HYGROTHERMAL DEGRADATION OF TOUGHENED ADHESIVE JOINTS: 
THE CHARACTERIZATION AND PREDICTION OF FRACTURE PROPERTIES

by

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The main objective of this work was to develop a framework to predict the fracture toughness degradation of highly toughened adhesive joints using fracture test data obtained by accelerated open-faced degradation method.

First, the mixed-mode fracture resistance (R-curve) behavior of two rubber-toughened epoxy-aluminum adhesive systems was measured and could be fit in a bilinear R-curve model. Then, open-faced DCB (ODCB) specimens of the same adhesive systems were aged over a relatively wide range of temperature, relative humidity (RH) and time, dried and tested to characterize the irreversible evolution of the mixed-mode fracture R-curves. The R-curve bilinear model parameters of adhesive system 1 varied significantly with degradation while that of adhesive system 2 remained unchanged.

The absorption and desorption of water in the adhesives cast wafers was measured gravimetrically. The absorption data were fitted to a new sequential dual Fickian (SDF) model while water desorption was modeled accurately using Fick’s law. A significant difference was observed between the amounts of retained water in the two adhesives after drying.
An exposure index ($EI$) was defined as the integral of water concentration over time and calculated at all points in the ODCB and closed DCB joints. The fracture toughness of the closed joints was then predicted from these calculated $EI$s by making reference to fracture toughness data from the ODCB specimens degraded to various $EI$ levels. To verify the predictions, fracture experiments and analyses were carried out for closed DCB joints. Good agreement was found between the predicted and experimentally measured fracture toughness values for the degraded closed DCB joints.

Furthermore, the crack path and fracture surface characteristics were evaluated as a function of the degree of aging using optical profilometry. The unexpected crack path in the mixed-mode fracture of unaged open-faced DCB specimens was addressed. The results showed a strong relationship between fracture surface parameters and the critical strain energy release rate, $G_{cs}$, irrespective of the type of adhesive and exposure condition.
Dedicated to my beloved, Nafiseh.
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Chapter 1: Introduction

1.1. Motivation

One of the main concerns with the use of structural adhesive joints is their long term durability. For example, adhesive joints in automotive applications may be exposed to aggressive environments such as high humidity and elevated temperature during their service life. Based on experimental observations, degradation mechanisms can be classified into two categories; namely, mechanisms of bulk degradation and mechanisms of localized (interface) degradation. Plasticization and hydrolysis of the adhesive layer are the main bulk degradation mechanisms, while oxide layer hydration, substrate corrosion, and cathodic delamination are the main interface degradation mechanisms [1-4]. In general, a combination of failure modes such as cohesive, adhesive, corrosion, and coating failures may occur, depending mainly on the type of adhesive [5] or surface pretreatment [6]. It is thus very important to develop a methodology for adhesive joint durability analysis, so that a joint can be designed with durability characteristics appropriate for its service life environment.

The parameters affecting the durability of adhesive joints can be classified into two main categories: environmental parameters determined by the service conditions and system parameters that are under the control of the joint designer. The main environmental parameters that reduce joint strength are exposure to liquids or their vapours [7], ions, elevated temperature [8], and stress [9]. The most important system parameters are adhesive and adherend properties [10] such as their mechanical, physical and chemical properties, the adherend surface pretreatment [11, 12] and morphology [13, 14], and the adhesive bondline thickness. A lack of an understanding of the mechanisms by which these factors affect the joint durability have hindered the development a comprehensive design procedure for predicting the durability, or generalizing published data for use in new systems or conditions.

Water may penetrate into adhesive joints by diffusion, osmosis, wicking, and/or capillary action. Many researchers have used a simple Fickian diffusion law to model the moisture uptake when the diffusion rate is more rapid than the polymer relaxation rate, which is related to the coupled motion of chain segments as the polymer temperature increases.
through the glass transition region [1]. When the rates of uptake and polymer relaxation are comparable, a dual stage Fickian moisture uptake profile is more appropriate [15]. Most of the work on diffusion available in the literature is limited to the measurement of the water diffusion properties of adhesives at a specific exposure environment. Therefore, it is desirable to conduct a thorough study on the water uptake behavior of adhesives and develop a predictive model that can be used over a wide range of temperature and relative humidity.

Typically, accelerated degradation methods rely on modification of the specimen geometry, increased aggressiveness of the degradation environment, or contamination of the surface. Water immersion, exposure to high relative humidity and/or elevated temperature, and application of a load during exposure all have been used to accelerate degradation. Direct exposure to water creates a very steep concentration gradient, while high temperature increases the rate of chemical reactions and the diffusion coefficient, thereby promoting water diffusion [16]. The main advantage of exposure to elevated humidity as opposed to water immersion is the ability to accurately control the moisture level to which the joint is exposed, and thereby control the equilibrium water concentration within the joint [3, 17]. In addition, the availability of atmospheric oxygen aids the degradation mechanisms [18]. Applied monotonous or cyclic loads lower the activation energy required for bond rupture, making adhesive bonds more vulnerable to degradation [19]. Most of the test methodologies used in these previous studies utilizes conventional degradation of closed joints. These tests are very time-consuming since there is a very long diffusion path.

Recently, an open-faced technique has been introduced to greatly accelerate the degradation of adhesive joints. A layer of adhesive is bonded to only one adherend, leaving the other face of the adhesive free to be exposed to a humid environment at elevated temperature. The specimen is then bonded to another adherend using a second layer of adhesive to form a complete fracture specimen. It has been shown that these open-faced specimens can be used to obtain a uniform level of degradation over the entire bondline [20]. Testing of double-cantilever beam and peel specimens made using this technique showed good repeatability in measured fracture strengths. It would be desirable to develop a methodology that can predict the residual strength of an adhesive system at any environmental condition,
i.e., arbitrary combination of relative humidity, exposure time, and temperature, using experimental data from an open-faced accelerated test procedure.

In the literature, very little attention has been paid to crack initiation and the subsequent progressive development of the damage zone ahead of the crack, which results in the rising part of fracture resistance curve. Usually, the steady-state value \( G_c \) of the critical strain energy release rate, \( G_c \) is used to predict the ultimate strength of an adhesive joint. However, joints with relatively short overlaps may reach their ultimate strength and fail catastrophically before \( G_c \) reaches its steady-state value, \( G_{cs} \). In this case, use of the \( G_{cs} \) as a fracture toughness criterion will overestimate the joint strength, and the ultimate strength must be based on values of \( G_c \) taken from the rising part of the \( R \)-curve at the appropriate crack length. Furthermore, the \( R \)-curve behavior changes with the degradation. Therefore, it would be of great value to develop a method to characterize the \( R \)-curve behavior of adhesive system and investigate the evolution of this behavior with degradation.

1.2. Objectives

The main objective of this thesis is to establish a framework to predict the durability of environmentally degraded adhesively bonded joints using data from accelerated joint degradation tests. The methodology should be generally applicable, with testing and analysis procedures that can be adapted to new adhesive systems. The research emphasis is on adhesive systems used in automotive structures with metal substrates. A second major objective is to develop a means of predicting the initiation fracture toughness in either fresh or degraded joints. This is of great importance in the analysis of relatively short joints bonded with highly toughened structural adhesives, and in the context of aged joints in which the joint toughness varies with the distance from the free edge. To achieve these primary objectives the following steps will be used:

(a) A methodology will be established to characterize the fracture resistance (R-curve) behavior of degraded and undegraded toughened adhesive joints.

(b) The water absorption/desorption behavior of the adhesives will be characterized, leading to the development of a predictive diffusion model.
(c) To characterize the degradation behavior, the critical strain energy release rate of open-faced specimens aged at different combinations of exposure temperature and relative humidity for varying times will be measured.

(d) The pathway independence of the degradation will be assessed, i.e., whether or not the effects of the exposure time and water concentration could be combined into a single parameter based on time integral of the water concentration.

(e) The results from the previous steps will be combined in order to predict the fracture toughness in a closed joint using the open-faced specimens. Experiments will be performed to test the validity of the prediction.

1.3. Organization of Thesis

Each of the chapters that follow represents a research article that has been published or is currently under peer-review for publication. Some chapters have or will soon be partially presented in the four consecutive Meetings of the Adhesion Society, 2008-2011.

Chapter 2, Fracture R-curve characterization of toughened epoxy adhesives, establishes the methodology to characterize the fracture resistance behavior of toughened epoxy adhesive joints using a bilinear R-curve model. The effects of loading mode mixity, adhesive bondline thickness, and crack initiation geometry on the fracture toughness are quantified.

In Chapter 3, Hygrothermal properties of highly toughened epoxy adhesives, the absorption and desorption of water in two different rubber-toughened epoxy adhesives are measured gravimetrically and a predictive dual stage Fickian diffusion model is proposed.

Chapter 4, Fracture R-curve of a toughened epoxy adhesive as a function of irreversible degradation, investigates the evolution of the fracture resistance behavior as a function of the environmental degradation of an aged toughened epoxy adhesive. The effects of water concentration, exposure temperature and relative humidity on the R-curve bilinear model parameters are quantified.

Chapter 5, Hygrothermal degradation of two rubber-toughened epoxy adhesives: Application of open-faced fracture tests, characterizes the steady-state critical strain energy
release rate of aged open-faced DCB joints as a function of exposure time, temperature and relative humidity for two substantially different adhesives. A degradation mechanism which accounts for the different characteristics of the two adhesive systems is proposed. The pathway independence of the degradation is also assessed.

Chapter 6, *Crack path selection in the fracture of fresh and degraded epoxy adhesive joints*, and Chapter 7, *Evolution of crack path and fracture surface with degradation in rubber-toughened epoxy adhesive joints: application to open-faced specimens*, investigate the changes in the crack path and fracture surface micro-topography caused by the degradation. The effects of adding the secondary layer on the primary aged layer, i.e. the change of the cure state and residual stress state are discussed. An unexpected crack path that is found for the undegraded open-faced DCB joints is explained in terms of the residual stress distribution in the layers. A crack growth mechanism, consistent with the highly three-dimensional nature of the fracture surface in undegraded joints, is proposed to explain the ductile-to-brittle transition that occurs in the fracture behavior of the joints as degradation progresses.

Chapter 8, *Prediction of environmental degradation of closed adhesive joints using data from open-faced specimens*, establishes the framework to predict the effective steady-state critical strain energy release rate of the closed DCB joints degraded at given exposure environments. The framework uses the experiments performed on open-faced specimens, together with the water absorption/desorption data and the exposure index concept. Results of tests performed on degraded closed DCB joints to validate the predictions of the framework and the validity of the degradation path independence are also presented.

Chapter 9 summarizes the major occlusions and recommended future work.
1.4. References

Chapter 2: Fracture $R$-curve characterization of toughened epoxy adhesives$^{1,2}$

2.1. Introduction

The prediction of the strength of adhesively bonded joints has been investigated using a variety of failure criteria such as maximum stress or strain, and fracture mechanics approaches [1-7]. Fracture mechanics approaches based on the critical strain energy release rate, $G_c$, for crack propagation are applicable to highly cross-linked structural adhesives and have the advantage of avoiding the explicit consideration of the bi-material singularities inherent in adhesive joints.

Crack extension in rubber toughened adhesive joints begins with the cavitation of rubber particles followed by void growth and induced shear yielding of the matrix. These processes and the development of micro-cracks lead to the progressive development of a damage zone [8]. As the load on the joint increases, the largest microcracks coalesce to form a macro-crack, which then grows as new microcracks and the damage zone advance into the adhesive layer [9-10]. During these early stages of fracture, the damage zone continues to expand ahead of the growing macro-crack, leading to a progressive toughening of the joint as increasing amounts of strain energy are dissipated by the plastic deformation and micro-cracking. This process results in the fracture resistance curve ($R$-curve) of $G_c$ versus the crack length. Eventually, the damage zone reaches a steady-state size and the $G_c$ becomes constant, no longer increasing with macro-crack length. This steady-state value of $G_c$ ($G_{cs}$) has been used to predict the ultimate strength of a wide range of adhesive joints [5]. However, joints with relatively short overlaps may reach their ultimate strength and fail catastrophically before $G_c$ reaches its steady-state value, $G_{cs}$. In this case, use of the $G_{cs}$ as a fracture toughness criterion

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will overestimate the joint strength, and the ultimate strength must be based on values of $G_c$ taken from the $R$-curve at the appropriate crack length.

The concept of the $R$-curve was initially introduced by Irwin to study crack growth in metals, and has been recognized in the fracture analysis of other materials such as composites, ceramics, polymers and quasi-brittle materials. Numerous researchers have investigated the effects of various factors such as specimen geometry and material properties on the $R$-curve, and have shown that it may be used in design methodologies [11-14].

There are only few recent studies on the $R$-curve behavior in adhesively bonded joints. Imanaka et al. studied the mode-II $R$-curve characteristics of rubber-modified and unmodified epoxies using end-notched flexure specimens in four-point bending. $R$-curve behavior was only observed with the rubber-modified epoxy, presumably because the unmodified epoxy did not develop an appreciable damage zone [15]. Imanaka et al. also compared the $R$-curves of two rubber-modified epoxy adhesives that were cast into bulk single-edge-notch bend specimens for mode I testing [16].

In this Chapter, the $R$-curves of two different rubber-toughened epoxy adhesives were measured using double cantilever beam (DCB) specimens tested under several mixed-mode loading conditions. The effect of bondline thickness was investigated, as was the relationship between crack initiation and the local geometry at the end of the adhesive bondline. The results have application for the prediction of the strength of adhesive joints with relatively short overlap lengths – shorter than required to reach $G_{cs}$.

2.2. Experimental procedures

2.2.1. Materials and joint fabrication

Two different adhesive systems were investigated in this study. Adhesive system is referred to a combination of specific adherend and adhesive with special surface treatment and known bondline thickness. DCB specimens (Fig. 2.1) of adhesive systems 1 and 2 were made using two different commercial heat-cured toughened structural epoxy adhesives (Table 2.1)
using the recommended curing profile of at least 30 min at 180°C, monitored using a thermocouple embedded in the adhesive layer of the joints.

![Diagram of DCB specimen](image)

**Figure 2.1:** DCB specimen geometry and dimensions.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Parameter</th>
<th>Size</th>
</tr>
</thead>
<tbody>
<tr>
<td>(L)</td>
<td>Specimen length</td>
<td>(\sim 250) mm</td>
</tr>
<tr>
<td>(h)</td>
<td>Adherend thickness</td>
<td>12.7 or 6.35 mm</td>
</tr>
<tr>
<td>(t)</td>
<td>Adhesive layer thickness</td>
<td>0.4 mm</td>
</tr>
<tr>
<td>(w)</td>
<td>Adherend width</td>
<td>19-21 mm</td>
</tr>
<tr>
<td>(a_0)</td>
<td>Precrack length</td>
<td>Variable</td>
</tr>
<tr>
<td>(\Delta a)</td>
<td>Crack length increment</td>
<td>Variable</td>
</tr>
<tr>
<td>(a)</td>
<td>Crack length</td>
<td>Variable</td>
</tr>
<tr>
<td>(P_1)</td>
<td>Upper adherend load</td>
<td>Variable</td>
</tr>
<tr>
<td>(P_2)</td>
<td>Lower adherend load</td>
<td>Variable</td>
</tr>
</tbody>
</table>

**Table 2.1:** Mechanical and physical properties of adhesives 1 and 2.

<table>
<thead>
<tr>
<th>Adhesive</th>
<th>Elastic modulus, (E), MPa</th>
<th>Poisson ratio, (\nu)</th>
<th>Tensile strength, (\sigma_y), MPa</th>
<th>Glass transition temperature, (T_g), °C</th>
<th>Cured density g/cm(^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adhesive 1</td>
<td>1.96</td>
<td>0.45</td>
<td>44.8</td>
<td>125</td>
<td>1.50</td>
</tr>
<tr>
<td>Adhesive 2</td>
<td>1.73</td>
<td>0.39</td>
<td>N/A</td>
<td>122</td>
<td>1.14</td>
</tr>
</tbody>
</table>

The DCB adherends were AA6061-T6 for the tests at lower mode ratios, and AA7075-T6 for the higher mode ratio tests in order to prevent adherend yielding. The crack paths were cohesive in all cases, so the change in adherends did not influence the measured \(G_c\). The adherends were pretreated using the P2-etch method [17] which included mechanical abrading, acetone immersion, and sulphuric acid etching to remove the existing aluminum.
oxide layer. In most cases, a precrack was created by embedding a folded 10 µm aluminum foil within the adhesive layer. To minimize the possibility of mechanical damage to the specimen edges after curing, the very small amount of residual adhesive that had flowed from the edges of the DCB specimens was removed using a gentle wet sanding process (final stage 300 grit). A very thin layer of white paper correction liquid, diluted with hexane, was applied to the specimen edges to assist in the identification of the macro-crack tip.

To investigate the effect of the precrack geometry on $G_c$ at initiation, $G_{ci}$, four different crack starting geometries were tested (Fig. 2.2). A folded aluminum foil was used to create relatively sharp precracks, while steel wire or PTFE sheet were used to simulate blunter adhesive end conditions. To evaluate the effect of adherend thickness on the $R$-curve behavior, DCB adherends of 12.7 and 6.35 mm thickness were employed. The bondline thickness and phase angle were kept at 0.4 mm and 27°, respectively, in all of these tests.

![Figure 2.2: Schematic of the sharp and blunted geometries used as the starting condition at the end of the adhesive bondline.](image)

**2.2.2. Fracture test methodology**

The fracture tests were conducted using a servo-electric load frame and the load jig of [18] (Fig. 2.3) which could generate the entire range of mode ratios using a single DCB specimen
geometry. For a given configuration of the links ($s_1$-$s_4$ in Fig. 2.3), the mode ratio was independent of the crack length. A second version of the load jig that had rollers in place of the two triangular end supports produced the same results.

Figure 2.3: (a) Photo of the experimental setup, and (b) Schematic illustration of mixed-mode loading system with DCB specimen in place [18].
Crack growth under displacement control was essentially stable with this system so that multiple crack extension events could be recorded with a single DCB. Two different methods were used to record the critical load at which a crack started to grow from either the as-bonded condition (with an artificial precrack) or from a growing crack. The crack length, \( a \) (Fig. 2.1), was determined to an accuracy of \( \pm 20 \) \( \mu m \) in both methods using an optical microscope on a micrometer stage having a field of view of 2 mm. In the first method, the specimen was loaded under displacement control at a crosshead speed of 1.5 mm/min until a maximum load was recorded. The crosshead was then stopped and the maximum load and corresponding crack length were used to calculate \( G_c \). It was observed that no crack extension occurred prior to the attainment of the maximum load. Because a small amount of overloading was inevitable in this approach, the crack was observed to grow unstably for 5-10 mm, making it difficult to obtain more than a few points on the rising part of the \( R \)-curve. In the second method, the specimen was loaded in discrete small steps while viewing the crack tip through the microscope to detect the onset of crack propagation at the critical load. This resulted in much shorter crack propagation increments (approximately 1 mm), allowing more data points to be recorded during the initial stages of the crack propagation on the rising part of the \( R \)-curve.

Crack initiation at a load \( P_{ci} \) was defined as the first crack extension of approximately 50 \( \mu m \) from the bondline terminus (foil, wire or PTFE precrack). This was the shortest extension that could be reliably detected. In some instances the first crack did not appear to grow from the terminus, but would be seen somewhere in a region within 50 \( \mu m \) of the foil, wire or PTFE.

### 2.3. Fracture toughness calculations

A beam-on-elastic-foundation model which accounts for the presence of the adhesive layer was used to calculate \( G_c \) [5]. The adherends were modelled using Euler-Bernoulli beam theory and the adhesive layer as an elastic foundation supporting transverse normal and shear stresses.

The load jig used for the fracture tests was statically determinate, and the upper and lower adherend loads \( P_1 \) and \( P_2 \) (Fig. 2.1) are given from equilibrium considerations of the link-arm system as:
\[ P_1 = P_c \left( 1 - \frac{s_1}{s_3} \right) \]  
(1)

\[ P_2 = P_1 \frac{s_1 / s_2}{1 + s_3 / s_4} \]  
(2)

where \( s_1, s_2, s_3 \) and \( s_4 \) are defined in Fig. 2.3b as distances between the pin centres and \( P_c \) is the critical load recorded at the onset of crack propagation. The nominal phase angle of loading is defined as:

\[ \psi = \arctan \left( \sqrt{\frac{G_{IIc}}{G_{Ic}}} \right) \]  
(3)

where 0° and 90° correspond to mode I and mode II, respectively. The final expressions for \( G_c \) and \( \psi \) are then [18]:

\[ G_c = \frac{(P_1 a)^2}{2D} \left[ 1 + \left( \frac{P_2}{P_1} \right) - \frac{1}{8} \left( 1 + \frac{P_2}{P_1} \right)^2 \right] \]  
(4)

\[ \psi = \arctan \left[ \frac{\sqrt{3}}{2} \left( \frac{P_1}{P_2} + 1 \right) \left( \frac{P_1}{P_2} - 1 \right) \right] \]  
(5)

where \( D \) is the flexural rigidity per unit width of the adherends defined as:

\[ D = \frac{Eh^3}{12} \]  
(6)

assuming the adherends are under plane stress. \( E \) and \( h \) are the Young’s modulus and thickness of the adherend, respectively (Fig. 2.1). This procedure yielded results that were very close to those calculated using the British Standard (BS7991:2001) [19], as shown in the Appendix.

2.4. Results and discussion

2.4.1. Validation of methods

Figure 2.4 shows the load versus crosshead displacement curves for five different crack growth events corresponding to the plateau part of the \( R \)-curve where \( G_c = G_{cs} \). The slope of the initial linear part of each curve beyond 0.3 mm displacement was used to calculate the compliance of the load jig/DCB system. The nonlinearity at smaller displacements was due to...
the settling of links in the load jig at the start of the test. The compliance of the load jig itself was measured using a stiff steel block in place of a DCB specimen. The joint compliance was then calculated by subtracting the load jig compliance from the total system compliance. Table 2.2 shows the critical load, specimen compliance, and specimen displacement at different optically measured crack lengths. As expected, the load decreased while the compliance and displacement of the specimen increased with crack length.

![Graph](image.png)

**Figure 2.4:** Load vs. crosshead displacement up to adhesive crack extension at different initial crack lengths for a DCB specimen in the load jig (Fig. 2.3).

**Table 2.2:** Critical load, specimen compliance, and loading pin displacement at the onset of crack propagation with different initial crack lengths for adhesive system 1.

<table>
<thead>
<tr>
<th>Crack length $a$ (mm)</th>
<th>Critical load $P_c$ (N)</th>
<th>Compliance $C$ (mm/N)</th>
<th>Displacement $\delta$ (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>80.6</td>
<td>2642</td>
<td>$6.8 \times 10^{-4}$</td>
<td>1.79</td>
</tr>
<tr>
<td>88.9</td>
<td>2335</td>
<td>$9.1 \times 10^{-4}$</td>
<td>2.12</td>
</tr>
<tr>
<td>97.7</td>
<td>2166</td>
<td>$1.14 \times 10^{-3}$</td>
<td>2.46</td>
</tr>
<tr>
<td>105.6</td>
<td>2032</td>
<td>$1.40 \times 10^{-3}$</td>
<td>2.85</td>
</tr>
<tr>
<td>115.3</td>
<td>1895</td>
<td>$1.74 \times 10^{-3}$</td>
<td>3.30</td>
</tr>
</tbody>
</table>
Figure 2.5 shows the average $G_{cs}$ values calculated using the three methods prescribed by British Standard BS7991:2001 [19] (see Appendix) and the data of Table 2.2. The simple beam theory (SBT), corrected beam theory (CBT), and experimental compliance method (ECM) gave very similar results. As expected, the SBT formulation resulted in the lowest value of $G_{cs}$, because it employs simple beam theory which assumes that the joint is a perfectly cantilevered DCB specimen, thereby underestimating the compliance. The CBT result was slightly greater than that of the SBT because of the crack-length correction factor which increases the effective crack length to compensate for the compliance underestimation. ECM, which uses the experimentally measured compliance to calculate $G_{cs}$, resulted in the highest value of $G_{cs}$ amongst the three methods of the British Standard. Figure 2.5 also shows that the $G_{cs}$ calculated using the present beam-on-elastic-foundation model (BoEF) was approximately 5% greater than those found with the CBT and ECM. A t-test analysis showed that the difference between these $G_{cs}$ values was not statistically significant with a confidence interval of 95%. A principal limitation of the three British Standard methods is that they cannot be used for mixed-mode loading; therefore, the BoEF method was used for all further calculations.
To investigate the accuracies of the optical crack length measurement and the determination of the critical load when using the manual start-stop methodology (i.e. loading in discrete small steps as described in Section 2.2), a series of automatic and start-stop fracture tests were compared under mode I loading. To avoid any specimen–to-specimen or batch-to-batch variation, comparisons of the loading methods were made using single DCB specimens of adhesive system 1 with a constant loading rate of 1.5 mm/min. Table 2.3 shows that the difference between the average $G_{cs}$ values using the automated and manual modes was approximately 5%, which was statistically insignificant at the 95% confidence level.

Table 2.3: $G_{cs}$ values measured using automated and manual loading modes at different crack lengths for adhesive system 1.

<table>
<thead>
<tr>
<th>Data point</th>
<th>$G_{cs}$ (Jm$^{-2}$)</th>
<th>Automated</th>
<th>Manual</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3397</td>
<td>3133</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>3163</td>
<td>3146</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>3220</td>
<td>3059</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>3269</td>
<td>3040</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>3337</td>
<td>3095</td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>3261</td>
<td>3095</td>
<td></td>
</tr>
<tr>
<td>SD</td>
<td>93</td>
<td>94</td>
<td></td>
</tr>
<tr>
<td>Difference</td>
<td>5%</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2.4.2. Characterization of $R$-curves

Figure 2.6 shows the critical load at the onset of crack extension as a function of crack length increment, $\Delta a$ (Fig. 2.1) for adhesive systems 1 and 2 at a phase angle of 27°. By employing the manual start-stop loading methodology, it was possible to record 30 to 40 data points within a crack growth range of less than 60 mm. The critical load increased significantly with crack length increment during the initial stages of crack propagation up to approximately $\Delta a=12$ mm, after which it decreased. The initial increase in critical load corresponded to the subcritical crack growth region in which the adhesive toughened as the damage zone developed until it reached a steady-state size. The second part of the curves, where the critical load decreases, was due to the increasing DCB compliance and the constant $G_{cs}$. 

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Figure 2.7 shows the typical $R$-curves obtained for adhesive systems 1 and 2 at a phase angle of 27°. The data fit well to a simple bilinear model as shown by the least-squares regression lines fitted to the rising and steady-state parts of the $R$-curve.

![Graph showing typical $R$-curves for adhesive systems 1 and 2.](image)

Figure 2.6: Critical load at the onset of crack extension versus crack length increment (Fig. 2.1) for both adhesive systems at a phase angle of 27°.

![Graph showing critical load at crack extension versus crack length increment.](image)

Figure 2.7: Typical $R$-curves of adhesive systems 1 and 2 and least squares regression lines for the rising and steady-state regions.

![Graph showing $R$-curves for adhesive systems 1 and 2.](image)
Three independent parameters were required to characterize the bilinear model (Fig. 2.8): the steady-state critical strain energy release rate, $G_{cs}$, the slope of the rising line, $(dG_{cr}/da)$, and the length of the rising part ($L_r = a_r - a_0$). $G_c$ as a function of crack length was thus represented as:

$$
G_c = \begin{cases} 
G_{cr}(a) = G_{ci} + \frac{dG_{cr}}{da}(a - a_0), & a_0 < a < a_r \\
G_{cs}, & a \geq a_r
\end{cases}
$$

where the subscripts $r$ and $s$ represent the rising and steady-state values of the critical strain energy release rate, respectively. The initial distance from the loading pins was $a_0$ and the crack length corresponding to the end of rising part was $a_r$. $G_{ci}$ was the initiation $G_c$ at which the crack started to grow from the adhesive terminus.

![Schematic representation of the bilinear R-curve model.](image)

To investigate the bilinear model further, six DCB specimens of adhesive system 2 with different precrack lengths ($a_0$, Fig. 2.1) were fracture tested at a phase angle of 27° using the manual loading methodology to obtain the $R$-curves. Figure 2.9 shows the rising parts of these six $R$-curves and the regression lines. Noting that only three out of the four parameters of the
bilinear model are independent, the averaged values of $G_{cs}$ and the length and slope of the rising part could be used to calculate the $G_{ci}$ for comparison with the measured values of $G_{ci}$. The average values and the standard deviations of the model parameters obtained from these tests are presented in Table 2.4. The average predicted $G_{ci}$ using the bilinear model parameters was 481 Jm$^{-2}$, which was 10% less than the average measured $G_{ci}$ of 537 Jm$^{-2}$. Noting that the standard deviation of the measured $G_{ci}$ was relatively high (25%), the calculated and measured values of $G_{ci}$ were in good agreement.

Figure 2.9: The rising parts of the $R$-curves and least squares regression lines for six different DCB specimens of adhesive system 2 tested at a phase angle of 27° with different folded foil precrack lengths, $a_0$.

<table>
<thead>
<tr>
<th></th>
<th>$G_{cs}$ (Jm$^{-2}$)</th>
<th>$dG_{cs}/da$ (Jm$^{-2}$/mm)</th>
<th>$L_R$ (mm)</th>
<th>$G_{ci}$ (Jm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ave.</td>
<td>4768</td>
<td>324</td>
<td>13.2</td>
<td>537</td>
</tr>
<tr>
<td>SD</td>
<td>186</td>
<td>41</td>
<td>1.0</td>
<td>139</td>
</tr>
</tbody>
</table>
2.4.3. The effect of adherend stiffness on the bilinear model parameters

It is known that in general the $R$-curve cannot be considered to be an intrinsic fracture characteristic of a material since it is geometry-dependent [20-22]. Hutchinson and Suo argued that a thicker and so stiffer beam should show a longer rising part, while the $G_{cs}$ is independent of the stiffness and is therefore a material property for a given composite laminate [20]. They reasoned that $G_{cs}$ is attained when a critical crack opening is achieved. For an adhesive joint of a given precrack length, stiffer adherends increase the resistance to adherend deflection and should thus yield a longer rising part of the $R$-curve.

In the present work, it was hypothesized that the $R$-curve dependence on adherend stiffness was relatively weak provided that the adherends deform only elastically. To investigate the sensitivity of the $R$-curve bilinear model parameters to changes in adherend stiffness, mixed-mode DCB fracture tests of adhesive system 1 were performed with two different adherend thicknesses – 12.7 mm and 6.35 mm. A finite element analysis and the absence of any residual curvature confirmed that the adherends remained completely elastic in both cases. There was no statistically significant difference between the average values (Table 2.5) of the $R$-curve bilinear model parameters for the two adherend thicknesses (t-test, 95% confidence). Therefore, the hypothesis was supported since a relatively large change in the adherend flexural rigidity (8 times) did not produce a significant change in the bilinear model parameters.

It was of interest to estimate the length of the process zone in joints made with these two adherend thicknesses since this should be proportional to the length of the rising part of the $R$-curve. Cohesive zone elements (ANSYS® 11, INTER 202) with a mode I exponential traction-separation law were used to model the crack path, and 2D structural solid elements (PLANE 182) with plane stress and plain strain options were used to model the adherends and adhesive, respectively. The maximum normal traction and the corresponding normal separation values were found using the experimental load-displacement curve and steady state $G_c$ obtained in mode I fracture testing of adhesive system 1. A process zone length (PZL) was defined as the distance from the crack tip to the point where the von Mises stress was 10% of the maximum seen at the crack tip. The PZL values for the adherend thicknesses of 12.7 mm and 6.35 mm were 7.9 mm and 5.5 mm, respectively. Thus an eight-fold increase in bending stiffness produced a 1.4 increase in the PZL. However, as mentioned above, the
The experimental data of Table 2.5 showed that this resulted in a statistically insignificant increase in the length of the rising part of the $R$-curve by a factor of 1.2.

Table 2.5: The average and standard deviation of the bilinear model parameters for adhesive system 1 with the adherend thicknesses of 12.7 mm and 6.35 mm. 12 and 4 DCB specimens were tested for the adherend thicknesses of 12.7 mm and 6.5 mm, respectively.

<table>
<thead>
<tr>
<th></th>
<th>6 mm</th>
<th></th>
<th>12 mm</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ave.</td>
<td>SD</td>
<td>Ave.</td>
<td>SD</td>
</tr>
<tr>
<td>$G_{cs}$ (Jm^{-2})</td>
<td>3960</td>
<td>515</td>
<td>4290</td>
<td>425</td>
</tr>
<tr>
<td>$G_{ci}$ (Jm^{-2})</td>
<td>620</td>
<td>55</td>
<td>535</td>
<td>95</td>
</tr>
<tr>
<td>$dG_{cs}/da$ (Jm^{-2}/mm)</td>
<td>456</td>
<td>89</td>
<td>413</td>
<td>102</td>
</tr>
<tr>
<td>$L_R$ (mm)</td>
<td>7.51</td>
<td>1.16</td>
<td>9.14</td>
<td>1.74</td>
</tr>
</tbody>
</table>

2.4.4. The effect of mode ratio on the $R$-curve bilinear model parameters

The ultimate strength of sufficiently long adhesive joints can be predicted using the fracture envelope; i.e. the steady-state critical strain energy release rate, $G_{cs}$, as a function of the mode ratio of loading. Prediction of the ultimate strength of shorter joints which might not attain sufficiently long crack lengths to establish a steady-state crack tip damage zone requires consideration of the dependence of the $R$-curve on the mode ratio.

Figures 2.10-2.12 show the variation of the bilinear $R$-curve model parameters with phase angle for both adhesive systems 1 and 2. As seen in Fig. 2.10, $G_{cs}$ and $G_{ci}$ both changed very little between phase angles of 0° and 27°, but increased considerably at higher phase angles. This highly nonlinear behavior of $G_{cs}$ with mode ratio agrees with previous experience in which relatively large increases in $G_{cs}$ were measured only at higher phase angles [5, 23]. It is interesting that $G_{ci}$ displayed a similar trend, albeit with greater scatter. The increased scatter in the $G_{ci}$ data is mainly a consequence of three factors: 1. Each data point is a single measurement, whereas $G_{cs}$ is an average of many crack growth events in the steady-state region of the $R$-curve. 2. Each crack initiation begins from a microscopically unique geometry and local environment. 3. There is a greater uncertainty in the detection of crack initiation than
in the identification of the load at which existing cracks extend. In the latter case, attention can be focused on the point where crack growth will occur and the likely critical load is also known.

As depicted in Fig. 2.11, the slope of the rising part \( \frac{dG_{cr}}{da} \) of the \( R \)-curve did not show any clear dependence on phase angle, implying that the rate of damage zone development was unaffected by the mode ratio. However, the length of the rising part of the \( R \)-curve increased with phase angle as shown in Fig. 2.12. This is consistent with the expectation that higher phase angles would produce more shear deformation causing micro-cracks to initiate over a longer distance ahead of the macro-crack tip. The damage zone was therefore longer at higher phase angles and consequently the \( G_{cs} \) was also greater (Fig. 2.10).

2.4.5. The effect of bondline thickness on the \( R \)-curve bilinear model parameters

It is known that the steady-state fracture toughness of adhesive joints increases with the bondline thickness [24-26]. For thin adhesive layers, the relatively larger constraint of the adherends constrains the damage zone, thus decreasing the fracture resistance. Duan et al. [26] showed that as long as the bondline thickness is much smaller than the adherend thickness, so that the adhesive bondline does not behave as a bulk sample, the steady-state fracture toughness increases linearly with bondline thickness.

![Figure 2.10: Variation of Gcs and Gci with phase angle for adhesive systems 1 and 2. Three replications of DCB fracture tests were conducted at each phase angle. Solid and hollow symbols denote Gci and Gcs, respectively. The lines connect the average values.](image-url)
Figure 2.11: Variation of the slope of the rising part of the $R$-curve with phase angle for adhesive systems 1 and 2. Three replications of DCB fracture tests were conducted at each phase angle. The lines connect the average values.

Figure 2.12: Variation of the length of the rising part with phase angle for adhesive systems 1 and 2. Three replications of DCB fracture tests were conducted at each phase angle. The lines show the least squares regression fits of the average values.
Figures 2.13-2.15 show the variation of the bilinear R-curve model parameters with the bondline thickness for adhesive system 1 at 27° phase angle. The increase of all model parameters with bondline thickness appeared to be approximately linear. When the bondline thickness increased, the adherend constraint on the layer decreased so that the damage zone developed faster and to a greater extent. Consequently, the slope and the length of the rising part of the R-curve increased with the bondline thickness (Figs. 2.14 and 2.15). The increase in both these parameters with bondline thickness resulted in an increased $G_{cs}$ (Fig. 2.13). As might be expected, $G_{ci}$ showed a weaker dependence on the bondline thickness than did $G_{cs}$; i.e. the rate of $G_{ci}$ increase with bondline thickness is 8 times smaller than that of $G_{cs}$ (Fig. 2.13). This is likely because the damage zone just starts to develop at the onset of crack propagation and so is relatively small and unaffected by adherend constraint.

![Figure 2.13: The variation of $G_{cs}$ and $G_{ci}$ with bondline thickness for adhesive system 1. Three replications of the fracture test were done at each thickness. Solid and hollow symbols denote $G_{ci}$ and $G_{cs}$, respectively. The line shows the least squares regression fit of the average values.](image-url)
Figure 2.14: The variation of the slope of the rising part with bondline thickness for adhesive system 1. Three replications of the fracture test were done at each thickness. The line shows the least squares regression fit of the average values.

Figure 2.15: The variation of the length of the rising part of the $R$-curve with bondline thickness for adhesive system 1. Three replications of the fracture test were done at each thickness. The line shows the least squares regression fit of the average values.
2.4.6. The effect of initial geometry on the R-curve bilinear model parameters

Figure 2.16 shows the $G_{ci}$ values for both adhesive systems 1 and 2 with the four precrack initial geometries of Fig. 2.2; i.e. foil, 45° and 90° PTFE sheet, and steel wire. The grand average of all $G_{cs}$ values obtained with the specimens used to test the different initiation geometries were 4456 Jm$^{-2}$ and 4360 Jm$^{-2}$ for adhesive systems 1 and 2, respectively. As expected, the difference between the steady-state fracture energies, $G_{cs}$, for the joints with different initial geometries was found to be statistically insignificant because of the crack propagation in the rising part of the $R$-curve. The differences in the $G_{ci}$ values for the four starting geometries were statistically significant at 95% confidence, and the $G_{ci}$ appeared to increase as the shape became blunter; i.e. the relatively sharp geometry produced by the foil, followed by the 45° PTFE sheet, the 90° PTFE sheet, and the bluntest produced by the steel wire.

Figure 2.16: $G_{ci}$ for different initial geometries. The results for the three replications of each fracture test are shown for each geometry and the average value is given within each column. Numbers 1 and 2 on the horizontal axis indicate the adhesive systems 1 and 2, respectively.
Even though the differences between $G_{ci}$ values for the four starting geometries were statistically significant, they were all considerably lower than the corresponding $G_{cs}$ values. In fact, the $G_{ci}$ values for the four starting geometries were 11 - 16% of the average $G_{cs}$ for adhesive system 1, and 9 - 14% of the average $G_{cs}$ for adhesive system 2. This relatively small variation of $G_{ci}$ with the four different precrack geometries suggests that a single value of $G_{ci}$ might be employed as an approximate measure of initiation strength, in some cases. For example, in automotive and other industrial applications there will inevitably be a wide range of local geometries at the ends of adhesive joints, and the estimate of the corresponding crack initiation loads cannot be made with great accuracy. The use of an average or lower bound $G_{ci}$ for all starting geometries may be useful in these cases.

Mohammed and Liechti have addressed the effect of initial geometry by looking at the effect of corner angle on bimaterial corner stresses [27]. They have shown that the change in the corner angle can significantly change the stress concentration at the bimaterial corner when the modulus elasticity ratio of the two materials is as high as 0.5. However, in the case of adhesive joints with stiff adherends, such as the aluminum adherends studied here, the elasticity modulus ratio of the adhesive layer ($E \approx 1.5$ GPa) and aluminum substrate ($E \approx 71$ GPa) is relatively small ($\approx 0.02$). This significantly reduces the effect of the corner angle on the stress concentration at the corner [27]. For example, for the ratio of 0.01, no change in the stress concentration factor was reported for a 45° change in the corner angle and that of the ratio of 0.02 was little [27]. This is consistent with the conclusion drawn here that the different starting geometries had little effect on the $G_{ci}$ and thus a single average or lower bound $G_{ci}$ could be suggested for all starting geometries in these adhesive systems.

Figures 2.17 and 2.18 show the slope and the length of the rising part of the bilinear $R$-curve model for the different starting geometries for adhesive systems 1 and 2. As expected, no clear trend was found between the slope or the length of the rising part and the sharpness of the initial geometry. It is logical to assume that the effects of starting geometry disappear after an approximately millimeter of crack growth. In the case of adhesive 2, the difference between both the slope and length of the rising part obtained with the foil and wire precracks was found to be statistically insignificant with a 95% confidence level. In the case of adhesive 1,
the PTFE precracks resulted in higher values of the slope and lower values of the rising length compared to those of the foil and wire precracks (t-test, 95% confidence). However, it is likely that these differences were an artifact of experimental scatter.

The length of the rising part of the $R$-curve, especially at the higher phase angles, appeared to be relatively long, approximately 20 mm. This places a lower bound on the overlap length of adhesive joints that are intended to reach their maximum ultimate strength as determined by $G_{cs}$. For instance, joints with adhesive 1 or 2 having an overlap length of 10-15 mm that are subject to mixed-mode loading with phase angles of roughly 45° to 55° will likely fracture before reaching $G_{cs}$ (Fig. 2.12). Predicting the ultimate load of such joints requires knowledge of $G_{cr}$ as a function of crack growth increment in the rising part of the $R$-curve. For example, if the overlap length of an arbitrary joint (mixed mode I-II) made of adhesive system 1 (bondline thickness of 0.4 mm) is 10 mm and is loaded with a phase angle of 47°, the predicted $G_{cr}$ when the crack reaches the end of the overlap based on the bilinear model is approximately 4,800 Jm$^{-2}$ while the $G_{cs}$ is 8,200 Jm$^{-2}$.

![Figure 2.17: The slope of the rising line for different initial geometries. The results for the three replications of each fracture test are shown for each geometry and the average value is given within each column. Numbers 1 and 2 on the horizontal axis indicate the adhesive systems 1 and 2, respectively.](image-url)
Figure 2.18: The length of the rising part for different initial geometries. The results for the three replications of each fracture test are shown for each geometry and the average value is given within each column. Numbers 1 and 2 on the horizontal axis indicate the adhesive systems 1 and 2, respectively.

Another implication of the work relates to the strength of adhesive joints that have degraded due to water diffusion from the end of the overlap. Since water diffusion will usually be limited to relatively short distances from the free edge of the bondline, the $G_{cr}$ values on the rising part of the $R$-curve will be degraded the most and will govern the ultimate strength of relatively short joints.

2.5. Conclusions

The $R$-curves for two different toughened epoxy adhesive systems were measured as a function of the mode ratio, bondline thickness, and initiation geometry at the end of the adhesive layer. The data could be fit to a bilinear model representing the rising part and steady-state region of the $R$-curve. The bilinear model parameters appeared to be largely independent of the precrack starting geometry, suggesting that the initiation fracture energy, $G_{ci}$, may be used as a measure of the initiation strength of manufactured joints where the adhesive layer local end geometry is quite variable. The bilinear model parameters did not show a significant dependence on the adherend thickness, suggesting that they can be uniquely determined for a given adhesive system which is loaded elastically. The initiation $G_{ci}$ the
steady-state $G_{cs}$, the slope and the length of the rising part of the $R$-curve all increased with the adhesive layer thickness. Increasing the phase angle of loading caused $G_{ci}$ and $G_{cs}$ to increase along with the length of the rising part of the $R$-curve. The slope of the rising part was not a significant function of the phase angle.

2.6. Appendix

Figure 2.5 compared the method used to calculate $G_c$ (Eqs. (1-6)) with the British Standard BS7991:2001 [19] that specifies three different methods for the calculation of mode I $G_c$:

a) Simple beam theory (SBT):

$$G_{tc} = \frac{4P_c^2}{Ew^2} \left( \frac{3a^2}{h^3} + \frac{1}{h} \right)$$ \hspace{1cm} (8)

where $P_c$ is the fracture load, $w$ is the adherend width, $a$ is the crack length, $E$ is Young’s modulus and $h$ is the adherend thickness.

b) Corrected beam theory (CBT):

$$G_{tc} = \frac{3P\delta}{2w(a + |\Delta|)}$$ \hspace{1cm} (9)

where $\delta$ is DCB joint displacement at the point where the load is applied, and $\Delta$ is a crack-length correction, defined as the x-axis intercept of the $C^{1/3}$ versus $a$ curve, where $C$ is the joint compliance.

c) Experimental compliance method (ECM):

$$G_{tc} = \frac{nP\delta}{2wa}$$ \hspace{1cm} (10)

where $n$ is the slope of the $\log(C)$-$\log(a)$ plot.
2.7. References


[19] BSI. Determination of the mode I adhesive fracture energy, GIC, of structural adhesives using the double cantilever beam (DCB) and tapered double-cantilever beam (TDCB) specimens. 2001:BS 7991.


Chapter 3: Hygrothermal properties of highly toughened epoxy adhesives

3.1. Introduction

It is widely known that the water ingress plays a significant role in the progressive degradation of the mechanical properties and hence the durability of epoxy adhesives. Many of the diffusion models that have been proposed to explain hygrothermal effects in epoxies fall into two categories. One is defined by the assumption that water diffuses into the epoxy and resides in the free volume of the material. The other assumes that absorbed water molecules couple strongly with certain hydrophilic functional groups such as hydroxyls in the epoxy resin. However, some researchers have shown that both physical and chemical mechanisms may occur simultaneously [1-4].

The simplest diffusion model is Fick’s law, which assumes that there are no interactions between the absorbed water molecules and the polymer chains. Simple Fickian behavior is observed in epoxies well above the glass transition temperature, $T_g$ [5]. In many cases, however, the simple Fickian model does not represent the absorption process and tends to overestimate water concentration [1-3, 6-9]. Such cases are called non-Fickian or anomalous.

One class of diffusion models proposed for the anomalous behaviour of water diffusion into epoxy adhesives is based on modifications to Fick’s law. For example, the dual Fickian diffusion model assumes that the diffusion is Fickian, but occurs through two different mechanisms acting in parallel with different diffusion properties [8-10]. The dual Fickian model is hence the superposition of two single Fickian models. Fick’s law has also been generalized by

---


introducing time-varying diffusion coefficients [1,7] or time-varying boundary conditions [1,2]. In these models, the diffusion coefficient or boundary condition is assumed to take the form of a Prony series which requires finding multiple coefficients and corresponding retardation times. These models introduce many degrees of freedom to the problem and the solution can be cumbersome and time-consuming.

Another class of anomalous diffusion models is based on a combination of physical diffusion and chemical interactions. Several studies, partially reviewed in [11], have been made to clarify the formation and existence of two different states of water molecules in epoxy, termed free and bound. Carter and Kibler [12] suggested a Langmuir-type two-phase diffusion model which assumes the existence of diffusing molecules in free and bound states. The Langmuir model has been used with some success at times [1,6,12].

Unlike absorption, water desorption behavior is normally Fickian [8]. The absorbed water in an epoxy cannot be completely removed in some cases and the existence of retained water after drying at temperatures below $T_g$ has been reported in the literature [13-16]. For example, Moy and Karasz [16] investigated epoxy–water interaction by differential scanning calorimetry (DSC), infrared spectroscopy (IR), nuclear magnetic resonance spectroscopy (NMR), and water absorption/desorption gravimetric experiments using a tetraglycidyl 4 4 diaminodiphenyl methane/diaminodiphenylsulphone (TGDDM/DDS) resin system. They observed a strong hysteresis related to the desorption process indicating retained amounts of water that could only be removed by heating the epoxy to temperatures above 100°C. Zhou and Lucas [14] showed that retained water after low-temperature desorption was related to the amount of water molecules forming stronger bonds (i.e. multiple hydrogen bonds) with the epoxy network.

In this Chapter, the absorption and desorption of water in two different rubber-toughened epoxy adhesives is measured gravimetrically over a relatively wide range of temperature and RH. The data are fitted to a new diffusion model in which Fick’s law was assumed to act in two sequential stages, each with its own diffusion coefficient and saturated water concentration. This “sequential dual Fickian” (SDF) model and a Langmuir-type diffusion model are both able to model the absorption behaviour. The dependence of the five SDF
model parameters on temperature and RH is investigated in detail. The two adhesives were selected to establish the generality of the SDF model and because they demonstrated different fracture durability behavior in a separate test program.

3.2. Mathematics of diffusion models

In this study, a newly developed type of dual Fickian model and a Langmuir-type model were used to characterize the anomalous behaviour of water absorption in two rubber-toughened epoxy adhesives, while a simple Fickian model was employed for the desorption modeling. Based on the size and shape of the wafer samples and the experimental setup, the diffusion was considered as one dimensional. The initial condition of absorption for both models was assumed to be zero water concentration and the constant saturation concentration value was taken as the boundary condition.

3.2.1. Dual Fickian model

In simple Fickian diffusion, it is assumed that the moisture flux is directly proportional to the concentration gradient in a material. The one-dimensional differential equation of Fickian diffusion, the boundary conditions and the initial condition for absorption to a plane sheet of thickness $2h$ are given as follows:

$$\begin{align*}
\frac{\partial C(x,t)}{\partial t} &= D \frac{\partial^2 C(x,t)}{\partial x^2} \\
C(x = \pm h, t) &= C_\infty \\
C(x, t \leq 0) &= 0
\end{align*}$$

(1)

where $C(x,t)$ is the water concentration (% by mass) at any spatial coordinate $x$ (m) and time interval $t$ (s), $C_\infty$ (%) is the saturated moisture concentration and $D$ (m$^2$/s) is the diffusion coefficient. The solution to the partial differential equation in Eq. (1) is given by:

$$\frac{C(x,t)}{C_\infty} = 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} (-1)^n \frac{\exp \left( -D(2n+1)^2 \pi^2 t \right)}{2n+1} \left(1 - \frac{2h}{x}\right) \cdot \\cos \left(\frac{(2n+1)\pi x}{2h}\right)$$

(2)
The fractional mass uptake, $M_t$ (i.e. the total mass uptake of water at time $t$ expressed as a percentage of the initial mass of the sample) can be obtained by integrating Eq. (2) over the spatial variable $x$:

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

(3)

where $M_\infty$ is the saturated fractional mass uptake, i.e. the mass uptake at saturation expressed as a percentage of the initial mass of the sample.

In the dual Fickian models present in the literature [8,9,17], two diffusion mechanisms are considered to be working in parallel such that the fractional mass uptake increases continuously until it reaches $M_\infty$. These models are called “parallel dual Fickian” (PDF). The Langmuir-type model and the gravimetric results in this study however indicated that there was a pseudo-equilibrium state at intermediate exposure times before reaching the final saturation (Section 4). This has been modeled in the present work by assuming that the pseudo-equilibrium corresponds to the completion of the first uptake mechanism and the start of the second one. Based on this assumption, a new “sequential dual Fickian” (SDF) model was developed in which the moisture concentration at any $t$ and $x$ is determined by:

$$
C(x,t) = \left[ 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \exp \left( - \frac{D_1(2n+1)^2 \pi^2 t}{4h^2} \right) \cos \left( \frac{(2n+1)\pi x}{2h} \right) \right] \times C_{1\infty} + \phi(t-t_d) \times \left[ 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \exp \left( - \frac{D_2(2n+1)^2 \pi^2 (t-t_d)}{4h^2} \right) \cos \left( \frac{(2n+1)\pi x}{2h} \right) \right] \times C_{2\infty}
$$

(4)

where $C_{1\infty}$ and $C_{2\infty}$ are the saturated concentrations of the first and second diffusion mechanisms such that $C_{1\infty}+C_{2\infty}=C_\infty$, where $C_\infty$ is the total saturation concentration. $D_1$ and $D_2$ are the diffusion coefficients of the first and second moisture uptake mechanisms, respectively. $t_d$ is the time at which the transition from the first diffusion mechanism to the second one occurs, and $\phi(t)$ is the Heaviside step function defined as:

$$
\phi(t-t_d) = \begin{cases} 
0, & t < t_d \\
1, & t \geq t_d 
\end{cases}
$$

(5)
The Heaviside step function in the second part of the right hand side of Eq. (4) ensures that the moisture concentration corresponding to the second mechanism is zero as long as the exposure time is less than \( t_d \). By integrating Eq. (4) over the spatial variable, the fractional mass uptake, \( M_t \) for the SDF model at any time \( t \) is given by:

\[
M_t = \left( 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp \left( -\frac{D_1 (2n+1)^2 \pi^2 t}{4h^2} \right) \right) \times M_{1\infty} + \phi(t-t_d) \times \left( 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp \left( -\frac{D_2 (2n+1)^2 \pi^2 (t-t_d)}{4h^2} \right) \right) \times M_{2\infty}
\]

where \( M_{1\infty} \) and \( M_{2\infty} \) correspond to the first and second uptakes, respectively and \( M_{1\infty} + M_{2\infty} = M_{\infty} \) (Fig. 3.1). The fractional mass uptake at any time \( t \), \( M_t \) was determined experimentally using gravimetric measurements and its value is given by:

\[
M_t = \frac{W_t - W_i}{W_i} \times 100\
\]

where \( W_i \) and \( W_t \) are the sample weights before any exposure and after an exposure time of \( t \), respectively. Thus the model has 5 parameters: \( D_1, D_2, C_{1\infty}, C_{2\infty} \) and \( t_d \). The present data were used to identify the dependence of these parameters on temperature, \( T \), and relative humidity, \( RH \), in order to make the model predictive for a range of environmental conditions.
3.2.2. Langmuir model

Carter and Kibler proposed a Langmuir-type adsorption theory to model the anomalous behaviour of moisture diffusion in polymers [12]. This model assumes the existence of diffusing molecules in mobile and bound states, each with probabilities of interchanging their states. Based on this model, for the one-dimensional case, the molecular number densities at exposure time \( t \) and spatial coordinate \( x \) satisfy the coupled pair of equations:

\[
D_L \frac{\partial^2 n_m}{\partial x^2} = \frac{\partial n_m}{\partial t} + \frac{\partial n_b}{\partial t}
\]  \hspace{1cm} (8)

\[
\frac{\partial n_b}{\partial t} = \gamma n_m - \beta n_b
\]  \hspace{1cm} (9)

where \( D_L \) is the diffusion coefficient, \( n_m \) and \( n_b \) represent the number of mobile and bound water molecules per unit volume. \( \gamma \) and \( \beta \) are the probabilities per unit time (s\(^{-1}\)) that mobile and bound molecules will change their respective states. Solving these equations with the equivalent initial and boundary conditions as for the SDF model gives the number of molecules at time \( t \) and position \( x \). The total number of water molecules per unit volume in an adhesive at time \( t \), \( N_t \) is approximated by [6]:

for short exposure times: \[
\frac{N_t}{N_\infty} \approx \frac{4}{\pi^{3/2}} \left( \frac{\beta}{\beta + \gamma} \right)^{\sqrt{4\kappa t}}
\]  \hspace{1cm} (10)

for long exposure times: \[
\frac{N_t}{N_\infty} \approx 1 - \frac{\gamma}{\beta + \gamma} e^{-\beta t}
\]  \hspace{1cm} (11)

where \( N_\infty \) is the total number of water molecules per unit volume at saturation and \( \kappa \) is defined as:

\[
\kappa = \frac{\pi^2 D_L}{4h^2}
\]  \hspace{1cm} (12).

The total number of water molecules per unit volume at the pseudo-equilibrium state, \( N_{pe} \) may be obtained as [6]:

\[
\frac{N_{pe}}{N_\infty} = \frac{\beta}{\beta + \gamma}
\]  \hspace{1cm} (13).
3.2.3. Fickian model in desorption

The desorption process was modeled using Fick’s law as:

\[
\begin{align*}
\frac{\partial C(x,t)}{\partial t} &= D_d \frac{\partial^2 C(x,t)}{\partial x^2} \\
C(x = \pm h, t) &= C_r \\
C(x, t \leq 0) &= C_\infty
\end{align*}
\]

where \( D_d \) and \( C_r \) are the diffusion coefficient of the desorption process and the minimum retained water concentration, respectively. The solution of this differential equation set for time \( t \) and spatial coordinate \( x \) is:

\[
\frac{C(x,t) - C_r}{C_\infty - C_r} = 4 \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \exp \left( \frac{-D_d (2n+1)^2 \pi^2 t}{4h^2} \right) \cos \frac{(2n+1)\pi x}{2h} 
\]

(14)

The fractional retained mass of water in the adhesive sample in percentage at time \( t \), \( M^f_t \), can be obtained by integrating Eq. (15) over the spatial variable:

\[
\frac{M^f_t - M_r}{M_\infty - M_r} = 8 \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp \left( \frac{-D_d (2n+1)^2 \pi^2 t}{4h^2} \right)
\]

(16)

where \( M_r \) is the minimum fractional retained water.

3.3. Experimental procedure

Two different proprietary, commercial DGEBA-based heat-cured rubber-toughened structural epoxy adhesives were studied (Table 3.1). The recommended curing profiles were at least 30 min at 180° C, monitored using a thermocouple embedded in the adhesive layer.

Table 3.1: Mechanical and physical properties of adhesives 1 and 2 as supplied by the manufacturers.

<table>
<thead>
<tr>
<th>Adhesive</th>
<th>Elastic modulus, ( E ), MPa</th>
<th>Poisson’s ratio, ( \nu )</th>
<th>Tensile strength, ( \sigma_y ), MPa</th>
<th>Glass transition Temp, ( T_g ), °C</th>
<th>Cured density, g/cm(^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adhesive 1</td>
<td>1.96</td>
<td>0.45</td>
<td>44.8</td>
<td>125</td>
<td>1.50</td>
</tr>
<tr>
<td>Adhesive 2</td>
<td>1.73</td>
<td>0.39</td>
<td>N/A</td>
<td>122</td>
<td>1.14</td>
</tr>
</tbody>
</table>
Adhesive wafers were cast between two aluminum plates coated with a polytetrafluoroethylene release agent. The wafer thickness of 0.8 mm was controlled using spacing wires. After curing, the adhesive wafers were cut to approximately 40 x 40 mm ensuring that the diffusion process was essentially one-dimensional in the thickness direction (the edge surface area was less than 4% of the total). A sharp knife was used to prevent edge cracking. XPS indicated some traces of release agent (fluorine) on the wafer surfaces; however, the gravimetric results did not change when this was sanded off.

To remove any absorbed moisture, the wafers were kept in a vacuum oven containing anhydrous calcium sulphate at 40°C for approximately 7 days. Mass uptake measurements were made under different combinations of temperature and RH as given in Table 3.2 along with the saturated salt solutions used to generate the atmospheres [18,19]. Table 3.2 also gives the amount of water present per unit volume of atmosphere at each exposure condition [20]. Airtight plastic containers were used as conditioning chambers within temperature-controlled ovens, and the wafers were placed on a grating with point contacts. Absorption and desorption measurements were repeated on three wafers at each exposure condition. Desorption was carried out in a vacuum oven containing anhydrous calcium sulphate at 40°C for up to three months. Some of the samples were analysed in fresh, saturated, and dried states using XPS to investigate changes in the composition due to water ingress.

Table 3.2: Different exposure conditions for adhesives 1 and 2 and saturated salt solutions used to achieve different levels of RH.

<table>
<thead>
<tr>
<th>RH (%)</th>
<th>Salt solution</th>
<th>Temperature (°C)</th>
<th>H₂O content (g/m³) Adh. studied</th>
<th>H₂O content (g/m³) Adh. studied</th>
<th>H₂O content (g/m³) Adh. studied</th>
<th>H₂O content (g/m³) Adh. studied</th>
<th>H₂O content (g/m³) Adh. studied</th>
</tr>
</thead>
<tbody>
<tr>
<td>31</td>
<td>MgCl₂</td>
<td>20</td>
<td>5.5 N/A</td>
<td>16.2 1</td>
<td>26.2 N/A</td>
<td>41.0 N/A</td>
<td></td>
</tr>
<tr>
<td>43</td>
<td>K₂CO₃</td>
<td>40</td>
<td>7.4 1</td>
<td>21.7 1</td>
<td>35.2 N/A</td>
<td>55.1 1</td>
<td></td>
</tr>
<tr>
<td>75</td>
<td>NaCl</td>
<td>50</td>
<td>12.9 N/A</td>
<td>37.9 1</td>
<td>61.4 N/A</td>
<td>96.1 N/A</td>
<td></td>
</tr>
<tr>
<td>82</td>
<td>KCl</td>
<td>60</td>
<td>14.1 1</td>
<td>41.5 1 &amp; 2</td>
<td>67.1 1</td>
<td>105.1 1 &amp; 2</td>
<td></td>
</tr>
<tr>
<td>95</td>
<td>K₂SO₄</td>
<td></td>
<td>16.3 1 &amp; 2</td>
<td>48.0 1 &amp; 2</td>
<td>77.8 1</td>
<td>121.7 1 &amp; 2</td>
<td></td>
</tr>
</tbody>
</table>
3.4. Results and discussion

3.4.1. Moisture absorption

Both the new sequential dual Fickian (SDF) and the Langmuir models were used to characterize moisture diffusion into adhesives 1 and 2. It was assumed that the diffusion coefficients \( D_1 \) and \( D_2 \) in the SDF model and \( D_L \) for the Langmuir model were independent of time. \( D_1 \) was determined by assuming a linear relationship between normalized mass uptake, \( M_t/M_{1\infty} \), and \( t^{1/2} \) during the initial stages of absorption. This linear relationship was approximated by [21]:

\[
\frac{M_t}{M_{1\infty}} = \frac{2}{h} \left( \frac{D_1 t}{\pi} \right)^{1/2}
\]  

(17).

It was assumed that the samples were fully saturated during the absorption period and the total saturated fractional mass uptake, \( M_{\infty} = M_{1\infty} + M_{2\infty} \) was determined from the gravimetric data. The other three parameters of SDF model \( (M_{1\infty}, t_d \text{ and } D_2) \) were determined by curve fitting. A nonlinear, least-squares optimization approach was developed using MATLAB® programming to find the best fit of Eq. (6) to the experimental data points. In the Langmuir model, the diffusion coefficient, \( D_L \) was assumed to be equivalent to \( D_1 \) in the SDF model. The probabilities \( \beta \) and \( \gamma \) were found by a least-square fitting of the analytical model to the experimental data points. Following the formulation and procedure given in [8,9], the parallel dual Fickian (PDF) model was also fitted to the experimental results using a least-squares optimization approach in MATLAB® to compare with the SDF and Langmuir models.

3.4.1.1. Fractional mass uptake profiles of adhesive 1

Figures 3.2-3.4 show the measured fractional mass uptake, \( M_t \) and the fitted SDF, Langmuir and PDF models versus the square root of time \( (t^{1/2}) \) for adhesive system 1 at different RH values for three temperatures. After the initial linear Fickian diffusion and the onset of a plateau, a second mass increase was observed in most of the exposure conditions. The single-stage Fickian model thus overestimated the experimental results, especially at high temperatures and RH, and at intermediate times.
Figure 3.2: Measured fractional mass uptake versus square root of time and the least-squares fits based on the SDF, Langmuir and PDF models at three RH levels for adhesive 1 at 20°C. Each data point is an average of three repetitions.

Figure 3.3: Measured fractional mass uptake versus square root of time and the least-squares fits based on the SDF, Langmuir and PDF models at five RH levels for adhesive 1 at 40°C. Each data point is an average of three repetitions.
Figure 3.4: Measured fractional mass uptake versus square root of time and the least-squares fits based on the SDF, Langmuir and PDF models at three RH levels for adhesive 1 at 60°C. Each data point is an average of three repetitions.

Tables 3.3 and 3.4 list the parameters of the SDF and Langmuir models, respectively, for adhesive 1 under the different exposure conditions. At the lower temperatures and RH (40°C-43%RH, 40°C-31%RH, 20°C-43%RH), the second diffusion mechanism disappeared and the fractional mass uptake profiles followed a simple Fickian diffusion behaviour \((D_2=0, \ t_d=\infty, \ M_{2\infty}=0)\). In these cases, the pseudo-equilibrium and final equilibrium states of the Langmuir model become coincident and there is no unique solution because any \(\theta\) with \(\gamma=0\) satisfies the model. Therefore, the Langmuir model was not used in these cases.
Table 3. 3: SDF model parameters obtained by curve fitting the experimental gravimetric results at different combinations of temperature and RH for adhesive 1. $M_{\infty}$ values obtained from PDF model are also given. Each data point is given as an average of three values obtained from the repetitions. SD shows the standard deviation.

<table>
<thead>
<tr>
<th>$T$ (°C)</th>
<th>$RH$ (%)</th>
<th>$D_1=\pm SD$ ($10^{-14}$ m$^2$/s)</th>
<th>$D_2=\pm SD$ ($10^{-14}$ m$^2$/s)</th>
<th>$M_{\infty,\pm SD}$ (%) (SDF)</th>
<th>$M_{\infty}=N_{\infty,\pm SD}$ (%)</th>
<th>$t_{d,1/2}$ (s$^{1/2}$)</th>
<th>$M_{\infty}$ (%) (PDF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>95</td>
<td>36±6</td>
<td>3.9±0.6</td>
<td>3.31±0.05</td>
<td>3.94±0.06</td>
<td>845</td>
<td>2.72</td>
</tr>
<tr>
<td></td>
<td>82</td>
<td>33±5</td>
<td>3.5±0.5</td>
<td>2.77±0.02</td>
<td>2.96±0.02</td>
<td>941</td>
<td>2.25</td>
</tr>
<tr>
<td></td>
<td>43</td>
<td>45±6</td>
<td>0.0</td>
<td>1.78±0.04</td>
<td>1.78±0.04</td>
<td>∞</td>
<td>1.78</td>
</tr>
<tr>
<td>40</td>
<td>95</td>
<td>134±17</td>
<td>3.8±0.7</td>
<td>3.36±0.09</td>
<td>4.78±0.15</td>
<td>536</td>
<td>2.80</td>
</tr>
<tr>
<td></td>
<td>82</td>
<td>142±6</td>
<td>3.3±0.4</td>
<td>2.71±0.04</td>
<td>3.55±0.06</td>
<td>524</td>
<td>2.34</td>
</tr>
<tr>
<td></td>
<td>75</td>
<td>159±25</td>
<td>3.6±0.6</td>
<td>2.21±0.05</td>
<td>2.79±0.06</td>
<td>521</td>
<td>1.97</td>
</tr>
<tr>
<td></td>
<td>43</td>
<td>113±11</td>
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<td>1.65±0.04</td>
<td>1.65±0.04</td>
<td>∞</td>
<td>1.65</td>
</tr>
<tr>
<td></td>
<td>31</td>
<td>139±19</td>
<td>0.0</td>
<td>1.26±0.04</td>
<td>1.26±0.04</td>
<td>∞</td>
<td>1.26</td>
</tr>
<tr>
<td>50</td>
<td>95</td>
<td>207±9</td>
<td>4.5±0.7</td>
<td>3.59±0.08</td>
<td>6.67±0.17</td>
<td>427</td>
<td>3.11</td>
</tr>
<tr>
<td></td>
<td>82</td>
<td>222±12</td>
<td>3.6±0.4</td>
<td>2.71±0.02</td>
<td>3.69±0.04</td>
<td>416</td>
<td>2.28</td>
</tr>
<tr>
<td>60</td>
<td>95</td>
<td>314±25</td>
<td>8.6±0.9</td>
<td>3.73±0.11</td>
<td>6.98±0.18</td>
<td>329</td>
<td>2.59</td>
</tr>
<tr>
<td></td>
<td>82</td>
<td>294±28</td>
<td>4.9±0.7</td>
<td>2.75±0.05</td>
<td>4.02±0.08</td>
<td>308</td>
<td>2.39</td>
</tr>
<tr>
<td></td>
<td>43</td>
<td>271±24</td>
<td>4.3±0.8</td>
<td>1.38±0.03</td>
<td>1.62±0.04</td>
<td>924</td>
<td>2.72</td>
</tr>
</tbody>
</table>

Table 3. 4: Langmuir model parameters obtained by curve fitting to the experimental gravimetric results at different combinations of temperature and RH for adhesive system 1. Each data point is given as an average of three values obtained from the repetitions. SD shows the standard deviation.

<table>
<thead>
<tr>
<th>$T$ (°C)</th>
<th>$RH$ (%)</th>
<th>$\beta=\pm SD$ ($10^{-7}$/s)</th>
<th>$\gamma=\pm SD$ ($10^{-7}$/s)</th>
<th>$N_{pe}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>95</td>
<td>3.23±0.19</td>
<td>0.68±0.03</td>
<td>3.23±0.08</td>
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<tr>
<td></td>
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<td>3.46±0.14</td>
<td>0.43±0.02</td>
<td>2.63±0.06</td>
</tr>
<tr>
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<td>95</td>
<td>4.07±0.26</td>
<td>1.94±0.12</td>
<td>3.20±0.09</td>
</tr>
<tr>
<td></td>
<td>82</td>
<td>3.66±0.18</td>
<td>1.23±0.05</td>
<td>2.66±0.07</td>
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<tr>
<td></td>
<td>75</td>
<td>3.43±0.16</td>
<td>0.88±0.04</td>
<td>2.18±0.04</td>
</tr>
<tr>
<td>50</td>
<td>95</td>
<td>4.97±0.22</td>
<td>5.31±0.28</td>
<td>3.20±0.08</td>
</tr>
<tr>
<td></td>
<td>82</td>
<td>4.78±0.15</td>
<td>1.75±0.06</td>
<td>2.69±0.06</td>
</tr>
<tr>
<td>60</td>
<td>95</td>
<td>10.9±0.81</td>
<td>12.86±0.73</td>
<td>3.21±0.11</td>
</tr>
<tr>
<td></td>
<td>82</td>
<td>6.88±0.43</td>
<td>3.22±0.22</td>
<td>2.75±0.05</td>
</tr>
<tr>
<td></td>
<td>43</td>
<td>2.52±0.14</td>
<td>0.53±0.04</td>
<td>1.36±0.04</td>
</tr>
</tbody>
</table>
3.4.1.2. Fractional mass uptake profiles of adhesive 2

Figure 3.5 shows the experimental fractional mass uptake, $M_t$ versus square root of time ($t^{1/2}$) and the fitted SDF, Langmuir and PDF models at 20, 40 and 60°C and 95% RH for adhesive 2. The corresponding parameters for both models are given in Tables 3.5 and 3.6.

![Fractional mass uptake profile graph](image)

Figure 3.5: Measured fractional mass uptake versus square root of time and the least-squares fits based on the SDF, Langmuir and PDF models at 95% RH and three different temperatures for adhesive 2. Each data point is an average of three repetitions.

Table 3.5: SDF model parameters obtained by curve fitting to the experimental gravimetric results at different combinations of temperature and RH for adhesive 2. $M_{1\infty}$ values obtained from PDF model are also given. Each data point is an average of three values obtained from the repetitions. SD shows the standard deviation.

<table>
<thead>
<tr>
<th>$T$ (°C)</th>
<th>RH (%)</th>
<th>$D_1=\overline{D}_1\pm SD$ (10^{-14} m^2/s)</th>
<th>$D_2\pm SD$ (10^{-14} m^2/s)</th>
<th>$M_{1\infty}\pm SD$ (%) (SDF)</th>
<th>$M_{\infty}=N_{\infty}\pm SD$ (%)</th>
<th>$t_{d^{1/2}}$ (s^{1/2})</th>
<th>$M_{1\infty}$ (%) (PDF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>95</td>
<td>26±4</td>
<td>6.8±1.2</td>
<td>2.31±0.04</td>
<td>2.99±0.06</td>
<td>631</td>
<td>1.87</td>
</tr>
<tr>
<td>40</td>
<td>95</td>
<td>87±11</td>
<td>4.1±0.8</td>
<td>2.83±0.06</td>
<td>3.75±0.09</td>
<td>386</td>
<td>2.41</td>
</tr>
<tr>
<td></td>
<td>82</td>
<td>104±13</td>
<td>9.8±1.5</td>
<td>2.14±0.06</td>
<td>2.27±0.07</td>
<td>497</td>
<td>1.78</td>
</tr>
<tr>
<td>60</td>
<td>95</td>
<td>248±29</td>
<td>8.1±1.5</td>
<td>3.16±0.09</td>
<td>4.78±0.12</td>
<td>219</td>
<td>2.59</td>
</tr>
<tr>
<td></td>
<td>82</td>
<td>208±24</td>
<td>9.6±1.3</td>
<td>2.38±0.03</td>
<td>2.8±0.04</td>
<td>273</td>
<td>1.99</td>
</tr>
</tbody>
</table>
Table 3.6: Langmuir model parameters obtained by curve fitting to the experimental gravimetric results at different combinations of temperature and RH for adhesive 2. Each data point is an average of three values obtained from the repetitions. SD shows the standard deviation.

<table>
<thead>
<tr>
<th>$T$ (°C)</th>
<th>RH (%)</th>
<th>$\theta \pm SD (10^{-7}/s)$</th>
<th>$\gamma \pm SD (10^{-7}/s)$</th>
<th>$N_{pe} \pm SD$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>95</td>
<td>10.88±0.73</td>
<td>5.8±0.34</td>
<td>2.06±0.04</td>
</tr>
<tr>
<td>40</td>
<td>95</td>
<td>10.64±0.84</td>
<td>4.7±0.29</td>
<td>2.58±0.08</td>
</tr>
<tr>
<td>82</td>
<td></td>
<td>12.5±0.87</td>
<td>1.1±0.06</td>
<td>2.08±0.07</td>
</tr>
<tr>
<td>60</td>
<td>95</td>
<td>22.3±1.38</td>
<td>12.9±0.69</td>
<td>3.10±0.10</td>
</tr>
<tr>
<td>82</td>
<td></td>
<td>24.2±1.82</td>
<td>0.5±0.03</td>
<td>2.32±0.06</td>
</tr>
</tbody>
</table>

The SDF model was able to characterize the anomalous diffusion behaviour of adhesives 1 and 2, showing a good agreement with the experimental results, the Langmuir model and the PDF model. Using the Langmuir model provides a means to estimate the relative amounts of bound and free water molecules in the adhesive. However, the probabilities $\theta$ and $\gamma$ have no physical significance in the diffusion process and also must be adjusted for any new exposure condition (Section 4.1.6). The SDF model divides the diffusion process into two separate stages governed by Fick’s law, which has a physical significance. The predictions of the SDF and PDF models were very similar, deviating the most at high RH and intermediate exposure times close to $t_d$. The $M_{1\infty}$ values obtained from the SDF model agree well with the total number of water molecules per unit volume in the pseudo-equilibrium state ($N_{pe}$) of the Langmuir model (average difference of 4%; see Section 4.1.5). This agreement adds physical significance to $M_{1\infty}$ in the SDF model. The $M_{1\infty}$ values obtained from the PDF model were always lower than the corresponding $N_{pe}$ values with an average difference of 15%. As will be discussed in Section 4.1.4, it is reasonable to assume that some of the water diffusion mechanisms occur after a delay time (i.e. $t_d$), leading to the second stage of water uptake; therefore, the SDF model is believed to represent a more realistic representation of water diffusion in the present adhesives.

Furthermore, it has been reported that in some cases the pseudo-equilibrium state ($M_{1\infty}$ occurring after $t_d$) for water absorption by DGEBA-based epoxies can be much longer than was found with the present adhesives [8, 22]. Since the PDF model assumes that both of the diffusion mechanisms start from the beginning of the absorption process, the predicted mass
uptake always increases with time and it is difficult to model such absorption behavior accurately. To deal with this limitation, Mubashar et al. [8] used a “delayed SDF” model by adding a power function to the SDF formulation. This delayed SDF model, however, adds three more constants and so increases the degrees of freedom of the problem, making it more difficult to develop the ability to predict how the model parameters vary with temperature and RH. As with the original PDF model, there is no physical significance to the added power function. On the other hand, by assuming two sequential water uptake stages, the SDF model provides a more general water absorption model that relates to the physical significance of Fick’s law and the Langmuir model.

In general, adhesive 2 appeared to be more resistant to water ingress than adhesive 1, and all five SDF parameters \((D_1, D_2, C_{1\infty}, C_{2\infty}, t_d)\) for adhesive 2 were always less than those for adhesive 1 at the same exposure condition. The \(D_1\) and \(M_{\infty}\) values of adhesive 2 were approximately 28% and 26% lower than those of adhesive 1, respectively.

In order for the SDF and Langmuir models to be predictive beyond the ambient conditions used in the experiments, it is necessary to identify the dependence of the model parameters on temperature and RH. This is discussed in the following subsections. It is noted that the present experiments did not investigate the possibility that the adhesive thickness influences the diffusion properties as reported in [9]. However, such changes were reported to be relatively small, being of the same order as the experimental scatter (e.g. Table 3.4). Moreover, ref. [9] did not provide an explanation for the observed dependency on adhesive thickness, and therefore the generality of this phenomenon remains unknown.

### 3.4.1.3. The effect of temperature and RH on the diffusion coefficients

Analysis of variance showed that \(D_1\) for adhesive 1 was independent of RH at all temperatures (95% confidence). Similarly, in the case of adhesive 2, a t-test showed that the average values of \(D_1\) were independent of RH at all temperatures. The second diffusion coefficient, \(D_2\) was always appreciably less than \(D_1\) for both adhesives (Tables 3.3 and 3.5). Excluding the inexplicably high \(D_2\) value at the 60°C-95% RH condition for adhesive 1, and unexpectedly low value at 40°C-95% RH condition for adhesive 2, analysis of variance revealed
that $D_2$ could be assumed independent of temperature and RH (95% confidence) for both adhesives.

The Arrhenius rate equation was used to investigate the effect of temperature on $D_1$:

$$D_1 = D_0 \exp \left( -\frac{Q}{RT} \right)$$

(18)

where $D_0$ and $Q$ are the diffusion constant and activation energy, respectively. $R$ is the universal gas constant (0.00198 kcal K$^{-1}$mol$^{-1}$) and $T$ is absolute temperature (K). Figure 3.6 shows $D_1$ versus inverse temperature, $1/T$ on a logarithmic scale for both adhesives. At a given temperature, $D_1$ was taken as the average obtained from the different RH conditions, since it was independent of RH as described above. Least squares regression showed that the $D_1$ variation with $\exp(1/T)$ was sufficiently linear in both adhesives during the first diffusion process to be modeled using Eq. (18). The calculated activation energy of the first diffusion process was essentially the same for adhesives 1 and 2; i.e. 10.2 and 10.6 kcal/mol, respectively.

![Figure 3.6: Variation of first diffusion coefficient, $D_1$, with temperature for adhesives 1 and 2. At each temperature, $D_1$ was taken as the average obtained from different RH conditions. Linear fit to the Arrhenius equation (Eq. (18)) with the slope equal to $-Q/R$.](image-url)
By way of comparison, Atkins reported that the energy required for breaking the hydrogen bonds present in liquid water (O-H\(-\)O) ranges from 5 to 20 kcal/mol [23]. The activation energy of the main-chain bonding of the epoxy network was reported to be 60-100 kcal/mol, and that of physical bonding (Van der Waals and/or dipole-dipole) is 0.5-2 kcal/mol [14]. Zhou and Lucas also reported the activation energy of water diffusion in a DGEBA-based epoxy to be 9.3 kcal/mol and attributed it to hydrogen bonding [14]. Therefore, the average activation energy of approximately 10 kcal/mol for both adhesives falls within the range reported for that of water diffusion in epoxy as well as the energy of hydrogen bonding given in the literature.

Popineau et al. [6] studied the kinetics of absorbed water in epoxy and concluded that the first diffusion mechanism corresponds to the diffusion of water molecules having strong interactions with the epoxy, while the water molecules absorbed during the second diffusion mechanism are relatively mobile. The second diffusion mechanism can then be related to a physical phenomenon such as clustering, in which the water molecules fill the free volume of the epoxy [9]. The water molecules within a cluster have no strong connections with the epoxy backbone and are essentially free.

3.4.1.4. The effect of temperature and RH on the saturated fractional mass uptakes

As seen in Fig. 3.7, \(M_{1\infty}\) increased significantly with RH, but it remained almost independent of temperature. This indicates that temperature affected only the rate of the first diffusion mechanism and not its saturation concentration value.

Figure 3.7 also shows that \(M_{2\infty}\) increased with both temperature and RH, although saturation in the second stage was not reached over the durations of the present experiments at the lowest temperature and RH exposure conditions (20°C-43%RH, 40°C-43%RH).
Figure 3.7: Variation of the first and second saturated fractional mass uptake values, $M_{1\infty}$ and $M_{2\infty}$ with temperature at 95%, 82% and 43% RH for adhesive 1. The lines are least square fits. Each data point is an average of three repetitions.

The dependence of $M_{2\infty}$ on RH and temperature can be explained in terms of the clustering of water molecules which is hypothesized to have occurred during the second uptake. One of the main factors that can increase the potential sites for the clustering is volumetric swelling of the adhesive due to water absorption, which will increase with both RH and temperature. The swelling strain is negligible during the initial stage of exposure but starts to increase (up to 10%) from medium exposure times [9,24,25]. It is then reasonable to assume that the volumetric expansion caused by the diffusion of water into the adhesive does not act immediately, which supports the assumption of a transition time $t_d$. The expansion causes the enlargement of the potential clustering sites within the adhesive and water molecules can then diffuse to fill these new voids.

An increase in the free volume for clustering and hence $M_{2\infty}$, can also occur because of thermal expansion and osmotic pressure within water clusters, both of which will depend on temperature and RH [26]. Osmotic pressure can be created by the diffusion of soluble components such as fillers into water clusters [27], thereby expanding the epoxy network. The water diffusion mechanism activated by osmotic pressure can then be assumed to start after
the formation of water clusters at a later time \((t_d)\) instead of the beginning of the diffusion \((t=0)\). The osmotic expansion and its contribution to \(M_{2\infty}\) will be proportional to the amount of absorbed water which is a function of temperature and RH. The absence of second stage within the period of the experiments at the lowest temperature and RH (20°C-43%RH, 40°C-43%RH) can be attributed to the relatively slow rate of volumetric expansion.

**3.4.1.5. The effect of temperature and RH on the transition time**

As seen in Table 3.3, \(t_d\) remained mostly unchanged with RH at different temperatures for adhesive 1, except for the 60°C-43%RH condition in which the transition time appeared to be unexpectedly long. It varied slightly with RH for the conditions studied with adhesive 2 (Table 3.5). Noting that the first diffusion mechanism was shown to be a chemical interaction (hydrogen bonding) which followed the Arrhenius rate equation, it is reasonable to assume that the time required for the first process to be completed \((t_d)\) depends on the rate of the process \((D_1)\). If it is hypothesized that \(t_d\) has an inverse linear relationship with \(D_1\) as:

\[
t_d = KD_1^{-1}
\]

(19)

where \(K\) is a constant, then substituting \(D_1\) from Eq. (18) into Eq. (19) results in

\[
t_d = t_{d0} \exp \left( \frac{Q}{RT} \right)
\]

(20)

where \(t_{d0} = KD_0\) is a transition time constant. To examine this hypothesis, the activation energy of the first diffusion mechanism, \(Q\) was calculated using Eq. (20) and the measured \(t_d\). Figure 3.8 shows the variation of \(t_d\) with inverse temperature on a logarithmic scale at 95% RH for both adhesives. Very similar results were observed at 82% RH for adhesive 1. A very good linear least squares fit between \(t_d\) and \(\exp(1/T)\) suggested that Eq. (19) was a valid assumption and using these fits, \(Q\) for adhesives 1 and 2 was found to be 9.7 and 10.2 kcal/mol, respectively. Using the results at 82% RH, \(Q\) for adhesive 1 was calculated to be 10.1 kcal/mol. These values compare well with those calculated for \(D_1\) using the data of Fig. 3.6, differing by only 5% and 3%, respectively.
Furthermore, the fractional mass uptake at \( t_d, \ M_{1,\infty} \), agrees well with the pseudo-equilibrium mass uptake, \( N_{pe} \) of the Langmuir model at any exposure condition with an average difference of about only 4% (Fig. 3.9). Therefore, \( t_d \) of the SDF model corresponds to the pseudo-equilibrium state of the Langmuir model. These results lend confidence that \( t_d \) as the time of saturation for the first diffusion mechanism was properly determined.

**Figure 3.8:** Variation of the transition time with temperature at 95% RH for both adhesives. Each data point is an average of three values obtained from the repetitions. The lines show least square regressions between \( t_d \) and \( \exp(1/T) \) and the slopes of the lines give the values of \( Q/R \).

**Figure 3.9:** Comparison between the first saturated fractional mass uptake, \( M_{1,\infty} \) of the SDF model and the pseudo-equilibrium mass uptake, \( N_{pe} \) of the Langmuir model at different combinations of temperature and RH. Each data point is an average of three values obtained from the repetitions.
3.4.1.6. The effect of temperature and RH on the $\beta$ and $\gamma$ probabilities of Langmuir model

Figure 3.10 shows the variation of $\beta$ and $\gamma$ with inverse temperature on a logarithmic scale at 82% RH for adhesive 1. The fair linear fits indicate that both probabilities varied approximately exponentially with $T$ and followed the Arrhenius rate equation at a particular RH. Similarly at 95% RH, both $\beta$ and $\gamma$ varied exponentially with $T$ but with different rates. Figure 3.11 shows that $\beta$ and $\gamma$ also depended strongly on RH, especially at higher temperature. Hence, although the form of the Langmuir model fits absorption data well, it does so with adjustable parameters $\beta$ and $\gamma$ that are unknown functions of both temperature and RH. This limits the use of the Langmuir model to environments where $\beta$ and $\gamma$ have been determined, and makes interpolation and extrapolation to different environments uncertain.

3.4.2. Moisture desorption

After the absorption process, the samples were dried in a vacuum oven at 40°C to measure the desorption profiles. The mass of samples decreased uniformly with drying time to minimum fractional retained water, $M_r$ (%), and remained unchanged, even after approximately 3 months. The simple Fickian model sufficiently characterized the desorption process in both
adhesives in terms of the desorption diffusion coefficient, $D_d$, the saturated fractional mass uptake, $M_\infty$ and the minimum fractional retained water, $M_r$. $D_d$ was determined in the same manner as $D_1$ using Eq. (17) and normalized mass loss profiles.

![Graph](image)

**Figure 3.11:** Variation of $\beta$ and $\gamma$ probabilities with RH at temperatures of 40°C and 60°C for adhesive 1. Each data point is an average of three values obtained from the repetitions. The lines are only to guide the trends.

### 3.4.2.1. Fractional retained mass profiles of adhesives 1 and 2

Figures 3.12-3.14 show the experimentally measured fractional retained mass, $M_f^t$, versus square root of time, $t^{1/2}$ and Fickian fits for the wafers of adhesive 1 that had been exposed to different RH at 20, 40 and 60°C. Figure 3.15 shows the same results for adhesive 2 with the exposure condition of 60°C-95% RH. No second slope was observed during desorption and the simple Fickian model adequately characterized the behaviour of both adhesives. The main difference between the fractional retained mass profiles of the adhesives 1 and 2 was the minimum fractional retained water, $M_r$; 1.4% and 0.16%, respectively, for the same $M_\infty$ of 4.8%. The $M_r$ value for adhesive 1 was approximately 30% of the corresponding $M_\infty$.

As mentioned previously, Marsh *et al.* [15] and Moy and Karasz [16] concluded that a drying temperature above $T_g$ was required to completely remove absorbed water from epoxy resin. Zhou and Lucas [14] observed some retained water in both DGEBA and TGDDM based epoxies after drying at temperatures up to 90°C, which was greater than $T_g$. They found that the amount of retained water eventually reached zero, but the activation energy required for high-temperature desorption was higher than that of low-temperature desorption. They
concluded that the water molecules retained after low-temperature desorption had multiple hydrogen bonds with the epoxy network.

Figure 3.12: Fractional retained mass during drying versus square root of time, fitted with the simple Fickian model for adhesive 1 initially saturated at 20°C and different RH. Each data point is an average of three repetitions.

Figure 3.13: Fractional retained mass during drying versus square root of time, fitted with simple Fickian models for adhesive 1 initially saturated at 40°C and different RH. Each data point is an average of three repetitions.
Figure 3.14: Fractional retained mass during drying versus square root of time and fitted simple Fickian models for adhesive 1 initially saturated at 60°C and different RH. Each data point is an average of three repetitions.

Figure 3.15: Fractional retained mass profile during drying versus square root of time and fitted simple Fickian model for adhesive 2 initially saturated at 60°C-95%RH. Each data point is an average of three repetitions.
### 3.4.2.1. The effect of temperature and RH on the minimum fractional retained water

Figures 3.16 and 3.17 show that $M_r$ was proportional to the temperature and RH during the absorption process for adhesive 1. At low temperature (20°C), $M_r$ remained relatively unchanged with RH (Fig. 3.17). Similarly, at low RH (43%), $M_r$ was largely independent of $T$. Figure 3.18 also shows that $M_r$ increased linearly with the ambient water concentration during absorption, regardless of temperature.

![Figure 3.16](image1.png)

**Figure 3.16:** Variation of minimum fractional retained water, $M_r$, with the temperature of absorption condition at different RH levels for adhesive 1. Each data point is an average of three repetitions. The linear least square fits show the general trends.

![Figure 3.17](image2.png)

**Figure 3.17:** Variation of minimum fractional retained water, $M_r$, with the RH of the absorption condition at different temperatures for adhesive 1. Each data point is an average of three repetitions. The linear least square fits show the general trends.
Figure 3.18: Variation of minimum fractional retained water, $M_r$, with the ambient water concentration achieved during different exposure conditions for adhesive 1. Each data point is an average of three repetitions. The linear least squares fit shows the general trend.

Figure 3.19 depicts the variation of minimum fractional retained water during the desorption process, $M_r$, with the saturated fractional mass uptake $M_{\infty}$ ($M_{1\infty}+M_{2\infty}=M_{\infty}$) which was obtained at different combinations of temperature and RH. $M_r$ increased linearly with $M_{\infty}$, independent of the original exposure condition. This finding may be useful in predicting the amount of retained water in the adhesive exposed to a varying environment.

Figure 3.19: Variation of minimum fractional retained water during the desorption process with the saturated fractional mass uptake, $M_{\infty}$, for adhesive 1. Each data point is an average of three repetitions. The linear least square fit shows the general trend.
3.4.3. XPS analysis

The significant difference between $M_r$ for these two adhesives was investigated using XPS. Table 3.7 shows the percentage of oxygen atoms associated with different chemical bonds (binding energies) for fresh (as-cured), saturated wet, and dried samples of adhesives 1 and 2. The O1sB peak corresponded to a bond associated with water molecules since it was present in the wet samples of both adhesives, but not in the fresh and dried samples of adhesive 2, nor was it significant in the fresh adhesive 1. As seen in Table 3.7, the atomic percentage of O1sB was 10% in dried samples of adhesive 1 which qualitatively supports the gravimetric results indicating that a considerable amount of absorbed water in the adhesive 1 could not be removed during the drying process at 40°C.

Table 3.7: Percentage of oxygen atoms associated with different chemical bonds with their binding energy for fresh, saturated wet and dried samples of adhesives 1 and 2. Each data point is an average of three repetitions.

<table>
<thead>
<tr>
<th>Exposure condition: 60°C-95% RH</th>
<th>O1s</th>
<th>O1sA</th>
<th>O1sB</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Atomic %</td>
<td>Binding energy (eV)</td>
<td>Atomic %</td>
</tr>
<tr>
<td><strong>Adhesive 1</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fresh ($M_t=0$)</td>
<td>84</td>
<td>532.7</td>
<td>12</td>
</tr>
<tr>
<td>Wet ($M_t=M_\infty=6.98%$)</td>
<td>67</td>
<td>532.6</td>
<td>15</td>
</tr>
<tr>
<td>Dry ($M_t=M_r=1.82%$)</td>
<td>76</td>
<td>532.7</td>
<td>13</td>
</tr>
<tr>
<td><strong>Adhesive 2</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fresh ($M_t=0$)</td>
<td>77</td>
<td>532.9</td>
<td>23</td>
</tr>
<tr>
<td>Wet ($M_t=M_\infty=4.78%$)</td>
<td>62</td>
<td>532.8</td>
<td>15</td>
</tr>
<tr>
<td>Dry ($M_t=M_r=0.20%$)</td>
<td>76</td>
<td>532.8</td>
<td>24</td>
</tr>
</tbody>
</table>

3.5. Conclusions

The water absorption and desorption of two different rubber-toughened epoxy adhesives were characterized using gravimetric measurements. A newly developed sequential dual Fickian (SDF) model was used to fit the fractional mass uptake profiles and agreed well with the Langmuir diffusion model. The diffusion mechanism in the first stage appeared to be
influenced by hydrogen bonding while the diffusion mechanism in the second stage was primarily physical in nature. The diffusion coefficients in both stages were found to be largely independent of RH, while the saturated fractional mass uptake values increased with RH. The diffusion coefficient of the first stage and the saturated fractional mass uptake of the second stage were both functions of temperature. These functional dependencies were described, making the SDF model predictive over the ranges of temperature and RH that were investigated.

The desorption during drying in both adhesives was described well by Fick’s law. Both gravimetric results and XPS revealed that there was a significant difference between the amounts of minimum fractional retained water in the two adhesives after drying. The relatively large amount of retained water in adhesive 1 was attributed to multiple hydrogen bonds between the water molecules and the epoxy or other constituents such as the rubber toughener particles or the filler. In a separate test program, it was found that these differences in water absorption-desorption corresponded to marked differences in the degradation of fracture toughness in hot-wet aging environments (to appear in a future publication).

The SDF model can be used to predict the water concentration distribution in adhesive joints exposed to environments of changing temperature and RH under the assumption of negligible interface diffusion.
3.6. References


Chapter 4: Fracture R-curve of a toughened epoxy adhesive as a function of irreversible degradation$^{1,2}$

4.1. Introduction

During the early stages of crack extension in toughened adhesive joints, the damage zone continues to expand ahead of the growing macro-crack, leading to a progressive toughening of the joint as increasing amounts of strain energy are dissipated by the plastic deformation and micro-cracking [1-2]. This process results in an $R$-curve where the critical strain energy release rate, $G_c$ initially increases with increasing crack length. Eventually, the damage zone reaches a steady-state size and $G_c$ attains a steady-state value, $G_{cs}$, which has been used to predict the ultimate strength of a wide range of adhesive joints [3-5]. However, joints with relatively short overlaps may reach their ultimate strength and fail catastrophically before $G_c$ reaches its steady-state value, $G_{cs}$. As shown in Chapter 2, this is of particular concern in highly toughened adhesive joints where $G_{cs}$ might only be reached after a significant amount of crack growth; e.g. up to 17 mm under a mixed-mode loading condition. In such cases, use of the $G_{cs}$ as a failure criterion will overestimate the joint strength, and predictions of the ultimate strength should be based on values of $G_c$ taken from the $R$-curve at the appropriate crack length. This approach can be facilitated using the bilinear $R$-curve model developed for highly toughened epoxy adhesives.

Traditional closed joints are not well suited for the study of degradation because the diffusion path of water into the adhesive layer is long and the degradation experiments are hence time-consuming. Moreover, the resulting degradation is not uniform after reasonable exposure times, with the exposed edges experiencing far greater strength loss than the central

---


portions of the joint. Since the results from testing such joints do not represent a discrete state of moisture degradation, it is impossible to directly apply the measured properties to other joint configurations or ageing conditions [6]. Open-faced specimens can be used to achieve a spatially uniform state of degradation and to accelerate the aging process by shortening the diffusion path of water into the adhesive layer [6-9].

It is well established that absorbed water plays a significant role in the progressive degradation of the mechanical properties of epoxy adhesives. It is thus important to characterize the water absorption and desorption behavior of adhesives in order to model degradation as a function of time. Some diffusion models assume that water diffuses into the epoxy and resides in the free volume of the material [10-12], while others propose strong chemical bonding between water molecules and certain hydrophilic functional groups in the epoxy resin such as hydroxyls [13-15]. Some researchers have shown that these physical and chemical mechanisms may occur simultaneously [14, 16-18].

Toughened epoxy adhesives usually exhibit anomalous diffusion behavior in which a simple Fickian model tends to overestimate the water concentration at a given time [14-17, 19-21]. In these cases, a dual Fickian model, which superimposes two Fickian models acting simultaneously [20-22] or sequentially, as proposed in Chapter 3, provides better accuracy.

This Chapter describes the fracture $R$-curves of a rubber-toughened epoxy adhesive that was degraded under a wide range of temperature and RH using open-faced specimens. The adhesive layer was then dried before fracture testing in order to measure the effects of irreversible degradation (i.e. without the reversible, plasticizing effect of absorbed free water) [7, 23-25]. The water uptake was predicted using an earlier sequential dual Fickian (SDF) model based on gravimetric measurements on bulk wafer samples. The fracture data revealed the effects of mode mixity, exposure time, temperature, RH, water concentration in the adhesive layer and the ambient water concentration on the $R$-curve bilinear model parameters.
4.2. Experimental procedures

4.2.1. Open-faced DCB specimen fabrication

As illustrated in Fig. 4.1, the primary adhesive layer (Table 4.1) of 0.4 mm thickness (controlled using spacing steel wires) was cured on the primary adherend using a backing plate coated with PTFE instead of the second adherend. After curing, the backing plate was removed and the open-faced specimens were degraded at the exposure conditions given in Table 4.2 for different predetermined time intervals. The degraded specimens were then dried in a vacuum oven containing anhydrous calcium sulphate at 40°C for approximately 7 days to remove any reversible effect of water ingress such as plasticization. Even though the effect of drying at such a low temperature for a relatively short time would be very small, the drying process was considered as a part of the degradation period and its effect was included in the calculation of the exposure index as will be discussed later in this Chapter. It has been established in the literature that the plasticization that occurs as a result of unbound diffused water molecules [13, 14, 26] can improve the durability of adhesive joints [7, 23-25]. For example, Wylde and Spelt fracture tested two toughened epoxy adhesives in both wet and dried conditions after exposure to varying environments, and observed that the existence of water in the adhesive in the wet case significantly increased the joint fracture toughness [7]. The water molecules that are tightly bound to the epoxy constituents are believed to cause irreversible damage such as chain scission, hydrolysis, crack initiation, crack growth, and subsequent loss of material [20, 27]. Drying the aged specimen before fracture testing removed the free water molecules and their subsequent plasticizing effect and hence facilitated the estimation of permanent damage in the adhesive layer.
Figure 4.1: Fabrication and aging of open-faced specimens.

Table 4.1: Mechanical and physical properties of the primary and secondary adhesives as supplied by the manufacturers.

<table>
<thead>
<tr>
<th>Adhesive</th>
<th>Elastic modulus, $E$, MPa</th>
<th>Poisson ratio, $\nu$</th>
<th>Tensile strength, $\sigma_y$, MPa</th>
<th>Glass transition temp, $T_g$, °C</th>
<th>Cured density, $g/cm^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary</td>
<td>1.96</td>
<td>0.45</td>
<td>44.8</td>
<td>125</td>
<td>1.50</td>
</tr>
<tr>
<td>Secondary</td>
<td>1.73</td>
<td>0.39</td>
<td>N/A</td>
<td>122</td>
<td>1.14</td>
</tr>
</tbody>
</table>

To ensure a strong mechanical interlocking between the primary and secondary adhesive layers, the primary adhesive layer surface was roughened using 100 grit sandpaper, wiped with a cheese cloth and acetone, and dried before the secondary bonding. The roughening process removed less than 25 μm of the primary adhesive layer. Fracture measurements on the effect of bondline thickness presented in Chapter 2 showed that this reduction in the nominal thickness of 400 μm would decrease $G_{cs}$ by less than 3%. The total bondline thickness of the primary and secondary adhesive layers was controlled using 0.8 mm spacing wires during secondary bonding. Figure 4.2 shows the final configuration and dimensions of the open-faced DCB joints.

The mode ratio of the DCB loading is given in terms of the phase angle, defined as $\psi = \arctan\left(\left(G_{II} / G_I\right)^{0.5}\right)$, where $G_{Ic}$ and $G_{IIc}$ are the mode I and II components of the strain energy release rate, respectively. The DCB specimens were made with AA7075-T6 aluminum alloy and pretreated using the ASTM 2651 P2-etch method [28] which included mechanical abrading, acetone immersion, and sulphuric acid etching to remove the existing aluminum.

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oxide layer. Crack paths in all specimens were cohesive, near the interface between the primary (aged) adhesive and the adjacent adherend.

The initiation geometry was created by embedding a folded 10 µm aluminum foil within the primary adhesive layer. To minimize the possibility of mechanical damage to the specimen edges after curing, the very small amount of residual adhesive that had flowed from the edges of the open-faced DCB specimens was removed using a gentle wet sanding process (final stage 300 grit). A very thin layer of white paper correction liquid, diluted with hexane, was applied to the specimen edges to assist in the identification of the macro-crack tip. The high volatility of hexane and the very small quantities applied ensured that it evaporated quickly and did not degrade the adhesive.

![Diagram of DCB joint](image)

**Figure 4.2**: The final configuration and dimensions of the open-faced DCB joint (not to scale).

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Parameter</th>
<th>Size</th>
</tr>
</thead>
<tbody>
<tr>
<td>$L$</td>
<td>Specimen length</td>
<td>~ 250 mm</td>
</tr>
<tr>
<td>$h$</td>
<td>Adherend thickness</td>
<td>12.7 mm</td>
</tr>
<tr>
<td>$t_p$</td>
<td>Primary bond thickness</td>
<td>0.4 mm</td>
</tr>
<tr>
<td>$t_s$</td>
<td>Secondary bond thickness</td>
<td>0.4 mm</td>
</tr>
<tr>
<td>$w$</td>
<td>Adherend width</td>
<td>19-21 mm</td>
</tr>
<tr>
<td>$a_0$</td>
<td>Starting length</td>
<td>~ 40 mm</td>
</tr>
<tr>
<td>$\Delta a$</td>
<td>Crack length increment</td>
<td>Variable</td>
</tr>
<tr>
<td>$a$</td>
<td>Crack length</td>
<td>Variable</td>
</tr>
<tr>
<td>$P_1$</td>
<td>Upper adherend load</td>
<td>Variable</td>
</tr>
<tr>
<td>$P_2$</td>
<td>Lower adherend load</td>
<td>Variable</td>
</tr>
</tbody>
</table>
4.2.2. Gravimetric measurements and open-faced aging

The water absorption properties of the primary adhesive were obtained from Chapter 3. These same conditions were used for the aging of the open-faced specimens over various saturated salt solutions in airtight plastic containers placed within temperature-controlled ovens (Table 4.2) [6, 29, 30]. Care was taken to ensure that the specimens had no direct contact with the salt solutions and were exposed solely to the humid air. At 95% and 82% RH, the open-faced DCB specimens were fracture tested after 12 different exposure times. At 43% RH, the number of exposure times was 8. In order to assess the repeatability of the measurements, three replications were made at 4 of these exposure times.

Table 4.2: Temperature and humidity conditions for gravimetric samples and open-faced specimens with the saturated salt solutions and the resulting ambient water concentration.

<table>
<thead>
<tr>
<th>RH (%)</th>
<th>Salt solution</th>
<th>Ambient water concentration (g/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>20°C</td>
</tr>
<tr>
<td>43</td>
<td>K₂CO₃</td>
<td>7.4</td>
</tr>
<tr>
<td>82</td>
<td>KCl</td>
<td>14.1</td>
</tr>
<tr>
<td>95</td>
<td>K₂SO₄</td>
<td>16.3</td>
</tr>
</tbody>
</table>

4.2.3. Fracture test methodology

Fracture test methodology was elaborated in Chapter 2 and is only briefly summarized here. The fracture tests were conducted using a servo-electric load frame and the load jig of [31] which could generate different mode ratios using a single DCB specimen geometry. Under mixed-mode conditions, the load applied to the primary adherend was greater than that on the secondary adherend so that the crack path tended toward the primary interface; i.e. nearer to the more highly-strained adherend. Following the procedures established in Chapter 2, the specimen was loaded in discrete small steps while viewing the crack tip through the microscope to detect the onset of crack propagation at the critical load. This resulted in shorter crack propagation increments of approximately 1 mm, allowing for enough data points to accurately define the rising part of the R-curve. The crack length, \( a \) (Fig. 4.2) was determined with an accuracy of ±20 μm using an optical microscope on a micrometer stage having a field of view of 2 mm. Crack initiation at a load \( P_{ci} \) was defined as the first crack extension of approximately 50
μm from the bondline terminus at the edge of the folded foil. In all cases, the crack grew cohesively within the primary adhesive layer.

4.2.4. Measurement of residual adhesive thickness and surface roughness

The average depth of the crack path was determined by measuring the thickness of the residual adhesive on the more highly strained adherend after fracture. Two datum points were established on the bare aluminum by first removing residual adhesive from 2 mm wide band on either side of the adherend using a solvent (mixture of methylene chloride and methyl alcohol; Glue Buster, Kosmic Surf-Pro Inc., Saint Amable, Quebec). Transverse line scans were then made from one datum to the other across the width of the specimen at several locations using an optical profilometer (Nanovea ST 400, Microphotonics Inc., Irvine, CA, USA) which also gave the average roughness of the fracture surface.

4.3. Results and discussion

4.3.1. Water diffusion

As developed in Chapter 3, the moisture concentration at any \( t \) and \( x \) in the sequential dual Fickian (SDF) model (Fig. 4.3) is determined by:

\[
C(x,t) = \left( 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \exp \left( - \frac{D_1 (2n+1)^2 \pi^2 t}{4h^2} \right) \cos \left( \frac{(2n+1) \pi x}{2h} \right) \right) C_{1\infty} \\
+ \phi(t-t_d) \left( 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \exp \left( - \frac{D_2 (2n+1)^2 \pi^2 (t-t_d)}{4h^2} \right) \cos \left( \frac{(2n+1) \pi x}{2h} \right) \right) C_{2\infty}
\]

where \( C_{1\infty} \) and \( C_{2\infty} \) are the saturation mass concentrations of the first and second diffusion mechanisms such that \( C_{1\infty} + C_{2\infty} = C_\infty \), where \( C_\infty \) is the total saturation mass concentration. \( D_1 \) and \( D_2 \) are the diffusion coefficients of the first and second moisture uptake mechanisms, respectively. \( t_d \) is the time at which the transition from the first diffusion mechanism to the second one occurs, and \( \phi(t) \) is the Heaviside step function which returns zero for negative values and one for positive values. By integrating Eq. (1) over the spatial variable, the fractional
mass uptake, $M_t$ (i.e. the total mass uptake of water at time $t$ expressed as a percentage of the initial mass of the adhesive) for the SDF model is given by:

$$M_t = \left\{ 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left(\frac{-D_1(2n+1)^2 \pi^2 t}{4h^2}\right) \right\} \times M_1^{\infty}$$

$$+ \phi(t-t_d) \times \left\{ 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left(\frac{-D_2(2n+1)^2 \pi^2 (t-t_d)}{4h^2}\right) \right\} \times M_2^{\infty}$$

(2)

where $M_1^{\infty}$ and $M_2^{\infty}$ are the fractional mass uptakes at saturation for the first and second diffusion mechanisms, respectively and $M_1^{\infty} + M_2^{\infty} = M^{\infty}$, where $M^{\infty}$ is the total saturated fractional mass uptake. Table 4.3 reproduces the parameters of the SDF model for the different exposure conditions obtained in Chapter 3. These parameters were used to calculate the water concentration at given degradation times in open-faced DCB specimens.

![Figure 4.3: Schematic illustration of the sequential dual Fickian (SDF) model.](image)

Table 4.3: SDF model parameters obtained by curve fitting the experimental gravimetric results at different combinations of temperature and RH. Each data point is the average of measurements on three wafers. SD is the standard deviation.

<table>
<thead>
<tr>
<th>$T$ (°C)</th>
<th>RH (%)</th>
<th>$D_1 = D_L \pm SD$ ($10^{-24}$ m$^2$/s)</th>
<th>$D_2 \pm SD$ ($10^{-24}$ m$^2$/s)</th>
<th>$M_1^{\infty} \pm SD$ (%)</th>
<th>$M^{\infty} = N^{\infty} \pm SD$ (%)</th>
<th>$t_{d1/2}$ ($s^{1/2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>95</td>
<td>36±6</td>
<td>3.9±0.6</td>
<td>3.31±0.05</td>
<td>3.94±0.06</td>
<td>845</td>
</tr>
<tr>
<td>40</td>
<td>95</td>
<td>134±17</td>
<td>3.8±0.7</td>
<td>3.36±0.09</td>
<td>4.78±0.15</td>
<td>536</td>
</tr>
<tr>
<td></td>
<td>82</td>
<td>142±6</td>
<td>3.3±0.4</td>
<td>2.71±0.04</td>
<td>3.55±0.06</td>
<td>524</td>
</tr>
</tbody>
</table>
4.3.2. *R*-curve bilinear model

Figure 4.4 shows the typical fracture resistance curves (*R*-curves) of the undegraded DCB joints obtained at phase angles of 27° and 48°. As expected, \( G_c \) was fairly low at initiation when the damage zone was small, and increased with the crack growth until it reached a steady-state value, when the damage zone was fully developed. As given in Chapter 2, a bilinear *R*-curve model was proposed for this same epoxy adhesive in terms of three independent parameters: the steady-state critical strain energy release rate, \( G_{cs} \), the slope of the rising line, \( (dG_{cr}/da) \), and the length of the rising part \( (L_r = a_r - a_0) \):

\[
G_c = \begin{cases} 
G_{cr}(a) = G_{ci} + \frac{dG_{cr}}{da}(a - a_0), & a_0 < a < a_r \\
G_{cs}, & a \geq a_r 
\end{cases}
\]  

(3)

where \( G_{cr} \) is the critical strain energy release rate in the rising part of the *R*-curve, \( a_0 \) and \( a_r \) are the initial distance from the loading pins and the crack length corresponding to the end of the rising part, respectively. \( G_{ci} \) is the initiation \( G_c \) at which the crack started to grow from the adhesive terminus. As seen in Fig. 4.4, the *R*-curve was well characterized by this bilinear model at both phase angles. Table 4.4 lists the average values and standard deviations of the three bilinear model parameters and \( G_{ci} \) for the undegraded DCB specimens tested at phase angles of 0, 27 and 48°. All the parameters except \( L_r \) increased with phase angle. The undegraded specimen values in Table 4.4 were used as a reference for the evolution of the *R*-curves with degradation in the present open-faced DCB specimens.

<table>
<thead>
<tr>
<th></th>
<th>43</th>
<th>113±11</th>
<th>0.0</th>
<th>1.65±0.04</th>
<th>1.65±0.04</th>
<th>∞</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>95</td>
<td>207±9</td>
<td>4.5±0.7</td>
<td>3.59±0.08</td>
<td>6.67±0.17</td>
<td>427</td>
</tr>
<tr>
<td></td>
<td>82</td>
<td>222±12</td>
<td>3.6±0.4</td>
<td>2.71±0.02</td>
<td>3.69±0.04</td>
<td>416</td>
</tr>
<tr>
<td>60</td>
<td>95</td>
<td>314±25</td>
<td>8.6±0.9</td>
<td>3.73±0.11</td>
<td>6.98±0.18</td>
<td>329</td>
</tr>
<tr>
<td></td>
<td>82</td>
<td>294±28</td>
<td>4.9±0.7</td>
<td>2.75±0.05</td>
<td>4.02±0.08</td>
<td>308</td>
</tr>
<tr>
<td></td>
<td>43</td>
<td>271±24</td>
<td>4.3±0.8</td>
<td>1.38±0.03</td>
<td>1.62±0.04</td>
<td>924</td>
</tr>
</tbody>
</table>
Figure 4.4: Typical R-curves of undegraded DCB joints tested at phase angles of 27° and 48° and linear least-squares fits for the rising and steady-state regions. The crack length and $G_c$ values at initiation and the onset of the plateau are labeled.

Table 4.4: The average and standard deviation of the bilinear model parameters and initiation $G_c$ for undegraded DCB specimens tested under different phase angles.

<table>
<thead>
<tr>
<th>$\psi$ (°)</th>
<th>$G_{c0}$±SD (Jm$^{-2}$)</th>
<th>$dG_{cs}/da$±SD (Jm$^{-2}$/mm)</th>
<th>$L_R$±SD (mm)</th>
<th>$G_{cs}$±SD (Jm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0*</td>
<td>3220±210</td>
<td>379±32</td>
<td>5.5±0.9</td>
<td>409±72</td>
</tr>
<tr>
<td>27**</td>
<td>4160±260</td>
<td>319±29</td>
<td>11.2±0.5</td>
<td>596±96</td>
</tr>
<tr>
<td>48*</td>
<td>6650±460</td>
<td>338±25</td>
<td>16.4±1.2</td>
<td>713±114</td>
</tr>
</tbody>
</table>

*: Three replications  **: Nine replications

4.3.3. Degradation of steady-state fracture toughness, $G_{cs}$

4.3.3.1. Effect of exposure time on $G_{cs}$

Figures 4.5 and 4.6 show the variation of mixed-mode $G_{cs}$ ($\psi = 27^\circ$) with exposure time for three values of RH at 60°C and 40°C, respectively. Also shown is the average $G_{cs}$ value of undegraded single layer DCB specimens with a bondline thickness of 0.4 mm, which was the same as the primary adhesive layer thickness in the open-faced DCBs. The coefficient of variance (defined as the standard deviation over the mean value expressed in percentage) of $G_{cs}$ values measured within single degraded or undegraded specimens was between 2% and 4% and that for the specimen-to-specimen variation in the three replications ranged between 6% and 11%. The standard deviations of the replications are given in Figs. 4.5 and 4.6.
In general, three stages of degradation were observed (Fig. 4.7). In the first stage, $G_{cs}$ decreased rapidly from the undegraded value of 4,160 Jm$^{-2}$ to approximately 800±150 Jm$^{-2}$ at 60°C, and 1,010±120 Jm$^{-2}$ at 40°C. A typical fracture surface corresponding to the first stage with a $G_{cs}$ value of approximately 3,000 Jm$^{-2}$ and an adhesive residue thickness, $t_r$ of 105 μm is given in Figure 4.7 (a). The duration of the first stage decreased with increasing both $T$ and RH.

During the second stage of degradation, $G_{cs}$ as well as the thickness of the primary adhesive residue left on the more highly-strained adherend, $t_r$, remained approximately constant regardless of the exposure time and condition (Fig. 4.7 (b)). The $t_r$ values corresponding to the second stage were smaller than those corresponding to the first stage, indicating that the crack path moved closer to the interface of the primary adherend as degradation advanced.

![Figure 4.5: Variation of $G_{cs}$ ($\psi = 27^\circ$) with the time of exposure at 60°C and three different RH. Each data point without error bars is an average of at least 20 measurements within one DCB specimen. Each data point with an error bar is an average value obtained from three different DCB specimens. Error bars show the specimen-to-specimen standard deviation.](image-url)
Figure 4.6: Variation of $G_{cs}$ ($\psi = 27^\circ$) with the time of exposure at 40°C and three different RH. Each data point without error bars is an average of at least 20 measurements within one DCB specimen. Each data point with an error bar is an average value obtained from three different DCB specimens. Error bars show the specimen-to-specimen standard deviation.

Figure 4.7: Schematic representation of $G_{cs}$ variation with exposure time during the three stages of the degradation. Typical failure surfaces and the thickness ($t_r$) of the residual adhesive layer on the more highly-strained adherend are given at each stage.
The third stage corresponded to relatively long exposure times, when the $G_{cs}$ and $t_r$ values dropped again to an average value of about $300\pm100$ Jm$^{-2}$ and less than $10$ μm, respectively. This happened about 365 days at 60°C – 95% and 82% RH (Fig. 4.5), and after 615 days at 40°C – 95% and 82% RH (Fig. 4.6). The average roughness of the fracture surfaces was always greater than $12$ μm in the first and second stages, while in the third stage it was approximately $2$ μm, the same value as on the pretreated adherends.

Typical $R$-curves in the three stages of degradation are shown in Fig. 4.8. In the first and second stages, the $R$-curves were similar to that corresponding to undegraded joints, but with much lower bilinear model parameters ($G_{cs}$, $dG_{cs}/da$ and $L_r$), particularly in the second stage. The rising part of the $R$-curve was not observed in the third stage, and $G_{cs}$ was lower than $G_{ci}$ in the other stages. The $R$-curve evolution with degradation will be discussed in more details in Section 3.4.

![Figure 4.8: Typical measured fracture $R$-curves ($\psi = 27^\circ$) of undegraded DCB joints and open-faced specimens in the three stages of degradation (Fig. 4.7). The lines show the bilinear $R$-curve model fits.](image)

The mode I $G_{cs}$ value corresponding to the second stage of the degradation varied between $510$ and $790$ Jm$^{-2}$ (see Section 3.5). It is interesting that this is comparable to the
values reported for the mode I $G_{cs}$ of DGEBA-based pure epoxy resin without rubber tougheners (the matrix of the present adhesive); i.e. approximately 600 Jm$^{-2}$ in [32] and 920 Jm$^{-2}$ in [34]. It is therefore hypothesized that during the first stage of the degradation, water progressively disrupted the bond between the rubber toughener particles and the epoxy matrix, thereby reducing the fracture toughness. At the end of first stage, $G_{cs}$ reached a value which corresponded approximately to the fracture toughness of the epoxy matrix (DGEBA) without rubber particles. Further degradation in stage two did not damage the epoxy matrix and $G_{cs}$ remained approximately unchanged until stage three, when further degradation became apparent resulting in near-interfacial fracture with a very low $G_{cs}$.

4.3.3.2 Effect of temperature on degradation of $G_{cs}$

Figures 4.9 and 4.10 show the variation of mixed-mode $G_{cs}$ ($\psi = 27^\circ$) with temperature for different exposure times at 95% and 82% RH, respectively. At a particular RH and exposure time, $G_{cs}$ was found to decrease exponentially with increasing temperature as:

$$G_{cs} = m \exp (-nT)$$  \hspace{1cm} (4)

where $m$ and $n$ are exponential fit coefficients. At a given RH, $n$ remained approximately unchanged and $m$ varied approximately linearly over the exposure time up to about 8 months (Table 4.5). This corresponded to stages 1 and 2 in Fig. 4.7, where it is hypothesized that the matrix epoxy remained intact.
Figure 4.9: Variation of $G_{cs}$ ($\psi = 27^\circ$) with temperature at 95% RH and five exposure times. Each data point without error bars is an average of at least 20 measurements within one DCB specimen. Each data point with an error bar is an average value obtained from three different DCB specimens. Error bars show the specimen-to-specimen standard deviation. The curves are least squares exponential fits (Eq. (4)).

Table 4.5: The coefficients of exponential fits (Eq. (4)) to the experimental $G_{cs} - T$ data points for open-faced DCB specimens conditioned at 95% and 82% RH.

<table>
<thead>
<tr>
<th>Time (month)</th>
<th>1</th>
<th>2</th>
<th>4</th>
<th>8</th>
<th>12</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n$ at 95% RH</td>
<td>0.033</td>
<td>0.035</td>
<td>0.034</td>
<td>0.035</td>
<td>0.047</td>
</tr>
<tr>
<td>$n$ at 82% RH</td>
<td>0.021</td>
<td>N/A</td>
<td>0.020</td>
<td>0.023</td>
<td>N/A</td>
</tr>
<tr>
<td>$m$ at 95% RH</td>
<td>7430</td>
<td>7040</td>
<td>6180</td>
<td>5110</td>
<td>5080</td>
</tr>
<tr>
<td>$m$ at 82% RH</td>
<td>6460</td>
<td>N/A</td>
<td>3700</td>
<td>2610</td>
<td>N/A</td>
</tr>
</tbody>
</table>
Figure 4.10: Variation of $G_{cs}$ ($\psi = 27^\circ$) with temperature at 82% RH and three exposure times. Each data point without error bars is an average of at least 20 measurements within one DCB specimen. Each data point with an error bar is an average value obtained from three different DCB specimens. Error bars show the specimen-to-specimen standard deviation. The curves are least-squares exponential fits (Eq. (4)).

The magnitude of degradation was defined as:

$$\Delta G_{cs} = G_{cs}^f - G_{cs}^d$$

where $G_{cs}^f$ is the $G_{cs}$ of the undegraded (fresh) specimens and $G_{cs}^d$ is the $G_{cs}$ after degradation.

Since the first diffusion coefficient ($D_1$ in Table 4.3) followed the Arrhenius rate equation as seen in Chapter 3, it was hypothesized that $\Delta G_{cs}$ would depend on temperature as:

$$\Delta G_{cs} = \Delta G_{cs}^0 \exp\left(-\frac{E_a}{RT}\right)$$

where $\Delta G_{cs}^0$ and $E_a$ are defined as a degradation constant and an activation energy, respectively. $R$ is the universal gas constant (0.00198 kcal K$^{-1}$mol$^{-1}$) and $T$ is absolute temperature (K). Figure 4.11 shows that Eq. (6) provides satisfactory agreement with the experimental $\Delta G_{cs} - T$ data points only at long exposure time (12 months). As seen in Fig. 4.12, both the activation energy and degradation constant decreased significantly with increasing exposure time implying that the degradation process accelerated with exposure time.
Figure 4.11: Measured $\ln(\Delta G_{cs})$ versus inverse temperature and the least-squares linear fits (Eq. (6)) at 95% RH and different exposure times.

Figure 4.12: Variation of activation energy, $E_a$, and degradation constant, $\Delta G_{cs}^0$, with exposure time obtained by fitting Eq. (6) to the experimental data points (Fig. 4.11).

4.3.3.3 Effect of ambient RH on degradation of $G_{cs}$

Figures 4.13 and 4.14 show the variation of $G_{cs}$ ($\psi = 27^\circ$) with RH for open-faced DCB specimens degraded at 60°C and 40°C for different exposure times. In all the conditions studied, $G_{cs}$ appeared to decrease linearly with increasing RH for a given exposure time and temperature. The strength of the dependency of $G_{cs}$ on RH decreased with time. For a given
exposure time, higher RH resulted in a larger number of water molecules available to interact with the adhesive constituents, particularly the rubber toughener particles or their bonds to the surrounding epoxy matrix, as hypothesized above. After relatively long exposure times (e.g. 8 months at 60°C), even the lower RH value (43%) provided enough water to eliminate the toughening mechanism completely.

Figure 4.13: Variation of $G_\text{cs}$ ($\psi = 27^\circ$) with RH at 60°C and three exposure times. Each data point is an average value obtained from three DCB specimens. Error bars show the specimen-to-specimen standard deviation. The lines are least-squares linear fits.

Figure 4.14: Variation of $G_\text{cs}$ ($\psi = 27^\circ$) with RH at 40°C and three exposure times. Each data point without error bars is an average of at least 20 measurements within one DCB specimen. Each data point with an error bar is an average value obtained from three DCB specimens. Error bars show the specimen-to-specimen standard deviation. The lines are least-squares linear fits.
Figure 4.15 shows the variation of $G_{cs}$ for a given exposure time with the ambient water concentration, combining the data for all temperatures and RH values. It is interesting that there was reasonable agreement between the power function fits and the experimental data even though the effects of temperature and ambient RH were combined into the ambient water concentration. This provides a mean to evaluate the $G_{cs}$ of an open-faced DCB joint as a function of exposure time at a given ambient water concentration without any knowledge about the water concentration in the adhesive layer itself. The ambient water concentration can be easily calculated for any given pair of $T$ and RH [29].

![Graph showing variation of $G_{cs}$ with ambient water concentration for three different exposure times. Each data point without error bars is an average of at least 20 measurements within one DCB specimen. Each data point with an error bar is an average value obtained from three different DCB specimens. Error bars show the specimen-to-specimen standard deviation. The curves are least-squares power function fits.]

4.3.3.4. Effect of adhesive water concentration on degradation of $G_{cs}$

Figure 4.16 depicts the variation of $G_{cs}$ ($\psi = 27^\circ$) with the adhesive layer average water concentration, $C(x,t)$ after each of the exposure periods for open-faced DCB specimens at different combinations of $T$ and RH. The SDF model parameters obtained for each exposure condition (Table 4.3) were used to calculate the water concentration at a given exposure time, $t$. Since the diffusion path through the primary adhesive layer thickness was only 0.4 mm, the
water concentration distribution over the bondline thickness was assumed to be uniform for the time intervals studied. At a particular exposure condition, $G_{cs}$ decreased almost linearly with increasing water concentration until saturation. Even though $G_{cs}$ continued to drop after saturation, the majority of the degradation occurred during the water uptake phase before saturation. Table 4.6 compares the decrease in $G_{cs}$ corresponding to the onset of water saturation ($\Delta G_{cs}^S$) and the total decrease in $G_{cs}$ obtained during stage 1 of the degradation ($\Delta G_{cs}^T$, the initial $G_{cs}$ minus the average value in stage 2). Therefore, between 71% and 93% of the total $G_{cs}$ decrease occurred during the water uptake phase leading to saturation. Furthermore, $\Delta G_{cs}^S$, the decrease to the onset of saturation was linearly proportional to the saturated water concentration in the adhesive, $C_\infty$, irrespective of $T$ and RH (Fig. 4.17). This suggests that the water molecules disrupted the bonds between the rubber particles and matrix immediately and degraded the toughening mechanism with almost no delay.

Figure 4.16: Variation of $G_{cs}$ ($\psi = 27^\circ$) with average adhesive water concentration for different exposure conditions during the period of water uptake. $C(x,t)$ was calculated using Eq. (1) with $x = 0.2$ mm (half of the primary bondline thickness) and the corresponding exposure time at each case. The lines are least-squares fits to the point of saturation.
Table 4.6: Comparison between the decrease of $G_{cs}$ from the start of the experiment to saturation and the total $G_{cs}$ decrease to the end of stage 2 under different exposure conditions.

<table>
<thead>
<tr>
<th>Exposure condition</th>
<th>Saturated water concentration, $C_{\infty}$ (%)</th>
<th>Saturatio time * (Day)</th>
<th>$G_{cs}$ decrease at saturation, $\Delta G_{cs}^S$ (Jm$^{-2}$)</th>
<th>Total $G_{cs}$ decrease, $\Delta G_{cs}^T$ (Jm$^{-2}$)</th>
<th>$\Delta G_{cs}^S / \Delta G_{cs}^T$</th>
</tr>
</thead>
<tbody>
<tr>
<td>60°C-95%RH</td>
<td>6.98</td>
<td>31</td>
<td>3130</td>
<td>3360</td>
<td>0.93</td>
</tr>
<tr>
<td>60°C-82%RH</td>
<td>4.02</td>
<td>66</td>
<td>2740</td>
<td>3360</td>
<td>0.82</td>
</tr>
<tr>
<td>60°C-43%RH</td>
<td>1.62</td>
<td>104</td>
<td>2400</td>
<td>3360</td>
<td>0.71</td>
</tr>
<tr>
<td>50°C-95%RH</td>
<td>6.67</td>
<td>56</td>
<td>3110</td>
<td>3360</td>
<td>0.92</td>
</tr>
<tr>
<td>40°C-95%RH</td>
<td>4.78</td>
<td>78</td>
<td>2840</td>
<td>3150</td>
<td>0.90</td>
</tr>
<tr>
<td>40°C-82%RH</td>
<td>3.53</td>
<td>92</td>
<td>2591</td>
<td>3150</td>
<td>0.82</td>
</tr>
</tbody>
</table>

*: Defined as the time at which $M_t = 0.99 M_\infty$ in Fig. 4.3.

4.3.4. R-curve degradation

4.3.4.1. Initiation $G_c$

Figure 4.18 shows the variation of mixed-mode initiation strain energy release rate, $G_{ci}$ ($\psi = 27^\circ$) with exposure time for open-faced DCB specimens degraded at 60°C and at three different RH. Nine replications of $G_{ci}$ for undegraded single layer DCB specimens are also given in the figure. The variation of $G_{ci}$ with the exposure time was of the same order as the scatter in the undegraded tests. Furthermore, a t-test revealed that the differences between the average $G_{ci}$ values obtained at each exposure condition (with varying exposure time) and that
of the undegraded specimens were not statistically significant at a 95% confidence interval. Therefore, it can be concluded that \( G_{ci} \) remained unchanged during the first and second stages of the degradation, irrespective of the exposure time, \( T \) and RH, and its grand average was calculated to be 580 Jm\(^{-2}\), which was in the same range as the values of \( G_{cs} \) seen in stage 2. It is therefore hypothesized that crack initiation is governed by the properties of the epoxy matrix and that the toughening action of rubber particles does not become appreciable until after a certain amount of crack extension (more than about 50 μm in the present case). This hypothesis is consistent with the fact that \( G_{ci} \) was independent of degradation, and with the earlier hypothesis that \( G_{cs} \) of stage 2 was also independent of further degradation because it corresponded to the epoxy matrix acting without the toughening action of rubber particles. Hence, \( G_{ci} \) was controlled by the stress state of the adhesive geometry at the start of the bondline (edge of the foil). The relatively high scatter in \( G_{ci} \) might be related to the difficulty in replicating this geometry accurately, and to the inherent limitations in detecting initiation.

![Graph showing variation of \( G_{ci} \) with time for different RH levels.](image)

Figure 4.18: Variation of mixed-mode \( G_{ci} (\psi = 27°) \) for undegraded closed DCB specimens and degraded open-faced DCB specimens exposed at 60°C and three different RH.

### 4.3.4.2. Toughening rate, \( dG_{cr}/da \)

The slope of the rising part of the \( R \)-curve (toughening rate) decreased with increasing exposure time until it reached an approximately constant value. The time to reach this
constant value varied with RH. This pattern of behavior of the toughening rate was the same as seen with $G_{cs}$ (Figs. 4.5 and 4.6) which suggests that the degradation of these two parameters was related. Figure 4.19 shows that the slope of the $R$-curve rising part varied linearly with the steady-state fracture toughness ($G_{cs}$), independent of the exposure time, $T$ and RH. The toughening rate could thus be expressed as:

$$dG_{cr}/da = \alpha G_{cs}$$

(7)

where $\alpha = 0.081 \text{ mm}^{-1}$ for this adhesive system (Fig. 4.19) and the intercept of the fitted line was negligible.

![Graph showing the variation of the slope of the rising part of the $R$-curve with $G_{cs}$. Each data point was calculated by fitting the bilinear $R$-curve model to the $G_{cr}$ vs. crack length measurements of DCB specimens aged under the various $T$ and RH conditions.](image)

$y = 0.081 \times$

$R^2 = 0.97$

4.3.4.3. Rising part length, $L_r$

Figure 4.20 shows the variation of the length of the $R$-curve rising part, $L_r$ with $G_{cs}$. In general, $L_r$ decreased with decreasing $G_{cs}$, independent of exposure time, $T$ and RH. Based on Eq. (3), the fracture toughness can be expressed as follows when $a = a_r$:

$$G_{cs} = G_{cr} (a_r) = G_{ci} + \frac{dG_{cr}}{da} L_r$$

(8)
Substituting Eq. (7) into Eq. (8) results in an empirical relationship between \( L_r \) and \( G_{cs} \):

\[
L_r = \alpha^{-1}(1 - G_{ci} G_{cs}^{-1})
\]

(9)

Figure 4.20 shows that the least-squares fit of Eq. (9) agrees very well with the experimental \( L_r \) versus \( G_{cs} \) data points. The \( \alpha \) and \( G_{ci} \) values calculated from the curve fit were found to be 0.080 mm\(^{-1}\) and 607 Jm\(^{-2}\), respectively. These values are in excellent agreement with \( \alpha = 0.081 \) mm\(^{-1}\) obtained from Eq. (7) and the grand average of \( G_{ci} = 580 \) Jm\(^{-2}\) presented in Section 3.4.1. This agreement implies that for all practical purposes, the slope and length of the rising part of the \( R \)-curve are independent of the \( T \) and RH aging conditions for the present adhesive system.

![Graph showing variation of \( L_r \) with \( G_{cs} \).](image)

Figure 4.20: Variation of the length of the \( R \)-curve rising part with \( G_{cs} \), combining data for all \( T \) and RH aging conditions. Each data point is calculated by fitting the bilinear \( R \)-curve model to the \( G_{cr} \) vs. crack length measurements of a DCB specimen aged at various \( T \) and RH.

The evolution of the bilinear \( R \)-curve model with degradation can thus be characterized in terms of only \( G_{cs} \) and \( G_{ci} \). Substituting Eq. (7) into Eq. (3) yields:

\[
G_c = \begin{cases} 
G_{cr}(a) = G_{ci} + \alpha G_{cs}(a - a_0), & a_0 < a < a_r \\
G_{cs}, & a \geq a_r
\end{cases}
\]

(10)
with

\[ a_r = L_r + a_0 = \alpha^{-1}(1 - G_{ci} G_{cs}^{-1}) + a_0 \]  

\(11\)

In summary, for any adhesive system with similar behavior to that studied, the parameters required to characterize the evolution of the \(R\)-curves with degradation are \(G_{cs}\), \(G_{ci}\) and \(\alpha\). All these three parameters can be obtained using open-faced DCB specimens aged at a single exposure condition (combination of \(T\) and \(RH\)) for varying exposure times which greatly reduces the experimental effort.

Furthermore, this model can be used in the \(R\)-curve prediction of closed joints. In practical joints, the water concentration and hence the level of degradation vary along the bondline, being maximum at the exposed end, and thus the degradation as well as toughening within the closed joint are functions of distance from the end. The steady-state \(G_c\) corresponding to a certain level of degradation at a given crack tip position can be evaluated using SDF diffusion model and the fracture test results of degraded open-faced DCB specimens. The initiation \(G_c\) and \(\alpha\) are constants for a given adhesive system. The proposed degradation model (Eq. (10)) can then be used to construct the \(R\)-curve which includes the effects of both toughening and irreversible environmental degradation in a closed joint.

4.3.5. Effect of phase angle on degradation

To investigate the sensitivity of the degradation to the loading mode, the variability of \(G_{cs}\) with exposure time was studied at different phase angles. It was found that the dependence of \(G_{cs}\) on the exposure time followed the typical three stage trend shown in Fig. 4.7, with the duration of the stages being independent of the phase angle. As depicted in Fig. 4.21, the degraded mixed-mode \(G_{cs}\) values obtained at both phase angles of 27° and 48° remained proportional to the degraded mode-I \(G_{cs}\), independent of the degradation time, \(T\) and \(RH\). The ratio between mixed-mode \(G_{cs}\) and that at mode I was 1.29 at 27° and 2.13 at 48°, independent of the level of degradation. It is interesting to note that the corresponding ratios for the undegraded single layer DCB specimens (bonded in one step) were found to be 1.29 and 2.06, respectively (Table 4.4). This implies that fracture envelope \((G_{cs} - \psi\) relationship) shifts
downward uniformly with degradation. Therefore, if the fracture toughness envelope for the undegraded case is known, it is possible to extract the entire fracture envelope for any level of degradation if the $G_{cs}$ is known for that level of degradation at a single phase angle.

$$y = 2.131x - 26$$

$R^2 = 0.98$

$$y = 1.296x + 8$$

$R^2 = 0.99$

Figure 4.21: Variation of mixed-mode $G_{cs}$ with mode-I $G_{cs}$ for open-faced DCB specimens degraded at the various combinations of $T$ and RH. The lines are least-squares linear fits.

The experimental $G_{cs}$ vs. $\psi$ data points for undegraded specimens of the studied adhesive system was found to fit a third order polynomial in the form of:

$$G_{cs}(\psi) = G_{ics} (1 + \alpha \psi + \beta \psi^2 + \gamma \psi^3)$$

(12)

where $G_{ics}$ is the mode-I $G_{cs}$ and $\alpha$, $\beta$ and $\gamma$ are the fit constants [34]. Since the ratio $G_{cs}(\psi)/G_{ics}$ remained unchanged with degradation (Fig. 4.21), the polynomial coefficients should also remain constant. Therefore, for any level of degradation, the measurement of $G_{ics}$ provides the information required to construct the corresponding fracture envelope using Eq. (12).

4.5. Conclusions

Open-faced DCB specimens of a toughened epoxy-aluminum adhesive system were degraded over a relatively wide range of temperature, RH and exposure time. The irreversible
effects were measured by drying the primary (aged) adhesive layer prior to closing the joint to form a DCB joint that was tested under mixed-mode loading conditions. Three stages of degradation were observed. In the first stage, the bilinear $R$-curve parameters ($G_{cs}$, $dG_{cr}/da$ and $L_r$) as well as the adhesive residual thickness ($t_r$) decreased in proportion to the exposure time until $G_{cs}$ reached a threshold value which corresponded to the fracture toughness of epoxy matrix (DGEBA) in the absence of rubber toughener. During the second stage, all bilinear $R$-curve model parameters and $t_r$ remained unchanged with time and the fracture remained cohesive, but close to the interface. With extremely long exposure, both $G_{cs}$ and $t_r$ decreased again to a very low value and no $R$-curve behavior was observed. This corresponded to the third stage in which the crack path was even closer to the interface, but with an extremely thin layer of epoxy remaining on a very smooth fracture surface.

In general, $G_{cs}$ decreased with increasing temperature, RH, water concentration in the adhesive layer and the ambient water concentration while $G_{ci}$ remained unchanged during degradation. A linear relationship was found between $dG_{cs}/da$ and $G_{cs}$, irrespective of the degradation parameters (Eq. (7)). An $R$-curve degradation model was proposed which greatly reduces the experimental efforts in the degradation characterization of similarly-behaved adhesive systems (Eq. (9)) and also has an application in the $R$-curve prediction of a closed joint having nonuniform degradation. Moreover, the degradation of fracture toughness was found to be insensitive to the phase angle. Consequently, the fracture toughness envelope shifts downward uniformly for a given level of degradation. This is a significant simplification since it is possible to extract the entire fracture envelope for any level of degradation if the $G_{cs}$ is known for that level of degradation at a single phase angle.

Future work should include the effects of various amounts of retained water in the aged adhesive. Previous experience suggests that unbound water plasticizes the adhesive matrix, increasing the fracture energy [7, 23-25].
4.6. References


Chapter 5: Hygrothermal degradation of two rubber-toughened epoxy adhesives: Application of open-faced fracture tests

5.1. Introduction

It is known that hygrothermal degradation of adhesive joints is closely related to water absorption and desorption by the adhesive [1-5]. Toughened adhesives usually exhibit an anomalous absorption behavior in which a simple Fickian model tends to overestimate the water concentration [6-8]. Dual Fickian models that superimpose two Fickian models either acting in parallel [6-7, 9], or sequentially, as introduced in Chapter 3, have been used successfully to characterize the anomalous water diffusion behavior. Unlike absorption, water desorption behavior is normally Fickian [10]. The existence of retained water after drying at temperatures below the glass transition temperature, \( T_g \), has been reported in the literature [11-14]. Zhou and Lucas showed that the retained water after low-temperature desorption was related to the amount of water molecules that formed strong bonds with the epoxy constituents [12].

The absorbed water molecules in an epoxy can exist in either the free or bound states [3, 4, 15]. Free water molecules act as a plasticizer, strongly reducing \( T_g \) and the modulus of elasticity [16]. The water molecules that are tightly bound to the epoxy constituents can act as intermolecular joints causing an increase in the modulus of elasticity [17]. Such bound water is believed to also cause irreversible damage such as chain scission, hydrolysis, crack initiation, crack growth, and subsequent loss of material [18]. In addition, water can disrupt the bonds at the interface between the adhesive layer and the adherends, causing irreversible damage in the interphase region [10].

Conventional closed joints are not well suited for degradation studies because the degradation is not uniform and the water diffusion path is long, causing degradation

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experiments to be lengthy. Since the fracture results from testing such joints do not represent a discrete state of moisture degradation, it is impossible to apply the measured properties directly to other joint configurations or ageing environments [19]. Therefore, open-faced specimens have been utilized to achieve a spatially uniform state of degradation, as well as to accelerate the aging process by shortening the diffusion path of water into the adhesive layer [19-22].

This Chapter describes the absorption and desorption profiles of two different rubber-toughened epoxy adhesives. XPS and DMTA analyses were carried out to explain the differences in the gravimetric measurements. Open-faced double cantilever beam (DCB) specimens were then used to accelerate the water absorption and desorption processes and measure the resulting change in fracture strength. A degradation model analogous to Fick’s law was proposed to characterize the loss of fracture strength in adhesive system 1, and the effects of changes in temperature, RH and water concentration on the model parameters were investigated. The relationship between the fracture strength and the exposure history was also evaluated (i.e. the effects of different combinations of water concentration and exposure time at a given temperature). A degradation mechanism was proposed which accounts for the different characteristics of the two adhesive systems.

5.2. Experimental procedure
The degradation of the fracture properties of two highly-toughened, heat-cured structural epoxy adhesives (Table 5.1) was measured using open-faced double cantilever beam (DCB) specimens (Fig. 5.1). Adhesive 2 was used as the secondary adhesive layer in all the joints. Gravimetric measurements on cast, bulk adhesive wafers were used to characterize the water diffusion behavior. The recommended curing profile of at least 30 min at 180°C was used for the primary and secondary bonds of the open-faced DCB fracture specimens, and the wafers used in the diffusion measurements. Cure was monitored using a thermocouple embedded in the adhesive layer.
Table 5.1: Mechanical and physical properties of adhesives 1 and 2 as supplied by the manufacturers.

<table>
<thead>
<tr>
<th>Adhesive</th>
<th>Elastic modulus, $E$, MPa</th>
<th>Poisson ratio, $\nu$</th>
<th>Tensile strength, $\sigma_y$, MPa</th>
<th>Cured density, g/cm$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adhesive 1</td>
<td>1.96</td>
<td>0.45</td>
<td>44.8</td>
<td>1.50</td>
</tr>
<tr>
<td>Adhesive 2</td>
<td>1.73</td>
<td>0.39</td>
<td>N/A</td>
<td>1.14</td>
</tr>
</tbody>
</table>

Figure 5.1: Configuration and dimensions of the open-faced DCB joints (not to scale).

5.2.1. Gravimetric measurements

Mass uptake measurements have been made under various combinations of temperature and RH on cast wafers of these same two adhesive in Chapter 3. Table 5.2 summarizes the environmental conditions that were used in Chapter 3, the saturated salt
solutions used to generate the atmospheres [19, 23], and the amount of water vapor present per unit volume of gas [24]. After saturation, the wafers had been dried in a vacuum oven containing anhydrous calcium sulphate at 40°C for up to 90 days. The absorption and desorption measurements had been repeated on three wafers at each exposure condition. The temperature-humidity conditions of Table 5.2 were also used for the aging of the present open-faced DCB specimens, as described below.

Table 5.2: Exposure conditions for the gravimetric samples of Chapter 3 and the present open-faced specimens, together with the saturated salt solutions used and the ambient water concentration achieved at each condition.

<table>
<thead>
<tr>
<th>RH (%)</th>
<th>Salt solution</th>
<th>Ambient water concentration (g/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>T=20°C</td>
</tr>
<tr>
<td>43</td>
<td>K₂CO₃</td>
<td>7.4</td>
</tr>
<tr>
<td>82</td>
<td>KCl</td>
<td>14.1</td>
</tr>
<tr>
<td>95</td>
<td>K₂SO₄</td>
<td>16.3</td>
</tr>
</tbody>
</table>

5.2.2. Dynamic mechanical thermal analysis

Cast wafers of adhesives 1 and 2 (approximately 10 x 20 mm with 0.8 mm thickness) in the fresh, wet and dried states were tested in a dynamic mechanical thermal analyzer. The wafers were subjected to a frequency of 1 Hz, a tensile strain of 0.1%, and a temperature ramp of 10°C/min between 30 and 190°C. The peak of the loss modulus versus temperature curve was used as an indicator of the glass transition temperature, \( T_g \).

5.2.3. Open-faced DCB specimen fabrication

The DCB adherends were AA6061-T6 aluminum alloy pretreated using the P2 sulfuric acid etch method [25]. The primary adhesive layer of 0.4 mm thickness was cured onto the primary adherend using a backing plate coated with a polytetrafluoroethylene release agent that had been baked dry (Fig. 5.1). After curing, the backing plate was removed and the open-faced specimens were degraded for varying times under the exposure conditions of Table 5.2. XPS analysis showed that insignificant amounts of the release agent transferred to the free surface of the primary adhesive. The degraded specimens were then dried in a vacuum oven.
containing anhydrous calcium sulphate at 40°C for approximately 7 days. The objective was to measure the irreversible effects of degradation by eliminating any reversible effects of water absorption such as plasticization [20]. To increase the mechanical interlocking and ensure a strong bonding between the primary and secondary adhesive layers, the primary adhesive layer surface was roughened using 100 grit sandpaper, acetone wiped, and dried before the secondary bonding. The roughening process removed less than 25 μm of the primary adhesive layer. To make a complete DCB joint, the open-faced specimen was then bonded to a second adherend using adhesive 2 and the same curing profile as for the primary bonding.

To investigate whether the second cure cycle had any effect on the fracture toughness of the primary layer of adhesive, fracture tests were carried out on un-aged closed DCB joints made from a single layer of adhesive 1. The difference between the average $G_{cc}$ values for specimens that were cured once and twice was only 4%, which was statistically insignificant (t-test, 95% confidence). It was thus assumed that the primary layer was fully cured during the first cure and unaffected by the secondary bonding process. Details about the open-faced fabrication procedure are given in Chapter 4.

The crack initiation geometry was created by embedding a folded 10 μm aluminum foil within the primary adhesive layer. To minimize the possibility of mechanical damage to the specimen edges after curing, the very small amount of residual adhesive that had flowed from the edges of the open-faced DCB specimens was removed using a gentle wet sanding process (300 grit). To further improve the visibility of the crack, the bondline was finished by hand with 600 grit sandpaper. A very thin layer of white paper correction liquid, diluted with hexane, was then applied to the specimen edges to assist in the identification of the macro-crack tip.

5.2.4. Fracture test methodology

The mixed-mode fracture tests were conducted using a servo-electric load frame and the load jig of [26]. All tests were conducted at a loading phase angle $\psi = 27^\circ$, where $\psi = \arctan \left( \left( \frac{G_{Ic}}{G_{IIc}} \right)^{0.5} \right)$, and $G_{Ic}$ and $G_{IIc}$ are the mode I and II components of the strain energy release rate. The specimen was loaded in discrete small steps while viewing the crack tip (the tip of the furthest advanced micro-crack) through a microscope to detect the onset of crack propagation.
at the critical load. The crack length, $a$ (Fig. 5.1), was determined to an accuracy of ±20 μm using an optical microscope on a micrometer stage having a field of view of 2 mm. A discussion of the discrete loading method methodology and its validity is given in Chapter 2. A beam-on-elastic-foundation model was used to calculate the steady-state critical strain energy release rate, $G_{cs}$ [27].

5.3. Results and discussion

5.3.1. Water absorption and desorption

Sequential dual Fickian (SDF) and simple Fickian models (see Chapter 3) were used to characterize the water absorption and desorption behaviors, respectively, in both adhesives. Figure 5.2 shows the gravimetrically measured fractional mass uptake, $M_t$, versus the square root of time ($t^{1/2}$), and the best fits based on the SDF model at 60°C – 95% RH and 60°C – 82% RH for adhesives 1 and 2. $M_t$ is defined as the total mass uptake of water at time $t$ expressed as a percentage of the initial mass of the adhesive. After the initial linear Fickian diffusion and the onset of a plateau, a second mass increase was observed for both adhesives in most of the exposure conditions. Hence, a simple Fickian model would overestimate the experimental results, especially at high $T$ and RH, and at intermediate times. As explained in Chapter 3, this anomalous behavior was captured by the SDF model. Figure 5.2 also depicts the fractional mass loss during drying versus $t^{1/2}$ and the least-squares fits based on a simple Fickian model for both adhesives. The mass of the samples decreased with drying time according to Fick’s law and reached a constant minimum value of fractional retained water, $M_r$ (mass of retained water expressed as a percentage of the initial mass of the adhesive). The required SDF absorption parameters ($D_1$, $D_2$, $M_{1\infty}$, $M_{2\infty}$, $t_d$) and the simple Fickian desorption parameters ($D_d$, $M_r$) for both adhesives are given in Chapter 3.
In general, adhesive 2 was more resistant to water absorption than adhesive 1, and so all the SDF parameters for adhesive 2 were less than those for adhesive 1 at the same exposure condition. The main difference between the desorption behavior of adhesives 1 and 2 was the minimum fractional retained water after drying, $M_r$ (see Chapter 3). For adhesive 1, $M_r$ increased proportionally with the increase of temperature, RH, $M_\infty$ (sum of $M_{1\infty}$ and $M_{2\infty}$) and the ambient water concentration. $M_r/M_\infty$, which represents the ratio between the bound and total water molecules (see Section 3.3), was negligible (approximately 3%) for adhesive 2 while it was much greater for adhesive 1, varying between 24% and 60% depending on the exposure condition. A higher temperature and lower RH resulted in higher values of $M_r/M_\infty$ and hence higher ratios of bound to free water molecules.
5.3.2. XPS analysis

The significant difference in the amount of retained water in adhesives 1 and 2 after drying was investigated using XPS on samples in three conditions: fresh (as-cured), saturated wet, and dried after saturation. The wet samples of adhesives 1 and 2 were saturated at 60°C – 95% RH giving $M_\infty$ of 6.98% and 4.78%, respectively. The dry samples were made by drying saturated wet samples at 40°C in a vacuum oven containing anhydrous calcium sulphate for one week. Three repetitions were carried out at each condition. Analysis areas had a diameter of 500 μm. Elemental compositions were determined from peak areas. Table 5.3 shows the O/C ratios for the two adhesives in the fresh, saturated wet and dried conditions. As expected, the ratios were largest in the wet condition, since the samples included free water molecules, and the values were proportional to $M_\infty$, being greater for adhesive 1 than for adhesive 2. Furthermore, the O/C ratio increased from the fresh state to the dried state after initial saturation. This increase was related to the chemical interactions between the adhesives constituents and water molecules such as hydrolysis, as has explained by Xiao et al. [28]. In the dried condition, the O/C ratio of adhesive 1 was greater than that of adhesive 2, which agrees qualitatively with the greater amount of retained water in adhesive 1.

<table>
<thead>
<tr>
<th>Condition</th>
<th>O/C ratio in percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Adhesive 1</td>
</tr>
<tr>
<td>Fresh</td>
<td>13.5</td>
</tr>
<tr>
<td>Saturated wet</td>
<td>22.6</td>
</tr>
<tr>
<td>Dried</td>
<td>18.3</td>
</tr>
</tbody>
</table>

Figure 5.3 shows the O1s peaks associated with various chemical bonds (binding energies) for fresh, saturated wet, and dried samples of adhesives 1 and 2. The O1s peak at approximately 533 eV was dominant in all cases and corresponded to the one observed in a cured di-glycidyl ether of bisphenol A (DGEBA) bulk epoxy sample as reported in [29]. O1sA at 534 eV was also detected in each case and was thus related to the adhesive constituents. It is hypothesized that the third peak, O1sB at 531.5 of eV, was related to a bond associated with
water molecules since it was present in the wet samples of both adhesives, but not in the fresh and dried samples of adhesive 2, nor was it significant in the fresh adhesive 1. The significant amount of O1sB present in the dried samples of adhesive 1 qualitatively supports the gravimetric results indicating that a considerable amount of absorbed water in adhesive 1 could not be removed during the drying process. The O1sB peak was not detected in the dried adhesive 2 samples, which was consistent with the negligible amount of retained water in adhesive 2.

Figure 5.3: XPS 1s oxygen peaks (O1s, O1sA and O1sB) for fresh, saturated wet and dried samples of adhesives 1 and 2.
Furthermore, XPS analysis of the fracture surfaces of aged and dried open-faced DCB joints (three replications) indicated the presence of O1sB in the fracture surface of joints in which adhesive 1 was the primary layer, but not in those in which adhesive 2 was the primary layer. This was expected since the open-faced joints had been aged and dried before the fracture tests, and so their XPS spectra resembled those of dried wafers. Indeed, the ratio of the O1sB peak height to that of the total O1s obtained from adhesive 1 open-faced joints (O1sB/O1s=13%) was comparable to that in the dried wafer sample of adhesive 1 (O1sB/O1s=10%).

5.3.3. Dynamic mechanical thermal analysis

Figures 5.4 and 5.5 show representative examples of the loss modulus, $E'$ as a function of temperature, $T$, for samples of adhesives 1 and 2, respectively, in the fresh, wet and dried conditions, as measured using the DMTA. Table 5.4 summarizes the conditioning history and the $T_g$ values measured from the $E'$ vs. $T$ curves for both adhesives. In the wet samples of both adhesives, the peak of the $E'$ vs. $T$ curves shifted to the left indicating a significant drop in $T_g$. Also, at elevated temperatures, the loss modulus of the wet samples became lower than that of the fresh adhesive as observed in [30, 31]. The rate of $T_g$ decrease for adhesives 1 and 2 was approximately 9°C and 7°C, respectively, per 1% increase in the water concentration. This is in good agreement with the value of 8°C per 1% reported for DGEBA epoxy resins [32]. As seen in Table 5.4, the plasticizing effect was reversible with drying causing $T_g$ to return to the value of the fresh samples in both adhesives, irrespective of the amount of retained water. Noting that the decrease in $T_g$ with absorbed water is attributed to the plasticization effect of free water molecules, it can be concluded that the retained water molecules in adhesive 1 were not free and were strongly bound to the adhesive constituents, since $T_g$ was unaffected by the presence of the retained water in adhesive 1.

To support this conclusion further, the DMTA temperature scan test was repeated on some of the wet and dried samples of adhesive 1. As expected, because of the high temperatures reached in the DMTA (up to 190°C), the gravimetric measurements taken after the first scan showed some mass loss in both wet and dry samples, as also reported in [12,18].
This mass loss during the first scan in the wet samples caused $T_g$ to increase from 75°C in the first scan to 111°C in the second scan. There was a negligible change in $T_g$ of the dried samples (112°C in the first scan and 113°C in the second scan), in spite of the decrease in the retained water during the first scan (1.68% and 1.26% before and after the first scan). Therefore, the retained water after drying had no plasticizing effect, supporting the conclusion that the retained water molecules were tightly bound to the adhesive constituents.

Figure 5.4: The variation of loss modulus versus temperature for fresh (Table 5.4: sample Fresh A1), wet (Table 5.4: sample Wet A1) and dried (Table 5.4: sample Dry A1) samples of adhesive 1.

Figure 5.5: The variation of loss modulus versus temperature for fresh (Table 5.4: sample Fresh A2), wet (Table 5.4: sample Wet A2) and dried (Table 5.4: sample Dry A2) samples of adhesive 2.
Table 5.4: The conditioning history and the fractional mass uptake, $M_t$, reached before DMTA testing, and $T_g$ for different samples of adhesives 1 and 2. The drying condition for the saturated samples was 14 days at 40°C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Conditioning</th>
<th>$M_t$ (%)</th>
<th>$T_g$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh</td>
<td>A1 cured and dried</td>
<td>0.00</td>
<td>121</td>
</tr>
<tr>
<td>Wet A1</td>
<td>saturated at 60°C-43%RH</td>
<td>1.62</td>
<td>111</td>
</tr>
<tr>
<td>Wet B1</td>
<td>5 days aging at 60°C-95%RH</td>
<td>4.54</td>
<td>75</td>
</tr>
<tr>
<td>Wet C1</td>
<td>7 days aging at 60°C-95%RH</td>
<td>4.81</td>
<td>81</td>
</tr>
<tr>
<td>Dry A1</td>
<td>saturated at 40°C-43%RH and dried</td>
<td>0.86</td>
<td>124</td>
</tr>
<tr>
<td>Dry B1</td>
<td>saturated at 60°C-43%RH and dried</td>
<td>0.98</td>
<td>122</td>
</tr>
<tr>
<td>Dry C1</td>
<td>saturated at 60°C-95%RH and dried</td>
<td>1.76</td>
<td>121</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>Conditioning</th>
<th>$M_t$ (%)</th>
<th>$T_g$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh</td>
<td>A2 cured and dried</td>
<td>0.00</td>
<td>75</td>
</tr>
<tr>
<td>Wet A2</td>
<td>saturated at 60°C-95%RH</td>
<td>4.78</td>
<td>42</td>
</tr>
<tr>
<td>Dry A2</td>
<td>saturated at 60°C-95%RH and dried</td>
<td>0.16</td>
<td>78</td>
</tr>
</tbody>
</table>

5.3.4. Fracture strength degradation

5.3.4.1. $G_{cs}$ of fresh joints

The fracture strength of the primary layer in undegraded open-faced specimens was difficult to measure because of the tendency of the crack to kink toward and propagate in the secondary layer even though it initiated at the foil embedded in the primary layer. This will be discussed further in Chapter 7. This problem did not occur when the primary layer was aged, since the reduced fracture toughness of the degraded primary layer compared to that of the fresh secondary layer resulted in a crack path that remained in the primary layer. Therefore, the $G_{cs}$ of the un-aged (fresh) open-faced DCB specimens was estimated using a standard closed DCB (single adhesive layer). It is known that the fracture toughness of adhesive joints is significantly affected by the bondline thickness in single-layered specimens [27, 33-35]. Therefore, in order to establish the $G_{cs}$ corresponding to a fresh open-faced specimen using a standard DCB with a single adhesive layer, it was necessary to determine whether to make the single layer equal to the primary adhesive thickness or the sum of the primary and secondary layers. Experiments were conducted with different combinations of primary and secondary adhesive thicknesses, and it was concluded that the thickness of the layer in which the crack
propagated (primary or secondary) was the parameter affecting the fracture strength of the joint, not the total thickness of the primary and secondary layers. In other words, the crack propagated in one adhesive layer as if the other layer did not exist. Therefore, the $G_{cs}$ of a single-layered DCB specimen with a bondline thickness equal to that of the primary layer in open-faced DCB specimens was used as the reference fracture toughness in the evaluation of the amount of degradation for aged open-faced DCB specimens. At a phase angle of 27° and a bondline thickness of 400 μm, these reference values were 4160 Jm$^{-2}$ (six replications with standard deviation of 260 Jm$^{-2}$) and 4380 Jm$^{-2}$ (six replications with standard deviation of 284 Jm$^{-2}$) for adhesive systems 1 and 2, respectively.

### 5.3.4.2. $G_{cs}$ degradation in adhesive system 1

The fracture strength of the degraded open-faced DCB specimens of adhesive system 1, measured as the steady-state critical strain energy release rate, $G_{cs}(t)$, was a strong function of the exposure time in the early stages of degradation. The amount of degradation was quantified by $\Delta G_{cs}(t)$, the decrease in $G_{cs}$:

$$\Delta G_{cs}(t) = G_{cs}(0) - G_{cs}(t)$$

where $G_{cs}(0)$ is the reference fracture strength of the undegraded specimens. Figures 5.6 and 5.7 show the variation of $\Delta G_{cs}(t)$ with the square root of exposure time (up to approximately 400 days) for adhesive system 1 at three different RH and temperatures of 60°C and 40°C, respectively. Figure 5.8 shows similar results for temperatures of 20°C (at 95% RH) and 50°C (at 95% RH and 82% RH) up to approximately 600 days. It is seen that the fracture strength decreased even at very short exposure times and at all water concentrations, even those that were very low. $\Delta G_{cs}(t)$ then reached a plateau value ($\Delta G_{cs}^{\infty}$). It was hypothesized that the variation of $\Delta G_{cs}(t)$ with time could be modeled using a simple Fickian-type relation since it appeared to depend mostly on the amount of water absorbed. Therefore,

$$\Delta G_{cs}(t) = \left[1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left(-\frac{D_{deg}t}{1+D_{deg}t}\right)\right] \times \Delta G_{cs}^{\infty}$$

105
where $D_{deg}$(day$^{-1}$) is defined as a degradation coefficient which reflects the rate of degradation. Figures 5.6 – 5.8 show the nonlinear least-squares fits of Eq. (2) to the experimental $\Delta G_{cs}(t) - t^{1/2}$ data. Overall, the agreement was reasonable, although Eq. (2) overestimated the degradation by approximately 10% near the end of the rising portion of the curves at higher RH. Although, this indicates that a dual Fickian-type model would result in a better representation of the fracture strength loss, similar to the dual stage Fickian behavior observed with water diffusion, a simple Fickian-type relation was assumed in this case because of the limited number of experimental data points available. One of the advantages of modeling the strength loss with Eq. (2) was that the influence of $T$, RH on the degradation behavior could be evaluated conveniently by assessing their effects on $\Delta G_{cs}^\infty$ and the degradation coefficient ($D_{deg}$).

![Figure 5.6](image)

Figure 5.6: Measured loss of $G_{cs}$ versus square root of exposure time and the least-squares Fickian-type fits at 60°C and three different RH. Adhesive system 1 tested at a phase angle of 27°. Each data point without an error bar is an average of at least 20 individual crack growth measurements within one DCB specimen. Each data point with an error bar (± standard deviation) is an average value obtained from three different DCB specimens (at least 20 individual crack growth measurements from each).
Figure 5.7: Measured loss of $G_{cs}$ versus square root of exposure time and the least-squares Fickian-type fits at 40°C and three different RH. Adhesive system 1 tested at a phase angle of 27°. Each single data point is an average of at least 20 crack growth measurements within one DCB specimen. Each data point with an error bar (± standard deviation) is an average value obtained from three different DCB specimens (at least 20 individual crack growth measurements from each).

Figure 5.8: Measured loss of $G_{cs}$ versus square root of exposure time and the least-squares Fickian-type fits at 20°C and 50°C. Adhesive system 1 tested at a phase angle of 27°. Each single data point is an average of at least 20 crack growth measurements within one DCB specimen. Each data point with an error bar (± standard deviation) is an average value obtained from three different DCB specimens (at least 20 individual crack growth measurements from each).
Table 5.5 shows the maximum decrease in $G_{cs}$ ($\Delta G_{cs}^\infty$) obtained by nonlinear curve fitting the data at different combinations of $T$ and RH (Figs. 5.6–5.8). It is seen that the dependence of $\Delta G_{cs}^\infty$ on RH was very weak at a given $T$. Moreover, $\Delta G_{cs}^\infty$ did not appear to follow a trend with temperature, and the maximum difference between the $\Delta G_{cs}^\infty$ values obtained at different temperatures was in the experimental scatter range (8%). Therefore, to a first approximation, the degradation condition ($T$ and RH) affected only the rate of fracture strength degradation and not the final amount. It is noted that the time to reach the plateau value, $\Delta G_{cs}^\infty$, was generally much longer than the time to saturate the adhesive layer of the open-faced specimen and the difference between these two times was a strong function of RH at a given $T$. For example, at 60°C, $\Delta G_{cs}^\infty$ was reached after about 40 days (at 95% RH), 170 days (at 82% RH) and 360 days (at 43% RH) while the corresponding water saturation times were approximately 31, 66 and 104 days, respectively.

### Table 5.5: Maximum $G_{cs}$ decrease ($\Delta G_{cs}^\infty$) obtained by curve fitting at different $T$ and RH combinations.

<table>
<thead>
<tr>
<th>RH (%)</th>
<th>$\Delta G_{cs}^\infty$ (Jm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T=20^\circ C$</td>
</tr>
<tr>
<td>43</td>
<td>-</td>
</tr>
<tr>
<td>82</td>
<td>-</td>
</tr>
<tr>
<td>95</td>
<td>3,180</td>
</tr>
<tr>
<td>Average</td>
<td>3,180</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>-</td>
</tr>
</tbody>
</table>

Figure 5.9 shows that the degradation coefficient, $D_{\text{degr}}$, which reflects the rate of degradation (Eq. (2)) increased with RH at any examined $T$, and was much more sensitive to RH above approximately 80%. At a given RH, the degradation coefficient varied linearly with $T$ between 20°C and 60°C (Fig. 5.10). It is reasonable to assume that the degradation rate was directly proportional to the water concentration in the primary adhesive layer. Since the time to water saturation was much less than the time to reach $\Delta G_{cs}^\infty$, the total fractional mass
uptake ($M_\infty$) was taken as a rough measure of the water content throughout the degradation; i.e. the lower concentration during the transient period of initial water uptake was ignored. As seen in Fig. 5.11, excluding the point (3.94, 0.004) corresponding to the 20°C - 95% RH condition, the degradation coefficient increased exponentially with $M_\infty$ independent of $T$ and RH. This is a useful result because it simplifies the measurement and analysis of toughness degradation.

![Graph showing variation of degradation coefficient with RH at 60°C and 40°C.](image1)

**Figure 5.9:** Variation of the degradation coefficient of adhesive system 1 with RH at 60°C and 40°C. The lines are to guide the eye.

![Graph showing variation of degradation coefficient with temperature at 95% and 82% RH.](image2)

**Figure 5.10:** Variation of the degradation coefficient of adhesive system 1 with temperature at 95% and 82% RH. The lines show the least-squares fits.
Figure 5.11: Variation of the degradation coefficient of adhesive system 1 with the total fractional mass uptake, $M_\infty$. The curve shows the least-squares exponential fit. Data points correspond to the nine $T$, RH conditions of Table 5.5.

5.3.4.3. $G_{cs}$ degradation in adhesive system 2

Figure 5.12 shows that the variation of $G_{cs}$ ($\psi = 27^\circ$) of adhesive system 2 with exposure time at 60°C was entirely different from the pattern seen with adhesive system 1 (Figs. 5.6 – 5.8). No statistically significant (95% confidence) decrease was observed in the adhesive system 2 fracture toughness at either RH, even after 560 days of degradation. The $G_{cs}$ value for the undegraded closed DCB specimens of adhesive system 2 (single-bonded DCB with a 400 $\mu$m bondline thickness) was 4,380 Jm$^{-2}$ with a standard deviation of 285 Jm$^{-2}$, and that of the degraded open-faced specimens, averaging all exposure times and conditions was 4,160 Jm$^{-2}$ with a standard deviation of 300 Jm$^{-2}$.

5.3.4.4. Degradation mechanisms

As discussed above, a key difference between the two adhesives was that adhesive 2 dried completely without retained water. Conversely, adhesive 1 retained a relatively large amount of water after drying, and consistent with the hypothesis that it was in the bound state (and therefore could not plasticize the matrix) the DMTA showed that $T_g$ was unaffected by this retained water. As explained below, it is hypothesized that this bound water was responsible for the marked degradation in the fracture toughness of adhesive system 1.

The relatively high toughness of rubber-toughened epoxy adhesives arises from the energy dissipation associated with the deformation occurring at the crack tip as it encounters
rubber particles within the epoxy matrix. Such deformation includes cavitation at the particle/matrix interface and shear yielding in the adjacent matrix [36-38]. These toughening mechanisms are strongly affected by the adhesion between the rubber particles and matrix [39-41]. Therefore, a possible explanation for the rapid fracture toughness degradation of adhesive system 1 is that the retained water molecules disrupted the chemical bonds between the rubber particles and the matrix by becoming bound at the rubber-matrix interface. This hypothesis is supported by an earlier observation in Chapter 4 that mode I fracture tests of degraded joints of adhesive system 1 produced a $G_{IC}$ that decreased to a constant value in the range $510 - 790$ Jm$^{-2}$, which was approximately equal to the mode I fracture strength reported for an untoughened DGEBA epoxy matrix (i.e. without rubber toughener particles); $G_{IC} = 600$ Jm$^{-2}$ in [42] and $920$ Jm$^{-2}$ in [43]. In other words, the fracture resistance of the degraded adhesive 1 was similar to that of an untoughened epoxy matrix.

Figure 5.12: Variation of $G_{IC}$ of adhesive system 2 tested at a phase angle of 27° with the exposure time at 60°C - 95% RH and 82% RH. Each data point without an error bar is an average of at least 20 measurements within one DCB specimen. Each data point with an error bar (± standard deviation) is an average value obtained from three different DCB specimens (at least 20 individual crack growth measurements from each).
5.3.4.5. Degradation dependence on EI pathway

It has been proposed that adhesive joint degradation at a given temperature is a function of the exposure index (EI), defined as the time integral of the water concentration in the joint [20]:

\[ EI = \int C(x, t) dt \]  \hspace{1cm} (3)

This concept was motivated by the desire to combine the effects of time and water concentration so that a single parameter could be used to quantify a given environmental aging condition. For example, it was of interest to see whether a long exposure to a low RH environment would be equivalent to a shorter exposure to a high RH at a given temperature.

Substituting \( C(x, t) \) from Eq. (4) of Chapter 3 into Eq. (3) and integrating over the absorption time gives the analytical expression for EI during the absorption as:

\[ EI_a = \left\{ t + \frac{16h^2}{\pi^3 D_1} \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)^3} \left[ \exp \left( -D_1 \left( \frac{2n+1}{2} \right)^2 \pi^2 t \right) - 1 \right] \cos \left( \frac{(2n+1)\pi x}{2h} \right) \right\} \times C_{1e} \]

\[ + \phi(t-t_d) \times \left\{ (t-t_d) + \frac{16h^2}{\pi^3 D_2} \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)^3} \left[ \exp \left( -D_2 \left( \frac{2n+1}{2} \right)^2 \pi^2 (t-t_d) \right) - 1 \right] \cos \left( \frac{(2n+1)\pi x}{2h} \right) \right\} \times C_{2e} \]  \hspace{1cm} (4)

where \( EI_a \) is the exposure index corresponding to the absorption process. Since the drying time of the open-faced specimens (7 days) was sometimes a significant fraction of the exposure time, the exposure index corresponding to the desorption process, \( EI_d \) was also considered.

Substituting \( C(x, t) \) from Eq. (15) of Chapter 3 into Eq. (3) and integrating over the desorption time, \( t' \) gives the analytical solution for \( EI_d \) as:

\[ EI_d = C_{1e} t' - \left\{ \frac{16h^2}{\pi^3 D_d} \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)^3} \left[ \exp \left( -D_d \left( \frac{2n+1}{2} \right)^2 \pi^2 t' \right) - 1 \right] \cos \left( \frac{(2n+1)\pi x}{2h} \right) \right\} \times (C_{1e} + C_{2e} - C) \]  \hspace{1cm} (5)

The total exposure index, \( EI_T \) from the time of first exposure to the hot-wet environment to the end of the drying period will then be:

\[ EI_T = EI_a + EI_d \]  \hspace{1cm} (6).
As shown in Chapter 3, at a given temperature, the diffusion coefficients $D_1$, $D_2$ and $D_d$ in Eqs. (4) and (5) were independent of RH, and for the open-faced specimens with a primary adhesive layer thickness of 0.4 mm, the variation of $EI_a$ and $EI_d$ through the thickness of the adhesive layer was negligible. $EI_T$ was therefore taken as a function of absorption and desorption times and instantaneous water concentration calculated at the mid-plane half way through the thickness of the primary adhesive layer.

The $EI$ concept is of use in quantifying environmental exposure only if the degradation is independent of the time-humidity path taken to reach a particular $EI$; i.e. the same amount of strength loss corresponding to a particular $EI$ is observed after exposure to different combinations of humidity and time which give the same $EI$. The path independency of $EI$ for adhesive system 1 was evaluated using combinations of three RH levels (95%, 82% and 43%) and different exposure times at 60°C and 40°C. Since there was no degradation in adhesive system 2 in the range of the exposure conditions and times studied, the path independency hypothesis could not be evaluated for this adhesive system.

Figures 5.13 and 5.14 show the average $G_{cs}$ values corresponding to particular $EI_T$ values achieved by three different paths (95%, 82% and 43% RH) at 60°C and 40°C, respectively, for adhesive system 1. Figures 5.15 and 5.16 show similar results at 50°C (95% RH and 82% RH) and 20°C (95% RH), respectively. $EI_T$ values were calculated using Eqs. (4) - (6) and the experimental data given in Chapter 3. A t-test showed that the difference between the $G_{cs}$ values achieved from the different paths at temperatures of 40°C, 50°C and 60°C was statistically insignificant with 95% confidence for $EI_T$ values greater than about $25 \times 10^6$ g/g·s. For example, at 40°C this value of $EI_T$ corresponds to 64 days of exposure at 95% RH and 86 days at 82% RH. This finding is of practical interest since it is usually intended to design adhesive joints for a long service life where $EI_T$ values would be large. For smaller $EI_T$, the degradation could not be said to be independent of the exposure history. For example, the 95% RH data points in both Figs. 5.13 and 5.14 lie below those for 82% and 43% RH. Because of the limited data available for smaller $EI_T$ values at 50°C, a strong conclusion could not be made about the degradation dependence on the exposure history at this temperature. Nevertheless, the master curves shown in Figs. 5.13 – 5.16 provide a useful envelope to estimate the amount
Figure 5.13: Variation of $G_{cs}$ of adhesive system 1 with $E_{IT}$ achieved using three different exposure paths (95%, 82% and 43% RH) at 60°C. Each single data point is an average of at least 20 individual crack growth measurements within one DCB specimen. Each data point with an error bar is an average value obtained from three different DCB specimens (each with at least 20 individual crack growth measurements). Error bars show the standard deviation. The curve is least-squares power function fit to all data points.

Figure 5.14: Variation of $G_{cs}$ of adhesive system 1 with $E_{IT}$ achieved by three different paths (95%, 82% and 43% RH) at 40°C. Each single data point is an average of at least 20 individual crack growth measurements within one DCB specimen. Each data point with an error bar is an average value obtained from three different DCB specimens (each with at least 20 individual crack growth measurements). Error bars show the standard deviation. The curve is least-squares power function fit to all data points.
Figure 5.15: Variation of $G_{cs}$ of adhesive system 1 with $EI_T$ achieved using two different paths (95% and 82% RH) at 50°C. Each single data point is an average of at least 20 individual crack growth measurements within one DCB specimen. Each data point with an error bar is an average value obtained from three different DCB specimens (each with at least 20 individual crack growth measurements). Error bars show the standard deviation. The curve is least-squares power function fit to all data points.

Figure 5.16: Variation of $G_{cs}$ of adhesive system 1 with $EI_T$ under the 95% RH and 20°C condition. Each single data point is an average of at least 20 individual crack growth measurements within one DCB specimen. Each data point with an error bar is an average value obtained from three different DCB specimens (each with at least 20 individual crack growth measurements). Error bars show the standard deviation. The curve is least-squares power function fit to all data points.
of $G_{cs}$ loss for any RH and exposure time at a given temperature. These relations can then be used to estimate the fracture strength of real joints that are exposed to varying condition (RH and temperature) during their service life by means of Eqs. (3)-(6).

Figure 5.17 shows the best fit curves of Figs. 5.13 – 5.16 for $E_{IT} > 25 \times 10^6 \text{ g/g·s}$ where the degradation was independent of the time-humidity pathway at a given temperature. It is seen that the degradation in the fracture strength increased with increasing temperature, tending to reach a quasi-steady level of residual strength for large values of $E_{IT}$ in each case. The decrease in $G_{cs}$ with increasing temperature was quite uniform over a wide range of $E_{IT}$, and only at relatively small $E_{IT}$ did the 20°C curve diverge from being parallel to the others, indicating a greater sensitivity to temperature at lower values of $E_{IT}$. To calculate $E_{IT}$ values at a new condition, the required diffusion properties can be estimated using the predictive SDF model developed in Chapter 3, and the corresponding $G_{cs}$ can then be extrapolated from Fig. 5.17 with known values of $E_{IT}$ and $T$. For example, Fig. 5.18 shows the variation of $G_{cs}$ with $T$ at selected $E_{IT}$ values extracted from Fig. 5.17. A relatively good linear fit to $G_{cs}$-$T$ data at a given $E_{IT}$ facilitates the calculation of $G_{cs}$ at a new condition.

![Figure 5.17: Variation of $G_{cs}$ of adhesive system 1 with $E_{IT}$ aged at the indicated temperatures. Data and humidity levels of Figs. 5.13-5.16.](image-url)
5.4. Conclusions

The differences between the absorption/desorption properties of two toughened epoxy adhesives were evaluated gravimetrically and by XPS and DMTA analyses. Both gravimetric and XPS results indicated that a significant amount of water was retained after drying in aged samples of adhesive 1, but a negligible amount was retained in adhesive 2. DMTA results showed that the retained water molecules in adhesive 1 were not free, but strongly bound with the adhesive constituents.

Mixed-mode fracture tests on degraded open-faced DCB specimens showed that the critical strain energy release rate, $G_{cs}$ of adhesive system 1 decreased with exposure time to reach a quasi-steady value that was similar to values reported for untoughened epoxy, while that of adhesive system 2 remained unchanged over a very long period. It was hypothesized that the differences in the degradation behavior and hygrothermal properties of the two adhesives were related to the presence of bound water molecules at the interface between the epoxy matrix and the rubber toughener in adhesive 1. A Fickian-type degradation model (Eq. (2)) was proposed to characterize the fracture toughness loss in adhesive system 1, and fairly
good agreement was observed between the model and the experimental results. The rate of
degradation predicted by the model is controlled by the coefficient, $D_{deg}$ which increased with
the increasing temperature, RH and saturated water concentration.

The dependency of fracture toughness degradation on the humidity-time exposure
history (pathway) was evaluated using the concept of exposure index, $EI$. Even though the
degradation could not be assumed to be fully independent of the exposure history, $G_{cs-EI}$
curves provide a useful envelope to estimate the amount of $G_{cs}$ loss at any exposure condition
(RH and $T$) after relatively long exposure times.
5.6. References


6.1. Introduction

The high fracture toughness of toughened epoxy adhesives can be attributed to their ability to form large crack tip damage zones prior to failure. One of the characteristics of toughened epoxy adhesive joints is the progressive development of the damage zone consisting of yielded material and distributed microcracks [1-5]. During the early stages of fracture, the damage zone continues to expand ahead of the growing macrocrack, leading to a progressive toughening of the joint as increasing amounts of strain energy are dissipated by different toughening mechanisms within the damage zone. This process results in the fracture resistance curve ($R$-curve) of the critical strain energy release rate, $G_c$, versus the crack length. Eventually, the damage zone reaches a steady-state size and $G_c$ becomes constant. The mechanisms resulting in the progressive toughening of rubber modified epoxy adhesive joints include stretching of rubber particles, cavitation, plastic dilatation of the epoxy matrix and shear bands formed between bonded or unbonded rubber particles [6-12].

Numerous researchers have investigated the damage zone around the crack tip either experimentally [6, 7, 13-15] or numerically [1, 16, 17]. For example, Lee et al. [15] measured the area of the damage zone in a bulk rubber-modified DGEBA based epoxy adhesive using optical microscopy and showed that it was closely correlated to the fracture toughness. In another work, they tested toughened epoxy-aluminum joints and observed the damage zone in both the crack tip region and the vicinity of the substrate interface, and concluded that the fracture toughness was affected significantly by bondline thickness because of the influence of the damage zones in these regions [13]. Some researchers have used stress or strain based criteria to approximately model the extent of the damage zone, neglecting a more detailed consideration of the actual mechanisms occurring in the vicinity of the crack tip. For example,
Sheppard et al. [1] developed finite element models of single lap and double strap joints made with aluminum or graphite-epoxy composite adherends and a toughened ductile adhesive, and used a critical von Mises strain criterion to predict the damage zone size. They showed a good correlation between the FE predicted and measured failure loads, and concluded that the model could be used for a broad range of joint configurations and loading conditions. Azari et al. [17] used a stress-based plastic zone model to explain the effect of applied strain energy release rate and mode ratio on the fatigue behavior of a rubber-modified epoxy adhesive.

Damage zone modeling and the distribution of stress and strain in the crack-tip region has been used frequently to explain the effects of adhesive yield stress, bondline thickness, adherend stiffness and mode ratio on adhesive joint strength [14, 17-22]. For example, Daghiyani et al. [22] and Hunston et al. [14] showed that the increase in mode-I fracture toughness with increasing bondline thickness corresponded to a decrease in the crack-tip constraint and so an increase in plastic deformation. Azari et al. [17] used estimates of the plastic zone size to investigate the effect of adherend stiffness and adhesive thickness on the crack growth rate and threshold strain energy release rate in the fatigue loading of adhesive joints.

There is an extensive body of work on the crack path in the fracture of adhesively bonded joints. Overall, four types of crack path have been reported: (a) cohesive failure, where the crack propagates through the adhesive layer; (b) interfacial failure, where the failure occurs at the interface between the adhesive and one of the adherends; (c) oscillatory failure, where the trajectory of the crack oscillates about the mid-plane of the bond but remains within the adhesive layer; and (d) alternating failure, where the crack alternates between the two interfaces [23-28].

The directional instability of cracks in adhesively bonded joints was experimentally addressed by Chai [23-25] who reported that the crack trajectory in the mode-I fracture of certain aluminum-epoxy joints and graphite reinforced epoxy laminates alternated periodically between the two interfaces. He related this phenomenon to the unavoidable imperfections in the adhesive layer. Cotterell and Rice [29] concluded that the longitudinal stress in the crack plane normal to the crack front (i.e. the $T$-stress) plays an important role in the directional
stability of crack propagation, with cracks being directionally stable if the $T$-stress is negative. Chen and Dillard [26] experimentally demonstrated the $T$-stress dependence of crack path selection in adhesively bonded joints using DCB specimens and a mechanical stretching procedure that could impose different $T$-stress levels. They observed that at relatively high positive $T$-stress levels, the crack periodically alternated between the two interfaces.

In addition to these studies of crack stability, different criteria have been proposed for crack path selection in brittle materials under mixed-mode loading conditions. The mode-I criterion assumes that the crack follows a pure mode-I path, where $K_{II} = 0$ [30-32]. Based on this criterion, Hutchinson and Suo [32] analytically derived the crack path as a function of the remote loading phase angle for different elastic mismatches in a multilayer. Sih [33] suggested that the fracture toughness and the direction of crack growth for mixed-mode problems are governed by the critical value of the strain energy density factor. Ergodan and Sih [34] suggested that the crack path is perpendicular to the direction of maximum opening stress at the crack tip. Palaniswamy and Knauss [35] proposed that the direction of crack propagation can be obtained by maximizing the energy release rate as a function of the angle of crack kinking. These criteria yield similar results and no experimentally distinguishable differences have been observed [26, 32, 36-37].

In this Chapter, the crack paths and fracture surfaces of fresh and degraded epoxy adhesive joints that fractured under mode-I and mixed-mode loading conditions were measured and characterized using an optical profilometer. These crack paths were then explained qualitatively in terms of a finite element model that was used to predict yielding in the adhesive as an approximate indicator of the extent of damage. The applicability of classical crack path selection criteria was evaluated and a crack growth mechanism was proposed that is consistent with the experimental observations and FE results.

6.2. Experimental procedures

The fracture test results used in this chapter have been reported in Chapters 2, 4 and 5, and the methods and data are only summarized briefly in Sections 2.1-2.3. The characterization
of the fracture surfaces of these same specimens and the finite element modeling has not been previously reported, and is described below in Sections 2.4 and 2.5, respectively.

6.2.1. Materials and DCB specimen preparation
DCB specimens were made using a commercial heat-cured rubber-modified DGEBA based structural epoxy adhesive. The adherends were AA7075-T6 aluminum alloy pretreated using the P2-etch method as described in Chapter 2. The bondline thickness of 385 μm was controlled using steel wires. The recommended curing profile of 30 min at 180°C was monitored using a thermocouple embedded in the adhesive layer of the joints. A folded 10 μm thick aluminum foil was embedded within the adhesive layer to initiate fracture. Details about the specimen preparation and fracture toughness results were reported in Chapters 2 and 4.

6.2.2. Open-faced specimen preparation
Open-faced technique has been repeatedly used in the literature to accelerate the degradation [39-41]. The open-faced specimen preparation procedure is fully described in Chapters 4 and 5. The primary adhesive layer, i.e. the layer to be degraded, of 385 μm thickness was first cured on the primary adherend using a backing plate instead of a second adherend. After curing, the backing plate was removed and the open-faced specimens were degraded under various combinations of temperature (60 and 40°C) and relative humidity (82 and 95 %) for different time intervals. The degraded specimens were then dried in a vacuum oven containing anhydrous calcium sulphate at 40°C for approximately 7 days to remove any reversible effect of water ingress such as plasticization. The primary adhesive was then very lightly sanded, wiped with acetone and dried before another layer of adhesive (termed the secondary adhesive) was used to bond the degraded open-faced specimen to a second adherend to make a complete DCB joint. The combined bondline thickness of the primary and secondary adhesive layers was controlled using 770 μm spacing wires during the secondary curing process. The dependence of fracture toughness on degradation was covered in detail in Chapters 4 and 5.
6.2.3. Fracture test procedure
As described in Chapter 2, the testing procedure employed a servo-electric load frame and the load jig of [42] which could generate mode-I as well as mixed-mode loading using a single DCB specimen geometry. The tests were carried out under displacement control, advancing the crosshead at 1.5 mm/min in small discrete steps while viewing the macrocrack tip through a microscope having a field of view of 2 mm.

6.2.4. Measurement of fracture surface profiles and crack path
The average depth of the crack path was determined by measuring the thickness of the residual adhesive on the more highly-strained adherend, which was the primary adherend in the open-faced specimens. Two datum points were established on the bare aluminum by first removing residual adhesive from a 2 mm wide band on either side of the adherend using a solvent (mixture of methylene chloride and methyl alcohol; Glue Buster, Kosmic Surf-Pro Inc., Saint Amable, Quebec). Transverse line scans were then made from one datum to the other across the width of the specimen at several locations using an optical profilometer (Nanovea ST 400, Microphotonics Inc., Irvine, CA, USA) to measure the adhesive residue thickness. Longitudinal and areal scans were also made in the same fashion to obtain two-dimensional and three-dimensional profiles of the fracture surfaces. The sampling rate was 500 data points per mm in all the scans. To assure the accuracy of this approach, the residual adhesive thickness was also measured on the opposing fracture surface to give the total bondline thickness. Doing this for three joints gave a maximum difference of 9% from the nominal bondline thickness of 385 μm.

6.3. Finite element modeling
The aluminum adherends (tensile elastic modulus, \( E = 71.7 \) GPa, tensile yield stress, \( \sigma_y = 460 \) MPa) did not experience any plastic deformation within the range of test conditions and were hence modeled using linear elastic, isotropic elements. The adhesive stress-strain behavior was approximated using a multi-linear isotropic hardening model derived from tensile test results provided by the manufacturer (Fig. 6.1) with a von Mises plasticity criterion. The
adhesive elastic modulus \( (E_a) \) and the proportionality limit were 1.5 GPa and 30 MPa, respectively. The plastic zone was defined as the regions with von Mises stress greater than the proportionality limit. The two-dimensional structural model used plane183 elements – an 8-node element with quadratic displacement behavior (ANSYS® 12, Ansys Inc., Canonsburg, PA) (Fig. 6.2). Plane stress and plane strain assumptions were employed for the adherends and the adhesive layer, respectively. The adhesive layer was meshed using elements having an average area of 32x32 μm\(^2\) while coarser meshes were used for the adherends. Twelve quarter-point singular elements arranged circumferentially around the crack tip were used to produce stress and strain singularities at the crack tip. The sensitivity of the FE model to the mesh density was assessed by varying the number of elements in the adhesive layer close to the crack tip. The changes in the plastic zone area and the crack tip von Mises and opening stresses were all less than 1% when the number of elements was doubled.

Figure 6.1: Multi-linear stress-strain curve for the adhesive.
It is emphasized that the current modeling of the adhesive plastic zone does not represent a model of the actual damage zone, since it neglects crack tip damage mechanisms such as cavitation and microcracking. However, it is reasonable to assume that the size of the damage zone will be proportional to that of the plastic zone. The intention of the current modeling was thus to determine the overall trends of the damage zone, not its actual size, as represented by the plastic zone trends. Also, it was used to identify the highly stressed regions in the constrained adhesive layer in an attempt to explain the three-dimensional nature of the fracture.

Two methods were evaluated to calculate the strain energy release rate in the FE model: (i) the virtual crack extension method in which
where $\Delta \Gamma$ is the change in the strain energy for a crack extension of $\Delta a$, and (ii) the J-integral was calculated in a contour within the adhesive surrounding the crack tip. It was found that these two methods differed by less than 1% for crack lengths on the lower half of the rising part of the $R$-curve (Fig. 6.3), with the difference increasing to approximately 3% for the steady-state critical strain energy release rate, $G_{cs}$. It was decided to use the J-integral method for all subsequent calculations. The values of $G$ calculated in this manner were indistinguishable from those calculated with the analytical beam-elastic-foundation (BOEF) model in Chapter 2.

Figure 6.3: Typical $R$-curves for a toughened epoxy adhesive measured at different phase angles. The lines are least-squares fits to the experimental data points based on the bilinear $R$-curve model.

6.4. Plastic zone evolution with crack growth ($R$-curve behavior)

In Chapter 2, it was shown experimentally that the current adhesive system exhibited $R$-curve behavior (Fig. 6.3) that could be approximated using a bilinear model having three independent parameters: the steady-state critical strain energy release rate, $G_{cs}$, the slope of the rising line, $(dG_{cr}/da)$, and the length of the rising part $(L_r=a_r-a_0)$. The critical strain energy release rate, $G_c$, as a function of crack length can thus be represented as:

$$ G = \frac{d\Gamma}{da} \approx \Delta \Gamma/\Delta a \quad (1) $$
\[ G_c = \begin{cases} G_{cr}(a) = G_{cl} + \frac{dG_{cr}}{da}(a - a_0) & \text{for } a_0 < a < a_r \\ G_{cs} & \text{for } a \geq a_r \end{cases} \]

where the subscripts \( r \) and \( s \) represent the rising and steady-state values of \( G_c \), respectively. The initial distance from the loading pins is \( a_0 \) and the crack length corresponding to the end of rising part is \( a_r \). \( G_{cl} \) is the initiation \( G_c \) at which the crack starts to grow from the adhesive terminus. These model parameters for different loading phase angles (defined as \( \text{atan} \frac{G_{II}}{G_I}^{0.5} \) where \( G_I \) and \( G_{II} \) are the mode I and II strain energy release rates, respectively) are given in Table 6.1, having been calculated using an analytical beam-on-elastic-foundation method that neglects adhesive yielding [42].

Table 6.1: The average and standard deviation of the bilinear \( R \)-curve model parameters and measured initiation \( G_c \), \( G_{cl} \) for DCB specimens tested under different phase angles, \( \psi \).

<table>
<thead>
<tr>
<th>( \psi (^\circ) )</th>
<th>( G_{cl}\pm\text{SD} ) (Jm(^{-2}))</th>
<th>( dG_{cr}/da\pm\text{SD} ) (Jm(^{-2})/mm)</th>
<th>( L_w\pm\text{SD} ) (mm)</th>
<th>( G_{cs}\pm\text{SD} ) (Jm(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3220(\pm)210</td>
<td>379(\pm)32</td>
<td>7.5(\pm)0.9</td>
<td>409(\pm)72</td>
</tr>
<tr>
<td>27</td>
<td>4160(\pm)260</td>
<td>319(\pm)29</td>
<td>11.2(\pm)0.5</td>
<td>596(\pm)96</td>
</tr>
<tr>
<td>48</td>
<td>6650(\pm)460</td>
<td>338(\pm)25</td>
<td>16.4(\pm)1.2</td>
<td>713(\pm)114</td>
</tr>
</tbody>
</table>

The crack lengths and critical loads on the arms of the DCB (Fig. 6.1) during the measurement of the \( R \)-curve under mode-I and mixed-mode (\( \psi=27^\circ \)) loading, as reported in Chapter 2, are given in Table 6.2. These critical loads were used in the present FE model to investigate how the plastic zone evolved with crack length as the adhesive joint toughened.

It is noted that \( R \)-curve development in the fracture of bulk toughened polymers [5,8] differs significantly from the behavior observed in thin, highly-constrained ductile adhesive layers, which generate very different states of stress. Toughening and crack growth resistance in such highly-constrained ductile layers is due to the development of an elongated damage (process or plastic) zone ahead of the crack tip [43, 45].
Table 6.2: Variation of critical loads (Fig. 6.2) and strain energy release rates with crack length under mode-I ($\psi=0^\circ$) and mixed-mode ($\psi=27^\circ$) loading. Crack length of 40 mm corresponds to crack initiation ($G_{ci}$), and the largest crack length at each phase angle corresponds to the onset R-curve plateau ($G_{cs}$).

<table>
<thead>
<tr>
<th>Mode-I ($\psi = 0^\circ$)</th>
<th>Mixed-mode ($\psi = 27^\circ$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crack length (mm)</td>
<td>$G_c$ (Jm$^{-2}$)</td>
</tr>
<tr>
<td>40</td>
<td>409</td>
</tr>
<tr>
<td>41.6</td>
<td>1000</td>
</tr>
<tr>
<td>42.9</td>
<td>1500</td>
</tr>
<tr>
<td>44.2</td>
<td>2000</td>
</tr>
<tr>
<td>45.5</td>
<td>2500</td>
</tr>
<tr>
<td>46.8</td>
<td>3000</td>
</tr>
<tr>
<td>47.5</td>
<td>3220</td>
</tr>
<tr>
<td>50.7</td>
<td>4000</td>
</tr>
</tbody>
</table>

Figures 6.4 and 6.5 illustrate the predicted variation of the plastic zone area (PZA) with $G_c$ as the crack grows (i.e. behavior corresponding to the R-curve) for mode-I and mixed-mode loading conditions, respectively.

Figures 6.4a and 6.5a represent the PZA corresponding to the strain energy release rate at crack initiation ($G_{ci}$), while Figs. 6.4d and 6.5d shows the PZA when $G_c=G_{cs}$ on the steady-state plateau of the R-curve. In both cases, the damage zone appeared to grow ahead of the crack as well as in the crack wake, as previously reported in [5, 46]. As expected, the damage zone under mode-I loading was symmetric. Under mixed-mode loading, however, two asymmetric critical locations were observed along the opposing interfaces. At a given $G_c$, the PZA corresponding to a phase angle of $\psi=27^\circ$ was always significantly larger than that for mode-I, and this ratio of PZA $\psi=27^\circ$/PZA $\psi=0^\circ$ increased with increasing $G_c$ (Table 6.3). It is hypothesized that the larger PZA and its faster growth at higher phase angles was due to the lower crack tip constraint at higher phase angles. For example, at $G= 600$ Jm$^{-2}$, the stress triaxiality factor (ratio of the mean stress to the von Mises stress at the crack tip) calculated by the FE model was

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approximately 4 at $\psi=0^\circ$ while at $\psi=27^\circ$, it was only 2. The larger stress triaxiality factor at mode-I indicates a more severe constraint of the adhesive in the vicinity of the crack tip [17, 22, 47].

Figure 6.4: Evolution of the plastic zone with the applied strain energy release rate (equal to $G_c$) during the rising part of the $R$-curve under mode-I ($\psi=0^\circ$). The dark region corresponds to von Mises stresses between 37.5 and 45 MPa and the grey region is between 30 and 37.5 MPa.

Figure 6.5: Evolution of the plastic zone with the applied strain energy release rate (equal to $G_c$) during the rising part of the $R$-curve under mixed-mode loading ($\psi=27^\circ$). For better visibility, the bondline thickness direction is shown with three times larger magnification than that in the crack growth direction. The dark region corresponds to von Mises stresses between 37.5 and 45 MPa, and the grey region is between 30 and 37.5 MPa.
Table 6.3: Variation of PZA with $G_c$ under mode-I and mixed-mode ($\psi=27^\circ$) and variation of PZA ratio with $G_c$.

<table>
<thead>
<tr>
<th>$G_c$ ($Jm^{-2}$)</th>
<th>PZA (mm$^2$)</th>
<th>PZA ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\psi=0^\circ$</td>
<td>$\psi=27^\circ$</td>
</tr>
<tr>
<td>600</td>
<td>0.11</td>
<td>0.43</td>
</tr>
<tr>
<td>1000</td>
<td>0.19</td>
<td>1.16</td>
</tr>
<tr>
<td>1500</td>
<td>0.27</td>
<td>2.44</td>
</tr>
<tr>
<td>2000</td>
<td>0.38</td>
<td>3.96</td>
</tr>
<tr>
<td>2500</td>
<td>0.45</td>
<td>5.20</td>
</tr>
<tr>
<td>3000</td>
<td>0.51</td>
<td>5.92</td>
</tr>
</tbody>
</table>

The PZA increased linearly with increasing $G_c$ during the rising part of the $R$-curves at both phase angles, as seen in Fig. 6.6, where $G_c$ and PZA values were normalized with respect to their ultimate values in the plateau region (Fig. 6.3). Thus the FE results were consistent with the idea that the increase in $G_c$ on the rising part of the $R$-curve was due to the enlargement of the damage zone as reflected by the plastic zone. On the plateau, the PZA became independent of the crack length, because the damage zone was fully developed and then advanced in a self-similar manner upon further crack growth, as described in Chapter 2 and has previously reported in [3, 32].

![Graph of Normalized $G_c$ and PZA vs Crack Length](image)

Figure 6.6: Variation of the normalized measured $G_c$ and plastic zone area (PZA) with crack length for mode-I ($\psi=0^\circ$) and mixed-mode ($\psi=27^\circ$) loading conditions. $G_c$ values correspond to the normalized
bilinear $R$-curve model (obtained from Table 6.1) and PZA was found using the corresponding critical loads in the FE model.

6.5. Steady-state plastic zone and phase angle

As reported in Chapter 2 and consistent with the observations in [48], the fracture toughness of these highly toughened epoxy adhesive systems increases with the phase angle. For example, Azari et al. [48] performed fracture tests on steel and aluminum joints made with the present adhesive at different phase angles from pure mode-I to 65°, and found that $G_{cs}$ increased with phase angle, consistent with the data of Table 6.1.

The amount by which $G_{cs}$ and PZA increased with increasing phase angle is defined as:

$$\Delta G_{cs} = G_{cs}(\psi) - G_{cs}(0) \tag{3}$$  
$$\Delta A = PZA(\psi) - PZA(0) \tag{4}$$

where 0 corresponds to mode-I and $\psi$ is any given phase angle. $\Delta G_{cs}$ was found using data presented in Table 6.4 from ref. [48] and $\Delta A$ was calculated using the PZA results from the FE model. $G_{cs}$ at mode-II ($\psi=90^\circ$) was extrapolated from the results given in Table 6.4 using a third-order polynomial fit as proposed in [48]. Figure 6.7 shows $\Delta G_{cs}$ and $\Delta A$ normalized by their respective maximum values at pure mode-II (termed $\Delta G_{cs}'$ and $\Delta A'$). Overall, the normalized $\Delta A$ showed a different dependence on phase angle than did the normalized $\Delta G_{cs}$, indicating that the damage zone processes leading to the critical strain energy release rate did not correlate well with the changes in PZA. In other words, changes in the onset of yield with phase angle did not explain the measured phase angle dependence of $G_{cs}$.

<table>
<thead>
<tr>
<th>$\psi$ (°)</th>
<th>0</th>
<th>16</th>
<th>27</th>
<th>47</th>
<th>54</th>
<th>55</th>
<th>65</th>
</tr>
</thead>
<tbody>
<tr>
<td>$G_{cs}$ (Jm$^{-2}$)</td>
<td>3860</td>
<td>3990</td>
<td>4060</td>
<td>7150</td>
<td>7810</td>
<td>7840</td>
<td>11850</td>
</tr>
</tbody>
</table>

To further investigate the effect of phase angle on $G_{cs}$, the maximum crack tip opening stress was calculated at each phase angle as illustrated in Fig. 6.8, using the FE model with a constant applied $G$ of 600 Jm$^{-2}$. As the amount of shear deformation grew with increasing phase angle, the PZA increased and $\sigma_y$ decreased. Both of these trends would have the effect
of toughening the adhesive joint with increasing phase angle, consistent with Fig. 6.3; i.e. the increase in PZA reflecting the growth in the damage zone, and the decrease in $\sigma_y$ corresponding to a reduced loading intensity at the crack tip.

![Figure 6.7](image1)

Figure 6.7: The variation of $\Delta G'_cs$, $\Delta A'$, $\Delta \sigma_y'$ and $|\Delta A'.\Delta \sigma_y'|$ with phase angle. The lines show the least squares third-order polynomial fits.

![Figure 6.8](image2)

Figure 6.8: Variation of PZA and $\sigma_y$ with phase angle at an applied $G$ of 600 Jm$^{-2}$. The lines show the least squares third-order polynomial fits.

The change in $\sigma_y$ with phase angle was defined as

$$\Delta \sigma_y = \sigma_y(\psi) - \sigma_y(0)$$  \hspace{1cm} (5)
and was normalized with respect to its maximum value at pure mode-I ($\sigma_y(0)$). As with the trend for $\Delta A$, Fig. 6.7 shows that the variation of the normalized $\Delta \sigma_y' (\Delta \sigma_y')$ had a different dependence on phase angle than did $\Delta G'_{cs}$. Interestingly however, the absolute value of their product ($|\Delta A'.\Delta \sigma_y'|$) showed an excellent agreement with the normalized $\Delta G_{cs}$ (Fig. 6.7). This phenomenological observation suggests that the dependence of $G_{cs}$ on phase angle is due to the combined effects of changes in the size of the damage zone (reflected by the PZA) and the level of crack tip opening stress. It is noted that the product $\Delta A'.\Delta \sigma_y'$ was first interpreted as being approximately equal to the irreversible work done on the plastic zone normalized by the irreversible work done at mode I, assuming that the opening stress is uniform in the plastic zone. However, the FE results revealed that the opening stress varied appreciably over the plastic zone and the energy calculated using the varying opening stress did not follow the trends given in Fig. 6.7. Therefore, the trend of $|\Delta A'.\Delta \sigma_y'|$ with phase angle in Fig. 6.7 remains a curiosity.

6.6. Crack path

6.6.1. Crack path in fresh joints under mode-I

6.6.1.1. Experimental observations

Figure 6.9 shows the 3-D fracture surface image (a) and typical longitudinal surface profile (b) for a DCB specimen tested under mode-I loading. The average crack path was measured to be approximately 190 μm from the upper adherend; approximately in the mid-plane of the 385 μm bondline. However, the fracture surface was not flat and in fact oscillated between the two interfaces with a maximum change in elevation of 350 μm, approximately the same as the bondline thickness. Also, the fracture surface revealed a pronounced three-dimensional characteristic both across and along the DCB.

To further investigate the crack growth mechanism, the visible edge of the adhesive layer around the crack tip was closely monitored using optical microscopy. As seen in Fig. 6.10 for mode-I loading, even though the macrocrack appeared at the upper interface, another opening propagated along the lower interface. Distinct microcracks were also observed
between the two interfaces. One possible reason for the macrocrack appearing in the interfaces, rather than at the expected location within the bondline, could be mechanical damage of the interfaces at the edges that might have been caused by the sanding process during the specimen preparation. This is supported by the fact that the interfacial crack path at the specimen edges was observed to be more pronounced when the edges were machined rather than sanded, because machining was a more aggressive process that caused more damage to the adhesive at the edges.

Figure 6.9: a) Typical 3-D image of the fracture surface under mode-I loading. The smooth regions at the edges correspond to bare aluminum with adhesive removed. Longitudinal corresponds to the
crack growth direction and transverse is the crack front across the joint width. b) Typical 2-D longitudinal fracture surface profile in mode-I loading condition. 0 and 385 μm on the vertical axis correspond to the upper and lower interfaces.

Figure 6.10: Photograph of the bondline edge under mode-I loading corresponding to $G_c = 3,220 \text{ Jm}^{-2}$. The upper interface opening corresponds to the macrocrack while the lower interface opening propagated parallel to the macrocrack. The image corresponds to a region in the wake of the crack; i.e. the tip of the macrocrack lies to the right of the image and is not shown.

6.6.1.2. Finite element analysis of crack path

Figure 6.11 shows the plastic zones in the vicinity of a crack representing the average crack plane at an applied $G$ of 600 Jm$^{-2}$ under mode-I loading, and assuming the plane strain conditions that exist across most of the joint width. As expected, one region of high stress was located around the crack tip and another region was located in the vicinity of the interfaces due to the constraint imposed by the adherends whose modulus of elasticity was approximately 50 times greater than that of the adhesive. This restrained the deformation of the adhesive close to the interfaces, creating higher stresses. Lee et al. [13] experimentally observed this same damage zone pattern in a rubber-modified epoxy adhesive in a compact tension fracture test. The stretching and cavitation of rubber toughening particles and the formation of shear bands are concentrated in these highly-stressed regions around the crack tip and along the interfaces. It is hypothesized that microcracks form in these regions and coalesce to create the jagged network of cracks that span from one interface to the other as observed in Fig. 6.9.
6.6.2. Crack path in fresh joints under mixed-mode loading

6.6.2.1. Experimental observations

Figure 6.12 shows the fracture surface topography of a DCB specimen tested under mixed-mode loading ($\psi = 27^\circ$). As in the mode-I case, the fracture surface was highly three-dimensional, oscillating between the two interfaces as seen in Fig. 6.12b. The average crack path was measured to be approximately 170 μm from the more highly-strained adherend, implying that the overall crack path deviated from the mid-plane by only 20 μm. Also, the maximum change in elevation was measured to be approximately 320 μm which was only slightly less than that of mode-I (350 μm).

The microscopic observation of the bondline edge indicated a stress transition from the upper to the lower interface ahead of the crack tip. As seen in Fig. 6.13, some discontinuous sharp openings were observed up to a distance of about 0.5 mm ahead of the macrocrack tip on the upper interface while the opening in the lower interface continued to a farther distance from the macrocrack tip, indicating the extent of the damage zone at this location.
Figure 6.12: a) 3-D image of the fracture surface under mixed-mode loading ($\psi=27^\circ$). The adherend surface at zero height corresponds to the interface with the more highly-strained adherend. The smooth regions at the edges correspond to bare aluminum with adhesive removed. b) Typical 2-D longitudinal fracture surface profile along the middle of the joint at $\psi=27^\circ$. 
6.6.2.2. Finite element analysis of crack path

Cracks initiating within a relatively brittle adhesive layer tend to begin to grow at an inclination of approximately 45° toward the more highly-strained adherend, such that the maximum principal stress is normal to the crack plane. This is illustrated in Fig. 6.14a using the present FE model, and is consistent with the results of refs [31, 32]. For relatively small phase angles, less than about 7° for the present adhesive system, a pure mode-I crack path exists within the adhesive parallel to the interface (Fig. 6.14b), and cracks will stabilize on this plane. For larger phase angles, such mode-I paths do not exist within the adhesive layer and crack growth in relatively brittle adhesives proceeds under mixed-mode conditions along the interface with the more highly-strained adherend; i.e. the path that maximizes the mode-I component of the strain energy release rate [31, 32]. These predictions for brittle crack growth, however, did not agree with the present observations, since as mentioned above, the average experimentally measured crack path was 170 μm from the upper interface, with local variations that reached almost from one interface to the other across the adhesive layer.

Figure 6.13: Micrograph of the edge of the adhesive joint in the vicinity of the macrocrack tip under mixed-mode loading (ψ=27°) with $G_c=4,160 \text{ Jm}^{-2}$. The macrocrack appeared at the upper interface when viewing the free surface of the bondline. Smaller cracks were observed along the lower interface ahead of the macro-crack which was growing from left to right.
To explain this contradiction, the von Mises stress distribution at crack initiation was examined using the FE model with $G_{cr}$ of 600 Jm$^{-2}$ for the bondline thickness of 385 μm with $\psi = 27^\circ$. Figure 6.15 shows that the maximum von Mises stress was located close to the upper adherend.
adherend, rather than at the assumed initial crack tip. This observation did not change for different assumed crack tip locations, and was consistent with the experimental observations that the first microcracking was observed at the upper interface and not at the tip of the foil starter crack when the specimen was tested under mixed-mode loading. It is also interesting to note the transition of the location of the maximum equivalent stress from the upper interface to the lower one as the distance from the crack tip increased. After a distance of approximately two times of the bondline thickness from the crack tip, the maximum von Mises stress was found to be at the lower interface (Fig. 6.15).

Figure 6.15: Plastic zone at $G=G_{c}=600 \text{ Jm}^{-2}$ under mixed-mode loading ($\psi = 27^\circ$). The dark region corresponds to the von Mises stresses between 37.5 and 45 MPa and the grey region is between 30 and 37.5 MPa. The squares show the maximum von Mises stress path ahead of the crack tip.

Figure 6.16 shows the variation of the von Mises stress, hydrostatic stress and shear stress as a function of distance from the crack tip on the maximum von Mises stress path (given in Fig. 6.15). Both the shear and von Mises stresses decreased initially and then started to increase when the path reached the lower interface at a distance of approximately 0.8 mm from the crack tip; beyond this point, their maximum values were always found at the lower interface. The hydrostatic stress was relatively constant over the thickness of the adhesive layer, and decreased with increasing distance from the crack tip after showing an initial increase. The magnitudes of all these stresses were still relatively high beyond 0.8 mm from the crack tip, increasing the probability of microcracking close to the lower interface.
Figure 6.16: Variation of von Mises, hydrostatic (mean) and shear stresses with the distance from crack tip on the maximum von Mises stress path shown in the upper diagram, for $G=600 \text{ Jm}^{-2}$.

Figure 6.17 shows the von Mises stress distribution within the adhesive layer when the crack was located in different positions. Figure 6.17a corresponds to the starter precrack in the adhesive layer mid-plane. The highly-strained region close to the upper interface caused the precrack to start to grow near the upper interface. As seen in Fig. 6.17b, when the crack was close to the upper interface, the maximum stress path within the adhesive layer was toward the lower interface, which caused the crack to deviate from the upper interface. Finally, when the crack reached the lower interface, the distribution of the most highly-strained regions in the adhesive layer tended to drive the crack back toward the upper interface (Fig. 6.17c). This mechanism generated the observed crack oscillation between the two interfaces (Fig. 6.12), leaving the average crack path approximately in the mid-plane.

Figure 6.12a showed that fracture oscillated between the interfaces in both the longitudinal and transverse directions of the joint. It is believed that this was a consequence of the distribution of the von Mises stress and strain combined with a random distribution of defects such as voids, or of nonuniformities in the toughening mechanism and epoxy matrix properties.
6.6.3. Crack path in degraded joints

6.6.3.1. Experimental observations

As explained in Chapters 4 and 5, three stages were observed during the degradation of the open-faced specimens irrespective of exposure condition. Initially, $G_{cs}$ decreased rapidly with exposure time from an undegraded value of 4,160 Jm$^{-2}$ to approximately 900 Jm$^{-2}$ (e.g. within 30 days at 60°C-95%RH and 120 days at 40°C-95%RH), and then remained unchanged. It decreased again after very long exposures (e.g. 365 days at 60°C-95%RH and after 615 days at 40°C-95%RH) to a very low value of approximately 300 Jm$^{-2}$. The first stage was believed to correspond to the gradual deterioration of the toughening mechanisms related to the rubber particles within the epoxy matrix, and $G_{cs}$ at the end of stage one (900 Jm$^{-2}$) was approximately the same as that of an untoughened DGEBA epoxy resin [49, 50]. After extremely long exposure times during the second stage, the DGEBA matrix also started to degrade, producing a rather abrupt further decrease of $G_{cs}$ at the beginning of the third stage.

Figures 6.18a and b show the 3-D images of the fracture surfaces of open-faced degraded specimens having $G_{cs}$ values of 900 Jm$^{-2}$ (stage two) and 300 Jm$^{-2}$ (stage three) at $\psi=$...
Figure 6.18: 3-D optical profilometer images of the fracture surfaces of degraded open-faced specimens having $G_{cs}$ values of: (a) 900 Jm$^{-2}$ and (b) 300 Jm$^{-2}$ for the joints tested under mixed mode loading ($\psi = 27^\circ$). The adherend surface at zero height corresponds to the interface with the more highly-strained adherend (primary adherend). The smooth regions at the edges correspond to bare aluminum with adhesive removed.

$27^\circ$. Figure 6.19 also shows the 2-D profiles measured along the centerline of the fracture surfaces of degraded specimens having $G_{cs}$ values of 900 Jm$^{-2}$ and 300 Jm$^{-2}$ at $\psi=27^\circ$. 

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Comparing these with the undegraded case shown in Fig. 6.12, it is clear that the crack plane became much flatter and closer to the more highly-strained as the degree of degradation increased and $G_{cs}$ decreased. This is reflected in Table 6.5, which lists the average crack path distance from the upper adherend, the roughness ($R_a$) of the fracture surfaces for the fresh and degraded joints, and the difference between the average of the 100 highest peaks and the average of the 100 lowest valleys. The latter parameter reflects the largest change in crack elevation within the bondline. It is seen that all these parameters decreased significantly after degradation.

![Graph (a)](image-a)

![Graph (b)](image-b)

Figure 6.19: Typical 2-D longitudinal fracture surface profiles measured along the centerline of degraded open-faced specimens having $G_{cs}$ values of: (a) 900 Jm$^{-2}$ and (b) 300 Jm$^{-2}$ for the degraded joints tested under mixed mode loading ($\psi = 27^\circ$). 0 and 385 μm on the vertical axis correspond to the upper (more highly-strained) and lower interfaces, respectively. The primary adhesive layer was 385 μm thick.
Table 6.5: Comparison of the average crack path depth, maximum fracture surface change in elevation, and fracture surface roughness values before and after degradation. The values represent the average results obtained from measurements on three different specimens at each case tested at $\psi=27^\circ$.

<table>
<thead>
<tr>
<th>Level of degradation</th>
<th>Crack path depth (μm)</th>
<th>Maximum change in elevation (μm)</th>
<th>Fracture surface roughness ($R_a$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Undegraded) $G_{cs} = 4160 \text{ Jm}^{-2}$</td>
<td>170</td>
<td>313</td>
<td>19</td>
</tr>
<tr>
<td>(Stage 2) $G_{cs} = 900 \text{ Jm}^{-2}$</td>
<td>45</td>
<td>136</td>
<td>11</td>
</tr>
<tr>
<td>(Stage 3) $G_{cs} = 300 \text{ Jm}^{-2}$</td>
<td>16</td>
<td>41</td>
<td>2</td>
</tr>
</tbody>
</table>

The decrease in the extent of crack tip damage in the degraded joints is also illustrated in Fig. 6.20 by an optical micrograph of the bondline edge of a degraded open-faced specimen tested under mixed-mode ($\psi=27^\circ$) loading corresponding to $G_{cs} = 900 \text{ Jm}^{-2}$. Comparing this to the bondline edge of an undegraded specimen that had significantly higher $G_{cs}$ values (Figs. 6.10 and 13), it is seen that no microcracking was observed across the bondline thickness and in the upper interface ahead of the macrocrack tip. This was expected because the lower fracture toughness of the degraded specimens corresponded to a smaller damage zone ahead of the macrocrack tip.

Figure 6.20: Optical micrograph of the bondline edge of a degraded open-faced specimen corresponding to $G_{cs} = 900 \text{ Jm}^{-2}$ under mixed-mode ($\psi=27^\circ$) loading. The upper interface opening corresponds to the well-defined macrocrack with no evidence of microcracking in the vicinity of the tip. Dashed line shows interface between primary and secondary adhesive layers.
**6.6.3.2. Analysis of crack path**

As aging progressed, the mixed-mode crack path in the aged adhesive tended to follow the trajectory characteristic of a brittle material near the interface of the more highly-strained adherend, in which the mode-I component of the fracture energy is maximized at the crack tip. This is clearly shown in Fig. 6.19 where the crack grows within the degraded adhesive layer, but very close to the interface of more highly-strained adherend. As mentioned above, degradation also made the fracture surfaces flatter and smoother (Figs. 6.12, 6.18 and 6.19). This is consistent with the hypothesis in Chapter 5 that the absorbed water disrupted the toughening mechanism in the adhesive, causing it to behave as a relatively brittle, pure epoxy resin. For example, Thomas *et al.* [49] reported that an untoughened DGEBA epoxy had a smooth and glassy fracture surface with only very slight indications of plastic deformation and shear banding. Figures 6.18 and 6.19 reflect such a trend toward brittle fracture behavior as degradation progressed.

In the case of undegraded joints, the toughening mechanisms (rubber particle stretching and cavitation) dissipated a relatively large amount of energy which resulted in higher stresses and a larger damage zone, and consequently a higher $G_c$. Under these circumstances, microcracks could initiate and propagate within the DGEBA epoxy matrix throughout the entire bondline thickness, resulting in a rough, 3-D fracture surface as described in Section 6.2. But in the case of degraded joints, the chance for microcracks to initiate and propagate across the entire bondline thickness was greatly reduced because of the significantly lower values of $G_c$ as illustrated in Figs. 6.18-6.20.

By definition, critical strain energy release rate is the amount of strain energy required to create a unit area of fracture surface. When the fracture is brittle, the crack faces are relatively smooth so that the nominal (apparent or projected area) and real fracture surface areas will be approximately the same. However, in the case of undegraded rubber-modified epoxy adhesive with 3-D fracture surface characteristics, the area of the actual fracture surface can be significantly higher than the corresponding nominal (projected) area. For example, the actual fracture surface areas of the 3-D profiles obtained from undegraded joints (Figs. 6.9 and 6.12) were calculated to be approximately 30% larger than the corresponding nominal areas.
For the degraded joints, this percentage was reduced to 16% and 11% in stages two and three, respectively (Fig. 6.18, Table 6.5). This is consistent with the observations of Chai who reported that the fracture energy was proportional to the roughness of the fracture surfaces in fibre-reinforced epoxy laminates [23]. The larger actual fracture surface area is consistent with the increased fracture toughness of the adhesive joint; i.e., because the rubber toughening particles create stresses that are more widely distributed, fracture occurs simultaneously over a larger volume of adhesive, which results in a rougher fracture surface.

6.7. Conclusions

The calculated crack tip plastic zone area increased with the amount of crack growth in a manner that was broadly consistent with the experimentally measured $R$-curves at two phase angles. Increasing the loading phase angle caused an increase in the plastic zone size and decreased the maximum opening stress for a given applied strain energy release rate. But both of these factors exhibited a markedly different dependence on phase angle than the measured steady-state critical strain energy release rate, $G_{cs}$. However, it was observed that the product of the normalized change in the crack tip opening stress and the change in the normalized plastic zone area provided an excellent fit to the $G_{cs}$ phase angle dependence. This purely phenomenological observation suggested that the dependence of $G_{cs}$ on phase angle is due to the combined effects of changes in the size of the damage zone (reflected by the plastic zone area) and the level of the crack tip opening stress.

Upon environmental degradation, a ductile-brittle transition was observed in the fracture behavior of the joints. All parameters related to the fracture surface including crack depth, roughness and maximum change in elevation decreased significantly after degradation, reflecting the reduced toughness of these joints. The maximum mode-I crack path selection criterion was applicable to the degraded joints with brittle characteristics, but could not predict the overall crack path in the undegraded specimens with ductile characteristics. A crack growth mechanism based on the distribution of the maximum von Mises stress was consistent with the experimental observations of the fracture surfaces of the undegraded joints. The relatively
high fracture toughness in the undegraded joints was partially attributed to the pronounced three dimensionality of the fracture surface.
6.8. References


Chapter 7: Evolution of crack path and fracture surface with degradation in rubber-toughened epoxy adhesive joints: Application to open-faced specimens

7.1. Introduction

It is well known that epoxy adhesives are susceptible to moisture ingress and their mechanical properties alter upon environmental exposure. Traditional closed joints are not well suited for the study of degradation because the diffusion path of water into the adhesive layer is long and the degradation experiments are hence time-consuming. Moreover, the resulting degradation is not uniform after reasonable exposure times. Since the results from testing such joints do not represent a discrete state of moisture degradation, it is impossible to directly apply the measured properties to other joint configurations or ageing conditions [1]. Open-faced specimens can instead be used to achieve a spatially uniform state of degradation and to accelerate the aging process by shortening the diffusion path of water into the adhesive layer [1-4].

Many researchers have studied the crack path in the fracture of adhesively bonded joints. Overall, four types of crack path have been reported: (a) cohesive failure, where the crack propagates through the adhesive layer; (b) interfacial failure, where the failure occurs at the interface between the adhesive and one of the adherends; (c) oscillatory failure, where the trajectory of the crack oscillates about the mid-plane of the bond but remains within the adhesive layer; and (d) alternating failure, where the crack alternates between the two interfaces [5-10].

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As summarized in Chapter 6, different criteria have been proposed for crack path selection in brittle materials under mixed-mode loading conditions. The mode-I criterion assumes that the crack follows a pure mode-I path, where $K_{II} = 0$ [11-13]. Ergodan and Sih [14] suggested that the crack path is perpendicular to the direction of maximum opening stress at the crack tip. Some strain energy based criteria have also been proposed [15, 16]. All these criteria yield similar results and no distinguishable differences in predicted crack path have been observed [8, 13, 17-19].

The directional instability of cracks in adhesively bonded joints was first experimentally addressed by Chai [5-7] who reported that the crack trajectory in the mode-I fracture of certain aluminum-epoxy joints and graphite reinforced epoxy laminates alternated periodically between the two interfaces. He related this phenomenon to the unavoidable imperfections in the adhesive layer. Cotterell and Rice [20] concluded that the $T$-stress (i.e. the longitudinal stress in the crack plane normal to the crack front) plays an important role in the directional stability of crack propagation, with cracks being directionally stable if the $T$-stress is negative. Chen and Dillard [8] experimentally demonstrated the $T$-stress dependence of crack path selection in adhesively bonded joints using DCB specimens and a mechanical stretching procedure that could impose different $T$-stress levels. They observed that at relatively high positive $T$-stress levels, the crack periodically alternated between the two interfaces.

The thermal residual stress developed in the adhesive layer after the curing cycle plays an important role in the crack path selection since it affects the $T$-stress [21, 22]. Yu et al. [23] measured the residual stresses in an epoxy-steel system using curvature in bi-material beams. They concluded that the residual stress due to cure shrinkage was negligible but considerable stresses developed when cooling due to the differential thermal contraction of the two materials. They also observed that the residual stress increased after a repeat of the thermal cycles and decreased upon moisture exposure. Daghyani et al. [21] studied the crack path in a rubber-modified epoxy adhesive bonding of both aluminum and carbon fibre/epoxy composite adherends. They calculated the thermal residual stress in the joints using a finite element analysis and showed that the type of adherend material influenced the level of the thermal
residual stress in the adhesive layer, which consequently resulted in different crack paths in the joints.

There is an extensive body of work on the characterization of fractured surfaces and their correlation with the fracture properties in metals, rock joints and concrete [24-28]. Fracture surfaces are thought to convey inherent fracture properties in response to the failure processes. However, only very limited attention has been paid to fracture surface characterization of adhesively bonded joints. The fractured surface can be related to the strength, fracture toughness and durability of the adhesively bonded joint [29]. Yee and Pearson [30] showed that the fractured surface for rubber-toughened epoxy adhesives is more complex than that for unmodified epoxy adhesives. Naito and Fujii [29, 31] studied the fracture surfaces of unmodified and rubber-modified epoxy adhesive joints fractured under static and fatigue mode-I loadings. They observed a larger strain energy release rate for more geometrically complex fracture surfaces (having higher roughness) and derived empirical equations showing the relation between fracture toughness and fractal dimension. They were also able to predict the fatigue crack growth rate by measuring the fractal dimension of the fracture surfaces.

In this Chapter, the crack paths and fracture surfaces of unaged and aged ODCB specimens using two rubber-modified epoxy adhesives that fractured under mixed-mode loading conditions were measured and characterized using optical non-contact profilometry. The issue of unexpected crack path in the mixed-mode fracture of unaged ODCB specimens was addressed by experimental examination of several hypotheses and finite element evaluation of the stress distribution in the plastic zone. The variation of the fracture surface characteristics including fracture surface roughness, average crack path depth and maximum elevation in the fracture surface profiles with aging and their relationships with the fracture toughness were then assessed.

7.2. Experimental procedure
As indicated below, some of the results used in this Chapter have been previously described in previous Chapters, and the methods and relevant data are only summarized briefly
in Sections 2.1-2.4. The residual stress measurement in the adhesive layers has not been previously reported and is described below in Section 2.5.

7.2.1. Materials
Two different commercial DGEBA-based heat-cured rubber-toughened structural epoxy adhesives were studied (Table 7.1). Unless otherwise stated, the recommended curing profile of 30 min at 180°C was used and monitored using a thermocouple embedded in the adhesive layer.

Table 7.1: Mechanical and physical properties of toughened epoxy adhesives A and B as provided by the manufacturers.

<table>
<thead>
<tr>
<th>Adhesive</th>
<th>Elastic Modulus, $E$, MPa</th>
<th>Poisson's Ratio, $ν$</th>
<th>Tensile Strength, $σ_y$, MPa</th>
<th>Glass Transition Temp, $T_g$, °C</th>
<th>Cured Density g/cm$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adhesive 1</td>
<td>1.96</td>
<td>0.45</td>
<td>44.8</td>
<td>125</td>
<td>1.50</td>
</tr>
<tr>
<td>Adhesive 2</td>
<td>1.73</td>
<td>0.39</td>
<td>N/A</td>
<td>122</td>
<td>1.14</td>
</tr>
</tbody>
</table>

7.2.2. ODCB specimen fabrication
The DCB adherends were AA6061-T6 aluminum alloy pretreated using the P2 sulfuric acid etch method. The primary adhesive layer was 385 μm thick and was made of either Adhesive 1 or Adhesive 2. It was cured onto the primary adherend using a backing plate coated with tetrafluoroethylene (TFE) dry lubricant (MS-122N/CO2 by Miller-Stephenson Co., Connecticut, USA) that had been baked for approximately four hours at 285°C [32]. After curing, the backing plate was removed and the open-faced specimens were exposed to a 60°C-95% relative humidity (RH) condition for varying times. The exposed specimens were then dried in a vacuum oven containing anhydrous calcium sulphate at 40°C for approximately 7 days to remove any reversible effect of water ingress such as plasticization. The primary adhesive layer was then very lightly sanded, wiped with acetone and dried before a layer of Adhesive 2 (termed the secondary adhesive layer) was used to bond the specimen to a second adherend to make a complete ODCB joint. Adhesive 2 was used as the secondary adhesive in all cases. If
the primary layer was Adhesive 1, the system was called “AB” and if both primary and secondary layers were made of Adhesive 2, the system was called “BB”. In the case of fresh ODCBs, the secondary bonding was done immediately after the primary bonding without the exposure and drying processes. The configuration and dimensions of a typical ODCB is depicted in Fig. 7.1. More details about the specimen fabrication are given in Chapters 4 and 5. Single-layered DCB specimens were made following the procedure established in Chapter 2.

![Figure 7.1: Configuration and dimensions of the ODCB specimen (not to scale).](image)

### 7.2.3. Fracture test procedure

As fully described in Chapter 2, the mixed-mode fracture testing procedure employed a servo-electric load frame and the load jig of [33]. All tests were conducted at a loading phase angle $\psi = 27^\circ$, where $\psi = \arctan \left( \sqrt{\frac{G_{II}}{G_I}} \right)$, and $G_I$ and $G_{II}$ are the mode-I and mode-II components of the strain energy release rate. The tests were carried out under displacement control, advancing the crosshead at 1.5 mm/min in small discrete steps while viewing the crack.
tip through a microscope having a field of view of 2 mm. The crack consisted of a macrocrack that extended continuously from the embedded aluminum foil, and a series of apparently disconnected microcracks that were seen ahead of the macrocrack tip up to a distance of no more than 3 mm. In Chapter 2, it was found that measurement of the furthest advanced microcrack ahead of the macrocrack gave the most consistent measurement of the crack length. However, with the present adhesive system, taking the crack length as the distance from the loading pins to the tip of the macrocrack produced little difference (less than 5%) in the calculated steady state critical strain energy release rate, $G_{cs}$. The onset of microcrack propagation at the critical load and the corresponding crack length were determined to an accuracy of $\pm 20 \mu m$ using a micrometer stage. A beam-on-elastic-foundation model was used to calculate the strain energy release rate, $G_C$, from the measured crack length and fracture load [34]. The use of small discrete steps in loading facilitated the measurement of the rising part of the fracture $R$-curves. More detailed information about the characterization of the $R$-curves and their environmental degradation in these adhesive systems is reported in Chapters 2, 4 and 5. The focus of this Chapter is only on the plateau values (steady-state $G_C$, $G_{cs}$), and not the rising parts of the $R$-curves.

7.2.4. Measurement of fracture surface profiles and crack path

As explained in Chapter 6, the average depth of the crack path was determined by measuring the thickness of the residual adhesive on the more highly-strained adherend, which was the primary adherend of the ODCB. Two datum points were established on the bare aluminum by first removing residual adhesive from a 2 mm wide band on either side of this adherend of the fractured joint using a solvent (mixture of methylene chloride and methyl alcohol; Glue Buster, Kosmic Surf-Pro Inc., Saint Amable, Quebec). Transverse line scans were then made from one datum to the other across the width of the specimen at several locations using an optical profilometer (Nanovea ST 400, Microphotonics Inc., Irvine, CA, USA) to measure the adhesive residue thickness. Longitudinal and areal scans were also made in the same fashion to obtain two-dimensional and three-dimensional profiles of the fracture surfaces. The sampling rate was 500 data points per mm in all the scans. To assure the
accuracy of this approach, the residual adhesive thickness was also measured on the opposing fracture surface to give the total bondline thickness. Doing this for three joints gave a maximum difference of 9% from the nominal bondline thickness of 385 μm in single-layered DCBs.

7.2.5. Residual stress measurement

To measure the residual stresses created within the adhesive layer due to the cure, Adhesive 1 was cured while clamped between a 0.6 mm thick, 20 mm wide strip of aluminum AA3003-H14 and a TFE-coated backing plate. The backing plate was removed immediately after finishing the cure, and the sample was allowed to bend freely as a result of the residual stresses created due to the coefficient of thermal expansion (CTE) mismatch between the aluminum strip and the adhesive layer during the cooling from cure temperature (180°C) to room temperature (20°C). The residual stress was then calculated based on the measurement of the sample’s curvature using the analytical formulation given in [23]. In the case of multiple cures, the sample was allowed to reach room temperature after each cure cycle.

7.3. Results and discussion

7.3.1. Fresh ODCB joints – unexpected crack path

The intention of making such joints was to measure the fracture toughness of the primary layer without any environmental exposure as a baseline for the degradation studies. Based on the pure mode-I ($K_{I}=0$) [11-13] and maximum opening stress [14] crack path selection criteria for brittle materials under mixed-mode loading, cracks should grow on the interface of the more highly-strained adherend for remote phase angles, $\psi$, greater than 7° in the present adhesive systems, as calculated in Chapter 6. Therefore, a phase angle of 27° was used in the mixed-mode fracture tests and the specimens were arranged such that the primary adhesive layer was located adjacent to the more highly-strained adherend to ensure that the crack would grow in the primary adhesive layer. Moreover, a folded aluminum foil was embedded in the primary adhesive layer to initiate the crack in this layer.
Figure 7.2a shows a typical fracture surface of an unaged ODCB of adhesive system AB tested with $\psi=27^\circ$. Similar observations were found with adhesive system BB. In both adhesive systems, the crack initially started to grow near the interface of the more highly-strained adherend from the tip of the embedded foil, but it was found that the crack kinked toward the secondary adhesive layer after growing approximately twice the total bondline thickness (~2 mm of crack growth) into the primary layer. The crack path then remained in the secondary layer (Fig. 7.2b). This was contrary to the predictions of the mode-I or maximum opening stress crack path selection criteria. The same crack path pattern was observed when the fresh ODCBs were tested at mode-I and even higher phase angles (up to $\psi=48^\circ$). The following sections examine several hypotheses in an attempt to explain the unexpected observation of crack path kinking in the unaged ODCB joints. It is noted that once the crack stabilized in either the primary or secondary adhesive layers, it was trapped in that layer and could not kink toward the other layer. It is plausible to assume that the interface between the two layers was relatively tough, such that the crack could not grow through it to kink toward the other layer. One possible reason for the very tough interface between the two layers is the mechanical interlocking due to the roughening of the surface of the primary adhesive layer before the secondary bonding to achieve a good bond.
Figure 7.2: (a) Crack path in the mixed-mode (ψ=27°) fracture of a fresh ODCB joint of primary Adhesive 1 (light gray color) and secondary Adhesive 2 (black). (b) Schematic of the crack path in the fracture of these unaged ODCB joints. Crack started to grow in the primary adherend very close to the interface with the primary adherend, but after approximately 2 mm of growth the crack kinked toward the secondary adhesive layer.

7.3.1.1. Curing cycle effect

One of the differences between the primary and secondary adhesive layers was the curing process. The secondary layer was cured only once (30 min at 180°C) during the secondary bonding while the primary layer experienced two curing cycles, each for 30 min at 180°C during the primary and secondary cures. It was hypothesized that the additional cure might have caused the primary layer to be tougher than the secondary layer, thereby causing the crack to grow in the secondary adhesive layer.

To examine this hypothesis, the effects of curing time and the number of cure cycles on the fracture toughness of single-layered DCB joints of Adhesive 1 were assessed. As seen in Table 7.2, no consistent trend was found between the average $G_{cs}$ and cure time. The maximum difference between the $G_{cs}$ values obtained at different cure durations was calculated to be approximately 13% which was well within the range of the coefficient of variance (COV) measured for multiple specimens at a single cure duration. This indicated that the differences in the fracture toughness of the specimens cured for different time periods were only in the range of experimental scatter. Moreover, the 60 min and 30 min cure times corresponded to those of the primary and secondary layers, respectively, and the slight decrease in $G_{cs}$ from 30 min to 60 min should have promoted the crack to remain in the primary layer since it had a slightly lower $G_{cs}$. Furthermore, three specimens were cured using two
consecutive complete cure cycles (each one including heating up, cure, and cooling down steps) in an attempt to exactly mimic the cure profile of the primary layer in ODCBs. Fracture tests of such joints showed no significant difference between $G_{cs}$ values corresponding to one or two cure cycles (t-test, 95% confidence, last row of Table 7.2). It was thus concluded that the fracture toughness of the primary layer was not affected by the secondary cure.

Table 7.2: $G_{cs}$ of single-layered DCBs of Adhesive 1 after different cure durations. Coefficient of variance (COV) defined as the standard deviation (SD) over the average value expressed as a percentage.

<table>
<thead>
<tr>
<th>Cure Time (min)</th>
<th>No. of repetitions</th>
<th>Ave. $G_{cs}$ (Jm$^{-2}$)</th>
<th>SD (Jm$^{-2}$)</th>
<th>COV (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>6</td>
<td>4160</td>
<td>336</td>
<td>8</td>
</tr>
<tr>
<td>45</td>
<td>3</td>
<td>3920</td>
<td>376</td>
<td>10</td>
</tr>
<tr>
<td>60</td>
<td>3</td>
<td>3890</td>
<td>543</td>
<td>14</td>
</tr>
<tr>
<td>90</td>
<td>3</td>
<td>3610</td>
<td>454</td>
<td>13</td>
</tr>
<tr>
<td>120</td>
<td>1</td>
<td>4020</td>
<td>486</td>
<td>N/A</td>
</tr>
<tr>
<td>60 (2x30 cure cycles)</td>
<td>3</td>
<td>3970</td>
<td>384</td>
<td>10</td>
</tr>
</tbody>
</table>

7.3.1.2. Effect of bondline thickness
In Chapter 2, it was shown that the fracture toughness of adhesives A and B increased significantly with increasing bondline thickness. It was thus assumed that decreasing the primary bondline thickness or increasing the secondary bondline thickness would cause the fracture toughness to be lower in the primary layer compared to that of the secondary layer, and that this could be used to keep the crack in the primary layer. Different combinations of primary and secondary adhesive layer thicknesses were examined and $G_{cs}$ was measured in each case as shown in Table 7.3. It was found that the crack path pattern did not change, and that the crack propagated in the secondary layer even when it was made much thicker and therefore supposedly tougher than the primary. This observation is similar to that reported in [9, 13] where cohesive crack growth occurred even when the adhesive layer fracture toughness was much higher than the interfacial fracture toughness. Hutchinson and Suo [13] have referred to this as an unexplained phenomenon. It was thus concluded that the fracture
toughness was not the main controlling parameter in determining the layer in which the crack propagated.

An unexpected observation in Table 7.3 was that the \( G_{cs} \) of the fresh ODCBs was only a function of the thickness of the secondary layer in which the crack propagated, and its value was nearly equal to the \( G_{cs} \) of an identical single-layered DCB joint with a bondline thickness equal to that of the secondary layer (Table 7.3). In other words, fracture in the ODCB proceeded in the secondary layer as if the primary layer were not present. This implies that the primary and secondary adhesive layers did not act as integrated layers with a bond thickness equal to the sum of the primary and secondary thicknesses. The explanation for this behavior is unknown.

Table 7.3: \( G_{cs} \) in the fracture of unaged ODCB specimens of system AB having different combinations of the primary (Adhesive 1) and secondary (Adhesive 2) bondline thicknesses. In each case, \( G_{cs} \) corresponded to crack growth in the secondary adhesive (Adhesive 2). The \( G_{cs} \) of identical single-layered DCB joints of Adhesive 2 with a bondline thickness equal to that of the secondary layer in the corresponding ODCB is also given.

<table>
<thead>
<tr>
<th>Bond thickness combination</th>
<th>( G_{cs} ) (Jm(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ODCB</td>
</tr>
<tr>
<td>Primary thickness (μm)</td>
<td></td>
</tr>
<tr>
<td>Secondary thickness (μm)</td>
<td></td>
</tr>
<tr>
<td>385</td>
<td>4310</td>
</tr>
<tr>
<td>125</td>
<td>3580</td>
</tr>
<tr>
<td>125</td>
<td>4270</td>
</tr>
<tr>
<td>125</td>
<td>6330</td>
</tr>
</tbody>
</table>

### 7.3.1.3. Residual stress effect

The third hypothesis for the unexpected growth of cracks in the secondary adhesive layer of the unaged ODCB joints was the potential influence of residual stress on the directional stability of the crack. The stability of a crack within an adhesive layer has been related to the \( T \)-stress, which is defined as the tensile stress in the crack plane normal to the crack front. The analytical approximate solution for the \( T \)-stress is given by [19]:

\[
T = \sigma_R + \left(\frac{1+\alpha}{1-\alpha}\right)^{0.5} C_1 K_{IC} t^{-0.5}
\] (1)
where $\sigma_R$ is the residual stress built up in the adhesive layer during the cure cycle and acting in the same direction as the $T$-stress, $K_{IC}$ is the mode-I stress intensity factor, $C_1$ is an empirical function of the Dundurs parameters, and $t$ is the adhesive layer thickness. $\alpha$ is one of the Dundurs parameters reflecting the mismatch in the shear modulus between the adhesive and the adherends, and defined as:

$$\alpha = \frac{\mu_1(k_2+1)-\mu_2(k_1+1)}{\mu_1(k_2+1)+\mu_2(k_1+1)}$$

where the subscripts 1 and 2 refer to the adherends and adhesive, respectively. $\mu$ is the shear modulus and $k = 3 - 4\nu$ for plane stress and $k = (3 - \nu)/(1 + \nu)$ for plane strain, where $\nu$ is the Poisson ratio. The criterion for straight, stable cracking in an adhesive layer is $T \leq 0$. The CTE of adhesives A and B was measured to be 85 and 83 ppm/°C using dynamic mechanical thermal analysis (DMTA) of their wafer samples, while that of aluminum is only 24 ppm/°C. This CTE mismatch would have created a tensile residual stress within the adhesive layers of the present ODCB specimens and probably a positive $T$-stress. A relatively large tensile residual stress of 60 MPa has been reported for a heat setting epoxy-aluminum system which resulted in a positive $T$-stress of greater than 30 MPa, and thus unstable crack growth and crack path kinking within the epoxy layer [35]. Yu et al. [23] reported a thermal residual stress of about 13 MPa in the interface of an epoxy-steel laminate.

If the $T$-stress in the secondary adhesive layer was negative or at least lower than that in the primary layer, the crack would then be predicted to be more stable in the secondary layer as was observed in the present experiments. The bondline thicknesses of the primary and secondary adhesive layers were equal (385 μm each) and to a rough approximation it could be assumed that the mechanical properties of the layers were the same, specifically in the case of adhesive system BB in which both layers were made of the same adhesive. The second term of the right hand side of Eq. (1) was thus the same for the primary and secondary adhesive layers. The only parameter that could be different was then the residual stress, and the only reason that could cause a difference in the residual stresses between the two layers was the difference in cure profiles, since the primary layer was cured twice while the secondary was cured only once.
The residual stress in Adhesive 1 increased slightly with the number of cure cycles up to the third cure, but remained approximately unchanged thereafter (Table 7.4). It is thus plausible that the tensile residual stress in the primary adhesive layer, which was cured twice, was greater than that in the secondary layer, thereby leading to a greater instability of the crack path in the primary layer compared to that in the secondary. Accordingly, it was hypothesized that a crack that had kinked to the secondary layer would tend to remain there. This argument would apply to ODCB specimens of systems AB and BB if it is assumed that the thermomechanical properties of adhesives A and B are approximately the same. To support the argument that the difference in the residual stress caused the crack to deviate from the primary and then remain in the secondary layer, two sets of experiments were carried out as described below.

Table 7.4: Variation of the residual stress with the number of cure cycles in Adhesive 1 cured on an aluminum strip.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Residual Stress (MPa)</th>
<th>1st Cure</th>
<th>2nd Cure</th>
<th>3rd Cure</th>
<th>4th Cure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>4.1</td>
<td>4.8</td>
<td>5.1</td>
<td>5.2</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>3.8</td>
<td>4.6</td>
<td>5.0</td>
<td>5.1</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>4.4</td>
<td>5.1</td>
<td>5.4</td>
<td>5.4</td>
</tr>
</tbody>
</table>

*Modified cure profiles*

Since the curvature measurements of Adhesive 1 cured on an aluminum strip showed that the residual stress did not change after the third cure cycle, it was hypothesized that the residual stresses in both ODCB adhesive layers would be equalized if the joints were cured for a prolonged time. To evaluate this hypothesis, two new cure profiles were examined in the manufacture of ODCBs of adhesive system AB: (a) adding one more cure cycle after the secondary bonding (i.e. the primary adhesive was exposed to three cure cycles), and (b) adding three more cure cycles after the secondary bonding (i.e. the primary adhesive was exposed to five cure cycles). In each cycle, the specimen was cooled to room temperature and then reheated. Figure 7.3 shows the fracture surfaces obtained after the mixed-mode testing of ODCBs prepared using these two cure profiles. As observed in the fracture testing of single-
layered DCBs cured for different times (Table 7.2), $G_{cs}$ was unaffected by the cure duration. However, the crack path pattern changed significantly with the additional cure cycles. When one more cure cycle was added to the ODCB fabrication, the crack path was mixed in the primary and secondary layers (Fig. 7.3a), while adding three more cure cycles caused the crack to propagate completely in the primary adhesive layer (Fig. 7.3b). Based on the residual stress results given in Table 7.4, it was then reasonable to assume that three more cure cycles in the manufacture of the ODCB would cause both adhesive layers to reach the same ultimate residual stress and result in equal crack path stability in the two adhesive layers. Since the primary layer was located adjacent to the more highly-strained adherend, and the precrack was placed in the primary layer, the crack remained in the primary layer as desired.

Figure 7.3: Fracture surfaces of adhesive system AB ODCB joints tested after multiple cures. (a) Mixed crack path in both primary and secondary adhesive layers corresponding to one additional ODCB cure cycle. (b) Crack path in the primary layer corresponding to three additional ODCB cure cycles. Light and dark regions indicate the primary (Adhesive 1) and secondary (Adhesive 2) layers, respectively.
**Hot-wet exposure**

It is known that exposing the cured adhesive layer to humidity results in residual stress relaxation [23, 36, 37]. It was thus assumed that if the primary adhesive layer was exposed to a humid environment for sufficient time, its residual stress and T-stress should decrease, thereby promoting greater stability in the primary layer. Therefore, before the secondary bonding, the primary adhesive layer of both adhesive systems AB and BB were exposed to a 60°C-95% RH environment for different time intervals and then dried at 40°C for approximately seven days. Gravimetric measurements on Chapter 3 showed that seven days of drying is sufficient for the desorption process and the amount of retained water does not change with further drying beyond seven days. While the amount of retained water after this drying in Adhesive 2 was reported to be approximately zero, that in Adhesive 1 was 1.7% of the sample original mass, this being equal to 25% of the saturated water concentration at this exposure environment. Table 7.5 shows the mixed-mode \((\psi=27^\circ)\) \(G_{cs}\) and crack path locations for both adhesive systems after different exposure times. \(G_{cs}\) in adhesive system AB started to decrease rapidly while that in adhesive system BB remained unchanged; however, in both adhesive systems, the crack remained in the primary adhesive layer. Therefore, hot-wet aging of the open-faced primary adhesive layer before the secondary bonding caused the crack path to remain within the primary layer as desired.

**Table 7.5:** \(G_{cs}\) and crack path location for adhesive systems AB and BB after different open-faced exposure times of the primary layer at 60°C-95%RH.

<table>
<thead>
<tr>
<th>Exposure Time (Day)</th>
<th>Adhesive System AB</th>
<th>Adhesive System BB</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(G_{cs}) (Jm(^{-2}))</td>
<td>Crack path</td>
</tr>
<tr>
<td>0 (Fresh)</td>
<td>4160</td>
<td>Secondary*</td>
</tr>
<tr>
<td>7</td>
<td>1670</td>
<td>Primary**</td>
</tr>
<tr>
<td>15</td>
<td>1420</td>
<td>Primary</td>
</tr>
<tr>
<td>30</td>
<td>1030</td>
<td>Primary</td>
</tr>
<tr>
<td>60</td>
<td>910</td>
<td>Primary</td>
</tr>
<tr>
<td>120</td>
<td>1120</td>
<td>Primary</td>
</tr>
</tbody>
</table>

*: Crack stabilized in the secondary adhesive layer after initiation in the primary layer (Similar to Fig. 7.2).

**: Crack remained in the primary adhesive layer and did not kink to the secondary layer.
Since the fracture toughness of adhesive system BB did not decrease after exposure (see Fig. 7.4), the change in the crack path pattern was not caused by degradation and therefore appeared to be related to the change in the residual stress caused by moisture absorption. During the exposure, stress relaxation occurred and resulted in a decrease of residual stress in the primary adhesive layer in a way that the final residual stress in the primary layer became less than that in the secondary and consequently the crack propagated stably in the primary layer. Since stress relaxation is a time dependent phenomenon, sufficient exposure time was required to significantly decrease the residual stress in the primary layer. For instance, as seen in Table 7.5, after an exposure of 15 days, the crack still deviated from the primary in system BB, but after 30 days exposure sufficient stress relaxation occurred to cause the crack to remain in the primary layer. In the case of adhesive system AB, a strong conclusion could not be drawn from this experiment owing to the fact that the fracture toughness of Adhesive 1 also started to decrease in the early stages of exposure. Hence, it was not clear whether the crack remained in the primary layer because of its degradation or because of the stress relaxation in the layer.

As addressed above, some difficulties occurred in driving the crack in the unaged primary layer of ODCB specimen when the recommended cure schedule was employed. However, once the crack propagated in the primary layer that had not been degraded (e.g. aged system BB and system AB with modified cure) the experimental fracture toughness measurements of the ODCB specimens consistently resulted in a $G_{cs}$ value that was in excellent agreement with the fracture toughness of the same adhesive system without the secondary layer. It can thus be concluded that, even though the addition of the secondary layer slightly changed the cure state and residual stress state of the primary layer, it did not have a distinguishable effect on the fracture toughness of the primary layer. Consequently, the decrease in the measured fracture toughness in degraded ODCB joints was solely due to the degradation of the primary adhesive layer.
7.3.2. Aged ODCB joints

7.3.2.1. Fracture toughness of aged ODCBs

Figure 7.4 shows the variation of $G_{cs}$ with the time of exposure for adhesives A and B. The data were obtained from mixed-mode fracture tests ($\psi=27^\circ$) on AB and BB ODCB joints that had been exposed to a 60°C-95% RH environment. The $G_{cs}$ of Adhesive 1 started to decrease from the very early stages of the degradation, within 4 days of exposure, while that of Adhesive 2 remained unchanged even after 540 days of exposure. As described in Chapters 4 and 5, this behavior was attributed to differences in the bonding between the absorbed water molecules and the rubber tougheners in the respective adhesives.

![Graph showing $G_{cs}$ vs. exposure time for adhesives A and B](image)

Figure 7.4: $G_{cs}$ of adhesives A and B as a function of exposure time at 60°C-95%RH. Data from ODCB joint systems AB and BB, respectively, that were fracture tested at $\psi=27^\circ$.

7.3.2.2. Fracture surface topography of aged ODCBs

Figure 7.5 shows the typical fracture surfaces of Adhesive 1 observed after different exposure times at 60°C-95%RH. The fracture surface of the unaged adhesive (Fig. 7.5a) corresponds to a single-layer DCB joint, and was completely cohesive, relatively rough and distant from the interface. As $G_{cs}$ decreased with increasing exposure time, the fracture surfaces became smoother and closer to the interface of the more highly-strained adherend (Figs. 7.5b and 7.5c). After a relatively long exposure time of 365 days, the crack path was still cohesive but very close to the interface, with a very smooth surface (Fig. 7.5d). At this stage, $G_{cs}$ was as low as 290 Jm$^{-2}$ [25]. Consistent with the stable $G_{cs}$ trend of Fig. 7.4, the fracture surfaces of Adhesive 2 (Fig. 7.6) were unaffected by the exposure, even after 540 days.
These relationships between the fracture surface characteristics and the fracture toughness were quantified using an optical profilometer to measure the average surface roughness ($R_s$), the average crack path depth ($t_r$) (average residual adhesive thickness on the surface of the more highly-strained adherend), and the maximum change in the fracture surface elevation ($E_m$) (difference between the average of the 100 highest peaks and the average of the 100 lowest valleys). The latter quantity reflected the range of the crack path oscillation within the primary layer.

It should be noted that in Figs. 7.5 to 7.8, (a) corresponds to the fracture surface of a fresh single-layered DCB with 385 μm bondline thickness, because the crack did not grow in the primary layer of an unaged ODCB when using the recommended cure profiles, as shown previously. However, based on the results given in Table 7.3, it was assumed that the $G_{cs}$ of the unaged primary layer of an ODCB would be the same as that in a single-layered DCB having the same bondline thickness as the ODCB primary layer.

![Figure 7.5](image_url)

Figure 7.5: (a) Single-layered DCB of Adhesive 1 with 385 μm bondline thickness. (b)-(d) Typical fracture surfaces of Adhesive 1 observed on the more highly-strained ODCB adherend (primary adherend) after different exposure times ($t$) at 60°C-95%RH.
Figures 7.7 and 7.8 show the typical joint centerline fracture surface profiles corresponding to Figs. 7.5 and 7.6, respectively. The fracture surfaces of both adhesives were very similar in the unaged condition, being rough and oscillating between the two interfaces (Fig. 7.7a and Fig. 7.8a). As the exposure time was increased, the fracture surfaces of Adhesive 1 became flatter, and the crack plane moved toward the more highly-strained adherend (Figs. 7.7b-d). However, for Adhesive 2, no significant effect of exposure time on fracture surface flatness and the crack plane location was observed (Fig. 7.8).
Figure 7.7: Typical centerline fracture surface profiles of Adhesive 1 specimens. (a) Single-layered unaged DCB of Adhesive 1 with 385 μm bondline thickness. (b)-(d) The more highly-strained ODCB adherend (primary adherend) after different exposure times (t) at 60°C-95%RH. 0 and 385 μm on the vertical axis correspond to the primary adhesive layer interfaces with the more highly-strained adherend and the secondary adhesive layer, respectively.
Figure 7.8: Typical centerline fracture surface profiles of Adhesive 2 specimens. (a) Single-layered unaged DCB of Adhesive 2 with 385 μm bondline thickness. (b)-(d) The more highly-strained ODCB adherend (primary adherend) after different exposure times (t) at 60°C-95%RH. 0 and 385 μm on the vertical axis correspond to the primary adhesive layer interfaces with the more highly-strained adherend and the secondary adhesive layer, respectively.

Figures 7.9 – 7.11 show that all of the fracture surface parameters measured for Adhesive 1 \((R_a, t_r, E_m)\) varied approximately linearly with \(G_{cs}\), the only exception being at the lowest \(G_{cs}=290 \text{ Jm}^{-2}\) where \(R_a\) was approximately the same as the roughness of the pretreated aluminum adhered surface (~2 μm) (Fig. 7.9) because the residual adhesive thickness, \(t_r\), was so small.

In the case of Adhesive 2, no significant change in the three surface parameters was observed when the exposure time was increased (t-test, 95% confidence; Table 7.6). Furthermore, the \(R_a\), \(t_r\), and \(E_m\) values corresponding to the unaged DCB specimens of adhesives A and B (with average \(G_{cs}\) values of 4160 and 4380 Jm\(^{-2}\), respectively) agreed closely, implying that the differences between the adhesives were due solely to their respective susceptibility to water degradation. All these findings indicated a strong relationship between fracture surface...
roughness, average crack path depth, maximum elevation in the profile and fracture toughness, irrespective of the adhesive; consistent with the results given in [29-31].

Figure 7.9: Variation of the fracture surface roughness of Adhesive 1 with $G_{cs}$. Each data point is the average of 9 replications measured on 3 specimens. Error bars show $\pm 1$ standard deviation. The line shows the least-squares fit.

Figure 7.10: Variation of the average residual thickness of Adhesive 1 with $G_{cs}$. Each data point is the average of 9 replications measured on 3 specimens. Error bars show $\pm 1$ standard deviation. The line shows the least-squares fit.
Figure 7.11: Variation of the adhesive maximum elevation difference of Adhesive 1 with $G_{cs}$. Each data point is the average of nine replications measured on three specimens. Error bars show ± 1 standard deviation. The line shows the least-squares fit.

Table 7.6: Fracture toughness, fracture surface roughness, crack path average depth, and maximum elevation difference in the fracture surface profiles for the fresh and aged specimens of Adhesive 2. Each data point in fresh case was an average obtained from 3 DCB specimens. The results in the aged case are the grand averages obtained from the ODCB specimens tested after 3 different exposure times (Figs. 7.6b-d) with 3 replications at each time.

<table>
<thead>
<tr>
<th></th>
<th>Fresh</th>
<th>Aged</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fracture toughness, $G_{cs}$ ±1SD ($Jm^{-2}$)</td>
<td>4380±280</td>
<td>4180±340</td>
</tr>
<tr>
<td>Roughness, $R_a$±1SD ($\mu m$)</td>
<td>19.4±2.4</td>
<td>18.1±2.8</td>
</tr>
<tr>
<td>Residual thickness, $t_{R}$±1SD ($\mu m$)</td>
<td>178±21</td>
<td>154±26</td>
</tr>
<tr>
<td>Maximum elevation, $E_m$±1SD ($\mu m$)</td>
<td>309±27</td>
<td>325±36</td>
</tr>
</tbody>
</table>

Figure 7.12 shows the variation of the ratio of the actual three-dimensional fracture surface area ($A$) to the projected area ($A_0$, the planar bond area) with $G_{cs}$ for system AB. It should be noted that throughout this work, $G_{cs}$ was calculated using projected area. This ratio is a three-dimensional relative measure of the roughness of the fracture surface, and is expected to increase with the toughness of the adhesive, reflecting the increased work of fracture. The $A/A_0$ ratio decreased from 1.31 in the case of the unaged DCB to 1.09 corresponding to the lowest $G_{cs}$ for system AB. As expected, the $A/A_0$ ratio for system BB remained constant at 1.33 irrespective of exposure time. These findings are consistent with the observations found in [5].
Figure 7.12: Variation of $A/A_0$ ratio of the fracture surface with $G_{cs}$ in system AB. Each data point is an average of 9 replications measured on 3 specimens. Error bars show ±1 standard deviation. The line shows the least-squares fit.

In the case of the degraded ODCBs of system AB, as explained in Chapters 4 and 5, first, the toughening mechanisms related to the rubber particles gradually deteriorated with aging time and then the DGEBA matrix also began to degrade, resulting in a very low $G_{cs}$ of 290 Jm$^{-2}$. Consequently, as explained in Chapter 6, after a sufficiently long exposure time, a transition from ductile to brittle behavior occurred in the fracture of system AB. For sufficiently long exposure times, the mixed-mode cracks tended to follow trajectories that maximized the mode-I component of the fracture energy at the crack tip (i.e., very close to the interface of more highly-strained adherend), a typically brittle material behavior. This is consistent with the hypothesis in proposed in Chapter 6 that the degraded Adhesive 1 acted as a relatively brittle, pure epoxy resin without any active toughening mechanism. This is also consistent with the work of Zhang et al., who reported a marked transition from brittle to ductile characteristics when toughening modifiers were added to a pure epoxy matrix [38]. Finally, the fracture surfaces of these aged specimens were smooth and glassy; similar to the observations for an untoughened DGEBA epoxy in [39].

The strong correlations between the fracture toughness and the fracture surface parameters irrespective of the type of adhesive and the aging time suggest that quantifying the fracture surface parameters in a post-failure analysis can reveal useful information about the
joint properties; e.g. the estimation of the fracture toughness at which a practical joint has failed or the level of degradation that it has experienced. Future work could focus on the developing a systematic predictive methodology.

7.3.3. Relation between crack path and plastic zone

Mode-I paths do not exist within the adhesive layer for phase angles greater than 7° in the studied adhesives and crack growth in relatively brittle adhesives proceeds under mixed-mode conditions along the interface with the more highly-strained adherend; i.e. the path that maximizes the mode-I component of the strain energy release rate. These predictions for brittle crack growth, however, did not agree with the present observations, since as mentioned above, the average experimentally measured crack path in the mixed-mode (ψ=27°) fracture of fresh joints was approximately in the bondline mid-plane and locally travelled almost from one interface to the other across the adhesive layer. For the degraded ODCB specimens, the lower the $G_{cs}$, the closer the crack path was to the highly-strained adherend interface. As discussed in the previous Chapter, finite element analysis of DCB joints made with Adhesive 1 revealed a transition of the location of the maximum von Mises stress from the more highly-strained interface to the opposing one as the distance from the crack tip increased. This analysis and the experimental observations were used to explain the unexpected crack path pattern in fresh DCB specimens of Adhesive 1.

A finite element model similar to that developed in Chapter 6 was used to assess the plastic zone and stress distribution in the undegraded ODCB joints. The primary and secondary adhesive layers stress-strain behavior was approximated using a multi-linear isotropic hardening model derived from tensile test results provided by the manufacturers. Very little difference was found between the mechanical properties of the two adhesives, and so the elastic modulus ($E_a$) and the proportionality limit of both were set to be 1.5 GPa and 30 MPa, respectively. Figure 7.13 shows typical plastic zones in the primary and secondary adhesive layers at an applied $G=1000$ Jm$^{-2}$ under mixed-mode loading (ψ=27°), corresponding to the critical strain energy release rate of these systems after approximately 2 mm of crack growth from the precrack tip, which coincided the crack path transition from the primary layer to the
secondary one (Fig. 7.2). It should also be noted that, at higher applied $G$ values, the plastic zone pattern was similar to the one given in Fig. 7.13, but at higher stress levels. Other than the very highly-stressed region close to the crack tip (black region in Fig. 7.13), two more highly-stressed regions were observed in the plastic zone. One was ahead of the highly stressed black region, located mostly in the primary layer (Region I in Fig. 7.13), while the other region was located in the secondary layer further from the aluminum foil precrack (Region II in Fig. 7.13). The transition of maximum von Mises stress path from the primary layer to the interface of the secondary one occurred at a distance of 1.8 mm from the precrack tip (Fig. 7.13). This was in good agreement with the location of the experimentally observed crack path kinking from the primary layer to the secondary (Fig. 7.2). The unexpected crack path kinking from the primary layer to the secondary one in the unaged ODCB joints was thus explained as follows.

At the moment of crack initiation within the primary layer (in the dark region, Fig. 7.13), micocracking also occurred within the secondary layer because of the relatively high stress levels (in region II, Fig. 7.13). As the load increased and the crack in the primary started to propagate (in region I, Fig. 7.13), the microcracks in the secondary layer also coalesced and formed a new crack. Since the residual tensile stress (and so $T$-stress) in the secondary adhesive layer was lower than that in the primary one (Table 7.4), the newly created crack in the secondary layer could grow more stably and hence the crack in the primary layer was arrested.
In the cases where the crack was observed to remain in the primary adhesive (unaged ODCBs of system AB with multiple cure cycles, and aged ODCBs of either system AB or BB), it was postulated that such microcracking still occurred in the secondary layer region II (Fig. 7.13), but that a macrocrack could not form before the extension of the crack in the primary layer region I.

7.4. Conclusions

The crack path and fracture surface in the mixed-mode fracture of two different rubber-toughened epoxy adhesives were evaluated using ODCB specimens in which the primary adhesive layer had been environmentally aged. First, the issue of unexpected crack path in the mixed-mode fracture of unaged ODCB specimens was addressed. Then, fracture surface parameters including average crack path depth, fracture surface roughness and maximum elevation in the profiles were quantified as a function of hot-wet aging time.

The second cure of the primary adhesive layer and different combinations of the primary and secondary adhesive layer thicknesses appeared to have no effect on the crack path pattern in the mixed-mode fracture of unaged ODCB specimens. In particular, cracks grew unexpectedly in the secondary adhesive layer of unaged ODCB joints. Two approaches were found to alleviate this difficulty and maintain crack growth in the primary adhesive layer: (i) increasing the number of curing cycles in unaged ODCBs of system AB, and (ii) exposing the primary layer of system BB ODCB specimens to a moist environment both resulted in equalized residual stresses in the primary and secondary adhesive layers and consequently no preference for the crack to grow in the secondary adhesive layer. The crack thus grew in the primary layer in these cases as desired. It was also found that adding the secondary layer had no distinguishable effect on the fracture toughness of the primary layer even though it slightly changed the cure and residual stress states of the primary layer.

A strong relationship was found between the fracture surface parameters \( R_a, t_R, E_m \) and the critical strain energy release rate, \( G_{cs} \), irrespective of the type of adhesive. In the case of Adhesive 1 where irreversible degradation observed, all these parameters varied approximately linearly with \( G_{cs} \). Upon degradation, a ductile-to-brittle transition was also
noticed in the fracture characteristics of Adhesive 1. In the case of Adhesive 2, aging did not result in the permanent degradation (unchanged $G_{cc}$) and all these fracture surface parameters remained unchanged with aging. The strong correlations that were found indicate that characterizing fracture surfaces as a post-failure analysis might be useful to estimate the fracture toughness at which a practical joint has failed.
7.5. References


Chapter 8: Prediction of environmental degradation of closed adhesive joints using data from open-faced specimens

8.1. Introduction

Traditional closed joints are not well suited for the study of degradation because the diffusion path of water into the adhesive layer is long, and so the degradation experiments are time-consuming. Moreover, the resulting degradation is not uniform after reasonable exposure times, with the exposed edges experiencing greater strength loss than the central portions of the joint. Since the results from testing such joints do not represent a discrete state of moisture degradation, it is impossible to directly apply the measured properties to other joint configurations or ageing conditions.

Open-faced specimens can be used to accelerate the aging process by shortening the diffusion path of water into the adhesive layer. Moreover, they achieve a spatially uniform state of degradation that can be associated with specific combinations of water concentration and exposure time. In the open-faced approach, the adhesive layer is first cast on only one adherend while its surface is left open to the aging environment. After aging the open-faced adhesive layer, the specimen is bonded to another adherend using another layer of adhesive to form a complete joint.

Spelt and Wylde used the open-faced method to measure the steady-state critical strain energy release rate, $G_{cs}$, of brittle epoxy adhesives that had been aged in hot-wet environments [1]. They tested the adhesive in both the wet and dry states (i.e. with and without water in the adhesive layer), and found that the strength of the dry specimens decreased monotonically with aging time while that of the wet specimens increased in the initial stages of aging due to the reversible plasticization effect of water. Loh et al. [2,3] used the open-faced configuration in the mixed-mode flexure and notched coating adhesion tests to study the environmental
degradation of the interfacial fracture energy in a rubber-toughened epoxy adhesive/steel joint. Similarly, Liljedahl et al. [4,5] employed the same tests in the damage modeling of environmentally degraded adhesively bonded aluminum and composite joints. In Chapters 4 and 5, the open-faced method was used in the characterization of the fracture degradation of two highly-toughened epoxy/aluminum adhesive systems aged under different combinations of temperature and relative humidity.

This Chapter establishes the framework by which the residual strength of a conventional closed DCB joint can be directly predicted using the results obtained from the fracture testing of degraded open-faced specimens. The framework integrated the fracture toughness results of degraded open-faced DCB specimens, the water diffusion properties of the adhesive, and the concept of the exposure index to estimate the residual strength of degraded closed joints. To verify the predictions, the fracture experiments and analysis were carried out for closed DCB joints degraded under two different exposure conditions. The validity of the degradation pathway independence in the predictions was also evaluated.

8.2. General framework

A framework for the assessment of the applicability of the open-faced technique to the prediction of the durability of closed DCB (CDCB) joints is shown in Fig. 8.1. The assessment methodology consisted of five major steps: a) Aging and fracture testing of open-faced DCB (ODCB) specimens, b) Gravimetric measurements and analysis in order to develop appropriate predictive models for water absorption and desorption during the aging and drying processes, c) Calculation of the $E_I$ values in both ODCB specimens and CDCB joints using the diffusion models and the temperatures and relative humidities of the exposure environments, d) Combining the results of the degraded ODCB fracture tests and $E_I$ calculations to construct fracture envelopes in which the fracture toughness is a function of $E_I$, e) Prediction of the fracture toughness of the degraded CDCB joints using the $E_I$ values corresponding to the aging
conditions and the $G_{cs}$-$EI$ fracture envelopes, and f) Aging and fracture testing of CDCB joints to compare with the predictions.

In previous work, the as-bonded (unaged) strength of regular closed adhesive joints has been accurately predicted using the characteristic “fracture envelope” for the adhesive system; i.e. the steady-state critical strain energy release rate, $G_{cs}$, as a function of the phase angle of loading, $\psi$ [6-8]. In this approach, the phase angle of the joint is calculated, and the joint critical load is computed as the one giving the corresponding $G_{cs}$ for the joint phase angle from the fracture envelope. The prediction of the strength of degraded joints follows the same pattern, with one additional variable, $EI$, reflecting the level and duration of water exposure and hence degradation. Therefore, the degraded fracture envelope for a particular adhesive system gives the measured $G_{cs}$ as a function of $\psi$ for a range of $EI$.

Figure 8.1: Framework for the assessment of the open-faced technique to predict the strength of environmentally degraded adhesive joints.
8.3. Experimental procedure

The methods and results pertaining to the water absorption/desorption measurements and analysis were reported in Chapter 3, while the aging and fracture testing of ODCB specimens was presented in Chapters 4 and 5. Therefore, these methods and data are only summarized briefly in Sections 3.1 and 3.2. The test methods, experimental results and fracture load predictions for the CDCB joints have not been previously reported, and are described in more detail in Sections 3.3 and 3.4.

Both the ODCB and CDCB specimens (Fig. 8.2) were made from aluminum AA6061-T6 adherends and a commercial DGEBA-based heat-cured rubber-toughened structural epoxy adhesive with a recommended curing profile of 30 min at 180°C. For all cast adhesive gravimetric samples, ODCB specimens and CDCB joints, the aging conditions were 60°C-95%RH and 60°C-82%RH obtained by placing the specimens in air-tight containers above different saturated salt solutions, while the drying condition was 40°C-0%RH, obtained using a vacuum oven containing anhydrous calcium sulphate as a desiccant.

![Diagram of CDCB joint](image)

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Parameter</th>
<th>Size</th>
</tr>
</thead>
<tbody>
<tr>
<td>(L)</td>
<td>Specimen length</td>
<td>~ 250 mm</td>
</tr>
<tr>
<td>(h)</td>
<td>Adherend thickness</td>
<td>12.7 mm</td>
</tr>
<tr>
<td>(t_p)</td>
<td>Primary bond thickness</td>
<td>0.4 mm</td>
</tr>
<tr>
<td>(t_s)</td>
<td>Secondary bond thickness</td>
<td>0.4 mm</td>
</tr>
<tr>
<td>(w)</td>
<td>Adherend width</td>
<td>19-21 mm</td>
</tr>
<tr>
<td>(a_0)</td>
<td>Starting length</td>
<td>~ 40 mm</td>
</tr>
<tr>
<td>(\Delta a)</td>
<td>Crack length increment</td>
<td>Variable</td>
</tr>
<tr>
<td>(a)</td>
<td>Crack length</td>
<td>Variable</td>
</tr>
<tr>
<td>(P_1)</td>
<td>Upper adherend load</td>
<td>Variable</td>
</tr>
<tr>
<td>(P_2)</td>
<td>Lower adherend load</td>
<td>Variable</td>
</tr>
</tbody>
</table>
Figure 8. 2: The configuration and dimensions of the open-faced DCB specimen (not to scale). Closed DCB joints had the same configuration and dimensions except the secondary adhesive layer was not present.

8.3.1. Gravimetric measurements

Cast adhesive wafers of 780 μm thickness (twice the bondline thickness of the joints) were cured and then cut to 40 x 40 mm samples, ensuring that the diffusion process was essentially one-dimensional in the thickness direction. After completely drying the wafers initially, mass uptake measurements were made after various exposure periods at 60°C-95% RH and 60°C-82%RH until saturation was reached. The wafers were then dried to obtain mass loss measurements until no further change was observed. More details about gravimetric measurements are given in Chapter 3.

8.3.2. ODCB preparation

The 385 μm thick primary adhesive layer (i.e. the layer to be degraded) was first cured on the primary adherend using a release-coated backing plate instead of a second adherend. After curing, the backing plate was removed and the open-faced DCB specimens were degraded at 60°C-95%RH and 60°C-82%RH exposure conditions for different time intervals. The degraded specimens were then dried for approximately 7 days to remove any reversible effects of water ingress such as plasticization. Another adhesive layer of 385 μm thickness (termed the secondary adhesive) was then used to bond the degraded open-faced specimen to a second adherend to make a complete DCB joint for fracture testing.

8.3.3. CDCB preparation

A normal closed DCB joint was made by curing a single 385 μm thick adhesive layer between two aluminum adherends (12.5 mm thick, 16 mm wide and 250 mm long). The surface treatment of the CDCB adherends was identical to the one used for the ODCB specimens described in Chapter 2. After curing, the bondline edges were slightly sanded to
remove any adhesive spew and allow direct exposure of the adhesive to the environment from both edges. The ends of the bondline across the width of the specimen were also exposed, but this was of no consequence because the calculation of the specimen average steady-state $G_{cs}$ (Section 3.4) only utilized data taken at crack lengths greater than 10 mm from the end of the joint, to avoid the effect of the rising part of the R-curve. Therefore the state of degradation was not a function of the distance from the ends. The closed joints were then exposed to 60°C-95%RH and 60°C-82%RH conditions for five months and subsequently dried for six months to remove the reversible effects of water ingress. The drying condition of the CDCB joints was the same as that of the ODCBs. Details about the exposure procedures can be found in Chapters 3 and 4.

It is noted that only one aging time was used with the CDCB joints while a range of aging times were used with the ODCB specimens. This was necessary in order to predict the varying level of degradation within a CDCB joint that resulted from the highly nonuniform water concentration within the closed adhesive layer. This is discussed further in Section 4. The aging temperature was 60°C in all cases, while the drying temperature was 40°C.

8.3.4. Fracture testing

The mode I and mixed-mode fracture tests were conducted on both the ODCB and CDCB specimens using a servo-electric load frame and the load jig of [6]. The mixed-mode tests were conducted at a loading phase angle, $\psi = 27^\circ = \tan^{-1}(G_{II}/G_I)^{0.5}$, where $G_I$ and $G_{II}$ are the mode I and II components of the applied strain energy release rate. The tests were carried out under displacement control, advancing the crosshead at 1.5 mm/min in small discrete steps while viewing the macrocrack tip through a microscope having a field of view of 2 mm. More details about the fracture testing and a discussion of the discrete loading methodology and its validity can be found in Chapter 2. A beam-on-elastic-foundation model was used to calculate the steady-state critical strain energy release rate, $G_{cs}$ [7]. The $G_{cs}$ measurements for the ODCB specimens degraded under different exposure conditions were reported in Chapters 4 and 5.
The fracture tests were conducted from initiation to crack lengths of up to approximately 100 mm. This generated a typical R-curve response (Fig. 8.3), where the critical strain energy release rate increased from the initiation value, $G_{ci}$, to the steady-state value at $G_{cs}$ after roughly 10 mm of crack extension.

![Figure 8.3: Schematic representation of the bilinear R-curve model from Chapter 2.](image)

8.4. Water diffusion results and analysis

In order to calculate the water concentration at locations within the closed DCB joints (CDCBs) as a function of exposure time in the two aging environments, it was necessary to model the water uptake of the adhesive.

8.4.1. Modeling absorption/desorption behavior

The water absorption and desorption behaviors of this adhesive were characterized in Chapter 3 using a sequential dual Fickian (SDF) and simple Fickian model, respectively. After the initial linear Fickian diffusion and the onset of a plateau, a second mass increase was observed before the final saturation (Fig. 8.4). This anomalous behavior was captured by the SDF model where the moisture concentration, $C(x,t)$ at any time, $t$ and position, $x$ is given by:
\[
C(x,t) = \left\{ 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \exp\left( -\frac{D_1 (2n+1)^2 \pi^2 t}{4h^2} \right) \cos\left( \frac{(2n+1) \pi x}{2h} \right) \right\} \times C_1 \infty \\
+ \phi(t-t_d) \times \left\{ 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \exp\left( -\frac{D_2 (2n+1)^2 \pi^2 (t-t_d)}{4h^2} \right) \cos\left( \frac{(2n+1) \pi x}{2h} \right) \right\} \times C_2 \infty 
\]

(1)

where \( C_1 \infty \) and \( C_2 \infty \) are the saturated concentrations of the first and second diffusion mechanisms (i.e. the first and second saturation plateaus) such that \( C_1 \infty + C_2 \infty = C \infty \), where \( C \infty \) is the total saturation concentration after long times. \( D_1 \) and \( D_2 \) are the diffusion coefficients of the first and second phases of moisture uptake, respectively. \( t_d \) is the time of the transition from the first diffusion phase to the second. \( 2h \) is the total length of the diffusion path, and \( \phi(t) \) is the Heaviside step function defined as:

\[
\phi(t-t_d) = \begin{cases} 
0, & t < t_d \\
1, & t \geq t_d
\end{cases}
\]

(2)

During the drying, the mass of the samples decreased with time according to Fick’s law and reached a constant minimum value of water concentration (\( C_r \)). The moisture concentration at any \( t \) and \( x \) is given by:

\[
\frac{C(x,t) - C_r}{C_\infty - C_r} = \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \exp\left( -\frac{D_d (2n+1)^2 \pi^2 t}{4h^2} \right) \cos\left( \frac{(2n+1) \pi x}{2h} \right)
\]

(3)

where \( D_d \) is the diffusion coefficient of the desorption process. For the present adhesive, the required SDF absorption parameters \( (D_1, D_2, C_1 \infty, C_2 \infty, t_d) \) and the simple Fickian desorption parameters \( (D_d, C_r) \) were measured in Chapter 3 and are summarized in Table 8.1.

<table>
<thead>
<tr>
<th>RH (%)</th>
<th>( D_1 \pm \text{SD} ) (10^{-14} m^2/s)</th>
<th>( D_2 \pm \text{SD} ) (10^{-14} m^2/s)</th>
<th>( C_1 \infty \pm \text{SD} ) (%)</th>
<th>( C_2 \infty \pm \text{SD} ) (%)</th>
<th>( t_d^{1/2} ) (s^{1/2})</th>
<th>( D_d \pm \text{SD} ) (10^{-14} m^2/s)</th>
<th>( C_r \pm \text{SD} ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>95</td>
<td>314±25</td>
<td>8.6±0.9</td>
<td>3.73±0.11</td>
<td>3.25±0.18</td>
<td>329</td>
<td>182±26</td>
<td>1.98±0.05</td>
</tr>
<tr>
<td>82</td>
<td>294±28</td>
<td>4.9±0.7</td>
<td>2.75±0.05</td>
<td>1.27±0.08</td>
<td>308</td>
<td>172±22</td>
<td>1.76±0.11</td>
</tr>
</tbody>
</table>
8.4.2. Water concentration profiles in ODCB and CDCB joints

The SDF model of absorption and the simple Fickian model of desorption with the parameters given in Table 8.1 were used in the water diffusion analysis of the ODCB and CDCB specimens for the 60°C-95%RH and 60°C-82%RH exposure conditions. These models were implemented in a MATLAB© (Mathworks, Natick, Massachusetts, USA) code to predict the temporal and spatial distribution of water concentration in the adhesive layer of the ODCB and CDCB joints at the end of the aging and drying processes.

The water diffusion path in the ODCB specimens was only the thickness of the primary adhesive, 385 μm, from the exposed surface of the adhesive to the adherend interface. This short diffusion path resulted in a uniform distribution of water concentration after aging for only approximately two weeks (saturation concentration level \(C_{1\infty}+C_{2\infty}\)) and in drying after only one week of drying (uniform level of the minimum retained water concentration \(C_r\)). Noting that the aging periods for ODCBs were chosen to span up to at least one year, each ODCB specimen with a specific aging time thus corresponded to a particular uniform level of
degradation. The drying time was shorter than the absorption time because drying was a Fickian diffusion process rather than a dual-Fickian process (Fig. 8.4).

In the case of CDCB joints, the water diffusion path length was half the joint width; i.e. 8 mm from each side toward the centerline of the bond. This long path resulted in a nonuniform water concentration, even after five months of aging. Figure 8.5 shows the predicted water concentration profiles across the bondline width after five months of aging as well as after the six months of subsequent drying at both the 60°C-95%RH and 60°C-82%RH exposure conditions. The predicted water concentration decreased rapidly with distance from the edge and reached a relatively uniform level toward the centerline. It is also seen that after six months of drying, the predicted water concentration within the bondline fell to the uniformly distributed level of the minimum retained water \( C_r \); i.e. approximately 1.98% and 1.76% for 95%RH and 82%RH, respectively (Table 8.1).

As discussed in Chapters 3 and 5, the absorbed water molecules in the present adhesive could be found in two forms; i.e. bound and mobile. The bound water molecules could not be removed even after a prolonged desorption period, and were responsible for the observed minimum retained water concentration \( C_r \).

The mobile water molecules contributed to the reversible degradation effect of water ingress by plasticizing the adhesive and increasing its fracture toughness. To ensure that the measured fracture toughness for both ODCBs and CDCBs reflected only the effects of irreversible degradation, the specimens were dried for a long enough period (one week for ODCBs and six months for CDCBs) that the mobile water molecules were completely removed from the specimens, resulting in a uniformly distributed water concentration that was very near to the minimum retained water concentration. A much long drying time was required for the CDBC, due to the much longer diffusion path across the specimen width.
8.4.3. Exposure index of degradation

To be able to use the degradation of ODCB specimens to predict the degradation of CDCB joints, it was convenient to define a parameter that reflected the extent of water exposure at a given location within an adhesive layer for a specified temperature. Previous work had suggested the utility of an “exposure index” ($EI$) defined as the time integral of the water concentration in the joint [1]:

$$EI = \int_{t_0}^{t} C(x, t) dt$$

where $C$ is the water concentration at time $t$ a distance $x$ from the free surface of the adhesive. The values of $EI(x, t)$ during the aging, $EL_a$, using the SDF model, and during the drying, $EL_d$, using the simple Fickian model were derived in Chapter 3 as:
\[ EI_a = \left\{ t + \frac{16h^2}{\pi^3D_1} \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)^3} \left[ \exp \left( -D_1 \frac{(2n+1)^2 \pi^2 t}{4h^2} \right) - 1 \right] \cos \left( \frac{(2n+1)\pi x}{2h} \right) \right\} \times C_{1e} \]

\[ + \phi(t - t_d) \times \left\{ \left( t - t_d \right) + \frac{16h^2}{\pi^3D_2} \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)^3} \left[ \exp \left( -D_2 \frac{(2n+1)^2 \pi^2 (t - t_d)}{4h^2} \right) - 1 \right] \cos \left( \frac{(2n+1)\pi x}{2h} \right) \right\} \times C_{2e} \]

(5)

and

\[ EI_d = C_e t' - \left\{ \frac{16h^2}{\pi^2D_d} \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)} \left[ \exp \left( -D_d \frac{(2n+1)^2 \pi^2 t}{4h^2} \right) - 1 \right] \cos \left( \frac{(2n+1)\pi x}{2h} \right) \right\} \times (C_{1e} + C_{2e} - C) \]

(6)

where \( t' \) denotes the time after the start of drying. The total exposure index, \( EI_T \) from the time of first exposure to the hot-wet environment to the end of the drying period is thus:

\[ EI_T = EI_a + EI_d \]

(7)

Therefore, Eq. (7) accounts for the degradation caused by water exposure during both the aging and the drying periods.

For ODCB specimens, the variation of \( EI_a \) and \( EI_d \) along the diffusion path, \( x \), through the thickness of the adhesive layer was negligible for most of the aging times because of the uniform water concentrations that were quickly achieved. Therefore, a single \( EI_T \) value, calculated using Eqs. (5)-(7) half-way through the thickness of the adhesive layer, could be used to represent the level of degradation in each ODCB joint.

In the case of the CDCB joints, the \( EI_T \) in the bondline was calculated as a function of distance from the edge, \( x \), using Eqs. (5)-(7). Figure 8.6 shows the \( EI_T \) profiles across the width of CDCB joints that were aged five months at 60°C-95%RH and 60°C-82%RH, and then dried for six months at 40°C. Because of the long diffusion path and resulting nonuniform distribution of the water concentration (Fig. 8.5), the variation of \( EI_T \) across the joint width was relatively large and a single \( EI_T \) value could not be used to represent the level of degradation. As expected, the maximum \( EI_T \) value was at the bondline edge and gradually decreased toward the center of the joint where there was relatively little water.
8.5. Fracture toughness of degraded specimens

8.5.1. \( G_{cs} \) in degraded ODCBs

The fracture toughness of ODCB specimens that had been degraded under different exposure conditions (combinations of temperature and RH) as a function of aging time was reported in Chapters 4 and 5. The relationship between the steady-state critical strain energy release rate, \( G_{cs} \), and \( E_{IT} \) for the 60°C-95%RH and 60°C-82%RH aging conditions for the loading phase angle of 27° is reproduced in Fig. 8.7. The least-squares best fits to these experimental data can be stated in a power form as:

\[
G_{cs} = \alpha E_{IT}^{-\beta}
\]

where \( \alpha \) and \( \beta \) are the empirical constants for each exposure condition. The data of Fig. 8.7 correspond to aging times of up to about 12 months at 95%RH and 18 months at 82%RH. It is
seen that, for this adhesive system, degradation in fracture strength occurs rapidly at first, but then slows to a gradual linear decline. As well, the amount of degradation after a given time was greater when aging occurred in a more humid environment.

Figure 8.7: Variation of $G_{cs}$ ($\psi = 27^\circ$) with EIT achieved using two different aging conditions (95% and 82% RH) at 60°C for ODCB specimens. The curves are least-squares power function fits to the data points at each RH. Data from Chapter 5.

8.5.2. $G_{cs}$ in degraded CDCB joints

Figure 8.8 shows the variation of the critical strain energy release rate, $G_{cs}$, with crack length for representative undegraded and degraded CDCB joints tested under $\psi = 27^\circ$ (aging for 5 months followed by drying for 6 months). The crack length is defined as the amount of crack growth, $\Delta a$, from the onset of initiation at the start of the adhesive layer. As discussed previously, the R-curve behavior was typical of this highly-toughened epoxy adhesive, with up to 10 mm of crack growth required to establish the steady-state damage zone corresponding to $G_{cs}$ (the plateau of each curve). Table 8.2 lists three repetitions of the measured $G_{cs}$ for degraded CDCB joints tested under mode I ($\psi = 0^\circ$) and mixed-mode ($\psi = 27^\circ$) loadings. As
reported in Chapter 2, the corresponding average $G_{cs}$ values in the undegraded CDCB joints are 3,220 Jm$^{-2}$ for $\psi=0^\circ$ and 4,160 Jm$^{-2}$ for $\psi=27^\circ$ with COV values of 6.5% and 6.2%, respectively. As seen in Table 8.2, the COV for the three tests at each condition were approximately the same as for the undegraded CDCB joints, implying that the test repeatability for degraded and undegraded CDCB joints was similar.

As was the case in the degradation of ODCB specimens, Table 8.2 and Fig. 8.8 show that $G_{cs}$ decreased after degradation for both conditions, but the decrease was greater when the joint was exposed to a higher RH. The $G_{cs}$ values dropped to approximately 25% and 50% of the undegraded value after five months of aging at the 60°C-95%RH and 60°C-82%RH conditions, respectively. Both the length and the slope of the rising part of the crack growth resistance curve also decreased after degradation, with the larger change occurring at the higher RH (Fig. 8.8). The initiation value of $G_c$ (i.e. $G_{ci}$) was largely unaffected by aging, as was the case in the degradation of ODCB specimens (see Chapters 4 and 5 for further discussion).

![Figure 8.8](image-url)
Figures 8.9a1 and 8.9a2 show the typical fracture surfaces of the CDCB joints that were aged for five months at 60°C-95%RH and 60°C-82%RH, respectively, dried for six months and then fracture tested at $\psi=27^\circ$. The fracture was cohesive and the fracture surfaces were fairly uniform, indicating that the interfaces did not degrade more than the adhesive layer. Figures 8.9b1 and 8.9b2 show the fracture surfaces of the degraded ODCB specimens that yielded approximately the same $G_{cs}$ for the same aging environment and phase angle. The fracture of degraded ODCB specimens was also cohesive and uniform. The fact that the failure modes were the same in both the CDCB and ODCB joints allows the degraded fracture strengths of ODCBs to be used to predict that in the CDCB. This would not be the case if, for example, one type of specimen failed interfacially while the other failed cohesively.

Figure 8.9: Photographs of the fracture surfaces of degraded CDCB joints (a1 and a2; aged for 5 months followed by drying for 6 months) and ODCB specimens (b1 and b2; aged such that $G_{cs}$ was same as in CDCBs) tested under mixed-mode loading ($\psi=27^\circ$). The upper adherend was the primary adherend in the ODCB specimens.
Table 8.2: Three repetitions of measured steady-state Gc for degraded CDCB joints tested under mode-I (ψ=0°) and mixed-mode (ψ=27°) loadings. COV is the coefficient of variance defined as the standard deviation divided by the mean. Aged for 5 months followed by drying for 6 months.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Gcs (Jm⁻²)</th>
<th>60°C – 95%RH</th>
<th>60°C – 82%RH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ψ=0°</td>
<td>ψ=27°</td>
<td>ψ=0°</td>
</tr>
<tr>
<td>N1</td>
<td>840</td>
<td>1,115</td>
<td>1,545</td>
</tr>
<tr>
<td>N2</td>
<td>880</td>
<td>1,205</td>
<td>1,680</td>
</tr>
<tr>
<td>N3</td>
<td>785</td>
<td>1,075</td>
<td>1,775</td>
</tr>
<tr>
<td>Ave.</td>
<td>835</td>
<td>1,060</td>
<td>1,660</td>
</tr>
<tr>
<td>COV (%)</td>
<td>5.7</td>
<td>6.6</td>
<td>6.9</td>
</tr>
</tbody>
</table>

8.6. Predicting fracture toughness of degraded CDCBs

The empirical relationship \( G_{cs}(EI_T) \) obtained from the degraded ODCBs tests (Eq. (8)) along with the \( EI_T \) profiles in the CDCB joints (Fig. 8.6) were used to determine the corresponding expected \( G_{cs} \) profiles across the joint width, as shown in Fig. 8.10. As expected, \( G_{cs} \) was lowest at the edges of the CDCB joints, where the greatest degradation occurred, and gradually increased toward the joint center. In unaged joints, the crack front during fracture tends to have a curved shape across the joint width, with its leading edge being relatively straight across the central half of the width and curving back with the trailing ends of the front being at the specimen edges. The effect of aging degradation tended to decrease this curvature, since fracture occurred more readily at the edges. Therefore, it was decided to use simply the average value of \( G_{cs} \) across the CDCB joint width to represent the effective fracture strength of the closed joint. For the 60°C-95% RH and 60°C-82% RH aging conditions this average \( G_{cs} \) was calculated to be 1,140 and 1,960 Jm⁻², respectively using data of Fig. 8.10.

Thus it was predicted that CDCB joints aged for five months and dried for six months should have \( G_{cs} = 1,140 \text{ Jm}^{-2} \) for the 60°C-95% RH aging environment and \( G_{cs} = 1,960 \text{ Jm}^{-2} \) for the less aggressive 60°C-82% RH aging condition.

These predicted fracture strengths, estimated from the degradation of ODCBs, agreed well with the experimentally measured \( G_{cs} \) values for CDCBs aged under these same conditions as seen from Table 8.2; i.e. \( G_{cs} = 1,060 \text{ Jm}^{-2} \) for the 60°C-95% RH condition, and \( G_{cs} = 2,120 \text{ Jm}^{-2} \)
for the 60°C-82% RH condition. The difference between the predicted and measured $G_{cs}$ values is approximately 8% at both RH conditions, which is only slightly greater than the range of the experimental scatter in the repetition of the fracture tests.

It is thus concluded that the measured $G_{cs}$-$E_{IT}$ relationship constructed using degraded open-faced specimens can be used to predict the fracture toughness of closed joints degraded under the same conditions of temperature and relative humidity. This is a significant result because the accelerated test data from open-faced specimens is obtained in a much shorter time than in closed joints. For example, in the current experiments, the time required to achieve the average $E_{IT}$ values of $32\times10^6$ and $17\times10^6$ g/g.s at 60°C-95%RH and 60°C-82%RH conditions using open-faced specimens was only about 2 months, including both the aging and drying steps. In comparison, the total process time for aging and drying the closed joints was 11 months, simply because of the longer diffusion path.

![Graph showing predicted $G_{cs}$ profiles across the width of CDCB joints obtained using $E_{IT}$ profiles of Fig. 8.6 and Eq. (8). 0 and 8 mm correspond to the joint center and edge, respectively.](image)

**Figure 8.10**: Predicted $G_{cs}$ profiles across the width of CDCB joints obtained using $E_{IT}$ profiles of Fig. 8.6 and Eq. (8). 0 and 8 mm correspond to the joint center and edge, respectively.
8.7. Degradation pathway independency

As discussed previously, the $EI$ concept was motivated by the desire to combine the effects of time and water concentration so that a single parameter could be used to quantify a given environmental aging condition. This concept is of great use in quantifying environmental exposure if the degradation is independent of the time-humidity path taken to reach a particular $EI$; i.e. the strength loss corresponding to a particular $EI$ is the same after exposure to different combinations of humidity and time which give the same $EI$. In Chapter 5, the path independency of $EI$ for the ODCB specimens of the current adhesive was evaluated using combinations of three RH levels (95%, 82% and 43%) and different exposure times at 60°C and 40°C. It was concluded that the fracture strength degradation can be assumed to be independent of the aging pathway with 95% confidence for $EI_T$ values greater than $25 \times 10^6 \text{ g/g.s}$.

The degree of degradation pathway independence for the present closed joints can be examined using Eq. (8) as a fit to all the $G_{cs}-EI_T$ data points obtained from different pathways in Chapter 5; i.e. aging ODCB specimens for a range of times at 43%, 82% and 95% RH. As given in Chapter 5, this was resulted in average $\alpha$ and $\beta$ coefficients of 4,744 and 0.384 at 60°C. Therefore the equation $G_{cs} = 4,744\cdot EI_T^{-0.384}$ can be taken to represent the effect of aging on fracture strength at 60°C regardless of the aging humidity. If this relationship is now used with the $EI_T$ distribution given in Fig. 8.6, the average $G_{cs}$ values across the CDCB joint width were calculated to be 1,290 and 1,730 Jm$^{-2}$ with standard deviations of 210 and 380 Jm$^{-2}$ for the 60°C-95%RH and 60°C-82%RH CDCB aging conditions, respectively. These predicted $G_{cs}$ values differ by 22% and 18% from their corresponding $G_{cs}$ values obtained from the experimental measurement of degraded CDCB joint (Table 8.2).

Even though the predicted CDCB degraded strength is not as accurate as when the $\alpha$ and $\beta$ parameters in Eq. (8) corresponded to the actual RH values used in the CDCB aging, the predictions are still good enough to be of value. The use of a single $G_{cs}(EI_T)$ relation to represent degradation over all RH aging conditions at a given temperature facilitates the prediction of the degraded fracture strength of closed joints exposed to environments where the humidity is changing over time.
It is noted that even though only one exposure temperature for CDCB joints was examined here, the fracture toughness of a closed joint degraded at a new temperature can be estimated using the degradation pathway independency and several $G_{cs}$-$EI_T$ envelopes provided for ODCB specimens of the current adhesive system at different temperatures in Chapters 4 and 5. To calculate $EI_T$ values of a closed joint at a new temperature, the required diffusion properties in aging and drying can be estimated using the predictive SDF and simple Fickian models given in Chapter 3, and the corresponding $G_{cs}$ values can then be determined with known values of $EI_T$ and temperature by extrapolation from the $G_{cs}$-$EI_T$ envelopes given in Chapter 4 and 5.

For practical applications, this framework provides a predictive tool to estimate the fracture toughness of a joint that is exposed to a condition with varying temperature and RH. Any exposure interval at a specified temperature and RH results in a certain increment in the exposure index, and so yields a known amount of fracture strength degradation. The overall fracture toughness loss after a series of such aging intervals would then be the sum of the losses.

8.9. Conclusions

A framework to predict the fracture toughness of degraded closed adhesive joints using fracture test data obtained from accelerated open-faced degradation specimens was established. The failure mode of both the closed and open-faced joints was found to be cohesive crack growth through the adhesive layer, for both mode I and mixed-mode loadings. After five months of degradation and six months of drying, the $G_{cs}$ values dropped to approximately 25% and 50% of their undegraded values, for aging conditions of 60°C-95%RH and 60°C-82%RH, respectively.

For the two utilized exposure conditions (60°C-95%RH and 60°C-82%RH), the open-faced fracture toughness results were used together with the water diffusion properties and the concept of the exposure index ($EI$) to predict the $G_{cs}$ of degraded closed joints. The predicted $G_{cs}$ values for the degraded closed joints determined in this manner agreed well with
those that were measured, with less than 10% difference. The ability to use open-faced accelerated degradation tests to predict the behavior of closed joints is of great practical importance since using the open-faced specimens significantly reduces the required exposure time.

Assuming a degradation that was independent of the time-humidity path taken to reach a particular $E_I$ resulted in the prediction of degraded closed joint fracture toughness with approximately 20% accuracy. Therefore, for practical design purposes, the knowledge of the degradation behavior at one RH level can be extended to other levels of RH using the degradation pathway independence characteristics of $E_I$. This is a promising result that needs to be validated over a wider range of exposure times.
8.10. References


Chapter 9: Conclusions and future work

9.1. Summary and conclusions

A framework was established to characterize the environmental degradation of two rubber-toughened epoxy adhesives and to predict the fracture toughness of the degraded closed joints using the data from open-faced experiments. The summary together with the important conclusions of each part is given below:

9.1.1. Water absorption/desorption behavior

The water absorption and desorption of two different rubber-toughened epoxy adhesives were characterized using gravimetric measurements. A newly developed sequential dual Fickian (SDF) model was used to fit the fractional mass uptake profiles and it agreed well with the Langmuir diffusion model. The diffusion mechanism in the first stage appeared to be influenced by hydrogen bonding while the diffusion mechanism in the second stage was primarily physical in nature. The diffusion coefficients in both stages were found to be largely independent of RH, while the saturated fractional mass uptake values increased with RH. The diffusion coefficient of the first stage and the saturated fractional mass uptake of the second stage were both functions of temperature. These functional dependencies were described, making the SDF model predictive over the ranges of temperature and RH that were investigated.

The desorption during drying in both adhesives was described well by Fick’s law. Both gravimetric results and XPS revealed that there was a significant difference between the amounts of minimum fractional retained water in the two adhesives after drying. The relatively large amount of retained water in adhesive 1 was attributed to multiple hydrogen bonds between the water molecules and the epoxy or other constituents such as the rubber toughener particles or the filler. It was found that these differences in water absorption-desorption corresponded to marked differences in the degradation of fracture toughness in hot-wet aging environments.
The SDF model can be used to predict the water concentration distribution in adhesive joints exposed to environments of changing temperature and RH under the assumption of negligible interface diffusion.

9.1.2. R-curves in fresh joints

Consideration of the adhesive joint R-curve is important in cases where joint failure might occur prior to the establishment of a steady-state damage zone corresponding to the critical strain energy release rate, \( G_{cs} \). The R-curves for two different toughened epoxy adhesive systems were measured as a function of the mode ratio, bondline thickness, and initiation geometry at the end of the adhesive layer. The data could be fit to a bilinear model representing the rising part and steady-state region of the R-curve. The bilinear model parameters appeared to be largely independent of the precrack starting geometry, suggesting that the initiation fracture energy, \( G_{ci} \), may be used as a measure of the initiation strength of manufactured joints where the adhesive layer local end geometry is quite variable. The bilinear model parameters did not show a significant dependence on the adherend thickness, suggesting that they can be uniquely determined for a given adhesive system which is loaded elastically. The initiation \( G_{ci} \), the steady-state \( G_{cs} \), the slope and the length of the rising part of the R-curve all increased with the adhesive layer thickness. Increasing the phase angle of loading caused \( G_{ci} \) and \( G_{cs} \) to increase along with the length of the rising part of the R-curve. The slope of the rising part was not a significant function of the phase angle.

9.1.3. Open-faced technique in adhesive systems with heat-cured secondary layer

The difficulties and issues in the application of the open-faced accelerated degradation methodology in the heat-cured highly-toughened adhesive systems were addressed. A secondary layer of heat-cured highly-toughened adhesive was chosen to fabricate fracture specimens since the room temperature-cured adhesives could not yield sufficient toughness to drive the crack in the primary layer. The effects of the application of the heat-cured secondary layer on the fracture toughness, cure state and residual stress state of the primary adhesive
layer were discussed. The residual stress and cure states of the primary layer changed slightly with the curing of the secondary layer. The fracture toughness of the primary layer however, remained unchanged with the curing of the secondary layer. Consequently, the change in the measured fracture toughness in the degraded ODCB joints was solely due to the degradation of the primary adhesive layer. It was thus concluded that the open-faced DCB specimens with the cured secondary layer can be used in the degradation characterization of the fracture toughness in these adhesive systems. Another support for the validity of the technique was the good agreement found between the fracture toughness results obtained from the closed and open-faced degraded specimens.

9.1.4. Evolution of $R$-curves with degradation

Open-faced DCB specimens of a toughened epoxy-aluminum adhesive system were degraded over a relatively wide range of temperature, RH and exposure time. The irreversible effects were measured by drying the primary (aged) adhesive layer prior to closing the joint to form a DCB joint that was tested under mixed-mode loading conditions. Three stages of degradation were observed. In the first stage, the bilinear $R$-curve parameters ($G_{cs}$, $dG_{cr}/da$ and $L_r$) as well as the adhesive residual thickness ($t_r$) decreased in proportion to the exposure time until $G_{cs}$ reached a threshold value which corresponded to the fracture toughness of epoxy matrix (DGEBA) in the absence of rubber toughener. During the second stage, all bilinear $R$-curve model parameters and $t_r$ remained unchanged with time and the fracture remained cohesive, but close to the interface. With extremely long exposure, both $G_{cs}$ and $t_r$ decreased again to a very low value and no $R$-curve behavior was observed. This corresponded to the third stage in which the crack path was even closer to the interface, but with an extremely thin layer of epoxy remaining on a very smooth fracture surface.

In general, $G_{cs}$ decreased with increasing temperature, RH, water concentration in the adhesive layer and the ambient water concentration while $G_{ci}$ remained unchanged during degradation. A linear relationship was found between $dG_{cr}/da$ and $G_{cs}$, irrespective of the degradation parameters. An $R$-curve degradation model was proposed which greatly reduces the experimental efforts in the degradation characterization of similarly-behaved adhesive
systems and also has an application in the $R$-curve prediction of a closed joint having nonuniform degradation. Moreover, the degradation of fracture toughness was found to be insensitive to the phase angle. Consequently, the fracture toughness envelope shifts downward uniformly for a given level of degradation. This is a significant simplification since it is possible to extract the entire fracture envelope for any level of degradation if the $G_{cs}$ is known for that level of degradation at a single phase angle.

9.1.5. Different fracture toughness characteristics of two toughened epoxy adhesives

The differences between the absorption/desorption properties of two toughened epoxy adhesives were evaluated gravimetrically and by XPS and DMTA analyses. Both gravimetric and XPS results indicated that a significant amount of water was retained after drying in aged samples of adhesive 1, but a negligible amount was retained in adhesive 2. DMTA results showed that the retained water molecules in adhesive 1 were not free, but strongly bound with the adhesive constituents.

Mixed-mode fracture tests on degraded open-faced DCB specimens showed that the critical strain energy release rate, $G_{cs}$ of adhesive system 1 decreased with exposure time to reach a quasi-steady value that was similar to values reported for untoughened epoxy, while that of adhesive system 2 remained unchanged over a very long period. It was hypothesized that the differences in the degradation behavior and hygrothermal properties of the two adhesives were related to the presence of bound water molecules at the interface between the epoxy matrix and the rubber toughener in adhesive 1. A Fickian-type degradation model (Eq. (2)) was proposed to characterize the fracture toughness loss in adhesive system 1, and fairly good agreement was observed between the model and the experimental results. The rate of degradation predicted by the model is controlled by the coefficient, $D_{deg}$ which increased with the increasing temperature, RH and saturated water concentration.

The dependency of fracture toughness degradation on the humidity-time exposure history (pathway) was evaluated using the concept of exposure index, $EI$. Even though the degradation could not be assumed to be fully independent of the exposure history, $G_{cs-EI}$
curves provide a useful envelope to estimate the amount of $G_{cs}$ loss at any exposure condition (RH and $T$) after relatively long exposure times.

9.1.6. Crack path and fracture surface characteristics

The crack path and fracture surface in the mixed-mode fracture of two different rubber-toughened epoxy adhesives were evaluated. The fracture surface parameters, i.e., crack depth ($t_R$), roughness ($R_\alpha$), and maximum change in elevation ($E_m$) were measured using optical profilometry. A finite element model was developed to obtain the plastic zone size and stresses.

A strong relationship was found between the fracture surface roughness parameters ($R_\alpha$, $t_R$, $E_m$) and the critical strain energy release rate, $G_{cs}$, irrespective of the type of adhesive. In the case of Adhesive 1 where irreversible degradation observed, all these parameters varied approximately linearly with $G_{cs}$. Upon degradation, a ductile-to-brittle transition was also noticed in the fracture characteristics of Adhesive 1. In the case of Adhesive 2, aging did not result in the permanent degradation (unchanged $G_{cs}$) and all these fracture surface parameters remained unchanged with aging. The strong correlations that were found indicate that characterizing fracture surfaces as a post-failure analysis might be useful to estimate the fracture toughness at which a practical joint has failed.

The maximum mode-I crack path selection criterion was applicable to the degraded joints with brittle characteristics, but could not predict the overall crack path in the undegraded specimens with ductile characteristics. A crack growth mechanism based on the distribution of the maximum von Mises stress was consistent with the experimental observations of the fracture surfaces of the undegraded joints. The relatively high fracture toughness in the undegraded joints was partially attributed to the pronounced three dimensionality of the fracture surface.

The issue of the unexpected crack path in the mixed-mode fracture of unaged ODCB specimens was addressed. The second cure of the primary adhesive layer and different combinations of the primary and secondary adhesive layer thicknesses appeared to have no
effect on the crack path pattern in the mixed-mode fracture of unaged ODCB specimens. In particular, cracks grew unexpectedly in the secondary adhesive layer of unaged ODCB joints. Two approaches were found to alleviate this difficulty and maintain crack growth in the primary adhesive layer: (i) increasing the number of curing cycles in unaged ODCBs of system AB, and (ii) exposing the primary layer of system BB ODCB specimens to a moist environment both resulted in equalized residual stresses in the primary and secondary adhesive layers and consequently no preference for the crack to grow in the secondary adhesive layer. The crack thus grew in the primary layer in these cases as desired.

9.1.7. Fracture toughness prediction of closed joints

A framework to predict the fracture toughness of degraded closed adhesive joints using fracture test data obtained from accelerated open-faced degradation specimens was established. The failure mode of both the closed and open joints was found to be cohesive crack growth through the adhesive layer, for both mode I and mixed-mode loadings. After five months of degradation, the $G_{cs}$ values dropped to approximately 25% and 50% of their undegraded values, for aging conditions of 60°C-95%RH and 60°C-82%RH, respectively.

For the two utilized exposure conditions, i.e. 60°C-95%RH and 60°C-82%RH, the open-faced fracture toughness results were used together with the water diffusion properties and the concept of the exposure index in order to predict the $G_{cs}$ of the degraded closed joints. The predicted $G_{cs}$ values for the degraded closed joints determined in this manner agreed well with those that were measured (with less than 10% difference). The ability to use open-faced accelerated degradation tests to predict the behavior of closed joints is of great practical importance since using the open-faced specimens significantly reduces the required exposure time.

Assuming a degradation that was independent of the time-humidity path taken to reach a particular exposure index resulted in the prediction of degraded closed joints fracture toughness with approximately 20% accuracy. Therefore, for practical design purposes, the knowledge of the degradation behavior at one RH level can be extended to other levels of RH using the degradation pathway independence characteristics of the exposure index, $EI$. 213
9.2. Future work

A very important future work would be to extend the application of the present work to practical sheet metal joints used in automotive industry. The experimental results obtained from this work can be used in developing a framework to design the practical joints made of the present adhesive systems. Such a framework may employ finite element analysis and may require some experimental verification.

The present work considered only the irreversible effects of water ingress (i.e. permanent degradation after drying). During actual service life, the reversible effects of water ingress such as plasticization may come into play. Previous experience suggests that unbound water in the adhesive layer might increase the fracture energy. So an insightful piece of future work would be to assess the fracture response of the system when it is not fully dried. This can be done by fracture testing of aged open-faced specimens having various amounts of unbound water.

The methodology developed here to predict the fracture toughness of degraded closed joints seems to be promising with relatively accurate predictions. The next step in this context would be to examine the methodology over a wider range of exposure conditions including environments with cycling temperature and humidity, and also on the other adhesive systems.