irregular surface topography. This effect was discussed in Section 2.4.5.2.



FIGURE 5.4 Scanning electron micrograph of a U/C PEEK substrate having received a simple abrasion-solvent wipe surface pretreatment. Magnification X750

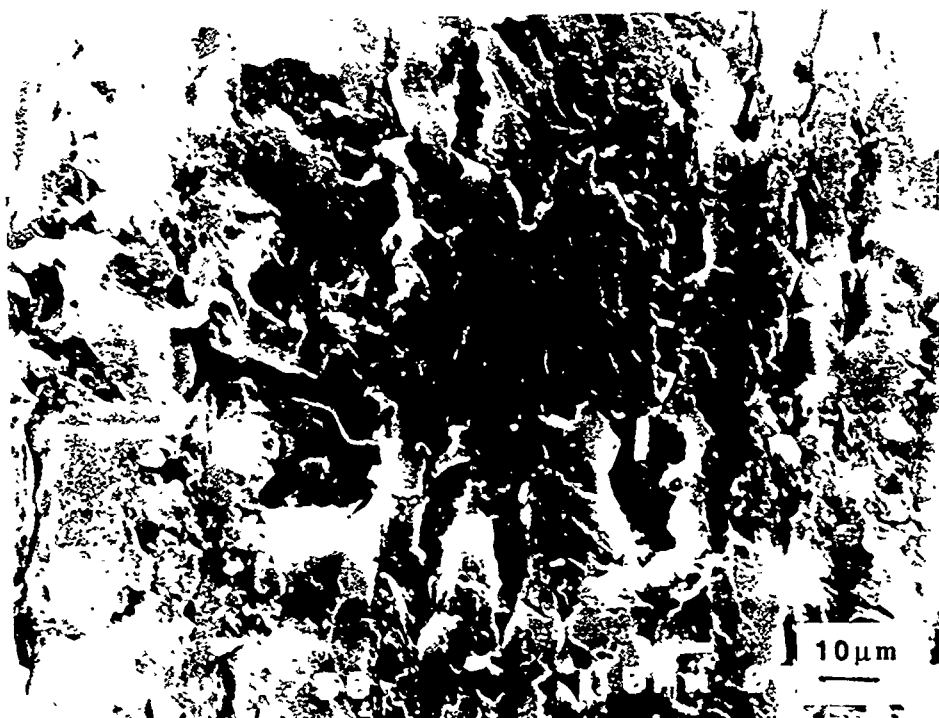


FIGURE 5.5 Scanning electron micrograph of a U/C PPS substrate having received a simple abrasion-solvent wipe surface pretreatment. Magnification X750



FIGURE 5.6 Scanning electron micrograph of a U/C PEEK substrate having received both an abrasion-solvent wipe and plasma treatment for 20 minutes. Magnification X750.



FIGURE 5.7 Scanning electron micrograph of a U/C PPS substrate having received both an abrasion-solvent wipe and plasma treatment for 15 minutes. Magnification X500.

5.3.5 Discussion of SEM Results

The micrographs shown in Figure 5.4 and Figure 5.5 show that the abrasion-solvent wipe surface pretreatment has roughened the surfaces of both the U/C PEEK and the U/C PPS substrates. It was noticeable that some fibre damage had occurred on the surface of the U/C PEEK substrates, and this had occurred to a lesser extent on the U/C PPS substrates. The micrographs shown in Figure 5.5 and Figure 5.6 indicated that additional effect of the plasma treatment was to cause further ablation of the matrix from the substrate surface and, in the case of the U/C PEEK substrates, to cause some pitting of the surface to occur.

In terms of surface roughness, there is no significant difference between the surfaces which had simply received the abrasion-solvent wipe treatment to those surfaces which had also received a plasma treatment. It is therefore unlikely that the improved joint performance can be attributed to an increased level of mechanical interlocking, following a plasma treatment. Indeed, it is questionable whether an adhesive will mechanically interlock with a surface in this condition. There is no reason why abrasion should have induced 'ink bottle' type cavities on the surface. It is therefore doubtful that mechanical interlocking contributes significantly to the intrinsic adhesion. There has been considerable debate as to whether mechanical interlocking is an important mechanism in abraded fibre-composite materials. Davies et al. [29] suggested that mechanical interlocking may be occurring, whereas Kodokian [2], and Evans et al. [24] concluded that the higher adhesive strengths were due to the removal of the weak interfacial layers and the increased surface polarity.

It is clear from this discussion that the degree of surface roughness does not satisfactorily explain the improvement in adhesion following a plasma treatment. The removal of weak surface layers is also an unlikely explanation because the abrasion-solvent wipe treatment alone would have achieved this. However, it was shown in Section 5.2.3 that the most reliable bonds were produced when abrasion was used in conjunction with plasma treatment. The most likely explanation of this result is that abrasion is not a necessary requirement for the attainment of strong joints unless a high level of surface contamination is present which the plasma treatment is unable to remove by itself. Therefore, the intrinsic adhesion arises from another source, i.e. by the formation of secondary, and possibly primary, intermolecular bonds across the adhesive-composite interface. The formation of these bonds will depend on the chemical species present in the surface region of the composite. These species can be detected by X-Ray photoelectron spectroscopy, which will now be discussed.

5.4 X-Ray Photoelectron Spectroscopy Studies

5.4.1 Introduction

In order to investigate the different effects of various surface pretreatments on the chemical characteristics of the fibre-composite surfaces, XPS was employed. From an engineering point of view, the surface chemistry is of interest for a number of reasons. Firstly, as was discussed in Section 2.2, the adsorption theory is the most widely accepted theory of adhesion. The short range intermolecular forces which this theory proposes are responsible for the intrinsic adhesion depend on the chemistry of the adhesive and the surface chemistry of the substrate. Using XPS, narrow scan spectra can be used to identify specific polar functional groups on a material's surface. It will be shown that a good correlation exists between the presence of specific functional groups on the surface of the substrate and the subsequent adhesive joint fracture behaviour. Secondly, the existence of surface contamination, even in small quantities, can interfere with adhesion. Contaminating species can also be detected by XPS. It will therefore be possible to investigate whether plasma treatment is able to remove heavy surface contamination, should it exist, and whether abrasion and plasma treatment together are more effective, as proposed in the previous Section.

Composite surfaces in four different conditions will be investigated. These conditions are (a) as moulded, (b) following an abrasion-solvent wipe, (c) following a plasma treatment in addition to an abrasion-solvent wipe and finally, (d) plasma treated only.

5.4.2 XPS Survey Scan Spectra

5.4.2.1 'As-moulded' composites

An examination of the survey scan spectra for the 'as-moulded' U/C PEEK and U/C PPS revealed a number of significant findings. Firstly, it can be seen that the moulded U/C PEEK surface was cleaner than the U/C PPS, which had been supplied by the manufacturer already moulded. The absence of silicon (from the mould releasing agent), detected in the form of the Si2p and Si2s photoelectron peaks at 99eV and 149eV respectively on the U/C PEEK surface confirm this. However, these peaks can be clearly seen on the U/C PPS spectra. Secondly, as would be expected due to the chemical structure of U/C PEEK, (as was shown in Figures 3.1), the elements carbon and oxygen were detected in the form of the C1s and O1s photoelectron peaks at 285eV and 533eV respectively. The U/C PPS chemical structure, (as shown in Figure 3.2) in addition, includes the element sulphur and this element can be clearly detected on the survey scan spectrum for this material in the form of the S2p and S2s

photoelectron peaks at 165eV and 229eV respectively. Thirdly, it can be seen that the relative magnitude of the C1s peak is greater than the O1s peak for both materials.

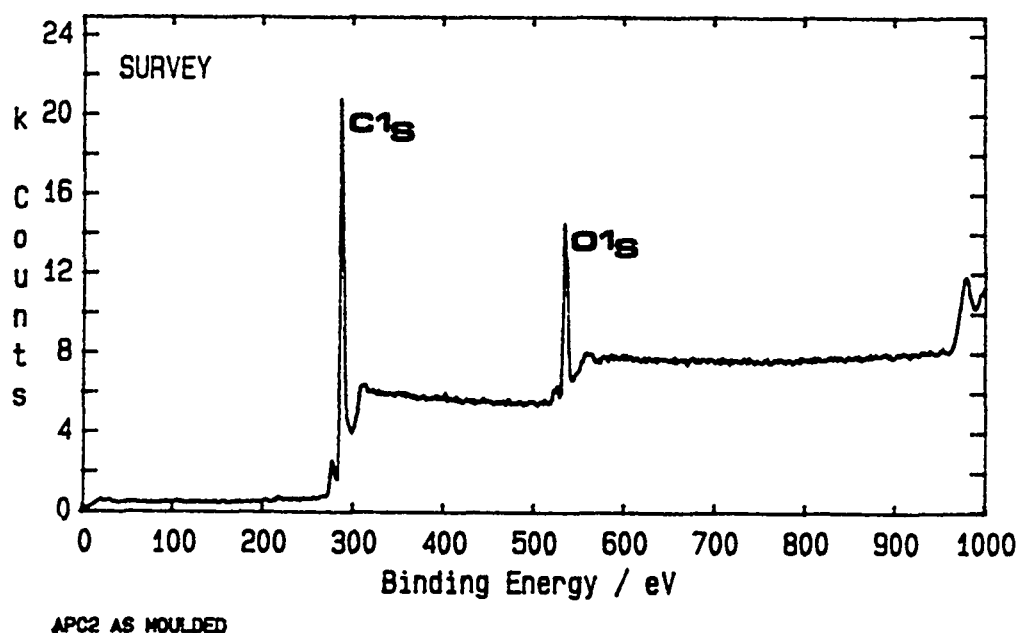


FIGURE 5.8(a) XPS Survey scan spectra for the 'as-moulded' U/C PEEK composite.

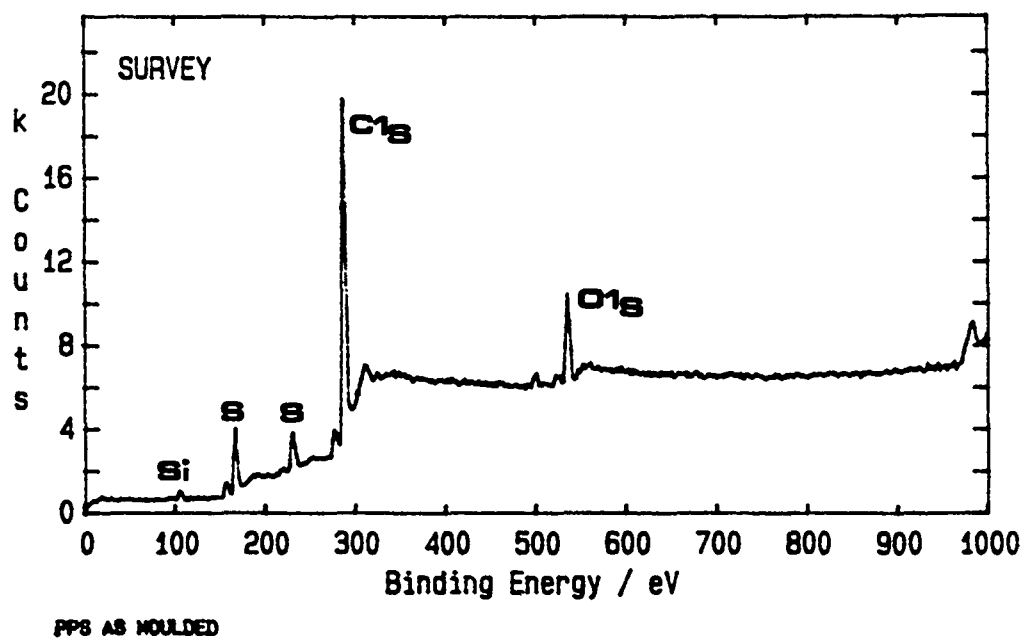


FIGURE 5.8(b) XPS survey scan spectra for 'as-moulded' U/C PPS composite

5.4.2.2 Abraded-solvent wiped composites

An examination of the XPS survey scan spectra for the abraded U/C PEEK and U/C PPS revealed two significant features. Firstly, the abrasion had very successfully removed the silicon contamination which had been present on the surface of the U/C PPS material. Secondly, the relative proportion of O1s to C1s decreased during the abrasion. A possible explanation for this is that the abrasion had removed some atmospherically oxidised species on the material surface.

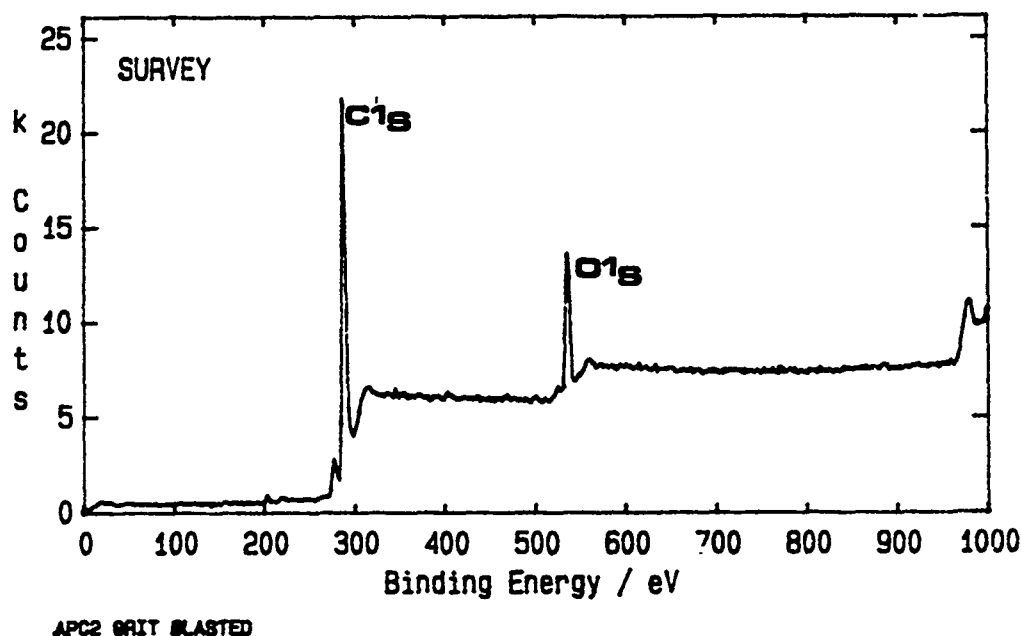


FIGURE 5.9(a) XPS survey scan spectra for abraded-solvent wiped U/C PEEK composite

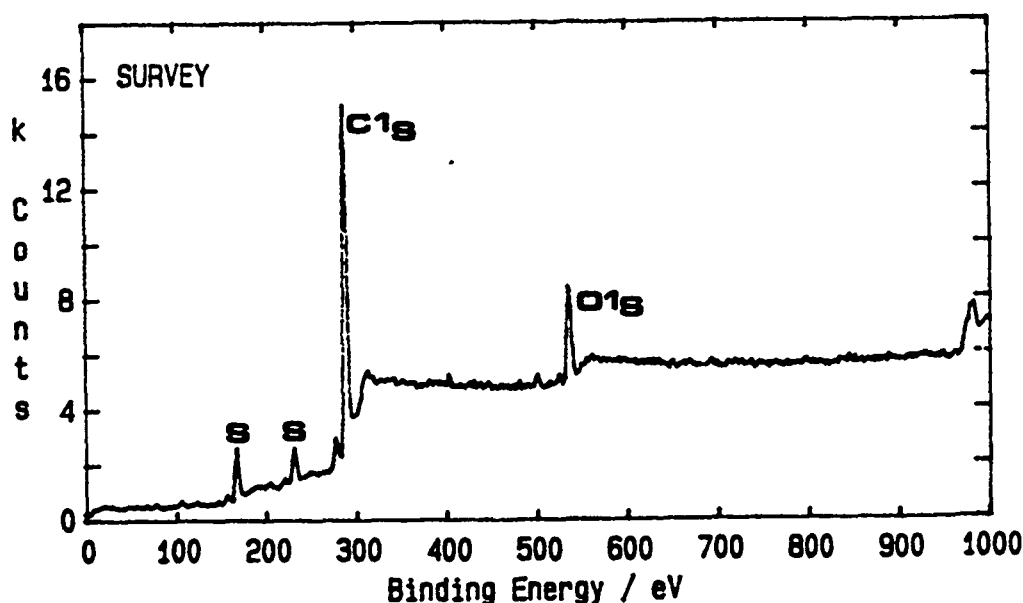


FIGURE 5.9(b) XPS survey scan spectra for abraded-solvent wiped U/C PPS composite.

5.4.2.3 Abraded and plasma treated composites

An examination of the XPS survey scan spectra for the U/C PEEK and U/C PPS which had received both abrasion and plasma treatment revealed several interesting points. Firstly, the oxygen plasma treatment had greatly increased the magnitude of the O1s peak relative to the C1s peak on both materials. This suggests that the treatment has effectively induced the oxidation of chemical species on the surface. Secondly, the plasma treatment has caused a small increase in the relative magnitude of the nitrogen N1s peak on both materials. This was probably caused by the presence of atmospheric air in small concentrations, either adsorbed onto the material surface, or was present in the plasma reactor chamber during treatment. The nitrogen present may then have combined with carbon, to form C-N, which was detected by the analyser. Finally, it was noted that after treatment, a trace amount of silicon was detected on the material surface. It was previously shown that the abrasion had removed this. Hence the plasma treatment had effectively reintroduced a very small amount of this contamination. The likely reason for this was the use of glass microscope slides in the reactor chamber to centrally position the substrates. Silicon from the slides may then have been deposited, in very small quantities, on the surface of the substrates.

It can be seen that abrasion alone effectively removed most of the surface contamination on the substrate surfaces. This would suggest that the level of surface contamination on these materials was not high. However, it was shown that abrasion was necessary for the attainment of joints of consistent strength, therefore abrasion is likely to be important for other reasons e.g. for increasing the surface area across which interfacial interactions can occur.

In order to examine in further detail the changes in the surface chemistry induced by the plasma treatment, the analyser step size was reduced from 1eV to 0.2eV, and narrow scan spectra were recorded for the U/C PEEK substrates. Substrates, which had been abraded and then plasma treated for periods up to 20 minutes at a power of 85W, were analysed. The elements included in the narrow scan were carbon, oxygen, nitrogen, silicon and fluorine. Particular attention has been paid to the C1s narrow scan spectra. The reasons for this are twofold. Firstly, it has been assumed that the polar functional groups which are induced by plasma treatment form between carbon atoms and either oxygen or nitrogen atoms. Hence the C1s narrow scan photoelectron peak should provide information on the nature of the bonding between these species. Secondly, the width of the C1s spectral peak is relatively broad (~10eV) which allows an accurate deconvolution of this peak to be undertaken. Although the O1s spectral peak contains much of the same information, most of the constituent species fall within a narrow range (~2eV). A deconvolution of this spectral peak would therefore be less accurate than that obtained from the C1s spectra.

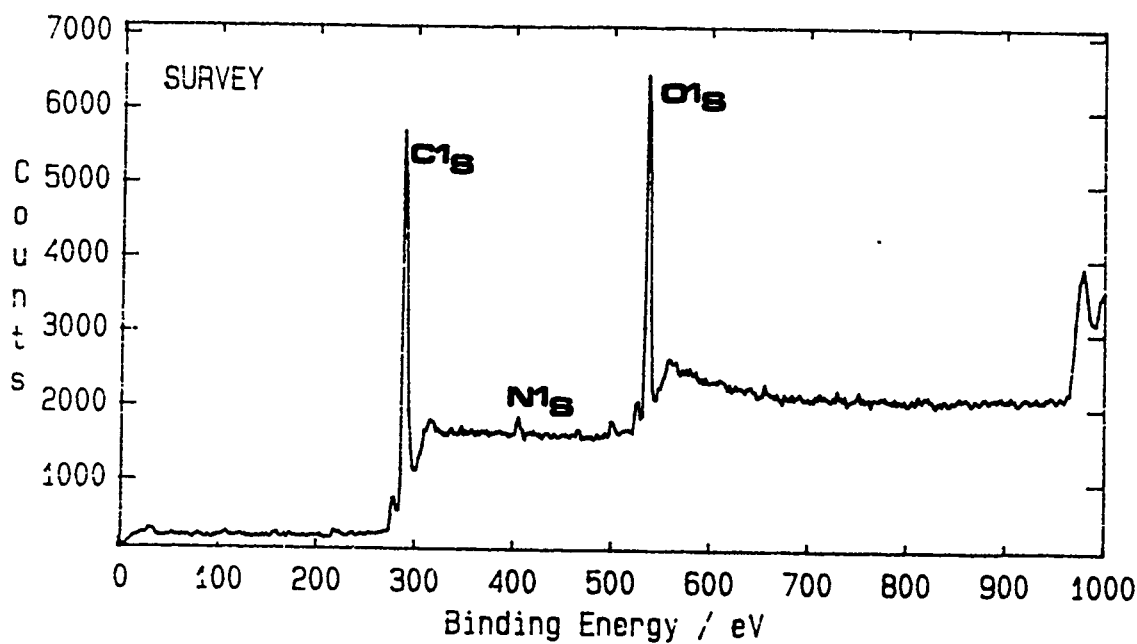


FIGURE 5.10(a) XPS survey scan spectra for the abraded and plasma treated U/C PEEK composite

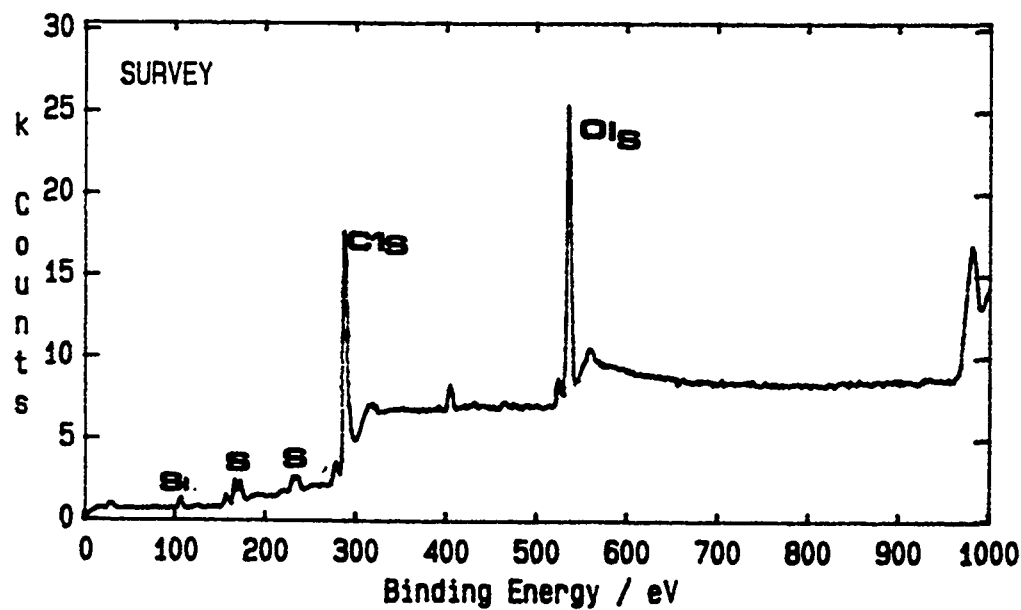


FIGURE 5.10(b) XPS survey scan spectra for the abraded and plasma treated U/C PPS composite

5.4.3 XPS Narrow Scan Spectra

Figure 5.13 shows the narrow scan spectra for the C1s peak for: (a) untreated; (b) abraded and (c) abraded and plasma treated U/C PEEK. It is interesting to note that the spectrum for the untreated U/C PEEK shows that a small secondary peak exists at about 294eV after the main C1s peak. This is an example of a shake-up satellite [75]. Shake-up satellites occur when an outgoing photoelectron simultaneously interacts with a valence electron and excites it (shakes it up) to a higher energy level. This interaction reduces the kinetic energy of the outgoing photoelectron which has the effect of increasing the measured binding energy (as is clear by reference to eqn. 3.2) associated with this photoelectron. A shake-up satellite is often observed in organic materials containing aromatic chain structures. In these instances, the satellite is referred to as the $\pi-\pi^*$ transition. Of course, the PEEK matrix contains such aromatic chain structures.

It can be seen that abrasion did not alter the C1s spectral peak of this material. No broadening of this peak had occurred and the $\pi-\pi^*$ transition was still visible. However, when a plasma treatment of just 2.5 minutes was applied, significant changes in this spectrum could be seen. Firstly, the plasma treatment had significantly broadened the C1s spectral peak. The increased width had been added to the high binding energy shoulder of the peak, indicating that a change in the nature of the carbon bonding had occurred. Secondly, the shake-up satellite was no longer visible after the plasma treatment. A possible explanation for its absence is that the plasma treatment may have broken down the aromatic chain structure on the material surface. This is certainly possible as it was reported in Section 2.4.2 that an oxygen plasma treatment could potentially break any organic bond [22]. In the next section, the deconvolution procedure applied to the C1s peak will be described.

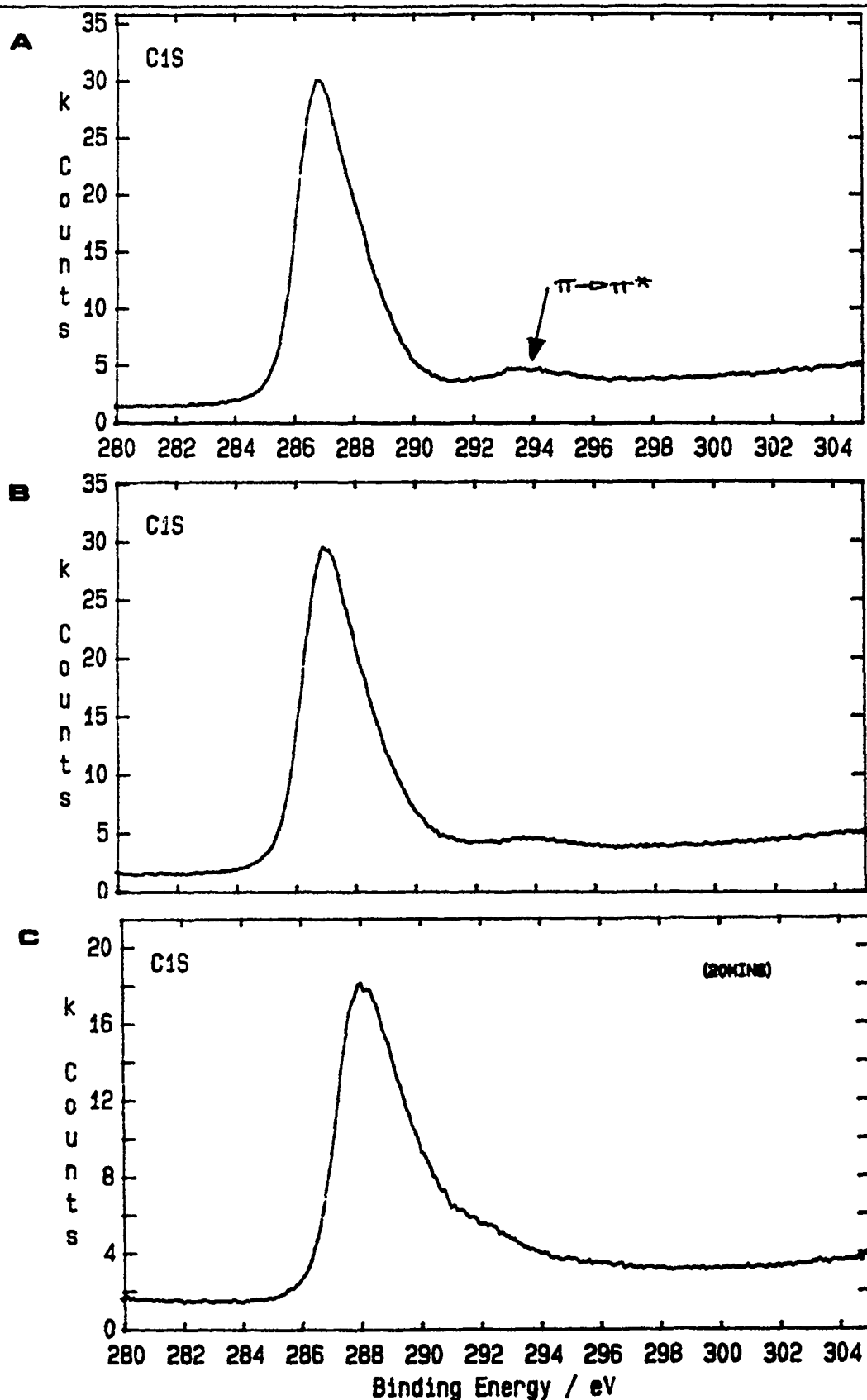


FIGURE 5.11 XPS narrow scan C1s spectra for the U/C PEEK composite in the following conditions: (a) Untreated , (b) Abraded ,(c) Abraded and plasma treated.

5.4.4 Peak Synthesis

The broadening of the high binding energy shoulder of the C1s spectral peak for the plasma treated U/C PEEK indicates the presence of oxygen or nitrogen rich carbon species [23, 86]. The binding energy of the emitted photoelectrons identifies whether the carbon is present in the form of C-H, C-N, C-O, C=O, or the O-C=O species. In each bonding configuration, the carbon atom will emit photoelectrons with a unique binding energy, as was discussed in Section 3.8. For the C1s spectral peak, these binding energies are well defined [86]. Knowing the binding energy centre for each characteristic constituent peak, it was possible to apply an iterative, least squares fitting routine on a dedicated computer in order to curve fit the constituent peaks to the main C1s peak.

The following procedure was adopted. Firstly, five peaks corresponding to the C-H, C-N, C-O, C=O, or the O-C=O species were identified at the following separations from the main C-H peak. The C-N species was fitted at +1.0eV, the C-O species was fitted at +1.6eV, the C=O species was fitted at +3.0eV and finally, the O-C=O species was fitted at +4.2eV. It was found necessary to fit an extra peak at +6.2eV from the C-H peak to account for the plasmon effect encountered. Secondly, the full width at half maximum (FWHM) value, which is an experimental parameter given by the spectrometer and material characteristics, was set and fixed at 1.75. Thirdly, thirty iterations of the curve-fitting routine were completed. This procedure was repeated for each spectrum in the set (i.e. for all the C1s spectra obtained from different treatment times). Fourthly, the average peak separations were then calculated for that set of spectra, and these average separations were then applied to each spectrum in the set and fixed. (By fixed, it is meant that the routine was unable to alter these values during iteration). Finally, the iterative curve fitting procedure was repeated and the percent area of each constituent peak was deduced. Figure 5.12 shows the way in which the C1s narrow scan spectra was curve fitted using this procedure.

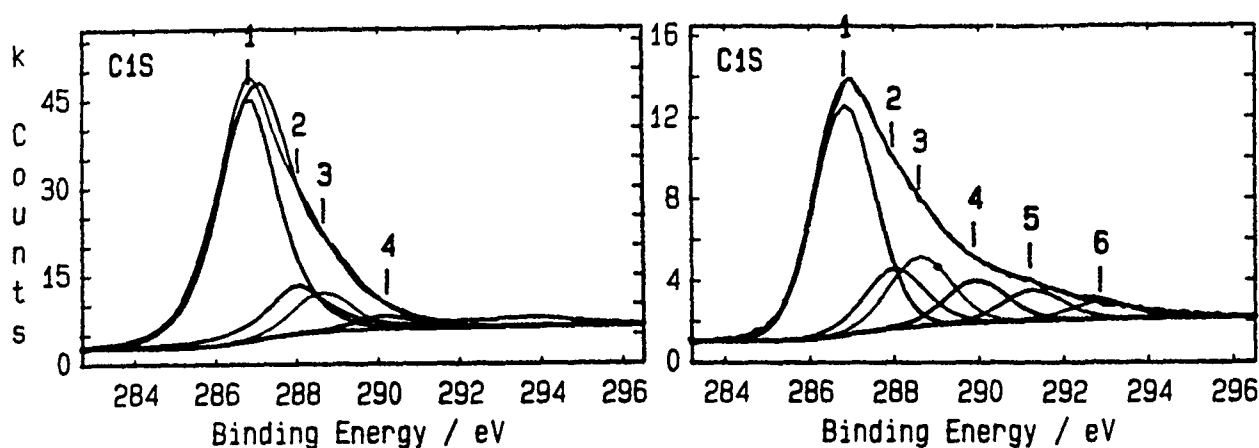


FIGURE 5.12 Curve fitted C1s spectra for (a) Untreated U/C PEEK and (b) Plasma treated (5 minutes) U/C PEEK.

5.5 The Correlation of XPS Results to Adhesive Joint Strength

5.5.1 Introduction

In Section 5.2 it was shown that an oxygen plasma treatment successfully enhanced the intrinsic adhesion of bonded fibre-composites. This was reflected in the locus of failure of the DCB joints no longer being at the adhesive-composite interface, but within the adhesive, and far higher values of the fracture energy, G_c , being recorded. In the previous Section, XPS was employed successfully to detect the changes in the surface chemistry of the treated fibre-composites resulting from a plasma treatment. In particular, it was demonstrated how very effectively the plasma treatment had been in increasing the surface concentration of polar groups, e.g. C=O and O-C=O. From the discussion on the theories of adhesion in Chapter Two, it is probable that the enhanced joint performance resulting from the plasma treatment are the result of various interfacial interactions including dipole-induced dipole, dipole-dipole, hydrogen bonds and possibly acid-base forces.

Due to the relative importance attributed to the adsorption theory in the literature, it is clearly of interest to attempt to correlate measurements of the surface chemistry with the joint fracture behaviour. Such an undertaking is not a simple matter due to the complexities involved in the adhesion process. In a recent review text, Yosomiya et al. [87], were unable to identify any simple correlation between the quantity of polar groups on the surface of a polymeric substrate and its subsequent joint strength. To relate the surface chemical compositions (obtained from

XPS analysis) to the values of γ_s^p , the polar component of the surface free energy, (obtained from contact angle measurements), Kinloch et al. [23] defined a parameter termed the 'weighted percentage dipole moment', Ω . They reported that a linear dependance existed between γ_s^p and Ω for a number of thermoplastic fibre-composites which had been treated to various levels of corona treatment and, most significantly, they reported that a critical value of Ω existed, termed Ω_c . They proposed that for all the fibre-composites treated, the criterion for avoiding interfacial failure, and thereby obtaining high values of the adhesive fracture energy, G_c , may be expressed as the need to attain a value of $\Omega = \Omega_c$. The applicability of this criterion will be considered in the following Sections. However, a simple measure of the increase in oxygen-rich species by a surface treatment technique is given by the atomic ratio of O1s to C1s and the O1s/C1s ratios for both corona-treated and plasma-treated U/C PEEK will now be discussed.

5.5.2 O(1s)/C(1s) Ratios for Corona and Plasma Treated U/C PEEK composite

Figures 5.13 and 5.14 show the atomic ratios of O1s/C1s as a function of surface treatment. The effects of both corona treatment and plasma treatment have been investigated so that any correlation in the measured value of O1s/C1s with adhesive joint strength may be observed more readily. It can be seen that both treatments increased the O1s/C1s ratio significantly. The untreated U/C PEEK composite possessed an O1s/C1s atomic ratio of approximately 0.15, which more than doubled when either a 20J/mm² corona treatment or a 15 minute plasma treatment was applied. These treatments had both proved sufficient to achieve a high fracture energy, cohesive locus of failure when bonding this composite with either adhesive.

The critical levels of corona energy required to achieve a high fracture energy, cohesive locus of failure were 10J/mm² and 20J/mm² for the epoxy-film and paste adhesives respectively. The corresponding plasma treatment times were ≤ 2.5 minutes and 12.5 minutes for the two adhesives respectively. {The value ≤ 2.5 implies that the critical value of plasma treatment was less than the minimum plasma treatment employed, and is thus not known precisely for the epoxy-film adhesive}

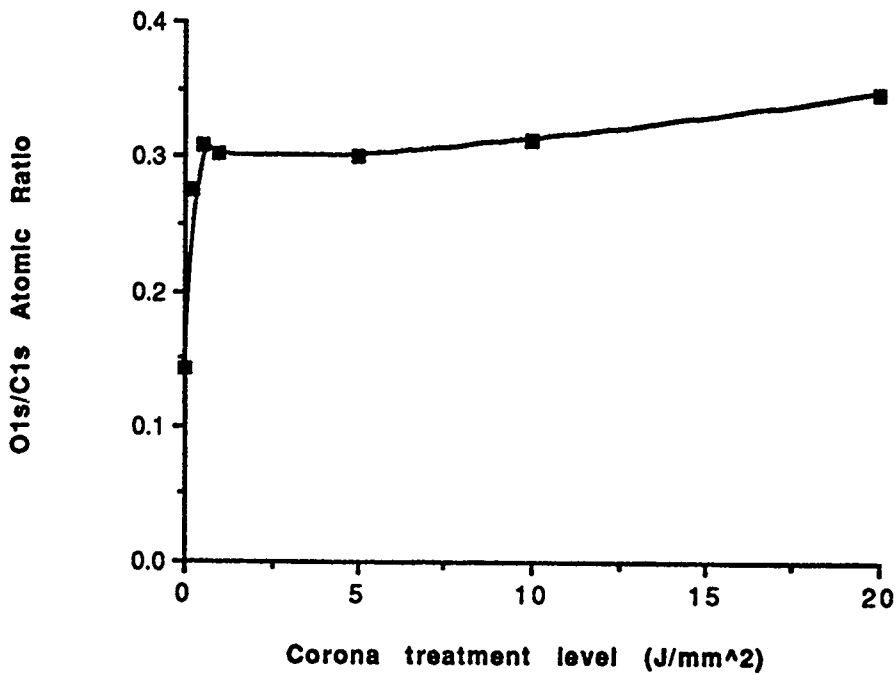


FIGURE 5.13 O1s/C1s atomic ratios for corona treated the U/C PEEK composite

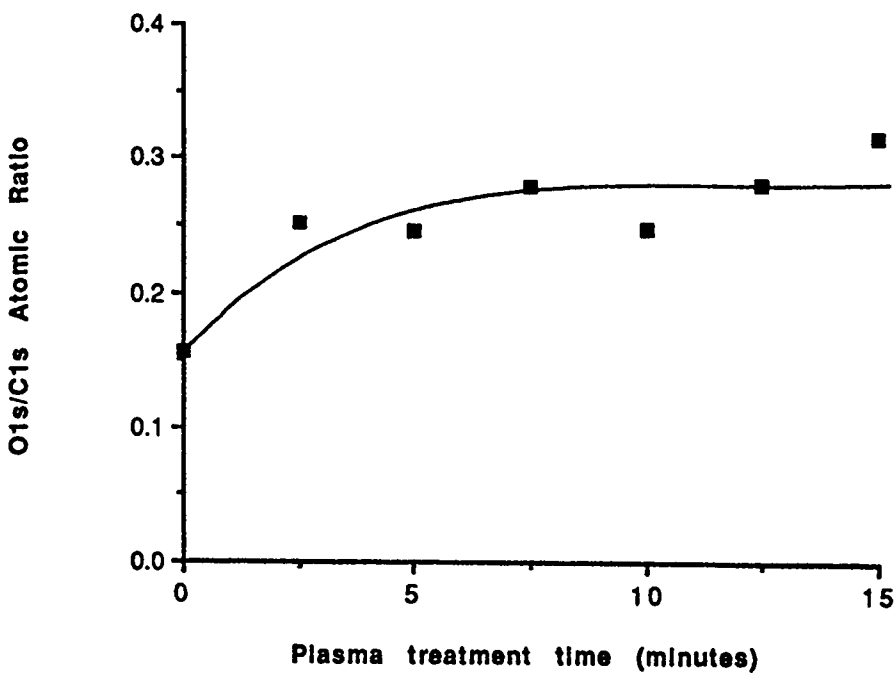


FIGURE 5.14 O1s/C1s atomic ratios for the plasma treated U/C PEEK composite

Now, the O1s/C1s ratios at these levels were 0.31 and 0.34 for the corona-treated U/C PEEK composite and 0.24 and 0.29 for the plasma-treated U/C PEEK composite. From these observations it would appear that the O1s/C1s ratios, although indicative of enhanced levels of oxygenated species on the composite surface, do not represent a criterion for the attainment of strong interfacial adhesion; i.e. the critical levels are dependent on the type of treatment employed. In the next Section another parameter, termed the weighted % dipole moment, will be considered.

5.5.3 The Weighted % Dipole Moment, Ω .

5.5.3.1 Introduction

In this Section, the data obtained from the XPS analysis will be employed to calculate the weighted % dipole moment, Ω , for both plasma treated U/C PEEK and corona treated U/C PEEK. It is clearly of interest to examine whether these values correlate to the fracture behaviour of the joints subsequently prepared with these substrates. However, before presenting these results, the procedure for calculating Ω will be described.

5.5.3.2 Calculation of the weighted % dipole moment

To deduce the value of the weighted % dipole moment, Ω , for a treated fibre-composite surface, the data from the deconvolution of the C1s narrow scans are employed. To deduce the concentration of the C-N, C-O, C=O, O-C=O species relative to all other groups on the composite surface, the concentrations of these species obtained by the deconvolution procedure described in Section 5.4.4 are multiplied by the atomic percentage of the parent C1s peak. The percentage values for each chemical group are then multiplied by their respective dipole moment (given in Table 5.2), to give their individual contribution to the total surface dipole moment. Then, having obtained the individual values, these are then summed and then normalized by 1 Debye to give the Ω value.

Before calculating the Ω values for plasma treated U/C PEEK, the technique was first applied to corona-treated U/C PEEK. The primary reason for this was to enable a comparison to be made with the earlier work reported by Kodakian [2] in which Ω values for corona-treated U/C PEEK were reported.

TABLE 5.2 Dipole moments for some chemical bonds

Chemical Species	Dipole Moment (Debye)
C-H, C-C	0
C-N	0.2
C-O	0.7
C=O	2.3
O-C=O	2.02

5.5.3.3 Ω values for corona treated U/C PEEK composite

Samples of U/C PEEK were prepared in the usual way, abraded and solvent cleaned and then corona-treated to energies ranging from 0 to 20J/mm². An XPS analysis was then carried out on the treated samples. Both wide scan and narrow scan spectra were obtained for the material in each condition. A peak synthesis of the C1s narrow scan spectrum was conducted, as described in Section 5.4.4. The deconvolution results are presented in Table A4.1 in Appendix 4.

The deconvolution results obtained via the XPS analysis of corona treated U/C PEEK were used to calculate Ω at each level of treatment, following the procedure described in Section 5.5.2. The results clearly indicate that the increase in surface polarity of U/C PEEK resulting from the corona treatment is largely the result of the increased proportion of the C=O and O=C-O groups present on the surface. Figure 5.15 shows the variation in the calculated value of Ω with corona energy. It can be seen from this figure that there is an initial rapid increase in Ω with corona energy, and that this increase levels off after further treatment.

From Figure 5.15 it is possible to define critical values of the weighted % dipole moment, Ω_c , for this substrate material bonded with either the epoxy-film or epoxy-paste adhesives respectively. In the present work, the critical levels of corona treatment, i.e. the treatment necessary to obtain high fracture energy values with the U/C PEEK substrates were 10J/mm² and 20J/mm² for the epoxy-film and epoxy-paste adhesives respectively. From Figure 5.15, the critical values of Ω may be deduced at these treatment levels. These values were $\Omega_c = 33\%$ and $\Omega_c = 35\%$ for U/C PEEK bonded with the epoxy-film and paste adhesives respectively.

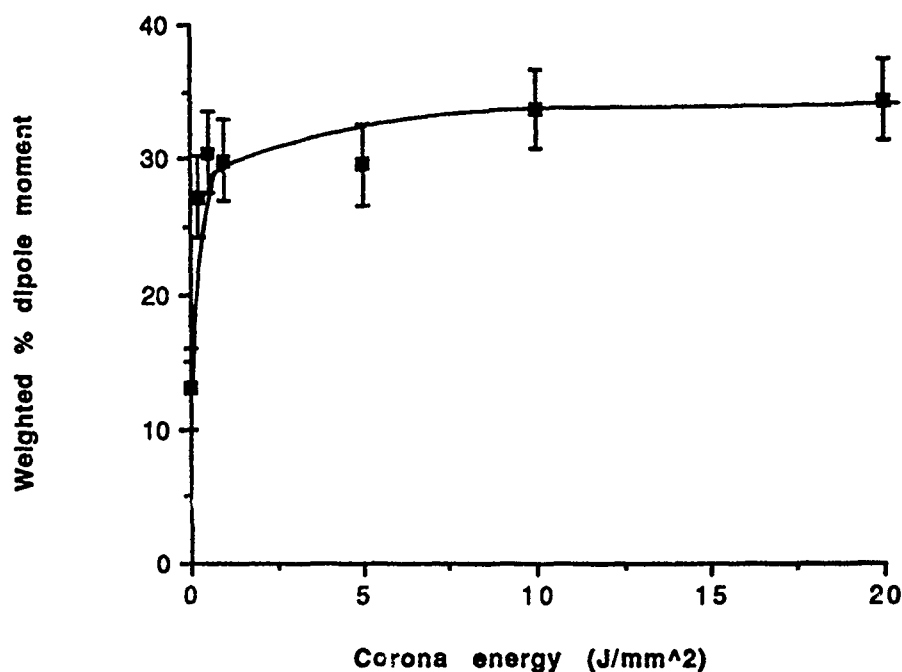


FIGURE 5.15 Variation in the weighted % dipole moment, Ω , with corona treatment energy for the U/C PEEK composite.

The values for Ω_c previously quoted in the literature were 25% and 28% for the U/C PEEK bonded with the epoxy-film and epoxy-paste adhesives respectively [2]. The values for Ω_c measured in the present work show the same trend as those previously measured, and differ from these values by less than 25%. It is considered that this difference could be the result of conducting the surface analysis at different periods after the corona treatment. Because the oxygenated species induced by the corona treatment are not stable [29, 2], then the value of Ω_c measured will be very sensitive to the delay between treatment and subsequent analysis. Therefore results obtained by different workers should be compared with caution. In the present work, XPS analysis was carried out 24 hours after treatment. The treated samples were stored in a dessicator immediately after treatment until ready for analysis.

5.5.3.4 Ω values for plasma-treated U/C PEEK composite

Samples of U/C PEEK were prepared in the usual way, abraded and solvent cleaned and then plasma-treated at a power of 85W for periods ranging from 0 to 15 minutes, as previously described. An XPS analysis was carried out on the treated samples. Both wide scan and narrow scan spectra were obtained in each condition in the same manner as before. The

results of the deconvolution of the C1s peak from the narrow scan spectrum can be seen in Table A4.2 in Appendix 4.

Several significant points emerge from Table A4.2. Firstly, both C=O and O-C=O groups increase significantly with the duration plasma treatment. A plasma treatment of 2.5 minutes has approximately the same effect on the polar groups as a corona treatment of 10J/mm². This agrees well with the experimental observation that, when the epoxy-film adhesive was employed to bond the U/C PEEK, then 2.5 minutes plasma treatment (or 10J/mm² corona treatment) was required to avoid interfacial failure with an associated low fracture energy. Secondly, the percentage of the C-N species was shown to decrease in with increasing duration of plasma treatment. The opposite effect was observed for the corona-treated materials. This can be readily explained because the corona treatment is carried out in atmospheric air, whereas the plasma treatment is carried out in pure oxygen. Thirdly, the results show that the plasma treatment has been effective in significantly increasing the C-O species on the surface. Surprisingly, the corona treatment had no significant effect on this group. These values were then used to calculate the variation in Ω for this material as a function of plasma treatment. The results are shown in Figure 5.16.

From Figure 5.16, the following observations can be made. Firstly, the critical values of Ω_c , for the plasma-treated U/C PEEK attained a somewhat higher value than were attained following a corona-treatment. This can be seen in Table 5.3. The value of Ω_c for plasma-treated U/C PEEK is 12.5% higher than for the corona-treated substrate when bonding with the epoxy-paste adhesive. This difference is not due to the time lag between treatment and analysis, because both sets of analysis were preformed after the same interval following treatment.

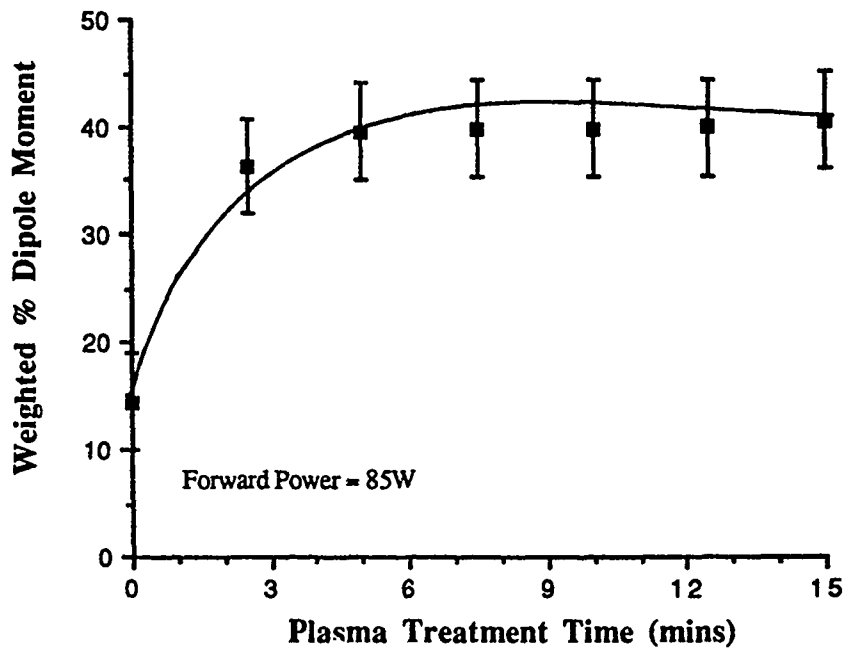


FIGURE 5.16 Variation in the weighted % dipole moment, Ω , with duration of plasma treatment for the U/C PEEK composite.

TABLE 5.3 Summary of the Ω_c results obtained for U/C PEEK substrates when bonding with the epoxy-film or epoxy-paste adhesive after surface treatment

Adhesive	Ω_c Corona-treated	Ω_c Plasma-treated
Epoxy-film	33	≤ 35
Epoxy-paste	35	40

From a close inspection of the data, it can be seen that the reason for the higher values in Ω_c being calculated after the plasma treatment is largely due to the higher concentrations of the C-O species, which has a dipole moment of 0.7 Debye . The increase in the C=O and O-C=O species from the corona and the plasma treatment were very similar, as is evident in Tables A4.1-2.

Thus, the values of Ω_c for a given adhesive are in broad agreement for both the plasma and the corona treatments. The use of the Ω_c values is far better than trying to use the O1s/C1s ratios to ascertain a criterion for the level of pretreatment needed. In addition, the trend of needing a higher value of Ω_c for the tougher epoxy-paste adhesive is seen for both types of treatment.

However, the values of Ω_c not precise and there is an overlap in the values for the different adhesives and treatments. Thus, a further refinement of this approach is needed.

5.6 Chapter Five Conclusions

The main conclusions from this Chapter are:

- 1 A plasma treatment was very effective in improving the level of intrinsic adhesion of the two thermoplastic fibre-composite materials investigated. This was demonstrated by a change in the fracture behaviour of joints prepared from U/C PEEK and U/C PPS substrates bonded with both epoxy-film and epoxy-paste adhesives.
- 2 When the U/C PEEK substrates were employed, the locus of joint failure changed from interfacial before treatment, with a value of $G_c = 0.21 \text{ kJ/m}^2$, to cohesive, in the adhesive, after a given duration of plasma treatment. The values of the adhesive fracture energy measured were: $G_c = 4.0 \text{ kJ/m}^2$ for the epoxy-paste adhesive and $G_c = 2.55 \text{ kJ/m}^2$ for the epoxy-film adhesive.
- 3 When the U/C PPS substrates were bonded with either adhesive, the locus of joint failure changed from interfacial before treatment, to interlaminar, after treatment with $G_c = 1.50 \text{ kJ/m}^2$ which was equivalent to $G_c(\text{il})$, i.e. the interlaminar value for the fracture energy for the composite material. In this case the composite substrates were the 'weakest link' and the higher fracture energy values associated with cohesive failure within the adhesive were not attained.
- 4 Scanning electron microscopy revealed that abrasion had removed a surface layer of matrix and roughened the surface. Also, this caused some fibre-damage, especially on the U/C PEEK substrates. It was also revealed that plasma treatment had resulted in ablation of the polymer matrix in the surface regions (especially on the U/C PEEK substrates), which exposed carbon fibres at longer treatment times.
- 5 X-Ray photoelectron spectroscopy demonstrated that the plasma treatment very effectively increased the atomic concentration of surface oxygen on the U/C PEEK substrates. A deconvolution of the C1s peaks obtained from U/C PEEK showed that the plasma treatment increased the proportion of oxygenated carbon in the form of C-O, C=O and O-C=O species. In contrast, when a corona discharge treatment was employed, similar increases in the C=O and O-C=O species were detected, but not in the C-O species. A good correlation existed

between the quantity of C=O and O=C-O species present on the surface and the subsequent joint fracture behaviour for both plasma and corona treatments.

6 When the weighted % dipole moment, Ω , was calculated as a function of treatment level, it was shown that the critical value, Ω_c , obtained depended on whether a corona-discharge or a plasma treatment was employed. For example, when bonded with the epoxy-paste adhesive, the oxygen-plasma treatment resulted in a Ω_c value of 40% whereas the corona treatment resulted in a Ω_c of 35%, i.e. the critical values were somewhat dependent on the type of treatment, as well as the adhesive employed. Thus, it is concluded that the weighted % dipole moment represents a more accurate predictor of joint fracture behaviour than the simple O1s/C1s ratio, but further refinement of this parameter is necessary.

Chapter Six

Joint Failure: Effects of Test Rate

6.1 Introduction

Adhesively-bonded structures are increasingly being employed in applications which are subjected to impact conditions. For example, bonded fibre-composites are now a popular choice of material for the manufacture of advanced automotive bodysheet structures. These structures may be subjected to a range of impact conditions, from the low energy road induced shocks and door slamming to the higher energy vehicle collision [4]. There is also a considerable interest in the use of these structures in military applications.

A key element of the fracture behaviour of bonded joints at higher rates of loading is the way in which the crack propagates from the initial starter defect. Under static loading conditions, i.e. at test rates $\leq 10^{-4}$ m/s, it was shown in Chapter Four that crack propagation was stable in mode I with the crack growing slowly, in a ductile manner (Type A). However, at higher loading rates, it will be shown that there was a transition from stable (Type A) to unstable (Type B) crack propagation in all the adhesive joint systems investigated. This is discussed in Section 6.4.

A consequence of experiencing unstable crack propagation during a fracture test is that the resulting force-time trace obtained from a load-cell device takes the form of a saw-tooth. The analysis of this type of data requires some special considerations. Firstly, it is not possible to use this data to deduce values of G_c for a joint using either the 'area' or 'compliance' techniques (i.e. eqns 2.14 or 2.17). The 'area method' calculates an average value of G_c over an increment of crack length, so a sudden, step-wise increase in the crack length cannot be handled by this technique. The 'compliance method' requires an accurate determination of dC/da , which requires a curve-fit calibration of C versus a (as shown in Figure 4.5). Since the parameters (P , δ and a) are only available at discrete points during an unstable DCB fracture test, an accurate calibration cannot be readily obtained. It was found that the most satisfactory way to approach the analysis of an unstable test was to employ beam theory. This is discussed in Section 6.3.

In order to employ the beam theory analysis described in Chapters Two and Four, it was shown that the experimentally determined values of the load, beam opening displacement and crack length were required. A high frequency response load-cell and a high-speed camera have been used to monitor these experimental variables during the high rate fracture tests. It will be shown in Section 6.2.4.1 that an inherent problem with high rate testing of the DCB geometry is that a large dynamic effect is encountered in the specimen at high rates. It is considered that this dynamic effect is mainly due to flexural stress wave reflections which interact with the propagating crack [88]. A consequence of the dynamic effect was that it became almost impossible to interpret the load-cell output at loading rates exceeding 2m/s. It will be shown that a beam theory analysis based upon the value of the opening displacement, δ , and the cantilever beam substrate modulus, E_s , has provided the most reliable approach from which to deduce values of G_c at high rates. Kinetic energy considerations are discussed in Section 6.3.5.

Close attention has been paid to determining the locus of joint failure in order to identify whether the corona-treated U/C PEEK substrates were more susceptible to interfacial failure in the joint than bonded U/C epoxy substrates at these higher rates. Finally, scanning electron microscopy has been employed to examine the fracture surfaces obtained at different rates. This has provided a useful insight into the micro-mechanisms operating within the rubber-toughened adhesives during fracture, and how these may have been affected by changes in the loading rate.

6.2 Interpretation of Experimental Data

6.2.1. Load Measurements

At slow to intermediate test rates, the load during the mode I DCB fracture test was monitored by a 1kN static load-cell, mounted on the screw-driven testing machine, as described in Section 3.3.1. At higher rates, (0.01m/s and above), the load was monitored by a high frequency response piezo-electric load-cell, as was described in Section 3.5 and shown in Figures 3.11-3.12. The output signal from this device was amplified and captured on the transient recorder. Some typical output signals obtained from tests on joints prepared with the U/C PEEK substrate bonded with the epoxy-film adhesive are shown in Figures 6.1-6.3 at increasing test rate. These Figures should be compared to Figure 4.13, which showed that the crack propagation in this adhesive was stable when loaded under static conditions.

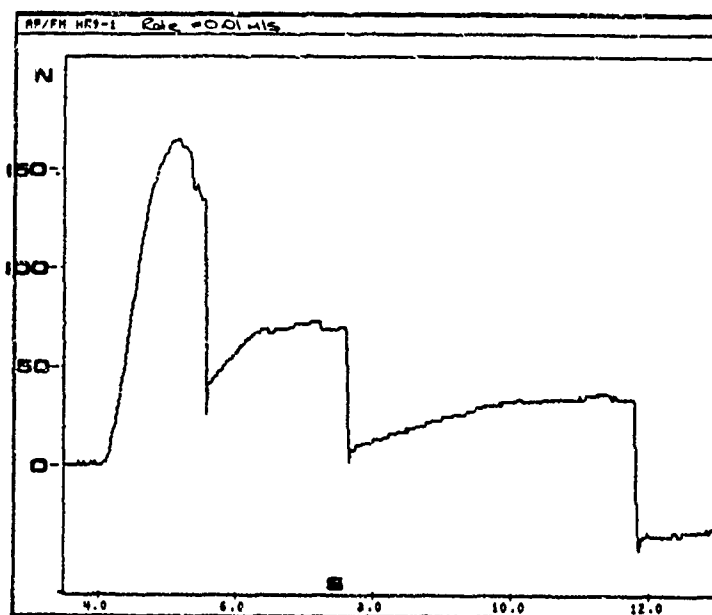


FIGURE 6.1 Load-time signal at a test rate of 0.01m/s for a joint prepared with U/C PEEK substrates, bonded with the epoxy-film adhesive. Locus of failure was cohesive. Crack propagation was unstable, stick-slip. The substrates had been corona-treated to $10\text{J}/\text{mm}^2$.

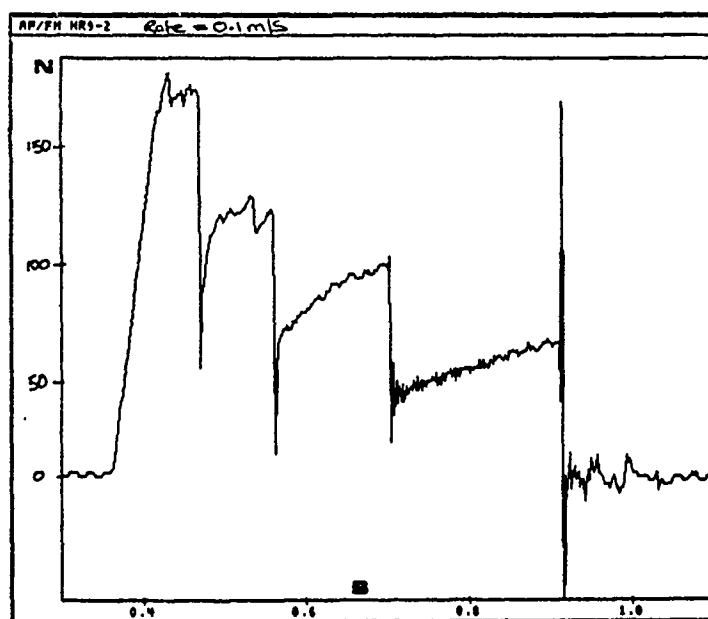


FIGURE 6.2 Load-time signal at a test rate of 0.1m/s for a joint prepared with U/C PEEK substrates, bonded with the epoxy-film adhesive. Locus of failure was cohesive. Crack propagation was unstable, stick-slip. The substrates had been corona-treated to $10\text{J}/\text{mm}^2$.

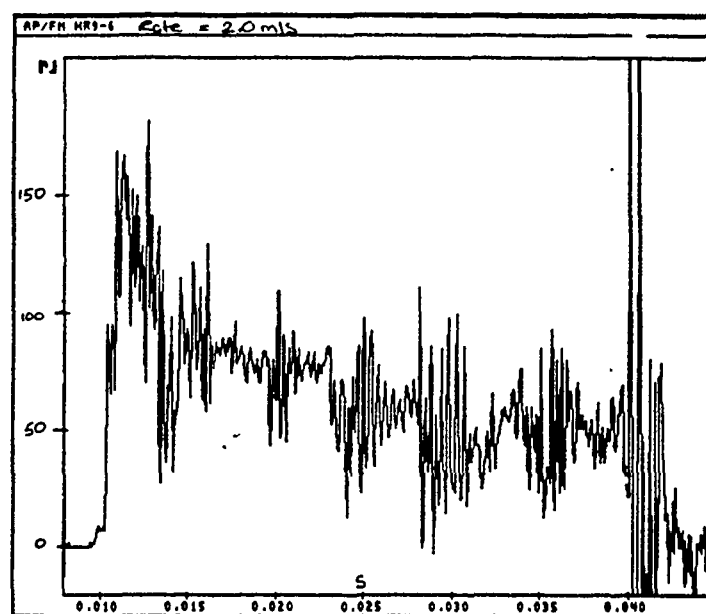


FIGURE 6.3 Load-time signal at a test rate of 2m/s for a joint prepared with U/C PEEK substrates, bonded with the epoxy-film adhesive. Locus of failure was cohesive. Crack propagation was unstable and the trace shows the 'dynamic oscillations'. The substrates had been corona-treated to 10J/mm^2 .

The unstable, stick-slip fracture behaviour can be seen clearly in Figures 6.1-6.2. The loading was linear up to a point just prior to crack initiation, after which time, some stable, cohesive crack growth was observed before the crack jumps cohesively through the adhesive and then arrests. The specimen arms are then reloaded, at the new crack length, until $G=G_c$ and again the crack initiated into the adhesive. Typically, some further stable, cohesive crack growth was again observed until the crack jumped again and the process was repeated.

As the loading rate was increased past 1m/s, interpretation of the load-time signal becomes increasingly difficult. Figure 6.3 shows a typical load-time trace obtained at 2m/s for the U/C PEEK composite bonded with the epoxy-film adhesive. The clarity of this trace is obscured by the dynamic oscillation. This oscillation is maximum at the instant when the crack jumps. At this instant, large flexural stress waves propagate through the arms of the specimen and are repeatedly reflected from both ends of the beam and from the crack tip [88, 89]. The flexural oscillations can be seen in the load-time signals and appear to be damped by the reloading of the specimen arms.

A further insight into the material response can be gained by examining the point of initiation of crack growth on the load-time signals. Figures 6.4-6.6 show the initial part of the load-

time signals for the three signals previously shown i.e at 0.01m/s, 0.1m/s and 2m/s. From the mode I static tests described in Chapter Four, it was decided that the most reliable definition of crack initiation was that point at which the first crack growth was recorded using high-speed photography. Other possible crack initiation points could be defined as the point of deviation from linearity or the point of maximum load on the load-time traces [81]. In the present work, the point of deviation from linearity was not employed due to the difficulty in obtaining consistent results when using this definition. It was noted also that the point of maximum load usually did not correspond to the point of visual crack initiation.

It is clear from Figures 6.4-6.6 that defining the point of crack initiation on the force-time signals is not a simple matter. There is no obvious point on the force-time signals which corresponds to this point. The procedure used for determining the point of crack initiation in the present work employed high-speed photography and this procedure is described in Section 6.2.2.

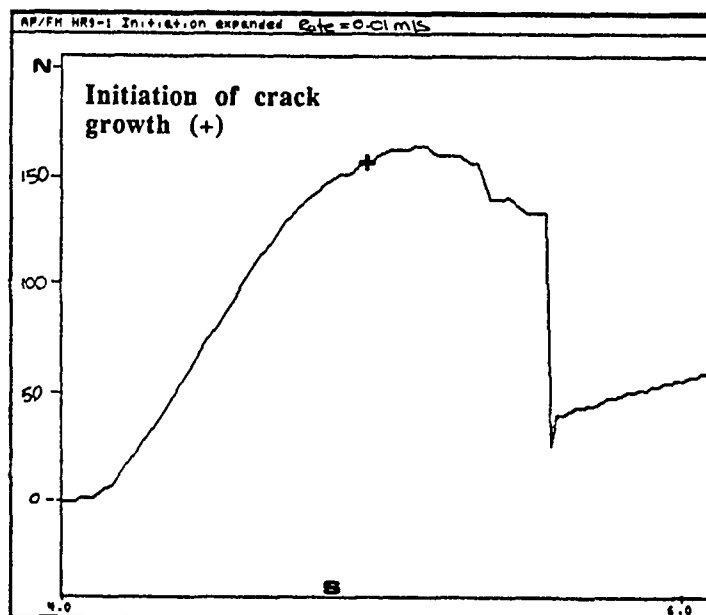


FIGURE 6.4 Load-time signal in the initial loading region at a test rate of 0.01m/s for a joint prepared with U/C PEEK substrates, bonded with the epoxy-film adhesive.

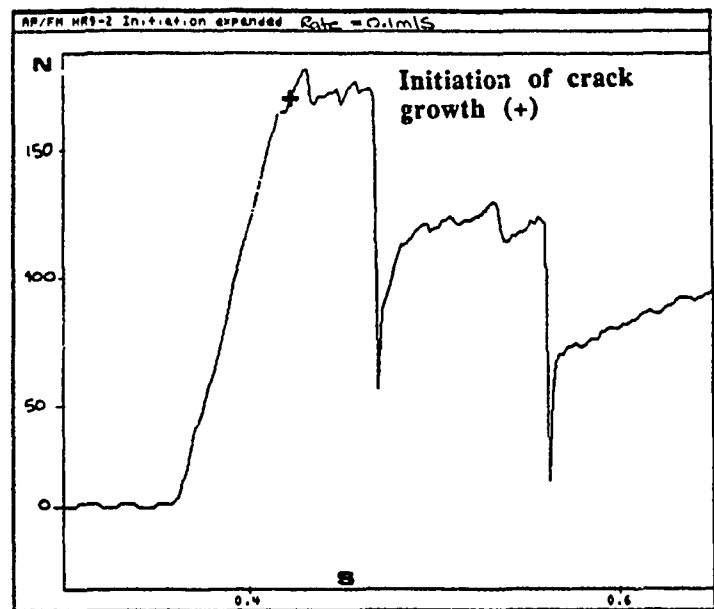


FIGURE 6.5 Load-time signal in the initial loading region at a test rate of 0.1m/s for a joint prepared with U/C PEEK substrates, bonded with the epoxy-film adhesive.

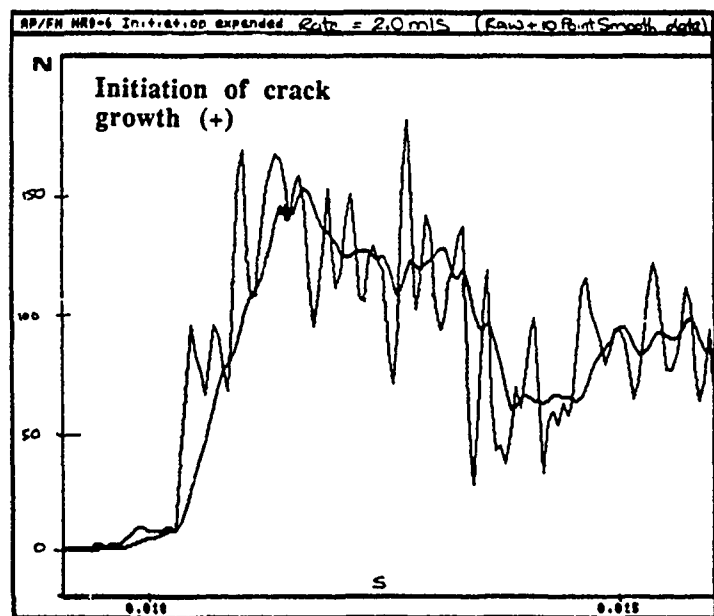


FIGURE 6.6 Load-time signal in the initial loading region at a test rate of 2m/s for a joint prepared with U/C PEEK substrates, bonded with the epoxy-film adhesive. (a) Unsmoothed and (b) smoothed traces are shown. Loading oscillations on trace (a) are inertial, and not associated with crack initiation.

6.2.2 High-Speed Photography

At all rates faster than 10mm/min (1.67×10^{-4} m/s), a high-speed camera was employed to record the beam opening displacement, δ , and the crack length, a , during the mode I DCB fracture tests. The 16mm high-speed camera was described in Section 3.5.3. Camera speeds from 100 pictures per second (pps) to 4000pps were selected, depending on the ram velocity employed in the test. In order to ensure sufficient exposure of the film, camera speeds in excess of 4000pps were not used.

A special feature of this camera was the half-frame converter, which split each picture into two frames. Thus, at a camera speed of 100pps, 200 frames per second (fps) were actually taken, and at 1000pps, 2000fps were recorded, and so on. The camera operating parameters are shown in Table 6.1.

TABLE 6.1 Experimental operating parameters selected for the high speed camera.

Ram Velocity (m/s)	Camera speed (pps)	Frame rate (fps)	Aperture setting
<0.01	100	200	f5.6
0.1	200	400	f4
0.5	400	800	f2.8
1.0	600	1200	f2.8
1.5	800	1600	f2.8
2.0	1000	2000	f2.8
3.5	2000	4000	f2.8
5.0	3000	6000	f2.8
10.0	4000	8000	f2.8

Notes: The lens used was a 45mm, f2.5 lens and the film used was Kodak 7250 Eastman colour film. Illumination was achieved via two Broadlite 1250W tungsten flood lights.

Film analysis was conducted using a 16mm analysis projector. The film recording of the fracture test was loaded into the projector, and each picture (showing two frames) was projected onto a screen in order to measure the beam opening displacement, δ , and crack length, a . For reasons which will be given in Section 6.3.4., particular attention has been directed towards determining the opening displacement, δ , at the point of crack initiation. This parameter will be denoted by δ_i .

The procedure adopted for measuring δ_i by film analysis was as follows. The initial starter defect length, a_0 , was recorded for each specimen. This was done following the separation of the substrates after the test because a more accurate result could be attained than by trying to measure a_0 prior to testing. The high-speed film was then analysed on the projector. Subsequent frames were viewed until the measured length of the crack exceeded the initial crack length, a_0 . Suppose that this occurred at frame number 'n'. Thus, at frame number n-1, crack initiation had not occurred, but by frame number 'n' it had. Now, the DCB specimen was fixed to the loading shackles during the test by two brightly marked pins. The initial pin separation (when $\delta=0$) was measured from the projected film image. Opening displacements were then measured from the movement of the moving pin during the test.

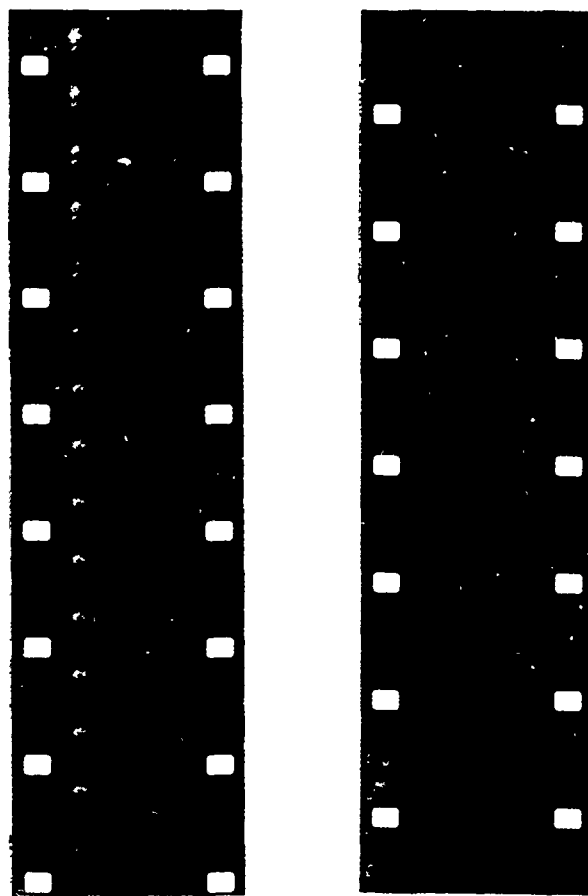


FIGURE 6.7 A high-speed film sequence at a ram velocity of 2m/s for the joint prepared with the U/C epoxy composite bonded with the epoxy-film adhesive.

Note that on the servo-hydraulic machine, the DCB was loaded from above and thus the lower pin remained stationary. On the screw-driven machine, the DCB was loaded from below and thus the upper pin remained stationary. The value of δ_i was then calculated from:

$$\delta_i = \delta_{n-1} + \frac{1}{2}(\delta_n - \delta_{n-1}) \quad \pm \frac{1}{2}(\delta_n - \delta_{n-1}) \quad (6.1)$$

where δ_{n-1} is the displacement measured from the frame 'n-1' and δ_n is the displacement measured from the frame 'n'. δ_i is therefore taken as the mean displacement of these two frames, so the maximum error in δ_i from this technique is clearly half of the displacement increment from frames 'n-1' to 'n'. Thus the error in the measurement of δ_i depends on the ratio of the ram velocity to the camera speed. To minimise errors, this ratio should be kept to an acceptable minimum, within the constraints imposed by the need to obtain sufficient film exposure.

An alternative procedure for the measurement of δ_i could be obtained from the relation:

$$\delta_i = \dot{\delta} t_i \quad (6.2)$$

where $\dot{\delta}$ is the ram velocity and t_i is the time to crack initiation. The value of t_i could then be deduced from the high-speed film in the same manner as δ_i was deduced previously, i.e. by multiplying the number of frames to crack initiation by the time interval per frame. This however, was less accurate because an initial framing zero error is encountered (i.e. the start of the test can only be pin-pointed to $\pm 0.5 \times$ time per frame). In addition, any error in the measurement of the ram speed would magnify the error in δ_i further. Finally, the value of t_i could be approximated from the load-time signal from the test. However, it was found that this was the least accurate method to use, particularly when the traces became severely influenced by the dynamic effects.

6.2.3 Joint Fracture Surfaces

Some typical fracture surfaces obtained from the high rate tests are shown in Figures 6.8 and 6.9. A careful examination of these surfaces revealed several valuable pieces of information. Firstly, the length of the starter crack, a_0 , was accurately determined from these 'post-failure' fracture surfaces. The crack length was an important parameter in the beam theory equations discussed in Chapter Four. Secondly, the locus of joint failure was visually ascertained from these fracture surfaces. When the failure locus was cohesive or interlaminar, as observed in these high rate tests, then this was clearly visible by eye. It will be shown in Chapter Seven that when the locus of failure appeared to be interfacial, then a more careful assessment of the locus was necessary.



FIGURE 6.8 Photographs of the fracture surfaces from failed joints at various testing rates. The adhesive was the epoxy-film adhesive and the substrate material was the U/C PEEK composite.

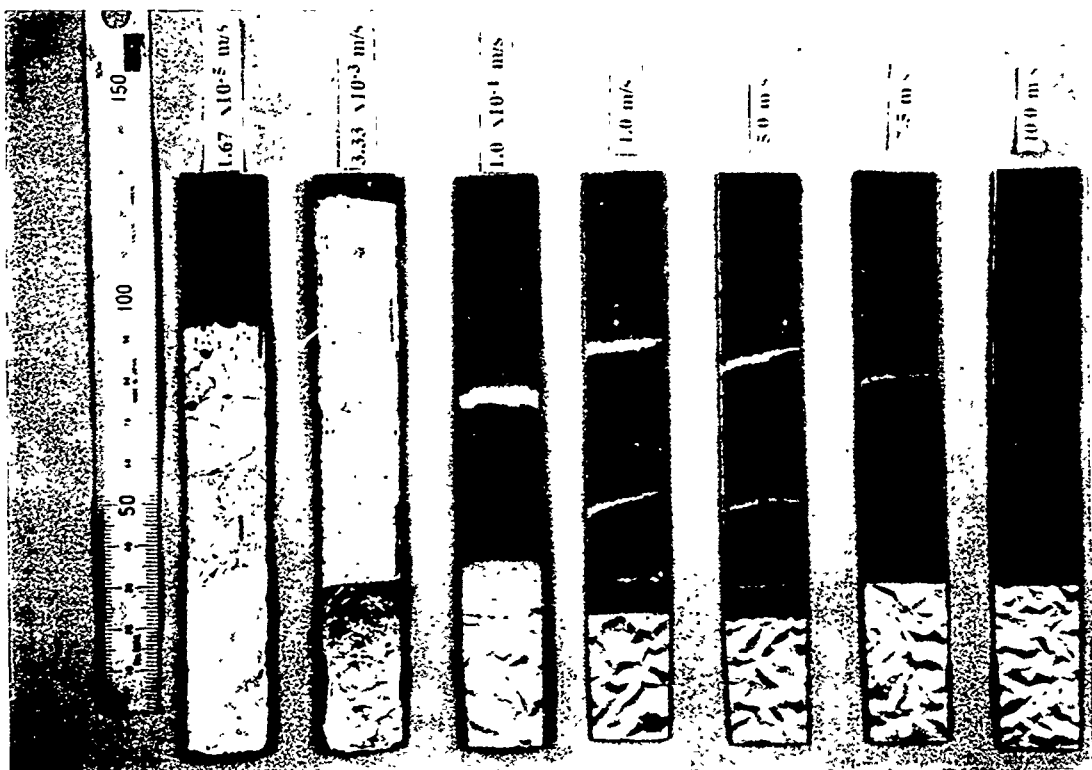


FIGURE 6.9 Photographs of the fracture surfaces from failed joints at various testing rates. The adhesive was the epoxy-paste adhesive and the substrate material was the U/C PEEK composite.

Finally, a microscopic examination of the fracture surfaces, using scanning electron microscopy, was used to identify the toughening mechanisms associated with the rubber particles within the epoxy adhesive. The effect of rate on these mechanisms was then identified and this will be discussed in Section 6.6.

6.2.4 Errors In Experimental Data

The experimental parameters required by the beam theory analysis were the load, P , the displacement, δ , the crack length, a , the beam width, B , and the beam thickness, h . The error in the measurement of the load will be considered first.

6.2.4.1 Errors in the load measurements

It was considered that the experimental measurement of the load represented the greatest source of error in the experimental data at high rates. It was shown in Section 6.2.1, that it became increasingly difficult to interpret the load-time signals at higher rates. In addition, due to the large dynamic effect experienced at rates above 2m/s, it was not possible to deduce any useful information from the piezo-electric load-cell at rates above this. In addition, at rates above 1m/s, it was necessary to smooth the load-time signal using a 10 point averaging technique on the signal analysis software. This technique averaged the ten points succeeding each data point and replaced the data point with this average. This clearly introduced another source of error. However, this procedure was only employed at rates between 1.5m/s and 2m/s. At 1m/s and below, no averaging was undertaken and only the raw data was analysed. At rates above 2m/s, it was not possible to interpret the load-time signal, and averaging was not undertaken. The errors encountered in measuring the load were estimated, and are shown in Table 6.2.

TABLE 6.2 Estimated errors in the load measurements for joints Prepared with the epoxy-film adhesive.

Rate (m/s)	Error in P (N)	% Error in P (%)
Static 10^{-5}	$\pm 2N$	1.3
10^{-4} - 10^{-2}	$\pm 5N$	3.3
10^{-2} - 10^{-1}	$\pm 10N$	6.6
10^{-1} -2.0	$\pm 20N$	13.3

Clearly, the inaccuracy in the measurement of the load may have introduced an error into the beam theory equations requiring this parameter. It will be shown in Section 6.3.3 that when the substrate modulus is calculated via eqn 4.6, then E_s was seen to decrease with increasing rate. This is a most unlikely result, and serves to highlight the error in the load measurements at the higher test rates.

It was considered that the most significant reason for the uncertainty in the load measurements was the existence of flexural waves within the specimen. The precise influence of flexural waves on the validity of the load measurements at higher testing rates is not fully understood. It is known however, that flexural waves produce bending moments. Smiley [59] used the constraint that, in order to neglect the effect of flexural waves, the critical bending moment to cause fracture must be very much greater than the bending moment induced by the flexural wave. This in turn, imposed a constraint on the maximum test rate employed. Wang and Williams [88] have recently modelled numerically the influence of flexural waves during a DCB test. They concluded that when flexural waves are considered, the value of G oscillates at the crack tip. They concluded that the dynamic value of G , termed G_{Dyn} , calculated numerically by considering the interaction of the stress waves with the crack tip, was greater than the value obtained by neglecting this interaction. This value was termed G_{Stat} , or static G . Therefore, when calculating the fracture energy, G_c , then lower values may be obtained if the stress wave interaction is not considered. In this instant, the value of the fracture energy calculated using static G measurements may be considered to represent a lower bound value to the fully dynamic solution.

6.2.4.2 Errors in the displacement measurements

The measurements of the beam opening displacement were made from the high-speed films. The error in this technique derived from the need to define the instant of crack initiation by an interpolation between two frames. The error so encountered was, therefore, proportional to the ratio of the ram velocity to the camera speed. At a ram velocity of 10m/s, and with the camera running at 4000pps (8000fps), a frame was recorded every 1.25mm of ram displacement. Thus the resolution of this measuring procedure was 1.25mm/frame at this rate. By linearly interpolating between two frames at this rate, the error in the measured value of the displacement was ± 0.625 mm, i.e. half of the displacement increment per frame. Typical values for the crack opening displacement at initiation ranged from 7mm to 9mm, thus at the highest rate, the typical percentage error in the displacement measurements were $\pm 8\%$. The errors in the measurement of δ for other test rates are shown in Table 6.3.

TABLE 6.3 The errors in the measurement of δ from a high-speed film.

Ram Velocity (m/s)	δ /fps (mm/frame)	Error in δ_i (mm)
0.0033	0.167	0.008
0.01	0.05	0.025
0.1	0.25	0.125
0.5	0.625	0.313
1.0	0.833	0.417
1.5	0.938	0.469
2.0	1.00	0.50
3.5	0.875	0.438
5.0	0.833	0.417
10.0	1.25	0.625

6.2.4.3 Errors in the measurement of a_0 , B and h.

The value of the starter crack length, a_0 , was measured accurately from the fracture surface after failure using vernier calipers. It was considered that this measurement may have contained an error of $\pm 0.1\text{mm}$. Given that a typical crack length was 30mm, then this represented a percentage error of $\pm 0.3\%$ in the measurement of a_0 .

The beam width, B, was measured also by vernier callipers to an accuracy of $\pm 0.01\text{mm}$ and the beam thickness, h, was measured by a micrometer screw gauge. It was considered that the maximum error in these measurements resulted from small variations in the values of B and h along the length of the beam. For the beam thickness and width measurements, ten separate measurements were made along the length of the beam, and an average was taken. The typical variation in the values of B and h along the beam length were: variation in B= 0.4mm or $\sim 2\%$ of the total width value, variation in h=0.015mm or $\sim 1\%$ of the total thickness value.

6.3 Analysis of Data

6.3.1 Beam Theory Methods

In Chapter Four, the various correction factors required for the beam theory analysis were described. The 'corrected load', 'corrected displacement' and 'corrected displacement-modulus' methods were given by eqns 4.10, 4.11 and 4.12 respectively and are shown again

below. The former equation is independent of the beam opening displacement and the latter is independent of the load. The relevant equations are:

$$G_c = \frac{12FP^2(a + \chi h)^2}{B^2 h^3 E_s} \quad (4.10)$$

$$G_c = \frac{F}{N} \frac{3P\delta}{2B(a + \chi h)} \quad (4.11)$$

$$G_c = \frac{F}{N^2} \frac{3}{16} \frac{\delta^2 h^3 E_{11}}{(a + \chi h)^4} \quad (4.12)$$

These equations have been used to calculate the mode I fracture energy of the DCB adhesive joint systems as a function of test rate. It will be shown in Section 6.3.5 that the kinetic energy was negligible at the test rates employed in this work {less than 2% of the adhesive fracture energy at 10m/s} and so the above equations were not modified for this effect. The errors described in Section 6.2.4 were used to estimate the likely errors encountered in the calculation of G_c by eqns. 4.10-4.12. Eqn. 4.10 gave the largest errors in G_c at all test rates. Under static test conditions, this equation gave an estimated error in G_c of 6.2%. However, at a test rate of 2m/s, the estimated error in G_c when calculated via eqn 4.10 increased to $\pm 30\%$. The estimated error in the value of G_c calculated via eqn. 4.12 at this test rate was $\pm 18\%$, i.e. eqn. 4.12 contained a considerably smaller estimated error than eqn. 4.10. It will be shown in Section 6.5 that when G_c is calculated via eqns 4.10-4.12, then considerably different results are obtained at high rates of testing and eqn. 4.12 has proved to be the most reliable.

A further complication at higher test rates is the need to input values of the substrate modulus and the correction factor χ . At lower rates, these parameters were deduced by a plot of $(C/N)^{1/3}$ versus 'a', as was described in Section 4.3.2. At higher rates, when the crack propagation was unstable, this procedure was not practical. These parameters will be discussed in the next two sections.

6.3.2 Shear Correction Term, χ

All of the beam theory equations require the value of the crack length, and therefore all need to be corrected for shear rotations and deflections of the beam at the crack tip, as was described in Chapter Four. For the static tests this term was calculated for each specimen in turn. At high rates, this procedure could not be followed and so an average χ value has been

determined for each composite material from a large number of static tests. For the U/C PEEK, a value of $\chi = 2.7$ has been employed, and for U/C epoxy, a value of $\chi = 3.8$ has been used. It was particularly important to use a corrected value of χ when considering crack initiation, since the shear correction term is more significant when considering short crack lengths.

6.3.3 Substrate Modulus Values

Eqns. 4.10 and 4.12 require a value for the substrate modulus. It was shown in Chapter Four that the substrate modulus may be deduced from beam theory. The equation:

$$E_s = \frac{P}{\delta} \frac{8N(a + \chi h)^3}{Bh^3} \quad (4.6)$$

can be used to calculate a point value. However, in order to retain the independence of eqns. 4.10, 4.11 and 4.12, an independent value of E_s should be employed. The use of eqn. 4.6 to calculate E_s was also restricted by the need to measure load. The substrate modulus for each fibre-composite material was measured at slow rate from three-point bend tests, as described in Section 3.4.1. The values obtained were $E_s = 110\text{GPa}$ for both U/C epoxy and U/C PEEK composites. These independently measured values were in very close agreement with the values calculated by eqn. 4.6 from the DCB joint tests conducted under at slow rates, i.e. at test rates below about $1.67 \times 10^{-2}\text{m/s}$ {see later, Table 6.4}.

In order to determine whether the moduli of the fibre-composites employed were rate dependent, dynamic mechanical thermal analysis (DMTA) was carried out as described in Section 3.4.2. In these tests the substrate modulus, E_s , was calculated as a function of the loading frequency. The resolution of this technique was poor due to limitations imposed by the specimen clamping conditions, but the results indicated that there was no change in the value of E_s over the frequency range of the test. These results are in agreement with those of Harding and co-workers [90,103,104] used a tensile version of the Hopkinson-bar apparatus to measure the tensile moduli for a U/C epoxy composite up to a strain rate of $\sim 450\text{s}^{-1}$. No rate dependence was found to exist for this material. Therefore, it has been assumed in the present work that the tensile substrate modulus, E_s , is independent of test rate.

It was however, still of interest to use eqn. 4.6 to calculate the modulus of the composite substrates upto the test rate of 2m/s . Table 6.6 shows the values of E_s calculated via eqn. 4.6 for the U/C PEEK substrates at rates up to 2m/s .

TABLE 6.4 Substrate axial modulus calculated from eqn. 4.6 as a function of test rate for the U/C PEEK composite.

Test Rate (m/s)	Substrate Modulus Eqn 4.6 (GPa)
1.67×10^{-5}	109
8.33×10^{-5}	116
1.67×10^{-4}	107
3.33×10^{-3}	109
8.33×10^{-3}	102
1.67×10^{-2}	108
1.00×10^{-2}	100
1.00×10^{-1}	101
5.00×10^{-1}	97
1.00×10^0	102
1.50×10^0	92
2.00×10^0	89

It can be seen from Table 6.4 that at test rates from 1.67×10^{-5} to about 1.67×10^{-2} m/s, the calculated value of E_s is in very close agreement with that value measured independently using the three-point bend tests. However, the table shows that as the rate of the DCB test is increased, then the value of modulus decreased from 109 GPa at slow test rates to 89 GPa at 2 m/s when calculated using eqn. 4.6. This was a very unlikely result and it was considered that the most likely reason for the decrease in the calculated values of E_s was the poor reliability of the load measurements at the faster rates. These results suggested therefore, that the measured load values were underestimated. Further, if the load was underestimated, then the values of the mode I fracture energy for the joints calculated via eqns. 4.10 and 4.11 would also give low values of G_c . However, eqn. 4.12 is independent of the load and therefore may be applied with greater confidence.

6.3.4 Analysis of Crack Initiation Data

The results that are presented in Section 6.5 show the joint fracture energy, G_c , versus the beam opening displacement rate at the point of crack initiation. Data at crack initiation were employed for three reasons. Firstly, the rate of strain at the crack tip is inversely proportional to the square of the crack length, i.e. the strain rate at this point decreases as the crack length

increases. Therefore, crack initiation from a constant initial crack length provides a consistent and repeatable event from which to measure G_c . Secondly, for unstable, stick-slip crack propagation, the values of force, displacement and crack length are most readily obtainable at this point. Thirdly, it was shown previously that no 'R-curve' exists for the adhesively-bonded DCB test specimens, and therefore G_c at initiation and propagation were equivalent. Finally, crack initiation was defined as the instant when the first crack growth was detected using high-speed photography. This definition proved to be the most repeatable in the present work.

6.3.5 Consideration of Kinetic Energy

The contribution made by kinetic energy to the Griffith energy balance was considered by Berry [91]. Including inertial effects, eqn. 2.13 may be expressed as:

$$G_{ic} = \frac{d(U_e - U_s - U_k)}{Bda} \quad (6.3)$$

where U_e is the external work done, U_s is the strain energy stored within the specimen and U_k is the kinetic energy imparted to specimen.

Smiley [59] considered the kinetic energy effects for the DCB geometry at crack initiation. By summing the kinetic energy of each beam element, the contribution to the energy balance was expressed as:

$$\frac{dU_k}{Bda} = \frac{33\rho h\dot{\delta}^2}{280} \quad (6.4)$$

where ρ is the density of the substrate beam, h is the beam thickness and $\dot{\delta}$ is the beam opening displacement rate. Semi-crystalline U/C PEEK has a density of 1600kg/m^3 [92] and of the two adhesives employed, kinetic energy effects were most significant in the epoxy-film adhesive, due to its lower static fracture energy. The contribution of kinetic energy to the energy balance of joints prepared with this adhesive is shown in Figure 6.10. It can be seen that at a displacement rate of 10m/s , kinetic energy accounts for less than 1.5% of the total mode I static fracture energy for the joint bonded with the epoxy-film adhesive. Clearly, if there is a reduction in the fracture energy at high rates, then the kinetic energy effects will become more significant.

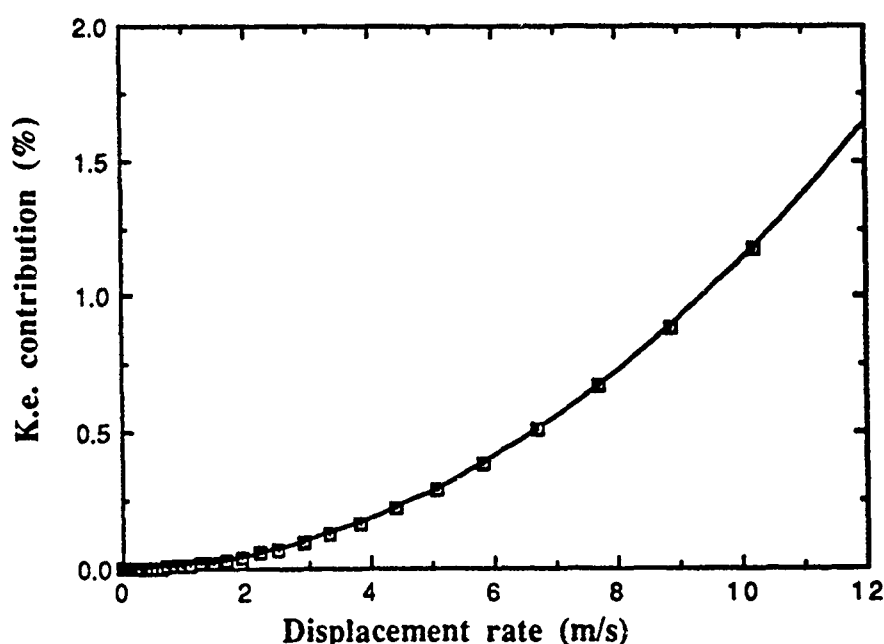


FIGURE 6.10 Kinetic energy contribution to the mode I fracture energy of the U/C PEEK composite bonded with the epoxy-film adhesive versus ram displacement rate.

6.4 Joint Fracture Behaviour

6.4.1 Stability Considerations

The stability of the crack propagation during a fracture test is controlled by the rate of change of G , i.e. dG/da [37]. If dG/da is positive, then crack propagation will tend to be unstable (provided dG_c/da is not also positive). If the specimen is loaded by a stiff machine, which is true in the present work, then a rapidly growing crack will be subjected to constant displacement conditions, provided that the crack speed during unstable growth is greater than the rate of displacement, i.e. that $a' \gg \delta'$. Thus, the condition for stable growth is:

$$\left(\frac{dG}{da} \right)_{\delta \text{ const}} \leq 0 \quad (6.5)$$

Williams [37] derived a general condition that if:

$$\frac{1}{2} C \frac{d^2 C}{da^2} \frac{1}{(dC/da)^2} \leq 1 \quad (6.6)$$

where C is the specimen compliance and a is the crack length, then the crack propagation will be stable. If this condition is applied to the DCB geometry, then it suggests that all crack propagation should be stable.

6.4.2 Static Crack Propagation Behaviour

Under mode I, static loading conditions i.e. at an opening rate of $1.67 \times 10^{-5} \text{ m/s}$, the DCB adhesive joint specimens exhibited stable (Type A) crack propagation. Force-displacement traces obtained during this type of crack propagation were shown in Figures 4.3 and 4.4 for the epoxy-film and epoxy-paste adhesives respectively.

6.4.3 Quasi-Static Crack Propagation Behaviour

However, as the beam opening displacement rate was increased, a transition from stable, cohesive (Type A) to unstable stick-slip (Type B) fracture behaviour was observed in both the epoxy-film and epoxy-paste adhesives, with either U/C epoxy or U/C PEEK substrates. It was noted that the transition from Type A to Type B crack propagation occurred at different rates in the two adhesives. The transition from Type A to B occurred at a slower rate in the epoxy-film adhesive than in the epoxy-paste adhesive i.e. the least tough of the two adhesives underwent the transition first.

TABLE 6.5 Transition rates from Type A to Type B crack propagation

Adhesive Type	Transition Rate (m/s)
Epoxy-film	3.3×10^{-3}
Epoxy-paste	1.67×10^{-2}

The transition rates are shown in Table 6.5. It can be seen that this transition was observed at a higher rate in the tougher, epoxy-paste adhesive. It was suggested by Kinloch and Williams [93] that the transition from stable to unstable crack growth in polymeric materials is controlled by a crack-tip blunting mechanism. They proposed that crack tip blunting caused the crack to arrest. Then, while the crack is stationary, continued loading of the specimen increased the strain energy available to grow the crack. Thus, when the crack does eventually propagate, there is an excess of energy available, and thus unstable crack growth resulted. However, this mechanism would suggest that a tougher adhesive should be more susceptible to unstable crack growth than less tough ones, and that unstable crack growth should be favoured by slow test rates and high test temperatures. It is therefore likely that other, more

subtle, mechanisms operate in the vicinity of the crack tip to control this transitional behaviour.

6.4.4 Dynamic Crack Propagation Behaviour

At opening displacement rates in excess of the transition rate for a particular adhesive, all crack propagation was unstable, stick-slip (Type B). It would, however, be inaccurate to describe this crack propagation as pure Type B, because, after crack arrest, there was usually a small amount of stable crack growth before the next unstable crack jump. In addition, as the opening displacement rate was increased, then the number of stick-slip bands in the epoxy-film adhesive increased, with each band accounting for less crack growth.

6.5 Results and Discussion

6.5.1 Effect of Rate on Joints bonded with the Epoxy-film Adhesive

The initiation values of the adhesive fracture energy, G_c , plotted against rate of loading, are shown in Figures 6.11 and 6.12 for the epoxy-film adhesive bonding the U/C epoxy and U/C PEEK composites respectively. The figures show the values of G_c calculated via eqns 4.10, 4.11 and 4.12. At slow rates, there was an excellent agreement between the values of G_c calculated by these three methods, as was shown in Chapter Four. However, as the rate of loading was increased, the differences between the values of G_c calculated via the different methods increased. When calculated via eqn. 4.10, consistently low values of G_c were recorded, with almost a 40% reduction in G_c being recorded at 2m/s, relative to the static value. It should be noted that this particular calculation method was highly dependent on the accuracy of the load measurements, i.e. the load value was raised to the the second power. When G_c was calculated via eqn. 4.11, then the reduction in the calculated value of G_c was less marked, with only a 20% reduction in the value of this parameter at 2m/s, relative to the static value. Eqn. 4.11 was dependent on the load value to the first power only. It should be remembered that load values were not recorded at rates exceeding 2m/s due to the difficulty of interpreting these traces at higher rates.

When G_c was calculated via eqn. 4.12, which was independent of the load measurements, then the value of G_c was seen to remain almost constant for this adhesive over the entire range of displacement rates employed. This result was of considerable interest because it implied that the declining G_c values obtained from eqns. 4.10 and 4.11 are not valid, but are an artifact

of the test, caused by inaccuracies in the load measurements at higher test rates. Further evidence to support the proposal that the load measurements were subject to error was given by the modulus calculations in Section 6.4.3. When the substrate modulus was calculated via eqn 4.6, then the value of E_s declined from 109GPa to 89GPa, which was an unlikely result, and is explained by the error in the load measurements at higher test rates.

Crack initiation in the epoxy-film adhesive was cohesive at all displacement rates. This result was of particular significance for the joints prepared with the U/C PEEK substrates, because it showed that the corona-treated surface provided an intrinsically strong interface between the composite and adhesive, even at high loading rates. All U/C PEEK substrates used for the rate testing with the epoxy-film adhesive received the same degree of corona treatment (i.e. 10J/mm²). It was interesting to note that at the maximum loading rate, some interlaminar crack propagation was observed at some distance down the specimen from the initiation of the crack. Further, at these high rates, post-mortem examination of the fracture surfaces suggested that the crack did not run straight through the centre of the adhesive layer, but appeared to have followed a sinusoidal path, approaching one interface at the peak, and the other interface at the trough of the wave motion. Indeed, it appeared to be at these maximum and minimum points that interlaminar crack growth was observed. A possible explanation for this observation was that, at the highest rates, the crack propagation behaviour was influenced by the dynamic flexural waves propagating in the arms of the specimen. However, as previously noted at crack initiation, all failure was cohesive for this adhesive.

Visually, the fracture surfaces looked duller at high rates (see Figure 6.9), but it will be shown in Section 6.6 that examination using scanning electron microscopy showed that there was still evidence of extensive particle cavitation and associated stress whitening in this adhesive, even at the highest loading rates.

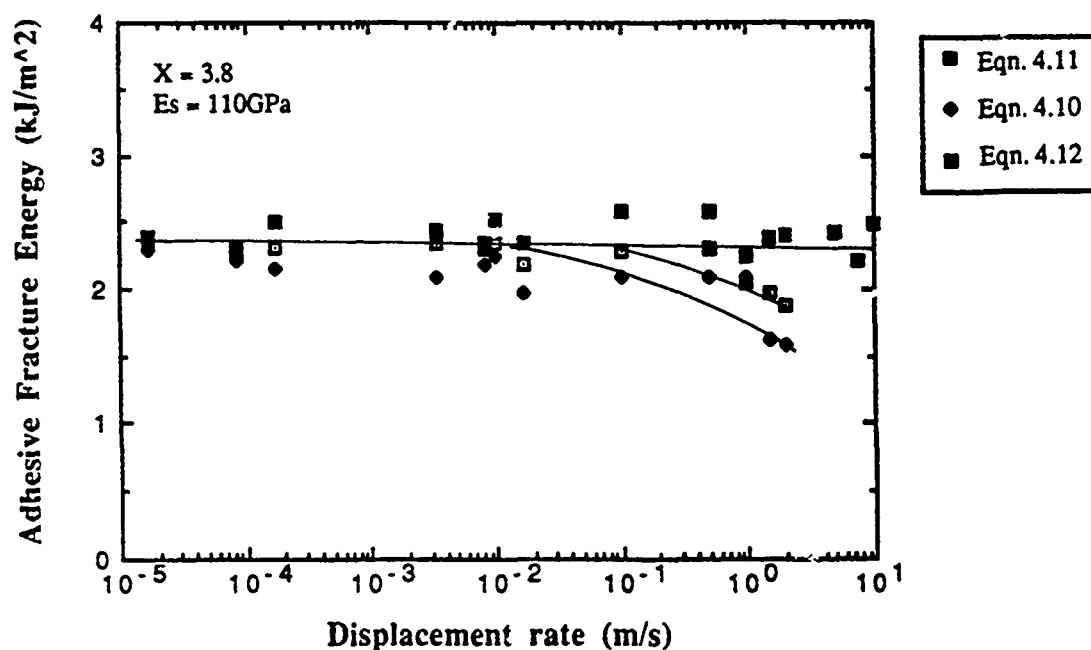


FIGURE 6.11 G_c versus ram displacement rate, deduced via eqns 4.10, 4.11, 4.12 at crack initiation for the U/C epoxy composite bonded with the epoxy-film adhesive. The locus of failure was cohesive at all rates.

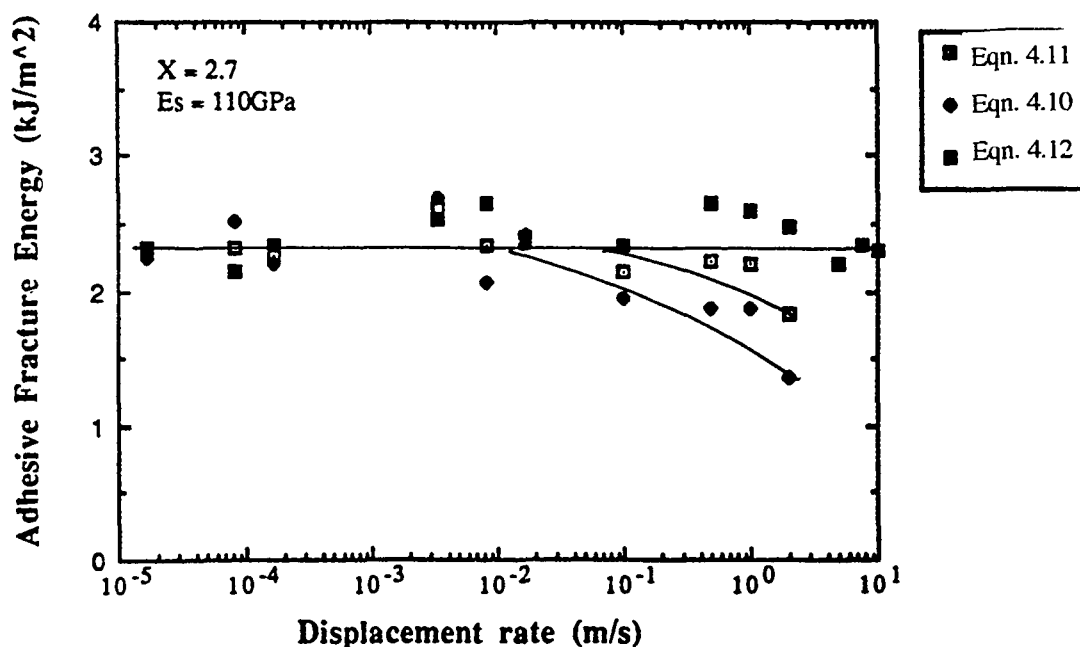


FIGURE 6.12 G_c versus ram displacement rate, deduced via eqns 4.10, 4.11, 4.12 at crack initiation for the U/C PEEK composite, corona treated to 10 J/mm^2 and bonded with the epoxy-film adhesive. The locus of failure was cohesive at all rates.

6.5.2 Effect of Rate on Joints bonded with the Epoxy-paste Adhesive

The initiation values of the adhesive fracture energy, G_c , plotted against the rate of loading, are shown in Figures 6.13 and 6.14 for the epoxy-paste adhesive bonding the U/C epoxy and U/C PEEK composites respectively. Once again, the figures show the values of G_c calculated via eqns 4.10, 4.11 and 4.12. It can be seen that there was good agreement between the values of G_c calculated by these three methods at slow rates. However, as the rate of loading was increased, the calculated values of G_c again began to diverge. However, for this adhesive, all three schemes for calculating the value of G_c predicted a reduction in the adhesive fracture energy at high rates. At a displacement rate of 10m/s, eqn. 4.12 shows that a 40% reduction in G_c had occurred. This reduction could not be due to inaccuracies in the load measurements, since eqn. 4.12 does not employ values of the load. Eqns 4.10 and 4.11 continued to predict even lower values for G_c , particularly at rates between 10^{-3} m/s and 2m/s; at higher rates the load was no longer measurable, as previously discussed.

A visual examination of the fracture surfaces of failed joints tested at 10^{-1} m/s revealed clearly the existence of two fracture regions. One region, associated with stable crack growth, was extensively stress whitened. The other region, associated with unstable crack growth, was darker and smoother in appearance, with no visible stress whitening. At rates up to 10^{-1} m/s, crack initiation clearly occurred with associated stress whitening. At higher rates, crack initiation occurred with little or no stress whitening. The micro-mechanisms operating will be discussed in more detail in Section 6.6.

Joints prepared with the U/C epoxy substrates exhibited a cohesive locus of failure up to a displacement rate of 5m/s, beyond which the failure locus became a mix of cohesive and interlaminar. Joints prepared with the U/C PEEK substrates exhibited a similar locus of failure, except the mixed locus was not observed below the displacement rate of 10m/s. It was again of particular interest to note that no interfacial crack growth was observed between the corona-treated U/C PEEK substrates and the epoxy-paste adhesive. Each U/C PEEK substrate was treated to the same level of corona treatment prior to bonding with this adhesive, (i.e. 20J/mm²).

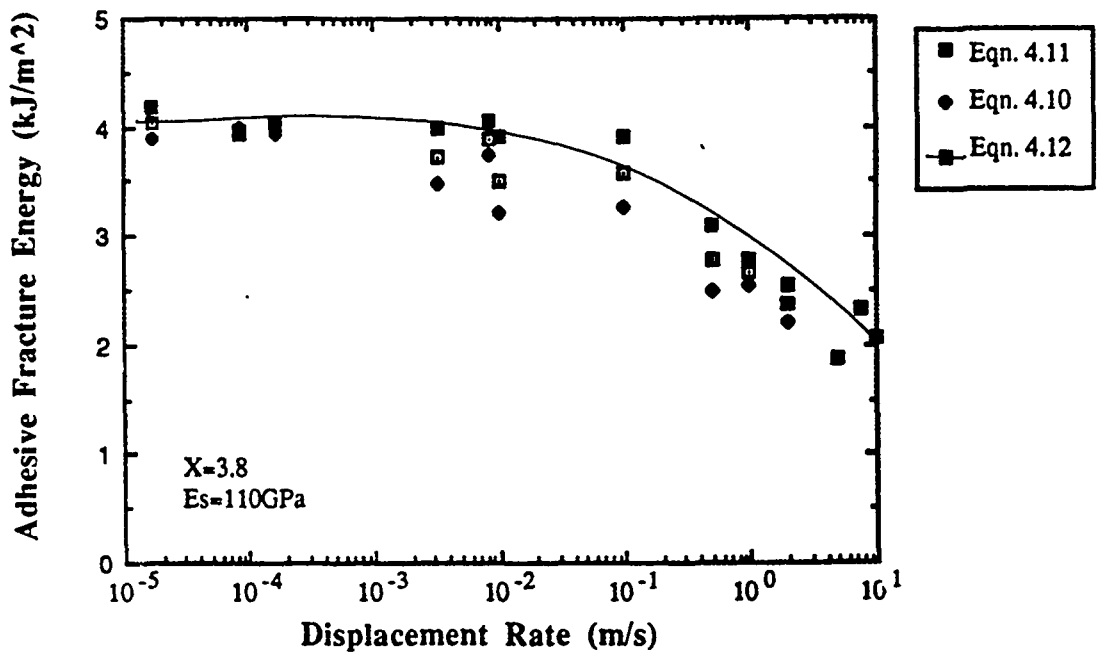


FIGURE 6.13 G_c versus ram displacement rate, deduced via eqns 4.10, 4.11, 4.12 at crack initiation for the U/C epoxy composite bonded with the epoxy-paste adhesive. The locus of failure was cohesive up to 5m/s, and then cohesive-interlaminar.

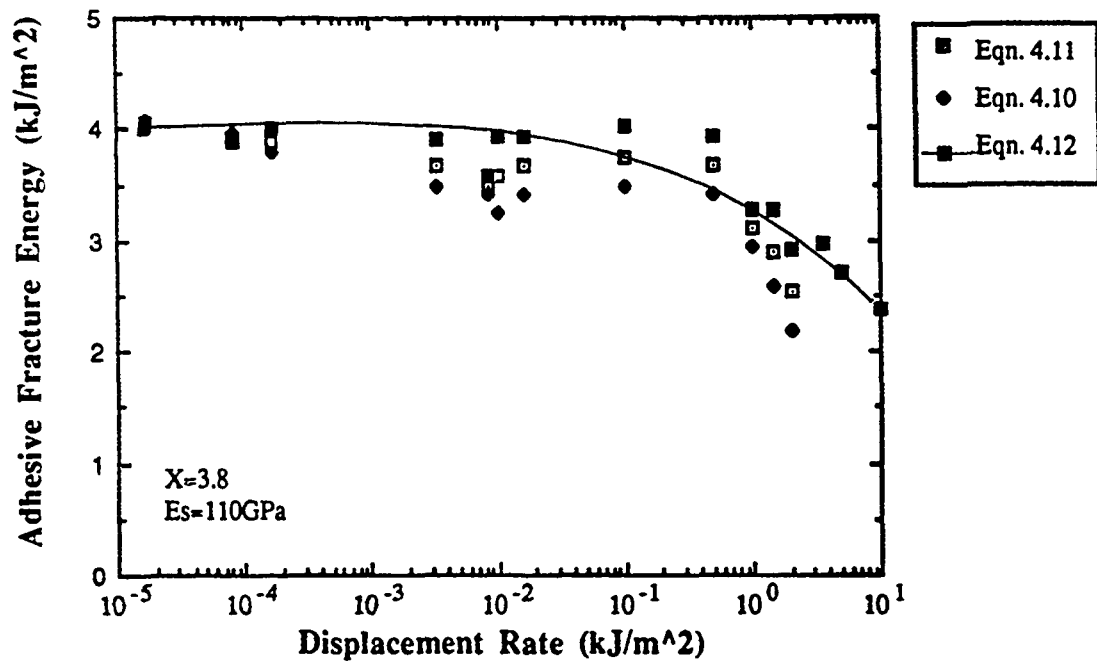


FIGURE 6.14 G_c versus ram displacement rate, deduced via eqns 4.10, 4.11, 4.12 at crack initiation for the U/C PEEK composite, corona treated to 20J/mm^2 and bonded with the epoxy-paste adhesive. The locus of failure was cohesive up to 7.5m/s, after which a mixture of cohesive and interlaminar fracture occurred.

6.5.3 Discussion of Fracture Results

It was shown in Figures 6.11 and 6.12 that when G_c was calculated using eqns. 4.10 and 4.11, a reduction was recorded for joints prepared with the epoxy-film adhesive. This reduction in G_c was seen to have occurred between 1-2m/s. These results should be treated with great caution, and indeed are incorrect, for two reasons. Firstly, when G_c was calculated by eqn. 4.12, which was independent of the measured load values, then no significant reduction was observed. Secondly, it was shown in Table 6.6 that when the substrate modulus was calculated via eqn. 4.6, then a decrease in modulus with rate was recorded. This result was most likely caused by a systematic underestimation of the load at these higher rates.

Figures 6.13 and 6.14 showed that when G_c was calculated for the joints prepared with the epoxy-paste adhesive by eqns. 4.10 and 4.11, then a reduction was again recorded. However, for the adhesive, a reduction in G_c was also given by eqn. 4.12. Thus all three equations suggested that there was a reduction in the value of G_c for this adhesive with increasing rate. Falling G_c values were first recorded at the displacement rate of 0.5m/s, and accounted for a 40% reduction in the value of G_c at 10m/s. However, again the values of G_c deduced using eqns. 4.10 and 4.11 are considered to be incorrect, due to the problems of determining accurate values of the load to use in these equations.

Therefore, by using a form of the analysis which was independent of the measurements of the load, it was shown that the adhesive fracture energy of the epoxy-film adhesive was not influenced by increasing the rate of the DCB test up to 10m/s. However, when the joints were prepared with the epoxy-paste adhesive, then a reduction in the adhesive fracture energy was observed.

It is clearly of interest to ascertain why the fracture energy of only one of the adhesives was dependent on rate. Kinloch and co-workers [47, 94] found that the difference between static and impact fracture energies for toughened epoxy adhesive joints was sensitive to the test temperature and as the glass transition temperature, T_g , of the adhesive was approached, then the difference between the static and impact values of the adhesive fracture energy became increasingly larger.

Hence, it is possible that the test temperature of 20°C relative to the T_g of the adhesives was a significant factor. This arises because the energy absorbed at the crack tip within the adhesive

is known to be highly sensitive to the yield stress of the adhesive. As the yield stress of the adhesive increases, the amount of shear yielding and particle cavitation would decrease. Thus, the amount of energy absorbed during crack propagation would decrease, resulting in lower values of G_c being measured. The hot-curing epoxy-film adhesive has a $T_g=90^\circ\text{C}$, whereas the cold curing epoxy-paste adhesive has a $T_g=59^\circ\text{C}$. Therefore, the epoxy-paste adhesive was being tested closer to its T_g than the epoxy-film adhesive, which could explain why a reduction in fracture energy was observed in the epoxy-paste adhesive, but not in the epoxy-film adhesive.

It is important to note that the reduction in the value of the adhesive fracture energy observed cannot be explained by a change in the locus of joint failure. The only significant change in failure locus was observed at 10m/s, at which point a mix of cohesive and interlaminar growth was observed. Given that a reduction was observed in the adhesive fracture energy starting at 0.5m/s in the epoxy-paste adhesive, then it must be due to changes in the micro-mechanisms operative at the tip of the crack within the adhesive. The tendency of a composite substrate to delaminate was discussed in Section 5.2.2. It was described how the propensity of a substrate to delaminate was governed by the value of the out-of-plane transverse tensile stress, σ_{yy} . Delamination of the substrate occurs if this value reaches a critical value, $\sigma_{yy,c}$, in the composite material. Since the crack-tip stress field was more intense in these joints at the higher test rates, then the composite substrates would have been more likely to delaminate under these conditions, as was indeed observed.

Finally, when the adhesive fracture energy, G_c , was calculated for each joint system using eqn. 4.12, then it was shown that the value of G_c was independent of the substrate employed. This would be expected, given that the locus of failure was cohesive, in the adhesive, for all crack initiation. It will be shown in Chapter Seven, that when these joint systems are exposed to hostile environmental conditions, then the value of G_c for the joint systems is dependent both on which substrate and which adhesive is employed.

6.6 Scanning Electron Microscopy Studies

6.6.1 Epoxy-film Adhesive Fracture Surfaces

The effect of displacement rate on the physical appearance of the fracture surfaces was studied using scanning electron microscopy. Figures 6.15-6.17 show typical fracture surfaces obtained from the mode I testing of joints prepared with the U/C epoxy substrates bonded with the epoxy-film adhesive. Figures 6.15(a and b) show the region of the fracture surface

just ahead of the aluminium starter foil. The starter foil is the smooth region at the bottom of the micrographs, and the direction of the crack growth was directly upwards. Figure 6.15(a) depicts a fracture surface obtained at a test rate of 1.67×10^{-5} m/s. The most noteworthy feature of this micrograph is the polyester mat carrier fibres, upon which the epoxy-film adhesive was carried. It is interesting to note how these fibres have been pulled from the epoxy-matrix of the adhesive in an interfacial manner. This may be deduced by the presence of long, clean fibres on the fracture surface, and the smooth indentations which these fibres have created on the epoxy surface. Figure 6.15(b) depicts a fracture surface obtained at a test rate of 10m/s. It can be seen from this micrograph that the polyester fibres were not pulled out from the epoxy matrix in the way that they were at slow test rates. At 10m/s, it appears that the fibres fractured with little 'fibre pull-out' being observed. The principal reason for the inclusion of these fibres was to support or "carry" the adhesive during handling and application. However, it was reported by Osiyemi [95] that the fatigue performance of this epoxy-film adhesive was significantly better than the tougher, epoxy-paste adhesive. It was concluded that this rather surprising result was due to the effect of the polyester mat carrier on the fatigue crack propagation, i.e. fibres bridged the crack and retarded the crack growth. It is clearly possible that the carrier material contributed more to the toughness of this adhesive under dynamic loading conditions.

Figures 6.16(a and b) again show a typical region of the fracture surface just ahead of the aluminium starter foil in the epoxy-film adhesive, but at the higher magnification of X750. Figure 6.16(a) was obtained from a joint tested at 1.67×10^{-5} m/s and Figure 6.16(b) was obtained from a joint tested at 10m/s. It was noted that both micrographs show evidence

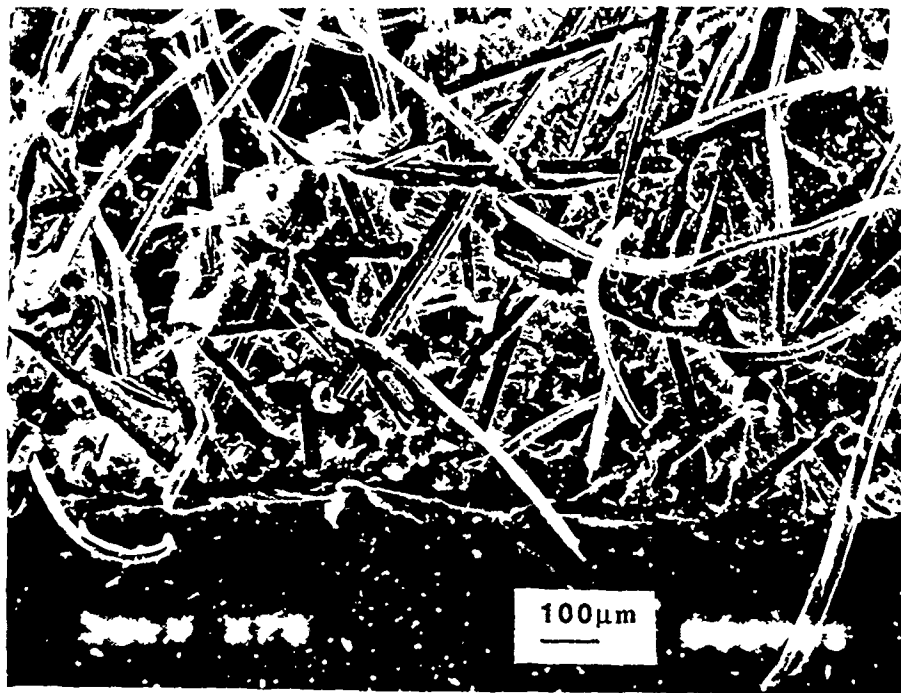


FIGURE 6.15(a) Scanning electron micrograph of an epoxy-film adhesive fracture surface directly ahead of the starter foil. The test rate was 1.67×10^{-5} m/s and the substrate material was U/C epoxy. Magnification X75.

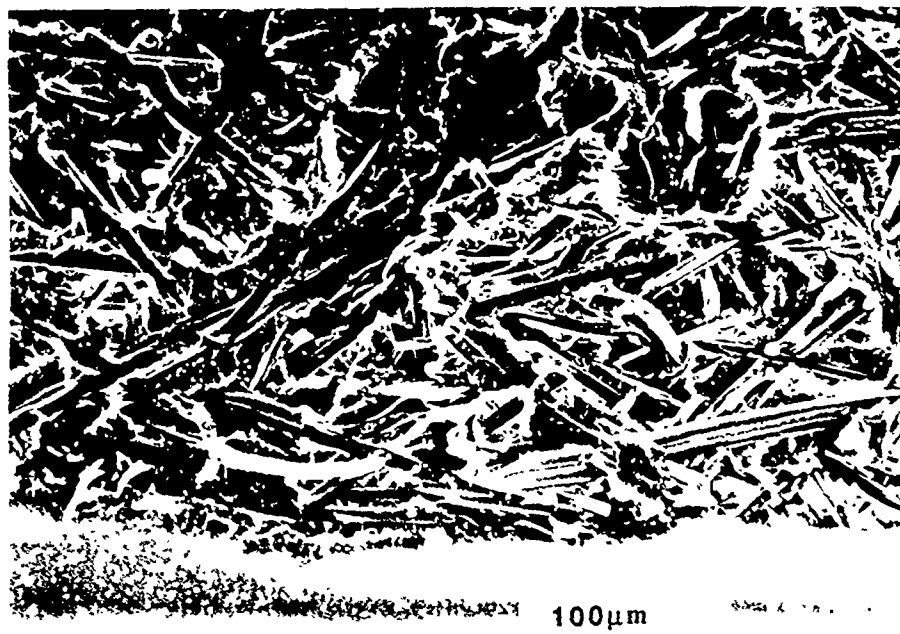


FIGURE 6.15(b) Scanning electron micrograph of an epoxy-film adhesive fracture surface directly ahead of the starter foil. The test rate was 10 m/s and the substrate material was U/C epoxy. Magnification X75.

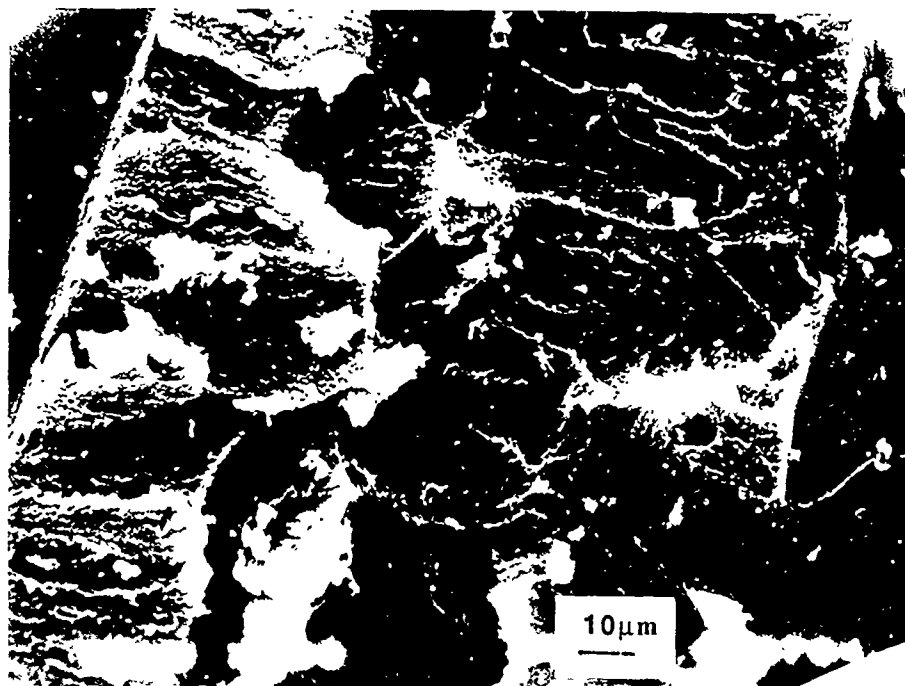


FIGURE 6.16(a) Scanning electron micrograph of an epoxy-film adhesive fracture surface directly ahead of the starter foil. The test rate was 1.67×10^{-5} m/s and the substrate material was U/C epoxy. Magnification X750.

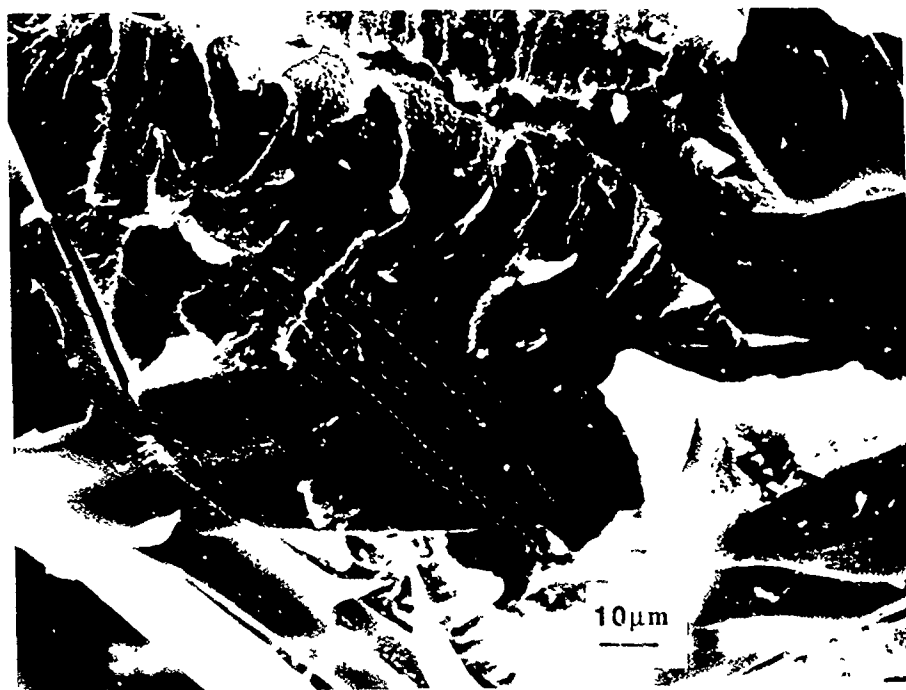


FIGURE 6.16(b) Scanning electron micrograph of an epoxy-film adhesive fracture surface directly ahead of the starter foil. The test rate was 10 m/s and the substrate material was U/C epoxy. Magnification X750.

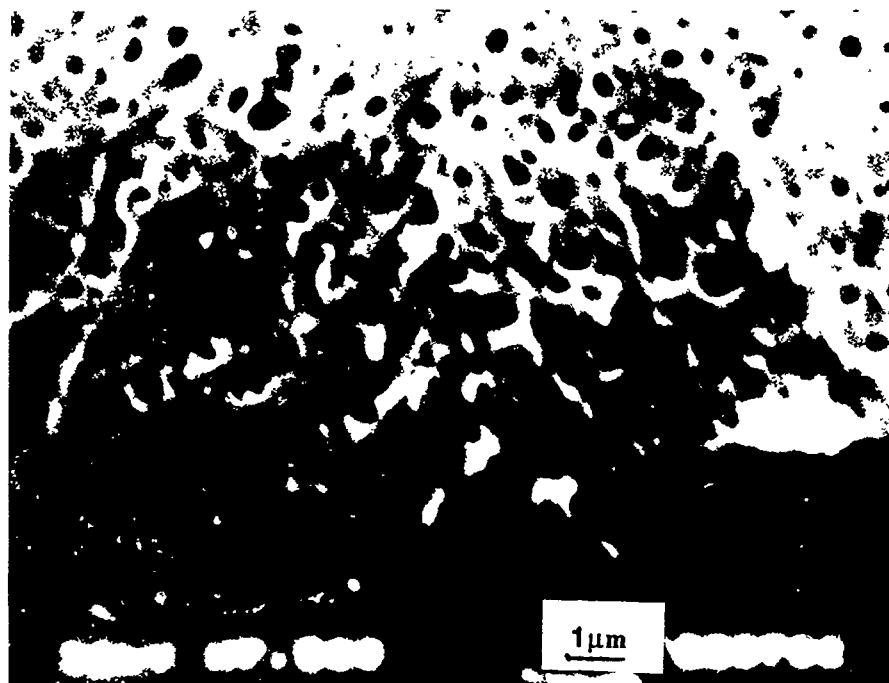


FIGURE 6.17(a) Scanning electron micrograph showing particle cavitation in the epoxy-film adhesive directly ahead of the starter foil. The test rate was 1.67×10^{-5} m/s and the substrate material was U/C epoxy. Magnification X7500.

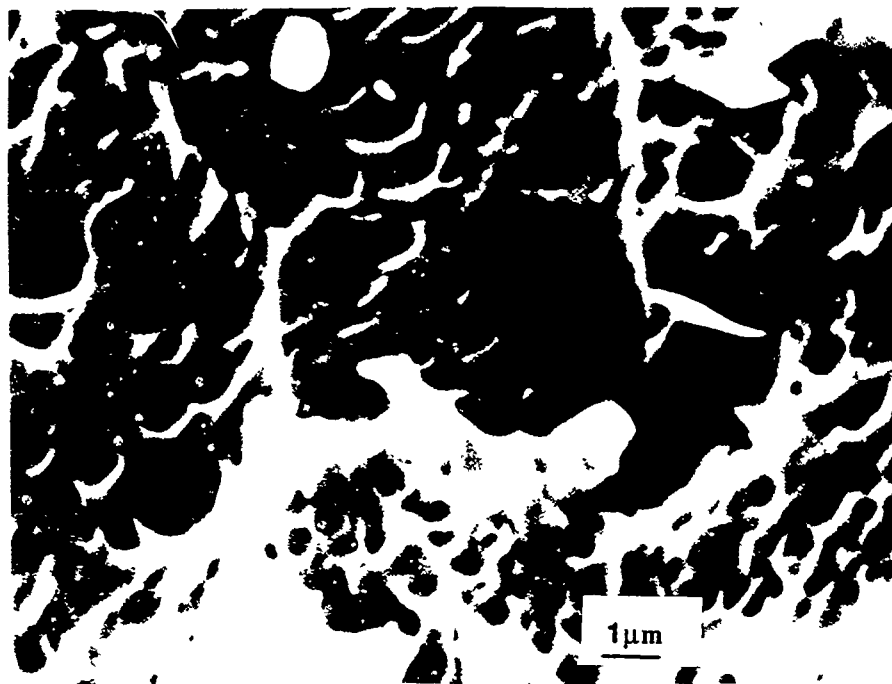


FIGURE 6.17(b) Scanning electron micrograph showing particle cavitation in the epoxy-film adhesive directly ahead of the starter foil. The test rate was 10 m/s and the substrate material was U/C epoxy. Magnification X7500.

plastic deformation and this suggested that shear yielding occurred at both slow and fast rates within the epoxy-film adhesive and therefore, this would suggest that this important energy absorbing mechanism was not significantly suppressed by increasing the rate of the test to 10m/s.

Another important energy absorbing mechanism which was discussed in Chapter Two was cavitation of the rubber particles, and associated particle hole growth, within the toughened adhesive. It was this micro-mechanism which gave rise to the stress whitening which was observed on visual inspection. Figures 6.17 (a and b) show the same fracture surfaces again, but at the higher magnification of X7500. At this magnification, the rubber particles are clearly visible, and there is no evidence to suggest that there is less particle cavitation at a high rate, Figure 6.17(b) than at a slow rate, Figure 6.17(a). This observation agrees with the mode I fracture results deduced from Eqn 4.12, which showed that G_c for the epoxy-film adhesive remained almost constant from static test rates up to 10m/s.

6.6.2 Epoxy-paste Adhesive Fracture Surfaces

Figures 6.18-6.20 show typical fracture surfaces obtained from the mode I testing of joints prepared with the U/C epoxy substrates bonded with the epoxy-paste adhesive. Figures 6.18(a and b) show the region of the fracture surface just ahead of the aluminium starter foil at a displacement rate of 1.67×10^{-5} m/s and 10m/s respectively. The direction of crack propagation was again directly upwards, at right angles to the starter foil.

The following features were visible in both micrographs. Firstly, short fibres could be seen. These fibres were added by the manufacturer to increase the viscosity of the adhesive. Secondly, glass spheres which were added to control the bondline thickness can be seen. The spheres are of two sizes. One size (5mil or 0.127mm) were added by the manufacturer and the larger size, (0.35mm) were added during preparation of the joints. Thirdly, a number of air bubbles or voids can be seen, which were introduced during mixing of the adhesive and hardener. Fourthly, an important difference between the two micrographs is the apparent roughness of the surface in Figure 6.18(a) and, in contrast, the apparent smoothness of the surface in Figure 6.18(b). This is particularly evident in the initiation region very close to the starter foil. In Figure 6.18(a) the fracture surface at crack initiation has a greater depth and a ridge can be clearly observed at this point. In contrast, the equivalent region in Figure 6.18(b) is very smooth, suggesting that the micro-mechanisms associated with crack growth were

occurring over a smaller volume. However, in order to examine these mechanisms more closely, it was necessary to examine these regions at higher magnifications.

Figures 6.19(a and b) show the same fracture surfaces of the failed epoxy-paste adhesive bonding the U/C epoxy substrates as previously, at a slow and a high rate respectively, but now at a magnification of X750. The difference between the two micrographs is striking. The fracture surface shown in Figure 6.19(a) clearly shows that particle cavitation has occurred within the adhesive during the fracture test at 1.67×10^{-5} m/s and this gives rise to the stress-whitening which was clearly visible on the fracture surfaces. However, the fracture surface shown in Figure 6.19(b) shows very little evidence to suggest that particle cavitation has occurred during the test at 10m/s. In fact, it is difficult to identify the rubber particles in this micrograph and no significant stress-whitening was observed on the fracture surfaces {as shown in Figure 6.9}.

This conclusion can be made more clearly by observing Figures 6.20(a and b). The epoxy matrix in the initiation region has been magnified to X2000. The difference between the slow and fast rate fracture surfaces is very clear in these micrographs. Figure 6.20(a) shows the slow rate fracture surface with extensive particle cavitation and a complex surface topography. The ridges and areas of "drawn" material are indications of extensive plastic deformation of the epoxy-matrix. Figure 6.12(b) shows the high rate fracture surface which is smoother and showing very much less particle cavitation.

These micrographs support the fracture results presented in section 6.5 and show clearly that the decrease in the value of G_c which was observed for the epoxy-paste adhesive may be explained in terms of a reduction in the energy absorbing micro-mechanisms occurring in the plastic zone ahead of the crack-tip at higher test rates.

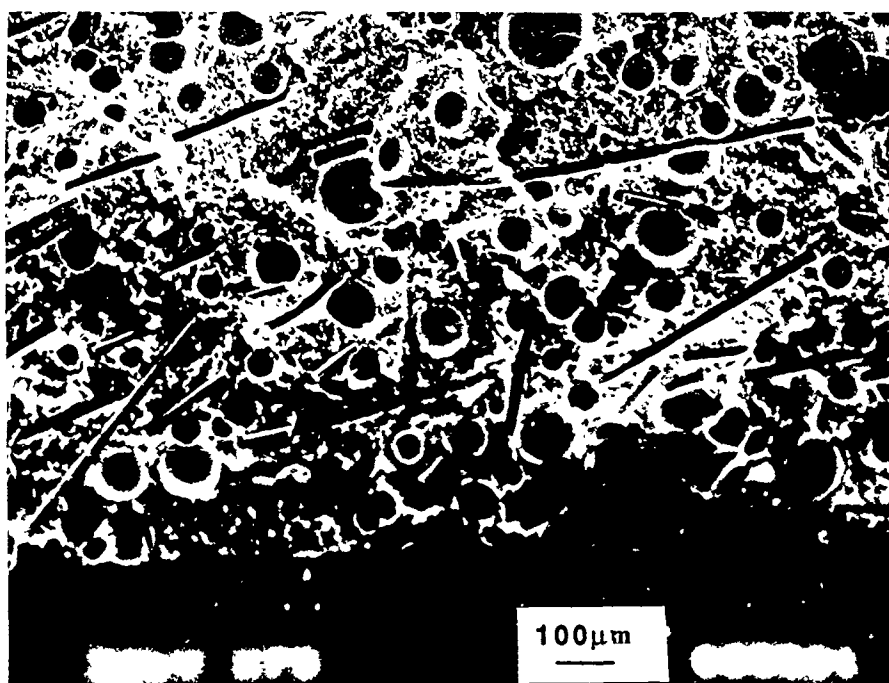


FIGURE 6.18(a) Scanning electron micrograph of an epoxy-paste adhesive fracture surface directly ahead of the starter foil. The test rate was 1.67×10^{-5} m/s and the substrate material was U/C epoxy. Magnification X75.

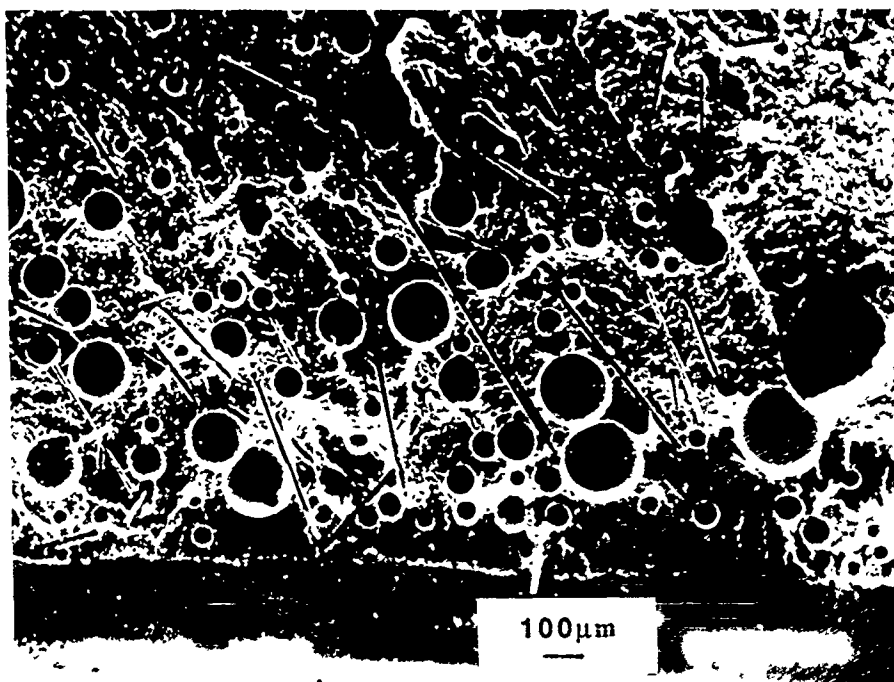


FIGURE 6.18(b) Scanning electron micrograph of an epoxy-paste adhesive fracture surface directly ahead of the starter foil. The test rate was 10 m/s and the substrate material was U/C epoxy. Magnification X75.

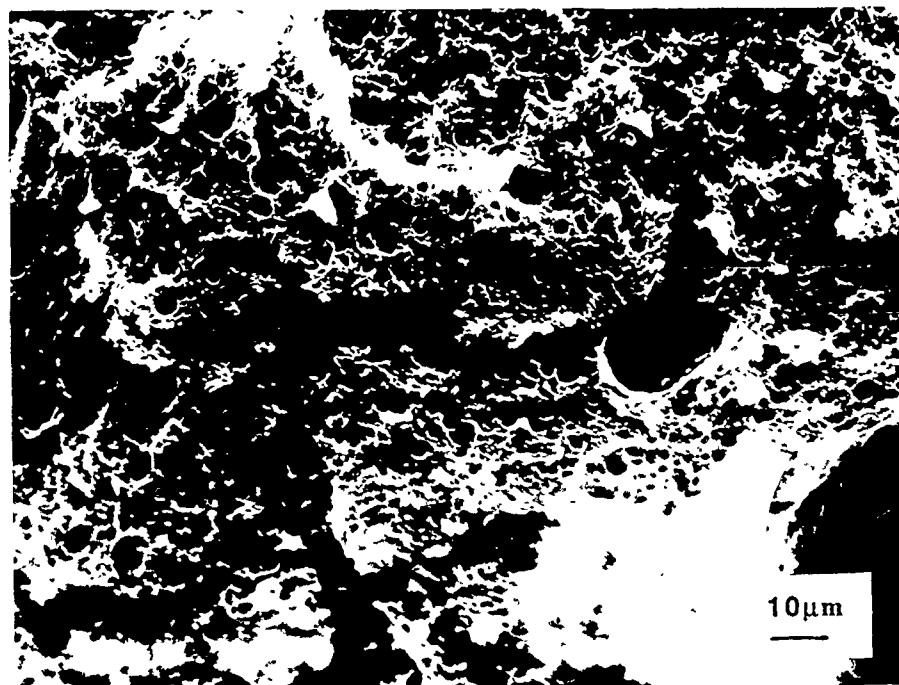


FIGURE 6.19(a) Scanning electron micrograph of an epoxy-paste adhesive fracture surface directly ahead of the starter foil. The test rate was 1.67×10^{-5} m/s and the substrate material was U/C epoxy. Magnification X750.

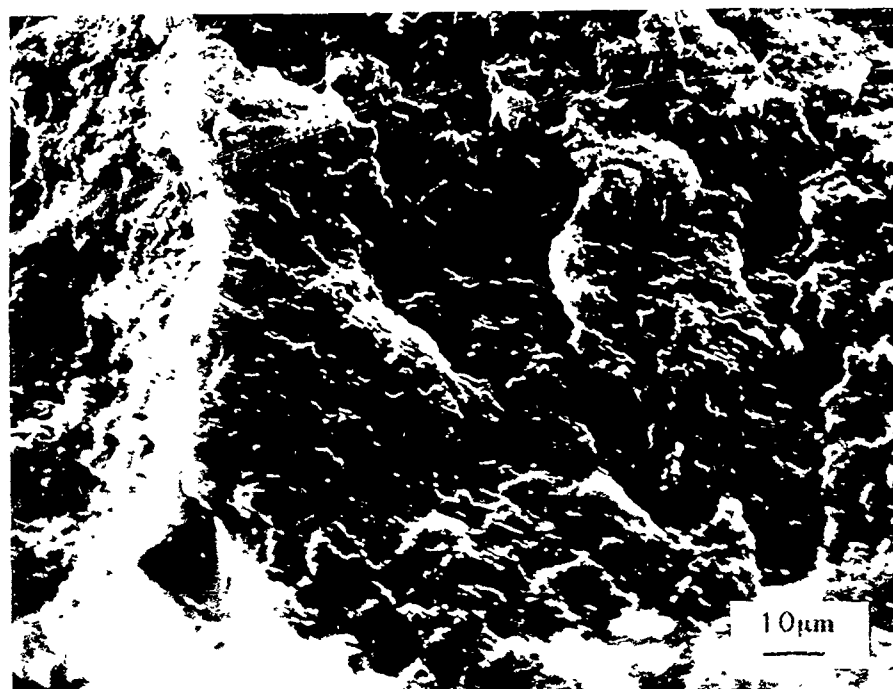


FIGURE 6.19(b) Scanning electron micrograph of an epoxy-paste adhesive fracture surface directly ahead of the starter foil. The test rate was 10 m/s and the substrate material was U/C epoxy. Magnification X750.

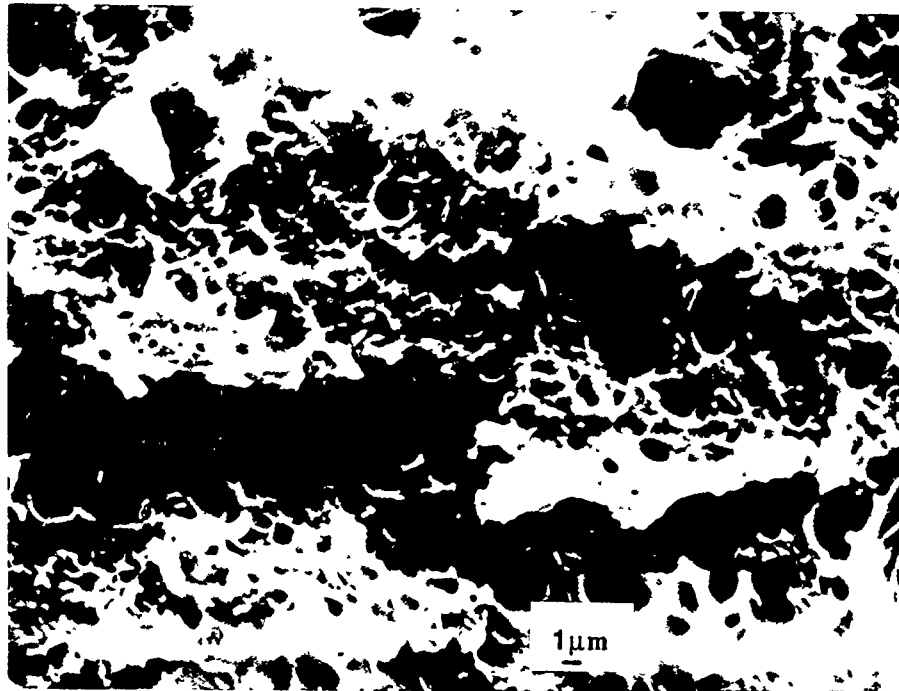


FIGURE 6.20(a) Scanning electron micrograph of an epoxy-paste adhesive fracture surface directly ahead of the starter foil. The test rate was 1.67×10^{-5} m/s and the substrate material was U/C epoxy. Magnification X2000.

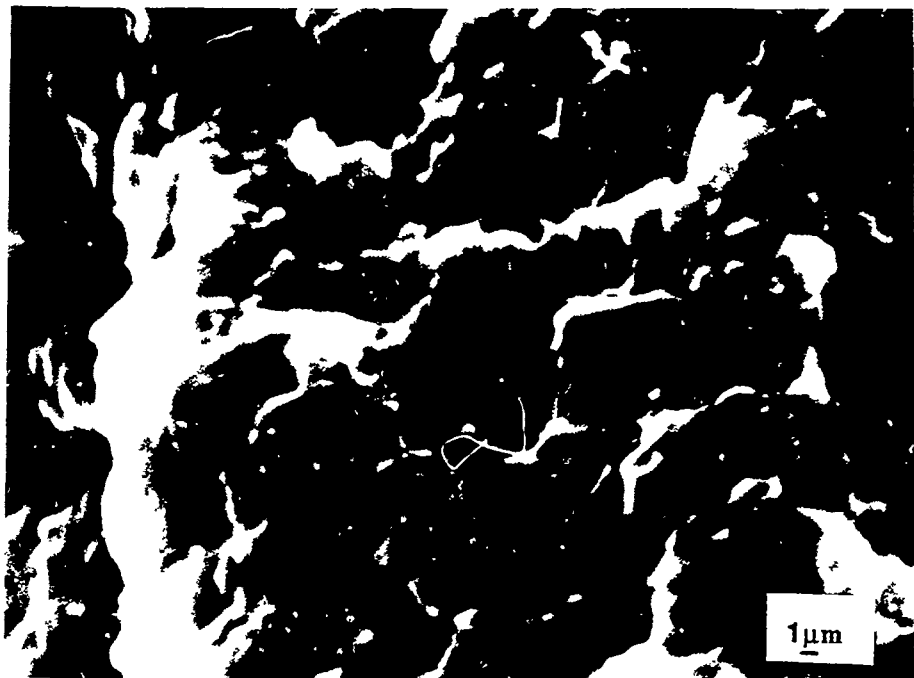


FIGURE 6.20(b) Scanning electron micrograph of an epoxy-paste adhesive fracture surface directly ahead of the starter foil. The test rate was 10 m/s and the substrate material was U/C epoxy. Magnification X2000.

6.7 Chapter Six Conclusions

The main conclusions from the work presented in Chapter Six are:

- (1) When calculating values of the adhesive fracture energy, G_c , at high test rates, misleading results may be obtained if the analysis requires values of the load to be used. This is due to the dynamic effects which are encountered in this test, which introduce large errors in the measured values of the load.
- (2) This problem may be overcome if a beam theory analysis based on the beam opening displacement and substrate modulus is used, so that there is no need to know accurate and valid values of the load. The beam opening displacement was determined using high-speed photography.
- (3) When the load independent method of calculating G_c was employed, then joints prepared with the epoxy-film adhesive showed that there was no effect of rate on the value of the fracture energy up to a rate of 10m/s i.e. the value of $G_c \approx 2.5 \text{kJ/m}^2$ at all the test rates employed. This was observed for both substrate materials.
- (4) However, when the epoxy-paste adhesive was employed, then a reduction in the value of G_c was observed. This reduction started at 0.5m/s and accounted for a 40% reduction in G_c at 10m/s, relative to the static value i.e. the value of G_c declined from 4.0kJ/m^2 to 2.4kJ/m^2 over this test range. This behaviour was observed for both substrate materials.
- (5) Scanning electron microscopy revealed that the micro-mechanisms of shear yielding and particle cavitation were observed to have occurred in the epoxy-film adhesive at all test rates employed. However, the interfacial debonding of the mat carrier from the epoxy adhesive which was observed at slow rates did not occur at fast rates. In the epoxy-paste adhesive, the micro-mechanisms of shear yielding and particle cavitation were observed at slow rates, but at high rates these occurred to a significantly lesser extent.
- (6) The difference in the fracture behaviour between the joints prepared with the different adhesives was attributed to the contrasting values of the glass transition temperature for each adhesive. The glass transition temperature of the epoxy-film adhesive was significantly higher than that of the epoxy-paste adhesive. Therefore, the epoxy-paste adhesive was tested at a temperature closer to its glass transition temperature.

(7) No interfacial failure was observed in any of the joint systems examined at any test rate. This observation was particularly significant for the U/C PEEK composite, since it shows that when testing at elevated rates, increased levels of corona treatment were not necessary.

Chapter Seven

Joint Failure: Effects of Test Environment

7.1 Introduction

In Chapter Two it was discussed how the mechanical properties of an adhesive joint may be affected by exposure to a hostile environment. Water, either in liquid or vapour form, was shown to be the most hostile environment which is commonly encountered by structural adhesive joints [61]. Mechanisms by which the ingressing liquid may modify the interface, the adhesive or the substrate material were also discussed. The main objective of this Chapter is to investigate the effect of prolonged exposure to a hostile environment (i.e. water at 50°C) on the mode I fracture behaviour of the bonded fibre-composite joints.

Firstly, the environmental durability tests were conducted in a hot-wet chamber. For the purposes of accelerating the test, the chamber was held at a constant temperature of 50°C. Therefore, in order to investigate whether the elevated temperature alone affected the fracture behaviour of the joints, a separate hot-dry chamber was also employed. The joints in this chamber were held in dry air at 50°C and removed periodically for testing. It should be noted that, in all the ageing tests, the U/C PEEK substrates were corona-treated to the level required to attain a high fracture energy, cohesive locus of failure when unaged. These treatment levels were 10J/mm² and 20J/mm² when bonding with the epoxy-film and epoxy-paste adhesives respectively.

Secondly, the joints were aged in the hot-wet environmental chamber for periods of up to one year, as described in Section 3.6. During this period no external stress was applied. Joints were removed at one monthly intervals and tested in order to measure the mode I value of the adhesive fracture energy, G_c . In addition, a number of joints which had been exposed in the hot-wet chamber for one year were removed and tested at high rates. Particular attention was paid to determining the locus of joint failure in these fracture tests.

Thirdly, in order to understand the observed fracture results, it was necessary to investigate the properties of the various adhesive-composite interfaces, and the properties of the bulk adhesives after ageing in water. Thus, the thermodynamic arguments advanced by Gledhill

and Kinloch, [5] which were discussed in Chapter Two, have been applied to the materials under investigation (i.e. the U/C epoxy or U/C PEEK composite bonded using either the epoxy-film or epoxy-paste adhesive) to assess the stability of the each interface in the presence of water. In addition, the effect of water on the bulk adhesive properties has been investigated in a series of water diffusion and tensile tests on aged adhesive specimens. This information provides a further insight into the observed fracture behaviour of the aged joints, and it is shown that the measured values of G_c do reflect the changes occurring at the interfaces and within the bulk adhesives.

Finally, scanning electron microscopy has been carried out in order to (a) identify the effect of water on the micro-mechanisms of fracture and (b) correctly ascertain the locus of joint failure.

7.2 Effect of Ageing Joints in a Hot-Dry Environment

7.2.1 Introduction

A commonly used method to accelerate an environmental durability test is to increase the temperature of exposure. Any degradation of the mechanical properties of an adhesive joint in water will occur more rapidly at say 50°C than at 20°C. For this reason, the environmental chamber used for these durability tests was heated to 50°C. Higher temperatures were not employed because, although many adhesives are themselves resistant to hydrolysis at moderate temperatures, this is not always the case at elevated temperatures, as was discussed in Chapter Two.

However, because the joints have been aged in a hostile water environment at 50°C, it was necessary to investigate the effect that the elevated temperature alone might have on the adhesive fracture energy. For this reason, adhesive joints were aged in a chamber, containing a drying agent, at a temperature of 50°C for up to 18 days.

7.2.2 Results from Ageing in the Hot-Dry Environment

The results of ageing in the hot-dry chamber are shown in Figure 7.1(a and b). The adhesive fracture energies of the joints bonded with the hot curing epoxy-film adhesive were unaffected. However, joints prepared with the cold curing epoxy-paste adhesive suffered almost a 40% reduction in fracture energy, relative to the unaged value. This reduction occurred within the first 96 hours, after which no further reduction in G_c was observed.

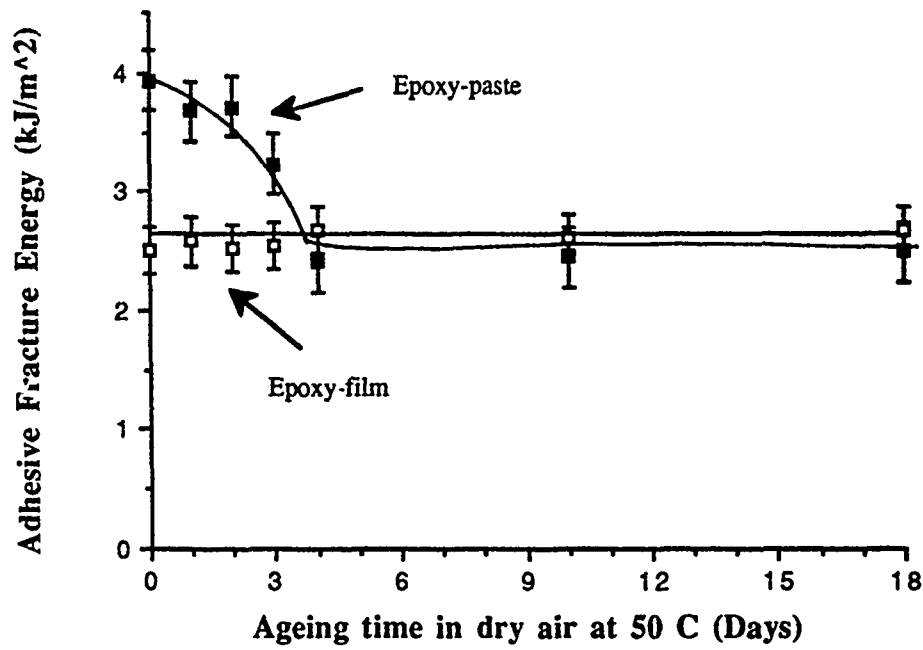


FIGURE 7.1(a) G_c -values versus ageing time in the hot-dry chamber. The substrate material was corona-treated U/C PEEK. Open points: Epoxy-film adhesive; Closed points: Epoxy-paste adhesive. (Data points are the mean of two tests, error bars show the coefficient of variation of the data) Locus of failure was cohesive.

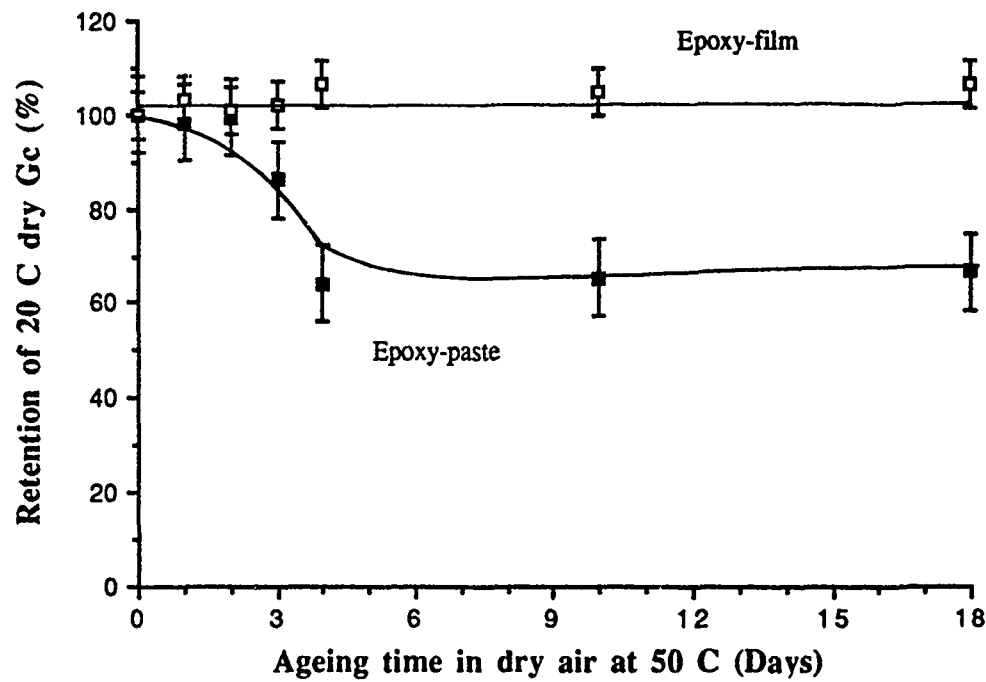


FIGURE 7.1(b) Retention of the 20°C dry G_c -values versus ageing time in the hot-dry chamber. The substrate material was corona-treated U/C PEEK. Open points: Epoxy-film adhesive; Closed points: Epoxy-paste adhesive.

The reason for the reduction in the value of G_c for joints prepared with the epoxy-paste adhesive was that this adhesive further cured at 50°C. This resulted in a more crosslinked, and thus more brittle adhesive, with a correspondingly lower fracture energy. The epoxy-film adhesive did not show this effect. Its cure temperature of 125°C is well above the chamber temperature, and it appeared that no further curing of this adhesive took place. Having established the effect of chamber temperature on G_c , the effect of water will now be investigated.

7.3 Effect of Ageing Joints in a Hot-Wet Environment

7.3.1 Introduction

In this Section, the results obtained from ageing the adhesive joint systems in distilled water at 50°C will be presented and discussed. In the durability tests the adhesive joints were aged for periods of up to one year. On removal from the environmental chamber, end-tabs were bonded onto the joints and the aged DCB specimens were then tested in mode I at a constant displacement rate of 2mm/min using a screw-driven tensile testing machine as described in Section 3.3.1. The adhesive fracture energy, G_c , was calculated via eqn. 4.11, as essentially stable crack propagation was observed. In addition to the slow rate tests, a number of aged joints were tested at high rates on the servo-hydraulic testing machine. These joints had all been aged in the hot-wet environmental chamber for one year. The adhesive fracture energies for the joints tested in this way were calculated via eqn 4.12, as was previously discussed in Section 6.5.

7.3.2 Durability Test Results

7.3.2.1 Effect of ageing joints bonded with the epoxy-paste adhesive

Figure 7.2 shows the effect of ageing joints bonded with the epoxy-paste adhesive on the value of G_c . The percentage retention of the 50°C dry value of G_c (i.e. the fully post-cured value) has been plotted in order to highlight the effect of water alone on the adhesive fracture energy, G_c .

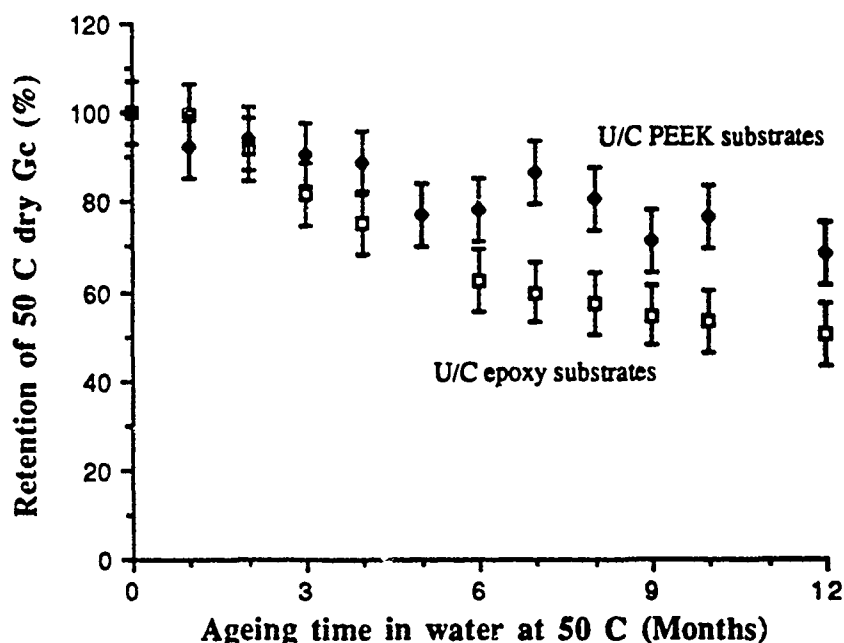


FIGURE 7.2 Retention of the 50°C dry G_c -values versus ageing time for joints bonded with the epoxy-paste adhesive. Square points indicate U/C epoxy substrates; Diamond points indicate U/C PEEK substrates. The U/C PEEK was corona treated to 20J/mm². All failure was predominantly cohesive. {Data points represent the mean of two tests, error bars show the coefficient of variation of the data}

It can be seen in Figure 7.2 that the joints bonded with the epoxy-paste adhesive show a significant reduction in the value of G_c after ageing in the environmental chamber for one year. The joints which were prepared with the corona-treated U/C PEEK substrates appeared to be somewhat more durable than those prepared with the U/C epoxy substrates. The joints which were prepared with the U/C PEEK substrates retained 70% of their 50°C, dry G_c after one year of exposure. The joints which were prepared with the U/C epoxy substrates retained 50% of their 50°C dry G_c value after one year of exposure. The absolute values of G_c after one year of exposure were: $G_c = 1.75 \pm 0.2 \text{ kJ/m}^2$ (for the U/C PEEK composite bonded with the epoxy-paste adhesive) and $G_c = 1.25 \pm 0.1 \text{ kJ/m}^2$ (for the U/C epoxy composite bonded with the epoxy-paste adhesive). All failure was predominantly cohesive.

Some typical fracture surfaces obtained from the testing of these joints can be seen in Figure 7.3(a and b). Figure 7.3(a) shows a photograph of fracture surfaces the U/C epoxy substrates bonded with the epoxy-paste adhesive. It is clear from this photograph that the exposure to water has changed the physical appearance of the fracture surfaces. Initially, in the unaged condition, the adhesive retains its usual colour with extensive stress-whitened regions across

the whole surface. However, after a period of three months in the environmental chamber, the adhesive fracture surface was noticeably discoloured. After a period of six months in the chamber, the adhesive became further discoloured and 'river lines' had started to form on the surface. These lines appear to divide smoother, less ductile regions from the rougher, more stress-whitened regions. As the duration of exposure was increased beyond six months, the smooth regions extended to cover a greater proportion of the fracture surfaces. In addition, small amounts of interfacial failure were observed to have occurred at the edges of the specimens. This was most noticable when the U/C PEEK substrates were employed, as shown in Figure 7.3(b). However, the locus of failure remained 90% cohesive.

The reduction in the surface roughness of the fracture surface which was observed, suggests that there has been a decrease in the amount of shear yielding and/or particle cavitation occurring during crack propagation within this adhesive. It will be shown in Section 7.6 that there has indeed been a reduction in the extent of cavitation at the rubber particle sites, observed using scanning electron microscopy. Both of these observations are consistent with the fracture results, namely that the toughness of the joints bonded with the epoxy-paste adhesive is significantly reduced by ageing in a liquid water environment.

It was noted that the joints prepared with the U/C PEEK substrates retained a greater proportion of their initial, unaged G_c value than equivalent joints bonded with the U/C epoxy substrates. Because the failure was essentially cohesive, it is possible that this difference was due to the different water diffusion properties of the two composite substrate materials. Wang and Spinger [96] measured the equilibrium water content of U/C PEEK to be 0.2% by weight and it has also been shown that the water uptake in the U/C PEEK composite is approximately one fifth of that observed with conventional epoxy resin composite systems [92]. The different diffusion properties of the substrates may have led to higher water concentrations at any given time in the adhesive when the U/C epoxy substrates were employed. Further, the higher water concentration in the U/C epoxy substrates may have resulted in more swelling of this substrate material, imposing swelling stresses on the adhesive. The water concentration distributions in the joints will be discussed further in Section 7.5.1.4.

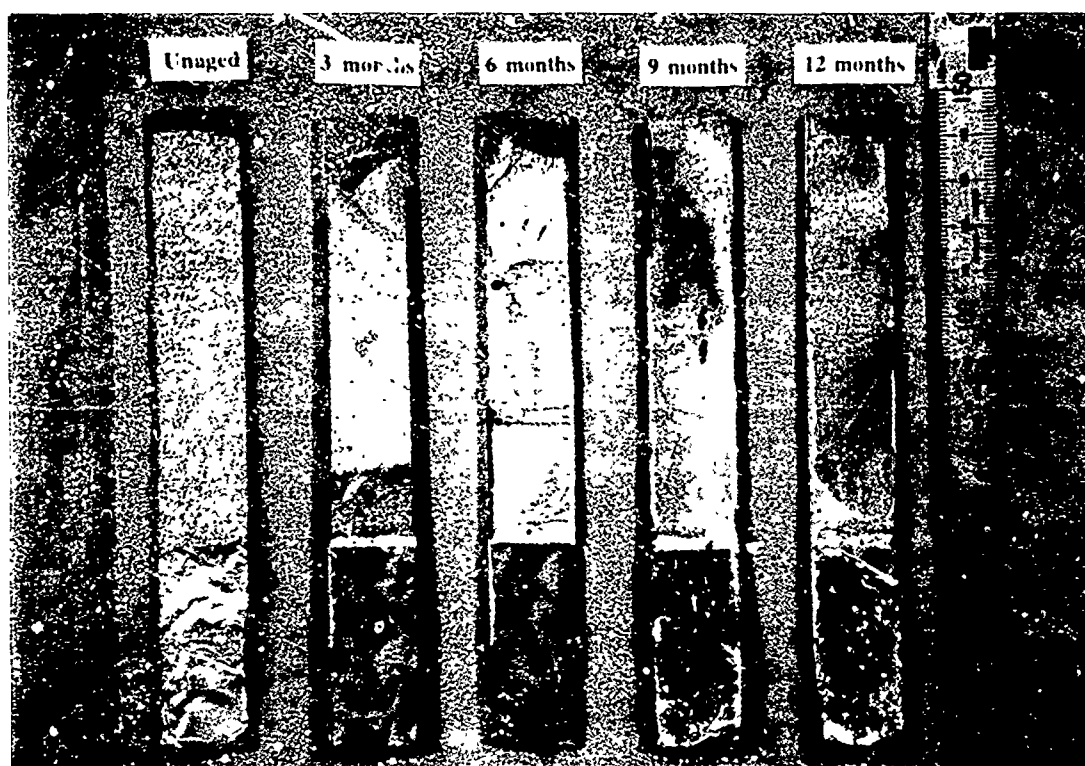


FIGURE 7.3(a) Typical fracture surfaces obtained from joints prepared with the U/C epoxy substrates bonded with the epoxy-paste adhesive after ageing in the hot-wet environmental chamber. Duration of exposure is shown.

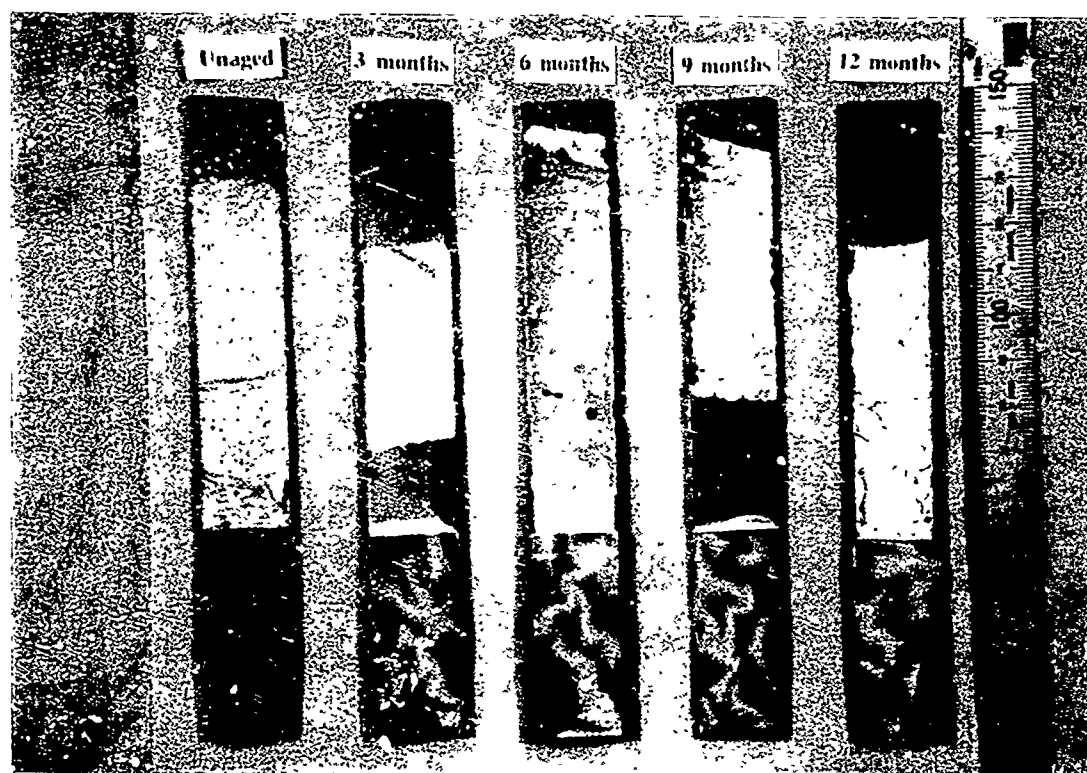


FIGURE 7.3(b) Typical fracture surfaces obtained from joints prepared with the U/C PEEK substrates bonded with the epoxy-paste adhesive after ageing in the hot-wet environmental chamber. The substrates were corona treated to 20J/mm^2 . Duration of exposure is shown.

7.3.2.2 Effect of ageing joints bonded with the epoxy-film adhesive

Figure 7.4 shows the effect of ageing in the hot-wet environmental chamber on the value of G_c for joints bonded with the epoxy-film adhesive. It was again particularly intriguing to note the significance of the substrate material on the long term durability of these joints. In contrast to the joints bonded with the epoxy-paste adhesive, a superior environmental durability was now observed when the U/C epoxy substrates were bonded with the epoxy-film adhesive. Figure 7.4 shows that when the U/C epoxy substrates were bonded with the epoxy-film adhesive, then the value of G_c initially increased somewhat with ageing, and then decreased significantly. No interfacial failure was observed in this joint system. However, when the corona-treated U/C PEEK was bonded with this adhesive, then the value of G_c immediately decreased and continued to fall until a lower plateau was reached.

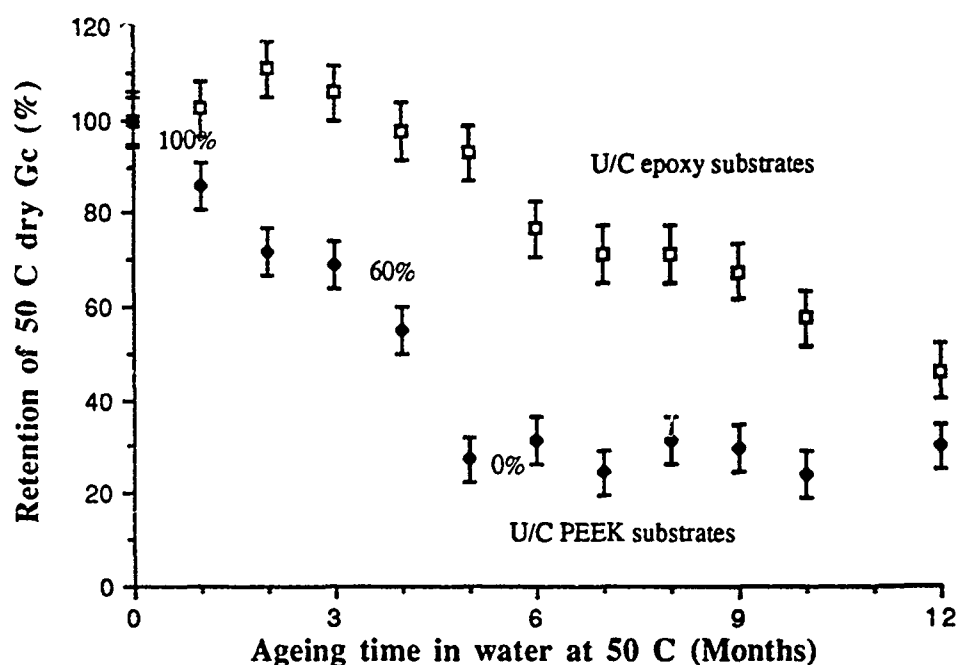


FIGURE 7.4 Retention of the 50°C dry G_c -values versus ageing time for joints bonded with the epoxy-film adhesive. Square points indicate U/C epoxy substrates; Diamond points indicate U/C PEEK substrates. The U/C PEEK was corona treated to 10J/mm². The numbers next to diamond data points show the % of cohesive failure. {Data points are mean of two tests, error bars indicate the mean scatter within the data set}.

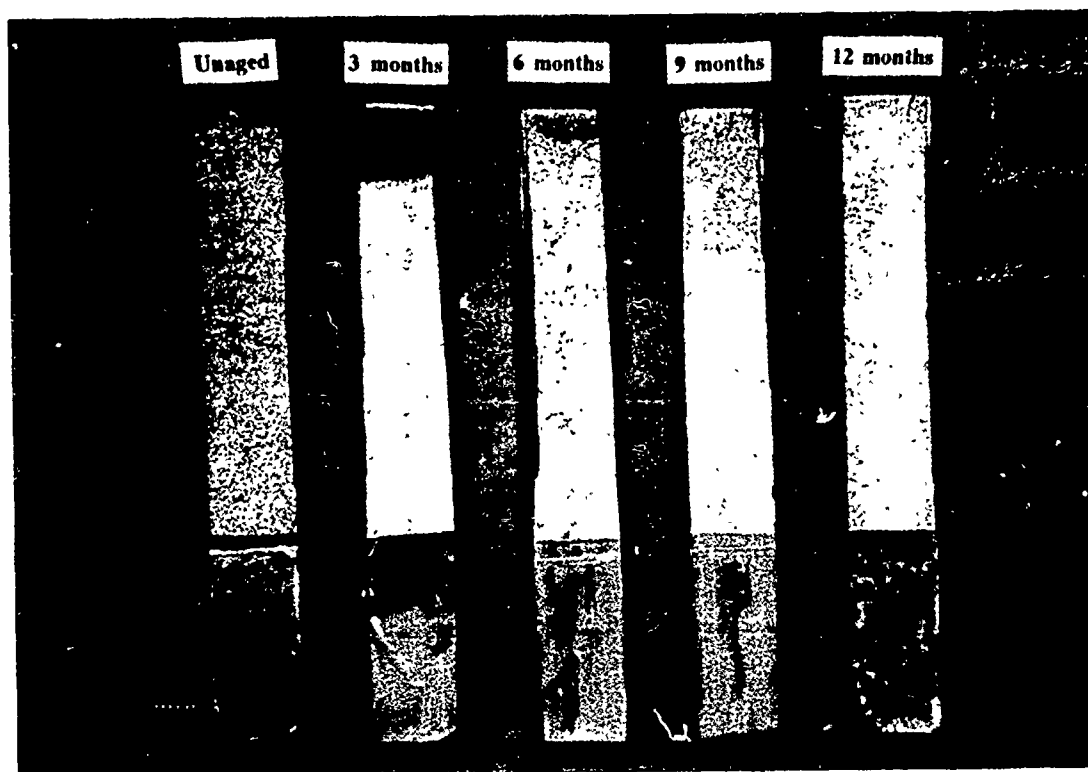


FIGURE 7.5(a) Typical fracture surfaces obtained from joints prepared with the U/C epoxy substrates bonded with the epoxy-film adhesive after ageing in the hot-wet environmental chamber. Duration of exposure is shown.



FIGURE 7.5(b) Typical fracture surfaces obtained from joints prepared with the U/C PEEK substrates bonded with the epoxy-film adhesive after ageing in the hot-wet environmental chamber. The substrates were corona treated to 10J/mm^2 . Duration of exposure is shown.

This decline was associated with a progressive change in the locus of joint failure, from cohesive to apparently interfacial. It should be noted that a corona treatment of 10J/mm^2 was sufficient to obtain high fracture energy, cohesive failure for this joint system in the unaged condition. Therefore, the effect of the environmental exposure has been to significantly reduce the level of intrinsic adhesion across the adhesive-composite interface in this joint system. Figure 7.4 shows that after one year of environmental exposure, the joints prepared with the U/C epoxy substrates bonded with the epoxy-film adhesive retained 50% of their initial, unaged value of G_c . Thus, for this joint system, the effect of the environment had reduced the value of G_c from 2.5kJ/m^2 to $1.25 \pm 0.1\text{kJ/m}^2$. However, the joints prepared with the U/C PEEK substrates bonded with the epoxy-film adhesive retained only 28% of their initial, unaged value of G_c . Thus, for this joint system, the effect of the environment had reduced the value of G_c from 2.5kJ/m^2 to $0.70 \pm 0.15\text{kJ/m}^2$.

Figure 7.5 shows some typical fracture surfaces obtained from the testing of joints bonded with the epoxy-film adhesive after ageing in the hot-wet environment. Figures 7.5(a) and (b) show joints prepared with the U/C epoxy and U/C PEEK substrates respectively. Figure 7.5(b) shows that when the substrate material was U/C PEEK, then there was a change in the locus of failure. This change in the failure locus occurred first at the sides of the joint, i.e. in the region most accessible to the ingressing water. Then, as the duration of exposure was increased, so the proportion of interfacial failure increased. After six months of exposure, the locus of joint failure was predominantly interfacial. This coincided with the lower 'plateau value' of G_c being attained, which was shown in Figure 7.4.

The initial increase in the value of G_c which was recorded for the U/C epoxy substrates bonded with the epoxy-film adhesive suggests that water initially plasticized the adhesive, resulting in a blunter crack tip and thus a higher G_c value was recorded. However, the significant reduction in the G_c value recorded after five months of exposure suggests that water has caused a further plasticization of the adhesive, which has caused a reduction in one or more of the energy absorbing mechanisms occurring within the plastic zone, ahead of the crack tip. This will be discussed in more detail in Sections 7.4 - 7.6.

In contrast, the fracture results obtained for the U/C PEEK substrates bonded with the epoxy-film adhesive were dominated by the failure of the adhesive-composite interface. The loss of toughness associated with the immediate attack of this interface appears to have more than countered the initial increase in G_c due to plasticization. The result was that the value of G_c immediately started to fall after ageing, and continued to fall steadily until the locus of failure

was entirely interfacial. This was an important result because it indicated that exposure to water may rapidly cause a deterioration of the fracture performance of this joint system. However, it was particularly intriguing to note that the interface between the U/C PEEK composite and the epoxy-paste adhesive was considerably more stable when tested under the same conditions and after an equivalent ageing time i.e. these joints failed with a predominantly cohesive locus of failure. It should be recalled that it was necessary to corona-treat the U/C PEEK substrates to a higher treatment level prior to bonding with the epoxy-paste adhesive, than when bonding with the epoxy-film adhesive. It was clearly of interest to determine whether it was the difference in treatment levels which may explain the different relative interfacial stabilities. This aspect will now be investigated.

7.3.2.3 Effect of corona treatment level on interfacial stability

A number of joints were prepared with U/C PEEK substrates which were corona treated to higher level than the 10J/mm^2 used in the above experiments. These substrates were then bonded using the epoxy-film adhesive. The joints were aged in the hot-wet environmental chamber for periods of up to one year. If the adhesive-composite interface of these joints were to remain stable, then higher corona treatment levels may be identified as a simple way to improve the long term durability of this joint system.

However, it is shown in Figure 7.6 that increasing the level of corona treatment to 15J/mm^2 has had no significant effect on the stability of this interface. As before, the effect of ageing in the hot-wet environment on this joint system was to progressively change the locus of joint failure from cohesive to interfacial during the fracture test.

The interfacial failure of this joint system in water was also reported by Osiyemi [95] during fatigue testing in water at 25 and 50°C. In addition, when joints prepared with the U/C PEEK substrates bonded with the epoxy-paste adhesive were tested in fatigue, then the locus of failure remained cohesive, in the adhesive. These results are similar to the results obtained in this work, and this indicates that the interface between the U/C PEEK substrates and the epoxy-paste adhesive is more resistant to water than the interface between the U/C PEEK substrates and the epoxy-film adhesive. The reasons for this will be further investigated in Sections 7.4-7.7. Firstly, however, the combined effect of ageing in water and testing at high rates will now be considered.

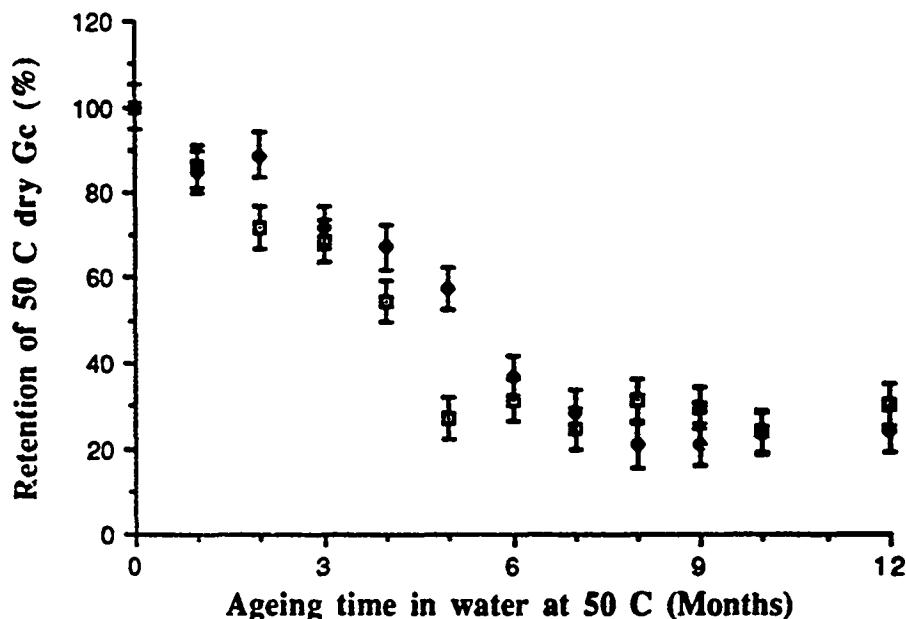


FIGURE 7.6 Retention of the 50°C dry G_c -values versus ageing time in water for the U/C PEEK substrates bonded with the epoxy-film adhesive. Square points indicate 10J/mm²; Diamond points indicate 15J/mm² of corona treatment. {Data points are mean of two tests, error bars are the coefficient of variation.}

7.3.3 Effect of High Test Rates on the Aged Joints

7.3.3.1 Effect of rate on fully aged epoxy-film adhesive joints

Joints which had been aged in the hot-wet chamber for one year (i.e. the maximum period used in the present work) were removed and tested using the servo-hydraulic tensile machine at three displacement rates (10⁻², 10⁻¹ and 2m/s). Only a small number of different test rates were employed due to the limited number of specimens available in this condition. Two tests were conducted at each rate, for each joint system.

Figure 7.7 shows the variation of G_c at crack initiation, versus rate for joints bonded with the epoxy-film adhesive. It can be seen that the U/C epoxy composite bonded with the epoxy-film adhesive showed no significant variation in G_c with test rate. The locus of failure remained fully cohesive. However, it was interesting to note that the crack propagated in a stable (Type A) manner at all rates. It was observed previously that crack propagation in this adhesive joint system when unaged, was unstable (Type B) at rates faster than 10⁻³m/s {Refer

to Table 6.5}. Therefore, the effect of the environment was to change the crack propagation behaviour from stick-slip (Type B) to stable (Type A), for rates up to 2m/s.

When the joints were prepared with the U/C PEEK substrates bonded with the epoxy-film adhesive, then the locus of failure was interfacial with associated low values of G_c recorded at all test rates. These results can also be seen in Figure 7.7

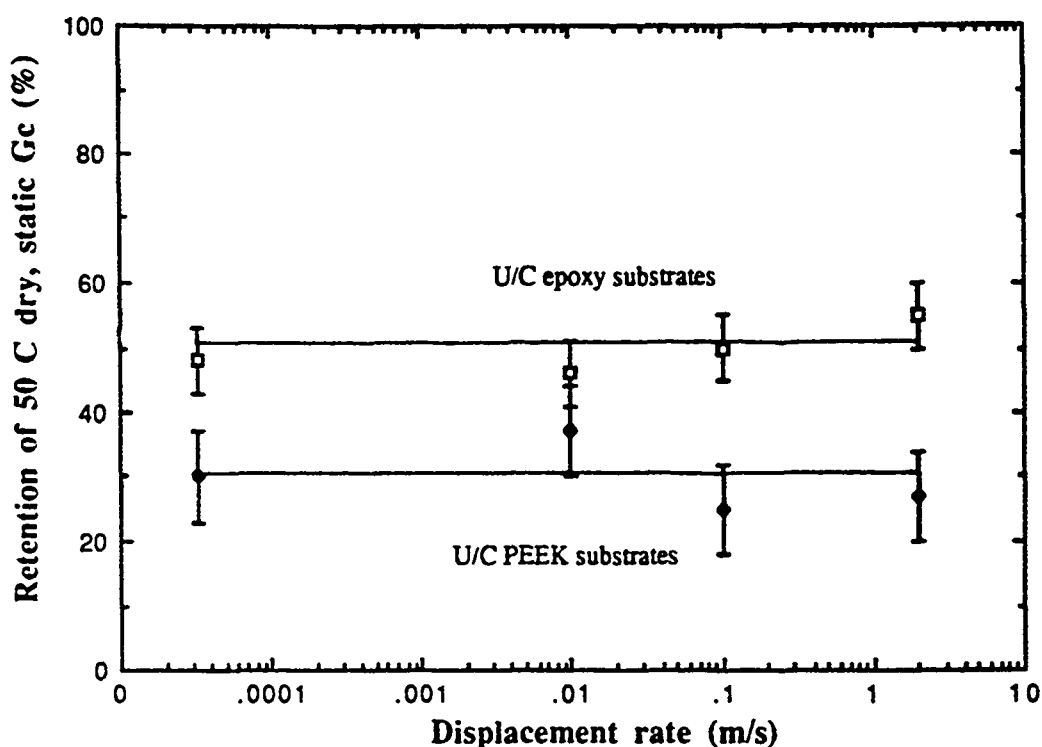


FIGURE 7.7 Graph showing the % retention of the 50°C dry, static G_c -values versus displacement rate for joints bonded with the epoxy-film adhesive and aged in the hot-wet environment for one year. Square points indicate U/C epoxy substrates, Diamond points indicate U/C PEEK substrates. {Data points are for the mean of two tests, error bars show max and min. values}.

7.3.3.2 Effect of rate on fully aged epoxy-paste adhesive joints

Joints consisting of the aged U/C epoxy substrates bonded with the epoxy-paste adhesive in the fully aged condition were unaffected by the test rate. The value of G_c remained constant with increasing rate over this range, as is shown in Figure 7.8. It was reported in Section 7.3.2 that these fully aged joints retained 50% of their 50°C dry G_c when tested at slow rate. These joints maintained this level of retention up to test rates of 2m/s. The previous decrease

in the G_c value observed when the unaged joints were tested at 1m/s {refer to Figure 6.13} was not repeated. However, the value of G_c recorded after one year of ageing was $1.25 \pm 0.1 \text{ kJ/m}^2$, i.e. significantly lower than the value measured at 10m/s in the unaged condition $\{\sim 2.5 \text{ kJ/m}^2 \text{ at } 2 \text{ m/s}\}$.

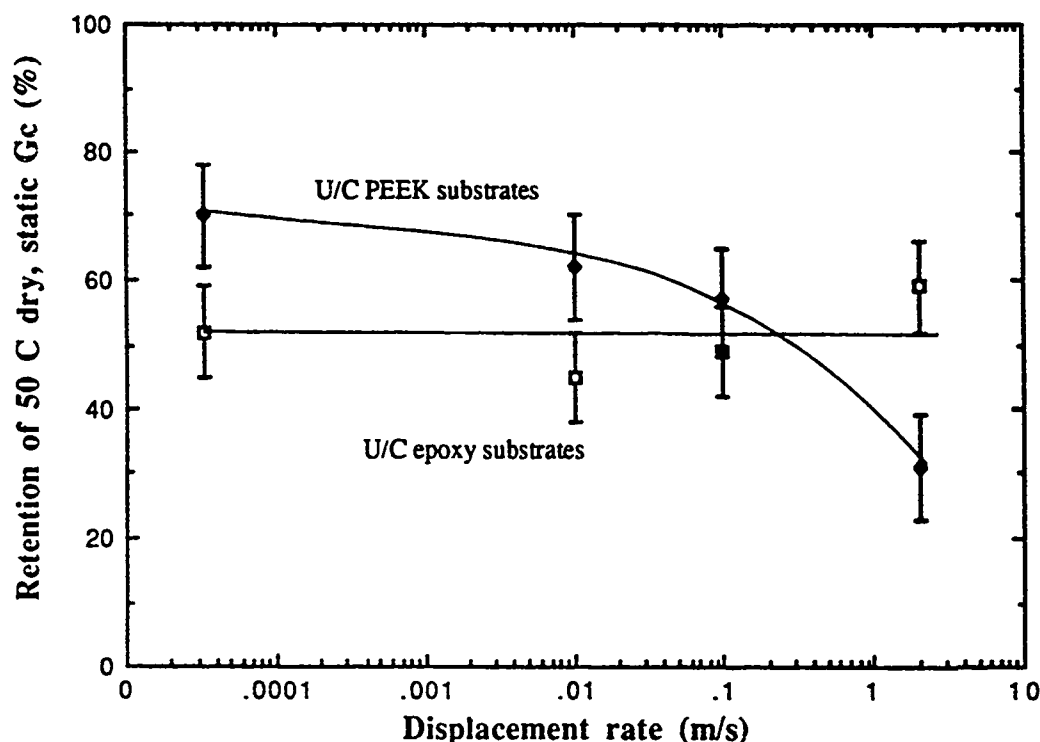


FIGURE 7.8 Graph showing the % retention of the 50°C dry, static G_c -values versus displacement rate for joints bonded with the epoxy-paste adhesive and aged in the hot-wet environment for one year. Square points indicate U/C epoxy substrates, Diamond points indicate U/C PEEK substrates. {Data points are for the mean of two tests, error bars show max and min values}.

However, when joints which had been prepared with the U/C PEEK substrates were bonded with the epoxy-paste adhesive and tested at high rates after ageing, it was noted that there was a significant decrease in G_c at the higher rates which was accompanied by a change in the locus of joint failure. At low rates, the fully aged joints failed in a predominantly cohesive mode (approx. 90% cohesive, 10% interlaminar). However, when these joints were tested at the higher rates, then an increasing proportion of the failure was at, or close to, the adhesive-composite interface, as is shown in Figure 7.9. This progressive change in the locus of joint failure was associated with a lower value of G_c being recorded. This would suggest that the crack resistance of this adhesive-composite interface has indeed been reduced by the combined effect of environmental ageing and testing at high rates.



FIGURE 7.9 Fracture surfaces obtained from joints prepared with the U/C PEEK substrates bonded with the epoxy-paste adhesive after ageing in the hot-wet environmental chamber for one year and then being subjected to various test rates. The substrates were corona treated to 26 J/mm^2 . The test rates are shown.

7.3.4 Discussion of Durability Results

The durability results show that the presence of water has had a significant and deleterious effect on the the fracture behaviour of all the joint systems employed. It would appear that ageing in water for extended periods has reduced the value of the adhesive fracture energy, G_c , for each joint system. This reduction was associated with both interfacial and bulk material effects. In order to gain a further insight into the observed fracture behaviour of the aged joints, the following areas will be investigated in some detail.

Firstly, the stability of each adhesive-composite interface will be assessed by the calculating the thermodynamic work of adhesion in an inert and a liquid environment. Such analyses should provide an indication as to which systems, if any, are more likely to suffer interfacial attack and weakening by the ingressing water. Secondly, the rate of both interfacial attack and the modification of the bulk adhesive properties will depend on the rate at which water is able to diffuse into the adhesive. Therefore, the water diffusion properties of both adhesives have

been measured in a series of water uptake tests. Of course, water may also diffuse through the substrates to reach the interface, but due to the exposed nature of the bondline in the DCB specimen and the higher diffusion and solubility coefficients of the adhesives, it has been assumed that the amount of diffusion through the substrate is small compared to the amount of diffusion through the adhesive. Thirdly, as was discussed in Chapter Two, the properties of the adhesive may be altered by water ingress. For this reason, the tensile properties of both bulk adhesives have been measured in a series of aged bulk tensile tests. These results would provide an insight into the fracture behaviour of each adhesive in the joint configuration.

7.4 Thermodynamic Work of Adhesion

7.4.1 W_A in an Inert Environment

The concept of the thermodynamic work of adhesion was discussed in Chapter Two. This can provide an indication of interfacial stability. The thermodynamic work of adhesion in an inert environment, W_A , was defined as the energy required to separate unit area of interface into two separate surfaces, assuming only secondary molecular forces are acting across the interface. The parameter W_A may be evaluated from eqn. 2.8. In order to employ this equation, the values of γ^D and γ^P , i.e. the values of the dispersion and polar force components of the surface free energy respectively, are required for the adhesive and substrate respectively. The values of γ^D and γ^P for the U/C PEEK and U/C epoxy composites, and the epoxy-film and epoxy-paste adhesives were calculated by Kodokian [2] using contact angle analysis. These values are given in Table 7.1.

TABLE 7.1 Surface free energies for the test substrates, adhesives and water.

Material	γ^D (mJ/m ²)	γ^P (mJ/m ²)
U/C PEEK substrate (a)	39.0	2.0
U/C PEEK substrate (b)	40.0	26.0
U/C PEEK substrate (c)	40.0	28.0
U/C epoxy substrate	31.3	7.2
Epoxy-paste adhesive	35.2	3.8
Epoxy-film adhesive	32.3	3.0
Water*	22.0	50.2

Notes: (a) Abraded; (b) corona treated to 10J/mm²; (c) corona treated to 20J/mm² * [1]

Now, in an inert medium, the work of adhesion, W_A , for an adhesive-substrate interface is usually positive, indicating that the interface is thermodynamically stable. However, in the presence of a liquid the thermodynamic work of adhesion, W_{AL} , (which may be calculated from eqn.2.9) may become negative, indicating that the interface is now unstable. If the presence of the liquid causes the work of adhesion to change from positive to negative, then this will provide the driving force for the displacement of the adhesive from the substrate surface by the liquid. This will in due course lead to the progressive weakening of the joint and also change the locus of failure from cohesive to interfacial.

7.4.2 W_{AL} in a Liquid (Water) Environment

TABLE 7.2. The thermodynamic work of adhesion in an inert medium (W_A) and in a liquid water environment (W_{AL}) for the test adhesive joints.

Substrate	Adhesive	W_A (mJ/m ²)	W_{AL} (mJ/m ²)
U/C Epoxy	Epoxy-paste	+76.8	+47.5
U/C Epoxy	Epoxy-film	+72.9	+48.9
U/C PEEK (a)	Epoxy-paste	+95.7	+22.5
U/C PEEK (b)	Epoxy-film	+89.6	+25.5

Notes: (a) corona treated to 20J/mm²; (b) corona treated to 10J/mm².

The values of W_A and W_{AL} are shown in Table 7.2 for the adhesive joint systems tested. It can be seen that all W_{AL} values remain positive, indicating that the interfaces should not spontaneously debond in water. However, the presence of water has caused the most severe reduction for the U/C PEEK joint systems (i.e. $W_{AL} \ll W_A$ for these systems). This indicates that the presence of the liquid environment has significantly reduced the thermodynamic work of adhesion between the U/C PEEK composite and either adhesive. Now, if the interface has weakened sufficiently to give an interfacial locus of failure, this will be reflected in a relatively low value of G_c needed to cause failure.

To summarize, the positive W_{AL} values indicate that, although the presence of water alone will not provide the driving force for the interfacial separation between the adhesive and substrate, such a separation might occur if external work is applied, e.g. during a fracture test. Because W_{AL} (U/C PEEK) < W_{AL} (U/C epoxy) when using either adhesive, then it follows that the joints prepared with the U/C PEEK will be more susceptible to interfacial failure than those prepared with U/C epoxy and, if this occurs, the U/C PEEK joints would be expected to

show a relatively greater decrease in the value of G_c .

7.5 Effect of Water on the Adhesive Properties

7.5.1 Water Diffusion Properties

7.5.1.1 Introduction

It was shown in Section 7.3 that when the U/C PEEK substrates were bonded with the epoxy-film adhesive and aged in the hot-wet environment, then the locus of joint failure changed from cohesive to interfacial. However, when the U/C PEEK substrates were bonded with the epoxy-paste adhesive, then the locus of joint failure remained essentially cohesive at slow test rates. It was shown that the thermodynamic arguments alone do not account for this behaviour. Another possible explanation for these results could be that water is able to diffuse into the epoxy-film adhesive more rapidly and attain a higher concentration at the adhesive-substrate interface than when bonding with the epoxy-paste adhesive. This higher concentration might exceed the critical water concentration, which was discussed in Section 2.8.2, and thus lead to interfacial attack. In order to investigate this possibility, the water diffusion properties of each adhesive will now be measured.

7.5.1.2 Water uptake tests

In order to measure the water diffusion and solubility parameters, a series of water uptake tests were performed, as was described in Section 3.6.4. Figure 7.10 shows the mass of water absorbed by the epoxy-paste and epoxy-film adhesive versus root-time. It can be seen that water was absorbed more rapidly, and reached a higher concentration, in the epoxy-paste adhesive than in the epoxy-film adhesive.

It was noted from Figure 7.10 that the mass of water absorbed by each adhesive was initially linear. This linear absorption behaviour is termed 'Fickian' and is commonly observed in epoxy adhesives at temperatures below their T_g [60]. After the initial linear region of water uptake, the epoxy-film adhesive reached an equilibrium plateau. This adhesive absorbed 75% of its equilibrium water concentration within 24 hours and reached equilibrium after 225 hours. However, the epoxy-paste adhesive not only absorbed water faster and reached a higher water concentration than the epoxy-film adhesive, but it showed a secondary absorption phase following an initial equilibrium after 157 hours of water uptake.

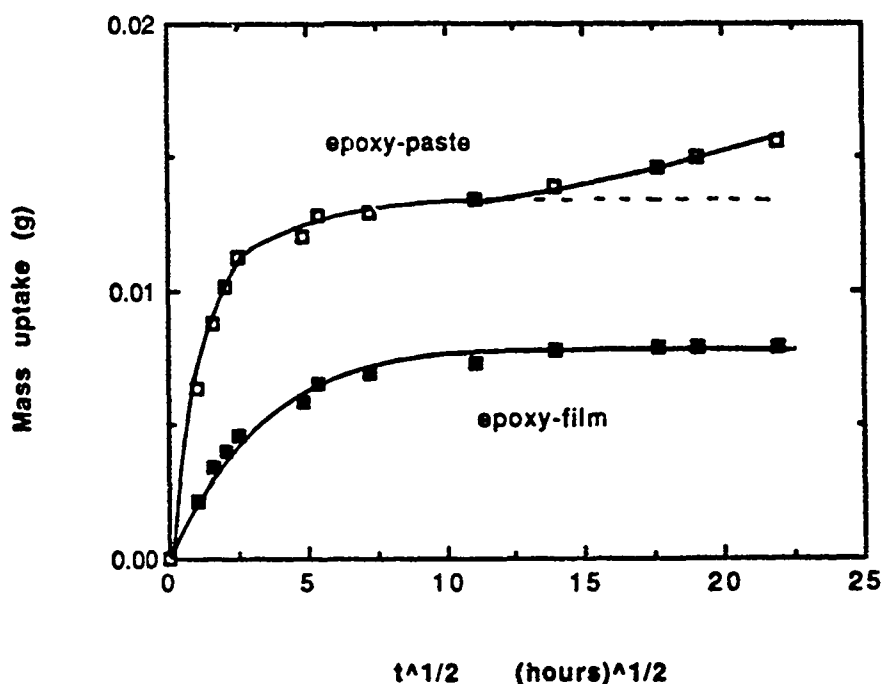


FIGURE 7.10 Mass uptake of water at 50°C by the test adhesives versus root time. Open points: Epoxy-paste adhesive; Closed points: epoxy-film adhesive.

The failure of the epoxy-paste adhesive to maintain its equilibrium water concentration in the diffusion tests may be taken as an indication that a secondary, water ingress mechanism started to operate. This type of behaviour was also reported by Comyn [60], who suggested that swelling stresses within the adhesive may have caused cracking to occur, and water was then able to penetrate into the cracks. If the stresses were tensile, then it is possible that void growth or particle cavitation may occur, again increasing the rate of water uptake. Comyn further suggested that hydrolysis of the adhesive, i.e. the chemical reaction between the adhesive and water, may explain this type of observation. However, this is not a likely explanation because thermosetting polymers, epoxies in particular, are stable in the presence of most organic solvents at moderate temperatures [1].

7.5.1.3 Calculation of the adhesive diffusion parameters

The parameters of interest are the water diffusion coefficient, D , the solubility coefficient, C_{∞} , and the water permeability coefficient, which is the product DC_{∞} . These parameters were discussed in Chapter Two. The diffusion coefficient, D , may be calculated from the linear region of a plot of M_t/M_{∞} versus root time / thickness, by application of eqn. 2.45. The M_t/M_{∞} versus root time / thickness data are plotted in Figures 7.11 and 7.12 for the epoxy-film and epoxy-paste adhesives respectively.

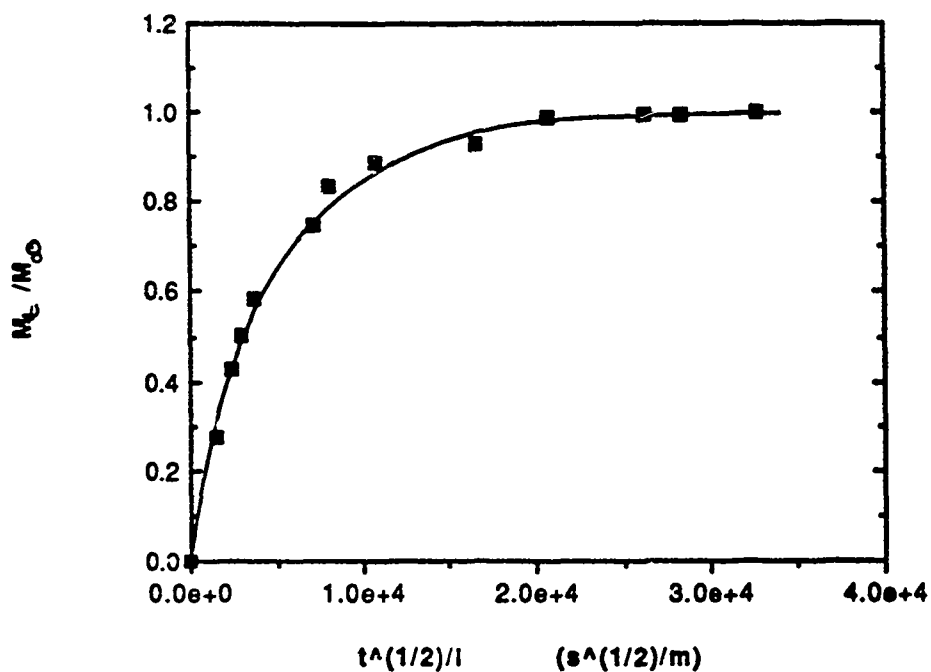


FIGURE 7.11 The fractional mass uptake of water (M_t/M_∞) plotted against $(t^{1/2})/l$ for the epoxy-film adhesive at 50°C.

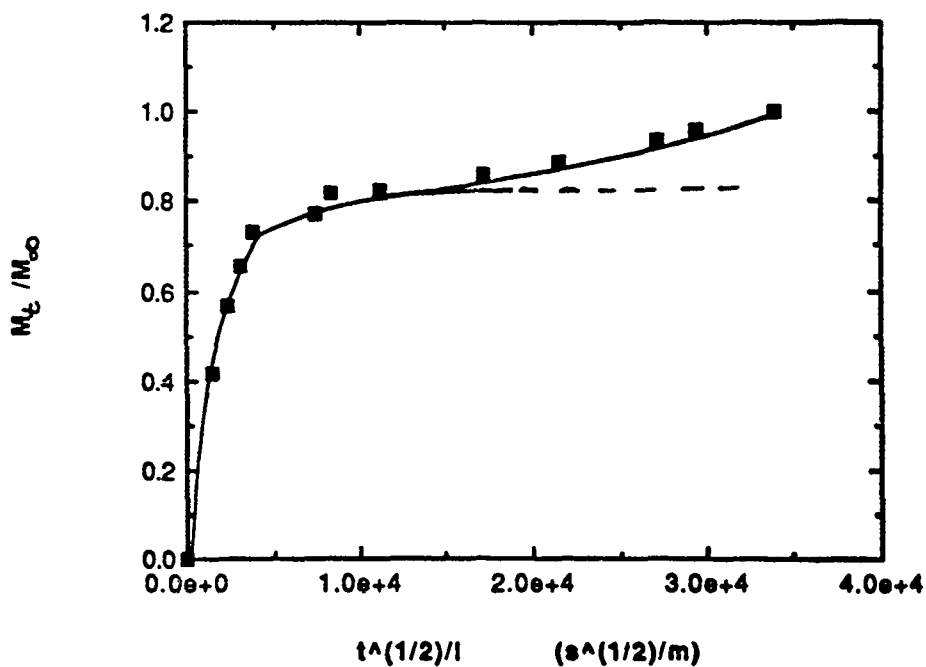


FIGURE 7.12 The fractional mass uptake of water (M_t/M_∞) plotted against $(t^{1/2})/l$ for the epoxy-paste adhesive at 50°C.

The diffusion coefficients were calculated for the two adhesives from eqn.2.45. The values are presented in Table 7.3. It can be seen that the initial rate of diffusion of water into the epoxy-paste adhesive at 50°C was significantly greater than the rate of diffusion into the epoxy-film adhesive. The solubility coefficient, C_{∞} , is defined as the mass of water absorbed in grammes per 100g of adhesive. The values measured for this parameter are shown in Table 7.3. Not only does water diffuse into the epoxy-paste adhesive more quickly, but it reaches a higher concentration than in the epoxy-film adhesive. This is demonstrated by the higher value of C_{∞} for the epoxy-paste adhesive.

The capacity of a material to transmit a permeant is indicated by its permeability coefficient, which is the product of the diffusion coefficient and the solubility coefficient, DC_{∞} . The values calculated for the permeability coefficients for the two test adhesives are shown in Table 7.3. It can be seen that the value of DC_{∞} for the epoxy-paste adhesive is almost three times greater than for the epoxy-film adhesive. Thus, the epoxy-paste adhesive transmits water more readily than the epoxy-film adhesive.

TABLE 7.3 Water diffusion and solubility parameters measured at 50°C for the test adhesives.

Adhesive	$D \times 10^{-13} \text{ (m}^2\text{s}^{-1}\text{)}$	$C_{\infty} \text{ (g per 100g)}$	DC_{∞}
Epoxy-film	5.7	2.53	14.4
Epoxy-paste	9.2	4.30	39.6

The low permeability coefficient of the epoxy-film adhesive may be, in part, due to the presence of the polyester mat carrier in this adhesive. Brewis et al [97] showed that the epoxy-film adhesive, FM 1000, was very much less permeable when prepared with an EP15 carrier material than when uncarried. They concluded that the carrier acted as an obstacle to the diffusing water.

7.5.1.4 Calculation of the water concentration distribution in the joints

In Section 7.5.2, the results obtained from the tensile testing of aged adhesive dumbbell specimens will be discussed. When correlating these results to joint fracture behaviour, it should be noted that when in the joint, water will take very much longer to reach equilibrium in the adhesive than in the thin sheet specimens used in these tests. This is because of the

relatively impermeable substrates used to prepare the DCB joints. Therefore the predominant diffusion path is through the adhesive layer, from the sides of the joint. The thickness of the adhesive diffusion slabs and adhesive dumbbells was about 0.35mm, whereas, in the DCB joint, the relevant dimension is the width of the joint, i.e. 20mm.

Having calculated the diffusion parameters for the two adhesives, it is possible to calculate the water concentration distribution profiles at various times for the adhesive layer in the DCB joint. Assuming that the substrates are impermeable to water, the concentration distribution within the adhesive layer can be calculated using a one-dimensional, non steady-state diffusion analysis [70], in which the adhesive layer is modelled as a plane sheet of thickness, l , and with a diffusion coefficient, D .

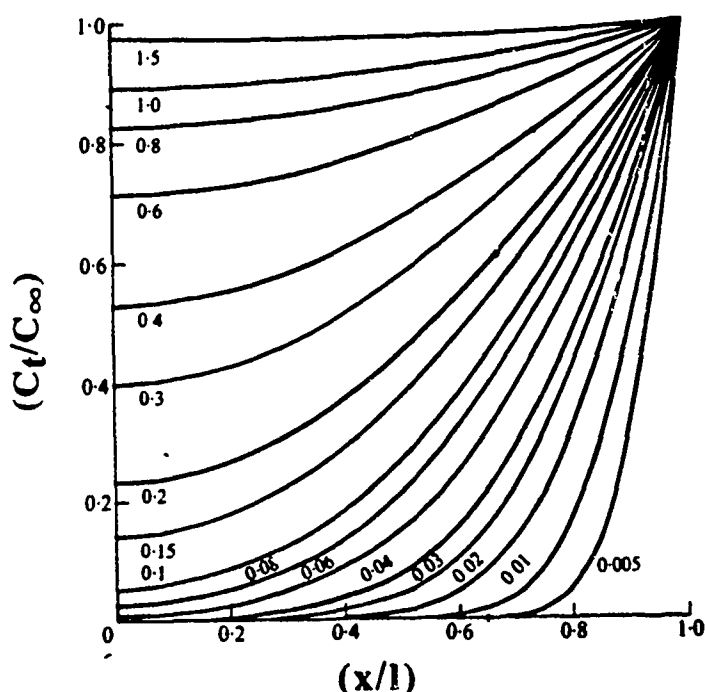


FIGURE 7.13 Concentration distributions at various times in the adhesive sheets. Initial uniform concentration was C_0 and surface concentration was C_1 . Numbers on curves are values of Dt/l^2 . Water distribution profiles for the two test adhesives in the DCB specimen are shown after one year of ageing. After Crank [70].

Using such an analysis, and the assumption that water only diffused in from the sides of the joint, it is clear that neither adhesive used in the bonding of the DCB specimens reached full equilibrium after one year of exposure to the hot-wet environment. At the mid-plane of the joint, the epoxy-film adhesive attained a concentration of $0.2C_\infty$ after one year, whereas the epoxy-paste adhesive attained a concentration of $0.4C_\infty$ after one year. Therefore, by

employing the values for C_{∞} presented in Table 7.3 for the two adhesives, the actual water concentrations at the mid-plane of the joints after one of ageing in the hot-wet environment were 0.56 and 1.72 grammes of water per 100 grammes of adhesive for the epoxy-film and epoxy-paste adhesives respectively. The water concentration distributions within the adhesive layer across the entire joint at various times can be seen in Figure 7.13.

It can be seen from the results in this Section that all the diffusion parameters calculated were greater for the epoxy-paste adhesive. Not only did water diffuse into this adhesive more rapidly, but it reached a higher concentration throughout the adhesive layer. The intriguing fracture results obtained in Section 7.3 can therefore not be explained solely by water diffusion or by the attainment of a critical water concentration at the adhesive-composite interface. It is clear that another factor must be responsible for the observed fracture results. In the next Section, the tensile properties of each adhesive will be measured.

7.5.2 Tensile Properties of the Adhesives

7.5.2.1 Effect of water uptake on the adhesive stress-strain behaviour

Dumbbell specimens of each adhesive were prepared as described in Chapter Three. These were then fully post cured {see Section 7.2 for details}, weighed using an analytical balance and suspended in a water bath at 50°C. Specimens of each adhesive were periodically removed from the water bath, carefully dried and reweighed to determine the fractional water uptake, and then tested in uniaxial tension as described in Section 3.6.5.

The variation in stress to failure, σ_f , and strain to failure, ϵ_f , was recorded as a function of water uptake for the two adhesives. The results are shown in Figures 7.14 and 7.15 respectively.

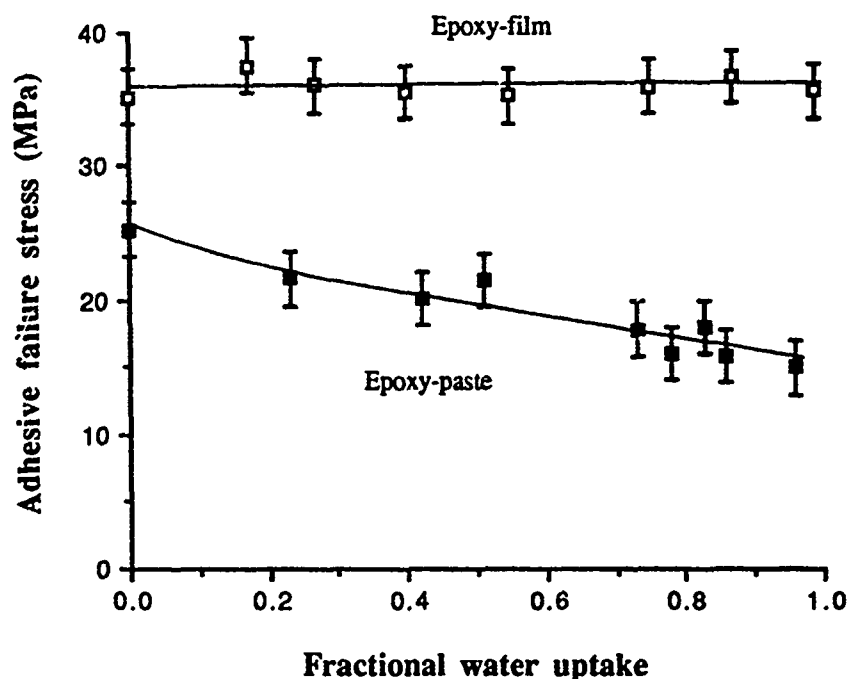


FIGURE 7.13 Adhesive failure stress, σ_f , versus fractional water uptake after ageing in the water bath at 50°C. Open points: Epoxy-film adhesive: Closed points: Epoxy-paste adhesive. (Data points are for the mean of two tests, error bars represent the coefficient of variation.)

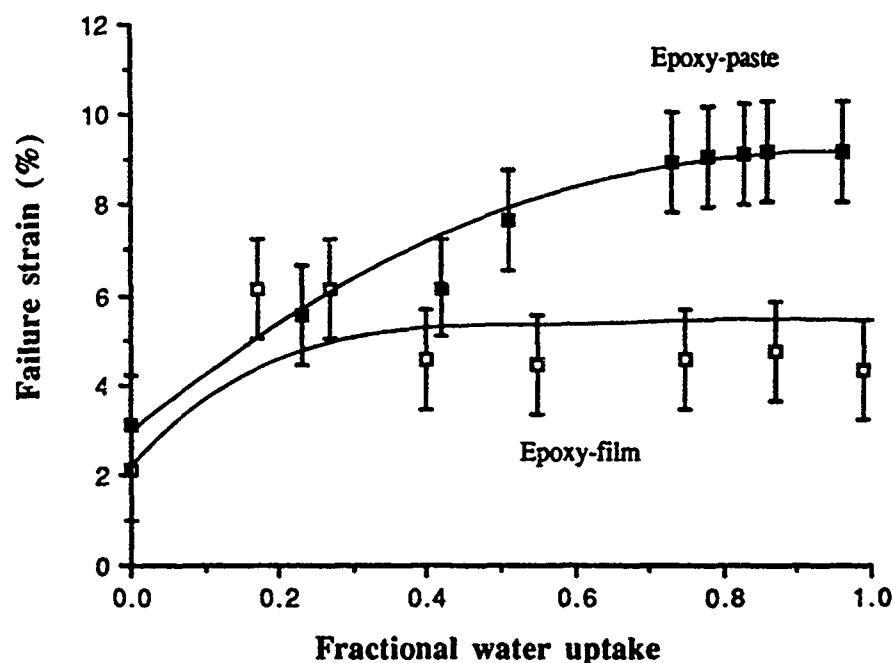


FIGURE 7.15 Adhesive failure strain, ϵ_f , versus fractional water uptake after ageing in the water bath at 50°C. Open points: Epoxy-film adhesive: Closed points: Epoxy-paste adhesive. (Data points are for the mean of two tests, error bars represent the scatter.)

It can be seen in Figure 7.14 that the value of σ_f for the epoxy-film adhesive was not affected by the uptake of water. The value measured was $\sigma_f = 36 \pm 2 \text{ MPa}$. However, the value of σ_f for the epoxy-paste adhesive decreased from 25.3 MPa in the dry condition, to 15.8 MPa after 120 hours in the water bath. It should be noted that all the dumbbell specimens had been dried out in the 50°C dry chamber for five days prior to immersion in water. Therefore, Figures 7.14 - 7.16 show the changes due to water absorption only, and not due to any post curing of the adhesive.

In terms of strain to failure, water diffusion increased the ductility of both adhesives, as can be seen in Figure 7.15. Initially, the value of $\epsilon_f = 2\%$ was recorded for the epoxy-film adhesive before immersion in the water. This value rapidly increased to 5% after immersion. The ductility of the epoxy-paste adhesive increased from $\epsilon_f = 3\%$ before immersion to $\epsilon_f = 9\%$ at its initial equilibrium plateau. The stress-strain behaviour for this adhesive in the secondary absorption region was not studied.

7.5.2.2 Effect of water uptake on the adhesive modulus

The 1% secant modulus was calculated from the stress-strain data. The variation in modulus with fractional water uptake is shown for both adhesives in Figure 7.16. It can be seen in Figure 7.16 that both adhesives suffer a significant reduction in the tensile modulus after immersion in the water bath. The modulus of the epoxy-film adhesive dropped from 2.5 GPa before immersion to 1.5 GPa upon saturation. The modulus of the epoxy-paste adhesive similarly dropped from 1.6 GPa to 0.9 GPa. This corresponds to a reduction in modulus of approximately 40% in each adhesive.

It can be seen that the absorption of water has had a significant effect on the tensile properties of both adhesives. However, perhaps the most significant result was the contrasting effect which water had on the values of the failure stress of the two adhesives, as shown in Figure 7.14. These results show that, after ageing in a hot-wet environment, the joints bonded with the epoxy-film adhesive will be subjected to a higher stress level than the joints bonded with the epoxy-paste adhesive. This important result will be discussed further in Section 7.7, after the surface analysis studies.

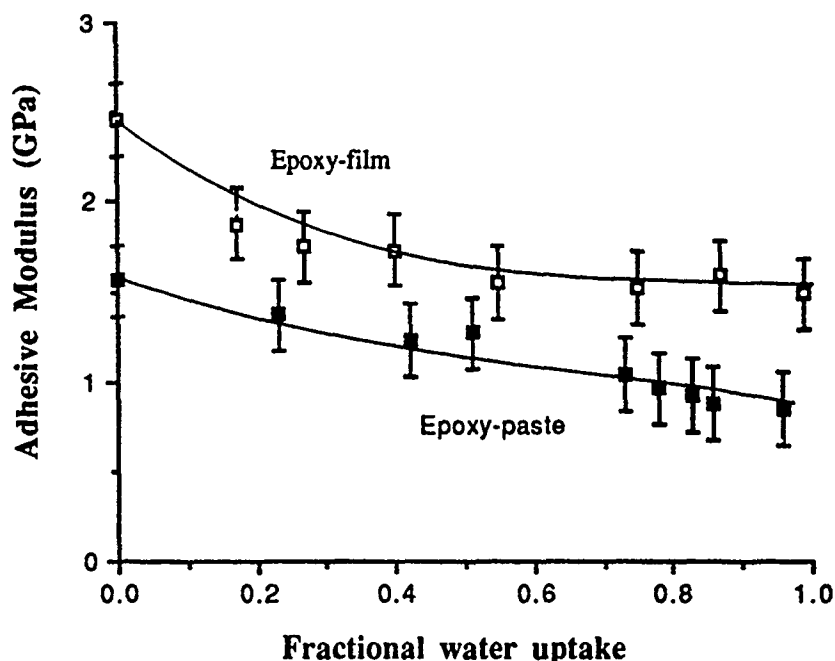


FIGURE 7.16 The 1% secant modulus versus fractional water uptake for the test adhesives after ageing in the water bath at 50°C. Open points: Epoxy-film adhesive; Closed points: Epoxy-paste adhesive. (Data points represent mean of two tests, error bars are the coefficient of variation.)

7.6 Surface Analysis Studies

7.6.1 Visual Assessment of Aged Fracture Surfaces

The visual observations made in the foregoing discussions will now be summarized. The effect of ageing each joint system in the hot-wet environment was:

(a) U/C epoxy substrates / epoxy-film adhesive.

The locus of failure remained fully cohesive, irrespective of the rate of test. The fracture surfaces became somewhat lighter and visibly smoother.

(b) U/C epoxy substrates / epoxy-paste adhesive.

The locus of failure remained cohesive, irrespective of the rate of test. The fracture surfaces became lighter, contoured and smoother.

(c) U/C PEEK substrates / epoxy-film adhesive.

The locus of failure was progressively altered by the presence of water. Joints failed in a

predominantly interfacial manner when tested at slow rate after ageing for six months in the hot-wet environment. Increased levels of corona treatment did not significantly delay this attack. At high rates, joints failed in an interfacial manner.

(d) U/C PEEK substrates / epoxy-paste adhesive.

The locus of failure remained predominantly cohesive (90% coh, 10% interfacial) when tested at slow rate after ageing for one year in the hot-wet environment. However, when tested at high rates, the locus of failure was progressively altered by increasing the rate, resulting in an interfacial locus of failure.

7.6.2 Scanning Electron Microscopy Studies

Figures 7.17 and 7.18 show clearly that water had a severe and deleterious effect on the micro-mechanisms of failure within both adhesives. Figure 7.17 shows a typical fracture surface from a joint prepared with the U/C epoxy composite bonded with the epoxy-film adhesive which had been aged in the hot-wet environment for one year. Comparing Figure 7.17(a) to Figure 6.16(a), i.e. comparing an aged fracture surface to an unaged fracture surface, it is apparent that water has changed the physical appearance of the surface. Figure 7.17(a) shows that the aged fracture surface is relatively featureless and considerably smoother than the unaged surface. This is even more apparent when Figure 7.17(b) is compared to Figure 6.17(b).

Figure 7.18(a) shows a typical epoxy-paste adhesive fracture surface after one year of ageing in the hot-wet environment. If this Figure is compared to Figure 6.18(a), i.e. a similar but unaged fracture surface, it can be clearly seen that water has created a much smoother surface. Figure 7.18(b) shows the same surface region in more detail. If this figure is compared to Figure 6.19(a), then the difference is striking. In the unaged condition, there was extensive evidence that particle cavitation had occurred at slow rate {see Figure 6.19(a)}. However, after ageing in the hot-wet environment for one year, Figure 7.18(b) shows that the extent of particle cavitation was much reduced.

Both Figures 7.17 and 7.18 support the fracture results obtained in Section 7.3, namely that when the U/C epoxy composite was bonded with either adhesive, then ageing in water caused a large (~ 50%) reduction in the adhesive fracture energy. This was associated with a reduction in the energy absorbing mechanisms of particle cavitation {as seen by SEM} and shear yielding {as seen visually on the fracture surfaces}.



FIGURE 7.17(a) Scanning electron micrograph of an epoxy-film adhesive fracture surface (cohesive region). The joint was aged in the hot-wet environment for one year and then tested under static conditions. The substrate was U/C epoxy. Magnification X500.



FIGURE 7.17(b) Scanning electron micrograph of an epoxy-film adhesive fracture surface (cohesive region). The joint was aged in the hot-wet environment for one year and then tested under static conditions. The substrate was U/C epoxy. Magnification X7,500.

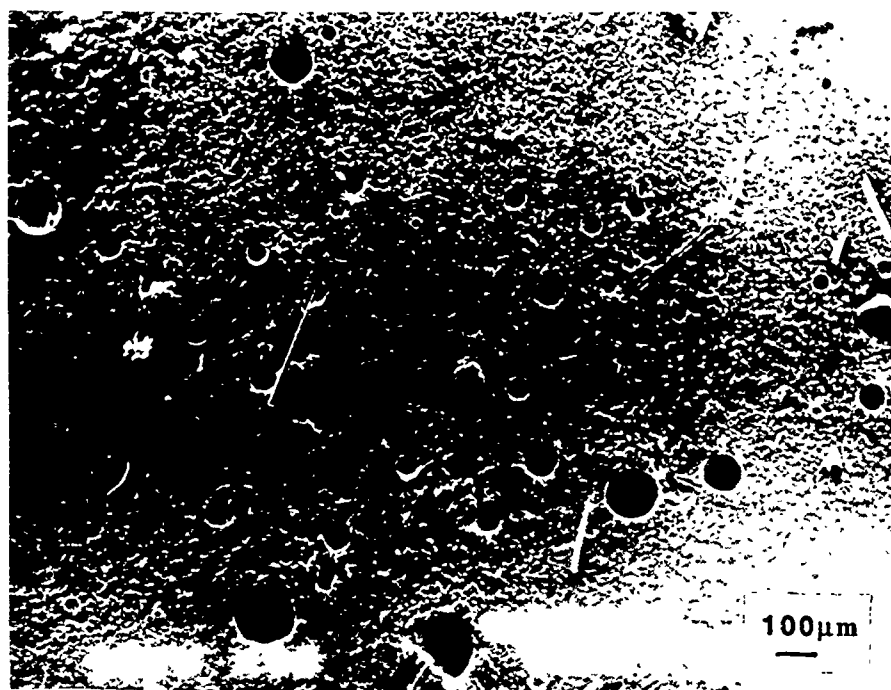


FIGURE 7.18(a) Scanning electron micrograph of an epoxy-paste adhesive fracture surface (cohesive region). The joint was aged in the hot-wet environment for one year and then tested under static conditions. The substrate was U/C epoxy. Magnification X50.

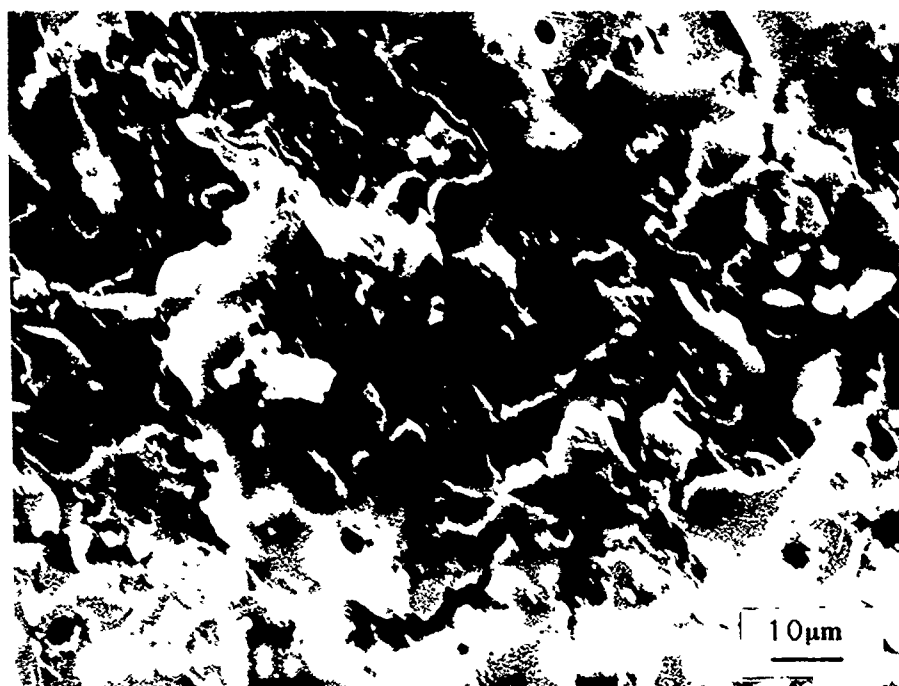


FIGURE 7.18(b) Scanning electron micrograph of an epoxy-paste adhesive fracture surface (cohesive region). The joint was aged in the hot-wet environment for one year and then tested under static conditions. The substrate was U/C epoxy. Magnification X1000.



FIGURE 7.19(a) Scanning electron micrograph of the adhesive part of an interfacial fracture surface between the U/C PEEK composite and the epoxy-film adhesive. The joint was aged in the hot-wet environment for six months and was tested under static conditions. Magnification X150.



FIGURE 7.19(b) Scanning electron micrograph of the composite part of an interfacial fracture surface between the U/C PEEK composite and the epoxy-film adhesive. The joint was aged in the hot-wet environment for six months and was tested under static conditions. Magnification X750.

However, when the U/C PEEK substrates were employed, it was found that water attacked the adhesive-composite interface. Figure 7.19 shows the two halves of a typical interfacial fracture surface obtained from the U/C PEEK, bonded with the epoxy-film adhesive and tested after ageing in the hot-wet environment for six months. Although fibre indentation marks can be seen on the adhesive side, (Figure 7.19(a)) due to curing against the composite in the joint, very few fibres have actually adhered to the adhesive. In addition, the composite half, (Figure 7.19(b) is relatively clean, showing that only small amounts of adhesive have adhered to this surface. These observations would confirm that the locus of failure was actually along the interface in this joint system, rather than within the adhesive or composite substrates.

7.7. Discussion of Results

7.7.1 Effect of Water on Interfacial Stability

The thermodynamic calculations of W_A and W_{AL} predicted that the interfacial stability of all the joint systems employed in this work would be reduced on exposure to a water environment. This reduction was predicted to be most severe when the U/C PEEK substrates were employed. This result does not confirm whether any of the test joints will fail in an interfacial manner during a fracture test, but only that the presence of water alone will not provide sufficient driving force for such a displacement. However, it was noted that the U/C PEEK substrates bonded with the epoxy-film adhesive failed in an completely interfacial manner after ageing in water for six months when tested at slow rate, but that this was not observed when the U/C PEEK was bonded with the epoxy-paste adhesive. Because the values of W_{AL} were approximately the same for these two joints and the water diffusion and solubility parameters were all greater for the epoxy-paste adhesive, then there must be an additional factor controlling the interfacial stability.

7.7.2 Effect of Stress on Interfacial Stability

For interfacial debonding to occur at the adhesive-composite interface, the interfacial forces of adhesion must be overcome [1]. This will occur if the transverse tensile stress, σ_{yy} , acting at the interface reaches the critical value, σ_{yyci} . This is analogous to the explanation proposed for why certain adhesive joints delaminate during a fracture test, as was discussed in Section 5.2.2. For delamination to occur within the composite, it was reported that the value of the transverse tensile stress, σ_{yy} , needed to overcome the value of the transverse tensile fracture

stress, σ_{yy} , in the composite material. Now, in the case of interfacial attack, σ_{yy} must exceed σ_{yyci} . This is shown schematically in Figure 7.20. Clearly, for an intrinsically strong interface, then the value of σ_{yyci} will be greater for an interface which has been weakened by a hostile environment.

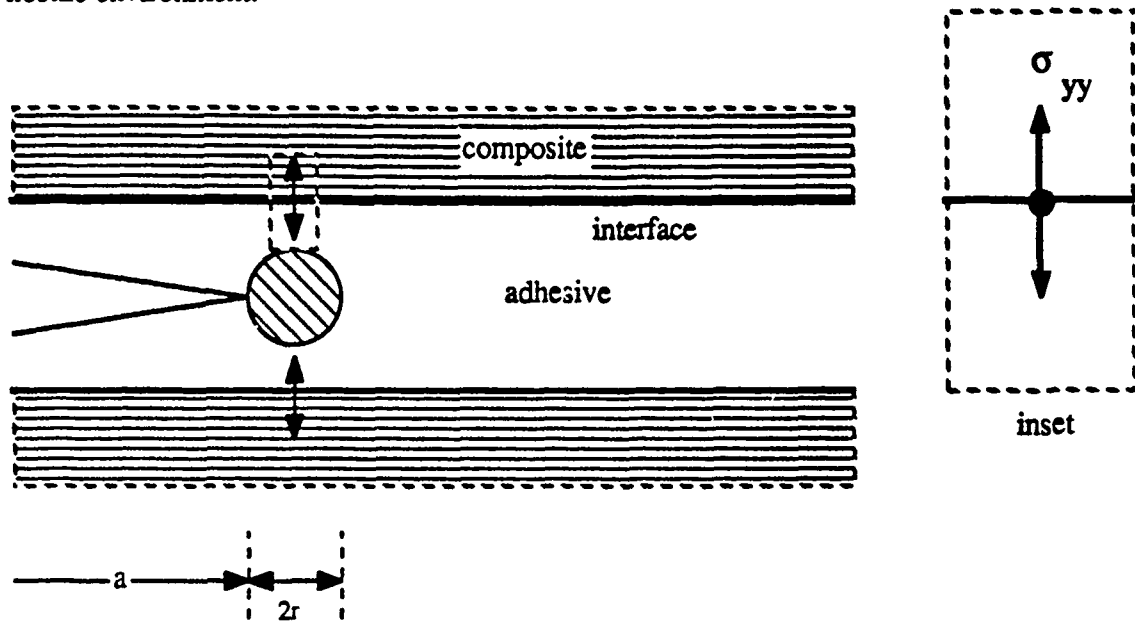


FIGURE 7.20 Stress acting on the adhesive-composite interface in the vicinity of the stress field of diameter $2r$ ahead of a sharp crack of length a in an adhesive joint.

The different interfacial stabilities observed for the U/C PEEK substrates bonded with the test adhesives may be explained by a consideration of the stresses in each joint. From the discussion in Chapter Two, it can be said that an adhesive-composite interface in the DCB joint will fail if the stresses at the interface are sufficient to to break the interfacial forces of adhesion, i.e. if the stresses can overcome the intrinsic adhesion across the interface. Now, in the unaged condition, the stresses on the interfaces within a joint bonded with the epoxy-paste adhesive are greater, due to the higher loads attained when testing this adhesive {see Figures 4.3 and 4.4}. It was for this reason that the U/C PEEK was treated to higher level of corona energy when bonding with the epoxy-paste adhesive. However, after ageing in the hot-wet environment, there are two mechanisms which reduce the stresses at the interface in joints bonded with the epoxy-paste adhesive which do not occur when the epoxy-film adhesive is employed. Firstly, the post-curing of the epoxy-paste adhesive caused not only a reduction in G_c , but also a reduction in the load at which crack propagation was observed. This reduced the stress acting at the adhesive-composite interface, σ_{yy} . Secondly, it was shown in Section 7.5.2 that water had little effect on the failure stress of the epoxy-film adhesive ($\sim 36\text{MPa}$), but that it lowered the failure stress of the epoxy-paste adhesive from 25.3MPa in the unaged but post cured condition, to 15.8MPa after 120 hours in water at 50°C . This result implies that

the effect of water on the joints bonded with the epoxy-paste adhesive would be to lower the failure stress of the adhesive, and thus lower the value of the transverse tensile stress, σ_{yy} , at the interface.

The effect of the hot-wet environmental exposure was therefore to significantly reduce the value of σ_{yy} for the U/C PEEK composite bonded with the epoxy-paste adhesive but not to reduce the value of σ_{yy} for the U/C PEEK composite bonded with the epoxy-film adhesive. Thus, $\sigma_{yy}(\text{epoxy-film}) \geq \sigma_{yyci} > \sigma_{yy}(\text{epoxy-paste})$. Hence, the critical transverse interfacial tensile stress, σ_{yyci} , was attained when the U/C PEEK was bonded with the epoxy-paste adhesive, which resulted in interfacial failure, but it was not attained when this composite was bonded with the epoxy-paste adhesive.

Interfacial failure was not observed when bonding the U/C epoxy composite due to the higher values of W_{AL} calculated for this joint. The higher values of W_{AL} resulted in a higher value of the critical stress required to cause interfacial debonding, σ_{yyci} , in the environmentally aged joints. Thus, for joints prepared with the U/C epoxy composite, $\sigma_{yyci} > \sigma_{yy}(\text{epoxy-film}) > \sigma_{yy}(\text{epoxy-paste})$. Therefore, for both adhesives, the stress acting across the interface was insufficient to overcome the interfacial forces of adhesion.

When the aged joints were tested at high rates, it was noticed that interfacial failure become the dominant mechanism for the U/C PEEK joints bonded with the epoxy-paste adhesive. Now, because epoxy adhesives are visco-elastic materials, as was discussed in Section 2.7.2, then the adhesive yield stress will be sensitive to the applied rate of strain. The effect of increasing the rate will be to increase the yield stress. It was shown in Chapter Six that the epoxy-paste adhesive was more sensitive to increasing rate than the epoxy-film adhesive. Testing at higher rates therefore increases the transverse tensile stress in the joint systems. Thus at higher rates, it appears that, $\sigma_{yy}(\text{epoxy-film}) > \sigma_{yy}(\text{epoxy-paste}) > \sigma_{yyci}$, when the substrate material was U/C PEEK. Therefore, at high rates, interfacial failure would be expected for U/C PEEK bonded with either adhesive, which is what was observed in Section 7.3.

7.7.3 Effect of Plasticization on the Value of G_c in Aged Joints

The tendency for water to cause plasticization of epoxy adhesives has been reported by many workers, e.g. by Mackie [98] and by Comyn [60]. A review of the literature confirms that water invariably causes a reduction in the strength properties of an adhesive. Such a reduction is most readily explained by the onset of plasticization. Some typical effects associated with plasticization are the lowering of the T_g , lowering of the modulus and yield stress, and

swelling of the adhesive.

However, the effect that plasticization of the adhesive would have on the adhesive fracture energy, G_c , is more complex. Ripling et al [99] observed that water increased the toughness of some epoxy adhesives after short periods of exposure. However, after longer periods of exposure, they reported that the toughness was decreased. Assuming Irwin's model [36] of the plastic zone at the crack tip, then the value of the adhesive fracture energy will depend on the adhesive yield stress, σ_y , and the crack tip opening displacement, δ_c .

$$G_c = \sigma_y \cdot \delta_c \quad (7.1)$$

Plasticization usually increases the value of δ_c , i.e. causes crack tip blunting which, other things being equal, will increase the value of G_c . The increasing strain to failure values measured in Section 7.5 is a indication that ageing in water has increased the values of δ_c for both the epoxy-film and epoxy-paste adhesives. Now, for the epoxy-film adhesive, the adhesive yield stress {which was approximately equivalent to the fracture stress} was not seen to decrease after water absorption in the uniaxial tensile tests. This suggests that, in the short term at least, the plasticization of the epoxy-film adhesive should increase the apparent toughness of this adhesive. It should be recalled that when the U/C epoxy composite was bonded with the epoxy-film adhesive, then an initial increase in toughness was indeed observed. A similar increase was not observed when bonding the U/C PEEK composite with this adhesive due to interfacial attack.

However, the yield stress of the epoxy-paste adhesive was significantly reduced by ageing in the water environment. Therefore, the combined effect of decreasing yield stress and crack tip blunting is more difficult to elucidate. The fracture results described in Section 7.3 showed that no initial increase in the value of G_c was observed for joints bonded with the epoxy-paste adhesive. It can be inferred from this observation that the decrease in yield stress of this adhesive more than countered any increase in G_c due to crack tip blunting.

The initial increase in G_c which was recorded for the U/C epoxy substrates bonded with the epoxy-film adhesive was reversed after four months of exposure. After one year of exposure, the joints retained only 50% of their initial, dry G_c value. It is possible that the yield stress of this adhesive decreased after ageing periods in excess of those used for the tensile tests, and that plasticization may account for the observed decrease in the adhesive fracture energy. The complex behaviour of epoxy adhesives aged for extended periods in water was reported

by Brewis et al [72]. They found that, although water decreased the adhesive T_g at short ageing times, after ageing for 10 months in water the T_g of each adhesive that they studied increased. However, it is likely that other mechanisms, e.g. physical ageing account for, at least in part, the decrease in G_c . It was concluded by Comyn [60] that it is unlikely that plasticization can satisfactorily explain the long term durability of adhesive joints, but that it is a contributory factor.

7.8 Chapter Seven Conclusions

The main conclusions drawn in this Chapter can be summarized as follows:

1. When aged in a hot-dry (50°C) environment, the epoxy-film adhesive showed no change in adhesive fracture energy, but the epoxy-paste adhesive suffered a 40% decrease in its unaged, room temperature, adhesive fracture energy. This was attributed to post curing of the room temperature adhesive at this temperature, resulting in a more crosslinked and thus more brittle adhesive. Thus, after ageing in these conditions, $G_c=2.5\pm0.2\text{kJ/m}^2$ for both the epoxy-film and epoxy-paste adhesives.
2. The effect of ageing joints consisting of the U/C epoxy composite bonded with either adhesive in a hot-wet environment for up to one year was to significantly decrease the adhesive fracture energies, but not change the locus of joint failure which remained cohesive, in the adhesive. When this substrate material was bonded with the epoxy-paste adhesive or the epoxy-film adhesive the joints retained about 50% of their 50°C dry G_c value after one year of exposure. Thus, after one year of exposure, $G_c=1.25\pm0.1\text{kJ/m}^2$ for the joints prepared with the U/C epoxy substrates bonded with either adhesive.
3. The effect of ageing the joints prepared with the U/C PEEK composite in the hot-wet environment for up to one year was to change both the locus of joint failure, and to decrease the joint fracture energy. When bonded with the epoxy-paste adhesive, after corona treating to 20J/mm^2 , then the joints retained 70% of their 50°C dry G_c value after one year of exposure. In addition, a small amount of interfacial failure (~10%) was observed. However, when bonded with the epoxy-film adhesive after corona treating to 10J/mm^2 , then the locus of failure changed to interfacial (~100%) and the joints retained only 28% of their 50°C dry G_c value after one year of exposure. Thus, after one year of exposure, $G_c=1.75\text{kJ/m}^2$ for the joints bonded with the epoxy-paste adhesive and $G_c=0.70\text{kJ/m}^2$ for the joints bonded with the epoxy-film adhesive.
4. Increasing the level of corona treatment applied to the U/C PEEK composite from

10J/mm² to 15J/mm², prior to bonding with the epoxy-film adhesive, did not improve the resistance to interfacial attack of this joint system.

5. The testing of fully aged (one year) joints consisting of the U/C epoxy composite bonded with either adhesive at high rates had no effect on the value of the adhesive fracture energy at crack initiation, and no effect on the locus of joint failure which remained cohesive. However, the testing of joints consisting of the U/C PEEK composite bonded with the epoxy-paste adhesive demonstrated that a further reduction in fracture energy was observed, and this corresponded to the locus of joint failure progressively switching from cohesive to interfacial at increasing test rates.

6. Calculations of the thermodynamic work of adhesion showed that the interfacial stability between the composite and adhesive was decreased for each joint system when exposed to water. This reduction was most severe when the U/C PEEK substrates were employed.

7. Water modified the bulk properties of both adhesives. The epoxy-film adhesive showed no change in its fracture stress, but suffered a 39% decrease in its tensile modulus and an 85% increase in its strain to failure after reaching equilibrium in water at 50°C. The epoxy-paste adhesive suffered a 38% reduction in tensile fracture stress, a 44% reduction in tensile modulus and a 300% increase in strain to failure.

8. It was proposed that the tendency of an interface to fail was governed by the need to attain a critical value of the transverse tensile stress, σ_{yyci} , at the adhesive-composite interface. This value of the critical stress is dependent on the W_{AL} value of the interface and the yield stress of the adhesive. Because the value of W_{AL} when bonding the U/C PEEK substrates is significantly less than W_{AL} for the U/C epoxy substrates, then joints consisting of the U/C PEEK composite are more likely to suffer from interfacial attack than those consisting of U/C epoxy. This is particularly significant after ageing in water when either (a) bonding the U/C PEEK composite with the epoxy-film adhesive, or (b) testing at high rates. These observations are due to the higher transverse tensile stresses imposed on the interface in these instances.

9. When the locus of failure remained cohesive, then the change in the adhesive fracture energy of the aged adhesive joints may be explained, at least initially, by the plasticization of the adhesive. However, after long exposure times, it is probable that other mechanisms were responsible for the degradation of the adhesive.

Chapter Eight

Thesis Conclusions

8.1 Introduction

The main conclusions which have been drawn in thesis are now drawn together and presented in this Chapter. Recommendations for future work will follow in Chapter Nine.

8.2 Conclusions

The concepts of continuum fracture mechanics have been successfully applied to the study of crack growth in adhesive joints. Several different data reduction schemes for calculating the adhesive fracture energy, G_c , from a mode I DCB test were investigated. It was shown that the values of G_c obtained from the "area method" contained a great deal of scatter, due to the approximations embodied in this technique. The "compliance method" was more accurate, but required a compliance calibration to be conducted. This would be difficult to achieve under certain test conditions e.g. at high rates.

By the application of simple beam theory, a further method of calculating G_c was employed. By modelling the DCB specimen as a built-in beam, three different beam theory equations could be derived for the calculation of G_c . These were termed the "load method", the "displacement method" and the "displacement, modulus method". However, the values of G_c calculated using these methods showed very poor agreement. The "load method" calculated low values of G_c , which increased with increasing crack length. In addition, when the substrate modulus was calculated using beam theory, then the value was seen to increase with increasing crack length.

However, it was shown that these inaccuracies could be corrected by the application of three correction factors, which accounted for the errors induced by the assumptions of the simple beam analysis. When correction factors accounting for the effects of shear, large displacements and end-block stiffening were employed, then excellent agreement was observed between the "corrected methods" for calculating G_c . Further, these methods now showed excellent agreement with the "compliance method" which was unaffected by the

correction factors. The "corrected-load method" now agreed with the other "corrected analyses" and showed that these joints did not exhibit an 'R-curve' effect, i.e. the value of G_c was independent of crack length. Also, when the substrate modulus was calculated by taking into account these correction factors, then the value of the modulus was shown to be independent of the crack length, which was the expected result.

All failure at slow test rates was cohesive and stable. The values of the adhesive fracture energy, G_c , were therefore independent of which fibre-composite was used as the substrate material under these test conditions. The value of G_c calculated for joints bonded with the epoxy-film adhesive was, $G_c\{\text{epoxy-film}\}=2.5\text{kJ/m}^2$ and the value calculated for joints bonded with the epoxy-paste adhesive was, $G_c\{\text{epoxy-paste}\}=4.1\text{kJ/m}^2$.

Joints bonded with the epoxy-film adhesive were loaded with different ratios of mode I to mode II using a modified version of the mixed-mode bending test apparatus. The values of G_I and G_{II} remained constant with increasing crack length, showing again that no 'R-curve' effect was seen for these materials. By employing the mixed-mode failure criterion proposed by Charalambides et al, the mixed-mode failure locus was drawn for these joints. In order to define the locus fully, it was necessary to measure the pure mode II value of the adhesive fracture energy, G_{IIc} . This was achieved for joints bonded with the epoxy-film adhesive using the end-loaded split (ELS) test apparatus. A Value of $G_{IIc}=4.4\text{ kJ/m}^2$ was recorded for this adhesive. Due to the higher toughness of the epoxy-paste adhesive, it was not found possible to achieve crack growth in joints bonded with this adhesive using the ELS apparatus. Further, when joints bonded with this adhesive were loaded under mixed-mode conditions on the modified MMB test rig, then crack growth was not achieved when the ratio of $G_I/G_{II} < 2$. However, for the joints bonded with the epoxy-film adhesive, it was shown that $G_{IIc} > G_{I/IIc} > G_{Ic}$, therefore mode I loading represented the most damaging loading mode for this adhesive.

As a possible alternative to the corona-discharge surface pretreatment technique, the effects of applying an oxygen plasma surface pretreatment were studied. Such a treatment was shown to very effectively improve the level of intrinsic adhesion of two thermoplastic based fibre-composites, U/C PEEK and U/C PPS. It was demonstrated that the application of an optimized plasma treatment was sufficient to obtain high fracture energy, cohesive failures with either the epoxy-film or epoxy-paste adhesives when the substrate was the U/C PEEK composite. However, when the substrate was the U/C PPS composite, then the fracture behaviour became dominated by interlaminar crack propagation, and the higher fracture energy, cohesive crack propagation was not observed.

A surface analysis of the plasma-treated substrates revealed that the resulting surface modifications were very similar in nature to those induced by the corona-discharge treatment. These modifications were concerned with both the physical and chemical characteristics of the surface. The most significant modification was to the surface chemistry of the plasma treated substrates. This was investigated using X-ray photoelectron spectroscopy (XPS). Deconvolution of the C1s spectra obtained by XPS showed that the plasma treatment had caused extensive surface oxidation of the substrates, greatly enhancing their adhesive properties. However, no completely satisfactory correlation between the surface chemistry and the subsequent adhesive fracture behaviour was shown to exist. The use of the O/C atomic ratios was shown to be an imprecise parameter for the prediction of the joint fracture behaviour. The weighted % dipole moment (WDM) parameter, Ω , was more precise, but again it failed to show a very good correlation with the joint fracture behaviour. The main obstacle was that the value of Ω attained a maximum value some time before fully cohesive crack growth was observed, and that the corona and plasma treatments imparted different critical values of Ω to the substrates. The WDM parameter is governed by the formation of major chemical groups on the substrate surfaces, and it could be that, in order to gain a full understanding of this complex phenomenon, then some of the more subtle chemical changes will have to be taken into account.

When testing the bonded DCB geometry at high rates, it was shown that the fracture behaviour of the adhesive joints became increasingly dominated by dynamic effects. The main source of the dynamic effect in this test is the propagation and reflection of flexural waves in the arms of the specimen. The presence of flexural waves very much reduce the accuracy of the load-cell measuring device by introducing violent force oscillations. Thus, it was concluded that misleading values of the adhesive fracture energy, G_c , were obtained when versions of the analysis requiring values of the load to be measured were used. Further, when the substrate modulus was calculated using the load values, then the modulus was seen to decrease with increasing rate. This was a highly unlikely result and further suggested that the load measurements were in error at high rates.

It was shown that the value of the beam opening displacement, δ , and the crack length, a , could be accurately monitored by the use of high-speed photography. The accuracy of these measurements was not reduced by the onset of dynamic oscillations. In addition, for the test rates employed, the assumption was made that the value of substrate modulus was independent of rate, so that there was no need to know accurate and valid values of the load. Results obtained by a dynamic mechanic thermal analysis and also from the literature showed

that this assumption was justified. Thus, calculating G_c via the load-independent method, i.e. using the "corrected-displacement, modulus method" was shown to be the most reliable.

An effect of increasing the rate of the test was to change the crack propagation behaviour from a stable, continuous propagation mode to an unstable, stick-slip propagation mode at higher test rates. As a consequence of this transition, only discrete values of G_c were attainable, and it was found that the first crack initiation values of G_c were the most repeatable, and thus these received the most attention. Using the "corrected-displacement, modulus method" to calculate G_c , it was shown that when the joints were prepared with the epoxy-film adhesive, then there was almost no effect of rate on the value of G_c up to the rate of 10m/s. However, when the epoxy-paste adhesive was employed, then G_c decreased with increasing rate. This reduction was first evident at 0.5m/s, and accounted for almost a 40% reduction in G_c at 10m/s. All failure was cohesive and independent of which composite was employed as the substrate.

Scanning electron microscopy revealed that the micro-mechanism of particle cavitation was observed to have occurred within the epoxy-film adhesive at all test rates. Further, a visual examination of the fracture surfaces of joints bonded with the epoxy-film adhesive suggested that extensive shear yielding had occurred in this adhesive at all test rates. However, the interfacial debonding of the mat-carrier from the epoxy-film adhesive which was observed at slow rates did not occur at high rates. In the epoxy-paste adhesive, the micro-mechanisms of shear yielding and particle cavitation were detected to have occurred extensively at slow rates, but at high rates these occurred to a significantly lesser extent. High rate testing did not compromise the stability of the various adhesive-composite interfaces. This was particularly significant for the bonding of the U/C PEEK composite, since it demonstrated that when testing at elevated rates, increased levels of corona treatment were not necessary.

When aged in a hot-dry environment, joints bonded with the epoxy-film adhesive showed no change in the value of G_c , but the joints bonded with the epoxy-paste adhesive retained only 60% of their unaged, room temperature G_c value after 18 days of exposure. This reduction was attributed to post curing of the adhesive due to its lower cure temperature i.e. room temperature rather than the 125°C required for the curing of the epoxy-film adhesive. The effect of post curing was to produce a more crosslinked and thus more brittle adhesive.

When aged in the hot-wet (water at 50°C) environment for periods of up to one year, the value of G_c for each joint system was significantly reduced. When tested at slow rate, the joints prepared with the U/C epoxy substrates bonded with either adhesive retained approximately 50% of their 50°C dry value of G_c after one year. The locus of failure remained cohesive.

However, joints prepared with the U/C PEEK substrates bonded with the epoxy-film adhesive suffered interfacial attack by the water. The locus of failure changed progressively from cohesive to interfacial. This change in the locus of failure was associated with a severe decrease in the measured fracture energy of the joint. After one year, this joint system retained only 28% of its 50°C dry value of G_c . When this composite was bonded with the epoxy-paste adhesive, the locus of failure remained predominantly cohesive (~10% interfacial after one year). This joint system retained 70% of its 50°C dry value of G_c after one year of ageing in the environmental chamber.

Joints which had been aged in the environmental chamber for one year were tested at high rates in order to observe the combined effect of high test rates and environmental exposure, as these conditions could possibly be encountered in service. It was concluded that for the joints prepared with either the U/C epoxy or U/C PEEK composite bonded with the epoxy-film adhesive, then no further reduction in the value of G_c was observed. When the substrate material was U/C PEEK, the locus of failure remained interfacial at all test rates. When the substrate material was U/C epoxy, the locus of failure remained cohesive. It was also noted that in this joint system the crack propagation behaviour was now stable even at high test rates. Thus, an effect of combining environmental ageing with increased rate was to prevent the usual unstable, stick-slip crack propagation from occurring.

When the U/C epoxy composite was bonded with the epoxy-paste adhesive and tested at high rates after ageing for one year, then no further reduction in adhesive fracture energy was observed. However, when the substrate was the U/C PEEK composite, then the locus of joint failure progressively changed from cohesive to interfacial as the test rate increased. This change in the failure locus was associated with a further decrease in the value of G_c . When tested at 2m/s, these joints now retained only 32% of their 50°C, dry static value of G_c .

It was shown that the interfacial failure between the U/C PEEK composite and the epoxy-film adhesive was not prevented by using a higher level of corona energy during surface preparation. Calculations of the thermodynamic work of adhesion showed that the interfacial stability between the composite and the adhesive was decreased for each joint system when exposed to water. The reduction was most severe when the U/C PEEK composite was employed. Water diffusion tests showed that equilibrium conditions were not achieved in the adhesive joints, even after one year of environmental exposure. However, water diffused into, and attained a higher concentration, in the epoxy-paste adhesive than in the epoxy-film adhesive.

Tensile tests on aged bulk adhesive samples showed that water significantly lowered the yield stress of the epoxy-paste adhesive. A reduction of 38% in σ_y was recorded for this adhesive. However, it was shown that the absorption of water did not lower the yield stress of the epoxy-film adhesive during the test. In the light of these observations, it was concluded that the tendency of an interface to fail was governed by the need to attain a critical value of the transverse tensile stress, σ_{yyci} , at the adhesive-composite interface. It was further concluded that the value of σ_{yyci} is dependent upon the W_{AL} value of the surface. Because the value of W_{AL} when bonding the U/C PEEK composite was significantly lower than the value of W_{AL} for the U/C epoxy composite, then joints consisting of the U/C PEEK composite are more likely to suffer from interfacial failure than those consisting of the U/C epoxy composite. Factors which subsequently increase the value of the transverse tensile stress, σ_{yy} at the interface further increase the risk of interfacial failure. Hence, interfacial failure was observed at slow rates when the U/C PEEK was bonded with the epoxy-film adhesive, because W_{AL} was low and σ_{yy} was high and thus σ_{yyc} was attained. However, when bonding with the epoxy-paste adhesive, σ_y was also low at slow rate so σ_{yyci} was not attained. However, at high rates, σ_y increased in the adhesives and thus σ_{yyci} was attained at higher rates when bonding with the epoxy-paste adhesive, thus interfacial debonding was observed under these test conditions.

Thus, the fracture behaviour of a number of different adhesive joint systems has been investigated over a wide range of test conditions. When tested at slow or fast rates in the unaged condition, the adhesive fracture energy for the joints consisting of either the U/C epoxy or U/C PEEK substrates was shown to be independent of which fibre-composite was employed, as all failure was essentially cohesive. However, after ageing these joints in a hostile environment for extended periods, it was shown that the subsequent joint fracture behaviour of the different joint systems was dependent upon which adhesive was employed to bond the joint and also, upon which fibre-composite substrate was employed.

Chapter Nine

Recommendations for Future Work

2.1 Introduction

During the course of this work, a number of areas were identified where future work would be beneficial. These areas will now be identified, and appropriate recommendations will be made.

2.2 Recommendations

Firstly, it was shown in Chapter Four that it was not possible to obtain the mixed-mode failure locus for the tougher, epoxy-paste adhesive, due to non-linear and plastic effects. It is recommended that these tests be conducted using thicker substrate beams, to reduce the large deformation experienced by the cantilever arms, and that a non-linear analysis be carried out in order to obtain accurate and valid values of G_{III} when using these tougher adhesives.

Secondly, it was shown that the weighted % dipole moment parameter showed a better correlation to the adhesive joint fracture behaviour than the O/C ratio. However, it appears that a further refinement of this parameter is required. This could possibly be achieved if a more detailed understanding of the surrounding chemical environment of each plasma induced species was obtained. This may be achieved by the use of advanced surface chemical analysis techniques, e.g. by the use of Infra-red reflection absorption spectroscopy.

Thirdly, it would be valuable to determine the fracture behaviour of these adhesive joint systems at test rates in excess of 10m/s. This would allow an assessment of whether these joint systems could be employed in structures which are likely to be subjected to even higher speed impacts. At higher test rates, a different test geometry could be employed, which is less prone to dynamic effects. A possible alternative to the DCB test specimen is the tapered double cantilever beam.

Fourthly, it would be of interest to investigate whether the problems associated with the environmental attack of the joints prepared with the U/C PEEK substrates could be overcome by the use of an oxygen plasma surface pretreatment. It is indeed possible that the oxygen

plasma might enable more durable joints to be prepared, especially since it was shown that the oxygen plasma-treated U/C PEEK substrates possessed a higher value of the WDM than corona-treated U/C PEEK. Thus, if the intrinsic adhesion across the adhesive-substrate interface is greater after an oxygen plasma treatment, then the use of this technique could well improve the environmental durability of adhesively bonded U/C PEEK.

Finally, it would be of much interest to assess the fracture behaviour of engineering structures following repair with a toughened adhesive. The repair of polymeric fibre-composite components with toughened adhesives is an area in which there is a growing interest, since the use of adhesives represents one of the most practical methods by which such repairs can be carried out.

Appendix One

θ Functions

The corrected equations discussed in Chapter Four incorporated the correction factors F and N , which were defined in eqns. 4.8 and 4.9. They included a number of θ functions which will now be defined.

(a) For the mode I DCB Test

$$\theta_1 = \frac{3}{10} \quad \theta_2 = \frac{3}{2} \quad \theta_3 = 1$$

$$\theta_4 = \frac{9}{8} \left\{ 1 - \left(\frac{l_2}{a} \right)^2 \right\} \quad \theta_5 = \frac{9}{35}$$

(b) For the mode II ELS Test

$$\theta_1 = \frac{3}{20} \left\{ \frac{15 + 50 \left(\frac{a}{L} \right)^2 + 63 \left(\frac{a}{L} \right)^4}{\left(1 + 3 \left(\frac{a}{L} \right)^3 \right)^2} \right\} \quad \theta_2 = \frac{-3 \left(\frac{a}{L} \right) \left\{ 1 + 3 \left(\frac{a}{L} \right)^2 \right\}}{\left\{ 1 + 3 \left(\frac{a}{L} \right)^3 \right\}}$$

$$\theta_3 = \frac{4}{\left\{ 1 + 3 \left(\frac{a}{L} \right)^3 \right\}}$$

$$\theta_4 = -\frac{9}{4} \frac{\left\{ \left(1 - \left(\frac{a}{L} \right) \left[1 + 3 \left(\frac{a}{L} \right)^3 \right] + 4 \left(\frac{a}{L} \right)^2 \left[1 - \left(\frac{l_2}{a} \right)^2 \left[1 + 3 \left(\frac{a}{L} \right)^2 \right] \right] \right\}}{\left[1 + 3 \left(\frac{a}{L} \right)^3 \right]^2}$$

$$\theta_5 = \frac{36}{35} \frac{\left\{ 1 + \frac{3}{8} \left(\frac{a}{L} \right)^3 \left[35 + 70 \left(\frac{a}{L} \right)^2 + 63 \left(\frac{a}{L} \right)^4 \right] \right\}}{\left\{ 1 + 3 \left(\frac{a}{L} \right)^3 \right\}^3}$$

Appendix Two

The Large Deflection correction for the modified MMB Rig

The expressions for G_I and G_{II} obtained using the modified MMB test apparatus were given in eqns. 4.14 and 4.15. These expressions contained the correction factors F_1 and F_2 , which corrected for the effective shortening of the bending moment arms due to large deflections in the beams. It was shown by Williams [80] that F_1 and F_2 could be expressed as:

$$F_1 = 1 - \left\{ \frac{3\alpha_1^2 + 4\alpha_1\alpha_2 + 8\alpha_2^2}{30} \right\}$$

$$F_2 = 1 - \left\{ \frac{3\alpha_1^2 + 4\alpha_1\alpha_3 + 8\alpha_3^2}{30} \right\}$$

where $\alpha_1, \alpha_2, \alpha_3$ are the slopes of the beam at the crack tip and loading points respectively. These slopes can be evaluated from:

$$\alpha_1 = \frac{2}{3L\xi} \{ n(L-b)^3 + a^3(1-8m) \} + \frac{b^2 - a^2}{\xi}$$

$$\alpha_2 = \alpha_1 + \frac{8qa^2}{\xi}$$

$$\alpha_3 = \alpha_1 + \frac{8mq a^2}{\xi}$$

where:

$$\xi = \frac{16a^3}{3\delta_{BD}}(q-m) \quad n = \frac{b}{L-b} \quad m = \frac{1 - \frac{b+c}{L}}{\left(1 + \frac{c}{b}\right)\left(1 - \frac{b}{L}\right)}$$

where b, c and L were defined in Figure 3.8(a), δ_{BD} is beam opening displacement and q is given by:

$$q = \frac{\frac{c}{b}}{\left(1 + \frac{c}{b}\right)\left(1 - \frac{b}{L}\right)}$$

Appendix Three

Parameters Required for the Mixed-mode Failure locus

It was discussed in Chapter Four how the mixed-mode failure locus was plotted for the adhesive joints bonded with the epoxy-film adhesive using eqn. 2.35. To employ this equation, it was first necessary to calculate values of G_0 , ψ_0 , and ω . The calculation of these parameters is discussed in [39]. The values may be given by:

$$G_0 = \frac{1}{1 - \Omega^2} \left\{ \left(\frac{G_{Ic} + G_{IIc}}{2} \right) - \sqrt{\left(\frac{G_{Ic} + G_{IIc}}{2} \right)^2 - (1 - \Omega^2) G_{Ic} G_{IIc}} \right\}$$

where,

$$\Omega = \frac{\sqrt{G_{Ic} G_{IIc}}}{2} \left\{ \frac{2}{G_{I/IIc}} - \frac{1}{G_{Ic}} - \frac{1}{G_{IIc}} \right\}$$

where $G_{I/IIc}$ is the value of the adhesive fracture energy when $G_I = G_{II}$; i.e. when $\psi = 45^\circ$, and

$$\tan^2 \psi_0 = \frac{1 - \frac{G_0}{G_{Ic}}}{1 - \frac{G_0}{G_{IIc}}}$$

Appendix Four

XPS Deconvolution Results

The following results were obtained from the deconvolution of the C1s narrow scans of the U/C PEEK composite following a corona and an oxygen plasma treatment.

TABLE A4.1 Deconvolution of the C1s peak from U/C PEEK composite subjected to a corona discharge treatment.

Corona Energy (J/mm ²)	C-H (%)	C-N (%)	C-O (%)	C=O (%)	O=C-O (%)
0	75	11	12	2	0
0.25	65	12	12	8	3
0.50	61	12	14	8	5
1.0	61	14	12	8	5
5.0	62	13	12	8	5
10.0	59	14	11	10	6
20.0	58	13	11	11	6.5

TABLE A4.2 Deconvolution of the C1s peak from U/C PEEK composite subjected to a oxygen plasma surface treatment.

Treatment Time (mins)	C-H (%)	C-N (%)	C-O (%)	C=O (%)	O=C-O (%)
0	72	15	10	3	0
2.5	55	14	16	8	7
5.0	54	12	17	10	7
7.5	54	11	18	10	7
10.0	54	13	16	10	7
12.5	54	11	16	10	8
15.0	54	10	16	11	8

References

- [1] Kinloch, A.J., *Adhesion & Adhesives: Science & Technology*. Chapman Hall London and New York. (1987).
- [2] Kodokian, G.K.A., *The Adhesive Bonding of Thermoplastic fibre-composites*. Ph.D. Thesis, Imperial College, London. (1989).
- [3] Kinloch, A.J. and G.K.A. Kodokian, *J. Adhesion*, **29**: p. 193-218. (1989).
- [4] Fay, P.A., R.E. Davis, and G.D. Suthurst; in proceedings of *Impact and fatigue testing of adhesives*. (1990). Society of Chemical Industry, Belgrave Square, London.
- [5] Gledhill, R.A. and A.J. Kinloch, *J. Adhesion*, **6**: p. 315-330. (1974).
- [6] Houwink, R. and G. Salomon, *Adhesion and Adhesives*. Vol. 1. Elsevier Publishing Co. London. (1965).
- [7] Voyutskii, S.S., *Adhesion & Autohesion of Polymers*, in *Adhesives Age*. (1962).
- [8] Deryaguin, B.V. and et.al., *Adhesion of Solids*. Consultants Bureau, New York & London. (1978).
- [9] Fowkes, F.W., *J. Adhesion*, **4**: p. 155. (1972).
- [10] Huntsberger, J.R., *Treatise on Adhesion and Adhesives*. ed. R.L. Patrick. Vol. 1. p. 119. Marcel Dekker, New York. (1967)
- [11] Orowan, E., *Journal Franklin Inst.*, **290**: p. 493. (1970).
- [12] Tabor, D., *Rep. Prog. Appl. Chem*, **36**: p. 621. (1951).
- [13] Andrews, E.H. and A.J. Kinloch, *Proc. R. Soc. Lond.*, **A332**: p. 385. (1974).
- [14] Gent, A.N. and A.J. Kinloch, *J. Polymer Sci.*, **42**: p. 659. (1971).
- [15] Gent, A.N. and J. Schultz, *J. Adhesion*, **3**: p. 281. (1972).

References

- [16] Gent, A.N. and A. Ahagon, *J. Polymer. Sci., Poly. Phys. Edit.*, **13**: p. 1285. (1975).
- [17] Klein, I.E. et al., *Int. J. Adhesion & Adhesives*, **3**: p. 159. (1983).
- [18] Webster, H.F. and J.P. Wightman, *J. Adhesion: Sci. & Tech.*, **5**: p. 93-106. (1991).
- [19] Fowkes, F.M. and M.A. Mostafa, *Ind. Eng. Chem. Prod. Res. Dev.*, **17**: (1978).
- [20] Bikerman, J.J., *Ind. Eng. Chem.*, **59**(9): p. 40. (1967).
- [21] Sharpe, L.H. in *proceedings of 15th Annual Meeting of the Adhesion Society*. Hilton Head, South Carolina. (1992).
- [22] Liston, E.H., *J. Adhesion*, **30**: p. 200. (1989).
- [23] Kinloch, A.J., G.K.A. Kodokian, and J.F. Watts, *Phil. Trans. R. Soc. Lond.*, **A.338**: p. 83-112. (1992).
- [24] Evans, J.R. et al., *J. Adhesion: Sci. & Tech.*, **1**(4): p. 291-302. (1987).
- [25] Chin, J.W. and J.P. Wightman, *J. Adhesion*, **36**: p. 25-37. (1991).
- [26] Carley, J.F. and P.T. Kitze, *Polymer Eng. & Sci.*, **18**(4): p. 326-334. (1978).
- [27] Schonhorn, H. and R.H. Hansen, *J. Polymer Sci.*, **B4**: p. 203. (1966).
- [28] Kodokian, G.K.A. and A.J. Kinloch, *J. Materials Sci. Lett.*, **7**: p. 625-627. (1988).
- [29] Davies, P. et al., *J. Materials Sci. Lett.*, **10**: p. 335-338. (1991).
- [30] Moyer, D.J.D. and J.P. Wightman, *Surf. Interface Anal.*, **17**: p. 457-464. (1991).
- [31] Griffith, A.A., *Phil. Trans. R. Soc.*, **A221**: p. 163-189. (1920).
- [32] Orowan, E., *Rept. Prog. Phys.*, **12**: p. 185. (1948).
- [33] Rivlin, R.S. and A.G. Thomas, *J. Polymer Sci.*, **10**: p. 291. (1953).

References

- [34] Hashemi, S., A.J. Kinloch, and J.G. Williams, *Proc. R. Soc. Lond.*, **A427**: p. 173-199. (1990).
- [35] Westergaad, H.H., *J. Appl. Mech.*, **June (1946)**. (1946).
- [36] Irwin, G.R., *Appl. Mat. Res.*, **3**: p. 65. (1973).
- [37] Williams, J.G., *Int. J. Fracture*, **36**: p. 101-119. (1988).
- [38] Reeder, J.R. and J.H. Crews, *AIAA Journal*, **27**: p. 1270. (1990).
- [39] Charalambides, M., *et al.*, *Int. J. Fracture*, **54**: p. 269-291. (1992).
- [40] Kinloch, A.J., *et al.*, to be published in *Composites Science and Technology*, . (1993).
- [41] Huang, Y., Ph.D. Thesis. Imperial College, London. (1991).
- [42] Kinloch, E.A.J., *Structural Adhesives: Developments in Resins & Primers*. ed. A.J. Kinloch. Appl. Sci. Pub. London. (1986)
- [43] Kinloch, A.J. and R.J. Young, *Fracture Behaviour of Polymers*. Elsevier Appl. Sci. London. (1983).
- [44] Young, R.J., *Introduction to Polymers*. Chapman Hall. London. (1981).
- [45] Ferry, J.D., *Viscoelastic Properties of Polymers*. John Wiley. New York. (1970).
- [46] Kinloch, A.J., G.A. Kodokian, and M.B. Jamarani, *J. Materials Sci.*, **22**: p. 4111-4120. (1987).
- [47] Kinloch, A.J. and G.K.A. Kodokian, *J. Adhesion*, **24**: p. 109-126. (1987).
- [48] Williams, J.G., *Fracture Mechanics Of Polymers*. Ellis Horwood. Chichester (1984).
- [49] Khalil, A.A. and M.R. Bayoumi, *Int. J. Adhesion & Adhesives*, **11(1)**: p. 25-29. (1991).

References

- [50] Gledhill, R.A. et. al., *Polymer*, **19**: p. 574-582. (1978).
- [51] Yamini, S. and R.J. Young, *Polymer*, **18**: p. 1075-1080. (1977).
- [52] Yamini, S. and R.J. Young, *J. Materials Sci.*, **14**: p. 1609-1618. (1979).
- [53] Beguelin, P., M. Barbezat, and H.H. Kausch, *Journal of Physics, III France* **1**: p. 1867-1880. (1991).
- [54] Mall, S., G.E. Law, and M. Katouzian, *J. Compos. Mater.*, **21**(6): p. 569-579. (1987).
- [55] Smiley, A.J. and R.B. Pipes, *J. Compos. Mater.*, **21**(7): p. 670-687. (1987).
- [56] Kinloch, A.J., J.G. Williams, and P. Yayla. in *proceedings of 2nd International Conference on Deformation and Fracture of Composites*. (1993). UMIST, Machester, U.K.
- [57] Kalthoff, J.F., *Int. J. Fracture*, **27**: p. 277. (1985).
- [58] Williams, J.G. and G.C. Adams, *Int. J. Fracture*, **33**: p. 209. (1987).
- [59] Smiley, A.J., *Rate Sensitivity of Interlaminar Fracture Toughness in Composite Mmaterials*. MSc. Thesis. University of Delaware. (1985).
- [60] Comyn, J., *Ch. 3 "Kinetics and Mechanisms of Environmental Attack, in Durability of Structural Adhesives*, A.J. Kinloch, Editor., App. Sci. Pub. London and New York. p. 85-129. (1983).
- [61] Kinloch, A.J., *Introduction Chapter, in Durability of Structural adhesives*, A.J. Kinloch, Editor. (1983), Applied Science Pubiishers: London and New York. p. 1-37
- [62] Atkins, R.W., S.S. Shaw, and D.A. Tod. in *proceedings of Adhesion in Hostlie Environments*. Belgrave Square, London. (1991).
- [63] Hand, H.M. et al., *Int. J. Adhesion & Adhesives*, **11**(1). (1991)

References

- [64] Cotter, J.L., *Developments in Adhesives-1*. ed. W.C. Wake. , pub. Applied Science Pub. London (1977).
- [65] Gledhill, R.A., A.J. Kinloch, and S.J. Shaw, *J. Adhesion*, **11**: p. 3-15. (1980).
- [66] Brewis, D.M., *et al.* in proceedings of *Adhesion '90*. (1990). Queens College, Cambridge.
- [67] Bowditch, M.R., D. Hiscock, and D.A. Moth, *Int. J. Adhesion & Adhesives*, **11**(3): p. 163-169. (1991).
- [68] Brewis, D.M., J. Comyn, and J.L. Tegg, *Int. J. Adhesion & Adhesives*, **1**: p. 35-39. (1980).
- [69] Powell, P.C., *Engineering with Polymers*. Chapman and Hall. London. (1983).
- [70] Crank, J., *Mathematics of Diffusion*. 2nd ed. Oxford University Press. Oxford. (1975).
- [71] Brewis, D.M., J. Comyn, and S.T. Tredwell, *Int. J. Adhesion & Adhesives*, **7**(1): p. 30-32. (1987).
- [72] Brewis, D.M., *et al.*, *Polymer*, **21**: p. 357. (1980)
- [73] Nowak, S., H.-P. Haerri, and L. Schlapbach, *Poly. Mat. Sci. & Eng.*, **62**: p. 437-441. (1990).
- [74] Joel, *JSM 5300 Instruction Manual*. Joel Ltd. Tokyo, Japan
- [75] Watts, J.F., *An Introduction to Surface Analysis by Electron Spectroscopy*. Oxford University Press. New York. (1990).
- [76] Seighbahn, K. and e. al., *ESCA: atomic, molecular, and solid state structure studied by means of electron spectroscopy*. Almquist and Wiksells. Uppsala, Sweden (1967).
- [77] Hashemi, S., A.J. Kinloch, and J.G. Williams, *J. Materials Sci. Lett.*, **8**: p. 125-129. (1989).

References

- [78] Williams, J.G., *Composites Sci. & Tech.*, **35**: p. 367-376. (1989).
- [79] Williams, J.G., *J. Compos. Mater.*, **21**(April): p. 330-347. (1987).
- [80] Williams, J.G., *J. Strain Analysis*, **24**(4): p. 207-214. (1989).
- [81] Davies, P., European Group on Fracture. Polymers and composites Task Group, . (1990).
- [82] ASTM, ASTM Standard E-399, . (1978).
- [83] Wang, Y. and J.G. Williams, *Composites Sci. & Tech.*, **43**: p. 251. (1992).
- [84] Charalambides, M., Ph.D. Thesis. Imperial College, London. (1992).
- [85] Bascom, W.D. and S. Oroshnik, *J. Materials Sci.*, **13**: p. 1441. (1978).
- [86] Briggs, D. and M.P. Seah, ed. *Practical Surface Analysis*. 2nd ed. John Wiley & Sons. Chichester. p657 (1990).
- [87] Yosomiya, R. et al., ed. *Adhesion and Bonding in Composites.*, Marcel Dekker, Inc., New York and Basel. p351. (1990).
- [88] Wang, Y. and J.G. Williams, to be published, . (1992)
- [89] Wang, Y. and J.G. Williams, Submitted for publication, *Engng. Fracture Mech.*, (1992)
- [90] Harding, J. and L.M. Welsh, *J. Materials Sci.*, **18**: p. 1810-1826. (1983).
- [91] Berry, J.P., *J. Mech. Phys. Solids*, **8**: p. 207-216. (1960).
- [92] Cogswell, F.N., *Thermoplastic Aromatic Polymer Composites*. 276. Butterworth Heinemann. Oxford. (1992).
- [93] Kinloch, A.J. and J.G. Williams, *J. Materials Sci.*, **15**: p. 987. (1980).
- [94] Kinloch, A.J. and G.K.A. Kodokian, *J. Materials Sci. Lett.*, **6**: p. 653-655. (1987).

References

- [95] Osiyemi, S.O., *The Fatigue Performance of Adhesively Bonded Fibre Composite Joints*. Ph.D. Thesis. Imperial College, London. (1992).
- [96] Wang, O. and G.S. Springer, *J. Compos. Mater.*, **23**: p. 434-447. (1989).
- [97] Brewis, D.M., *et al.*, *Europ. Polym. J.*, **17**: p. 127. (1981).
- [98] Mackie and N. Su. in proceedings of *PRI.*, University of Bristol. (1992).
- [99] Ripling, E.J., S. Mostovoy, and C.J. Bersch, *J. Adhesion*, **3**: p. 145. (1971).
- [100] Zanni-Deffarges M.P. and M.E.R Shanahan in proceedings of *Structural Adhesives in Engineering III*, University of Bristol. (1992).
- [101] Kinloch A.J., and S. Osiyemi., in proceedings of *Structural Adhesives in Engineering III*, University of Bristol. (1992).
- [102] Parker B.M., *Int. J. Adhesion and Adhesives* **10** No 3, p187 (1990).
- [103] Harding J., and K. Saka OUEL Report 1682/87.
- [104] Harding J., and Y.L. Li., *Composites Sci. and Tech.* **45** pp161-171. (1992).
- [105] Kinloch A.J., *Developments in Adhesives-2*. App. Sci. Pub. London. (1981).
- [106] Hull D., *An Introduction to Composite Materials*. Cambridge University Press. Cambridge. (1988).
- [107] Kodokian G.K.A., and A.J. Kinloch. *J. Adhesion* **29** pp193-218 (1989).
- [108] Watts J.F., and E.M. Gibson. *Int. J. Adhesion and Adhesives* **11** No 2 pp105-108 (1991).
- [109] Fakes *et al* *Surface and Interface Anal.* **10** pp416-423 (1987).
- [110] *Proceeding of the Sixteenth Annual Meeting of the Adhesion Society*. Blacksburg. Virginia USA (1993).