The Strength of Adhesively Bonded Joints Degraded by Moisture

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Abstract

This research aims to fill a gap in the current adhesives durability modelling field by providing the first steps of a comprehensive predictive package. The specific area considered concerns those joints whose degraded failure locus is cohesive within the adhesive rather than interfacial. The modelling package presented covers the whole process of absorption of environmental moisture into the adhesive layer of a joint, the resulting degradation of the adhesive material and the final reduction in time of the strength of the joint. The kinetics of moisture diffusion and the environmental degradation have been experimentally measured and modelled. A particular finding was that water uptake by bulk adhesives was found not to conform to the most basic form of the Fickian diffusion model so often adopted by other authors. In addition to a thickness effect, uptake was found to be a two-stage process.

Experimental bulk adhesive and adhesive joint programmes have provided a broad base of moisture-dependent bulk properties and residual joint strength data for combinations of two epoxide adhesives (E32 and AV119), two exposure temperatures, two substrate materials and two joint geometries. Also, a wide range of absorbed moisture levels were studied for both the bulk adhesive and joint programmes, thus providing a useful breadth of environmental data. In summary, nearly fully saturated, E32 experienced reductions in elastic modulus and ultimate tensile strength (UTS) of 83% and 58%, respectively. AV119 experienced 34% and 55% reductions. Moving onto the joints, independent of geometry, typical losses in residual strength were found to be between 20% and 40% for an approximate fractional uptake level of 0.25.

Resulting water uptake and moisture-dependent elastic-plastic material models have then been incorporated into a quasi-static structural ABAQUS finite element analysis framework. After evaluating various additional finite element variations, a combination of a linear Drücker-Prager yield model and a global limit state failure criterion was found to give accurate prediction of environmentally degraded residual strength for a thin, plane steel-E32 butt joint.
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Declaration

I declare that the work presented in this thesis is both appropriate to the subject area and original. It is also my own work in its entirety, except for some of the raw experimental water uptake data. This extra data was kindly provided by Miss. Kallirroi Petropoulou as part of her individual Final Year undergraduate project and added breadth to my modelling work.
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Nomenclature

**Arabic**

- $a$: location of crack in adhesive layer
- $c$: local diffusant concentration
- $c_s$: concentration of diffusant at surface
- $c_\infty$: ambient equivalent diffusant concentration; also equilibrium concentration
- $D$: Fickian diffusion coefficient
- $D_1$: Fickian diffusion coefficient of first stage of two-stage diffusion model
- $D_2$: Fickian diffusion coefficient of second stage of two-stage diffusion model
- $d$: cohesion in Drucker-Prager yield model definition
- $d_{bunt}$: adhesive layer thickness for a butt joint
- $d_{lap\text{-}shear}$: adhesive layer thickness for a lap-shear joint
- $E$: elastic modulus
- $E_c$: overall elastic modulus of composite
- $E_{\text{dry}}$: elastic modulus of dry composite
- $E_f$: elastic modulus of filler/fibre component of two-phase composite
- $E_m$: elastic modulus of matrix component of two-phase composite
- $E_{\text{wet}}$: elastic modulus of fully-wet composite
- $F$: function defining locus of Drucker-Prager yield surface
- $f()$: function
- $G$: shear modulus
- $G_1$: shear modulus of first phase of two-phase composite
- $G_2$: shear modulus of second phase of two-phase composite
- $G_{1c}$: critical fracture energy for a Mode I crack
- $G_{1}^*$: upper bound of composite shear modulus
- $G_{2}^*$: lower bound of composite shear modulus
- $i$: $x$-step index in finite difference scheme
- $J_x$: diffusion flux in the $x$-direction
- $K$: bulk modulus
- $K_1$: bulk modulus of first phase of two-phase composite
\( K_2 \)  
bulk modulus of second phase of two-phase composite

\( K_{1c} \)  
critical fracture toughness for a Mode I crack

\( K_1^{*} \)  
upper bound of composite bulk modulus

\( K_2^{*} \)  
lower bound of composite bulk modulus

\( k \)  
time-step index in finite difference scheme

\( L \)  
non-dimensional ratio in evaporative boundary diffusion model \((= l \alpha /D)\)

\( L_{\text{eff, bulk}} \)  
effective length of bulk tensile specimen

\( l \)  
half-length or half-thickness of an uptake specimen

\( l_1 \)  
original length of gauge length section of simplified tensile specimen

\( l_2 \)  
original total length of tapered sections of simplified tensile specimen

\( l_3 \)  
original total length of end-tab sections of simplified tensile specimen

\( m \)  
mass uptake

\( m_{\text{eqo}} \)  
equilibrium mass uptake contribution of Fickian diffusion stage

\( m_r \)  
mass uptake contribution of relaxation stage

\( m_{\text{eqo}} \)  
equilibrium mass uptake contribution of relaxation stage

\( m_{\infty} \)  
equilibrium mass uptake

\( m_{\text{eq1}} \)  
equilibrium mass uptake of first stage of two-stage diffusion model

\( m_{\text{eq2}} \)  
equilibrium mass uptake of second stage of two-stage diffusion model

\( n, n \)  
index of terms in an infinite series

\( p \)  
hydrostatic stress

\( q \)  
von Mises effective stress

\( R \)  
ratio of yield stress in triaxial tension to yield stress in triaxial compression

\( RF_{B,C,D,E} \)  
reaction force at Node B, C, D or E

\( r \)  
third invariant of deviatoric stress

\( s_{\text{bulk}} \)  
crosshead speed when testing a bulk tensile specimen

\( s_{\text{but}} \)  
crosshead speed when testing a butt joint

\( s_{\text{lap-shear}} \)  
crosshead speed when testing a lap-shear joint

\( T \)  
temperature

\( t \)  
time

\( t' \)  
pseudo-time quantity in diffusion \((= \sqrt{t/\bar{D}}) [10^{-5} \sqrt{\text{sec}/\text{m}^2}]\)

\( t_\sigma \)  
an alternative form of effective stress

\( U \)  
fractional uptake

\( U_{xy} \)  
overall fractional uptake in 2-dimensional diffusion system
**Nomenclature**

- $U_x$: $x$-component of diffusion in 2-dimensional system
- $U_y$: $y$-component of diffusion in 2-dimensional system
- $v_f$: volume fraction of filler/fibre component of two-phase composite
- $v_1$: volume fraction of first phase of two-phase composite
- $v_2$: volume fraction of second phase of two-phase composite
- $w_1$: width of gauge length section of simplified tensile specimen
- $w_2$: width of tapered sections of simplified tensile specimen
- $w_3$: width of end-tab sections of simplified tensile specimen
- $x, y, z$: Cartesian axis directions

**Greek**

- $\alpha$: surface resistance term in evaporative boundary diffusion model
- $\beta, \beta_n$: term (or series of terms) in evaporative boundary diffusion model
- $\delta_{B,C}$: half of crack separation at Node B or C
- $\delta_1$: elongation in gauge length section of simplified tensile specimen
- $\delta_2$: total elongation in tapered sections of simplified tensile specimen
- $\delta_3$: total elongation in end-tab sections of simplified tensile specimen
- $\delta_{tot}$: total elongation in tensile specimen
- $\varepsilon$: overall or common uniaxial strain
  - $\varepsilon_1$: strain in gauge length section of tensile specimen
- $\dot{\varepsilon}_{\text{axial, bulk}}$: uniaxial strain rate in bulk tensile specimen
- $\dot{\varepsilon}_{\text{axial, butt}}$: axial strain rate in adhesive layer of butt joint
- $\dot{\varepsilon}_{\text{eff, bulk}}$: effective strain rate in bulk tensile specimen
- $\dot{\varepsilon}_{\text{eff, butt}}$: effective strain rate in adhesive layer of butt joint
- $\dot{\varepsilon}_{\text{eff, lap-shear}}$: effective strain rate in adhesive layer of lap-shear joint
- $\varepsilon_f$: uniaxial strain in filler/fibre component of two-phase composite
- $\varepsilon_m$: uniaxial strain in matrix component of two-phase composite
- $\phi_{1,2,3,...}$: constants
- $\dot{\gamma}$: rate of shear strain in adhesive layer of lap-shear joint
Nomenclature

\( \nu \)  
Poisson's ratio

\( \theta \)  
friction angle in Drucker-Prager yield model definition

\( \sigma \)  
overall or common uniaxial tensile stress

\( \sigma_{ic} \)  
\( i \)th uniaxial stress value in compression

\( \sigma_{it} \)  
\( i \)th uniaxial stress value in tension

\( \sigma_t \)  
tensile yield (or other key) stress

\( \sigma_y \)  
yield stress in uniaxial tension

\( \sigma_u \)  
uniaxial stress in gauge length section of tensile specimen

\( \sigma_f \)  
uniaxial stress in filler/fibre component of two-phase composite

\( \sigma_m \)  
uniaxial stress in matrix component of two-phase composite

\( \Omega \)  
time constant

\( \psi \)  
dilation angle in Drucker-Prager yield model definition

Key to acronyms

A-187  
designation for \( \gamma \)-glycidoxypropyltrimethoxysilane primer

UTS  
ultimate tensile strength

SEM  
scanning electron microscopy

DMTA  
dynamic mechanical thermal analysis

DSC  
differential scanning calorimetry

DGEBA  
the diglycidyl ether of bisphenol-A

DAPEE  
\( \text{di}(1\text{-aminopropyl-3-ethoxy}) \) ether

TETA  
triethylene tetramine

DAB  
1, 3-diaminobenzene

DDM  
4, 4'-diaminodiphenyl methane

DMP  
tris(dimethylaminomethyl) phenol

BF3MEA  
boron trifluoride monoethylamine

DDS  
4, 4'-diaminodiphenylsulphone

TGDDM  
tetraglycidyl-4, 4'-diaminodiphenylmethane
1 Introduction

Adhesives are now becoming accepted amongst designers for use as practical mechanical joining techniques, competing against such traditional methods as welding, riveting and bolting. However, to be more extensively utilised by industry, adhesion science has had to overcome certain weaknesses. For all their strengths in being able to join dissimilar materials, distribute stress, be aesthetically unobtrusive and be lightweight, they lose their appeal for such reasons as limited capacity to cope with high temperature and their susceptibility to environmental attack. In particular - and the subject of this research - it is accepted that exposure to moist environmental conditions can sometimes markedly degrade the strength of adhesive joints. The additional fact that this effect is hard to quantify has therefore provided one important reason why adhesives are not specified as much as they perhaps could be - or why it is hard to optimise engineering designs that make use of adhesives. Despite the wide use of structural adhesives, such as phenolics and epoxides, in the performance and quality-conscious automotive and aircraft industries, the reliable prediction of environmental durability still represents an important goal for engineers today.

Two points immediately come to mind from a general knowledge of the literature (this being discussed fully in Chapter 2). Firstly, the bulk of the work carried out focuses on the environmental durability of the interfacial regions of adhesive joints. Secondly, there seems to exist very little predictive cohesive durability work. Certainly, no complete models have been presented. However, as much as absorbed moisture may sometimes tend to promote interfacial weakening of an environmentally exposed joint, there is significant evidence in the literature that suggests that some joints fail cohesively within the adhesive layer. Thus, this research aims to provide a cohesive environmental durability modelling technique which fills a gap left by the existing literature.
1.1 Methodology of this research

Figure 1-1 first shows an overall visualisation of the environmental durability issue, including various dependencies. In this work, interfacial durability is put aside and cohesive effects considered. Thus, a complete methodology of cohesive environmental durability prediction is presented in this research. This starts with the exposure of an adhesive joint to moist (and hot) conditions, then links to the degradation of bulk adhesive properties, and finally predicts strength degradation of the whole joint. And as such, this represents a more complete and useable solution than offered elsewhere in the current literature.

This methodology investigates each link in the chain of moisture absorption, degradation of adhesive properties and structural response of the joint. Experimental programmes of work were carried out to measure the rate of water uptake by adhesives as well as moisture-dependent mechanical properties of bulk adhesives and bonded joints. Analytical work then attempted to model the above measured behaviours, these various models then being incorporated into a finite element stress analysis approach to overall durability prediction.
Thus, the work can be broken down as follows:

- measurement and modelling of the rate of water uptake by adhesives - Gravimetric uptake tests were used to evaluate the classical Fickian diffusion model, resulting in the development of more accurate models
- measurement and modelling of moisture-dependent bulk adhesive properties - Quasi-static tensile tests were carried out on absorbed, thin dogbone specimens. Moisture-dependent uniaxial stress-strain characteristics were measured, these elastic-plastic properties then being characterised using various methods
- linking of uptake and properties models in order to predict the properties profile in an adhesive layer as a function of time of exposure
- structural analysis of a joint using the above properties profile - finite elements were used and material models and failure criteria evaluated before final implementation of a full 3-dimensional durability analysis of an adhesive joint
- supporting experimental programme to measure residual strengths of exposed joints - the above finite element predictive durability results were validated against experimental moisture-dependent residual strength data

Although it is proposed that the suggested modelling technique can be developed for use with other structural adhesives and joint geometries, the current work specifically studies two epoxide adhesives. The first adhesive is a two-part, chalk-filled cold-cured epoxide called E32 and supplied by Permabond, and the second is a single-part, rubber-toughened, hot-cured epoxide called Araldite AV119 and supplied by Ciba Geigy. Continuing the search for cohesive failure, even when significantly environmentally exposed, two joint geometries and two substrate materials were investigated. The two geometries were the single lap-shear joint and the butt joint. The two substrate materials were steel and aluminium alloy, both with a suitable surface pretreatment to protect the interfaces and encourage cohesive failure. Finally, to broaden experimental data and to investigate the viability of accelerated uptake tests, exposure to moisture was carried out using liquid water at both room temperature and at 55 °C.
Chapter 1: Introduction

The reason for the choice of quasi-static finite element structural durability analysis, as opposed to a creep analysis, etc., is that a well-designed joint should experience reasonably low stresses and not fail in a time-dependent manner. Thus, the modelling work in this research focuses on practical engineering joints and the way in which they fail. Therefore, it is suggested that failure is an instantaneous response to degradation in adhesive properties caused by absorbed moisture. Also, as this is the first such investigation into this method of predicting environmental durability in this Group, a situation of sequential environmental exposure and loading is considered. Modelling of simultaneously exposed and loaded joints waits for the initial results of the current work and is therefore reserved for future research projects.

1.2 Structure of the thesis

The structure of this thesis essentially follows the structure of the methodology shown above. Following a broad literature review presented in Chapter 2 and a brief description of the chosen adhesives and basic bulk specimen manufacture presented in Chapter 3, Chapter 4 then discusses water uptake properties of the adhesives. A programme of gravimetric uptake tests was first carried out, these data then being used to evaluate the classical Fickian diffusion model often used by durability researchers. However, the current research will show that this model is inadequate and will propose more accurate alternatives.

Chapter 5 then addresses the mechanical properties of the chosen adhesives. Again an experimental programme was followed by characterisation work. In accordance with the requirement to incorporate data into a quasi-static finite element model making use of elastic-plastic adhesive properties, a series of tensile tests was carried out. The uniaxial stress-strain response of dry and absorbed thin dogbone specimens was measured using a servo-mechanical Instron tensile testing machine. The resulting data were then used as the basic for analytical work to characterise parameters such as elastic modulus and ultimate tensile strength as a function of absorbed moisture.

Next, to provide underlying adhesive joint durability data, Chapter 6 presents a purely experimental programme of work to measure environmental residual strength. Suitably
pretreated steel and aluminium alloy butt and single lap-shear joints were prepared using both adhesives. These joints were then immersed for various durations in distilled water at either room temperature or 55 °C. and then tested for residual strength on the Instron. In all cases, locus of failure was estimated. This programme of work provided a good breadth of experimental data for the joint systems investigated, against which to test later durability models.

The main technical content of this thesis then concludes with a chapter on the proposed overall finite element durability modelling technique. Choosing to focus on the steel-E32 butt joint for the remainder of the research, Chapter 7 first shows the finite element implementation of the improved uptake model suggested earlier in Chapter 4. After showing how the moisture profile in an adhesive layer can be successfully determined using a diffusion analysis, 2-dimensional linear structural analyses of a dry joint are then used in an initial assessment of failure criteria. Then, developing the technique further, more modelling accuracy is added, concluding with full nonlinear 3-dimensional analyses of dry and wet joints. In carrying out these analyses, both yield models and failure criteria were evaluated, the end result being the proposal of a durability modelling package which accurately predicts moisture-dependent residual strength for the chosen joint type.

Chapter 8 then collects together all the issues addressed earlier in the thesis and presents conclusions. At various points, these conclusions point to problems that were encountered, such as the unconventional water uptake characteristics displayed by both adhesives. These problems and the further work they may suggest are also discussed in this chapter.
1.3 Major achievements of this research

In attempting to provide a complete cohesive environmental durability model starting with
the absorption of moisture and finishing with failure, this work presents various major
achievements. These are as follows:

- the classical simple Fickian diffusion model, adopted by some authors, is shown not to
  be adequate to predict moisture absorption by adhesives
- a two-stage water uptake model has been developed which agrees with complex
  experimental diffusion patterns measured experimentally
- the elastic-plastic properties of bulk adhesives have been determined and shown to be
  consistently degraded by absorbed moisture
- the uptake and constitutive models and methodology have been used to predict the
  spatial properties profile in an adhesive layer as a function of either moisture content or
  time of environmental exposure
- as a result of bulk adhesive uptake and properties and experimental joint work, initial
  indications suggest that accelerated hot-absorption tests may well be valid for use in
  the durability prediction chain, thus allowing the gathering of experimental data in
  much shorter times. Certainly, further studies are warranted.
- various finite element yield models and failure criteria were evaluated and a proposal
  made that a Drucker-Prager yield model together with a limit state failure criterion can
  provide good durability predictions for joints that fail cohesively.
2. Literature review

Structures which are bonded with organic polymers are to some degree generally susceptible to the effects of environmental attack, sometimes resulting in premature failure of bonded structures. Also, as the precise mechanisms of environmental weakening still remain uncertain, this can result in a lack of confidence amongst designers to specify adhesives - especially as it is not always certain whether or how much a joint will suffer a strength loss in time. However, in support of the main research and to provide a solid background, this literature review seeks to collect and present a broad range of durability work carried out by other researchers in the field. Following the structure of the overall project, this review is divided up into various component aspects of environmental durability of adhesives, as follows:

- general overview of durability
- water uptake of adhesives
- mechanical properties of adhesives
- environmental performance of adhesive joints
- modelling of environmental durability of joints

2.1 General observations of environmental durability effects

It is generally accepted that environmental conditions of a moist atmosphere, elevated temperatures and applied stress can often result in the weakening of structural adhesive joints, and there is plenty of evidence of this in the literature [1, 2, 3, 4, 5, 6, 7, 8]. It is regarded, however, that moisture and elevated temperatures provide the most aggressive forms of attack and this is summed up in a diagram presented in a review paper by Kinloch [3]. This diagram is reproduced and shown here in Figure 2-1. One fundamental factor which contributes to this effect is the fact that organic polymers are themselves hydrophilic. Add to this that the occurrence of water is very common and environmental attack of adhesive joints becomes a significant problem.
Figure 2-1 Effect of hot/wet and hot/dry environments and stress on adhesive joint strength [3]

However, although the precise mechanisms involved in environmental weakening still remain uncertain, certain factors reliably seem to have an influence on either the initial, dry strength of an adhesive joint or on its residual strength after exposure. Note here that durability is a function of both a joint's dry strength and its resistance to subsequent environmental attack, i.e. time-based reduction in strength. So, the factors that can be expected reliably to affect the environmental durability of an adhesive joint include:

- the joint geometry
- the choice of substrate material
- the choice of adhesive
- the choice of substrate pretreatment
- the choice of substrate primer
- the harshness of the environment to which the joint is exposed

Although aspects specifically related to the environmental performance of joints will be discussed at greater length later in this review, it is useful in this introductory section of the literature review to demonstrate a few of the above points, thus giving a broad overview of durability factors. Gledhill and Kinloch [1] exposed some mild steel-epoxy butt joints to
various hot/wet environments. They then periodically measured the residual strength of these joints, the results being reproduced here in Figure 2-2. This figure summarises the effect of severity of environment and exposure time on the residual strength of adhesive joints. It can been seen that generally, increases in temperature and attack by moisture lead to a fall-off in joint strength with time. However, at 55% relative humidity (RH), there is no significant weakening over extended time periods. This apparent insensitivity of adhesive joints to low humidities has prompted some authors [1, 2, 9, 10] to propose that there is a minimum water concentration within a joint below which no environmental weakening occurs. Other work presented by Kinloch [11] shows the same effect with aluminium lap-shear joints and is summarised in Figure 2-3. This lack of sensitivity to low RH conditions represents the basis of a much-referenced paper which describes Gledhill et al.'s proposed interface-based durability model [2], which is discussed later in this review.

![Figure 2-2](image-url)  
*Figure 2-2 Fracture stress of epoxy/mild steel butt joints exposed to various environments as a function of time [1]*
Bearing in mind the previous comment, which hints at the importance of interfacial resilience against environmental attack, the next diagram, Figure 2-4 [12], shows how the choice of substrate pretreatment (often allied with a subsequent primer) can affect durability. Again, a lengthier discussion on this issue can be found in the adhesive joint durability section of this literature review. However the figure clearly shows that a wise choice of pretreatment (either mechanical, chemical or electrochemical) can have a very pronounced effect (and sometimes a negative effect) on both the initial, dry strength or the strength loss of the joint after environmental exposure. Note that, although this research focuses on cohesive durability effects and joint failure, choice of pretreatment still had to be addressed in order to encourage the required cohesive locus of failure for the experimental work on adhesive joints.

Now that it has been shown that exposure to moist environments often has a marked weakening effect on adhesive joints, it has to be considered how the moisture gets into the joint. For the purposes of this research, only non-permeable metallic substrates have been considered. Therefore, ingress of water into a joint must be by way of the adhesive layer or the interfacial regions of the joint. Accordingly, it is generally accepted that moisture enters a well-made joint by way of diffusion through the bulk adhesive, as opposed to...
transport along the interface [1, 2, 3, 4, 13, 14]. Therefore, the absorption of water into the bulk adhesive in the glueline of a joint lies at the basis of durability work. Therefore, a first step in a typical durability study might be to measure the uptake behaviour of adhesive materials. Uptake information from the literature is discussed in more detail in the next section of this review chapter, but perhaps it is relevant to mention here that various techniques have been suggested, the most common being gravimetric experiments [2, 15, 16, 17, 18, 19]. Using this type of technique, bulk adhesive specimens (often thin films or sheets) are exposed to either water or water vapour, specimen mass then being recorded as a measure of water uptake. With this type of test, however, only the bulk mass of absorbed water can be estimated and not the full local water concentration profile. Also, if absorbing by immersion in liquid water, it is assumed that any mass increase in an uptake specimen is due solely to absorbed water, i.e. no account is taken of possible leaching out of components of the adhesive into the water.

![Figure 2-4](image)  
**Figure 2-4** Effect of surface pretreatment on joint strength for epoxy/aluminium alloy joints [12]
Assuming aspects of diffusion of water into an adhesive joint are understood and accepting that water has been absorbed into the adhesive layer, the water can either attack the interfacial regions, or it can attack the bulk adhesive itself (or a combination of the two). Some proposed interfacial and cohesive degradation mechanisms are listed below:

- within the adhesive ("cohesive"):
  - plasticisation of adhesive
  - swelling of the adhesive
  - hydrolysis of the adhesive
  - cracking or microcracking of the adhesive

- at the adhesive/substrate interface:
  - rupture of interfacial primary bonds
  - rupture of interfacial secondary bonds
  - hydration and weakening of the oxide layer on metallic substrates
  - hydrolytic attack on an adhesive boundary layer, which may differ in chemical/physical structure to the rest of the bulk adhesive
  - hydrolysis of the primary bonds of any primer present, leading to cohesive failure through the primer layer
  - displacement of adhesive from substrate

Again, although many authors have followed up with interfacially-controlled durability studies, perhaps building on Gledhill et al.’s previously referenced model [2], this project is concerned with cohesive failure and therefore focuses on the environmental response of the adhesive material within the exposed joint. Although detailed discussion of the mechanisms and degree of cohesive environmental degradation of adhesive materials belongs in a later section of this review chapter, there is evidence in the literature to support more investigation into cohesive environmental effects [9, 15, 16, 17, 19, 20, 21, 22, 23, 24]. Certainly in the case of metallic substrates bonded with typical structural adhesives, a well-designed and made joint should ideally be expected to fail cohesively. Furthermore, even though environmental ageing may change the mechanical properties of the adhesive, a cohesive mode of failure should still be retained. Bearing this engineering
design ideal in mind, however, the literature suggests that cohesively-controlled environmental failure has been largely neglected.

In quantifying environmental durability, the literature would first suggest that durability is measured either in terms of residual joint strength after a certain duration of exposure to environmental conditions of a certain severity or in terms of the rate of crack propagation in the adhesive layer or along the interface of a continuously exposed and loaded joint. However, in environmentally conditioning a joint to be tested, a cautionary note must be raised. Using hot absorption conditions for the measurement of either bulk adhesive uptake characteristics or the measurement of mechanical properties or the environmental performance of adhesive joints may result in misleading data. With regard to applying room temperature-measured but hot-absorbed bulk adhesive mechanical properties to adhesive joint or bulk adhesive structural analyses, this may lead to unforeseen errors. This problem could arise because exposure to elevated temperature conditions might have irreversibly changed the structure, and so the mechanical properties, of the adhesive. Gledhill and Kinloch [1] warn that, as they doubt that cooler environments of lower RH values cause any degradation to adhesive joints, accelerating water uptake by using elevated absorption temperatures may result in misleading performance of the joints being tested. Also, Parker [25] suggests that joints absorbed to target uptake levels under hot conditions give different failure loads and failure loci than room temperature-absorbed joints.

It should also be borne in mind that other possible sources of misleading or inappropriate environmental data may include unexpected specimen thickness effects [26] during uptake experiments as well as an unexpected tensile specimen thickness-dependence of mechanical properties [27]. Although the use of thin uptake specimens can dramatically reduce experiment durations to reasonable limits, it is possible that uptake data derived from the absorption of thin film adhesive specimens may not be applicable to the uptake behaviour occurring across the typically longer adhesive layer dimensions of a lap-shear joint. Similarly, it may not be valid to apply tensile mechanical property data obtained from a thick dogbone specimen in an analysis of a joint with a thin adhesive layer.
2.2 Water uptake by adhesives

Despite the fact that typical structural adhesives are polymeric in nature, i.e. plastics, they are not actually "waterproof". They do, in fact, significantly absorb gaseous and liquid solvents. Specifically, adhesives absorb moisture from typical humid working environments. Depending on the structure of the polymer, its stress state, the ambient water concentration and temperature, adhesives can absorb water up to an equilibrium level equivalent to perhaps 10% mass gain [2, 4, 9, 15, 23, 28, 29, 30, 31], leading to the degradation problems introduced earlier.

2.2.1 Experimental techniques

Thus, one of the essential building blocks in developing an understanding of environmental durability of adhesives is to measure the water uptake behaviour of adhesive materials. Although it has been tried to develop in situ experimental techniques [32], whereby water uptake can be measured directly by analysing the adhesive layer within a real joint, the most common technique is to use bulk adhesive specimens and to take gravimetric measurements [2, 15, 16, 17, 18, 19]. Because water uptake is a relatively slow process, even in hot conditions, thin film specimens are used to ensure reasonable experimental timescales. Specimens are exposed to either liquid water or water vapour and periodically weighed in order to determine the amount of water that has been absorbed. If absorbing from water vapour within an environmental chamber, apparatus is available which allows weight data to be logged automatically, using a recording microbalance [9, 26]. Thus, water vapour absorption experiments can be more convenient, although the equipment is more complicated and expensive, due to the need to automatically record specimen weight as well as needing to maintain the required temperature and relative humidity. But an additional point in favour of absorbing from vapour is that there is not such a strong physical path for components of the adhesive to be leached out, and thus any weight changes can more confidently be attributed to water absorption alone. However, absorbing from liquid water requires simpler equipment and tends to result in a higher, more effective equilibrium water content, as is discussed later in this section and in the main thesis. For gravimetric uptake tests absorbing from liquid water, a thin film of bulk adhesive is typically immersed in a thermostatted bath of distilled/deionized water and then
periodically removed, blotted dry (superficially) and weighed on a conventional microbalance. This technique has negative points in terms of the requirement of manual intervention and temporary removal from the test environment and also because of the possibility of uptake measurement errors due to specimen mass loss component arising from leaching. However, as stated above, gravimetric uptake experimental techniques are the most common, very often absorption being from liquid water. In fact, Shen and Springer [18] give a very good account of the experimental procedure they used.

Note, however, that this type of method can only give an estimate of the bulk mass of absorbed water within the whole uptake specimen. If testing a proposed water uptake model, it might be of interest to analyse the local water concentration profile within an uptake specimen or the adhesive layer within a joint. Thus, for this and other reasons, other techniques have been proposed [33]. These include:

- Reflection Coefficient Sensing
- Viscosity Dependent Fluorescence
- Infra-Red Spectroscopy
- Dielectric Spectroscopy

However, these methods tend to be costly and awkward to implement and have not been significantly reported in the literature.

Adopting a gravimetric uptake measurement technique, thin films of adhesive can be used in order to provide one-dimensional diffusion data in a relatively short time. Thin bulk adhesive films can be prepared using one of a variety of methods [9, 22, 28, 34, 35] and placed in liquid water or water vapour at a given temperature and static pressure, and the uptake behaviour measured. Using thin film or plane sheet bulk adhesive specimens also tends to avoid edge effects, i.e. if the ratio of the specimen thickness to the length or width is too high, significant water is absorbed through the specimen edges and distorts the measured mass uptake away from the required one-dimensional behaviour. One-dimensional uptake is usually focused on as, for an isotropic material, the one-dimensional behaviour is relatively simple and the corresponding two- and three-dimensional
behaviours can be generated at an uptake modelling stage by combining the component one-dimensional behaviour as appropriate.

2.2.2 Mechanisms and classification of uptake behaviour

Now that the existence of water absorption by adhesives has been established, as have available experimental measurement techniques, it now follows to discuss observed water uptake characteristics in more detail. An in-depth discussion of uptake modelling is presented in Chapter 4, but it serves well at this point to outline some basics in order to be able to assess some of the observations found in the literature.

Kaltenecker-Commerçon et al. [36] introduced a useful physical visualisation of the process of diffusion of a solvent within a polymeric substrate. They described the process as a random wandering of small solvent molecules into and out of microscopic holes or pores within the polymeric substrate (adhesive) structure. Further, for the case of a polymer in its leathery state, i.e. significantly above its glass transition temperature, it is generally accepted that the diffusion process follows Fick's laws [4, 15, 16, 26, 28, 29, 34, 36, 37, 38]. Fickian diffusion is discussed in detail in Chapter 4, but a quick description is that Fickian diffusion prescribes a linear local diffusant concentration gradient-driven diffusion "flux" within the substrate [39]. This model is similar to a purely resistive electrical model, where a potential difference is applied across a resistor, causing a current to flow. Comparing the two models, the potential difference becomes a local concentration gradient with the substrate, the electric current becomes the diffusion flux and the electrical resistance becomes the Fickian diffusion coefficient. In his important diffusion paper, Fujita [40] notes that diffusion can be termed "Fickian" only if the diffusion coefficient is either constant or a function of diffusant concentration alone. Assuming for a moment that the diffusion coefficient is taken to be constant, the solution for Fickian uptake in a thin, plane substrate film, both faces being exposed to a constant temperature and relative humidity, gives linear mass uptake behaviour up until about 60% of equilibrium uptake [4, 40] when uptake (or % mass gain) is plotted against the square root of exposure time. Beyond this point, still judged on a root time basis, the uptake slows down fairly smartly and approaches an equilibrium value. Note also that the basic Fickian model requires that the surfaces of the uptake specimen reach an equilibrium concentration instantaneously,
this value being directly dependent on the ambient water concentration and also being equal to the eventual equilibrium bulk uptake concentration. For true Fickian uptake with a constant diffusion coefficient and with no boundary effects, there is only one possible uptake curve shape. In fact, if the uptake axis is defined as fractional uptake (normalised against equilibrium uptake) and the time axis is defined as the square root of time divided by the specimen half-thickness (in the case of a "reduced uptake plot"), and if the axes of all uptake plots have the same scaling and length, then there is genuinely only one single curve representing simple Fickian uptake. And, given that the uptake axis shows fractional uptake, this curve can be totally defined by the constant Fickian diffusion coefficient alone. Therefore, bearing in mind individual scaling of mass uptake and root time axes, it is easy to test whether a set of experimental uptake data is Fickian or not. As a useful reference, the basic Fickian uptake curve form is shown in Figure 2-5.

Figure 2-5 Standard reduced sorption curve shape for constant diffusion coefficient Fickian uptake
Moving on to discuss departures from basic Fickian diffusion, various alternative uptake plot shapes have been observed and modifications or extensions to Fick's model have been suggested. Some authors [21, 28, 41] have observed various other uptake characteristics, as listed below:

- initial Fickian linear uptake, attainment of a mass peak and subsequent slow mass loss
- as per simple Fickian uptake, uptake slowing down but equilibrium mass uptake never being achieved
- initial Fickian uptake and plateau, followed by a second slow uptake stage leading to final equilibrium ("two-stage" behaviour)

In seeking to explain observations of non-Fickian behaviour, some authors [36, 38, 40, 42, 43, 44] refer to a classification system first proposed by Alfrey et al. [45], which takes into consideration relaxation effects occurring simultaneously with the diffusion process. They define "Case I", "Case II", and "anomalous" modes of diffusion, Case I being simple Fickian. For Fickian diffusion to be achieved, the diffusion process should be much slower than any simultaneous relaxation process occurring in the substrate material. For Case II, the situation is reversed and the diffusion process should be much faster than any relaxation process. This is consistent with the generally expected Fickian diffusion in rubbery polymers, where the structure is more mobile than the relatively rigid structure of glassy polymers. Looking at the early diffusion behaviour and wanting formally to define the various modes of diffusion, they introduce the following expression:

\[ m = \phi_1 t^{\phi_2}, \text{ where} \]

\( m \) represents the mass of absorbed penetrant, \( t \) is time and \( \phi_1 \) and \( \phi_2 \) are constants. Simple Fickian uptake then requires \( \phi_2 \) to take a value of 0.5 and Case II requires a value of 1.0. Thus, simple Fickian uptake gives initially linear behaviour when plotted against the square root of time and Case II gives initially linear behaviour when plotted against time itself. Furthermore, Case I and Case II define upper and lower bounds for diffusion, real processes often lying somewhere between and changing between modes as uptake progresses. These processes are termed "anomalous" and result from diffusion and relaxation processes occurring at comparable rates, this possibly explaining observations of
two-stage uptake. Berens and Hopfenberg [46] attempted to separate the proposed diffusion and relaxation effects on uptake. Leaving the diffusion process to be defined by simple Fickian uptake with component equilibrium uptake and diffusion coefficient, he suggests the superposed relaxation contribution might take an equilibrating exponential form with its own defining equilibrium uptake and time constant parameters, as discussed in Chapter 4.

Tai and Szklarska-Smialowska [44] extend the classification system above by further introducing the terms "pseudo-Fickian" and "super Case II", these requiring values for $\phi_2$ of less than 0.5 and greater than 1.0, respectively. However, for all the detailed subdivision of this framework, it rapidly becomes rather academic and arbitrary. For the purposes of this work, therefore, it is perhaps best to note the possibility of parallel diffusion and relaxation processes and bear it in mind for later modelling of non-Fickian uptake. Certainly, however, as Fickian uptake tends to feature in any diffusion process to a greater or lesser extent, it makes sense to use it as a foundation stone to any uptake measurement or modelling work.

Discussing possible reasons for failure to obey simple Fickian uptake, it is perhaps useful to be aware of the current glass transition temperature of the absorbing adhesive. Bearing in mind that it might at first seem that Fickian uptake applies only to leathery polymers, the fact that many authors [15, 16, 19, 20, 23, 26, 28, 35, 47, 48, 49] have measured a decrease in glass transition temperature with increasing absorbed water becomes important. Therefore, depending on the absorption temperature, an initially glassy polymer may become leathery as the uptake process proceeds, thus entering a Fickian regime [26]. Although some authors [16, 20] have measured the glass transition temperature, using dynamic mechanical thermal analysis (DMTA), of typical dry epoxide adhesives to be between about 70 and 140 °C., Brewis et al. [37], using the same technique, found the glass transition temperature of a dry epoxide-polyamide adhesive to be only 34 °C. This creates a degree of uncertainty as to the structural state of typical adhesives at a given temperature and uptake level, however, combining with Wright's [49] stated rule of thumb that a typical epoxide adhesive may drop 20 °C. in transition glass temperature for every 1% in mass uptake does suggest a tendency for Fickian uptake to be achieved as uptake
progresses. Even so, various authors [2, 26, 28, 36] suggest that it is common for adhesives to display simple Fickian uptake, even whilst in a glassy state.

2.2.3 Relationship between uptake parameters

Adopting Fickian diffusion as a basis for further discussion and analysis of observed uptake behaviour, and remembering that Fickian uptake (with constant diffusion coefficient) is defined by an equilibrium uptake and a diffusion coefficient, it would be useful here to outline the expected dependencies of these two parameters on environmental variables such as temperature and relative humidity. The effect of applied stress can also be considered, as can the possibility of Fickian uptake with a variable diffusion constant or with a more complex boundary model. Concentrating on the basic factors of temperature and relative humidity (if exposure to water vapour is being considered), Collings [30] and Brewis et al. [26] state that diffusion coefficient is expected to be a function of temperature only and that equilibrium uptake is expected to be a function of relative humidity only. Further, Brewis et al. [26] say that a dependence of diffusion coefficient on relative humidity would imply contravention of the zeroth law of thermodynamics. Referring to the dependence of diffusion coefficient on temperature, and bearing in mind the expected nonlinearity of behaviour, it is common amongst researchers to plot the relationship as the logarithm of diffusion coefficient against the reciprocal of absolute temperature, this type of plot being called an "Arrhenius plot". According to the literature [2, 30], a linear relationship between the logarithm of diffusion coefficient and the reciprocal of absolute temperature is often observed, as follows:

\[ \ln(D) \propto \frac{1}{T} \]  

This relationship then suggests that the diffusion coefficient increases more and more rapidly as temperature increases. Note also that diffusion coefficient, being related to the initial slope of the fractional uptake against root time plot, gives a direct idea of the time taken to achieve equilibrium uptake.
Moving onto the comparison between liquid water and saturated water vapour (100% RH) uptake environments, several authors [9, 34, 50, 51] note that the two environments are equivalent for any given temperature and that, therefore, values of diffusion coefficient and equilibrium uptake can be expected to be same in both environments. However, Musty et al. [52] add a cautionary note about comparison of uptake parameters determined from saturated water vapour and liquid water sorption tests. They say that reported discrepancies can often be accounted for by virtue of intended saturated water vapour not actually being saturated. Therefore, specimens absorbed by suspending above a reservoir of liquid solvent may not actually experience the imagined 100% RH. They continue to suggest that, within a shallow layer of vapour above a reservoir of liquid solvent, there exists a small but critical temperature gradient. This results in the vapour not achieving true saturation and consequently apparent mismatches in diffusion parameters.

As a point of interest, Shen and Springer [18] discuss the equilibrating of temperature within a sample of absorbing adhesive. They note that the rate of attainment of thermal equilibrium is typically one million times faster than the corresponding rate of uptake equilibration. Therefore, the temperature throughout an uptake specimen can safely be assumed to be constant and always equal to the ambient temperature.

The issues of local diffusant concentration-dependent and stress-dependent uptake are perhaps secondary to the primary issues of the effects of temperature and relative humidity. Fujita [40] presents a good analysis of diffusant concentration-dependent diffusion coefficient sorption of penetrants in polymers and makes some interesting points on the effects on the process. As with constant diffusion coefficient Fickian uptake, he notes that the initial section of the reduced sorption plot is again linear. Furthermore, for markedly increasing functions of diffusion coefficient with concentration, the linear region can be expected to continue a little further towards the equilibrium uptake point. Fujita then states that, whilst a heavy dependence of diffusion coefficient on concentration affects the spatial concentration profile within the polymer, the resulting bulk uptake curve is not nearly as sensitive. Thus, a constant diffusion coefficient equivalent usually provides a good substitute.

Then discussing techniques for deducing the functional form of the dependence of diffusion coefficient on concentration, Fujita presents a method based on measuring the
initial slopes of both absorption and desorption curves. He then presents diffusion coefficient variations for two polymer-penetrant systems, these being polymethyl acrylate-ethyl acetate and polymethyl acrylate-benzene. For both systems, he reports that the diffusion coefficient increases markedly with concentration as well as with temperature, the increase with concentration typically being up to 1000-fold at room temperature (although the increases became smaller at higher temperatures). Importantly, however, Fujita then considers polymer-diffusant systems where the diffusant has a low affinity to the polymer and does not act as a solvent as such. Thus, he presents diffusion coefficient findings for polymethyl acrylate-water, showing virtually no dependence on concentration throughout the 10 to 60 °C. range investigated.

Considering first the possibility of dependence of diffusion coefficient on local diffusant concentration with a typical adhesive substrate material, many authors discuss the issue, although it is often dismissed for epoxide adhesive materials. So, bringing in other evidence from the literature [18, 23, 26, 30, 53, 54], it would appear that there is a strong case for independence of diffusion coefficient on concentration.

On the subject of the analysis of stress-dependent diffusion, Roy [55] and Roy and Reddy [56, 57] make use of the Lefèbvre [58] diffusion model, which is based on a free volume concept. Here, the diffusion coefficient is defined in terms of the local strain state, temperature and water concentration. With or without this free volume visualisation, other authors have also discussed models [54, 59] or experimental observations [2, 3, 5, 17, 20, 23, 30, 60, 61, 62, 63] in their analyses of stress-dependent uptake, Morgan et al. [17] suggesting that an increase in applied stress leads to an increase in free volume and consequent increase in equilibrium uptake. However, the study of stress-dependency lies outside the bounds of this research and further discussion in this review chapter is not appropriate.

Finally, the possibility of effects leading to non-simple Fickian thickness effects should be considered. Although stress-dependency of uptake and variable diffusion coefficient have been discussed, but may not after all be of prime importance with this research, a thickness effect will remain a key issue. As discussed before, simple Fickian uptake in bulk material in combination with the basic instantaneous equilibrating boundary condition gives a single locus of uptake curve in the fractional uptake versus square root of time divided by
half-thickness plane. Thus, on this basis, uptake curves for all specimen thicknesses converge on the same line. However, the introduction of a gradually developing boundary concentration condition gives a characteristic uptake curve separation for different thicknesses, the boundary diffusion effect influencing the bulk behaviour. Crank [39] proposes several forms of gradually developing boundary concentration condition. Again, these are discussed in Chapter 4.

2.2.4 Experimental observations of uptake characteristics

The results of various gravimetric uptake studies, particularly with epoxide and phenolic adhesives, have indicated that Fickian diffusion often occurs in the adhesive layer of a joint [4, 15, 16, 18, 28, 32, 64]. Shen and Springer [18] carried out diffusion experiments using rectangular sheets of both composite and homogeneous materials, exposed to humid air and liquid water on one or both faces of the sheet. Their application of one-dimensional Fickian diffusion analysis was supported well by their experimental results, i.e. initial water uptake was found to be linear with root time, levelling off towards an equilibrium value at extended time.

Althof [15] studied water diffusion in five different structural adhesives used in the aerospace industry. These adhesives were modified epoxides, epoxy-nitriles and a phenol-polyvinyl adhesive and were supplied in the form of films, some containing a carrier of woven fabric. He noted that Fickian analysis could be used as long as the diffusing water did not alter the chemical structure of the adhesive. He tested thin sheet specimens (1 x 60 x 60 mm) as well as layers of adhesive sandwiched between impermeable aluminium foil film, this latter specimen geometry intended to represent more closely the longer diffusion path lengths met in lap-shear joints. The results of these tests suggested different values for diffusion coefficient for the two specimen geometries. Brewis et al. [26] carried out a series of experiments on thin sheets of DGEBA-DAPEE. Specimen thickness ranged from 0.050 to 0.170 mm and absorption was from water vapour, mass gain being measured using a vacuum microbalance and chart recorder set-up. The resulting reduced uptake plots for various thicknesses of specimen, all absorbing from the same relative humidity and temperature conditions, seemed to give different diffusion coefficient values. Together
with Althof's [15], this might suggest a possible thickness-dependence of diffusion coefficient. However, there is little representation of this issue elsewhere in the literature.

Althof also observed examples of a second uptake stage with some epoxide adhesives at high relative humidity and temperature, when there was a secondary water uptake stage after an initial apparent equilibrium. Althof attributed this second uptake stage to structural changes within the adhesive and noted that temperatures in excess of 60 °C. seemed to result in changes to the adhesives studied. This highlights the dangers of using elevated temperatures in order to accelerate laboratory environmental durability experiments, as diffusion and degradation mechanisms which would not occur under ambient conditions may well occur at higher temperatures.

De Nève and Shanahan [16] carried out mass uptake experiments using 130 x 115 x 4 mm specimens of DGEBA/Permabond ESP 470 epoxy adhesive exposed to water vapour at 70 °C. and 100% RH. Their results also showed two uptake stages. The initial uptake stage did show linear Fickian characteristics, however, and gave a value for diffusion coefficient of $11.9 \times 10^{-13} \text{ m}^2\text{s}^{-1}$. They proposed that the second uptake stage was due to hydrothermal ageing of the adhesive, resulting in changes to its mechanical properties through plasticisation. This would appear to be consistent with Althof's warning of accelerated laboratory uptake tests at elevated temperatures possibly bringing about environmentally-unrealistic mechanical changes in some adhesives.

Brewis et al. [28] carried out uptake tests on a DGEBA epoxy resin with six different hardeners using thin plate specimens of 20 x 20 x 0.35 mm. Specimens were immersed in distilled water at 25, 45 and 70 °C. They were periodically removed from the water, dried with filter paper, weighed and then returned. Again, they reported various different water uptake patterns, including simple Fickian. However, all adhesives over the temperature range studied displayed an initial Fickian linear uptake stage. In cases displaying initial linear Fickian behaviour followed by a mass fall-off, the diffusion coefficient was calculated by extrapolating the mass fall-off part of the plot back to zero time in order to determine equilibrium uptake. In general, final equilibrium was reached after between 2 and 4 months.
Comyn [4] also determined diffusion coefficients for epoxide and phenolic adhesives based on Fickian analysis and mass uptake in thin adhesive films (less than 0.5 mm thick) exposed to thermostatted distilled water. Periodically, films were removed from the water, dried between paper tissues, weighed and returned to the water. Results for a nitrile-phenolic adhesive showed Fickian diffusion with linear uptake versus root time, smoothly leading to equilibrium. However, as have other authors and as reported earlier, he observed some exceptions to this type of uptake. In these diffusion experiments, he also observed departures from the simple Fickian uptake pattern, namely an initial linear uptake followed by a steady fall-off in mass.

Other published uptake data, which at first appears to display conventional, constant diffusion coefficient Fickian uptake behaviour, in fact seems not to conform to this pattern. Several published uptake plots have been compared to the fundamental simple Fickian curve shape and, although some of this experimental data showed very close agreement with simple Fickian behaviour, uptake behaviour presented by Althof [15] and Roberts and Yates [65] seemed to show sub-Fickian uptake behaviour at intermediate times (around the crook of the uptake curve). Althof studied a range of epoxide adhesives, including the unsupported Ciba BSL 313A. His thin film uptake curves for both 40 °C./70% RH and 70 °C./95% RH conditions seemed to suggest significantly diffusion that was lower and flatter than the simple Fickian pattern. Roberts and Yates [65] studied the thin-film diffusion behaviour of Ciba AV119 in environments of 60 °C./70% RH and 30 °C./water. In the former case, their experimental data agreed quite closely to the simple Fickian uptake curve shape, with only slight evidence of sub-Fickian behaviour at the crook of the curve. But in the latter case, their experimental data appears to lie significantly below the equivalent simple Fickian curve. Again, these anomalies perhaps suggest that a simple constant diffusion coefficient Fickian uptake model may not in fact accurately describe the water absorption behaviour of some common adhesives under certain absorption conditions.

Addressing the experimentally observed relationship between relative humidity, temperature, equilibrium uptake and diffusion coefficient, Brewis et al. [28], perhaps as expected, found no strong dependence of equilibrium uptake on temperature for any of the DGEBA-based adhesives they tested. Shen and Springer [18] add to this by suggesting that, whilst temperature does not affect the value of equilibrium uptake, the time taken to
reach maximum water concentration is affected by temperature through a temperature-dependent diffusion coefficient. Shen and Springer [18] also suggest that the moisture content of the environment affects equilibrium uptake, although equilibrium uptake is constant for a material immersed in liquid. They go even further by proposing that there is a simple power law relating equilibrium uptake to the relative humidity of the environment. Also, the time taken for a material to attain equilibrium, and therefore diffusion coefficient, appeared unaffected by the moisture content of the environment.

Althof [15], carried out uptake experiments using various thin sheet epoxy adhesives. In moist air conditions, he found that both equilibrium uptake and diffusion coefficient increased with increasing temperature at constant RH, these findings for equilibrium uptake perhaps contradicting [18] and [28] above. Also, equilibrium uptake increased with increasing RH at constant temperature, especially at high values of relative humidity. Then, conversely, he found that diffusion coefficient decreased with increasing RH at constant temperature. Shen and Springer [18], from their work on CFRP composites, support this observation. Wright [49] carried out some experiments on cast sheets of epoxy resin exposed to water vapour and liquid water. In the case of the water vapour experiments, he found that equilibrium uptake increased quite markedly with increasing RH, the rate of change increasing rapidly between 95 and 100% RH. This last observation agrees with [15] above. Then, equilibrium uptake also increased with increasing temperature but this effect was not as pronounced. His 100% RH experiments also suggested that the diffusion coefficient increased with temperature, with large increases above 50 or 60 °C. Again, this general trend is supported by [28] above. Supporting the observations of [15] and [49], Collings [30] carried out uptake experiments using CFRP laminates and found that equilibrium uptake increased with increasing RH at a constant 60 °C. Equilibrium uptake also increased slightly with increasing temperature at a constant 75% RH.

Noting that both [15] and [49] above observed relatively large increases in equilibrium uptake at very high RH, Brewis et al. [9] found different characteristics. In tests on DGEBA-DAB from water vapour at 50 °C., they found that equilibrium uptake increased steadily with increasing RH but flattened off between 95 and 100%. Diffusion coefficient was then seen to increase with increasing RH, slowly at first but increasing faster and faster right up to the 100% point. However, this trend in diffusion coefficient appears to
contradict the experimental observations of [15] above as well as El Sa'ad et al. [50]. These authors carried out uptake experiments with rubber-toughened DGEBA-based adhesives. They found that, between room temperature and 60 °C., diffusion coefficient decreased with increasing RH, this perhaps agreeing with [15] above.

Other results of El Sa'ad et al.'s [50] experimental work, agreed with the usual finding in that equilibrium uptake increased with temperature from room temperature to 60 °C., even using the low RH value of 11 to 12%. Supporting this finding, similar increases of equilibrium uptake were also seen over the same temperature range at 75 to 76% RH and in liquid water, the increases being more pronounced at higher RH values. Further supporting this work, Kanellopoulos et al. [66] carried out tests on CFRP composites and found an increase in equilibrium uptake with increasing temperature over a range of 20 °C. to 60 °C. and at a constant RH of 12%. But at a constant RH of 76% and over the same temperature range, equilibrium uptake was observed not to vary significantly. Then, their uptake tests from liquid water over a range of 20 °C. to 40 °C. suggested that equilibrium uptake increases with increasing temperature.

In summary, when considering variations in equilibrium uptake and diffusion coefficient with temperature and relative humidity, different adhesive systems can produce conflicting observations. It seems to be consistently accepted that equilibrium uptake is seen to increase with increasing relative humidity. However, an inconsistency lies in the fact that Althof [15] and Wright [49] specifically mention relatively large increases in the 95% to 100% RH range, whereas Brewis et al. [9] found that equilibrium uptake stabilised in this range. Then, considering the differences in the relationship between equilibrium uptake and temperature for adhesives absorbing from water vapour and liquid water, Shen and Springer [18] would maintain that equilibrium uptake remains unaffected by temperature changes if absorbing from liquid water. However, Kanellopoulos et al. [66] found that liquid water uptake experiments gave an increasing trend of equilibrium uptake with temperature, whilst changing to water vapour resulted in equilibrium uptake remaining virtually unchanged with increases in temperature. Brewis et al. [9], Shen and Springer [18] and Althof [15], respectively, observed increasing, unchanging and decreasing variations of diffusion coefficient with increasing relative humidity.
In a more detailed study of uptake characteristics, Brewis et al. [26] considered the possibility of a variable diffusion coefficient. They considered a concentration-dependent diffusion coefficient and investigated the variation by carrying out uptake tests over a range of relative humidities. They carried out tests on DGEBA-DAPEE at 48 °C. and in all cases uptake was found to be Fickian. Their results also showed the diffusion coefficient to be independent of concentration in this particular system. Constancy of diffusion coefficient has also been observed for some other water-epoxide systems [18, 23, 30, 53, 67], but there are reports of systems where diffusion coefficient increases with water concentration [68, 69].

One explanation to support the proposition of an independence of diffusion coefficient upon water concentration is that most of the absorbed water exists in clusters within the epoxide [26]. A relatively small amount of water remains molecularly dispersed in the adhesive, and except at very low overall concentrations, its amount remains constant over the whole range of vapour pressure. Only the dispersed water molecules will contribute to the diffusion process.

2.2.5 Conclusions

- no single uptake model can guarantee accurately to model the absorption characteristics of all adhesives, each system should be judged separately
- simple Fickian diffusion often does not describe water uptake by adhesives very well
- variable diffusion coefficients or gradual boundary equilibration conditions can be used to modify uptake characteristics, although the former technique results in only moderate modification [40]
- two-stage uptake behaviour can occur and can be explained by the presence of a relaxation process in addition to diffusion. The relative rates of the two processes dictates the overall uptake curve shape
- elevated temperatures can result in an irreversible change in the mechanical structure of an adhesive, non-Fickian diffusion then being assumed. This also questions the validity of measuring mechanical properties of hot-absorbed adhesives for later stress analysis
- applied tensile stress can increase rate and equilibrium level of uptake
2.3 Moisture-dependent mechanical properties of bulk adhesives

In considering the effects of environmental exposure on the degradation of the cohesive mechanical properties of bulk adhesives, Ashcroft and Spinks [13] state that absorbed water tends to degrade adhesives and that possible mechanisms include plasticisation, swelling, hydrolysis and cracking or microcracking. It should be noted that the first two of these mechanisms are regarded as reversible, mechanical integrity being regained with redrying [4, 21]. Hydrolysis and cracking, however, are irreversible and often the result of elevated temperature excursions. Under realistic, lower-temperature environmental ageing conditions, many authors measuring a degradation in mechanical properties in response to absorbed water attribute the observed degradation to plasticisation of the adhesive [16, 17, 21, 23, 37, 48, 61]. Also, Crocombe [70] notes that plasticisation and any resulting changes in mechanical properties is effectively instantaneous.

2.3.1 Test methods

In order to measure the moisture-dependent mechanical properties of adhesives, the variation being due to one or more of the above mechanisms, researchers have used a range of tests on both dry and absorbed adhesives. Typically, two types of property are measured, these being shear or tensile constitutive properties and glass transition temperature.

Uniaxial tensile (or compressive) or shear tests, nominally under quasi-static loading conditions, can be carried out in order to calculate the stress-strain behaviour of the adhesive material. Test speeds are set low enough to avoid rate effects, yet fast enough to avoid creep effects. For shear testing, various methods have been used, although it is common to use a joint type of specimen. Here, such a geometry is chosen that the adhesive layer is subjected to a near-uniform shear stress. It is also required that all of the material within the adhesive layer is homogeneous and mechanically representative of that particular bulk material. Although no environmental ageing was involved, Lilleheden [27] carried out a study using the thick adherend shear test (TAST) joint set-up, making use of a non-contact, Moiré fringe strain measurement technique. For his TAST substrates, he used
a strong aircraft grade aluminium alloy with acid etching and priming to give a strong interface, these being bonded together with American Cyanamid FM 73 epoxide adhesive. From these tests, Lilleheden concluded that there was no mechanical boundary effect in the adhesive layer and that shear strain was uniform, going from one interface to the other. Using such a joint test, a good pretreatment also ensures that there is no interfacial debonding and therefore no underestimation of shear properties. Apart from the above-mentioned TAST geometry, another commonly used set-up is the napkin ring test, originally devised by Gillespie and Rideal [71] - or a modified version of it [19, 24]. Conventional tensile tests can also be carried out, and these typically make use of bulk adhesive specimens, either in a cylindrical dumbbell or flat dogbone geometry, standards for various specimen types being laid down in ASTM D638-91. Both shear and tensile test types give stress-strain characteristics from which moduli, yield, ultimate stress and ultimate strain information can be determined for modelling comparison reasons. Standard elastic relationships can then be used, if necessary, to compare tensile and shear moduli for consistency.

Various forms of DMTA test can also be used to measure the time-dependent, viscoelastic properties of bulk adhesive specimens. Here, the specimen is cyclically loaded at a certain frequency between appropriate displacement or load cycle limits whilst also being heated slowly through a prescribed temperature range. The dynamic response to the loading is measured, a variable lag typically being observed between the former and the latter. Thus, an elastic modulus together with an associated phase angle (or damping effect) are output as a function of temperature. From these results, it is possible to estimate an effective static elastic modulus at any temperature within the range tested. Also, and perhaps the most useful output of this type of test, glass transition temperature can be estimated, it being customary to take the position of the primary peak of the phase angle curve as the required temperature.

Whether DMTA or another technique, such as differential scanning calorimetry (DSC), is used to determine glass transition temperature, this information provides a useful reference point in terms of whether an adhesive material will be in its glassy or leathery state under certain intended test or service conditions. This is important to know, as this transition corresponds to a sudden change in mechanical properties. Also, exceeding the glass transition temperature can lead to irreversible structural changes within the adhesive [35,
72], thus shedding doubt as to whether room temperature-measured mechanical properties obtained from a hot-absorbed adhesive specimen are valid to be used within a subsequent room temperature structural analysis [1, 15, 34]. As is discussed in the following paragraphs, glass transition temperature is often seen to decrease with absorbed moisture. Thus, the interaction between temperature, absorbed moisture, degraded mechanical properties and decreasing glass transition temperature can be complex, an adhesive specimen quite possibly changing from glassy to leathery as absorption continues.

As a cautionary note, however, it must be remembered that a typical DMTA test on an environmentally aged adhesive specimen can take 30 minutes or an hour to complete, the specimen being exposed to relatively high temperatures for much of the time. This therefore introduces problems with drying out of the specimen, thus not producing mechanical results in respect of adhesive at a constant moisture content level. Also, this type of test does not only measure purely moisture effects but will record effects purely due to temperature. Therefore, high up the temperature range of a typical DMTA test, not only might the specimen have significantly dried out but irreversible structural changes may be introduced and distort the data.

2.3.2 Experimental observations

De Nève and Shanahan [16] carried out both DSC and DMTA tests on a DGEBA-dicyandiamide epoxide adhesive to investigate the effects of environmental plasticisation and lowering of the glass transition temperature on durability. After ascertaining the optimum curing conditions by using DSC to monitor glass transition temperature, further DMTA tests conducted in compression-compression mode at a frequency of 5 Hz on dry adhesive fixed the glass transition temperature at 126 °C. Elastic modulus, defined as the absolute part of the complex modulus, was found to be approximately 4000 MPa at 20 °C. - and therefore with the adhesive still in its glassy state. Other bulk adhesive specimens were aged for various times from zero to over 1200 hours at 70 °C. and 100% RH. Similar DMTA tests on these specimens showed that glass transition temperature decreased with ageing, dropping by 39% of the dry value, to 77 °C. at 1261 hours. The 20 °C. elastic modulus was also found to decrease, although this dropped by only 5% of the dry value, to 3800 MPa. As even 1261 hours of ageing gave a glass transition temperature of 77 °C., this
means that all these elastic modulus values correspond to the adhesive's glassy state. Note also that these mechanical properties trends were measured only as functions of ageing time in the chosen environment and not of uptake levels.

Although they give no details of specimen geometry or other test parameters, Bowditch [61] reports environmental failure stress characteristics for both a chalk-filled and an aluminium-filled epoxide adhesive. Again, the lack of specimen geometry information makes it impossible to estimate the levels of absorbed moisture, but specimens were immersed in water at 50 °C. and failure stress measured as a function of ageing time. These results are presented in diagrams which have been summarised and combined and are shown here in Figure 2-6.

![Figure 2-6 Environmental degradation of failure stress for a chalk-filled and an aluminium-filled epoxide adhesive after immersion in water at 50 °C.](image)

Reference to this figure clearly shows that both adhesives suffer a marked loss in ultimate stress with ageing, the chalk-filled adhesive falling from a dry failure stress of about 22 MPa to under 2 MPa after 2000 hours' immersion (a 92% loss). The aluminium-filled adhesive then loses 76% of its failure strength, its dry value of 46 MPa falling to 11 MPa.
after the same maximum duration of immersion. Also, after 2000 hours of immersion, the strength loss of both adhesives appear to be stabilising at the quoted levels.

Gledhill and Kinloch [1] carried out static tensile tests on DGEBA/Ciba Geigy HY 959 epoxy adhesive. They used dumbbell specimens with a gauge length of 30 mm and a cross-sectional area of 12 mm² and they tested at 20 °C. at a constant strain rate of 1.4 × 10⁻³ s⁻¹. Although, in this paper, they omitted to enumerate exposure times, they say that cohesive breaking stress was not particularly affected by ageing in water at temperatures of 20, 40 and 60 °C. At 90 °C. However, they state that failure stress decayed with ageing time. This ties up with their fundamental suggestions that less aggressive environments hardly degrade adhesive joints and also that environmental degradation of adhesive joints is essentially interfacially-controlled. Interestingly, they then warn of using accelerated uptake tests as a basis for durability studies due to the possibility of introducing different degradation mechanisms at higher temperatures.

Brewis et al. [9] compression-tested 12 mm long and 8 mm diameter cylindrical specimens of DGEBA/DAB epoxide adhesive, both dry and after exposure to water, in a Mayes MPU 500 mechanical testing machine at a crosshead speed of 2 mm/min. The exposed specimens were immersed in water at 100 °C. in a Soxhlet apparatus for 500 hours, calculations using predetermined diffusion parameters suggesting that an equilibrium uptake of 1.9% had essentially been achieved by this time. The results of their compression tests suggested an elastic modulus of 1400 MPa in the dry condition, reducing to 800 MPa in the saturated condition. For the same conditions, yield stress varied from 124 MPa down to 104 MPa and ultimate stress varied from 169 MPa down to 163 MPa in the saturated condition.

Roberts and Yates [65] carried out tensile tests on 100 x 10 x 1.5 mm specimens of AV119 using an Instron 1185 tensile testing machine. Two environments were used to age specimens prior to room temperature-testing, these being immersion in liquid water at 30 °C. and exposure to 70% RH at 60 °C. Tests were carried out over a range of fractional uptake values ranging from dry to partially or fully-saturated. The maximum fractional uptake of test specimens aged in water at 30 °C. was about 0.9, equilibrium uptake being extrapolated to about 5.5%. The specimens exposed to 70% RH at 60 °C. actually reached
equilibrium uptake of about 3.5%. Tensile strain was measured using a 25 mm gauge length contact extensometer. The crosshead speed used for all tensile tests was 1 mm/min.

The results of these tests suggested that the elastic modulus of the specimens aged in water at 30 °C. decreased from about 3150 MPa at the dry condition to about 2780 MPa at the maximum uptake condition (about 5% mass uptake, corresponding to 0.9 fractional uptake). This represents a drop of 11.7%. For the 70% RH/60 °C. specimens, elastic modulus was seen to decrease from about 3150 MPa, again at the dry condition, to about 2800 MPa at the equilibrium uptake condition, this representing a drop of 11.1% covering the whole uptake range.

Morgan et al. [17] carried out tensile tests on TGDDM-DDS bulk epoxy adhesive dogbones with a gauge length of 30 mm and cross-section of 4 x 0.6 mm. They used an Instron TM-S-1130 table model tensile testing machine set at a strain rate of 0.01 min⁻¹ (0.3 mm/min). They tested adhesive specimens with a range of water contents and tested at a range of temperatures. Being an aerospace research project, their work concentrated on the effect of continuously varying the ambient temperature to simulate the widely varying operating conditions of supersonic aircraft. With respect to the effects of absorbed water, they claim that elastic modulus, UTS and strain to failure all decrease with increasing mass uptake at testing temperatures from 23 °C. to 150 °C., noting that this degradation is due to plasticisation. Specimens were tested either dry or absorbed to approximately 4% mass gain by exposing for 3 hours to steam at 120 °C. in an autoclave. Note, however, that no equilibrium uptake values were quoted. Looking at plotted uniaxial tensile mechanical properties at the lower end of the above-mentioned temperature range, elastic modulus is seen to decrease from about 2120 MPa in the dry condition to about 1880 MPa in the wet condition - a drop of 11.3%. UTS fell 9% from 67 to 61 MPa. Finally, engineering strain to failure perhaps only marginally decreased from the dry to the wet condition at 23 °C., the drop being perhaps only 4% of the 4% dry strain to failure value. However, this decrease was more significant at temperatures in the middle of the range studied.

Ashcroft and Spinks [13] developed a technique of using micro-indentation to link between water uptake and mechanical properties. The indenter employed a triangular-based sharp point with a face angle of 65.3°, giving an identical depth to projected contact area ratio as a Vicker's indenter. Their work also took account of the variation in water concentration at
different depths for less than saturated specimens, noting that different indentation loads would not lead to identical mechanical property values as it would in the case of homogeneous materials (e.g. either completely dry or fully saturated adhesives). They used their technique to test a two-part filled epoxide adhesive, Araldite K138, care being taken to avoid non-representative inhomogeneities with the indenter. Hardness and elastic modulus values were calculated from load/depth data using a method described by Oliver and Pharr [73], elastic modulus values being based upon elastic unloading. Although they admit that this method is based upon an elastic-plastic material response, and so it is not directly applicable to viscoelastic polymers, they say that the method still serves as a useful comparative tool. Tests on dry and aged adhesive specimens were carried out both in air and also \textit{in situ}, i.e. under water for the wet specimens. Acknowledging that the method of calculating elastic modulus left something to be desired and presenting the \textit{in situ} results, they measured a definite decrease in modulus with increased ageing in water at 20 °C. Typical values plotted suggest a dry elastic modulus at 20 °C. of about 4500 MPa, falling to about 2800 MPa after 2 hours immersion. As this work aimed mainly to test the indentation-uptake-properties correlation technique, as there was an admission of doubt as to accuracy of calculated elastic modulus values and as this technique probes only just beneath the surface of the specimen, these results need to be viewed with caution. However, it would appear that they observed genuinely decreasing elastic modulus of the Araldite K138 epoxide adhesive with increasing ageing time.

Althof et al. [74] tested a range of dry and environmentally aged epoxide adhesives using both tensile shear and dynamic torsion-pendulum tests. The shear tests made use of a TAST joint geometry with overlap length 5 mm, width 25 mm and a slightly variable adhesive layer thickness of approximately 0.1 mm. The shear stress was assumed constant along the overlap length and therefore simply estimated as the load divided by the in-plane cross-sectional area - this assumption of uniformity was checked with a finite element model and found to be realistic. Then, using special contact extensometry and taking account of substrate distortion, the shear strain was calculated from adhesive layer thickness and relative shearing displacement of the substrates. For the dynamic torsion-pendulum tests (to DIN 53 445), shear modulus was calculated over a range of temperature by using an expression combining dynamic motion and geometric parameters. Noting that the mechanical properties of plastics are dependent on the type of test used as well as being time-dependent, Althof et al. analysed the results from both types of test and concluded
that absorbed water generally softens adhesives. They suggest that the mechanism involves adsorption of small diffused water molecules within the adhesive, resulting in weakening or even neutralisation of subsidiary valence bonds. They add that the addition of elevated temperatures tends to favour this process. This then leads to a reduction in shear modulus and yield. They also note that moisture effects are reversible.

Looking specifically at their plotted results for one of the modified epoxide adhesives, plastic fabric-carried FM 73, it can be seen clearly that storage in fairly neutral ambient conditions of room temperature (20 °C.) and 65% RH leads to very little change in static shear stress-strain behaviour, except for an approximate 6% increase in ultimate shear stress after one year - due perhaps to postcure. Upon ageing under relatively wet conditions of 20 °C. and 95% RH for eight weeks, the shear modulus appears virtually unchanged, although the ultimate shear stress decreases from a dry value of 45 MPa to about 42 MPa, representing a 6.7% drop. Moving onto the plotted dynamic test results for FM 73, it would appear that even as long as one year's exposure to 20 °C. and 95% RH fails to reduce the dry glass transition temperature of 124 °C.

Then, turning to the uncarried epoxide-nylon adhesive, FM 1000, and using TAST joints of the same dimensions as before, it can be seen that storage for up to 12 weeks under neutral conditions of 20 °C. and 65% RH seems to decrease shear modulus significantly, reduce yield but perhaps has negligible effect on ultimate shear stress. Then, ageing for 9 weeks at 20 °C. and 95% RH sees a marked decrease in shear modulus to perhaps only a third or even a quarter of the dry value, this effect being far more pronounced than the dry storage time effect. Under the same conditions, both yield and ultimate shear stress also decrease, shear yield stress falling from a dry value of about 35 MPa to a value at 9 weeks of about 5 MPa - an 86% drop. However, as with all the data in this paper, mechanical properties are measured only with respect only to time of exposure to various environments. Thus there is no direct indication of fractional uptake values or probably non-uniform concentration profiles (and consequently, stress distribution) within the TAST adhesive layer.
John et al. [23] carried out static tensile tests on dry and aged specimens of epoxide adhesives. They studied two relatively tough, two-part paste adhesives, namely Redux 410 (supplied by Ciba-Geigy) and Hysol 9321 (supplied by Hysol Dexter). For the purposes of environmental ageing, specimens were exposed at 40 °C. and 90% RH. Although no details of testing temperature, specimen dimensions or crosshead speed are given (and therefore no estimation of bulk mass uptake is possible), they observed steady decreases in elastic modulus and failure stress with exposure times of up to one year for both adhesives. Redux 410 had a dry elastic modulus of 1400 MPa, dropping by 15.4% to 1185 MPa after one year's ageing. Failure stress dropped 12.9% from 33.3 to 29.0 MPa with the same ageing time. The Hysol 9321 adhesive was stronger and stiffer, its dry elastic modulus of 2276 MPa dropping by 35.2% to 1475 MPa after one year's exposure. Then, it's failure stress dropped 15.2% from 46 MPa to 39 MPa subjected to the same exposure time. However, whereas failure strain remained much the same, at about 3% for the Hysol 9321 adhesive, Redux 410 displayed a marked decrease in failure strain with ageing. In the dry condition, this adhesive registered 12.0% strain to failure, whilst after one year's exposure the value fell to 8.5%. They also undertook DSC tests to measure the glass transition temperatures of the two adhesives studied. Redux 410 gave a dry glass transition temperature of 58 °C., this falling to 53 °C. after one year's ageing at the above-mentioned conditions. Hysol 9321 gave a dry value of 57 °C., which fell only slightly, to 56 °C., after the same length of exposure. However, they note that ageing can have postcure effects on the adhesive, tending to increase the glass transition temperature. Thus, they say that it might be unwise to use glass transition temperature to gauge the amount of environmental plasticisation (and thus water uptake) in an aged adhesive. They also carried out TAST tests in order to measure the shear properties of the adhesives in question, noting that this type of test gives reasonably genuine estimates of mechanical shear properties as long as premature interfacial failure of the joint specimens does not occur and thereby interfere with the measurements. Thus they also present shear modulus, ultimate shear stress and shear strain to failure data for the dry and unaged adhesives. These are fairly consistent with the corresponding tensile data. Again, all mechanical property measurements were presented with respect only to time of exposure to the chosen environment.

Zanni-Deffarges and Shanahan [19] carried out both modified napkin ring and bulk adhesive DMTA tests in order to measure the mechanical properties of dry and aged DGEBA/TGMDA-DICY epoxide adhesive. The modified napkin ring torsion set-up took
the form of a 3 mm-thick plate bonded to a hollow cylinder of external and internal radii 10 and 5 mm respectively, both substrates being made of stainless steel and suitably pretreated. Taking account of substrate distortion and assuming a uniform shear stress distribution in the adhesive layer bonding the plate and cylinder together, they used this test to measure shear modulus and ultimate shear strain, noting that ultimate strain values for an aged adhesive layer can sometimes be underestimated due to partial interfacial disbonding.

Noting that they determined the diffusion coefficient to be $1.5 \times 10^{-12} \text{ m}^2\text{s}^{-1}$ and the equilibrium mass uptake to be 4% at their chosen 70 °C. and 100% RH ageing conditions, this provides a link between measured mechanical properties and water content in the adhesive. However, in trying to relate mechanical properties directly to local moisture concentration, they warn of possible ambiguities in calculated shear modulus values arising from non-uniform, pre-equilibrium concentration profiles within the adhesive layer. Thus, using a constant relative rotational speed of $2 \times 10^{-5} \text{ rad.sec}^{-1}$ and an adhesive layer thickness of 1 mm, they present mainly dry and fully saturated results, stating that the dry shear modulus was found to be about 800 MPa, whilst the fully saturated value had dropped 25% to 600 MPa. Noting that ultimate shear strain decreases markedly with ageing time (from about 20% dry to about 2% fully saturated), they then make certain elastic-plastic assumptions within the adhesive layer and calculate ultimate local shear stresses, deducing that the dry value of 41 MPa falls 75.6% to 10 MPa in the fully saturated condition. Further to the modified napkin ring tests, their DMTA work suggested that absorbed water also decreased the value of glass transition temperature from 140 °C. in the dry condition to 130 °C. in the fully saturated condition. Using standard relationships between shear and elastic moduli, and assuming that Poisson's ratio is not affected much by the ageing process, they then stated that there was good agreement between moduli values measured using both the modified napkin ring and DMTA test techniques.

In other work [24], the above authors used the same DGEBA/TGMDA-DICY epoxide adhesive and carried out bulk tests on an Instron tensile testing machine at a crosshead speed of 1 mm/min. Tensile specimens were of dimensions 110 x 10 x 2 mm and, again, they tested both dry specimens and specimens aged for various times under the previous conditions of 70 °C. and 100% RH. The results of these tests showed that elastic modulus fell by 20% from an initial dry value of about 2430 MPa to 1940 MPa at equilibrium.
uptake. Noting, above, that a corresponding drop in shear modulus of 25% was measured with the viscoelasticimetric technique, this observed drop in static tensile elastic modulus is fairly consistent, although any discrepancies could perhaps be accounted for by way of test type-dependence of mechanical properties as well as the significant scatter apparent in the authors' plotted results.

Harris and Tod [75] mechanically tested an un-named one-part, hot-cure toughened epoxide adhesive which had had process oil, similar to that used in steel milling plant, mixed in with it to a level of 3.3% by weight prior to cure. They carried out conventional tensile testing on both dry and aged specimens, ageing consisting of immersion in water at 20, 40 or 60 °C. Tensile testing was carried out at 21 °C. using dumbbell specimens 2 mm in thickness. Although equilibrium uptake values are not clear from the presented data and although it is not clear at which temperature the tensile test specimens were aged, some plotted results show clearly that elastic modulus and ultimate stress are significantly reduced with increasing absorbed water. Over what is perhaps a range of dry to fully-saturated (at least, if absorption was from water at 20 °C.), this particular oil-impregnated adhesive would appear to lose approximately 40% of its elastic modulus. Ultimate tensile stress is correspondingly reduced by perhaps 30%. Moving onto ultimate strain, however, it appears that this is increased with increasing absorbed water, from about 4.5% in the dry condition to about 6.5% in advanced states of uptake. Although the observed decreases in elastic modulus and ultimate stress are generally consistent with the other literature, it would appear that it is more common to see a decrease in the ultimate tensile strain sustainable by typical epoxide adhesives [17, 19, 23]. As to the possible unusual effects of the absorbed oil, the authors offer no real discussion on this point relevant to ultimate strain observations.
2.3.3 Modelling of the mechanical properties of composites or filled adhesives

If there is a requirement to develop a mechanistic constitutive material model for a composite material, such as a filled or toughened adhesive, based on the properties and interaction of the different component phases, the literature contains various studies which are of interest. Hashin and Shtrikman [76] used a variational approach in modelling the overall elastic moduli of arbitrary geometry composite materials from the moduli of the component phases of the \( n \)-phase composite, noting that the simple uniform stress and the uniform strain mixture laws always provide absolute minimum and maximum bounds of composite modulus. Hashin and Shtrikman's bounds further improved on those proposed by Paul [77], also being applicable to undefined geometries. With the constraint that the component phases should be elastic, isotropic and homogeneous and have similar stiffnesses, Hashin and Shtrikman go on to develop their general \( n \)-phase model, giving expressions for upper and lower bounds of bulk and shear moduli, before simplifying to fit a two-phase situation. They then applied their model to a tungsten carbide/cobalt alloy as a case study, claiming positive results. They then note an uncertainty in fixing definitely the bounds for shear modulus. Also, because of the constraint that the component phase moduli should be similar (the biggest ratio encountered in their case study was a shear moduli ratio of 3.6), they note that their model is unsuitable to model situation of holes or rigid particles within a matrix material - the model then predicting either zero or infinite moduli bounds. Walpole [78] then discusses Hashin and Shtrikman's work, criticising it for a lack of general applicability, and then develops composite moduli bounds that can be applied even to anisotropic phases.
2.3.4 Conclusions

- adhesives are generally degraded by absorbed moisture
- if excessively elevated temperatures are avoided, redrying a plasticised adhesive can result in at least partial recovery of the original properties
- the use of joint specimens to test bulk properties can be satisfactory as long as premature interfacial failure is avoided by the use of a durable surface pretreatment
- whilst some authors, including Gledhill and Kinloch [1] doubt any significant degradation in mechanical properties at lower ageing temperatures, others have indeed observed degradation at around room temperature [13, 65, 74]
- glass transition temperature, elastic modulus and ultimate tensile strength generally decrease with increasing absorbed water
- ultimate strain is sometimes seen to decrease, yet at other times seen to increase
- environmental degradation of adhesive materials can be used as a basis for the prediction of the durability of adhesive joints
2.4 Environmental performance of adhesive joints

This section of the literature review seeks to present reported observations of joint strength and locus of failure characteristics with respect to environmental ageing. However, we find ourselves addressing perhaps the biggest issue within the subject area of adhesive joint environmental durability - the divide between cohesive and interfacial locus of failure. Foundation durability work carried out by Gledhill et al. [2] concluded emphatically that environmental susceptibility of adhesive joints was primarily due to the sensitivity of the interfacial regions under attack by absorbed moisture. They even suggested that the plasticising action of absorbed water on the bulk adhesive within the bondline actually improves durability, this being echoed by both Li et al. [48] and Kinloch [79]. Then, together with the fact that exposure to moisture is often observed to worsen durability, this led to their conclusion of interface-controlled environmental weakening. Coupled with the observation that environments with low water concentrations did not degrade joint strengths, they then offered an explanation involving the absorption of moisture through the adhesive, migration of that moisture to the interface, progressive attainment of a critical water concentration and final thermodynamics-predicted interfacial debonding. Thus, an environmental crack develops as more moisture is absorbed, reaches the interface and surpasses a critical interfacial concentration value. Fracture mechanics theory, with a Griffith's critical flaw size criterion is then used to predict failure of the joint.

Whatever the details of Gledhill et al.'s durability model, the importance of interfacial integrity is universally accepted and many researchers have accepted this idea of interfacial control and have focused on it as a basis for their own developments. Thus, much of the durability literature concentrates, perfectly legitimately, on the application of pretreatments and primers and other techniques of providing a very initially strong as well as durable interface. As much as these aspects are discussed in this review, the balance with regards to this cohesive durability project is simply to acknowledge the environmental sensitivity of adhesive joint interfaces and to note some of the pretreatments which give good interfacial resilience - thus tending to drive locus of failure towards the required fully cohesive within the adhesive. A full parametric study of pretreatments therefore falls outside the bounds of this project, the main point of interest being the cohesive environmental performance of adhesive joints. So, of most interest here are reported
observations of environmentally-affected joint strengths, supported by the occurrence of cohesive locus of failure.

Here, it is worthwhile to reiterate the difference between initial (or dry) joint strength and durability, especially in the context of surface pretreatments. Initial joint strength is purely the ultimate load capacity of an unaged adhesive joint, whereas environmental durability is the capacity of that joint to sustain its initial strength for extended periods whilst under environmental attack. Changing the pretreatment may actually decrease the initial strength of a joint, although it may result in better durability, i.e. that lowered initial strength is sustained better when attacked by moisture. Obviously, a combination of both good initial strength as well as good environmental durability gives the best situation, however, it is important to note the distinction made here.

2.4.1 The effects of substrate surface pretreatments on durability

There is truly a vast wealth of literature available on the effect of using various pretreatments and primers on the environmental durability of adhesive joints. Again, a very detailed study of the literature lies outside the bounds of this research, although interfacial resilience is such an important issue that no durability literature review would be complete without some analysis of these aspects. Typical pretreatments applied to the bonding surfaces of adhesive joint substrates include mechanical, simple degreasing-only, chemical and electrochemical processes. They are all intended to provide a more durable bond between the adhesive and substrate surfaces. Whereas mechanical pretreatments, such as wire brushing, application of Scotchbrite™ or grit-blasting, aim to improve interfacial durability by larger-scale roughening of the substrate surface topography (perhaps leading to greater surface area and mechanical interlocking), chemical or electrochemical processes are used to modify and stabilise both the smaller-scale topography and chemical structure of the surface oxide layer in the case of metallic substrates. With poor surface pretreatment, a weak oxide layer is often the product and this can lead to a locus of failure which passes through the layer itself. In support of this, various authors [51, 80, 81, 82, 83, 84, 85] have used surface analysis techniques on failed adhesive joints and have found that locus of failure was within the oxide layer itself.
Primers can be used alone or additionally to the prior application of another surface pretreatment in order to improve durability. Providing a suitable choice is made, a primer can increase the strength of an adhesive joint by promoting the formation of strong covalent bonds both at the interface between the substrate oxide layer and the primer layer and at the interface between the primer layer and the adhesive [86]. Perhaps the most commonly represented group of primers in the literature is the organosilane, or "silane", type. Furthermore, one silane primer discussed often is γ-glycidoxypropyltrimethoxysilane, the typically-used Union Carbide product designation being A-187.

Still with regard to metallic substrates, most pretreatment literature discusses either mild steel or aluminium alloy, interest in the former arising primarily from the automotive industry and interest in the latter arising from the aircraft industry. Information on the adhesive bonding of other metals, such as titanium, can also be found more and more frequently [60, 61] - especially as new, advanced materials come into use. However, as the experimental adhesive joint work carried out in this research made use of mild steel and aluminium alloy substrate materials, further discussion in this section will be restricted to these.

For aluminium alloy substrates, chemical and electrochemical pretreatments are generally regarded as having the most potential for improving durability, a very comprehensive survey having been undertaken by Critchlow and Brewis [87]. These break down most popularly into acid etching and acid anodising processes, each one typically not consisting of only a single chemical treatment but in fact a succession of stages including degreasing and rinsing. Perhaps the most famous acid etch process is the Forest Products Laboratory (FPL) process, as defined by Eickner and Schowalter [88]. The original FPL process was in fact based upon a dichromate-sulphuric acid etch. Sometimes, however, the original specification would be optimised by changing the levels of chromate present in order to further improve its performance. Also, more recently environmental pressures have led to the substitution of non-chromate etch components in place of the original toxic ones [83]. Thus, there are various different acid etch processes available. Another note is that some authors erroneously use the term "FPL etch" to cover all chromic acid etches.
Often, however, even better durability has been effected by the use of an acid anodisation process subsequent to an acid etch. Various processes are available, perhaps the most famous anodising process being the phosphoric acid-based Boeing BAC 5555 pretreatment [89], which specifically includes the FPL etch as one of its several stages. Hardwick *et al.* [84] say that this improvement could be as a result of the formation of a thicker oxide layer in the case of an additional acid anodising stage to the process and they quote a typical thickness of 40 nm for an FPL etch versus 300 nm for a complete BAC 5555 treatment. Also, the oxide layer produced by acid anodising typically has a more intricate, adhesion-promoting microstructure than the native layer [90]. As before, it is possible to modify the components within any acid etch or anodising process in order to yield the required durability from an adhesive joint in question. Thus, it is common to encounter also chromic acid [3, 14, 25, 32, 48, 61, 63, 82, 85, 87, 91, 92, 93, 94] and sulphuric acid [61, 83, 95, 96] anodising pretreatments in the literature.

It has also been observed that the composition of the alloy can have an effect on adhesive bond strength [3, 82, 87, 93]. Commonly, high magnesium or copper concentrations in an aluminium alloy are seen to lead to poor strength and durability, Critchlow and Brewis [87] maintaining that an FPL etching process can be used to remove magnesium-rich oxide layers.

### 2.4.2 Experimental observations on the effects of pretreatments

Now discussing in more detail the experimental adhesive joint durability work carried out by other researchers, Bishopp *et al.* [91] carried out some durability tests using a floating roller peel joint geometry. The substrate material used was 2024-T3 clad aluminium alloy and the adhesive was an experimental carried toughened epoxy. Various mechanical and chemical pretreatments were investigated, as was a phenolic/epoxy primer. Some joints were aged at 70 °C and 85% RH for up to 30 days. When tested for durability, the primed joints gave a ranking of PAA>potassium dichromate/sulphuric acid pickle>CAA. They also reported that priming made little difference to the already good durability performance of the PAA pretreatment. However, they stated that joints aged for the full 30 days rarely displayed deeply cohesive locus of failure, suggesting that environmental attack preferentially degraded the interface.
Bowditch and Gardham [61] carried out a series of stress rupture tests using NS4 aluminium alloy bonded with a chalk-filled epoxide adhesive - note that one of the adhesives studied in the current research is similar. Environmental exposure of the test specimens consisted of immersion in water at either 40 or 50 °C. Again, various chemical pretreatments were tried and ranked for durability performance. Interestingly, they observed that, in the case of ageing at 50 °C., locus of failure was predominantly cohesive within the adhesive, resulting in little differentiation between applied pretreatments. However, at 40 °C., the interface appeared to suffer the worst environmental degradation, with a corresponding change in locus of failure and the choice of pretreatment now coming much more into play. From the set of joints aged at 40 °C., the durability ranking of pretreatments became PAA>CAA>CAA+PAD>SAA+SAA+PAD>acid etch only. Also, for some PAA joints, they observed an increase in joint strength with time of exposure. In response to this they suggest that, given the highly environmentally resistant PAA interface, the action of the absorbed water tends to relax internal stresses within the adhesive arising from the cure shrinkage, thus increasing the capacity of the joint to sustain external loading.

Brewis et al. [14] used variously pretreated pure aluminium clad alloy together with a DGEBA-based epoxide adhesive to bond single lap-shear joints, which were then tested either in the dry condition or after various period of ageing at 50 °C. and 97-100% RH of up to one year in duration. Initial, dry joint strengths led to a pretreatment ranking of CAE>CAA>sandblast>degrease, although they say that CAA might usually be expected to do better than CAE. Their plotted results for the exposed joints then showed some interesting trends. Although the CAE joints showed a decrease in joint strength with ageing time, the CAA joints were seen to increase in strength by 35% after about 4000 hours of exposure. Similarly to Bowditch and Gardham, above, they explain this trend by way of a stress-relieving action of absorbed water. Then, considering locus of failure, a cohesive mode was certain in only the dry CAA joints, the dry CAE joints perhaps only just failing through the adhesive. Certainly, with ageing, locus of failure tended towards interfacial for all joint types.

Digby and Packham [83] used the Boeing Wedge test (to ASTM D3762) to assess the durability properties of various chemical pretreatments. L165 clad aluminium alloy was used as the substrate material, Redux 312/5 epoxy resin being selected as the adhesive.
Environmental ageing was at 50 °C and at 95% RH. A phosphoric acid anodising treatment to BAC 5555 specifications was used as a reference. Also, as a replacement for the FPL etch within the BAC 5555 treatment, they tried a ferric sulphate/sulphuric acid etch, which they designated "P2". Sulphuric acid anodising and phosphoric acid dip pretreatment components were also investigated. Noting that it is often difficult to predict the durability of any one particular package of combined pretreatments, they report that the best durability performance was given by an FPL+PAA+PAD treatment. Comparing the FPL and P2 acid etching alternatives, they state that they give similar durability. Moving onto consider locus of failure of the wedges, they note that only pretreatments including a PAA stage gave reliably cohesive failure. For other pretreatment combinations, the locus was more interfacial, that for one SAA-based pretreatment being through the oxide layer.

Poole and Watts [93] used the modified film epoxide adhesive, Redux 312/5, to bond Boeing Wedge joints. They studied four different aluminium alloys and used environmental ageing conditions of up to 288 hours' exposure to 50 °C. and 96% RH for their durability tests. Both BSL 157 and 7075-T6 alloys gave the same durability ranking of E+PAA>E+CAA=CAA>E>GB>DG. Then, the two clad alloys, BSL 152 and Alclad 7075-T6, gave E+PAA=E=GB>E+CAA=CAA>DG. Apart from degreased-only wedges, locus of failure was observed generally to be cohesive within the adhesive.

Various authors also investigate the use of primers on variously pretreated aluminium substrates [87, 97]. Critchlow and Brewis [87] observed fair durability performance after treating grit-blasted aluminium substrates with a A-187 silane primer solution. Stone and Sutton [97] then used an unclad BSL 157 aluminium alloy in a wedge test configuration to study durability. As well as applying an A-187 silane primer in various concentrations of aqueous solution to the surface of the substrates, they also tried mixing the silane with the epoxide adhesive before cure. Upon exposure to water vapour at 50 °C. and 96% RH, they found that, for premixed silane within the adhesive, the lowest tested concentration level of 0.15 ml/100g gave the best durability in terms of crack propagation speed. However, even better durability was achieved by applying the silane in the form of a solution to the substrates prior to bonding.

For steel substrates, favoured surface preparations tend to focus on mechanical pretreatments and the application of primers. Fay and Maddison [5] studied the durability
of mild steel joints using the Maddison-type perforated single lap-shear geometry [98] (with 3 mm diameter holes instead of the usual 4 mm ones). This geometry is used for durability assessment because the holes in the overlap section of the joint create extra faces for water absorption and also reduce the length of water absorption paths into the adhesive layer. Also, as the holes are positioned in the centre of the adhesive layer, where a lap-shear joint is least stressed, the perforations do not unduly weaken the joint. They used BS1449:CR1E steel, blanked into 60 x 20 x 0.9 mm coupons, these being spaced with 250 μm ballotini and bonded with a single-part, hot-cured, toughened epoxy paste (Permabond ESP 110). Environmental ageing was achieved by exposure to salt spray conditions for up to 56 days as well as to cyclic hydrothermal stress conditions to BS3900 Part F2. Surface pretreatments investigated consisted of various combinations of oiling, degreasing and the application of either A-187 silane or the proprietary Accomet C treatment. In the case of the silane primer, coupons were dipped in a 1% aqueous solution and then air-dried. If Accomet C was selected, coupons were immersed in a 5% deionized water solution of the primer, the resulting layer then being roller reduced to yield a dry film coating weight of 0.45-0.50 gm⁻². The coated coupons were then air-drying and stoved at 110 °C. Upon assessing durability, they first note that the silane primer gave rise to better dry strengths than Accomet C, although Accomet C gave better durability. Joint strengths were universally observed to decrease with exposure, although both primers dramatically improved durability compared to basic degreasing-only.

Gettings and Kinloch [99] bonded 25.4 mm cubes of BS9, EN3B mild steel together using a DGEBA-based epoxide adhesive to form a butt joint configuration. Copper wire pieces were used within the adhesive layer to provide a thickness of 0.50 mm and the bonding faces of all substrates were pretreated by degreasing and grit-blasting with white alumina. In addition to that, some substrates were treated with one of three different primers. After bonding, some joints were then immersed in water at 60 °C. for up to 1500 hours. Joints were then gradually fractured in tension. All exposed joint strengths were observed to decrease with immersion time, joints treated with A-187 silane primer achieving the best dry strength as well as durability. Then, importantly, they note that the other two primers actually decreased both dry strength and durability compared to the degreased and grit-blasted-only joints. This last observation provides a warning that, as with any pretreatment, the application of a primer does not necessarily have a beneficial effect.
Brockmann and Jopp [100] studied the durability performance of mechanically pretreated mild steel. They used a single lap-shear joint geometry and a DGEBA-DICY epoxide adhesive. Various grit-blasting media were investigated, including white alumina, glass beads and steel shot. They environmentally aged their joints by exposure for 4 weeks to conditions of 80 °C. in either water or 95% RH humidity. Salt spray was also used in some tests. Although no dry strength data is discussed in their paper, the exposed joint tests showed grit-blasting with steel shot or white alumina to give markedly better durability than grit-blasting with glass beads for all three ageing environments. Although the other two environments led to very similar durability performance with alumina and steel shot grit-blasting, the water vapour environment favoured steel shot even more, this giving the highest overall durability.

Neeb and Brockmann [101] also studied the effects of mechanical pretreatments on mild steel substrates. A wide range of grit-blasting media were tried, along with various adhesives, including a two-part polyamine-cured epoxide. The single lap-shear joint geometry was selected and some joints were environmentally aged by immersion in deionized water at 80 °C. prior to tensile testing. In this paper, both initial, dry joint strengths are discussed as well as the usual residual strength results for the exposed joints. Considering only the epoxide-bonded joints, both white alumina and glass bead grit-blasting media seemed to give relatively poor initial strength, whereas glass grit, ceramic beads, steel shot and steel grit gave much better strength (steel shot perhaps being the best in terms of initial strength). Then, moving onto consider residual strength (as a percentage of initial strength), glass beads and glass grit gave poor strength retention, steel shot gave fair strength retention and ceramic beads, white alumina and steel grit gave good strength retention (ceramic beads and steel grit perhaps being equal best). Although perhaps still arbitrary, combining initial and residual strength by multiplying them together produces an overall durability ranking of ceramic beads>steel grit>steel shot>white alumina>glass grit>glass beads, the spread being fairly even (except that ceramic beads and steel grit give very similar overall durability).

Both Brockmann and Jopp [100] and Neeb and Brockmann [101] propose reasons why the use of grit-blasting media may have an effect on adhesion strength and long-term durability. They variously suggest mechanisms including cleaning effect, increase of surface area and micro-mechanical interlocking as well as chemical effects caused by
embedded media in the surface of the substrate. They state that, even after ultrasonic
degreasing, remaining ions such as silicon or aluminium from embedded grit combine with
the adhesive to form a chemically-different interphase which controls adhesion. Also,
water diffusing through the adhesive layer can reach the interface, causing pH changes
which affect bond strength.

Gledhill et al. [102] did an interesting study of the effects of silane application parameters
on environmental durability. Degreased, alumina grit-blasted and primed mild steel
substrates were used in a butt joint geometry with an adhesive layer thickness of 0.5 mm.
The adhesive used was DGEBA-based. Five different silane primers, including A-187,
were investigated in their study of the effects of solution age, solution pH and drying
conditions. Some joints were aged for up to 1500 hours by immersion in water at 60 °C.,
with a general observation that joint strengths were seen to degrade with increased
immersion time. In investigating the effects of solution age, A-187 was used in aqueous
solutions of 1% v/v. After initial preparation of the solution, it was then left to stand at
room temperature for varying periods up to 1440 minutes. These joints were then aged as
above for 1500 hours before tensile testing for residual strength. The results from these A-
187 solution age tests showed that optimum joint strength was achieved using solutions left
to stand between about 30 and 90 minutes before application to the substrates. In
investigating the effects of silane coating drying temperature, they then reported that
elevated temperatures tended to reduce the residual strength of aged joints, their lowest
drying temperature of 20 °C. giving the strongest joints. Finally, in analysing the effects of
pH on durability, they explain that pH is basically a function of the solvent used (e.g. water
or ethanol), solution age and the nature of the silane primer itself. They then tabulate how
solution age affected the pH of aqueous solutions of all five silanes tested, different silanes
displaying different pH variation profiles with time. Focusing back on A-187, they then
show that increasing pH from about 2 to 10 results in a marked decrease in initial, dry joint
strength. When this result is matched with the solution age pH trends, it would again
confirm that better joint strength would be achieved by letting the freshly mixed silane
solution stand for about an hour before application and drying. In conclusion, however,
they note that, because of the parameters involved, choice of primer application conditions
can have a very sensitive effect of durability, sometimes the application of a primer
actually being disadvantageous.
Thus, for aluminium alloys, the literature strongly suggests that optimum durability is achieved by the application of a phosphoric acid anodising treatment. Furthermore, to possibly still increase initial strength and durability and also as a means of prolonging the useable life of freshly anodised surfaces prior to bonding, the application of a final primer should be considered. Then, for steel substrates, grit-blasting (in combination with prior or subsequent degreasing) with ceramic or white alumina media might be considered. And again, a final priming treatment could give similar advantages to those gained with aluminium substrates. However, as occasionally mentioned in previous paragraphs, positive durability effects resulting from the random combination of a surface pretreatment package with a substrate surface can never be guaranteed, sometimes the environmental durability performance of the resulting interface being worse than if no pretreatment had been used.

2.4.3 Experimental observations of cohesively failed joints

Leaving behind interface-controlled studies and moving onto observations more specifically involving environmental strength of joints that have failed with a cohesive locus of failure, Brewis et al. [14] observed a linear decrease of joint strength upon total water uptake for a number DGEBA-DAPEE-bonded aluminium alloy lap joints. Some of his results for a chromic acid anodising and sand-blasting pretreatments are shown in Figure 2-7. Other experiments with this adhesive, where a different chromic acid anodising pretreatment was used as a surface pretreatment, showed a linear increase in joint strength with increase in water uptake. This could be due to stress-relieving effects of adhesive plasticisation by water ingress. Other adhesives tested have shown a marked non-linearity under conditions of high water uptake, e.g. in the case of the epoxide-polyamide adhesive FM 1000 [4, 64].

Within the MTS adhesives programme, under the durability section, some useful joint testing was carried out [103]. Especially useful, with regards to this project, is the fact that the adhesive used was AV119. Their data showed that, for several joint geometries considered, the locus of failure remained predominantly cohesive within the adhesive, even for environmentally degraded joints. Therefore, this data tends to confirm the validity of developing a cohesive durability model. T-Peel, cylindrical butt and Boeing wedge joints
were all either immersed in water at 60 °C. or exposed to hot humid conditions before testing. With suitable pretreatments previously applied to the aluminium substrates (up to and including phosphoric acid anodising), observed failure modes were almost all cohesive.

Thus, in addition to the notes on the wise use of surface pretreatments to provide good interfacial resistance against environmental attack, the above observations tend to support this research's cohesive approach to the modelling of adhesive joint durability. And this should be seen as complementing interfacial durability models, such as the well-known one presented by Gledhill et al. [2].

![Figure 2-7](image)

**Figure 2-7** The linear relationship between epoxy/aluminium joint strength and adhesive layer bulk fractional uptake, as found by Brewis et al. [14]
2.4.4 Conclusions

- absorbed moisture generally degrades adhesive joint strengths
- occasionally, absorbed moisture can initially increase joint strength. Brewis et al. [14] suggest that this is due to a stress-relieving action in the slightly plasticised adhesive
- Gledhill et al. [2] proposed a durability model in which moisture is transported to the interfaces of a joint via diffusion through the adhesive. Predicted by thermodynamic work of adhesion considerations, progressive attainment of a critical water concentration at the interface causes debonding and the formation of an environmental crack front. Fracture mechanics were then used to predict failure
- increased absorbed moisture tends to move failure locus from cohesive towards interfacial
- contrary to this interfacial approach, cohesive locus of failure has often been observed for environmentally exposed joints. this suggests that degradation of bulk adhesive mechanical, properties can be a controlling factor for environmental durability
- good substrate surface pretreatments can give very environmentally durable interfaces
- aluminium alloys benefit most from electrochemical treatments, such as acid etching or anodising. Processes including acid anodising treatments are generally the best
- steels respond best to mechanical treatments, such as grit-blasting. Alumina is an effective blasting medium for increased durability
- adhesion promoters, or primers, may additionally improve environmental durability. A-187 silane, applied in a very weak solution (typically 1% v/v) to the substrate surfaces prior to bonding, often provides best durability
2.5 Modelling of the environmental durability of adhesive joints

Kinloch [79] presented a good overall study of environmental durability modelling, noting that it is still in its infancy. However, he listed five different approaches as given below:

- mechanistic approach
- fracture mechanics approach
- stress analysis approach
- using adhesive layer water uptake correlations
- extrapolating accelerated ageing tests

A mechanistic approach would take into consideration a knowledge of the detailed kinetics and mechanisms of environmental attack and then a fracture mechanics or stress analysis approach would be used to predict residual strength of the exposed adhesive joint. Perhaps within a mechanistic model, then, a fracture mechanics approach would be used to predict the stability of a flaw in the adhesive layer, this flaw being moisture-induced. Also, the mechanical properties, and hence fracture toughness or critical energy release rate (fracture energy), could be a function of absorbed water content. Next, a stress analysis approach would not necessarily take into account detailed mechanisms occurring in the adhesive joint but would build upon previously measured moisture-dependent material properties together with a suitable failure criterion to predict joint failure. Here, Kinloch notes that this technique is more successful for the study of cohesive failure than interfacial failure situations. The approach of using adhesive layer water uptake correlations is perhaps less flexible in that experimental bulk or adhesive layer water uptake level and experimental residual joint strength correlations are derived and used as a basis for prediction of residual strength of other joints. Finally, the use of accelerated uptake data can be used in the prediction of the residual strength of adhesive joints exposed to less harsh, but more natural, environments. The water uptake section of this review chapter has already mentioned some possible pitfalls in using experimentally obtained water uptake data as part of a durability model. Specifically, problems associated with accelerated uptake tests and possible thickness-dependence of uptake parameters have been flagged. Thus, these modelling components must be used with caution.
2.5.1 The Gledhill et al. model and other mechanistic critical water concentration-based approaches

As discussed earlier in this section, perhaps one of the most well-known durability models was that developed by Gledhill et al. [2] and was based upon two basic experimental observations. Firstly, they noticed that, whilst exposure of adhesive joints to relatively wet environments resulted in degradation in strength with time, exposure of the same joints to lower RH conditions did not lead to any significant degradation. Secondly, they observed that the locus of failure of their environmentally exposed joints was predominantly interfacial in nature. Given the assumption that moisture is absorbed into a joint through the bulk adhesive in the bondline, from where it gradually penetrates through to the interfacial regions of the joint, they then suggest a developing front of interfacial adhesive material attaining a critical water concentration. This critical water content level forms part of a thermodynamics work of adhesion analysis which dictates that an interfacial adhesive-substrate bond should lose all its strength when the required critical absorbed moisture level is reached. Thus, in the real joint scenario, when exposed to relative humidity conditions corresponding to a sufficient bulk moisture equilibrium level that surpasses the critical level, the interfacial regions experience a gradually spreading debond front. This then equates to a developing environmental crack, to which Gledhill et al. apply a Griffiths critical flaw size fracture mechanics technique in order to predict joint failure. Thus their model combines a mechanistic, thermodynamics-based analysis of moisture-induced interfacial debonding with a standard fracture mechanics approach to determine the current stability of an environmental crack. As input to their model, it was required to already have previous bulk adhesive Fickian uptake parameters as well as the critical water content level for that particular adhesive-substrate system. Also, for the fracture mechanics stage, the geometry factor for the joint type in question was needed. Upon testing their model with epoxy-mild steel butt joints, they reported a good success rate. Figure 2-2, already presented in the introduction to this review chapter, shows their results.

Further work has also been carried out on the proof of existence and determination of the critical water concentration. Brewis et al. [9] studied both a bulk epoxide adhesive and steel joints bonded with the same adhesive. Although the joints displayed strength loss only when exposed to water vapour activities above a threshold value, sorption isotherms for the same bulk adhesive showed no such discontinuities, thus not supporting Comyn et
al.'s suggestion of water clustering within the adhesive [26, 64]. Therefore, this lent confidence to the assumption of an interface-controlled environmental degradation mechanism. They then suggested that this interfacial degradation mechanism involved the hydration of salts trapped within the interfacial regions of a joint.

Lefebvre et al. [104] carried out tests on various DGEBA and DGEBF epoxide adhesives, using a scrape test to ASTM D2197. Here, glass plates were given a 25 µm epoxy coating before being exposed to equilibrium uptake, and then the force required to scrape the adhesive coating cleanly off the glass plate was measured. For one of the adhesives, they noted a discontinuity in a scrape force against RH graph which corresponded to a pronounced rate of increase of equilibrium uptake with respect to RH, this being at the 70% RH point. Supported by other experiments in which salts were added to a basic adhesive and then the uptake behaviour was re-measured, they concluded that there was indeed a critical water concentration and that it was attributed to water clustering within the adhesive which, at a certain water concentration, leads to water molecules condensing on the -OH groups of the polymer. At the interface, this would then break inter-chain hydrogen bonds and displace adsorbed -OH groups from the surface of the substrate.

Considering mechanistic approaches which incorporate the idea of a critical water concentration and subsequent displacement of adhesive molecules from the surface of the substrate, such as the above models, the measurement of the critical concentration value is not trivial. In Lefebvre et al.'s work, above, they happened to observe a connection between discontinuities in scrape force and bulk adhesive diffusion parameter plots, allowing them to suggest a critical concentration for their system. However, other systems may not display such obvious characteristics. Also, other interfacial degradation mechanisms such as the rupture of primary bonds, hydration of an oxide layer, hydrolytic attack on an adhesive boundary layer (or interphase) or hydrolysis of a primer layer may be responsible for environmental degradation of joint strengths. However, the precise nature of interfacial degradation mechanisms and kinetics is still a very complex and uncertain area.
2.5.2 Lavrentyev and Rokhlin's interfacial durability models

Lavrentyev and Rokhlin [105] present two interfacial durability models in their paper, noticing that locus of failure became more interfacial with ageing as well as observing a correlation between aged joint strength and the frequency shift of a minimum in the spectrum of a reflected ultrasonic signal. Their work focuses mainly on analysing the correlation between the interface properties-sensitive angle-beam reflection ultrasonic spectra and interfacial degradation, but they present their models in support of their experimental findings. The first of their two models visualises a two-part inhomogeneous interphase with a soft, damaged phase and a dry, undamaged phase. As the interface is attacked by absorbed moisture, the proportion of the soft, damaged phase is imagined to increase. The second model visualises the environmentally degraded primer layer as an array of interfacial disbonds filled with water, these then being represented by transverse nonlinear springs.

Experimentally, they made up aluminium single lap-shear joints using an aircraft grade alloy and applying a PAA pretreatment followed by a BR-127 corrosion-inhibiting primer. The adhesive used was an FM-73 prepreg film giving an adhesive layer thickness of between 100 and 160 µm. Some of the joints were simultaneously stressed and aged by immersion in a saturated sodium chloride (NaCl) solution at 68 °C. At various times, joints were removed and the ultrasonic analysis technique applied at the centre of the overlap. After ultrasonic analysis was completed, joints were then broken and the surfaces inspected for locus of failure. However, the authors do not mention any residual strength data here, this work focusing mainly on mechanisms of failure as opposed to prediction of environmental joint strengths. Upon inspection of the failure surfaces and comparison with the ultrasonic spectra, they noticed a correlation between the percentage of interfacial failure over the bond area and certain characteristics of the ultrasonic spectra.

In presenting the first of their two models, they considered an environmentally aged interphase region at the adhesive-substrate junction. They then visualised this interphase or primer layer as consisting of proportions of dry and wet spots, assigning stiff elastic properties to the former proportion and viscoelastic properties to the latter, softer proportion. An increase in ageing was modelled as an increase in number or size of the wet
spots, the wet areas promoting interfacial failure and the dry areas failing cohesively. Thus, this was consistent with their observations of generally mixed mode failure and that the proportion of interfacial failure over the overlap length increased with ageing with their single lap-shear joints. They then combined the properties of the two phases to calculate the effective elastic properties of the "composite" interphase and used this within a computer simulation to predict the phase shift of the minimum in the ultrasonic spectrum as a function of the proportion of interfacial failure, obtaining accurate results.

In the case of the second model, the water was visualised to diffuse towards the interface and to form circular, water-filled areas of disbond of approximately zero thickness. The degree of interfacial degradation thus became equivalent to the proportional area of disbonds compared to the whole nominal bonded area of the joint. They then addressed the boundary conditions at the degraded interface and stated that slip conditions could be applied to areas of disbond, whereas still-bonded areas should retain rigid conditions. The whole interface was then represented by complex transverse spring boundary conditions. Using fracture mechanics based on the assumed pattern of disbonds as well as elastic constants of the interacting dissimilar substrate and adhesive materials, they then calculated the required spring constants. Again, using knowledge of the response of the ultrasonic signal to the disbonds at the interface, they then compared modelled and experimental frequency shift versus fractional interfacial failure area. As with the first model, they obtained good agreement.

2.5.3 The fracture mechanics approach

Moving on to consider the possible role of fracture mechanics within durability modelling, a suitable joint type can be selected, for which the geometry factor is known - e.g. plain or tapered double cantilever beam (DCB or TDCB). Then, by measuring crack growth and displacement as a function of load, it is possible to estimate the Mode I fracture toughness, \( K_{1c} \), and critical strain energy release rate, \( G_{1c} \). Being material properties, they can then be transferred to analyses of other joint geometries for prediction of crack stability. However, there are limitations to this transferability of \( K_{1c} \) and \( G_{1c} \). Depending on how brittle the adhesive is and how thick the adhesive layer is, \( K_{1c} \) and \( G_{1c} \) values obtained from one test may not be realistic for use in another situation. Also, if Mode I values are being measured.
with the simple test geometry, they may not be valid in the analysis of a more complex geometry, where mixed mode stress fields occur. It will also be necessary to assume the presence of an initial flaw in a joint geometry being analysed. The length of that flaw also needs to be estimated. Then, moving onto environmental aspects, it would be necessary not only to measure $K_{1c}$ and $G_{1c}$ for the dry adhesive material but also for wet adhesive. This might pose problems in that it would be essentially impossible to ensure uniform moisture distributions within the relatively wide adhesive layer in a typical DCB or TDCB joint.

However, if the above method can be used, then it provides a powerful technique for quantifying the stability of an adhesive joint interface without either having to know the details of mechanisms or having to analyse the stresses or strains and apply an assumed failure criterion within the complex interfacial regions all within a finite element analysis. Although not popular with Gledhill et al. [2] and Kinloch [79] in the case of wet joints, a similar technique can be used for analysing cohesive failure. Again, either a joint test specimen geometry or a bulk adhesive specimen can be used, such as a compact tension specimen.

2.5.4 The stress analysis approach

Stress analysis can be also used as a vehicle for environmental durability modelling. Particularly for cohesive failure with joint geometries of any significant complexity and if detailed stress and strain profiles are required, then a finite element analysis approach is appropriate. For the modelling of interfacial failure loci, the representation of the interface becomes very complex indeed. Although this technique bypasses the requirement of detailed knowledge of the mechanisms and kinetics of environmental degradation, it does require the input of a suitable material model as well as the application of an appropriate failure criterion. Perhaps it is the latter which can be the most contentious issue, as the choice can appear to be arbitrary, often based on convenience rather than on any solid engineering concept. Thus, various authors have used different criteria in their finite element approaches to cohesive durability modelling.

John et al. [23] used a COSMOS finite element package to model double lap-shear joints comprising CFRP substrates bonded with one of two epoxide adhesives, either Redux 410
or Hysol 9321. Joints were environmentally aged at 40 °C. and 90% RH for up to one year, when failure for joints with shorter overlap lengths was observed still to be cohesive within the adhesive layer. However, they focus mainly on the effects of overlap length and fail to present directly any effects of ageing on residual strength. In their analysis work, they used a two-dimensional model with previously measured moisture-dependent linear elastic material properties, along with a Fickian-based calculations of water distribution. Noting that there are no universally accepted failure criteria for use with composites or adhesives, they adopted a failure criterion based on a critical stress acting over a critical distance. They predicted a reducing ultimate load with increasing ageing time which was in good agreement with their experimental results.

Roy [55] and Roy and Reddy [56, 57] used a two-dimensional finite element representation of an adhesive butt joint with elastic metallic substrates to model its creep response and delayed failure. Stating that the presence of moisture can change the stress state of adhesives, they modelled the ingress of water into the adhesive layer using Fickian uptake laws combined with Lefebvre's nonlinear, free volume-dependent diffusion coefficient [58], this then being expressed as a function of temperature, penetrant concentration and dilatational strain. They used Schapery's viscoelastic constitutive material equation [106] and an energy-based delayed failure criterion developed by Reiner and Weisenberg [107]. The Flory-Huggins lattice model for polymer-solvent interaction provided the link between uptake (or penetrant concentration) and viscoelastic response of the adhesive, this interdependence being solved iteratively. Running their model using the NOVA finite element software, with the joint subjected to a fixed displacement, they compared uptake profiles within the adhesive layer resulting from varying degrees of coupling between diffusion coefficient, penetrant concentration and dilatational strain. Viscoelastic stresses and strains in the adhesive layer were also analysed on a similar basis. They then ran the model again, but this time with the joint subjected to a range of constant axial tensile loads, for the purpose of testing the applied delayed failure criterion. However, they did not appear to model the effects of absorbed water in conjunction with their failure criterion, and no experimental work was carried out to support their modelling conclusions. Also, by using a viscoelastic constitutive material model, they were modelling the creep response of environmentally aged adhesive joints. However, as a well-designed joint should not fail by this mechanism and as this research focuses on the prediction of static residual strength, their work is not directly relevant here.
2.5.5 The use of water uptake correlations

Using water uptake correlations bypasses both a knowledge of detailed mechanisms and kinetics of environmental degradation and the need to carry out stress analyses with moisture-dependent adhesive properties. Also, there is not the major issue of choice of failure criterion which has to be addressed when using a structural finite element analysis approach. With this approach, either bulk adhesive or in situ adhesive layer water concentration distributions are measured and then correlated to experimental environmental joint strengths. Brewis et al. [14] made up single lap-shear joints using pure aluminium-clad alloy to BS3 L73 and a DGEBA-based epoxide adhesive, exposing some of them for up to one year at 50 °C. and 97-100% RH. Various pretreatments were used on the aluminium substrates prior to bonding. Upon measuring joint strengths after various ageing times and then linking them to bulk adhesive layer mass uptake values determined using Fickian analysis, they universally found linear relationships between joint strength and fractional uptake - independent of whether locus of failure was cohesive or interfacial. However, it must be noted that their experiments covered virtually the complete uptake range, some adhesive layers being essentially fully-saturated. Therefore, they had no need to rely on extrapolation of limited wetness joint strength data to predict residual strengths after longer ageing times, as might be required in other modelling situations.

The same authors also encountered a nonlinearity in joint strength versus adhesive layer bulk uptake with an epoxy-nylon adhesive. Here, they found a steep drop-off in joint strength at or after the exposure time required to achieve equilibrium uptake in the adhesive layer. Therefore, this perhaps throws doubt on the idea, implied above, that there is a unique and instantaneous relationship between joint strength and water uptake.

2.5.6 Extrapolation of accelerated ageing tests

The use of bulk adhesive uptake and joint strength data obtained from accelerated laboratory tests can also be used to estimate environmental durability in cases where there is limited time in which to gather experimental information. Certainly, when considering using a new adhesive system or designing with a structure with a new joint geometry, existing data may not yet be available and it may be impractical to wait a long time to
gather durability data. However, as tempting as it would be to carry out a series of hot-absorbed adhesive joint and uptake experiments and to use the results to deduce uptake and joint strength performance in more natural environments, this technique has its pitfalls. Typically, hot-absorption can lead to irreversible mechanical property changes with certain adhesives which would not occur in more natural environments [1, 15, 34], thus possibly introducing errors in subsequent durability predictions. Also, using scaled-down models of an intended joint geometry for tests may create errors if stress fields are not subject to the same scaling and if an assumption of Fickian thickness scaling is wrongly assumed in the calculation of moisture profiles.

2.5.7 Conclusions

- there is still a great need for complete environmental durability predictive models, cohesive models being absent
- as comprehensive as Gledhill et al.'s [2] model is, it considers only interfacial degradation and also requires the prior determination of critical water concentration - this is not trivial
- Lavrentyev and Rokhlin [105] also concentrate on the modelling of interfacial degradation only
- the finite element stress analysis approach developed by Roy [55], Roy and Reddy [56, 57] and Lefebvre et al. [58] does not model the practical quasi-static mode of failure of well-designed adhesive joints, using instead a viscoelastic material model. Nor do they present supporting experimental results
3. Choice of adhesives and basic specimen preparation

This chapter introduces the adhesives used in the environmental durability studies carried out within this research. It also describes the procedure used to prepare parent thin sheet specimens, from which individual specimens were finally profiled and then used in the experimental water uptake and mechanical properties work described in Chapters 4 and 5 of this thesis. This final profiling of rough uptake or tensile test blanks cut from the parent sheets is described as appropriate in those later chapters.

3.1 Nature of the adhesives

Permabond E32 and Ciba “Araldite” AV119 epoxy resins were chosen for the purposes of this research. E32 is a two-part, nominally room temperature-cured, chalk-filled adhesive, and AV119 is a single-part, rubber-toughened, hot-cure adhesive.

E32 was chosen firstly because some existing properties data was available within the Research Group, thus augmenting any experimental data obtained here. Also, E32's mechanical properties are not over-sensitive to changes in temperature, making later tensile testing of bulk adhesive specimens at room temperature more convenient. Then, AV119 is an adhesive which has been studied by other researchers. Hence published data is fairly common and provides a background against which to judge the current research. Finally, these two materials represent two different classes of structural adhesive (cold-cure, filled and hot-cure, unfilled), thus providing the opportunity of generating a useful range of durability data and models.
3.2 Bulk specimen preparation

For the purposes of the experimental water uptake and subsequent mechanical properties measurement work on the two chosen bulk adhesives, relatively thin specimens were used. The reason for using relatively thin specimens for both sets of experimental work was that the uptake process is known to be slow, thin specimens helping to ensure realistic absorption times for required uptake levels. With regard to the later mechanical properties work on wet adhesive, it was intended to expose ready-profiled tensile specimens. Thus, mechanical test specimens were required to be thin also. Bearing in mind that a typical Fickian diffusion coefficient for a polymer might be of the order of $10^{-13} \text{ m}^2\text{s}^{-1}$ from liquid water at about 20 °C., this suggests an exposure time of approximately one month for a film 1.0 mm thick to reach 95% of maximum water content. Therefore, in order to make the absorption process quick enough to fit into the timescales available whilst still being able to prepare and handle the specimens efficiently, it was decided to make specimens of both adhesives approximately 0.4 mm thick for the bulk of the experimental studies carried out here. During the later stages of the water uptake work, it was decided specifically to investigate the effect of specimen thickness on the rate of diffusion. For these experiments, thicker parent bulk adhesive sheets were required. However, the procedure employed to prepare these sheets was essentially identical, only differing in the thickness of spacing shims used with the plate mould described shortly.

To prepare parent sheets of bulk E32 or AV119, a small mound of adhesive was ejected from the cartridge and pressed between the upper and lower plates of a two-piece mould assembly shown in Figure 3-1. These plates were each 25 mm thick and 200 mm square, ground flat on the inner faces and being made of mild steel. A caphead bolt was used at each corner to force the plates together onto the mound of adhesive and a silicone-coated “Melinex” film lining placed between the adhesive and the plate surfaces was used to prevent bonding of the adhesive to the mould itself. Suitably sized pieces of silver steel gauge plate were used to space the two mould plates apart at the required specimen thickness.
Chapter 3: Choice of adhesives and basic specimen preparation

Side View: plates 25 mm thick by 200 mm square

4 x M12 caphead bolts
2 x ground mild steel mould plates

4 x peripheral spacers
Silicone-coated Melinex film

mound of adhesive

Figure 3-1 Sketch of mould plate assembly used to prepare bulk adhesive specimens

Before each mound of adhesive was laid onto the Melinex-lined bottom plate prior to fitting the top plate, the cartridge of either E32 or AV119 was preheated in a temperature-controlled oven in order to reduce viscosity of the adhesive and so ease application and spreading. This cartridge preheating was carried out for 30 minutes at 40 °C. for both adhesives.

It was also found that air pockets tended to be introduced into the adhesive as it was squeezed from its cartridge onto the mould plate. This was minimised by keeping the cartridge nozzle under the surface of the mound of adhesive as it formed. Air was also found to be present within the adhesive as supplied. However, with careful selection, void-free rectangular uptake or tensile test blanks could successfully be cut from the parent sheets.

In the case of E32, being a two-part adhesive which is dispensed from a double-barrelled cartridge via a mixing nozzle, it was found that even the longer of the two available nozzles did not give full mixing, this being obvious even on a visual level. To prevent this problem, two of the longer 150 mm mixer nozzles were cut and joined together with adhesive tape. This gave an extended mixer nozzle approximately 230 mm in length and resulted in much better mixing of the resin and cross-linking agent. Once the mound of
either E32 or AV119 was laid, the upper Melinex lining and top mould plate were positioned, the gauge plate spacers were inserted round the mould edges and the four caphead bolts were evenly tightened in order to squeeze the adhesive down to the correct thickness. At that point, the mould plate assembly was ready to be placed into the oven for the main cure, as described below.

3.3 Curing of E32 and AV119 bulk specimens

In order to ensure consistent mechanical properties of the two adhesives, curing procedures were standardised. Being a nominally room-temperature cure adhesive, E32 was cured at 40 °C. in an oven for 48 hours in order to be certain of full cure. As this curing time was relatively long, it was decided that there was no need to preheat the thick steel mould plates. At the end of the cure, the mould plate assembly was removed from the oven, the caphead bolts removed, the Melinex film lining carefully peeled off and the adhesive sheet labelled and placed into a desiccator for storage and later use.

Being a hot-cure adhesive, the AV119 thin film specimens were cured by placing the mould plate assembly into an oven set at 120 °C. Following previous practice in the Group, it was required to expose the adhesive film itself to two hours at 120 °C. However, initial heating and cooling rate tests suggested that the heavy steel mould plate assembly had a large thermal inertia. Figures 3-2 and 3-3 show these heating and cooling characteristics. For these tests, the mould plate assembly was placed into an oven preheated to 120 °C for heating; for the cooling cycle, the oven was switched off, the door left closed and the oven left to cool naturally before removal of the mould. In order to measure local adhesive sheet temperature, a thermocouple was embedded in a dummy mound of adhesive and a digital meter used to log the output. During the heating and cooling cycles, temperature was recorded every minute for later plotting against time. Although the high thermal inertia rendered it impossible to expose the curing adhesive to a step of 120 °C. for the required time, the characteristics shown in Figures 3-2 and 3-3 suggested that a total oven time of three hours would ensure that the adhesive layer experienced between 115 and 120 °C. for the required two hours.
Figure 3-2 Heating characteristics of mould plate assembly for the curing of AV119

Figure 3-3 Cooling characteristics of mould plate assembly for the curing of AV119
After the mould plate assembly had cooled sufficiently for handling following the cure (perhaps as long as twenty hours after switching the oven off), the mould was removed from the oven and then split in order to remove the adhesive film. This was then labelled and put into a desiccator for drying.

As mentioned earlier in this chapter, final profiling of individual water uptake and tensile test specimens from the above parent bulk adhesive sheets is described in the appropriate chapters later in this thesis. In preparation for that stage, however, rough rectangular blanks were manually cut from the parent sheets, typically obtaining three or four blanks per sheet.
4. Water Uptake by adhesives

The uptake part of this research project lies at the very basis of the proposed approach to modelling the environmental durability of bonded joints. The literature universally agrees that it is the absorption of water into the adhesive layer of a joint which causes structural degradation and consequent reduction in residual strength or service life of the joint. Therefore, to measure and then to be able to characterise the moisture uptake behaviour of adhesives provides the foundation to the later mechanical properties and structural modelling stages of the proposed approach to durability prediction.

The moisture uptake work falls clearly into two categories, these being experimental studies and subsequent modelling of the observed behaviour. Based on an initial programme of gravimetric experimental uptake studies with E32 and AV119, an investigation of the classical Fickian diffusion model formed the basis of the analytical uptake work. Many authors [4, 15, 16, 26, 28, 29, 34, 36, 37, 38] state that Fick's laws adequately describe the absorption of moisture by adhesives, however this work set out to fully test this model for the adhesives chosen here. As part of this analysis of the Fickian model, uptake experiments have been carried out using a range of specimen thicknesses in order not only to test for correct profile of individual uptake plots but also to test for Fickian response to varying specimen thickness. The majority of the literature would appear to accept the basic Fickian model with its response to varying specimen thickness, however the possibility of a non-Fickian thickness effect has important implications when modelling the durability of adhesive joints. If underlying uptake behaviour has been measured using thin bulk adhesive specimens, predicting the moisture profile in the deep adhesive layer of a joint using the basic Fickian model could lead to large errors. Therefore, to build in thickness effects, time-dependent boundary conditions were investigated as an addition to the basic Fickian model.

As allowed in Fickian uptake, the effect of concentration-dependent diffusion coefficient has also been investigated. This study was undertaken bearing in mind Fujita's [40] hint at the relative lack of movement in modelled uptake plot in response to introducing a concentration-dependence of diffusion coefficient. If, for example, introducing such a
dependence can be shown to have little effect on uptake behaviour, then this can be 
discounted as a reasonable explanation for experimental observations of pronounced 
deviations from the Fickian diffusion pattern.

In addition to the thickness response which is inherently part of the basic form of the 
Fickian model, the effects of absorption temperature and applied stress have been 
investigated. Apart from the testing of conformity to uptake models, the provision of hot-
absorbed uptake data has important consequences for overall durability modelling.
Accepting the literature's view that that diffusion coefficient, and perhaps equilibrium 
uptake, increase with increasing temperature, target moisture levels can be achieved much 
more quickly if accelerated uptake tests are allowed. Thus, if the elevated absorption 
temperature itself does not otherwise influence the adhesive, the use of accelerated 
experiments can vastly speed up the acquisition of residual joint strength data. Therefore, 
as groundwork for the later durability work presented in this thesis, uptake was measured 
both at room temperature and at 55 °C.

As the overall aim of this research is to model sequentially exposed and then loaded 
bonded structures, the stressed uptake work is not carried forwards beyond this chapter. 
However, stress effects investigated here will be incorporated into future fully-coupled 
durability modelling work, where the environmental degradation of simultaneously loaded 
and exposed joints will be predicted.

In addition to using the basic Fickian model as a vehicle to study the effects of absorption 
temperature, specimen thickness, concentration-dependent diffusion coefficient and 
applied stress, two-stage models were also investigated. Various authors [21, 28, 40, 41, 
45, 46] have observed generally low-lying uptake behaviour with initial partial 
equilibration followed by a secondary uptake stage, this behaviour often being attributed to 
a simultaneous relaxation process and not being able to be described by a purely single-
stage diffusion model.

In summary, this modelling work was carried out in order both to understand the 
underlying mechanisms of the process and to provide a mathematical representation of 
uptake behaviour for linking to degraded cohesive mechanical properties and use within 
the proposed overall durability model. In this chapter, the water uptake studies are
arranged in the order of experimental work followed by theory and available models. The application of these models to characterise the experimentally observed uptake behaviour for both adhesives then concludes this chapter.

**Special note**

In this chapter, classical Fickian diffusion has been used throughout as a basis for the moisture uptake modelling part of the work. However, as various modifications to the most basic Fickian form have been investigated, terms have been introduced here accordingly. To avoid possible confusion between similar uptake model variants, the following note aims to provide some introductory definitions.

Fickian diffusion essentially defines a flow or flux of diffusant which is locally and instantaneously proportional to the spatial diffusant concentration gradient, as defined later in Equation (3). Thus, Fickian diffusion merely describes the diffusion behaviour within the bulk of a piece of substrate material. However, it is meaningless as a complete solution unless a boundary condition is specified. Therefore, practical literature tends to present various forms of the Fickian uptake model with such a boundary condition.

Any complete form of Fickian diffusion in an infinitely large plane sheet exposed on both surfaces to moisture is therefore effectively defined by two things. These are the coefficient of proportionality controlling the flux in the bulk material (the diffusion coefficient) and the rate of equilibration of the surfaces of the sheet. In the most basic form of Fickian uptake commonly adopted by the literature, the boundary equilibration is taken to be instantaneous and the diffusion coefficient constant. Throughout this chapter, the term "simple Fickian" diffusion refers to this case. Moving one step further, Fickian diffusion also allows a concentration-dependent diffusion coefficient. General use of the unqualified "Fickian" term will refer to such a case where the diffusion coefficient may vary.

Making changes to the default instantaneous boundary equilibration condition represents a move less commonly considered in the durability literature. For this reason, any modification to a time-dependent boundary condition will always be specifically qualified in the text. For example, the phrase "Fickian diffusion with exponential time-dependent
boundary condition" refers to that particular boundary condition combined with either constant or concentration-dependent diffusion coefficient. Often, individual references to Fickian-based uptake models will be defined locally in detail.

4.1 Experimental programme

In order to provide a basis for the later development of mathematical models for the water diffusion behaviour of bulk adhesives, the absorption behaviour of both E32 and AV119 was measured experimentally, with a view to investigate possible stress and thickness effects. For reasons of convenience and to follow convention, it was decided to use a gravimetric technique, as described well by Shen and Springer [18]. Using this method, bulk specimens are exposed to the required environmental conditions and occasionally weighed in order to estimate the absorption of water. Although this technique can only give estimates of bulk mass uptake and not the local absorbed moisture profile and although it does not differentiate between uptake and mass loss due to leaching, this method is fairly easy to implement in the laboratory.

Other uptake measurement techniques have been proposed [33], including reflection coefficient sensing viscosity-dependent fluorescence infra-red spectroscopy and dielectric spectroscopy. However, these methods were discarded for the purposes of this research as they also have limitations, tend to be costly and are complicated to implement.

4.1.1 Organisation of uptake tests

In organising the gravimetric uptake test schedule, it was necessary to address various issues. These included choice of stress levels, choice of thicknesses, specimen sizing and preparation, what ageing environments to choose and other details of the gravimetric experimental programme.
4.1.1.1 Choice of environmental exposure conditions

Two temperatures were chosen at which to investigate the unstressed water diffusion behaviour of the two adhesives under examination. Room temperature ("RT"), of 22 °C., was chosen in an attempt to simulate realistic environmental exposure. The temperature of 55 °C. ("Hot") was also chosen, as the diffusion process, including equilibration, is faster at that temperature, enabling useful uptake results to be obtained more quickly and the possibility of using accelerated uptake tests within the overall context of durability studies. Perhaps for this reason, many other researchers have also carried out diffusion experiments at similar temperatures, resulting in good availability of data. It had to be borne in mind, however, that using an artificially high absorption temperature may irreversibly affect the subsequent room temperature mechanical properties of the chosen adhesives. The validity of the accelerated tests was addressed when bulk adhesive mechanical properties data had been obtained later on in the research. Note that the effect of absorption temperature on uptake behaviour was investigated using unstressed specimens of a single approximate thickness. Thus, no hot-absorbed stress or specimen thickness investigations were undertaken here.

Mainly for convenience purposes and also to encourage reasonable levels of equilibrium uptake, absorption was carried out from liquid distilled water, as opposed to air/water vapour mixtures at various RH values. A compact temperature chart recorder was used to monitor room temperature for the appropriate tests, giving a continuous record of ambient temperature during periods of uptake testing. From these records and for the purposes of all work in this project, room temperature was found to be 22 ±1 °C.

For the tests at 55 °C, a thermostatically controlled oven was used to keep vessels containing test specimens at the required temperature. A thermometer was placed in the oven near the vessels in order to measure the temperature accurately. The oven temperature was found to vary from the 55 °C. average by a range of ±2 °C. Also, loose aluminium foil covers were placed over the tops of the vessels to prevent excessive evaporation of distilled water at the higher temperature.
4.1.1.2 Choice of loading levels for stressed uptake tests

Although it was never intended to carry out an intensive study of stressed diffusion or to use the results within the proposed durability modelling programme, a limited series of experimental room temperature uptake tests using specimens in the thinnest category (see later) was undertaken. As it was preferred to use relatively thin uptake specimen, as discussed later, and as such thin specimens would be prone to buckling under compressive loads, all specimens in this programme were tested in tension. Also, only one thickness of specimen (approximately 0.4 mm) was used for these stressed uptake tests so as not to confuse any stress effect with thickness effect. After reference to Gomersall et al. [108], who suggest that minimal creep effects occur with AV119 at load levels less that 50% of ultimate tensile strength (UTS), it was decided that two non-zero load levels of 25% and 50% of a typical wet UTS value should be used for both adhesives studied here. In addition to unstressed reference tests, preliminary thin bulk dogbone tensile test results suggested approximate applied tensile stress levels of 8 MPa and 16 MPa for AV119 and 6 MPa and 12 MPa for E32.

After some time and before equilibrium uptake had been achieved, however, both the stressed E32 specimens broke, the more highly-stressed specimen breaking relatively early on during absorption. This suggested that E32 was not very resilient under simultaneous environmental and stress conditions, calling for a specimen to be tested at an even lower stress level. Thus, a target of 2 MPa was chosen for a new specimen, this representing only about 8% of the adhesive's preliminarily-measured wet UTS value. Therefore, within this programme of stressed, room temperature uptake experiments using ~0.4 mm specimens, and in addition to reference unstressed specimens of similar thickness, two AV119 specimens and one E32 specimen were tested essentially to full-term. With regard to the failed medium-stressed E32 specimen (target 6 MPa), some useful uptake data was obtained. Finally, as the most highly-stressed E32 specimen broke relatively early, this test gave minimal useful data.

As the specimens were loaded by means of fixed masses, the target stress levels above were not achieved precisely. However, the actual values are summarised along with all other uptake test schedule information later in Table 4-1.
Stressed uptake test set-up

Although an unstressed uptake specimen could simply be immersed in a beaker of distilled water, the apparatus requirements for the stressed experiments needed more thought. It was necessary to immerse a specimen completely in water whilst at the same time applying a constant tensile load. It was decided that loads should be applied simply by suspending dead-weights from the ends of specimens, making use of specially-designed self-locking end grips and a framework. In addition to ease and speed of attachment and release, these end grips were designed to hold the specimen close to its extreme ends, thus minimising unstressed regions. The framework was then placed in a plastic container of approximate dimensions 100 x 300 x 300 mm. This was then filled with distilled water. The stressed specimens took longer to extricate from the apparatus than the freely immersed unstressed specimens, thus going against the need for a quick gravimetric measurement cycle time in order not to overly disturb environmental exposure. However, the apparatus was designed to allow relatively easy removal and replacement of specimens. This apparatus for the stressed tests is shown in Figure 4-1.

Figure 4-1 Apparatus for carrying out stressed uptake experiments
4.1.1.3 Choice of uptake specimen thickness and other dimensions

In order to measure the water uptake behaviour for an isotropic material, it is usual to use plane films of the bulk material in order to force the process to be essentially one dimensional. Also, as the uptake process is generally very slow, relatively thin specimens are used. As we shall see later, this has implications with respect to various potential thickness effects. Firstly, as thick specimens cannot be used for reasons of excessively long uptake test durations, the dependence of uptake on specimen thickness can never realistically be fully investigated. Secondly, if thin tensile test specimens are used (as they can be absorbed to target moisture levels fairly quickly), any thickness-dependence of mechanical properties will not be measured, either. However, certainly to investigate thickness-dependent uptake effects, it was decided to test a range of specimen thickness - whilst still retaining sensibly short uptake test durations. Thus, nominal guideline target specimen thicknesses were chosen to be 0.4, 0.8 and 1.5 mm. Also, the effect of thickness on uptake behaviour was investigated on the basis of unstressed, room temperature absorption experiments only. As for the specimen plan, a simple rectangular shape was chosen with dimensions 80 x 30 mm. This specimen size rendered the thickness-to-surface area ratio suitably small, ensuring that the diffusion process is essentially one-dimensional. As with the actual load levels for the stressed uptake experiments, the actual specimen thicknesses varied slightly from their planned target values due to the nature of the mould system used. Again, all the relevant uptake schedule information can be found below in Table 4-1.

4.1.1.4 Summary of test schedule

Table 4-1 below summarises the various temperature, specimen thickness and applied stress combinations investigated within the uptake test programme. Again, it can be seen that the effect of temperature on uptake behaviour was investigated using unstressed specimens of the smallest thickness (~0.4 mm). The effect of thickness was then investigated by way of room temperature-absorbed, unstressed specimens. Finally, the effect of stress was investigated using ~0.4 mm-thick, room temperature-absorbed specimens.
Chapter 4: Water uptake by adhesives

Table 4-1 Summary of Overall Uptake Test Schedule

<table>
<thead>
<tr>
<th>Specimen ID</th>
<th>Adhesive</th>
<th>Absorption Temperature (°C.)</th>
<th>Specimen Thickness (mm)</th>
<th>Actual Applied Tensile Stress (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H01*</td>
<td>E32</td>
<td>22</td>
<td>0.36</td>
<td>0</td>
</tr>
<tr>
<td>R12*</td>
<td>E32</td>
<td>22</td>
<td>0.47</td>
<td>0</td>
</tr>
<tr>
<td>R19</td>
<td>E32</td>
<td>22</td>
<td>0.43</td>
<td>2.2</td>
</tr>
<tr>
<td>R13**</td>
<td>E32</td>
<td>22</td>
<td>0.45</td>
<td>6.2</td>
</tr>
<tr>
<td>R14**</td>
<td>E32</td>
<td>22</td>
<td>0.45</td>
<td>11.8</td>
</tr>
<tr>
<td>R15</td>
<td>E32</td>
<td>22</td>
<td>1.56</td>
<td>0</td>
</tr>
<tr>
<td>H02</td>
<td>E32</td>
<td>55</td>
<td>0.36</td>
<td>0</td>
</tr>
<tr>
<td>R01*</td>
<td>AV119</td>
<td>22</td>
<td>0.42</td>
<td>0</td>
</tr>
<tr>
<td>R02*</td>
<td>AV119</td>
<td>22</td>
<td>0.41</td>
<td>0</td>
</tr>
<tr>
<td>R04</td>
<td>AV119</td>
<td>22</td>
<td>0.42</td>
<td>7.2</td>
</tr>
<tr>
<td>R05</td>
<td>AV119</td>
<td>22</td>
<td>0.41</td>
<td>16.7</td>
</tr>
<tr>
<td>R17</td>
<td>AV119</td>
<td>22</td>
<td>0.88</td>
<td>0</td>
</tr>
<tr>
<td>R08</td>
<td>AV119</td>
<td>22</td>
<td>1.54</td>
<td>0</td>
</tr>
<tr>
<td>H04</td>
<td>AV119</td>
<td>55</td>
<td>0.39</td>
<td>0</td>
</tr>
</tbody>
</table>

* Duplicate thin, unstressed, room temperature-absorbed E32 or AV119 specimens.
** These stressed uptake specimens broke prematurely, giving only limited useful data.

4.1.1.5 Preparation of uptake specimens

Using the mould plate assembly described in Chapter 3 earlier gave large, plane, uniform films of adhesive, the thickness being controlled by the use of spacers placed around the periphery. Individual uptake specimens were then cut from these parent sheets by scoring with a sharp blade and then manually snapping out the rectangles. Whilst avoiding unnecessary contamination with grease, etc., the edges of each uptake specimen were lightly abraded with sandpaper in order to remove loose pieces of adhesive which might otherwise fall off during the uptake test and result in gravimetric errors. The main faces of each specimen were then cleaned with Inhibisol degreasant in order to remove any traces of dirt or grease which might have inadvertently come into contact with the specimen during handling. Specimens were then dried in an oven at 40 °C. and then stored in a desiccator at room temperature for at least a week before commencing uptake testing.

4.1.1.6 Gravimetric uptake measurement technique

For the purposes of environmental ageing, rectangular specimens of both adhesives, prepared as described above, were simply immersed in containers of distilled water at the
required temperature. For an unstressed test, it was adequate simply to immerse a specimen in a beaker filled with water, although a stressed test required the more complex apparatus for the application of load under water, as described earlier. Water uptake was determined by periodically removing a specimen from the water, blotting the surfaces dry with analytical grade tissue paper and then weighing using a Mettler M5 analytical microbalance. This approach is commonly accepted practice and is reported well in the literature [18]. Using this method does, however, make the assumption that any observed mass gain is attributable only to the absorption of water by the specimen. It is also assumes that no component of the immersed polymer is dissolved and leached out by the water, although this has been observed by other authors, as discussed in the Literature Review chapter. Another potential problem with this gravimetric technique is the possible evaporation of water from the specimen during weighing. However, at the level of accuracy being used here, stability of quickly-repeated mass readings suggested this was not a significant effect.

Although the Mettler M5 microbalance has a resolution of 1 µg, this level of accuracy was not required. As the anticipated equilibrium mass gain of a typical adhesive was expected to be several percent of its original dry mass and as a typical uptake specimen might weigh just a few grams, it was decided that recording specimen mass only to the nearest 0.1 mg would be sufficient to achieve satisfactory accuracy of results. Before use, the balance was physically levelled and calibrated to zero before weighing each specimen. The zero calibration was then re-checked after each weighing was completed.

Care was taken not to cause significant evaporation of water absorbed within the bulk of the adhesive by avoiding excessive heating due to manual handling and by returning the specimen to its beaker of water as soon as possible after removal and weighing. Thus, if a series of specimens was scheduled to be weighed in the same session, each individual specimen was removed, weighed and replaced before moving onto the next one, as opposed to leaving all the specimens to be weighed out of water for longer than necessary. After blotting the surfaces dry, and following Brewis et al. [26], an anti-static gun was used to remove the charge on the specimen, as it had been found from preliminary uptake tests that a specimen receiving a static charge during blotting caused the microbalance to give large and erratic errors. As another anti-static safeguard, each specimen to be weighed
was placed inside a simple aluminium foil folder. This folder was weighed beforehand and its mass subtracted from the recorded combined mass value in order to determine the specimen mass. Each weighing was repeated at least twice, whilst making sure to return the specimen to its beaker of water as quickly as possible to reduce the effects of disturbing the uptake process. Between each weighing of the same specimen, it was removed from the foil folder, dusted, statically discharged, replaced into the folder and reweighed to confirm the specimen mass.

Each initially dry specimen was weighed immediately after being taken from previous storage in a desiccator before the beginning of its uptake test. As the uptake process is non-linear, starting off quickly and then moving towards equilibrium, appropriate time intervals were chosen. Furthermore, it was found that the choice of weighing interval was best made on the basis of previous preliminary trial uptake tests. Therefore, weighing was carried out every few hours for a room temperature test at first but slowing down to intervals of more than a week as each test progressed. Uptake tests at 55 °C. were observed to have reached equilibrium uptake much more quickly, approximately one week after the start of the test. Thus shorter weighing intervals were required for the hot tests, i.e. controlling the weighing interval enabled a balance to be struck between over-disturbance of the specimens, perhaps resulting in artificially low uptake measurements, and obtaining too few data points on the uptake curve.

### 4.1.2 Experimental results

The results of the overall uptake test programme will be discussed in the following categories, noting changes in uptake curve shape:

- basic uptake behaviour, including effect of temperature
- effect of specimen thickness
- effect of applied stress

As explained earlier, the default uptake parameters used within this programme of work consisted of a specimen thickness of approximately 0.4 mm, room temperature absorption and zero applied stress. Therefore, for investigation of the effect of absorption temperature,
thickness or applied stress, the relevant parameter was varied whilst the others were left at their default values. Note that all specimens which fall approximately within one of the three chosen nominal target thickness categories, even though there may be a small variation, are regarded as having the same thickness for initial analysis purposes.

As it is both conventional and useful to discuss experimental uptake characteristics within the context of a formalised theoretical or modelling background, and although the theory of diffusion is presented later in this chapter, it helps in the following sections to be able to refer to the classical Fickian pattern of water uptake. As discussed briefly in the Literature review chapter of this thesis, basic Fickian diffusion requires instantaneous specimen boundary equilibration and describes local diffusant flux (controlled by a coefficient of diffusion) in a substrate material and thus defines a specific shape of uptake curve. Furthermore, although Fickian uptake allows for a concentration-dependent diffusion coefficient which results in slightly increased flexibility in the shape of the uptake curve, references in this thesis to "simple Fickian uptake" refer specifically to the single, fundamental, constant diffusion coefficient Fickian curve shape. Other behaviours will be considered in a later section. Again, as described in the Literature review chapter, such a simple Fickian uptake curve is usually plotted as mass uptake or fractional uptake (mass uptake divided by equilibrium uptake) against the square root of time. Describing the shape of an uptake curve plotted in this way, simple Fickian uptake defines an initial linear region extending to at least 0.6 fractional uptake, the slope of which is directly related to the value of the diffusion coefficient. This is then followed by a reasonably rapid slowing down and equilibration of uptake. Note that this curve is linearly scalable but it has only one unique mathematical shape. Another crucial characteristic of the Fickian uptake curve shape is that, even for a case of variable diffusion coefficient (whether it is a function of concentration, time or position), there is still only one curve shape for a range of specimen thickness if the horizontal axis is plotted as the square root of time divided by specimen thickness or half-thickness, $\sqrt{t/l^2}$. Thus, for any truly Fickian uptake situation with instantaneously equilibrating boundary condition, this thickness scaling property is a firm requirement and a test of whether experimental uptake conforms to this model. Therefore, the standard approach taken here will be to plot $\sqrt{t/l^2}$ on the horizontal axis, this immediately making clear any non-Fickian thickness effect.
4.1.2.1 Basic experimental uptake behaviour

Here we are looking at the room temperature and hot experimental uptake behaviour for both E32 and AV119. Again, comparing for now only the ~0.4 mm, unstressed specimens, this includes specimens H01, H02, H04, R01, R02 and R12. Note that specimens H01/R12 and R01/R02 represent duplicate test sets carried out to check the consistency of the experimental gravimetric uptake measurement technique. These experimental results are plotted in Figure 4-2.

![Figure 4-2 Basic RT and Hot experimental uptake using unstressed, thin specimens](image)

This figure shows immediately that the duplicate room temperature E32 and AV119 specimen sets produced essentially identical pairs of uptake curves, helping to confirm the accuracy of the experimental technique itself. Then, the figure shows that increasing the absorption temperature leads to an increase in the rate of water uptake, although any trend in equilibrium uptake is not absolutely certain. Although the literature suggested varying characteristics, the findings here seem to be consistent with the majority view. This is that rate of uptake generally increases and equilibrium uptake sometimes increases with increasing temperature. Note particularly that the hot-absorbed E32 curve shows a fundamentally different behaviour with initial peaking of specimen mass followed by a
very marked fall-off before apparently approaching an overall equilibrium. This type of behaviour has been reported in the literature [28] and tends to be a characteristic of absorption from liquid water at relatively high temperatures, in which case components of the adhesive can be leached out. Thus, a water uptake process occurs simultaneously with a mass transfer process, confusing the interpretation of experimental gravimetric uptake data.

When taking into consideration that E32 is chalk-filled and that chalk is effectively water-soluble, it is suggested that perhaps the chalk (or some other component of the adhesive) is leached out, resulting in the observed eventual mass decrease. It is interesting to consider whether the same type of behaviour would have eventually been observed at the lower temperature if time had been permitting, although perhaps the shape of the uptake curve did suggest that a single equilibrium condition would genuinely be achieved at this temperature. However, this unconventional and ambiguous behaviour of hot-absorbed E32 is one reason why further treatment of E32 is limited later in this work.

Although no formal comparison with mathematical uptake models is discussed at this stage, reference to the standard simple Fickian curve shape in Figure 2-5 of the Literature Review chapter gives an initial suggestion that the remaining experimental uptake curves for both adhesives may not conform to this model. Indeed, they consistently fail to show the linear then rapidly equilibrating behaviour of the simple Fickian model. Furthermore, as Fujita [40] suggests that a concentration-dependent diffusion coefficient can only ever slightly adjust the shape of simple, constant diffusion coefficient Fickian uptake, it looks unlikely that even that could be responsible for the shallow shape of most of the experimental uptake data seen here. As is discussed both in the Literature Review chapter and in later sections of the current chapter, the introduction of a concentration-dependent diffusion coefficient gives at best only moderate levels of flexibility of shape to the Fickian uptake curve.

These basic thin, unstressed uptake results show unusual behaviour, the room temperature results for both adhesives perhaps not even having reached equilibrium. However, Table 4-2 attempts to give an estimate of equilibrium uptake values as well as time to reach equilibrium although more formal application of uptake models and parametrisation of experimental uptake data is presented later in this chapter.
As discussed earlier, formal characterisation and modelling of the observed uptake behaviour of E32 and AV119 is reserved for later sections of this chapter. Thus, further presentation of diffusion parameters such as diffusion coefficient and equilibrium uptake values will be carried out then. However, it is already apparent at this stage that the chosen adhesives display unconventional uptake behaviour and will require an in-depth modelling approach.

<table>
<thead>
<tr>
<th></th>
<th>Equilibrium Uptake (%)</th>
<th>Time to Achieve Equilibrium (weeks)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E32 (RT)</td>
<td>9.7</td>
<td>300***</td>
</tr>
<tr>
<td>E32 (Hot)</td>
<td>7.1*</td>
<td>0.3/14**</td>
</tr>
<tr>
<td>AV119 (RT)</td>
<td>5.1</td>
<td>&gt;350***</td>
</tr>
<tr>
<td>AV119 (Hot)</td>
<td>6.6</td>
<td>3</td>
</tr>
</tbody>
</table>

* This value obtained using Brewis et al.'s \[28\] of back-extrapolation of uptake curve to uptake axis for calculation of equilibrium uptake (and determination of diffusion coefficient).

** Time to reach mass peak followed by time to achieve final, complete equilibrium

*** Estimated

Table 4-2 Estimates of equilibrium uptake and time taken to achieve equilibrium for ~0.4 mm thick, unstressed E32 and AV119

4.1.2.2 Effect of specimen thickness

Here, unstressed, RT-absorbed specimens of different thickness were used for the investigation of effect of thickness on uptake. Bearing in mind the simple Fickian characteristics of thickness scaling, as described earlier, that uptake curves for all thicknesses of specimen of a certain material absorbing from water at a given temperature (and at a certain applied stress level) should follow one single locus in the \( U \) v. \( \sqrt{t/l^2} \) plane, this subset of uptake tests was seen as important and potentially illuminating. Indeed, in addition to the analysis of basic uptake curve shape, the conformity, or otherwise, to the Fickian thickness constraint provides another solid test of uptake régime.

With the reference unstressed, ~0.4 mm, room temperature-absorbed specimens from §4.1.2.1 included, using only the R12 duplicate for E32 and the R02 duplicate for AV119, Figures 4-3 and 4-4 show the effect of specimen thickness on the experimental uptake behaviour of E32 and AV119.
During the timescales available to this research, equilibrium uptake levels (which we would expect to be the same for all thicknesses of the same adhesive) have not been achieved for the thicker specimens for either adhesive. However, it is immediately obvious from the early behaviour that both E32 and AV119 display a non-Fickian thickness scaling of uptake curve. As the specimen thickness for both adhesives increases from approximately 0.4 mm to 1.5 mm, plotting mass uptake against $t/l^2$ gives a clear movement of the locus of curve. Again, this is fundamentally non-simple Fickian. Indeed, and as discussed in the theory and modelling sections, the behaviour seen for both adhesives is neither simple-Fickian nor Fickian with variable diffusion coefficient. Looking at the figures more closely, the results for E32 and AV119 show consistently that an increase in specimen thickness drives the uptake curve progressively higher, tending to suggest a genuine effect. Thus, we appear to have a non-Fickian thickness effect on uptake and this is discussed in more detail in the modelling sections of this chapter. Note that equilibrium uptake levels for unstressed, room temperature absorbed E32 and AV119 are indeed assumed to be independent of thickness for later analyses in this thesis.

![Figure 4-3 Dependence of uptake on specimen thickness for E32 (RT, unstressed).](image)
4.1.2.3 Effect of applied stress

Although having no place in the later durability modelling stages of this research, the effect of applied stress on water uptake was studied in order more fully to understand diffusion and to prepare the ground for future fully-coupled diffusion-structural analyses. For the purposes of the stressed uptake programme of tests, ~0.4 mm, room temperature-absorbed specimens of both E32 and AV119 were used. Similarly to before, Figures 4-5 and 4-6 show the effect of applied stress on the uptake behaviour of the two adhesives.

As noted in the figure for E32, relatively highly loaded specimens R13 and R14 broke prematurely, therefore limiting the amount of useful information available. Then, concentrating on the remaining results for this adhesive, the data fails to show a clear increase in rate or equilibrium level of uptake. Note that, as diffusion coefficient is a function of the initial slope of the uptake curve scaled against equilibrium uptake, it is actually not certain whether this is increased (i.e. plotting percentage mass uptake and observing an increase in both equilibrium uptake and initial slope might result in no change of diffusion coefficient, \textit{per se}).
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Figure 4-5 Dependence of uptake on applied stress for E32 (RT, thin)

Figure 4-6 Dependence of uptake on applied stress for AV119 (RT, thin)

However, being prepared to trust the small amount of pre-failure uptake data obtained from the most highly stressed Specimen R14 (11.8 MPa), there does appear to be a definite indication that increasing the applied stress level does indeed tend to increase both the rate and equilibrium value of uptake. In the case of the relatively lightly loaded Specimen R19
(2.2 MPa), though, this seems to display a lower rate and equilibrium uptake value. However, one must ask whether experimental error is to blame for this apparent feature.

Moving onto AV119, the data seems more consistent than in the case of E32, although the situation may have been helped by the fact that the stress levels were higher and none of the three specimens tested failed prematurely. So, for AV119, it would appear that an increase in applied stress leads to a consistent increase in both rate and equilibrium level of uptake. Again, and for the same reasons as explained above, any trend in diffusion coefficient is not certain, although it can always be calculated (assuming uptake conforms to the Fickian model in the first place) from the rate and equilibrium value.

Again, this investigation into stress effects on uptake is not to be carried further for the purposes of the current research. However, this preliminary work does seem to have initially confirmed that an increase in applied stress generally increases the rate at which moisture is absorbed into adhesive materials. This, then, potentially has a knock-on effect on the rate of degradation of simultaneously loaded and exposed adhesive joints and therefore requires appropriate allowance in such a durability model.
4.2 Uptake theory and modelling

In the following sections, classical diffusion theory as well as some adaptations are presented. This available theory has then been applied to the previously presented experimental uptake behaviour recorded for E32 and AV119 in order to characterise the observed behaviour mathematically and therefore to be able to incorporate it in the proposed broader finite element durability model. In presenting the theoretical water uptake models that have been investigated for this research, a division between bulk effects and surface effects has been visualised, both of these elements giving different key characteristics to the shape of the uptake plot. In the case of the uptake behaviour in bulk adhesive materials, classical Fickian uptake has been used as a foundation stone, concentration-dependent diffusion coefficient also having been considered. However, in consideration of experimental observations of non-Fickian uptake, especially two-stage behaviour, dual sorption model combinations have also been investigated. Leading on from suggestions in the literature that uptake can be influenced by a relaxation process occurring in parallel with the diffusion process, a dual model consisting of Fickian diffusion superposed on a relaxation-controlled uptake component has been considered. For the purposes of that investigation, the functional form of the relaxation component suggested by Berens and Hopfenberg [46] has been used. For reasons of ease of finite element implementation, a dual Fickian diffusion model has been compared to the Fickian diffusion-relaxation model.

Bearing in mind the pronounced non-Fickian thickness scaling effect observed in the experimental uptake programme described earlier, more complex boundary conditions than the standard instantaneous equilibration condition have been investigated. As discussed in the Literature review chapter of this thesis, Crank [39] presents various gradually developing boundary concentration conditions, which he combines with constant diffusion coefficient Fickian diffusion in the bulk material. As appropriate, the above uptake model variations have been studied parametrically in order to understand their fundamental characteristics. Depending on the form of the equations defining each model under consideration, solution methods have been suggested. The final intention is to implement selected models within the parent finite element framework chosen for the overall durability modelling research. However, for the purposes of studying the characteristics of
the various uptake models outside of the wider durability modelling environment, spreadsheet solutions and FORTRAN-coded finite difference solution schemes have been developed.

Once the various chosen uptake model components and their characteristics have been described, they have been selectively applied to the experimental uptake data in order to achieve sufficiently accurate mathematical characterisations for use in the later durability modelling stages. If custom writing of special uptake analysis modules is to be avoided, then chosen models must conform to those already available within ABAQUS. Therefore, even if one model is more mechanistically sound, a close alternative may finally be chosen for implementation reasons.

4.2.1 Single-stage uptake models

Although single-stage uptake models cannot be used to characterise experimentally observed two-stage behaviour, they lie at the foundation of all diffusion studies and therefore provide the required basic insight into uptake as a whole. In this section, various forms of Fickian uptake are discussed, their defining equations, solution methods and characteristics also being presented. Although, for example, useful thickness effects can be implemented by combining a single-stage bulk uptake model with a time-dependent boundary model, this is left to a later section of this chapter.

4.2.1.1 Simple constant diffusion coefficient Fickian model

This simple Fickian model forms the basis of most uptake modelling work presented in the adhesives durability literature, often being accepted in its unmodified form as adequately representing experimentally observed moisture absorption by adhesive materials. In order first to visualise the physical situation being modelled, Figure 4-7 shows a plane sheet (theoretically of infinite main surface area) of substrate material exposed to moist ambient conditions on both faces. As with all uptake models presented in this thesis, the sheet of substrate material is of thickness 2l, symmetry allowing for uptake modelling to describe the developing moisture profile over only one half-thickness, the x position ordinate extending from x = 0 on the centreline to x = l at the free surface of the substrate. Also, for
a given temperature (and applied stress level), there is a unique dependence of equilibrium concentration, \( c_{\infty} \), within the substrate material on the ambient moisture concentration level, the latter usually being expressed in terms of relative humidity. Also, all particular solutions to the uptake models here refer to the case where the material is dry throughout at zero time.

\[
J_x = -D \frac{\partial c}{\partial x}
\]  

(Fick's first law)

Figure 4-7 Uptake specimen set-up as used as a basis for all analytical models

Fick suggested that both heat and mass transfer processes were governed by the random motion of particles. He then suggested that Fourier's heat conduction equation could be applied to the directly analogous situation of diffusion. Hence, the rate of diffusant transport ("flux"), \( J_x \), would be proportional to the local spatial diffusant concentration gradient, and this is Fick's first law. Expressed in its simplest one-dimensional form, and corresponding to the set-up shown in the previous figure, Fick's first law can be written:
Then, applying conservation of mass considerations, the local time-rate of change of concentration can be expressed as follows:

$$\frac{\partial c}{\partial t} = -\frac{\partial J_x}{\partial x}$$  \hspace{1cm} (4)

This then gives the general case of:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(D \frac{\partial c}{\partial x}\right)$$  \hspace{1cm} (5)

Again, Equation (5) represents the general case of Fickian diffusion, allowing for variable diffusion coefficient. However, first analysing the constant diffusion coefficient, "simple" Fickian uptake model, this particular case leads to the simplified Equation (6).

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}$$  \hspace{1cm} (6)

Note at this point that diffusion can potentially be a three-dimensional process in x, y and z-directions, with varying concentration gradients and therefore fluxes. Also, in the case of anisotropic materials, there may well be varying diffusion coefficient values in these three directions, further complicating the situation. However, in all this work, only one-dimensional uptake processes have been considered and so only the x-direction and a single diffusion coefficient are considered. For later characterisation of moisture absorption into joints, the adhesives have been assumed to be isotropic, therefore allowing the synthesis of the multi-dimensional behaviour by simply building up from one-dimensional uptake components.

Solution

Whether the diffusion coefficient is constant and whether a complex boundary condition is to be applied to the bulk uptake model very much affect the method and nature of the solution. In this simple, constant diffusion coefficient case, an analytical solution is available, one form of which is given below:
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\[
\frac{c(x, t)}{c_\infty} = 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)^2} \exp \left( -\frac{D(2n+1)^2 \pi^2 t}{4l^2} \right) \cos \left( \frac{(2n+1) \pi x}{2l} \right)
\]

(7)

This solution gives the development of concentration in both one-dimensional space and time. Also, the above particular solution is for material which is initially dry, i.e. has zero concentration of diffusant throughout at zero time. Also, it is assumed that the surfaces of the thin film specimen attain equilibrium concentration instantly upon contact with the diffusant, i.e. there is no time-dependent boundary effect requiring a non-trivial boundary model. Thus, this model describes the basic case of simple Fickian bulk uptake with the standard instantaneous boundary equilibration condition. Note also that Equation (7) can be evaluated directly and requires no more than a simple spreadsheet treatment for initial parametric studies.

However, against the context of an experimental programme of gravimetric uptake studies, it is more usual to record and analyse data in terms of bulk mass uptake as a function of time only, as opposed to local diffusant concentration as a function of position and time. Thus, Equation (7) is usually integrated to give the following bulk uptake form of the solution:

\[
\frac{m(t)}{m_\infty} = U = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp \left( -\frac{D(2n+1)^2 \pi^2 t}{4l^2} \right)
\]

(8)

In Equation (8), the parameter \( U \) is introduced. This represents fractional uptake and will be used throughout discussion in this thesis. As in the case of Equation (7), Equation (8) can be evaluated directly and requires initially no more than a relatively simple spreadsheet implementation. As the form presented here is expressed as a summation of an infinite series, it is important to include a sufficient number of terms. The required minimum number of terms also depends on the magnitude of diffusion coefficient and half-thickness. However, all investigations within this research used a summation of the first 50 terms of Equation (8). Solutions were initially tried with fewer terms, but satisfactory accuracy and effective convergence were easily achieved by using 50 terms.
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At this stage, it is important to note that bulk fractional uptake history for the simple Fickian model is purely a function of diffusion coefficient. Or, if bulk mass uptake itself is being considered, its history is a function of diffusion coefficient and equilibrium uptake. Also, and with all considered cases of diffusion models with instantaneous boundary equilibration (i.e. just bulk diffusion alone), equilibrium uptake acts simply as a linear scaling factor. Thus, in any work where experimental uptake behaviour is to be represented using a simple Fickian uptake model, it is necessary to deduce both the diffusion coefficient and the equilibrium uptake for substitution of the values into the model expression. This in turn ideally requires the undertaking of a full-term uptake test, i.e. effectively to equilibrium.

For some later investigations of the behaviour of the simple Fickian model, especially where more flexible analytical manipulation and evaluation of fractional uptake at any required time were required, Equation (8) was replaced by a more easily-manipulated algebraic expression, which is discussed in §4.2.2.2.

Model characteristics

As it is, Equation (8) is not useful when trying to deduce the value of the diffusion coefficient from an experimental uptake curve which is already known to conform to the unique and fundamental simple Fickian pattern. However, remembering that simple Fickian diffusion gives initially linear uptake and assuming full-term uptake date to be available (and thus knowledge of equilibrium uptake), Equation (9) can be used to determine the diffusion coefficient. This gives a very close approximation to Equation (8) up to approximately \( U = 0.6 \) and gives diffusion coefficient directly from the slope of the \( U \) v. \( \sqrt{\frac{t}{I^2}} \) curve.

\[
U = 2 \frac{D}{I} \sqrt{\frac{t}{\pi}}
\]  

(9)

To recap discussions presented in the Literature Review chapter and earlier on in the current chapter, and also to describe further the properties of simple Fickian uptake, it is crucial to emphasise that this model has only one mathematical shape. Although this becomes a family of linearly scalable curve shapes in the \( m \) v. \( \sqrt{\frac{t}{I^2}} \) plane (or the \( U \) v. \( \sqrt{\frac{t}{I^2}} \) plane)
The simple Fickian model can truly be represented by one single curve in the $U \times \sqrt{D t / l^2}$ plane, this being shown in Figure 4-8. Therefore, when using this model in an attempt to match experimental uptake data, it is a simple matter to identify whether this model is adequate. By the same token, however, this property gives very little model flexibility when attempting to match experimental uptake data.

This also has important implications when investigating Fickian conformity of specimen thickness scaling. The above simple Fickian requirement of one unique locus in the $U \times \sqrt{D t / l^2}$ plane dictates that uptake curves for all thicknesses should have precisely the same locus. Thus, when comparing experimental data with the simple Fickian model, this provides an additional requirement or check beyond pure curve shape in the case of data for multiple thicknesses. If, however, experimental data shows a family of uptake curves for different thicknesses, this either implies that uptake is fundamentally non-Fickian or perhaps that a complex boundary effect is occurring in addition to the (possibly still Fickian) adjacent bulk diffusion process. Again, it is a formal requirement of all basic Fickian uptake models that the surfaces of a specimen should instantaneously assume equilibrium uptake, this local cohesive concentration level being uniquely dependent on the ambient moisture concentration (or relative humidity) for the material in question.
4.2.1.2 Fickian model with concentration-dependent diffusion coefficient

Although basic Fickian uptake models lack flexibility in that they require an instantaneous boundary equilibration condition, they allow a variable diffusion coefficient. When considering this option, Fujita [40] states that it is common to investigate diffusion coefficient as functions of local concentration, position or time. However, in response to the other literature [18, 23, 26, 30, 53, 67] and for physical realism, only concentration-dependent diffusion coefficient has been considered for the purposes of this research. This type of Fickian uptake is now discussed, first looking at the changes in formulation of the underlying partial differential equation, then looking at methods of solution and finally analysing its characteristics.

As it does for the simple Fickian model, Equation (5) still holds. However, with diffusion coefficient now being a function of concentration, Equation (6) no longer applies and is replaced by Equation (10).

\[
\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} + \frac{\partial D}{\partial x} \frac{\partial c}{\partial x} \tag{10}
\]

or:

\[
\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} + \frac{dD}{dc} \left( \frac{\partial c}{\partial x} \right)^2 \tag{11}
\]

This concentration-dependent Fickian model is now mathematically more complex than its predecessor and has no general analytical solution. Simple, direct spreadsheet treatments become impossible and a numerical solution approach is now required. A proposed scheme is presented in the following section, followed in turn by analyses of the model for cases where diffusion coefficient varies linearly and exponentially with concentration.

Solution

As the implementation of a naturally stable and convergent implicit numerical scheme was over-complicated at this early stage, an explicit finite difference scheme was drawn up in
order to solve Equation (11). Figure 4-9 shows a visualisation of this spatially one-dimensional scheme, using a grid to represent time and position stepping, symmetry allowing the modelling of only half of the specimen. Note that, in contrast to the system used in all the analytical uptake expressions presented in this chapter, position, $x$, is defined as being zero on free surface of specimen, increasing to $l$ on the centreline.

The chosen scheme represents the second spatial derivative of concentration in Equation (11) by a central difference of accuracy $O[(\Delta x)^2]$, as follows:

$$
\frac{\partial^2 c}{\partial x^2}_{i,k} = \frac{c_{i+1}^k - 2c_i^k + c_{i-1}^k}{(\Delta x)^2}
$$

(12)
The first spatial derivative of concentration was represented by another central difference, again of accuracy $O((\Delta x)^2)$, as follows:

$$\frac{\partial c}{\partial x_{i,k}} = \frac{c_{i+1}^k - c_{i-1}^k}{2\Delta x}$$  \hspace{1cm} (13)$$

Then, for the time derivative of concentration, a forward difference of accuracy $O((\Delta t))$ was used, as follows:

$$\frac{\partial c}{\partial t_{i,k}} = \frac{c_{i}^{k+1} - c_{i}^k}{\Delta t}$$  \hspace{1cm} (14)$$

As for the function $D(c)$, only prescribed analytical forms were investigated, so nodal values of diffusion coefficient could be calculated directly, as could values for $dD/dc$. Combining nodal diffusion coefficient information with Equations (12), (13) and (14) gives the following expression for nodal concentration at the end of the current timestep:

$$c_{i}^{k+1} = c_{i}^k + \Delta t \left[ D_i \left( \frac{c_{i+1}^k - 2c_i^k + c_{i-1}^k}{(\Delta x)^2} \right) + \left( \frac{dD}{dc} \right)_i \left( \frac{c_{i+1}^k - c_{i-1}^k}{2\Delta x} \right)^2 \right]$$  \hspace{1cm} (15)$$

In implementing the basic instantaneous equilibration boundary condition of Fickian diffusion, all surface nodes in the $(x, t)$ plane were set to $c_\infty$ for all time. For the centreline boundary condition, $\partial c/\partial x$ was taken to be zero. Then, at zero time, all nodes (excluding the surface node) were set to zero concentration, representing initially dry material. This concentration-dependent Fickian bulk uptake model can also be combined with a more complex boundary effect, such a boundary condition being implemented by appropriate alternative assignment of surface node concentration values. However, later studies found this approach to be of little value here, and such models were not investigated.

Two functional forms of concentration-dependent diffusion coefficient were investigated, these being linear and exponential, the latter decreasing with increasing concentration. Decreasing functions of diffusion coefficient were favoured because of the generally flat, low nature of the experimental uptake plots already obtained. Also, attempting to provide a
physical justification, it is possible that a proportion of moisture diffusing through an adhesive material may become bound and so immobilised from further ingress. This would then tend to reduce the remaining available free volume and resist the diffusion process. For the purposes of the description of diffusion coefficient value with concentration, diffusion coefficient was expressed in terms of normalised concentration, \( \frac{c}{c_\infty} \), i.e. relative to equilibrium concentration (corresponding to integrated equilibrium bulk mass uptake). So, for the linear case:

\[
D(c) = \phi_1 + \phi_2 \left( \frac{c}{c_\infty} \right) \tag{16}
\]

with:

\[
\frac{dD}{dc} = \frac{\phi_2}{c_\infty} \tag{17}
\]

And for the exponential case:

\[
D(c) = \phi_1 + \phi_2 \exp \left( -\phi_3 \frac{c}{c_\infty} \right) \tag{18}
\]

with:

\[
\frac{dD}{dc} = -\frac{\phi_2 \phi_3}{c_\infty} \exp \left( -\phi_3 \frac{c}{c_\infty} \right) \tag{19}
\]

In choosing a suitable timestep size to achieve convergence, no formal treatment of the scheme represented by Equation (15) was available for selection of correct sizing. Therefore, the maximum timestep criterion was based on that commonly accepted as the limit for a similar finite difference scheme applied to the simple, constant diffusion coefficient case (Equation (6)). For this case, which is exactly equivalent to the heat conduction equation in one dimension, Carnahan et al. [109] showed that the timestep should follow the following criterion:
\[\Delta t \leq \frac{(\Delta x)^2}{2D}\]  

(20)

Displacement step sizing was determined by running the finished code and experimenting with different numbers of nodes across a typical specimen half-thickness. These investigations suggested that accurate results were achieved given 20 nodes across a half-thickness of 0.2 mm. Node spacing of at least this level of refinement was therefore retained for all analyses with this finite difference model.

Because of the increased numerical complexity over the analytical solution of the constant diffusion coefficient model, the finite difference concentration-dependent diffusion coefficient uptake model, with either the linear or exponential \(D(c)\), was implemented using a FORTRAN 77 programme running on a SUN UltraSparc computer. This programme, shown in Appendix A, wrote spatial concentration and bulk mass uptake output to files, which could then be transferred to a PC for manipulation and plotting using a spreadsheet as before. Thus, the characteristics of the concentration-dependent diffusion coefficient Fickian uptake model were investigated. The results of this study are discussed in the next section.

Model characteristics

Testing of the finite difference numerical model for the concentration-dependent diffusion coefficient case was not as simple as testing the model for the simple Fickian case. As there was no analytical solution available, ABAQUS finite element analyses were used to test the finite difference solutions. In all cases where the finite difference model converged properly, the predicted bulk uptake being essentially identical to that produced by the corresponding ABAQUS analysis. This gave confidence in all sensible results from the finite difference model. However, for large negative values of \(dD/dc\) at low concentration, the model was found to converge on a false solution. Reference to Equation (11) suggests that such a highly negative value would tend to "overbalance" the uptake process and result in a falsely predicted drying out behaviour. This is fundamentally incorrect and brings into question the limits of the model's ability and the physical significance of high negative values of \(dD/dc\) at low diffusant concentrations.
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However, once the concentration-dependent diffusion coefficient model was being used with confidence, its properties could be analysed. Whereas the simple Fickian model gives only one mathematical uptake curve shape, the concentration-dependent diffusion coefficient solution gives a whole range of curves in the $U \text{ v. } \sqrt{t/\delta}$ plane, depending on the form of $D(c)$. However, for a fixed $D(c)$ (independent of form), there is again only one curve in the $U \text{ v. } \sqrt{t/\delta}$ plane. However, that curve will vary slightly from the shape of the simple Fickian shape. This again shows that, for any given $D(c)$, when uptake is plotted against $\sqrt{t/\delta}$ for a single material absorbing from the same ambient concentration and temperature conditions, data from specimens of different thickness still lies along the same locus. Again, this becomes an important point when analysing experimental uptake data.

- Characteristics for linear $D(c)$

Studying the output of this model, it was found that this form of the variable diffusion coefficient Fickian model always gave uptake curves whose loci were similar to the single simple Fickian shape. Therefore, this was an immediate indication that allowing variation of diffusion coefficient with concentration would never introduce high levels of uptake curve flexibility, as confirmed by Fujita [40]. Again, uptake curve shapes always showed vaguely (although not exactly) linear initial uptake behaviour, followed by progress towards equilibrium. In fact, varying the diffusion coefficient as a function of concentration served mainly either to slightly sharpen or to slightly flatten the knee of the curve. However, the knee could never be moved very far up or down the fractional uptake axis, always remaining at approximately $U = 0.8$. Of course, there was the additional constraint of the still-Fickian, single locus, thickness $\sqrt{t/\delta}$ uniformity.

Although it was apparent from fairly early on that the variable diffusion coefficient Fickian model gave only limited room for manoeuvre and would probably not be all that useful in modelling experimental uptake data, a limited parametric study was carried out. Obviously, there are an infinite number of linear diffusion coefficient functions. However, an interesting characteristic became apparent shortly after starting the testing programme. Therefore, the general properties of the linear variable diffusion coefficient model are presented here against the background of this particular characteristic. As before, for convenience and standardisation purposes, it will be usual to talk in terms of diffusion coefficients as functions of normalised concentration, $c/c_\infty$. 

100
Describing the characteristic mentioned above, it was noticed that all uptake curves defined by linear variable diffusion coefficient models where $D(c)$ passed through the same $c/c_\infty = 2/3$ point had virtually identical initial regions. Therefore, sets of linear $D(c)$ curves crossing at different fractional uptake values would produce a corresponding family of uptake curves with similar initial regions. This effect is demonstrated in Figures 4-10 and 4-11, showing two such sets of $D(c)$ and uptake curves. Table 4-3 explains the legends accompanying these figures. Note that, for sets of uptake curves with similar initial regions, variations in the form of $D(c)$ give very little flexibility in the position and curvature of the knee. Therefore, if fitting a model of this type to experimental data showing a strong initial linear behaviour, there is little room for manipulating the other model parameters to fit other uptake curve characteristics.

<table>
<thead>
<tr>
<th>Legend</th>
<th>$D$ at $c/c_\infty = 0$ $(10^{-14}\text{ m}^2\text{s}^{-1})$</th>
<th>$D$ at $c/c_\infty = 1.0$ $(10^{-14}\text{ m}^2\text{s}^{-1})$</th>
<th>$D$ at $c/c_\infty = 2/3$ $(10^{-14}\text{ m}^2\text{s}^{-1})$</th>
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<td>1</td>
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<td>3</td>
<td>5</td>
</tr>
<tr>
<td>2 (constant $D$)</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>7</td>
<td>5</td>
</tr>
<tr>
<td>4</td>
<td>18</td>
<td>6</td>
<td>10</td>
</tr>
<tr>
<td>5 (constant $D$)</td>
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<td>10</td>
<td>10</td>
</tr>
<tr>
<td>6</td>
<td>2</td>
<td>14</td>
<td>10</td>
</tr>
</tbody>
</table>

**Table 4-3** Linear $D(c)$ parameters chosen for investigation

**Figure 4-10** Linear $D(c)$ functions chosen for investigation
Again, and apart from this $c/c_w = 2/3$ correlation, it can be seen that allowing a variation of diffusion coefficient gives limited flexibility of model, the knee of the uptake curve always lying at approximately $U = 0.8$. However, the Figures show that an increasing linear function of diffusion coefficient slightly sharpens the knee of the corresponding uptake curve, which also overshoots the constant diffusion coefficient locus. A decreasing function slightly flattens the knee and gives an uptake curve which undershoots the corresponding constant diffusion coefficient uptake curve locus. Note that, if uptake had been plotted against $\sqrt[3]{Dt/l^2}$ and not $\sqrt{t/l^2}$, all uptake curves would have been very similar.

- Characteristics for exponential $D(c)$

Bearing in mind the limited flexibility of uptake curves displayed by the linear variable diffusion coefficient Fickian uptake model, an exponential form of $D(c)$ was investigated to see whether more movement could be achieved. In the light of initially seemingly low, flat uptake curves obtained from the experimental work, it was decided to investigate the effects only of decaying exponential functions of concentration-dependent diffusion coefficient. Furthermore, although it seemed unlikely that this exponentially variable form of the Fickian model would follow exactly the same $c/c_w = 2/3$ correlation as the linear model, it seemed that the value of diffusion coefficient at relatively high concentration
levels was of key influence. Therefore, as a starting point for the study of the characteristics of the exponential model, a series of $D(c)$ curves were chosen which all passed through the same diffusion coefficient value at $c/c_\infty = 2/3$. Referring to Equation (18) in §4.2.1.2 for definition of $D(c)$ parameters, Table 4-4 defines the curves investigated. Note that the units for constants $\phi_1$ and $\phi_2$ are $10^{-14} \text{m}^2\text{s}^{-1}$ and that $\phi_3$ is dimensionless.

<table>
<thead>
<tr>
<th>Legend</th>
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<th>$\phi_2$</th>
<th>$\phi_3$</th>
</tr>
</thead>
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<tr>
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<td>-</td>
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</table>

Table 4-4 Exponential $D(c)$ parameters chosen for Investigation

Figures 4-12 and 4-13 show these $D(c)$ functions and the resulting uptake curves graphically. It can be seen from the uptake curves that the exponential form of $D(c)$ does seem to give slightly more flexibility in terms of curvature of the whole uptake curve, especially with the relatively quickly initially decaying diffusion coefficient cases ("initially" referring to low concentration, as opposed to time). However, for all the $D(c)$ forms tested here, the knee of the resulting uptake curve still remained firmly around the $U = 0.8$ mark. Thus, for all constant and concentration-dependent diffusion coefficient Fickian uptake models investigated here, there is limited flexibility. And as with any concentration-dependent Fickian model with an instantaneous equilibration boundary condition, there is still no variation with thickness in the $U \times v(t^2)$ plane.
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4.2.2 Two-stage uptake models

In response to observations both here and in the literature of apparently anomalous or two-stage uptake, it has been sought in this research to find uptake models which can produce these characteristics. It has so far been clear that a single component Fickian uptake model, with or without concentration-dependent diffusion coefficient, cannot reproduce the
complex uptake curves often seen experimentally. In particular, a low first partial equilibration is often seen, this followed after some time by a second uptake stage. Sometimes, this second uptake stage is not very pronounced and becomes more like a persistent linear phase after initial partial equilibration. In wanting to develop a model which can predict this type of behaviour, and realising the limitations of single Fickian-based components, a possible technique is to consider multi-part, superposed uptake models. As the quantity of possible combinations that could be assembled is large, however, only a representative subset of cases is studied here. In particular, as the earlier discussion on concentration-dependent Fickian diffusion models showed limited variation from the simple Fickian diffusion reference, two-stage combinations of these will not be considered here. Thus, only two-stage models with simple Fickian diffusion contributions have been selected and these are discussed in the following sections.

4.2.2.1 Simple Fickian diffusion with relaxation contribution

It has been suggested by some authors [36, 38, 40, 42, 43, 44, 45, 46] that a relaxation process can occur simultaneously with the diffusion process, thus producing apparently two-stage uptake behaviour. It has been suggested [45] that this relaxation process is a swelling response to osmotic pressure induced by water diffusing into the structure of a polymer. Berens and Hopfenberg [46] carried out work to investigate the relative contributions of the two processes, suggesting a Fickian definition for the diffusion part and a relaxation part described by the following purely phenomenological expression:

$$m_r(t) = m_{\infty}(1 - e^{-\omega t})$$  \hspace{1cm} (21)

The diffusion and relaxation contributions to the overall uptake, defined by Equations (8) and (21), are then simply added together, noting:

$$m_{\infty} = m_{\infty0} + m_{\infty0}$$  \hspace{1cm} (22)
Given a known total equilibrium uptake value, this two-stage diffusion-relaxation model requires only the following parameters to be optimised when fitting experimental uptake data:

- Simple Fickian diffusion component
  - equilibrium uptake, \( m_{\infty} \)
  - diffusion coefficient, \( D \)
- Relaxation component
  - time constant, \( \Omega \)

**Solution**

Using an overall uptake model consisting of a superposition of a simple Fickian diffusion component and the above-described relaxation component, a simple spreadsheet solution method is adequate to study the model characteristics in the first instance.

**Model characteristics**

Using Equation (21) to define a relaxation contribution to the overall uptake behaviour, this combined model can give the general form of sorption plot shown in Figure 4-14. Immediately it can be seen that this model has the ability to give a two-stage uptake effect, this having been observed both elsewhere in the literature and during the experimental uptake programme here.

![Figure 4-14 Uptake curve characteristics available using two-stage diffusion-relaxation model](image-url)
Note that this type of relaxation component will result in different overall uptake curve loci in the $U \sim \sqrt{t}$ plane for specimens of different thickness. Therefore, the figure presented here is relevant for only one specimen thickness, this and the other model parameter values being tabulated in Table 4-5. Although, therefore, this model produces a thickness effect, it achieves it simply by not representing thickness at all in the relaxation component. As is discussed in later sections, a boundary effect would seem to be a more meaningful tool with which to model a non-Fickian thickness effect. Furthermore, the relaxation part of the model characterises uptake only at the integrated bulk level and thus cannot produce a spatial concentration profile. For these reasons and because of the later need to implement any finally chosen uptake model using ABAQUS finite element software, this model has limited attraction. Also, it will be noticed in a later section that a dual simple Fickian uptake model (which can be directly implemented in ABAQUS) can produce similar characteristics to this Fickian diffusion-relaxation model. This renders it more immediately useful, within the chosen durability modelling framework.

<table>
<thead>
<tr>
<th>Specimen half-thickness = 0.2 mm; total equilibrium uptake = 5%</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Fickian Diffusion Component</strong></td>
</tr>
<tr>
<td>Equilibrium Uptake, $m_{d,e}$ (%)</td>
</tr>
<tr>
<td>Diffusion Coefficient, $D \times 10^{-14}$ m$^2$s$^{-1}$</td>
</tr>
<tr>
<td>3</td>
</tr>
<tr>
<td>10</td>
</tr>
<tr>
<td><strong>Relaxation Component</strong></td>
</tr>
<tr>
<td>Equilibrium Uptake, $m_{r,e}$ (%)</td>
</tr>
<tr>
<td>Time Constant, $\Omega$ (s$^{-1}$)</td>
</tr>
<tr>
<td>2</td>
</tr>
<tr>
<td>$1 \times 10^{-7}$</td>
</tr>
</tbody>
</table>

*Table 4-5 Parameter values used to obtain Figure 4-14*

### 4.2.2.2 Dual simple Fickian model

In attempting to develop another two-stage model which could be directly implemented in ABAQUS whilst retaining the ability to model anomalous uptake characteristics, the properties of a dual simple Fickian model were investigated. As with the previously proposed two-stage model, the two components act separately and in parallel. Equation (8) is used twice to define the individual mass uptake behaviours which are simply added together to generate the combined effect. To obtain the required two-stage characteristics, each of the two simple Fickian components should typically assume different defining parameter values.
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Noting again that component equilibrium uptake values add together to give the known overall value, optimisation of this model requires the determination of the following three parameters only:

- First component
  - diffusion coefficient, $D_1$
  - equilibrium uptake, $m_{eq1}$
- Second component
  - diffusion coefficient, $D_2$

Solution

As the single simple Fickian model has an analytical solution (Equation (8)), it was again convenient to implement an initial solution using a spreadsheet. However, although this was a satisfactory approach for simple forward-manipulation of the double simple Fickian model, the complexity of the infinite series nature of the solution of each component caused problems when higher levels of solution manipulation were required. For example, during later fitting to experimental uptake data, it became necessary to use an optimisation tool within the spreadsheet software. As the evaluation of the various terms of the series expressions increased the mathematical complexity of the spreadsheet document, however, the software was unable to carry out the optimisation. Therefore, noting the simple unique locus and scaling properties of the simple Fickian model, it was replaced by a close polynomial curve-fit for the more complex manipulation work. This technique was also useful, especially when evaluation of fractional uptake at specific required time points was required (for summing component uptake values at equivalent time values).

The polynomial replacement to the infinite series simple Fickian model could again be used only because of the simple scaling properties of the model. For a randomly chosen diffusion coefficient of $13 \times 10^{-14}$ m$^2$s$^{-1}$, the single simple Fickian uptake curve is closely approximated by the following expressions:

$$0 \leq t' \leq 60; \quad U = f(t') = \frac{\phi_1 + \phi_2 t' + \phi_3 t'^2 + \phi_4 t'^3}{1 + \phi_3 t' + \phi_6 t'^2 + \phi_7 t'^3}, \quad \text{and} \quad (23)$$
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\( t' > 60; \quad U = 1.0 \) \hspace{1cm} (24)

where:

\[
t' = 10^{-5} \sqrt{\frac{t}{I^2 \left[ \frac{s^{1/2}}{m} \right]}} \hspace{1cm} \text{(25)}
\]

and:

\[
\phi_1 = 0.003427589 \\
\phi_2 = 0.041168924 \\
\phi_3 = -0.00103212 \\
\phi_4 = 5.19582 \times 10^{-5} \\
\phi_5 = -0.01536310 \\
\phi_6 = 3.85146 \times 10^{-5} \\
\phi_7 = 4.51962 \times 10^{-5}
\]

To give the single simple Fickian uptake curve for other values of diffusion coefficient, \( f(t') \) can be scaled as follows:

\[
0 \leq t' \sqrt{\frac{D}{\nu_{13}}} \leq 60; \quad U = f\left(t' \sqrt{\frac{D}{\nu_{13}}} \right), \quad \text{and} \hspace{1cm} (26)
\]

\[
t' \sqrt{\frac{D}{\nu_{13}}} > 60; \quad U = 1.0 \hspace{1cm} (27)
\]

For \( D \) in units of \( 10^{-14} \text{m}^2 \text{s}^{-1} \).

For quick studies of model behaviour and for experimental data-fitting, the above approximation to the basic simple Fickian shape proved invaluable. With regards to closeness of fit to the original Fickian uptake curve shape, there is no visible deviation between the two lines right up to equilibrium.
Model characteristics

Figure 4-15 shows the characteristics of the model when used with differing diffusion coefficient and equilibrium uptake values. Table 4-6 accompanies the figure and shows the selected parameters. Note that it is important to control the balance between component equilibrium values, as this governs the relative proportions of the different phases of the combined behaviour.

The Figure shows that this two-stage model can produce similar uptake behaviour to the previous simple Fickian-relaxation model. As well as creating the secondary linear uptake phase, the double simple Fickian model can give a generally low-lying uptake curve, as often observed experimentally in this research. However, as this model is a simple superposition of two Fickian bulk models with no special boundary resistance component, this compound model again displays no non-Fickian specimen thickness effect. Thus, in
the $U \text{ v. } \sqrt{t/l^2}$ plane, this compound model produces a single curve for all thicknesses of specimen.

As will be seen later, however, this two-stage model can be used as a useful component in a more complex model, this bringing in the required thickness effect. Also, bearing in mind that the dual simple Fickian model consists of components that can be directly implemented in ABAQUS, this model is especially attractive for further development.

4.2.3 Single-stage uptake models combined with time-dependent boundary conditions

Up to this point, no genuine attempt at modelling non-Fickian thickness effects has been made. The previous two-stage model combining a simple Fickian diffusion component with a relaxation component did produce a spread of curves in the $U \text{ v. } \sqrt{t/l^2}$ plane for different thicknesses (as seen with the experimental results), but it was felt that this thickness effect was rather ad-hoc. Therefore, looking for an uptake model component which is likely to be more faithful to the mechanisms actually occurring, boundary models were considered. In this initial study, these boundary effects were combined with single-part Fickian bulk uptake models.

Previously, it has been seen that any single or dual uptake model based only on constant or variable diffusion coefficient Fickian diffusion components can never produce the required thickness effect. This limitation is a direct result of the fact that these models all make use of the basic Fickian instantaneous equilibration boundary condition. However, if the instantaneous equilibration condition is replaced by a gradual, time-dependent surface concentration development condition, a specimen thickness effect is introduced. No longer is the overall uptake behaviour controlled by the bulk diffusion process alone but it becomes influenced by a surface resistance effect also.

Crank [39] presents various time-dependent boundary conditions which he combines in turn with a simple Fickian diffusion bulk model. Three of these boundary conditions, acting in combination with single-stage Fickian bulk diffusion models, are discussed in the following sections.
4.2.3.1 Boundary conditions

Three of Crank's proposed boundary conditions are mentioned here. The first condition defines a surface concentration which increases linearly with time. However, this implies no final equilibration of concentration at the surface, suggesting in turn that the overall uptake process will never reach equilibrium. This is not what is observed in practice and therefore this condition is not considered further.

The other two conditions, however, do indeed equilibrate with time and are therefore discussed here at greater length. These more appropriate conditions can be expressed as follows:

\[ -D \frac{\partial c}{\partial x} = \alpha (c_\infty - c_s) \]  \hspace{1cm} (28)

\[ c_s = c_\infty (1 - e^{-\Omega}) \]  \hspace{1cm} (29)

Equation (28) perhaps most commonly represents a situation where a specimen is being exposed to water vapour. In such cases, it is possible for evaporative effects to disturb the uptake behaviour. This condition is equilibrating in nature and defines a spatial concentration gradient at the surface which is held proportional to the difference between ambient and surface concentration values. Just as simple Fickian bulk diffusion is analogous to heat conduction, the evaporative diffusion boundary condition is exactly equivalent to the convective surface heat transfer equation and can therefore be directly implemented using conventional thermal finite element analysis software. The boundary effect is then controlled by the parameter \( \alpha \), which is exactly equivalent to the convective heat transfer coefficient, \( h \), used in thermal boundary layer analysis.

The second remaining condition, defined by Equation (29), again has the required equilibrating nature but is purely an exponential function of time. The boundary effect of this model is thus controlled by the time constant parameter, \( \Omega \).
4.2.3.2 Study of combined bulk/boundary uptake models

Having defined two time-dependent boundary conditions that are of interest for further analysis, it was required to combine them in turn with a single-stage bulk uptake model. As discussed previously, two useful boundary conditions remain (Equations (28) and (29)), and either can be combined with potentially any single-part bulk uptake model. However, bearing in mind the relative lack of flexibility gained from introducing a concentration-dependent diffusion coefficient, use here of such a bulk uptake model was rejected. Considering also the finite element implementation weaknesses of other bulk uptake models, the decision was made to use only the constant diffusion coefficient simple Fickian model to describe diffusion in the bulk material.

Simple Fickian bulk model combined with evaporative boundary condition

Crank [39] presents an analytical solution to the case of a simple Fickian bulk uptake model of Equation (6) in combination with the evaporative boundary condition of Equation (28), as shown below.

\[
\frac{c(x, t)}{c_\infty} = 1 - \sum_{n=1}^{\infty} \frac{2L \cos(\beta_n x/L) \exp\left(-\beta_n^2 Dt/L^2\right)}{2 \beta_n^2 + L^2 \cos \beta_n} \tag{30}
\]

Where the \( \beta_n \) values are the positive roots of:

\[
\beta \tan \beta = L \tag{31}
\]

and:

\[
L = \frac{l\alpha}{D} \tag{32}
\]

Here, we can see the introduction of a non-dimensional term, \( L \), which can be seen as representing the balance between surface and bulk diffusion processes. Also, it now starts to become apparent that changing specimen thickness is likely to have more of an effect than with the purely bulk Fickian uptake models with their instantaneous equilibrating
boundary condition. Again, as it is more useful when comparing a modelled uptake curve to experimental data to have an expression for integrated bulk mass uptake, the following expression is available:

\[
m(t) = U = 1 - \sum_{n=1}^{\infty} \frac{2L^2 \exp\left(-\frac{\beta_n^2 \cdot Dt}{L^2}\right)}{\beta_n^2 \left(\beta_n^2 + L^2 + L\right)}
\]

- Solution

As this solution is analytical in nature, a spreadsheet can be used when studying the characteristics of this model. Unlike the case of the simple Fickian bulk model alone, there is no simplified equivalent of Equation (9) to help in determining the diffusion coefficient given an experimental uptake curve. This limits the ease of backwards-manipulation and parameter optimisation of Equation (33), but it is still helpful to be able to change the parameters of the equation and plot the results using a spreadsheet.

In using a spreadsheet to study this compound uptake model, the transcendental Equation (31) was solved using the bisection root-finding method, allowing for values of \( L \) between 0.1 and 100. This range of \( L \) values gave a wide range of boundary resistance levels and was considered adequate for these studies.

- Model characteristics

It is most convenient to study the behaviour of the current model by plotting fractional uptake against \( \sqrt{Dt/L^2} \). Viewing the results in this way, it can be seen that each value of \( L \) gives a different bulk mass uptake curve, as shown in Figure 4-16. Note that, as \( D \) is a property only of the bulk material property and \( \alpha \) is a property only of the surface, the specimen half-thickness, \( l \), influences the balance of the overall uptake behaviour. Thus, the half-thickness effectively controls the ratio of surface effect to bulk effect. If either the diffusion coefficient of the bulk material, the thickness of the material or the boundary resistance value, \( \alpha \), is changed, the uptake rate is also changed. Thus, unlike the action of a bulk uptake model alone, the boundary resistance model acting together with any given bulk diffusion process gives this distinction of thickness between uptake specimens.
Figure 4-16 Characteristics of evaporative boundary condition when combined with simple Fickian bulk uptake model

Looking now at the results of the single-stage Fickian with evaporative boundary condition model, it can be seen that low L (corresponding to low α) values give the most pronounced relative boundary effect. In these cases of significant boundary resistance, it can be seen that a concavity is introduced into the early region of the uptake process, whilst the general uptake rate is suppressed compared to a sole simple Fickian bulk uptake process. Towards the other extreme, high L or α values correspond to a low boundary effect, converging to simple Fickian uptake. However, it must be noted that all runs of this model with pronounced boundary effect still show the knee of the predicted uptake curve to occur at a point higher than U = 0.8, even if other characteristics of the uptake curve can be varied. So, although this model provides a valuable characterisation tool for bringing in a thickness effect, it would be impossible to use this uptake model on its own to fit two-stage experimental data with low initial partial equilibrium uptake.
Simple Fickian bulk model combined with exponential boundary condition

For this combination of the exponentially equilibrating boundary concentration model of Equation (29) with the simple Fickian bulk diffusion defined by Equation (6), Crank [39] again quotes an available analytical solution for local penetrant concentration as follows:

\[
c(x, t) = \frac{c(x, t)}{c_\infty} = 1 - \frac{\cos \left( \frac{\Omega}{D} \right)^{0.5}}{\cos \left( \frac{\Omega}{D} \right)^{0.5}} \exp (-\Omega t) - \frac{16\Omega^2}{\pi} \sum_{n=0}^\infty \frac{(-1)^n}{(2n+1)^2} \frac{\exp \left( -D(2n+1)^2 \pi^2 t / 4l^2 \right)}{2n+1} \cos \left( \frac{2n+1}{2n+1} \right) \exp \left( -\frac{D(2n+1)^2 \pi^2 t}{2n+1} \right)
\]

(34)

The above can then be integrated to give bulk mass uptake, this being defined below:

\[
\frac{m(t)}{m_\infty} = U = 1 - \left( \frac{D}{\Omega^2} \right)^{0.5} \exp (-\Omega) \tan \left( \Omega^2 / D \right)^{0.5} - \frac{8}{\pi^2} \sum_{n=0}^\infty \exp \left( -\frac{(2n+1)^2 \pi^2 D t / 4l^2} \right) \left[ 1 - \left( 1 - \frac{D \pi^2}{4\Omega^2} \right) \right]
\]

(35)

• Solution

As in the case of the previous boundary model combination, the availability of an analytical solution enables this model to be studied using a spreadsheet. Furthermore, unlike the last model, this model does not require the numerical solution of a transcendental equation as part of the overall solution process. Similarly to the previous model, the non-dimensional quantity \( \Omega^2 / D \) controls the uptake curve locus in the \( U \) v. \( \sqrt{D t / l^2} \) plane

• Model Characteristics

Figure 4-17 shows the behaviour of this particular uptake model combination. Although the precise curve shapes differ slightly from those produced by the previous model, especially in terms of the more pronounced initial concavity, the current model does give very similar behaviour, the knee again occurring at approximately \( U = 0.8 \). As this research does not aim to provide an exhaustive mathematical treatment of all combinations of
model, and as there is no immediately available finite element solution module for this boundary condition, this combined model will not be discussed further.

![Graph showing characteristics of exponential time-dependent boundary condition](image)

**Figure 4-17** Characteristics of exponential time-dependent boundary condition when combined with simple Fickian bulk uptake model

**Rationalisation of single-stage uptake models with boundary effects**

Two combinations of single-stage uptake models with time-dependent boundary conditions have been discussed above. A direct comparison can thus be made between simple Fickian bulk uptake combined with either of Crank’s two equilibrating boundary conditions. Again, both conditions give similar thickness-dependent uptake behaviour, but the evaporative boundary model has the attraction of being able to be implemented directly within the ABAQUS finite element software chosen for the overall durability modelling programme. Therefore, for later requirements of a two-stage uptake model component that can give a genuine thickness effect, the simple Fickian bulk model with evaporative boundary condition will be taken forward.
4.2.4 A two-stage uptake model including time-dependent boundary condition

As the experimental uptake results showed clear examples of two-stage uptake behaviour, and as the various single-stage Fickian uptake models (either with or without concentration-dependent diffusion coefficient or boundary effect) could never produce these characteristics, there seemed a definite need for further development of a two-stage model for use within the final durability modelling stages of this research. However, not only was two-stage uptake required from the model but the characteristics of the experimental uptake data required that the model had to bring in a thickness effect, this suggesting the incorporation of a time-dependent boundary condition component. Also, as discussed previously, it was important that any final uptake model could be directly implemented within ABAQUS.

It was decided to build a final compound uptake model composed of a simple Fickian bulk model with an evaporative boundary component added to a single simple Fickian model which would retain the instantaneous equilibration boundary condition. Thus, it was hoped that the incorporation of a boundary component would give the thickness discrimination and that the double model set-up would allow for two-stage uptake behaviour. As before, it is assumed that an experimental uptake curve with known equilibrium uptake is to be fitted. As component equilibrium values simply add together as usual, optimisation of this model requires determination of the following parameters:

- **First stage**
  - surface resistance value, $\alpha$
  - diffusion coefficient, $D_1$
  - equilibrium uptake, $m_{\alpha 1}$
- **Second stage**
  - diffusion coefficient, $D_2$
4.2.4.1 Solution

As both main components of this model were separately able to be implemented using a spreadsheet, this two-stage model was treated in the same way. The simple Fickian with evaporative boundary model component was evaluated by summing a number of terms of its defining series, and the simple Fickian-only model component replaced by the curve-fit described in §4.2.2.2.

4.2.4.2 Model characteristics

Moving on to discuss more fully the behaviour of this model, it should first be noted that its characteristics can be complicated. Graphical characteristics for this model are presented later in §4.3.3, when this model is used for final characterisation of unstressed, room temperature-absorbed uptake behaviour of E32 and AV119. However, some of the more obvious model characteristics are discussed here.

Investigating this combined model set up with significant contributions from each part, as well as setting a significant boundary resistance within the simple Fickian-boundary model component, it was found (for given component bulk diffusion coefficients and α value) that varying the specimen thickness had quite a complex effect. Reducing the thickness results in the simple Fickian-boundary model component placing a greater importance on the boundary effect, transferring the early concavity through to the combined uptake curve. Increasing the thickness, however, results in the simple Fickian-boundary model component tending towards pure simple Fickian behaviour, the overall combined effect tending towards that of a combination of two superposed purely simple Fickian behaviours. Thus, a low knee and relatively flat secondary phase can be produced. Also, noting from before that the simple Fickian-boundary model converges with increasing thickness, such an increase causes the boundary contribution of this component to become insignificant. This in turn causes the combined model to converge in the \( U \) v. \( \sqrt{\frac{d}{k}} \) plane and for further increases in thickness not to have any effect. Again, this gives the superposition of two simple Fickian behaviours with a secondary linear region (see §4.2.2.2 on the dual simple Fickian model).
Because of the complexity of this combined model and the large range of possible predicted uptake curves, and also because the individual component behaviours have been presented earlier, it was felt superfluous and impractical to present graphical examples here. Thus, any further discussion of behaviour of this compound uptake model is carried out within the context of characterisation of the experimental AV119 and E32 uptake data in §4.3.3.
4.3 Application of uptake models to characterise experimental data

As stated earlier, the experimental study of the effects of stress on uptake behaviour were never intended to be carried further forward in this research. Therefore, the observations from §4.1.2.3 should simply be noted, whilst this research carries on to consider unstressed uptake only. That leaves both the effect of thickness and absorption temperature to be considered in the remaining sections of this chapter. The latter has important later implications to the validity or otherwise of using accelerated ageing tests, where inconsistencies between room temperature and hot mechanical degradation measurements may shed doubt as to the usefulness of this technique. Referring back to Figure 4-2 showing basic experimental uptake results, and with regard specifically to hot-absorbed E32, it has been decided not to attempt to model the observed experimental data because of the very unconventional shape of the mass gain curve, this possibly being a result of the chalk filler leaching out into the water. Therefore, the remaining in-depth treatment of uptake data will be restricted to room temperature-absorbed E32 and to room temperature and hot-absorbed AV119.

Also, whether the models presented under §4.2. are a phenomenological or mechanistic representation, it is important for the furtherance of the durability modelling stages of this research that a choice of model should be made here. Ideally, the mechanisms of uptake should be fully understood and a model directly derived from that knowledge. However, a minimum requirement here is that the observed experimental uptake behaviour should be at least characterised.

4.3.1 Initial characterisation of data using single-stage simple Fickian model

Viewing the experimental uptake data in the light of the characteristics of the presented uptake models, it immediately comes to mind that any single Fickian uptake model, with the basic instantaneous boundary equilibration condition, cannot possibly be used to characterise the uptake curve spread seen for varying specimen thickness. Therefore, for final characterisation, a model system which includes an evaporative boundary condition was finally chosen and this is discussed in later sections of this chapter. However, as a first
step in formally analysing the remaining experimental uptake data, it has been attempted to find closest possible fits using the simple, constant diffusion coefficient Fickian model. Again, already accepting that the thickness effect cannot be modelled without resort to something like a boundary effect, only the ~0.4 mm specimens have been treated at this stage. Obviously, with the shape of the experimental uptake curves (but not the equilibrium value) changing with varying specimen thickness, the optimum simple Fickian diffusion coefficient values will change. However, the results of this simple Fickian model fitting to the remaining ~0.4, unstressed specimens are shown in Figure 4-18. Table 4-7 then brings forward the equilibrium uptake values tabulated earlier in §4.1.2.1 and adds the best-fit Fickian constant diffusion coefficient values.

Figure 4-18 Best attempts at fitting remaining unstressed, thin, RT and Hot-absorbed experimental uptake data for E32 and AV119

<table>
<thead>
<tr>
<th></th>
<th>Diffusion Coefficient (10^{14}\text{m}^2\text{s}^{-1})</th>
<th>Equilibrium Uptake (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E32 (RT)</td>
<td>1.6</td>
<td>9.7</td>
</tr>
<tr>
<td>AV119 (RT)</td>
<td>2.9</td>
<td>5.1</td>
</tr>
<tr>
<td>AV119 (Hot)</td>
<td>13</td>
<td>6.6</td>
</tr>
</tbody>
</table>

Table 4-7 Best-fit parameter values for simple Fickian model, applied to remaining unstressed RT and Hot E32 and AV119
Looking at Figure 4-18, it can be seen straight away that the simple Fickian model generally cannot satisfactorily match the experimental data. Even in the best-approximated case of hot-absorbed AV119, the simple Fickian uptake curve shape seems not to match the inflections displayed by the experimental data. Then, in the room temperature-absorbed E32 and AV119 cases, the best attempts at a fit fall ridiculously short. Because the experimental uptake data tended not to fit the unique simple Fickian curve shape, a simple recipe was followed in choosing the "best fit" diffusion coefficient value. Once vertical scaling has been set by working to the appropriate equilibrium uptake level, the diffusion coefficient is the only remaining parameter available to define the locus of the modelled uptake curve. Therefore, the universal fitting approach taken here was to manipulate the value of the diffusion coefficient in order to match the initial slope of the experimental data. However, given the inability of the simple Fickian uptake model either to match single uptake curves or the thickness effect seen in the experimental data, a more complex approach was required.

4.3.2 Characterisation using single-stage concentration-dependent diffusion coefficient models

Again, independently of attempting to model the thickness effect, the issue in hand was to try to model the generally flat and low experimental uptake data. As discussed in the previous modelling sections of this chapter, another tool available to manipulate the shape of an uptake curve is to allow a concentration-dependent diffusion coefficient. However, referring back to Figures 4-10 to 4-13 in §4.2.1.2, it can be seen that a variable diffusion coefficient can be made to give only a relatively small manipulation in the shape of the uptake curve. Furthermore, it is suspected that the incorporation of a concentration-dependent diffusion coefficient within a more complex, multi-part uptake model would still not give the flexibility required. For this reason, this approach has been discarded from further characterisation work.
4.3.3 Characterisation using the two-stage Fickian model with evaporative boundary effect

From the model characteristics analysis carried out in §4.2 and its subsections, it can be seen that the experimentally observed thickness deviation in the $U$ v. $\sqrt{t/\ell^2}$ plane and the generally low-lying uptake data require the introduction of a boundary effect. As seen earlier, this component to any uptake model brings in a response to the balance between surface resistance and bulk diffusion effects, thus generating the required movement in the $U$ v. $\sqrt{t/\ell^2}$ plane. Then, the observation of low-lying uptake with a secondary linear phase, this perhaps being two-stage behaviour, points strongly to using a compound model. For these reasons, it was concluded that the two-stage model consisting of a simple Fickian uptake component superposed onto a simple Fickian bulk uptake model with an evaporative boundary model (as described in §4.2.4) should be used.

As hot-absorbed uptake data for AV119 had been obtained for a specimen thickness of ~0.4 mm only and thus was not as comprehensive as the room temperature data, characterisation could not be attempted with the current uptake model. Concentrating, therefore, on the unstressed, room temperature-absorbed, thickness-dependent data for both adhesives, this model was applied to the data shown in Figures 4-3 and 4-4 in §4.1.2.2 and a best fit sought. Remembering from §4.2.4 that this two-part model requires optimisation of the four parameters of a surface resistance value, $\alpha$, a diffusion coefficient value and an equilibrium uptake value for one component and a diffusion coefficient for the other component, significant mathematical effort was required. At first, this optimisation was attempted simply by trial and error but this soon became unrealistic. Whilst it was possible, looking at the pronounced thickness effect, to make an estimate of magnitude for the surface resistance parameter for the first model component, the interacting effects of the four parameters led to a very complex behaviour of the compound model. Therefore, using a series summation for the Fickian component with boundary effect and a polynomial representation for the pure Fickian component (as described in §4.2.2.2), a spreadsheet was used to carry out the optimisation. The solver used within the spreadsheet programme makes use of the Generalized Reduced Gradient (GRG2) nonlinear optimisation code developed by Leon Lasdon, University of Texas, and Allan Waren, Cleveland State University. However, attempting to optimise all four parameters using this solver caused
problems. Therefore, for each adhesive, one parameter was set purely from trial and error experience and optimisation carried out on the remaining three. Figures 4-19 and 4-20 show the resulting best fits for E32 and AV119, Table 4-8 listing the required model parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>E32</th>
<th>AV119</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a \times 10^{-11} \text{ms}^{-1}$</td>
<td>5.00</td>
<td>4.88</td>
</tr>
<tr>
<td>$D_1 \times 10^{-14} \text{m}^2\text{s}^{-1}$</td>
<td>13.75</td>
<td>10.0</td>
</tr>
<tr>
<td>$m_{\infty 1} %$</td>
<td>4.53</td>
<td>2.71</td>
</tr>
<tr>
<td>$D_2 \times 10^{-14} \text{m}^2\text{s}^{-1}$</td>
<td>6.07</td>
<td>10.0</td>
</tr>
<tr>
<td>$m_{\infty 2} %$</td>
<td>5.17</td>
<td>2.39</td>
</tr>
<tr>
<td>Converged thickness (mm)</td>
<td>16</td>
<td>18</td>
</tr>
</tbody>
</table>

Table 4-8: Best-fit parameter values for two-stage model with boundary effect, applied to unstressed RT-absorbed E32 and AV119 specimens of varying thickness

![Figure 4-19](image-url)  

**Figure 4-19** Best attempt at fitting unstressed, thin, RT-absorbed experimental uptake data for E32 using two-stage model with boundary effect (also showing model convergence).
These figures suggest that this most comprehensive model still fails to characterise the uptake behaviour of both E32 and AV119 accurately. However, not only does the model respond to the experimentally observed thickness effect, but it successfully reproduces the variation in uptake curve shape as thickness changes. The experimental data for both adhesives shows two-stage behaviour for thinner specimens, whilst thicker specimens display behaviour more akin to the single, rapid equilibration of the simple Fickian model. This transition is modelled well.

The above thus increases confidence that the current compound uptake model genuinely responds to the underlying mechanisms occurring in the diffusion process. Accepting that the model displays the main required properties as described above, the convergence behaviour with increasing thickness has important implications to durability modelling. Noting that the model shows convergence at a thickness of 16 mm for E32 and 18 mm for AV119, this quantifies the extent to which thin specimen uptake data would be in error when applied to joints with larger characteristic adhesive layer dimensions. Conversely, the model shows that, when the characteristic dimension of a joint reaches its converged value, boundary effects can be ignored.
In conclusion, whilst the fits to the experimental data are not ideal, the proposed compound model satisfies all the main characteristic behaviour patterns required. In addition to the basic thickness effect, this model successfully reproduces the transition from the two-stage uptake behaviour of thin specimens to the more conventional equilibration of thicker specimens. Also, this model comprises component building blocks which are all directly implementable using a standard thermal finite element analysis. Thus, it has been carried forwards and used as the final uptake model in the durability modelling work presented later in this thesis.

4.4 Conclusions

- the simple Fickian diffusion model with constant diffusion coefficient and instantaneous boundary equilibration fails to characterise experimental water uptake for both adhesives studied
- uptake response to varying specimen thickness is also non-simple Fickian, suggesting gradual boundary equilibration
- modelling work suggested that E32 does not assume Fickian-like thickness uptake scaling for specimen thicknesses less that 16 mm - and 18 mm for AV119. This warns of possible errors when using thin specimen uptake data to predict moisture profiles in adhesive layers with relatively large characteristic dimensions
- the introduction of a concentration-dependent diffusion coefficient does not have much influence on the resulting Fickian bulk uptake curve - the knee always remaining at approximately 0.8 fractional uptake. Although some authors have studied possible \( D(c) \) forms, the current research suggests that this cannot explain significantly non-simple Fickian uptake
- applied tensile stress increases uptake activity, suggesting increased degradation and with implications to the modelling of simultaneously exposed and loaded adhesive joints
- in final conclusion, a two-stage uptake model with additional boundary effect was chosen to represent the moisture absorption characteristics of the two adhesive studied. This model reproduced well both the thickness effects and the general undulating uptake curve shapes (characteristic of two-stage processes) observed experimentally
5. Moisture-dependent elastic-plastic properties of bulk adhesives

This chapter describes both the experimental and modelling aspects of work carried out on the mechanical properties of bulk adhesives. With regard to the experimental studies, it was hoped that results would be generally consistent with the literature and that mechanical properties would be found to be significantly moisture-dependent and thus support the proposition of a cohesive environmental durability model. Furthermore, the intention was to provide moisture-dependent elastic-plastic material models for E32 and AV119 for use within the chosen finite element durability modelling framework. Thus, moisture-dependent uniaxial tensile properties were measured for both E32 and AV119, the adhesives selected for this project.

Various approaches to the characterisation of mechanical properties were then investigated, making use of these uniaxial stress-strain data. These included the consideration of both mechanistic models and phenomenological curve-fitting of individual parameters such as elastic modulus and ultimate tensile strength as functions of water concentration. Finally, with a view to providing material models within ABAQUS, the complete measured stress-strain curves used as a basis for moisture-dependent material definitions. Together with the previous water uptake modelling work and the assumption that moisture concentration is instantaneously and uniquely related to bulk adhesive degradation [70], this programme of mechanical properties work therefore provides the next important link in the environmental durability chain.

5.1 Experimental programme

The purpose of this work was first to confirm the moisture-dependence of mechanical properties of E32 and AV119 and then to obtain uniaxial tensile stress-strain curves as a basis for characterisation and later provision of elastic-plastic material definitions within ABAQUS. Although water uptake was studied at both room temperature and at 55 °C., all
Chapter 5: Moisture-dependent elastic-plastic properties of bulk adhesives

mechanical properties measurement and subsequent modelling work has been carried out at room temperature conditions.

5.1.1 Choice of mechanical testing technique

As this research aims to predict the residual strength of sequentially exposed and loaded adhesive joints, a quasi-static uniaxial tensile testing technique was selected as the method of obtaining mechanical properties data for the two bulk adhesives being investigated. Thus, the required elastic-plastic stress-strain behaviour could be measured over a full range of strain, up to final failure.

In the early planning stages of this section of the research, dynamic mechanical thermal analysis (DMTA) was also considered and some initial tests carried out, but this technique outputs largely time and temperature-dependent data which is of less relevance here. Useful information is therefore limited and typically obtained over only a small range of strain. Also, the mechanical properties of the bulk adhesives were not required over the extended temperature range available to the DMTA technique. As all final strength and durability modelling was to be at ambient temperature, mechanical properties were required only at room temperature.

Therefore, a programme of dry and environmentally exposed bulk adhesive testing work was implemented, making use of an Instron 6025 servo-electromechanical testing machine. For the purposes of this work, only axial strain data was required.

5.1.2 Test specimen design and manufacture

Considering the relative slowness of the water uptake process, it was decided to make use of thin flat dogbone specimens for the tensile testing programme. Also, bearing in mind the need not to drive out absorbed water from wet specimens, it was decided that the dogbones should be manufactured to their final profile prior to ageing. The alternative of absorbing a large sheet of adhesive to a target moisture content and then cutting out individual dogbone specimens was felt to be too awkward and likely to interfere with uptake levels. Thus, dogbones were manufactured before ageing from dry thin parent sheets of bulk adhesive,
the latter having previously been prepared as described in Chapter 3. For testing of an aged batch of specimens, it was then intended to remove the specimens from water and test them on the Instron with as little delay as possible.

To keep ageing times to a minimum and to follow the specimen manufacturing procedures used in the previous chapter, it was decided to carry out the tensile testing using dogbones approximately 0.4 mm in thickness, this corresponding to the standard minimum thickness category of specimen used in the previous uptake work. Although using specimens of this limited thickness risked creating handling difficulties, it was considered to be the best overall option. Figure 5-1 shows the geometry of these specimens. Again, using thin specimens enabled target moisture levels to be absorbed into the adhesives reasonably quickly, pre-cutting the dogbones to the final profile avoiding the risks associated with excessive physical handling before testing. To have an already-profiled specimen and to be able to test very soon after removal from water was felt very important, as it was felt that excessive handling of dogbones after ageing would lead to the generation of heat and evaporation of absorbed moisture.

![Figure 5-1 Profile of tensile dogbone specimen](image)

The dogbone specimens were machined from thin rectangular blanks of bulk E32 and AV119, roughly cut from dry parent sheets of adhesive. A Deckel CNC milling machine, together with a suitable program, was used to produce the profile to a high degree of consistency and accuracy. Up to half a dozen blanks were stacked together and cut in each session. Each stack was first clamped to a special, custom-made jig mounted on the table of the milling machine, clamps purchasing on the central region of the uppermost blank top surface. A small hole was then drilled through the stack of blanks on the centreline and towards each wider end of what would eventually be the finished dogbone profile. The
central clamps were then removed and the two through-holes used, together with an upper aluminium clamping plate (with a profile just smaller all round than the finished dogbone), to sandwich and fix the blanks firmly onto the jig for machining of the final profile with an edge milling cutter. Bearing in mind the very brittle nature of both adhesives, especially dry and in thin sections, this machining process gave a very low specimen breakage rate and good edge finish. Nevertheless, each specimen was lightly abraded to prevent any loose particles falling off during water absorption and affecting the back-checking of water uptake via mass measurement.

5.1.3 Design of test programme

In order to retain a broad range of experimental mechanical properties data and to continue to consider the possible use of accelerated uptake tests as part of durability prediction, it was decided to age dogbone specimens at both room temperature and at 55 °C. Even thought it was previously seen that E32 responded very unconventionally with respect to its hot uptake behaviour, mechanical testing was still carried out on E32 absorbed at the higher temperature. Again noting that all mechanical testing was carried out at room temperature, the hot-absorbed adhesive specimens were thin enough to cool very rapidly to ambient temperature in the short gap between removal from water and testing. Furthermore, having already measured the uptake behaviour of E32 and AV119 specifically in the 0.4 mm thickness range, these curves could be used directly in determining required immersion times, without reference to suggested uptake models. As an additional check on uptake level, however, each dogbone was weighed after removal from water, this consistently confirming initial estimates.

A fast, consistent and efficient procedure of removal from water and tensile testing was developed in order to minimise water loss due to evaporation. First of all, the Instron was fully set up. Then, once a batch of dogbones had been removed from water at the required time, mass uptake was checked by weighing individual specimens before placing them in a close-fitting and sealable plastic bag, where they remained until mounted in the Instron for testing. Even considering that it was usual to test a batch of four wet specimens at a time, the delay between removal from water and testing was kept down to between 15 minutes
and 1 hour. Again, as the cooling process for hot-absorbed specimens was achieved in a matter of seconds, executing the testing quickly did not interfere with this.

In cases where a batch of specimens was hot-absorbed to a target moisture level, another batch was simultaneously stored in a desiccator within an oven at the same temperature. This was done in order to check whether the elevated temperature conditions themselves led to further postcure of the adhesives and thus influenced the mechanical properties. As a by-product of this, the number of batches of dry dogbone specimens tested was increased substantially. Whether hot postcuring in the desiccator had an effect on the mechanical properties of the adhesives is discussed later in this chapter. With respect again to testing two parallel batches of specimens, the wet batch was tested first in order to cut down any unnecessary delay between removal from water and testing.

Next, the choice of moisture levels was addressed and it was decided that in addition to reference dry tests, batches of specimens of each adhesive should be absorbed to two moisture levels at each temperature. These moisture levels would be very approximately half-saturated and fully-saturated, relative to the corresponding absorption temperature. In the event of obvious inconsistencies between room temperature and hot-absorbed mechanical properties, this would give a minimum useful 3 data points for each adhesive at each absorption temperature. With regard to achieving the fully-saturated condition at room temperature, however, the earlier experimental uptake work suggested that very lengthy ageing times would be required. For this reason, target room temperature-absorbed moisture levels were reduced slightly. Even so, for all four adhesive and absorption temperature combinations, mechanical properties would be produced for the dry, moderately wet and heavily wet material. Whether or not the hot-absorbed data would be consistent with the room-temperature-absorbed data, and whether it would be subsequently used, was considered when all the results were available. This point has important implications as to the viability of using accelerated uptake tests as part of durability modelling and this is discussed later in this chapter. Comparing with experimental equilibrium uptake values presented in Table 4-2 in the last chapter, uptake values actually achieved for the tensile dogbone specimens are shown below in Table 5-1, as are ageing times.
## Chapter 5: Moisture-dependent elastic-plastic properties of bulk adhesives

<table>
<thead>
<tr>
<th></th>
<th>RT-absorbed</th>
<th>Hot-absorbed</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$m$ (%)</td>
<td>$U$ (-)</td>
</tr>
<tr>
<td>E32 (slightly wet)</td>
<td>4.53</td>
<td>0.467</td>
</tr>
<tr>
<td>E32 (heavily wet)</td>
<td>9.14</td>
<td>0.942</td>
</tr>
<tr>
<td>AV119 (slightly wet)</td>
<td>2.28</td>
<td>0.447</td>
</tr>
<tr>
<td>AV119 (heavily wet)</td>
<td>3.55</td>
<td>0.696</td>
</tr>
</tbody>
</table>

Table 5-1 Uptake levels achieved for experimental mechanical properties programme

With regard to hot-absorbed E32, all moisture levels were treated with caution due to this adhesive's unconventional uptake behaviour at elevated temperatures. Note that Brewis et al.'s [28] technique was used to determine effective equilibrium uptake for hot-absorbed E32. Using this technique, the mass fall-off part of the gravimetric curve is extrapolated back to the uptake axis to estimate diffusion-only equilibrium. Furthermore, for any one batch of aged specimens, the thickness of individual dogbones typically varied slightly from the nominal target 0.4 mm. As all specimens within a batch were aged for the same time, this led to a corresponding slight variation in moisture level. However, as individual specimen weighings were always consistent with both the target moisture level and thickness, the mass uptake values calculated from individual post-ageing specimen weights were averaged across each batch to produce a single representative moisture level for that batch. Also, bulk moisture levels were assumed to act uniformly within a specimen, effects of locally varying concentration evening out.

Finally, it was decided for duplication purposes that each batch of specimens, dry and wet, should usually consist of up to 4 dogbones. Occasionally, a specimen would break prematurely or would give obviously erroneous mechanical properties data, this resulting in the number of stress-strain curves obtained being reduced. However, this was never felt to be a problem.
5.1.4 Test details

As there was significant complexity involved in the tensile testing procedure itself, various issues are discussed in detail in the following sections. These include the physical set-up on the Instron, as well as strain measurement and determination of suitable crosshead speeds.

5.1.4.1 Instron set-up

An Instron 6025 static tensile testing machine fitted with a 5 kN load cell was used to carry out the uniaxial tensile tests, all being carried out at a room temperature of 22 ±1 °C. A conventional 25 mm, knife-edge, contact extensometer was used to record axial strain but problems were encountered with the experimental set-up. This at times necessitated calculation of strain using crosshead position data, as described in later sections of this chapter. Although various details are discussed later, Figure 5-2 shows the tensile test set-up. Note the use of supporting blocks placed behind the specimen and level with the knife-edges of the extensometer. 30 kN wedge grip jaws (Instron catalogue number 2716-015) were used to hold the specimens.
5.1.4.2 Load measurement

Load was measured using a 5 kN load cell (Instron catalogue number 2518-805) mounted in the top frame of the Instron 6025 machine. Its accuracy is specified as 0.1% of cell-rated output or 0.5% of indicated load, whichever the greater. Quick initial calculations knowing the approximate specimen cross-section and based on an estimate of maximum possible ultimate stress then suggested that the load cell should be operated at its 500 N sub-range in order to maximise accuracy. This setting was used for all tensile tests within this programme, and possible errors due to changing between ranges were thus avoided.

5.1.4.3 Strain measurement

Although load measurement is perhaps fundamentally easier to achieve with accuracy, strain measurement was more difficult because of the thinness of the specimens being
tested. Initially, a standard 25 mm gauge length axial knife-edge contact extensometer (Instron code number 248), as shown schematically in Figure 5-2, was used to measure strain. In order to prevent the self-weight of the extensometer causing excessive distortion of the specimen, it was supported by a vertical length of cord attached to a convenient point on the Instron frame. However, it was found that the position of attachment of the cord to the extensometer body had a pronounced effect on strain output.

This was first suspected when elastic modulus values for dry E32 and AV119 specimens, determined from preliminary tests, were calculated to be in the region of approximately 1000 to 2000 MPa. Generally available information, however, suggested that these values were perhaps unrealistically low. However, subsequent manual calibration tests on the same extensometer suggested very accurate operation. This caused a false sense of security in the validity of the axial strains recorded during many of the tensile tests and delayed further investigation until near the end of the programme.

When the problem was eventually addressed formally, it was considered possible that either the extensometer legs were slipping on the specimen or that the specimen distortion caused by the clamping reaction of the extensometer was causing erroneous strain measurements. To investigate this, a specimen was set up in the Instron, with the axial extensometer attached as usual. In addition, however, a travelling microscope was positioned adjacent to the specimen in order to provide another measure of axial strain by way of directly measuring the distance between the extensometer leg knife-edges. Then, as a third indication of strain, crosshead position data was also recorded.

Once this three-fold axial strain measurement set-up was complete, the crosshead was driven to a predetermined load and then held at that position. Then, working quickly in order to avoid inaccuracies due to specimen relaxation, extensometer strain, crosshead position and travelling microscope measurements were taken. When all this data had been recorded, the crosshead was restarted and driven to the next load point and the various strain measurements taken again. About ten equally-spaced load points, spread over the expected load range of the specimen, were planned.

This calibration test produced some interesting results. Analysing specimen strain and extensometer knife-edge displacement determined using the above methods, it was first
confirmed that the slight distortion of the thin specimen due to the attachment of the extensometer was not significantly influencing strain measurement. However, it appeared that although the knife-edges were not slipping on the specimen, the strain output from the extensometer was far in excess of the actual strain being experienced by the specimen - hence the lower than expected elastic modulus results being calculated.

Eventually, it was decided to check whether the extensometer support system was affecting the strain output. The original set-up had the cord attached to the junction of the built-in upper leg and the extensometer body. However, the support was changed, with the extensometer now supported by a vertical cord attached to the rearmost extreme of it's body casing. Again, crosshead position and travelling microscope readings were used to confirm actual strain. It now appeared that the extensometer was giving accurate strain results. This test was carried out yet again with a fresh specimen. Again, extensometer, crosshead and travelling microscope data were all consistent. Therefore, with the repositioning of the support, it was felt that the extensometer could now be used to measure strain with more confidence.

However, for all tensile tests that had been carried out prior to rectifying the above problem, alternative methods had to be used to provide correct axial strain data. The following sections describe these alternative calculations.

**Calculation of unyielded strain from crosshead position data**

Where extensometry was thought to have been in error, crosshead displacement data was used to estimate specimen strain. For later calculation of elastic modulus, where just the early part of the stress-strain behaviour was required, it was possible to use a simple correlation using a constant proportion of crosshead displacement to estimate strain. Bearing in mind the actual profile of the dogbone tensile test specimens, previously shown in Figure 5-1, it can be visualised that yielding will occur first in the thinner gauge section of the dogbone, whereas the wider end tab sections remain unaffected. This local yielding will result in a differential weakening of the dogbone as stress increases. However, it can be assumed that, for lower loads generating maximum axial stresses well short of any yield behaviour, the dogbone material can be assumed to have constant elastic modulus throughout. Thus, early strain was calculated from crosshead position data simply by
apportioning the total specimen extension between grips in accordance with the changing specimen width. To simplify the curved arcs of the specimen shoulders in these calculations, the actual specimen shape was replaced by the geometric approximation shown in Figure 5-3.

![Figure 5-3 Geometric approximation to the actual dogbone profile](image)

Taking sections 1, 2 and 3 to refer to the gauge length, trapezoid and free end-tab regions of the above stylised dogbone profile, respectively, it is assumed that the specimen is under load with the gauge length section experiencing an axial stress, \( \sigma_1 \). The elongation in the gauge length section thus becomes:

\[
\delta_1 = \frac{l_1 \sigma_1}{E} \quad \text{(36)}
\]

Noting that axial stress is inversely proportional to local specimen width, and using a single mean specimen width for the trapezoidal regions, elongations for sections 2 and 3 can be written:

\[
\delta_2 = \frac{l_2 w_1 \sigma_1}{w_2 E}, \quad \text{and} \quad \delta_3 = \frac{l_3 w_1 \sigma_1}{w_3 E} \quad \text{(37, 38)}
\]

where \( l_2 \) and \( l_3 \) represent total lengths of the relevant specimen sections. The total specimen elongation between jaws thus becomes:
\[ \delta_{\text{tot}} = \delta_1 + \delta_2 + \delta_3 = \left( l_1 + \frac{l_2 w_1}{w_2} + \frac{l_3 w_1}{w_3} \right) \sigma_1 \frac{\varepsilon}{E} \]  

(39)

Then, the ratio of gauge length elongation to total specimen elongation becomes:

\[ \frac{\delta_1}{\delta_{\text{tot}}} = l_1 \left/ \left( l_1 + \frac{l_2 w_1}{w_2} + \frac{l_3 w_1}{w_3} \right) \right. \]  

(40)

Finally, using the specific dimensions in Figure 5-3, the strain in the gauge length section can be written:

\[ \varepsilon_1 = 100 \cdot \frac{\delta_{\text{tot}}}{\left( l_1 + \frac{l_2 w_1}{w_2} + \frac{l_3 w_1}{w_3} \right)} = 1.20 \delta_{\text{tot}} \cdot \varphi \]  

(41)

with \( \delta_{\text{tot}} \) in mm. Thus, assuming uniform unyielded elastic modulus, gauge length strain can be calculated from total crosshead displacement. With the extensometer set up properly, uniaxial stress-strain curves generated from crosshead displacement data were compared to extensometer-based results. This comparison was very favourable over a good proportion of ultimate strain. Figure 5-4 shows an example comparison for a moderately wet AV119 specimen.

![Figure 5-4](image)

**Figure 5-4** Comparison of extensometer strain and strain determined from crosshead displacement data assuming uniform, unyielded elastic modulus
Calculation of ultimate strain from crosshead position data

In addition to elastic modulus values calculated from crosshead position data, ultimate axial strain values were also calculated. Whereas the elastic modulus calculations assumed no yielding and used low strain crosshead position data, different assumptions were made when calculating ultimate strain. Here it was assumed that, even at failure, the wider end tabs of the dogbone specimen would not have yielded, i.e. those regions would have retained their original elastic modulus value. This in turn is dependent on the assumption that a specimen would not suffer from excessive post-yield hardening, and this was generally borne out by existing load-displacement curves which showed smart transition into plastic behaviour after the initial linear region. Neither was there ever any visible evidence of local specimen necking which might have invalidated this approach. Replacing the curves shoulder regions of the specimen by a sudden step between end-tab and gauge section widths, strain at failure in the end-tabs could be estimated using elastic modulus and ultimate load data. This could then be subtracted from the total crosshead displacement-to-failure, giving the ultimate strain of the yielded gauge section of the specimen.

As an additional check as to the validity of assuming that the end tabs remain unyielded, Figure 5-4 can again be referred to. The uniaxial stress-strain data for this moderately wet AV119 specimen shows a UTS of approximately 42.5 MPa and a yield stress of perhaps 26 MPa. Using a simple specimen width ratio between gauge length and end-tab regions, and taking a condition of ultimate load in the former region, gives an estimated stress in the end-tab regions of only a little over 18 MPa. This is well below yield and thus supports the proposed method for estimation of ultimate strain. As before, strain data from the correctly-working extensometer was compared to estimated results. This comparison again confirmed the validity of the above calculations.

5.1.4.4 Logging of test data

A virtual instrument panel written in National Instruments LabView software running on an Apple Macintosh platform was used to log load, displacement and extensometer strain via the Instron console’s RS232 data port. The virtual instrument automatically sensed the
start and end of each tensile test and issued a prompt to save the recorded data to the Apple Macintosh's hard disk. Subsequently, these text files could be loaded into Microsoft Excel for further manipulation of data.

5.1.4.5 Determination of crosshead speeds

When considering the choice of crosshead speed for the various tests, it was decided to attempt to keep the total test duration approximately constant for all tests. The aim was to have a slow enough crosshead speed in order to avoid rate-dependence becoming a factor and to have a high enough speed to avoid creep effects. It was therefore decided to aim for a test duration of 5 minutes, this also helping to avoid excessive evaporation of water from wet specimens. Initial trial and error tensile tests suggested that both E32 and AV119 should be tested at a crosshead speed of 0.5 mm/min in the fully-dry condition. Moving onto the fully-wet condition, however, both adhesives became more compliant - especially E32. This led to a crosshead speed range requirement of between 1 and 3 mm/min for the wet adhesives, depending on the level of moisture content.

5.1.4.6 Details of test execution

After removing the specimen to be tested from the sealed bag used to store the absorbed dogbones between removal from water and testing (only in the case of wet specimens), a micrometer was used to measure the cross-sectional dimensions of the gauge length section of the thin dogbone. Working quickly to avoid excessive evaporation, the specimen was then clamped centrally in the jaws of the tensile testing machine. The axial extensometer was then attached to the specimen, taking great care not to exert any undue force. The crosshead was then driven downwards just enough to take out any excessive initial slack in the specimen. After checking the seating and alignment of the extensometer, the load cell and extensometer were then zeroed ready for the start of the test. The LabView data logging software, as described in §5.1.4.4, was also set up and made ready to record load, strain and crosshead position data upon test commencement.

With the appropriate crosshead speed selected, the test was started and allowed to run until specimen fracture, the aim being to capture the mechanical behaviour of the specimen up
to and including the plastic region of the stress-strain curve. Upon test completion, the data logged using LabView was saved to file and later processed using a spreadsheet. Any remaining tests in the session were carried out as quickly as possible. As discussed earlier, a typical batch of wet specimens consisted of four dogbones. Working quickly and taking into consideration the target test duration and set-up time for each specimen, a batch of four specimens typically took perhaps a little over half an hour to test, the use of a sealed plastic bag for wet specimen storage further helping to avoid moisture loss.

5.1.5 Experimental results

After carrying out the above programme of environmental mechanical properties testing of both adhesives, the text files created by LabView were processed using a spreadsheet. Taking strain (either calculated using the above techniques or directly from the extensometer output) and calculating axial stress by dividing recorded load by specimen cross-section, uniaxial stress-strain curves were generated for every specimen tested. These results are shown in Figures 5-5 and 5-6. Again, a typical dry or wet dogbone test duration would be approximately 5 minutes.

![Strain-axial stress diagram](image_url)

**Figure 5-5 Basic tensile test results for individual E32 dogbones**
Firstly, it can be seen for both adhesives that dry heated postcuring (to create parallel batches of tensile specimens in the hot-absorbed cases) did not discernibly influence the measured mechanical properties. Then, it can immediately be seen that absorbed moisture leads to a pronounced degradation in mechanical properties for both adhesives. Although perhaps some of the wet specimen curves for E32 show significant spread within batches, the grouping is reasonably tight and produces a clear picture of the effects of absorbed moisture. However, more detailed observations as well as whether hot-absorbed data is consistent with room temperature-absorbed results are discussed in the following sections.

5.1.5.1 Moisture-dependent mechanical properties of E32

Accepting that the individual specimen tensile results fit together to provide a consistent view of the effects of environmental ageing, it helped to take these results and produce average curves for each absorption condition. This aids both the current discussion of mechanical properties trends and also provides a clear foundation for characterisation work presented later in this chapter. Thus, Figure 5-7 shows the five averaged and representative environmental stress-strain curves for E32. Deciding to characterise the general behaviour as elastic-plastic, but with more detail than elastic-perfectly plastic, these curves were then inspected and broken down into parameters of elastic modulus, $E$, yield stress, $\sigma_y$, ultimate
tensile stress (UTS) and the strain at which UTS is effectively achieved (or pre-perfectly-plastic strain, PPPS). These are shown in Table 5-2. Ultimate strain is not tabulated, as this parameter later takes no part in either moisture-dependent mechanical properties modelling or in the overall finite element environmental durability modelling stages of this research. Note also that yield stress and PPPS are hard to define clearly and are very subjective. Furthermore, there often being no clearly linear stress-strain behaviour for E32, elastic modulus has been calculated from a chord joining the origin of the axis system to the yield point. This was felt to give a value which would be a genuine representation of material behaviour over a finite stress range, and thus more valid than an instantaneous, initial tangential value. All these calculated parameters find their main use in the sections on mechanical properties modelling later in this chapter, but they are also useful here as an addition to the graphical results.

![Graph](image)

**Figure 5-7 Averaged stress-strain curves for E32**

<table>
<thead>
<tr>
<th>Condition (%(temp.))</th>
<th>Elastic Modulus (MPa)</th>
<th>Yield Stress (MPa)</th>
<th>UTS (MPa)</th>
<th>PPPS (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry</td>
<td>2008</td>
<td>15.1</td>
<td>31.7</td>
<td>3.9</td>
</tr>
<tr>
<td>3.11(Hot)</td>
<td>1130</td>
<td>14.6</td>
<td>20.4</td>
<td>3.1</td>
</tr>
<tr>
<td>4.53(RT)</td>
<td>538</td>
<td>10.6</td>
<td>17.5</td>
<td>27</td>
</tr>
<tr>
<td>6.06(Hot)</td>
<td>369</td>
<td>4.86</td>
<td>15.9</td>
<td>30</td>
</tr>
<tr>
<td>9.14(RT)</td>
<td>338</td>
<td>6.17</td>
<td>13.2</td>
<td>27</td>
</tr>
</tbody>
</table>

**Table 5-2 Moisture-dependent mechanical properties parameters for E32**
Concentrating on the mass uptake levels only, as individual fractional uptake values are dependent on the relevant absorption temperature-dependent equilibrium level, Figure 5-7 shows a clear reduction in both key parameters of elastic modulus and ultimate strength going from the dry condition to the wettest. Across the whole fractional uptake range tested (0 - 0.942), these parameters experienced reductions of 83% and 58%, respectively. At the two wettest conditions of 6.06% (Hot) and 9.14% (RT), however, no certain distinction can be made. Then, turning to ultimate strain, this can be seen to increase consistently and very markedly over the moisture level range.

With regards to the consistency between room temperature and hot-absorbed mechanical properties, Figure 5-8 shows the above-tabulated mechanical properties parameters plotted against mass uptake. Looking first at the more easily determined parameters of elastic modulus and UTS, the figure shows reasonably smooth progressions throughout the wetness range, irrespective of absorption temperature, thus indicating that the latter does not influence the mechanical properties of E32 - at least, up to 55 °C. These trends also suggest that degradation slows down as moisture is absorbed, perhaps explaining why the 6.06%(Hot) and 9.14%(RT) cases show similar properties. Yield stress and PPPS, however, do not produce smoothly decreasing curves as in the case of the previous parameters, although they do still show a generally consistent environmental response. Therefore, whilst taking care in the interpretation of mechanical properties data, it looks feasible that accelerated uptake tests, using absorption temperatures of up to 55 °C., can indeed be used as part of a durability modelling framework.

In summary, E32 shows a clearly pronounced degradation in environmental mechanical properties. It also appears that room temperature and hot-absorbed mechanical properties are consistent throughout the wetness range tested and thus supports the possibility of using accelerated uptake tests as part of a wider durability modelling programme. However, despite this apparent convenience, it must be borne in mind that mass uptake was difficult to define bearing in mind E32's unconventional hot uptake behaviour.
* As for E32, these averages determined visually.
5.1.5.2 Moisture-dependent mechanical properties of AV119

Referring back to Figure 5-6, no discernible effect of hot postcure was seen between the different batches of dry specimens, and both room temperature and hot-absorbed results were taken together. Figure 5-9 shows the five averaged uniaxial stress-strain curves for dry and wet AV119. Table 5-3 then shows elastic modulus and other parameters calculated from these curves. Although not generally necessary with E32, the measured mechanical properties data for dry AV119 required a small degree of extrapolation in order to estimate UTS. Figure 5-9 and Table 5-3 both reflect this slight adjustment but do not distort the following interpretation of environmental response.

Again, Figure 5-9 shows a general degradation of mechanical properties with increasing absorbed moisture, although perhaps this is not as clear for intermediate moisture levels as in the case of E32. Here, the curves appear not to be in the anticipated relative positions. Particularly, elastic modulus and UTS for the 2.28% (RT) and 3.55% (RT) cases seem to be in the wrong order, the properties for the latter case appearing less degraded than for the former.
Chapter 5: Moisture-dependent elastic-plastic properties of bulk adhesives

Figure 5-9 Averaged stress-strain curves for AV119

<table>
<thead>
<tr>
<th>Condition (%) (temp.)</th>
<th>Elastic Modulus (MPa)</th>
<th>Yield Stress (MPa)</th>
<th>UTS (MPa)</th>
<th>PPPS (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry</td>
<td>2294</td>
<td>30.0</td>
<td>66.3</td>
<td>5.0</td>
</tr>
<tr>
<td>2.28(RT)</td>
<td>2052</td>
<td>26.7</td>
<td>42.6</td>
<td>8.0</td>
</tr>
<tr>
<td>3.55(RT)</td>
<td>2262</td>
<td>30.7</td>
<td>45.0</td>
<td>3.0</td>
</tr>
<tr>
<td>3.60(Hot)</td>
<td>1919</td>
<td>25.4</td>
<td>45.1</td>
<td>3.8</td>
</tr>
<tr>
<td>5.73(Hot)</td>
<td>1516</td>
<td>19.9</td>
<td>29.7</td>
<td>2.9</td>
</tr>
</tbody>
</table>

Table 5-3 Moisture-dependent mechanical properties parameters for AV119

Both these sets of results were generated from extensometer data after the strain measurement problem had been rectified, so this potential error can be eliminated. Furthermore, the two curves for the very similar mass uptake levels 3.55%(RT) and 3.60%(Hot) show significantly different elastic modulus values whilst retaining virtually identical UTS. This further confuses detailed interpretation of moisture-dependent mechanical properties for AV119, although the dry and 5.73%(Hot) curves do seem to suggest definite environmental degradation over a wide range of absorbed moisture levels. Working across this approximately complete fractional uptake range, elastic modulus and UTS decrease by 34% and 55% , this relative reduction in elastic modulus being much less than corresponding one for E32. However, the question as to the validity of using
accelerated uptake tests for environmental durability modelling purposes is hard to answer with certainty.

Although the detailed response of mechanical properties to absorbed moisture at intermediate uptake levels is not clear for AV119, a plot of the parameters shown in Table 5-3 above is presented in Figure 5-10. This figure helps in the visualisation of the effects of moisture and confirms the differences in environmental response of AV119 to the case of E32. Whilst noting possible inconsistencies between the 3.55%(RT) and 3.60%(Hot) data points, an overview perhaps suggests a generally linear decrease in elastic modulus. With regards to UTS, the limited experimental data again allows at most the suggestion of a linear decrease with absorbed moisture. Given the currently available data, the form of this degradation with respect to moisture content would be hard to determine precisely.

The results shown previously in Figure 5-9 show additionally that, unlike the case of E32, ultimate strain appears to decrease with increasing absorbed moisture. However, just as it seemed to lie at the basis of the inconsistency above, the 2.28%(RT) curve breaks the trend by displaying an uncharacteristically large ultimate strain value of nearly 10%. Note that the literature [17, 23, 75] is divided on the effect of absorbed moisture on ultimate strain.

![Figure 5-10 Moisture-dependent mechanical properties parameters for AV119](image-url)
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Given the fact that elastic modulus for AV119 seems less relatively degraded by moisture than for E32, perhaps this supports the fundamental concept that the elastic modulus of an unfilled, highly cross-linked material is more difficult to change. Bearing in mind that AV119 is toughened by a much smaller volume content of relatively water-resistant rubber particles, as opposed to the sensitive chalk filler particles of E32, perhaps this is not surprising. Finally, although it is not certain whether room temperature and hot-absorbed mechanical properties are consistent from the limited range of experimental data presented here, it remains a strong possibility.

5.1.6 Conclusions

- absorbed moisture substantially degrades both E32 and AV119. Over an effectively complete saturation range, E32 experiences an 83% reduction in elastic modulus and a 58% decrease in UTS. Over a slightly reduced saturation range, corresponding reductions for AV119 are 34% and 55%, respectively
- experimental results for E32 support the validity of using mechanical properties measured using hot-absorbed specimens in the prediction of room temperature durability. AV119 requires further investigation

5.2 Characterisation of moisture-dependent bulk adhesive elastic-plastic properties

The previous sections of this chapter have already shown a definite influence of absorbed moisture on the mechanical properties of E32 and AV119. In the case of AV119, the behaviour at moderate moisture levels was perhaps vague, although overall degradation was seen over a wider range of ageing. In the case of E32, however, the environmental degradation trend in the various chosen mechanical properties parameters was more consistent across the different moisture levels and absorption temperatures. In this and following sections, these parameters are characterised as functions of moisture content in order further to quantify environmental degradation and establish any trends. It has also been sought to define these trends in such a way that full moisture-dependent elastic-plastic material definitions can be provided for use within the finite element durability modelling programme presented in Chapter 7. Various characterisation approaches have
been investigated here, starting with mechanistically-based modelling of individual stress-strain parameters presented previously in Tables 5-2 and 5-3.

5.2.1 Mechanistic approach using mixture laws

Although this treatment cannot be applied to the characterisation of yield stress or UTS, mixture laws are commonly used to estimate the elastic modulus of composite materials from a knowledge of geometry, volume fraction of the component phases and component elastic properties. In the case of this research, either of the two adhesives being studied can possibly be regarded as a "composite" for two reasons. Firstly, both can be considered to be physical composites due to the fact that they are particulate-filled or toughened adhesives. Whereas E32 is filled with chalk particles (of approximate average diameter 2 µm), AV119 is toughened by the addition of much smaller rubber particles of typical diameter less than 0.1 µm. Alternatively, however, the physical composite nature of an environmentally aged adhesive can be ignored and it can instead be seen as a conceptual "composite" consisting of a mixture of fully-wet and completely dry phases.

5.2.1.1 Introduction to mixture law models

Various mixture law models were tested against experimental mechanical properties data for the two adhesives. Two bounding models most obviously suited to unidirectional fibre reinforced composites (the uniform strain and the uniform stress models) were investigated first. Then, Hashin and Shtrikman's model [76] was investigated. These models are introduced in the following sections, noting again that volume fraction values can refer either to literal filler particles or to conceptual proportions of fully-wet adhesive. Note, however, that mixture law approaches are not necessarily ideal when modelling either holes or rigid particles within a physical composite matrix. In such cases, predicted modulus bounds can become either zero or infinite and thus serve little practical use. This comment is aimed particularly at E32, with its chalk filler particles. As is discussed later, chalk in its dry state has a much greater stiffness than a typical epoxy resin and thus approximates to a greater or lesser extent to being rigid. However, chalk's physical response to becoming wet is to disintegrate completely. Used as filler particles within an adhesive, the chalk could therefore begin to act as voids within the resin.
Uniform strain model

Figure 5-11 shows a schematic of an idealised fibre-reinforced composite loaded in tension in line with the direction of the fibres.

Matrix \((E_m, \sigma_m)\)

\[ \varepsilon \]

Fibres \((v_f, E_f, \sigma_f)\)

\[ \varepsilon \]

**Figure 5-11** Schematic of uniform strain mixture law model for elastic modulus

For the set-up shown above, the fibres have an elastic modulus, \(E_f\), the matrix has an elastic modulus, \(E_m\), and there is a volume fraction of fibres, \(v_f\). In the context of modelling elastic modulus for wet adhesives, the matrix could represent the resin and the fibres could represent the rubber or chalk particle filler in the adhesive. Alternatively, the matrix and fibre components could be made to represent symbolic dry and fully-wet zones within some partially-wet adhesive. The composite is then loaded with total, overall stress, \(\sigma\), due to which the composite experiences an axial strain of \(\varepsilon\). Because of the geometry of the composite and the direction of loading, both the fibres and the matrix experience the same strain. Applying conventional linear elastic theory to the model above, and equating strains in the direction of loading, the following standard result is obtained for overall composite elastic modulus:

\[
E_c = \frac{\sigma}{\varepsilon} = v_f E_f + (1 - v_f) E_m
\]

The above represents the classical uniform strain model which always gives an extreme upper bound to the prediction of elastic modulus in any composite material. For given component elastic modulus values, this model represents a straight line composite modulus between the two as volume fraction varies from zero to unity. Note also that this model is stable for cases where one phase has zero elastic modulus.
Figure 5-12 shows another schematic of an idealised fibre-reinforced composite, this time loaded in tension transversely to the direction of the fibres.

\[ E_c = \frac{\sigma}{\varepsilon} = \frac{1}{\frac{v_f}{E_f} + \frac{(1-v_f)}{E_m}} \]  

The above equation then gives the other classical mixture law model for elastic modulus, this time providing a lower bound. Unlike the straight line characteristics of the uniform strain model, the uniform stress model represents a "sagging" composite modulus curve between the two extreme component modulus limits as volume fraction varies. Also unlike the uniform strain model, the uniform stress model is not defined for cases where one phase has zero elastic modulus.
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Hashin and Shtrikman's model

Another composite stiffness model used to investigate the variation of mechanical properties with respect to water content was one developed by Hashin and Shtrikman [76]. This model predicts improved upper and lower composite moduli bounds in terms of component moduli and volume fraction information. Stated to be one of its strengths, this model can be successfully applied to a wide range of composite geometries, as long as the moduli of the two phases are comparable. Although their model can be written for an n-phase composite, the moduli bounds for the two-phase case can be expressed as follows:

\[ K_1^* = K_1 + \frac{v_2}{K_2 - K_1} + \frac{3v_1}{3K_1 + 4G_1} \]  \hspace{1cm} (44)

\[ K_2^* = K_2 + \frac{v_1}{K_1 - K_2} + \frac{3v_2}{3K_2 + 4G_2} \]  \hspace{1cm} (45)

\[ G_1^* = G_1 + \frac{v_2}{G_2 - G_1} + \frac{6(K_1 + 2G_1)v_1}{5G_1(3K_1 + 4G_1)} \]  \hspace{1cm} (46)

\[ G_2^* = G_2 + \frac{v_1}{G_1 - G_2} + \frac{6(K_2 + 2G_2)v_2}{5G_2(3K_2 + 4G_2)} \]  \hspace{1cm} (47)

Then, to convert from Hashin and Shtrikman's shear and bulk modulus system, the following elastic relationships can be used to determine elastic modulus and Poisson's ratio values:

\[ K = \frac{E}{3(1 - 2\nu)} \]  \hspace{1cm} (48)

\[ G = \frac{E}{2(1 + \nu)} \]  \hspace{1cm} (49)
However, it must again be noted that this model is not appropriate in cases where one phase assumes very different elastic properties to the other, in which case the upper and lower moduli bounds move further and further apart and become of little use.

5.2.1.2 Use of mixture laws to model elastic modulus for E32

Referring back to Figure 5-8 and Table 5-2, showing the variation of mechanical properties parameters with absorbed moisture, it can be seen that elastic modulus seems to be a gently downward curving function of uptake, perhaps levelling off towards the fully-wet end of the scale. As both the room temperature and hot-absorbed data seemed consistent, it was considered together. Also, for consistency of plotted fractional uptake values here, mass uptake percentages for the two hot cases were normalised against room temperature equilibrium uptake. In cases where wet adhesive is to be modelled as a mixture of dry and fully-wet portions, it is useful to provide a value for composite elastic modulus in the fully-wet condition before commencement of modelling. Following the smooth pattern of degradation already seen for E32, and noting that there was a near-saturation modulus value at 9.14% (U = 0.942), a value of 317 MPa was estimated for U = 1.0. Other information available included volume fraction of chalk filler particles and their (dry) elastic modulus and Poisson's ratio. Bysh et al. [110] quoted a filler volume fraction of 12% for E32, the chalk particles having a (dry) elastic modulus in the range 10000 to 17000 MPa and a Poisson's ratio of 0.2. They also measured E32's overall Poisson's ratio to be 0.406.

Firstly, considering environmentally aged E32 to consist of a mixture of fully-dry and fully-wet proportions of adhesive, whereby volume fraction becomes identical to fractional uptake, the uniform strain model defines a linear variation of composite modulus with respect to absorbed moisture level. It has already been seen, however, that this is not the case. In fact, with the downward sagging characteristics of the uniform stress model, this would seem to be a better candidate. Given the experimentally measured dry composite elastic modulus value of 2008 MPa and the estimated fully-wet value of 317 MPa, Figure 5-13 shows how both the uniform strain and uniform stress models fit the experimental data. Next, Hashin and Shtrikman's model was applied to the same dry-wet "composite" visualisation for E32. Figure 5-13 also shows the bounds defined by this model, with the
assumption that absorbed moisture does not affect the 0.406 Poisson's ratio of E32. The figure clearly shows the inadequacy of the uniform strain model in matching the experimental data. Both the uniform stress and Hashin and Shtrikman's model, however, provide closer fits.

Next, environmentally aged E32 was visualised as a literal composite, with the chalk filler assuming its actual volume fraction of 12%. With this visualisation, the modelling of the effects of increasing absorbed moisture has to work differently. Some assumptions have to be made about the environmental response of the resin and filler phases and then the various mixture law models can be used to fill in the gaps.

Using first the simple uniform strain model to experiment with manipulation, and bearing in mind the various unknowns, two assumptions were made. Firstly, from physical experience, it was assumed that the chalk filler in fully-wet E32 would attain zero elastic modulus. Then, it was assumed that the resin itself was not degraded at all by moisture. Thus, using overall elastic modulus values at the fully-dry and fully-wet, the uniform strain model was made to fit those two end points by choosing a dry elastic modulus for chalk of 14090 MPa. Note that this value is consistent with the range quoted by Bysh et al. [110]. However, this implementation of the model does not define a path between the two end
points. And certainly, no assumption was made about the behaviour of chalk as it becomes partially-wet. Unless an assumption can be made as to the continuous environmental degradation of the filler, this model cannot be used to predict moisture-dependent overall composite elastic modulus. Furthermore, there is no mention in the literature to support the postulation that unfilled epoxy adhesives do not environmentally degrade like their filled counterparts, thus making unsound the assumption that the resin phase maintains constant elastic modulus. Moving on then to consider the uniform stress and Hashin and Shtrikman's models, neither is meaningful in cases where one phase attains zero elastic modulus. Therefore, for such a chalk-filled adhesive, these models are fundamentally inappropriate.

In summary, the most successful application of mixture laws to model moisture-dependent elastic modulus for E32 was when the adhesive was not visualised as a literal composite but as a conceptual composite consisting of fully-dry and fully-wet proportions. Taking the experimentally measured dry elastic modulus value of 2008 MPa and the estimated fully-wet elastic modulus value of 317 MPa, both the uniform stress and Hashin and Shtrikman's models produced reasonable fits to the intermediate-wetness experimental data. However, despite the more complex formulation of Hashin and Shtrikman's model, the appreciable range of environmental elastic modulus drives the upper and lower bounds apart more than would be liked. Although this model successfully characterises the general curved variation in experimentally measured elastic modulus, the uniform stress model produces the closest fit.

Thus, the best mixture law attempt at modelling moisture-dependent elastic modulus for E32 can be written as follows:

\[
E_c = \frac{1}{\frac{U}{E_{\text{wet}}} + \frac{1-U}{E_{\text{dry}}}} \tag{50}
\]

where \(E_{\text{wet}}\) assumes the estimated fully-wet value of 317 MPa and \(E_{\text{dry}}\) assumes the experimentally measured dry value of 2008 MPa. Note again that fractional uptake, \(U\), is defined here as either room temperature or hot-absorbed mass uptake divided by the room temperature equilibrium uptake value of 9.7% for E32.
5.2.1.3 Use of mixture laws to model elastic modulus for AV119

Two things are apparent with AV119 when considering the viability of the physical composite model. Firstly, the mechanical properties data for AV119 was not as well-ordered and consistent between absorption temperatures as it was for E32. Secondly, it is very difficult to determine the environmental response of the rubber toughening particles present in AV119. As the dry-wet "composite" visualisation looked most promising for E32, however, a similar approach was taken with AV119.

Discarding the hot-absorbed 5.73% data point because it exceeds the adhesive's room temperature equilibrium uptake value of 5.1%, the remaining four points perhaps suggest a linear degradation of elastic modulus with absorbed moisture. Note for now that the seemingly inconsistent elastic modulus value at the 3.55%(RT) is ignored. This implies that the uniform strain model would be appropriate to characterise the experimental data, rather than the uniform stress and Hashin and Shtrikman's models.

With an estimated elastic modulus value for the fully-wet condition of 1750 MPa, Figure 5-14 shows the linear fit using the uniform strain model to visualise AV119 as a mixture of fully-dry and fully-wet proportions. Again, using this visualisation, fractional uptake becomes exactly equivalent to volume fraction. The figure also superposes uniform stress and Hashin and Shtrikman fits for information purposes.

It can be seen that the wet-dry conceptual "composite" implementation of the uniform strain model characterises the experimentally degraded elastic modulus for AV119 well. Thus, moisture-dependent elastic modulus for AV119 can be characterised closely as follows:

\[ E_c = U E_{\text{wet}} + (1 - U) E_{\text{dry}}, \]

where \( E_{\text{wet}} \) assumes the estimated fully-wet value of 1750 MPa and \( E_{\text{dry}} \) assumes the experimentally measured dry value of 2294 MPa. As in the case of E32, fractional uptake, \( U \), is defined here as either room temperature or hot-absorbed mass uptake divided by the room temperature equilibrium uptake value of 5.1% for AV119.
5.2.2 Characterisation using curve-fitting

Although the previous application of mixture laws produced fair estimates of moisture-dependent elastic modulus for both adhesives, the post-yield hardening behaviour could not be successfully modelled. Thus, this approach was not adequate for the planned elastic-plastic finite element durability work. The finite element modelling requires the provision of moisture-dependent definitions of global uniaxial stress-strain behaviour for the two adhesives. Therefore, it was decided to investigate curve-fitting as a technique to characterise the moisture-dependent mechanical properties of E32 and AV119.

Retaining the dry-wet conceptual composite uniform stress mixture law fit for E32 elastic modulus (Equation (50)) and uniform strain mixture law fit for AV119 elastic modulus (Equation (51)), curve-fits as functions of room temperature-normalised fractional uptake were used to characterise yield stress, UTS and PPPS for both adhesives. Although elastic modulus and UTS are more easy to define, the more subjectively estimated properties of yield stress and PPPS are retained to aid visualisation of environmental degradation. Elastic modulus and UTS alone cannot adequately give a feel of the variation in uniaxial stress-strain behaviour as moisture is absorbed. Again, ultimate strain was not formally modelled as this was hard to define reliably from the experimental results.
5.2.2.1 Curve-fitting of yield stress, UTS and PPPS for E32

Referring back to Figure 5.7 and Table 5-2 showing moisture-dependent yield stress, UTS and PPPS values for E32, curve-fitting software was used to characterise each of these parameters as a function of room temperature-normalised fractional uptake. Considering the apparently nonlinear relationship between each of the properties parameters and uptake, appropriate smooth curve fits were selected in an attempt to retain the essential behaviour of the experimental data. Also, as no experimental mechanical properties data points seemed obviously inconsistent, nothing was discarded at this stage.

The apparently sigmoidal behaviour of both yield stress and PPPS highlighted one of the problems associated with a strict interpretation of the original experimental stress-strain data. Without careful control of subjective points such as yield and PPPS, resulting simple curve fits can produce inconsistencies when using this technique to reconstitute stress-strain behaviour at any chosen uptake level. For example, in early curve fitting attempts for the mechanical properties parameters of E32, the above uncertainty in fixing yield and PPPS caused erroneous inflections in modelled stress-strain curves. However, to demonstrate that the curve fitting principle can be successfully used to characterise moisture-dependent stress-strain behaviour, Figures 5-15 and 5-16 show the individual parameter curve-fits and a series of sample reconstituted moisture-dependent stress-strain curves. Although not overlaid for reasons of clarity, this model reproduces the key properties very closely at the experimentally measured uptake points.
5.2.2.2 Curve-fitting of yield stress, UTS and PPPS for AV119

Similar to the approach taken for E32 and referring back to Figure 5-10 and Table 5-3, curve-fits were used to model yield stress, UTS and PPPS as functions of room temperature-normalised fractional uptake for AV119. Inspecting the figure and remembering that elastic modulus was modelled as a linear function of uptake in the
application of mixture laws, it would appear that linear functions could be applied to the other mechanical properties parameters, too. Certainly, in this case, the figure does not suggest more complex functional relationships than linear. Again, preferring to standardise by normalising fractional uptake against room temperature conditions, the last experimental data points at a hot-absorbed 5.73% were discarded. Assuming these linear curve-fits, Figures 5-17 and 5-18 show the characterisation of the individual properties parameters as well as the resulting reconstituted stress-strain curves at sample uptake levels.

![Figure 5-17](image-url)  
**Figure 5-17** Curve-fitted moisture-dependent yield stress, UTS and PPPS for AV119

![Figure 5-18](image-url)  
**Figure 5-18** Curve-fits used to model moisture-dependent stress-strain behaviour for AV119
5.2.3 Definition of moisture-dependent mechanical properties using complete uniaxial stress-strain curves

Thinking still of the later finite element durability modelling, the above proposed models must now be compared to the conventional way in which moisture-dependent elastic-plastic material properties are defined within ABAQUS. In conjunction with additional material models defining 3-dimensional yielding and flow, it would be normal to use experimentally measured uniaxial stress-strain curves to define material properties. Thus, for example, using a number of experimental data points, stress can be defined as a function of plastic strain and moisture concentration. From this discrete data, ABAQUS then linearly interpolates between nearest supplied points to calculate material properties at any given concentration and strain. However, although fine discretisation of stress-strain curves can be used to define material properties, the interpolation procedure cannot be controlled.

5.2.4 Conclusions

- uniform strain and uniform stress mixture law models successfully characterised moisture-dependent elastic modulus for both E32 and AV119. In both cases the adhesive was represented not as a literal composite but as a mixture of dry and fully-wet portions
- additional curve-fitting of the other individual properties parameters allowed the full range moisture-dependent elastic-plastic behaviour to be characterised, although care must be taken not to apply this technique to an excessive number of subjective or imagined stress-strain points (e.g. yield stress)
- for ease of use, however, it is suggested that finely discretised complete uniaxial stress-strain curves should be used to define adhesive mechanical properties within later durability modelling work (Chapter 7). With additional experimental mechanical data at more frequent uptake levels, accuracy would be improved still further
6. Experimental adhesive joint durability studies

A programme of experimental adhesive joint durability studies was undertaken in order to confirm that joint strengths were degraded by moisture and that the mode of failure for significantly degraded joints could be cohesive, thus supporting the development of a cohesively-controlled durability model. Also, it was necessary to provide experimental data against which to validate the later finite element durability modelling work presented in this research. It was planned to age a series of E32 and AV119 adhesive joints by immersion in water and then to measure residual strength as a function of moisture content in the adhesive layer. Whereas much of the durability literature presents environmental degradation information against exposure time, the previously-obtained uptake results enable residual strength to be related directly to moisture content. As in the case of the previous experimental bulk adhesive mechanical properties work, all joint testing was carried out at a room temperature of 22 ±1 °C. As before, to retain breadth of experimental data and to further consider the validity of using accelerated tests as part of durability prediction, both room temperature and hot-absorption were retained for the joint programme. Also, and importantly, all joints were to be aged in an unstressed condition and then tested for residual strength afterwards. The environmental response of a simultaneously loaded and exposed joint was not investigated within this research, the current work focusing on a sequential ageing and loading scenario.

Residual strength testing itself involved loading of the joints using the Instron 6025 machine. The set-ups and determination of the crosshead speeds used are discussed later in this chapter. Test results data universally consisted of load and time data, from which failure loads were extracted. Failure loci were also determined by visual inspection, this being supported by both macro photography and scanning electron microscopy (SEM).
6.1 Choice of joint geometry

It was decided to study two joint geometries, these being single lap-shear and thin, plane butt. The single lap-shear geometry is forgiving of slight lay-up inaccuracies and gives good joint strength but typically presents a long path for water uptake into the middle of the adhesive layer. The butt geometry, on the other hand, is more sensitive to lay-up inaccuracies and gives relatively poor joint strength but presents a much shorter path for water uptake - and so, more immediate durability data. Also, both of these geometries are common and are represented well in the literature.

6.2 Choice and sizing of substrate raw materials

Looking for suitable substrate materials to give good interfacial strength and so encourage cohesive failure, it was decided to concentrate on steel and aluminium alloy. These are two very common substrate materials, with particular applications in the automotive and aircraft industries. There is also much information in the literature about the use of suitable surface pretreatments to ensure good resistance to environmental attack. Both suggested substrate materials were investigated with a view to finding at least one system which gave reliably cohesive environmental failure.

Besides making a good choice of substrate material and pretreatment in order to ensure durable interfaces, it was important to size the steel and aluminium lap-shear substrates such that joint failure was encouraged to be cohesive within the adhesive. In the case of this geometry, excessive bending or failure in the substrate due to undersized dimensions were to be avoided. This sizing was carried out using Crocombe et al.'s adhesive joint stress analysis method, which takes account of substrate bending. Using estimates of failure load and adhesive layer dimensions, a maximum combined bending and axial tensile stress of 550 MPa was predicted in the substrate for a particular grade of high tensile steel available in a stock thickness of 3.20 mm. As a previous tensile test on this material had given a 0.1% proof stress of 580 MPa, it was considered that substrates of this thickness would experience little significant strain or yielding. Thus, this grade of steel was used in strips of a standard size of 12.65 mm width by 3.20 mm thickness. The individual
lap-shear substrates were then cut from the raw strip to a finished length of 150 mm. For the less critical butt geometry, mild steel plate of thickness 2.90 mm was sufficient.

The use of aluminium alloys with their generally lower strengths required more thought, however. With this in mind, it was decided to make use of existing stocks of aircraft grade BS L 157 - T6 alloy for both the butt and lap-shear aluminium substrates. This particular grade of alloy with the T6 heat treatment has a specified minimum 0.2% proof stress of 390 MPa and minimum ultimate tensile strength of 440 MPa. Thus, this alloy is of high strength and was considered suitable to resist substrate failure or excessive lap-shear substrate bending under load. For the manufacture of aluminium butt substrates, it was decided to make use of some existing 2.50 mm sheet and for lap-shear specimens it was decided to use 4.20 mm plate. Further supporting calculations using Crocombe et al.’s [111] method gave an estimated maximum tensile stress in an aluminium substrate of this grade of 308 MPa, this being below the 0.2% proof stress quoted in the British Standard. The lap-shear substrates were cut from this plate to dimensions of 12.65 mm in width and 102 mm in length, the latter being the full width of the raw plate stock.

6.3 Choice of surface pretreatments

Surface pretreatments were used on both the steel and aluminium alloy substrates for both the butt and lap-shear joints in order to maximise interfacial durability. The literature suggests different classes of pretreatment for steel and aluminium. The general conclusion is that mechanical pretreatments, possibly with additional priming, gives the best durability for steel and that acid etches and anodising treatments give the best results for aluminium alloys. The following sections discuss the final choices in more detail.

6.3.1 Pretreatment used for steel substrates

Considering first the steel substrates, the literature [5, 100, 101, 102] would seem strongly to recommend a pretreatment combination of degreasing, grit-blasting and the application of a silane coupling agent. With regards to degreasing, it was decided to use two consecutive ultrasonic baths of analytical grade acetone. Then, turning to the grit-blasting medium, reference to the literature [100, 101] suggested that white alumina gave both good...
dry strength and durability. With that in mind, 180/220-grit white alumina was chosen as the blasting medium to be used to treat the bond areas of all steel substrates in this adhesive joint testing programme. This was applied using a Redashe grit-blasting machine operated at 90 PSI and with the applicator pistol held approximately 70 mm away from, and perpendicular to, the substrate. The silane solution application parameters were considered next. As discussed in the Literature Review chapter of this thesis, Gledhill et al. [102] carried out such a study. Focusing on γ-glycidoxypropyltrimethoxysilane (Union Carbide A-187), they found that a 1% aqueous solution produced best durability results when left to age at room temperature after initial mixing for between approximately 30 and 90 minutes before application. Therefore, the above pretreatment scheme was used here for steel, the following list giving the full application details:

- initial degrease in liquid acetone using a stiff brush to remove and dissolve gross surface contaminants
- grit-blast with 180/220-grit white alumina
- remaining alumina dust blown off surfaces with high-pressure nitrogen
- first ultrasonic degreasing bath in liquid acetone for 15 minutes
- removal from first ultrasonic bath and draining
- second ultrasonic degreasing bath in liquid acetone for 15 minutes
- removal from ultrasonic bath and excess contaminated acetone immediately blown off with high-pressure nitrogen
- bond areas of substrates dipped in aqueous silane solution for 4 minutes
- removal from silane solution and excess blown off with high-pressure nitrogen
- final drying of substrates in oven for 5 minutes at 40 °C.
- substrates removed from oven and bonded within 10 minutes

As the above stages were fairly simple to implement, the pretreatment of the steel substrates was carried out in-house in the Adhesives Group laboratories.

6.3.2 Pretreatment used for aluminium alloy substrates

Again, the literature suggests that aluminium alloys require different pretreatment to steel and it is commonly accepted [14, 87, 91] that acid etches and anodising treatments give the
best interfacial durability. With this in mind, all aluminium alloy butt and lap-shear substrates were given a phosphoric acid anodising pretreatment, closely based on the classic Boeing BAC 5555 procedure but with slightly changed alkaline cleaning and acid etch processes. In accordance with Digby and Packham [83], the originally specified BAC 5514 alkaline cleaner was replaced by the Minco N24205 alkaline cleaner and the FPL etch was replaced by the DEF STAN 03-2 chromic acid etch. Furthermore, as the processes involved are fairly hazardous and require significant investment of time and money to set up, the aluminium substrates were pretreated off-site at DERA, Farnborough. The details of this treatment are summarised below:

- Minco N24205 alkaline cleaner applied
- rinse
- DEF STAN 03-2 chromic acid etch applied
- rinse
- phosphoric acid anodising treatment applied
- rinse
- dry
- surfaces protected from contamination and bonded within two hours

Despite the fact that the aluminium substrates were pretreated off-site, close communication was maintained and arrangements were made to collect the substrates and bring them back to the University laboratories for immediate bonding. Thus, the requirement to bond within two hours of the final drying process was met with ease.

### 6.4 Detailed design of substrates and joint lay-up

In order to prevent the impedance of water uptake into the adhesive layer of the joints, it was felt that the manufacturing procedure should be designed to produce joints with an uninterrupted adhesive layer. Although it is common practice to use spacers of one form or another embedded in the adhesive layer itself, alternative substrate design and lay-up techniques were sought here. Whilst ballotini or lengths of wire embedded within an adhesive layer may not significantly affect the strength of a dry joint, these may well affect the ingress of water during environmental ageing of joints. And as this work intends to rely
Chapter 6: Experimental adhesive joint durability studies

upon the previous water uptake modelling to predict the moisture profile within the adhesive layer, this supported the need for the adhesive layer to be free of any obstructions. Therefore, adhesive layer thickness for all joints was controlled by the use of spacers placed externally to the adhesive layer.

The above decision to externally space lap-shear and butt substrates also influenced the choice of laying-up procedures. In the case of the butt joints, this decision also influenced the design of the substrates themselves. For both the steel and aluminium butt joints, specially slotted substrates were designed, which provided a central bond surface with remote outer lands for placement of spacers. A hole was also provided towards the rear of the substrate and on its axial centreline for application of loading during measurement of residual strength. Figure 6-1 shows this butt substrate design along with key dimensions. Control of the adhesive layer was achieved by wrapping several layers of conventional adhesive tape over the two outer lands of one of the two substrates used for each joint. Although a cure temperature of 120 °C. was used for AV119 joints, the adhesive tape used for adhesive layer control withstood these conditions without leading to increased scatter of layer thickness between joints. Using four layers of tape gave an approximate adhesive layer thickness for all butt joints of nearly 0.5 mm.

![Figure 6-1 Butt substrate design, allowing spacing externally to adhesive layer](image)

Figure 6-1 Butt substrate design, allowing spacing externally to adhesive layer
For the purposes of laying-up the butt joints, it was decided to assemble each joint individually. First, a strip of silicone-coated Melinex release film was placed against a simple mild steel backing plate of length somewhat longer than the completed joint. The bottom substrate was then placed against the Melinex and held to the backing plate with a spring clip. Holding the assembly near-vertically, a bead of adhesive was then applied along the central bond surface of this bottom substrate. The top substrate (one of them already having been spaced with tape) was then brought in and slid gently onto the bottom substrate and into visibly assessed alignment. A second spring clip was then applied to the top substrate, thus keeping the whole joint pinned flat to the backing plate. Very carefully, the adhesive layer region was then swept with a small straight edge on both the main face and on the slotted sides in order to remove any excess adhesive. As it was important to control the uptake of moisture into the adhesive layer, fillets were to be avoided. Typically, batches of twelve joints were made up in each session, the joints being stood near-vertically in a slotted wooden base for curing in the oven. This procedure was easy to implement and produced clean, accurate joints with a well-defined and neat adhesive layer. Using the bulldog clips and backing plate also ensured that the joints were kept flat, thus avoiding unwanted out of plane bending during later tensile testing. Figure 6-2 shows the above laying-up arrangement used for all butt joints.

Figure 6-2 Butt joint lay-up
The lap-shear joints required a different approach to the butt joints, as no special substrate profiling was needed. However, it was still required to externally space the adhesive layer. This time, an existing clamping jig was used to hold a complete batch of joints together in a single stack for curing. The jig was similar to a spring-loaded vice with a flat bed which both applied pressure to the stack of joints and also ensured lateral alignment of all joints. For the purposes of spacing, adhesive tape was again used. Dummy substrates (of the same dimensions as the actual substrates) were covered with several layers of adhesive tape, any excess being carefully trimmed off with a sharp knife. This produced substrate-like spacers of extra thickness, giving the required 0.25 mm adhesive layer thickness. Figure 6-3 shows this set-up and how the substrates and spacers were assembled to give a fillet-free adhesive layer. Thus, each joint assembly consisted of a block of two substrates and two spacers, a single blob of adhesive being applied to the centre of the overlap area of one substrate before placement of the other pieces. Note that a dry film mould release spray was used to coat the spacers to avoid them bonding onto the joint itself. Also, substrates were marked on their edges with a felt-tipped pen prior to bonding in order to aid judgement of overlap length, the target for both steel and aluminium joints being 12 mm. Strips of silicone-coated Melinex release film were also placed between each joint assembly in the stack, thus preventing adjacent joints bonding together during cure. Once the stack was assembled and the spring-loaded clamp applied, a tissue was used carefully to wipe away any excess adhesive from the sides of the adhesive layers. The jig was then placed into the oven at the required temperature to cure the joints.

**Figure 6-3 Lap-shear lay-up arrangement**
6.5 Curing of joints

Chapter 3 described the manufacture of thin sheet bulk adhesive specimens for both the adhesive uptake and the bulk mechanical properties work. It also discussed the curing temperature and duration requirements for E32 and AV119. However, the curing time for the AV119 joints was reduced to a more standard two hours at 120 °C. in the absence of the heavy steel plate moulds used for the bulk specimens. For E32, the original 48 hours at 40 °C. was retained. All cured joints were then stored in a desiccator at room temperature until required for ageing or testing, this storage duration being variable but typically a few weeks.

6.6 Individual measurement of adhesive layers

Even though the previously-described joint lay-up procedures were designed to control substrate alignment, the adhesive layers of all manufactured joints were individually measured to check consistency of manufacture. Because of the fine substrate manufacturing tolerances specified, adhesive layer length and width were not individually measured for the butt joints. Values of 10.0 mm and 2.90 mm, respectively, were used for all the steel butts and 20.0 mm and 2.50 mm for the aluminium butts in respect of these dimensions. However the following butt joint dimensions were measured on an individual basis:

- average adhesive layer thickness
- taper along the length of the adhesive layer

These individual butt joint adhesive layer thicknesses and tapers were measured using a shadowgraph machine in surface mode. Taking the steel and aluminium butt joints together, this programme of individual measurements gave a minimum adhesive layer thickness of 0.42 mm and a maximum of 0.54 mm, the mean of the whole group being 0.48 mm. This value is used in the finite element durability analysis in Chapter 7. With regard to butt joint adhesive layer taper, the 10.0 mm-long adhesive steel layers experienced a range of taper between zero (parallel) and 13%. The 20.0 mm-long aluminium butt joint adhesive layers had tapers up to 17%. However, taper was not
modelled at the finite element analysis stage and was noted purely in case of unexpected experimental residual strength results. No such inconsistency was positively identified.

In the case of the lap-shear joints, only the adhesive layer width was taken constant for all steel and aluminium joints, this being 12.65 mm for both materials. For the single lap-shear geometry, bearing in mind possible bending, yielding and exaggeration of destructive peel stresses at the ends of the overlap, substrate thickness is of great importance. As quoted previously, these dimensions were 3.20 mm for the steel substrates and 4.20 mm for the aluminium ones. Although the chosen joint lay-up procedures again encouraged uniformity of other lap-shear adhesive layer dimensions, the following were subject to greater variability and were measured individually for every joint manufactured:

- average adhesive layer thickness
- length of adhesive layer (or overlap length)

The shadowgraph was again used to measure the individual lap-shear adhesive layer lengths, but the average thicknesses were measured using a micrometer. First, the overall joint thickness across both substrates and adhesive layer was measured at the centre of the overlap and then twice the measured substrate thickness subtracted to give the adhesive layer thickness. Taking steel and aluminium joints together, the results of this individual lap-shear measurement programme showed that adhesive layer thickness varied from 0.17 mm to 0.38 mm, with 0.24 mm mean. With regards to overlap length, these varied from 11.2 mm to 12.2 mm, with a mean of 11.85 mm.

In the later presentation of lap-shear joint residual strengths, nominal average shear stress at failure was calculated as failure load divided by individual overlap area. Although noting the complex non-uniform stress distribution and effects of substrate bending in the case of the lap-shear geometry, it was felt important to reflect individual joint overlap differences in quoted results. In conclusion to the various adhesive joint dimensions presented here and in earlier sections, Table 6-1 summarises the appropriate details. As butt joint adhesive layer taper did not appear to affect residual strength and as it is not modelled in the later finite element work, these values are not tabulated. Also, Figures B-1 to B-4 in Appendix B show graphs of all individual adhesive layer thicknesses.
Environmental ageing and estimation of immersion times

In addition to dry tests, it was decided to aim for two levels of water content for each type of joint tested. As with the previous water uptake and bulk adhesive mechanical properties work, hot absorption was still retained in order to investigate further the validity of using accelerated laboratory tests to predict durability. However, considering the relatively long normal paths for diffusion of water into the adhesive layer of a joint - especially in the case of the lap-shear geometry - it was not attempted to reach a near-saturation value. As it was considered that achieving only an outer border of aged adhesive layer would probably give significant residual strength degradation for both the butt and lap-shear joints, relatively low target fractional uptake values were accepted. After initial calculations using joint dimensions and room temperature and hot-absorbed uptake data from earlier stages of the research, it was decided to aim for target fractional uptake levels of 0.125 and 0.25. Unlike the previously presented work on bulk adhesive mechanical properties, these fractional uptake values were calculated as normalised to their respective room temperature or hot equilibrium uptake values.

Not all joint types were tested at all uptake level and absorption temperature combinations. As the residual strength results began to come through, it became apparent that some joint types were prone to varying degrees of unwanted interfacial failure. In such cases, further tests at increased uptake levels were generally abandoned. The lap-shear joints were particularly prone towards more definite interfacial failure, the fracture surface often crossing from at or near one interface to the other. Then, for some wet joints of both geometries, a border of interfacial failure was observed. However, the programme of joint ageing and testing was carried out over many weeks and results continually monitored in
order to guide its direction. Despite abandoning various joint type and ageing combinations part of the way through the programme, all joint types were tested in the dry, 0.125(RT) and 0.125(Hot) conditions.

The required immersion time calculations were based on the ~0.4 mm bulk adhesive uptake results presented in Chapter 4. Because of the effect of thickness on uptake, discovered later, the joints would have achieved a higher than expected water content in the time allotted. Measuring the moisture content in the adhesive layer by weighing a joint was impractical because of the barely significant mass contribution of the layer and because of likely mass changes to the substrates due to corrosion or oxidation. Therefore, fractional uptake levels presented in this chapter should be taken only as a very rough guideline to increasing environmental ageing. Whilst it would be possible to modify the estimated 0.125 and 0.25 moisture levels using the more recent thickness-dependent uptake models for E32 and AV119, this could be done only for the room temperature-absorbed joints as the thickness effect was not investigated for hot-absorption. Therefore, the moisture levels presented in this chapter of the thesis serve only as approximate relative ageing markers or general tags. During the later finite element durability modelling of the room temperature-absorbed steel E32 butt joint, the diffusion part of the analysis determines the full 3-dimensional water profile in the adhesive layer using the final thickness-dependent uptake model presented in Chapter 4. Therefore, any values presented in this chapter are not critical to the overall durability modelling procedure.

Considering particularly the immersion of steel joints in water, initial tests with spare substrates showed that the usual distilled water caused severe rusting of the metal and the formation of a thick deposition within 24 hours at room temperature. Not wanting to accelerate possible corrosion-induced interfacial delamination of the adhesive layer, water used for adhesive joint ageing was "swept" clear of absorbed oxygen by bubbling nitrogen through it for half an hour beforehand, followed by a subjection to partial vacuum for a further half an hour. Further tests with treated water showed this procedure to markedly reduce the rusting problem.

Although, both the aluminium and steel butt joints had a bond area with significant width to length ratio, immersion time calculations for the nominal target bulk moisture levels were based on the previously-obtained one-dimensional thin specimen experimental
diffusion results. Thus, steel or aluminium adhesive layer half-width became equivalent to plane uptake specimen half-thickness, \( l \). In the case of the lap-shear geometry, a two-dimensional diffusion calculation was used with superposition to two mutually perpendicular one-dimensional effects, as follows:

\[
(1 - U_y) = (1 - U_x)(1 - U_y)
\]  

(52)

Thus, for the two-dimensional diffusion situation, the target 0.125 or 0.25 overall \( U_y \) value could be used, with appropriate half-thicknesses in the two directions, to identify the required immersion time from the raw one-dimensional diffusion results. For the butt joints, immersion times could be read directly off the experimental uptake plots with no two-dimensional to one-dimensional fractional uptake conversion.

6.8 Summary of joint testing programme

Collecting together the points outlined in the previous sections, the following combinations were planned for the programme of dry and aged adhesive joint residual strength testing:

- 2 substrate materials - steel ("MS") and BSL 157-T6 aluminium alloy ("AL")
- 2 joint geometries - butt ("B") and single lap-shear ("LS")
- 2 adhesives - E32 and AV119
- 3 nominal target moisture levels - dry, \( U = 0.125 \), \( U = 0.25 \)
- 2 absorption temperatures - RT and 55 °C.

This therefore gave eight joint "types", each to be aged at either room temperature or at 55 °C. up to an estimated fractional uptake level of 0.25, depending on the promise shown by the initial dry and moderately aged joints. Thus, for example, using terminology to be retained throughout this thesis, a steel single lap-shear joint bonded with AV119, will be referred to as type "MS-LS-AV119". Then, when referring to this type of joint being aged in hot water to an approximate 0.25 fractional uptake, the label "0.25(Hot)" will typically be added. Note that the "MS" label originated from "mild steel" and is loosely applied as a general material descriptor to both butt and lap-shear substrates, even though the material used for the lap-shear joints was of a stronger grade.
Considering batch numbers, it was planned to allow a basic three or four duplicates for each joint type and ageing combination, depending on availability of the previously-manufactured joints and on the remaining planned tests. Eventually, this joint testing programme gave residual strength data for the eight joint types at the ageing conditions shown in Table 6-2. For the combinations tested, the table shows the immersion times used to give the estimated target uptake levels.

<table>
<thead>
<tr>
<th>Joint Type</th>
<th>Dry</th>
<th>0.125(RT)</th>
<th>0.125(Hot)</th>
<th>0.25(RT)</th>
<th>0.25(Hot)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MS-B-E32</td>
<td>0</td>
<td>18.7</td>
<td>1.3</td>
<td>75</td>
<td>-</td>
</tr>
<tr>
<td>AL-B-E32</td>
<td>0</td>
<td>13.8</td>
<td>1.0</td>
<td>55</td>
<td>-</td>
</tr>
<tr>
<td>MS-B-AV119</td>
<td>0</td>
<td>11.5</td>
<td>4.0</td>
<td>38</td>
<td>8.9</td>
</tr>
<tr>
<td>AL-B-AV119</td>
<td>0</td>
<td>8.5</td>
<td>3.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>MS-LS-E32</td>
<td>0</td>
<td>85</td>
<td>6.0</td>
<td>370</td>
<td>-</td>
</tr>
<tr>
<td>AL-LS-E32</td>
<td>0</td>
<td>85</td>
<td>6.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>MS-LS-AV119</td>
<td>0</td>
<td>55</td>
<td>9.9</td>
<td>182</td>
<td>45</td>
</tr>
<tr>
<td>AL-LS-AV119</td>
<td>0</td>
<td>55</td>
<td>9.9</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 6-2 Joint type and ageing condition combinations tested, giving immersion times in days. 4 joints in all dry joint batches; 3 joints in all aged joint batches

For every test combination represented in the above table, one joint was macro-photographed in order to present locus of failure information in support of the visual estimates made for each test. Some of this macro photography is discussed later in this chapter. Similarly, to support measured environmental degradation and visually estimated locus of failure, a programme of scanning electron microscopy was carried out on the fracture surfaces of dry and aged joints. As with the macro photography work, this is discussed later in this chapter.

6.9 Testing

The following sections describe the mechanical testing aspects of the residual joint strength programme. This includes the test set-up and determination of suitable crosshead speeds. As in the case of the previous bulk adhesive mechanical properties work, the Instron 6025 tensile testing machine was used to provide static residual joint strength data.
6.9.1 Selection of crosshead speeds

Although rate-dependence was not thought to be a significant issue with either E32 or AV119, it was intended to use crosshead speeds which would subject the adhesive layer in the joints to similar levels of equivalent strain rate experienced by the bulk adhesive dogbone specimens used for the mechanical properties work. As practicality suggested only one speed for all lap-shear joints and one or all butt joints, crosshead speed calculations were based on a nominal representative bulk adhesive dogbone test speed. Therefore, it was decided to base the joint test crosshead speeds on a typical value of a wet uniaxial bulk tensile test crosshead speed of 3 mm/min. Also, in the following calculations, other typical data was used. These included butt and lap-shear adhesive layer thicknesses of 0.48 mm and 0.24 mm and other joint dimensions (as given in Table 6-1), as well as substrate and adhesive material property estimates. An effective uniform bulk tensile specimen length of 88 mm was also used.

6.9.1.1 Calculation of crosshead speed for butt joint tests

The resulting von Mises effective stresses in response to applied direct strains to both a uniaxially-loaded bulk tensile specimen and an axially-loaded butt joint were estimated using simple linear stress-strain relationships and the von Mises expression. These were then equated to give the required butt joint crosshead speed as a factor of the dogbone test crosshead speed.

For the uniaxial bulk tensile situation, the effective axial strain rate can be written as follows:

\[ \dot{\varepsilon}_{\text{eff,bulk}} = \dot{\varepsilon}_{\text{axial,bulk}} = \frac{s_{\text{bulk}}}{L_{\text{eff,bulk}}} \]  \( (53) \)

In the case of the butt joint, however, the Poisson effect within the adhesive layer gives rise to an extra stress component in the direction of the adhesive layer length. Thus, the von Mises effective axial strain rate in the adhesive layer of the butt joint becomes:
\[
\dot{\varepsilon}_{\text{eff, butt}} = \dot{\varepsilon}_{\text{axial, butt}} \frac{\sqrt{\nu^2 - \nu + 1}}{(1 - \nu^2)}, \text{ where (assuming the substrates are rigid):} \\
(54)
\]

\[
\dot{\varepsilon}_{\text{axial, butt}} = \frac{s_{\text{butt}}}{d_{\text{butt}}} \\
(55)
\]

Equating effective strain rates for the uniaxial bulk and butt joint specimens then gives the required crosshead speed for the butt joint tests:

\[
s_{\text{butt}} = \frac{s_{\text{bulk}} d_{\text{butt}}}{L_{\text{eff, bulk}}} \frac{(1 - \nu^2)}{\sqrt{\nu^2 - \nu + 1}} \\
(56)
\]

Thus, substituting values for the bulk specimen Poisson's ratio, effective specimen length and bulk test speed as well as adhesive layer thickness, the required crosshead speed for the butt joint tests becomes 0.016 mm/min.

6.9.1.2 Calculation of crosshead speed for lap-shear joint tests

For the lap-shear case, effective strain rates were again equated between the joint and bulk tensile dogbone cases. Using a method developed by Crocombe et al. [11], the shear and direct stress field at the end of a single lap-shear overlap was estimated from typical failure load of 5 kN, material properties and adhesive layer dimension data. Using standard elastic relationships and then Mohr's circle of strain, principal strains were determined from this stress field. These were found to be 0.72\(\gamma\) and -0.35\(\gamma\), where \(\gamma\) is the shear strain in the direction of loading. Assuming plane strain, these values then gave a von Mises effective strain rate, which was related to geometry as follows:

\[
\dot{\varepsilon}_{\text{eff, lap-shear}} = 0.63\gamma = 0.63 \frac{s_{\text{lap-shear}}}{d_{\text{lap-shear}}} \\
(57)
\]

Then, equating effective strain rates between the uniaxial bulk tensile case and the lap-shear joint, again making use of Equation (53), the required crosshead speed for testing the joints can be estimated:
Using typical values, this gave a suggested crosshead speed for the lap-shear joints of 0.013 mm/min.

6.9.1.3 Final selection of crosshead speeds

Initial tensile tests on preliminary steel and aluminium butt and lap-shear joints with the above-suggested crosshead speeds highlighted some problems. The equivalent bulk-to-joint strain rate-based methods used above for determination of crosshead speeds should also result in approximate equivalence of test duration. However, preliminary tests on aluminium butts and aluminium and steel lap-shears gave test durations up to an order of magnitude longer than the average 5-minute duration of a bulk adhesive dogbone test. This suggested large errors in the assumptions made in the crosshead speed calculations. Note that the originally-calculated 0.016 mm/min crosshead speed successfully gave the required test duration for the steel butt joints and was thus retained.

Although the general joint geometry suggests minimal compliance in the load path, it was found that a significant proportion of crosshead displacement was being taken up with distortion of the substrate material around the loading holes in the case of the aluminium butt joint. As the substrates had been assumed completely rigid, the adhesive layer was not experiencing the calculated strain rate. Therefore, more preliminary tests were undertaken and the crosshead speed increased simply by trial and error until the test duration decreased to appropriate levels. This gave a final crosshead speed of 0.1 mm/min for all dry and aged E32 and AV119 aluminium butt joints.

The error in the predicted test duration was even worse for the lap-shear joints. In this case, clearly visible substrate bending could be seen as the load increased. Again, this substrate distortion was taking up most of the crosshead displacement. As the free substrates had again been assumed rigid in the original calculations, this represented a vast underestimation of adhesive layer strain. As with the aluminium butts, further preliminary tests were carried out with both aluminium and steel lap-shear joints and the crosshead
speed increased until a suitable duration was achieved. Despite the very different geometry
to the butts, 0.1 mm/min was again required to give the correct test duration and was
therefore used for all dry and aged steel and aluminium lap-shear joints.

6.9.2 Test set-up

In order to maintain correct alignment and consistency of joint loading, great care was
taken in setting up both the butt and lap-shear joints in the Instron. In the case of the butt
geometry, it was especially important not to exert any out-of-plane bending on the joint.
For the single lap shear geometry, peel stresses are unavoidable. However, care was taken
in alignment in order to avoid Mode III loading of the adhesive layer.

6.9.2.1 Butt joint set-up

For the butt joints, the 30 kN Instron chromed wedge-grip jaws were used in conjunction
with clevis pin attachments in order to apply the load as axially as possible and to avoid
application of moments to the substrates. Placing the hole towards the rear of each
substrate helped ensure pure axial tension in the substrate above the adhesive layer. Figure
6-4 shows this set-up.

![Butt joint set-up in Instron](image)
6.9.2.2 Lap-shear joint set-up

To enhance alignment, 25 mm-long pieces of spare substrate material were bonded to the inner face of each substrate end. Once the joint symmetry had been compensated in this way, the joint was then clamped centrally in the self-tightening wedge-grip jaws of the Instron. As all lap-shear substrates were 12.65 mm in width, compared to the 25.4 mm width of the jaw faces, the centrelines of both the joint and the jaws were marked before setting up. This helped to ensure no lateral twisting, resulting in inadvertent and unwanted Mode III loading. Figure 6-5 shows this lap-shear set-up.

![Figure 6-5 Lap-shear joint set-up in Instron](image)

Figure 6-5 *Lap-shear joint set-up in Instron*
6.10 Results of residual joint strength tests

As it was not possible to measure local substrate or adhesive layer strain, adhesive joint loading data was logged against time only. As with the previous bulk adhesive mechanical properties work, the same LabView data logging software (mentioned in §5.1.4.4) was used to capture load measurements in real time. Nominal average stresses were then calculated for both joint geometries. Although the stress fields are not uniform or uniaxial and therefore butt and lap-shear cases cannot be compared, it was felt that this calculation of a nominal average shear stress to quantify failure strength for the latter geometry was still useful in that it took account of slightly varying bond areas between individual joints.

By way of introducing the joint test results, Figures 6-6 and 6-7 show the nominal average tensile or shear stress response of the butt and lap-shear joints against time for the various joint types and ageing conditions tested, results for E32 and AVI19 not having been separated here. Figure 6-6 shows two clear groups of curves for the butt joints, and this is caused by the much higher crosshead speed used for the aluminium butts, in compensating for the distortion of the softer substrates around the loading holes. However, for both adhesives and for all ageing conditions, and independently of locus of failure, the stress against time response of the butt joints was essentially linear right up to sudden failure.

![Graph](image)

Figure 6-6 Butt joint load-time characteristics (one curve for each joint type and ageing condition combination)
Turning to Figure 6-7, representing the lap-shear joints, it can be seen that failure is not so sudden and definite as in the butt joint case. This is perhaps an indication of progressive failure of the lap-shear bondline due to the non-uniform stress field and bending at the ends of the overlap.

The ultimate stresses from the complete programme of residual joint strength tests were then plotted against ageing condition for each of the eight joint type categories. These plots are shown in Figures 6-8 to 6-15 and are also annotated with visual estimations of locus of failure. More detailed individual joint adhesive layer thicknesses and failure loads are shown in Tables B-1 to B-8 in Appendix B. For the purposes of this research, identification of locus of failure was made on a visual level. As such, a failure surface displaying the appearance of the original unbonded metal substrate is labelled "interfacial". However, even a very light visible layer of adhesive on a substrate surface would result in the label "cohesive". Furthermore, for some aged butt and lap-shear joints, there was observed a definite border of interfacial failure around the exposed edges of the adhesive layer, almost certainly corresponding to the radial ingress of moisture. In the case of the lap-shear joints, it was normal for the fracture surface to zig-zag through the thickness of the adhesive layer, the path crossing from near one interface to the other.
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Figure 6-8 Failure stresses for MS-B-E32 joints

Figure 6-9 Failure stresses for AL-B-E32 joints

Figure 6-10 Failure stresses for MS-B-A V119 joints

Figure 6-11 Failure stresses for AL-B-A V119 joints

Figure 6-12 Failure stresses for MS-LS-E32 joints

Figure 6-13 Failure stresses for AL-LS-E32 joints
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Figure 6-14 Failure stresses for MS-LS-AV119 joints

Figure 6-15 Failure stresses for AL-LS-AV119 joints

Note that the annotations of "C", "C+IFB" and "IF" describe visually estimated locus of failure and have the meanings "cohesive", "cohesive with interfacial border" and "interfacial" respectively.

Together with the literature, the results of this programme of environmental adhesive joint residual strength testing suggest various aspects for investigation. Supported where appropriate with macro photography and scanning electron microscopy, these aspects are listed below:

- the effect of absorbed moisture on locus of failure
- the effect of absorbed moisture on residual strength
- the effect of absorbed moisture on adhesive and fracture surface texture and colour
- the effect of choice of adhesive on locus of failure
- the effect of joint geometry on locus of failure
- the effect of absorption temperature on residual strength and locus of failure

Before discussing the residual joint strength results, it must be noted that comparing results across butt and lap-shear geometries should be avoided due to the different loading situations present. E32 and AV119 results should also be considered separately. However, it may be valid from time to time to compare loosely between steel and aluminium results within each adhesive and geometry classification. First discussing Figures 6-8 to 6-15, it is immediately apparent that increased moisture content generally leads to a decrease in residual strength. Figure 6-13 for the AL-LS-E32 joints, is the only case where the opposite might be concluded. Although this joint type was tested in only the dry,
0.125(RT) and 0.125(Hot) conditions, all other E32 joint types show a degradation in residual strength over this range of ageing conditions. This one inconsistent set of results for the AL-LS-E32 joints could perhaps be explained by absorbed moisture relieving a higher stress concentration generated by aluminium substrates. For now, however, it is accepted that absorbed moisture does generally degrade adhesive joints. Table 6-3 summarises this observed decrease in residual strengths together with corresponding locus of failure.

<table>
<thead>
<tr>
<th>Joint type</th>
<th>Maximum nominal fractional uptake level tested</th>
<th>Average dry failure stress (MPa)</th>
<th>% degradation in residual stress over tested uptake range</th>
<th>Change in locus of failure</th>
</tr>
</thead>
<tbody>
<tr>
<td>MS-B-E32</td>
<td>0.25</td>
<td>50.6</td>
<td>41</td>
<td>remains C</td>
</tr>
<tr>
<td>AL-B-E32</td>
<td>0.25</td>
<td>49.4</td>
<td>41</td>
<td>remains C</td>
</tr>
<tr>
<td>MS-B-AV119</td>
<td>0.25</td>
<td>78.9</td>
<td>40</td>
<td>C → C+IFB</td>
</tr>
<tr>
<td>AL-B-AV119</td>
<td>0.125</td>
<td>84.2</td>
<td>28</td>
<td>C → C+IFB</td>
</tr>
<tr>
<td>MS-LS-E32</td>
<td>0.25</td>
<td>33.5</td>
<td>19</td>
<td>C → C+IFB</td>
</tr>
<tr>
<td>AL-LS-E32</td>
<td>0.125</td>
<td>27.3</td>
<td>-14</td>
<td>remains C</td>
</tr>
<tr>
<td>MS-LS-AV119</td>
<td>0.25</td>
<td>50.1</td>
<td>30</td>
<td>remains IF</td>
</tr>
<tr>
<td>AL-LS-AV119</td>
<td>0.125</td>
<td>49.6</td>
<td>7.9</td>
<td>remains IF</td>
</tr>
</tbody>
</table>

Table 6-3 Summary of environmental residual strength and locus of failure results

Figures 6-8 to 6-15 also show, over the fractional uptake range studied, that absorbed moisture can tend to move locus of failure from cohesive to interfacial, this being the general view of the literature. Types MS-B-AV119, AL-B-AV119 and MS-LS-E32 display this trend. However, this effect is dependent on choice of adhesive and the range of fractional uptakes studied, some joint types here always failing cohesively. Any change of locus from cohesive to interfacial was generally observed to be a local effect within any one adhesive layer. The result of environmental ageing giving an outer ring of wet adhesive whilst inner regions of the layer remained dry was often to produce a failure which was interfacial around the edge but still cohesive in the centre. To describe this locally-changing locus of failure, the term "interfacial border" (or "IFB") is used here. Thus, for meaningful discussion, locus of failure for an aged joint should potentially be analysed with reference to position within the adhesive layer.
To further discuss the residual strength work it serves best to present a series of macro photographs, these being shown in Figures 6-16 to 6-22. These offer visual texture and locus of failure information in support of the previous series of Figures. Referring to the series of macro photographs, it can be seen that locus of failure for some adhesive-substrate systems moves from cohesive to interfacial with increasing absorbed moisture.

Figures 6-16 and 6-17 for dry and 0.125(Hot) AL-B-AV119 joints, respectively, show that the apparently brittle and uniform centrally cohesive failure for this joint type becomes interfacial in the outer regions as moisture is absorbed. Although not presented here, the steel equivalent of the AL-B-AV119 joint type also showed fairly stable, central cohesive locus of failure in the dry condition. Figure 6-18 for the 0.125(Hot) MS-B-AV119 joint then shows again the pronounced shift towards interfacial failure in the aged regions of the adhesive layer, the original granular surface of the grit-blasted steel substrate clearly showing through. Moving on, Figure 6-19 shows this interfacial border effect for the lap-shear geometry. This time, an E32 joint is shown. The macro photograph of this 0.125(Hot) MS-LS-E32 joint shows a border of lighter and more granular grit-blasted steel. Thus, Figures 6-17, 6-18 and 6-19 show the interfacial border effect for both adhesives and both geometries often observed for aged joints.

Note that the AV119 joints discussed above seemed to display more interfacial locus of failure, even when dry. Figure 6-20 demonstrates this effect with AV119, and the original grit-blasted steel surface of the dry MS-LS-AV119 joint clearly shows through. As ageing increased to 0.25(RT) and 0.25(Hot) for this joint type, the interfacial failure mode was retained with a very similar visual fracture surface. On the other hand, however, E32 showed a definite tendency with both geometries to retain cohesive failure, even when aged.
Figure 6-16 Macro photograph of dry AL-B-AV119 centrally cohesive failure surfaces

Figure 6-17 Macro photograph of 0.125(Hot) AL-B-AV119 failure surfaces, showing outer border of visually interfacial failure

Figure 6-18 Macro photograph of 0.125(Hot) MS-B-AV119 failure surfaces, showing outer border of visually interfacial failure
Figure 6-19 Macro photograph of 0.125(Hot) MS-LS-E32 cohesive failure surfaces, showing characteristic zig-zagging of fracture locus

Figure 6-20 Macro photograph of dry MS-LS-AV119 failure surfaces, showing both wholly visually interfacial failure and zig-zagging of fracture locus
Figure 6-21 Macro photograph of dry MS-B-E32 centrally cohesive failure surfaces

Figure 6-22 Macro photograph of 0.25(RT) MS-B-E32 centrally cohesive failure surfaces, showing outer border of adhesive with different colouring
The locus of failure annotations in Figures 6-8, 6-9 and 6-13, showing residual strengths for MS-B-E32, AL-B-E32 and AL-LS-E32 joints, suggest that these types were found to retain cohesive failure throughout the wetness ranges tested, the two butt types certainly retaining fully cohesive failure up to 0.25 fractional uptake. Turning to the macro photography in support of this assertion, Figures 6-21 and 6-22 showing dry and 0.25(RT) MS-B-E32 joints clearly show this cohesive locus retention over the whole bond area. Interestingly, Figure 6-22 shows that the texture of the cohesive fracture surface becomes rougher in the aged condition. Note also that this figure shows a border of darker coloured adhesive, corresponding to the wetter regions of the adhesive layer. However, the main point with regards to the wider issues of this research is that, with good selection of joint geometry and substrate pretreatment, E32 retains a wholly cohesive mode of failure even when regions of the adhesive layer are heavily exposed to moisture.

As already seen in the various macro photographs presented here, the butt geometry generally favours a more stable, central cohesive locus (even for unaged AV119), whereas it was universally observed that the fracture surface for the lap-shear joints crossed from on or near one interface to on or near the other. Figures 6-21, 6-22 and 6-16, covering a mixture of dry and aged E32 and AV119 butt joints, show that, where cohesive failure occurs, it is reliably central. However, Figures 6-20 and 6-19 show the wandering fracture locus always seen with the lap-shear joints, independent of adhesive, substrate material and ageing condition.

Finally, it is important to continue to investigate the validity of hot-absorbed adhesive joint durability data. The possible time advantages of measuring the environmental degradation of both bulk adhesive and adhesive joint specimens based upon accelerated, hot uptake are very significant and so this point must be addressed. Although the conclusions made in the previous bulk adhesives mechanical properties chapter can legitimately stand alone on this issue, these adhesive joint residual strength studies should be taken in support. Attempting to make useful deductions, although the nominal fractional uptake levels presented here are affected by the recently-identified thickness effect, the question here is whether room temperature and hot-absorbed residual strength results are equivalent for similar uptake levels. Referring again to Figures 6-8 to 6-15 and comparing room temperature and hot-absorbed pairs of results, there seems good evidence for most joint types that absorption temperature does not affect strength. Whilst MS-B-AV119 and AL-B-AV119 joint types
show strength differences between room temperature and hot-absorbed 0.125 conditions, MS-B-E32, AL-B-E32, AL-LS-E32 and MS-LS-AV119 types show very good consistency. Note that there is strong evidence that failure locus is very much transitional at this moisture level, requiring caution in residual strength comparisons.

6.11 Supporting scanning electron microscopy

In support of experimental residual strength and locus of failure results and the macro photography, a programme of scanning electron microscopy was undertaken. First investigating the physical nature of a typical dry cohesive E32 failure surface, Figure 6-23 (1500x magnification) shows the typical topography for a butt joint. Although this adhesive is filled with relatively large chalk particles, it was impossible to locate areas visibly highly populated with obvious particles, the figure being genuinely representative of the failure surface as a whole. Thus, this observation suggested that the failure locus in dry E32 tends to be through the resin itself. Increasing the magnification also failed to detect any obviously particulate topography.

With this dry E32 surface as reference and moving to the periphery of a 0.25(RT) butt joint, Figures 6-24 (1500x magnification) and 6-25 (4000x magnification) show a much higher density of exposed filler particles. As these micrographs were captured very near the outer regions of the adhesive layer, the adhesive here would have been markedly environmentally degraded. As before, the topography shown in these figures was representative of the wet region of the fracture surface as a whole. Additionally, Figures 6-24 and 6-25 show that virtually all of the exposed filler particles have become debonded from the adhesive matrix and sit apparently loosely in cavities. This finding is consistent with observations made by Bowditch [61]. Therefore, it appears that an increase in absorbed water causes the failure locus for E32 to deviate through filler particle sites, implying a less brittle, plasticised adhesive matrix in the wetter condition. Also, the free space around the chalk particles in the aged adhesive might imply either swelling of the resin matrix or shrinkage of the chalk.

Looking now at the effect of absorption temperature on the cohesive E32 failure surface, peripheral micrographs (1500x magnification) of 0.125(RT) and 0.125(Hot) butts are
shown in Figures 6-26 and 6-27. Comparing these micrographs shows that absorption temperature makes no discernible difference to the topography of the failure surface or the microscopic locus of failure. This adds weight to the validity of accelerated uptake tests in environmental durability modelling.

Moving onto cohesive AV119 failure surfaces, Figure 6-28 shows a reference dry surface for a butt joint. Especially with this adhesive, increasing the magnification beyond the 1500x used here failed to give any further obvious information, even at magnifications which might have been expected to reveal AV119's sub-micron rubber toughening particles. Figure 6-29, showing a peripheral micrograph of a 0.25(Hot) AV119 butt failure surface, shows that increasing the moisture content fails to make an obvious difference to the topography. Perhaps the only possible observation is that the increased ageing results in a coarser larger-scale topography, leaving the smaller-scale details effectively unaffected.

Figure 6-30 then seeks to confirm the partial interfacial failure of a 0.125(Hot) MS-B-AV119 joint. Referring back to Figure 6-18, this joint type gave a visually interfacial locus around an outer border of the adhesive layer. The micrograph shown in Figure 6-30 was taken centrally within the area of apparent interfacial failure and suggests obviously different topography to the cohesive fracture surfaces shown in the previous Figures 6-28 and 6-29. This tends to confirm the presence of a different material at this assumed interfacial failure site, thus supporting the use of visually determined locus of failure for adhesive joints.
**Figure 6-23** Scanning electron micrograph (1500x) of dry MS-B-E32 cohesive failure surface

**Figure 6-24** Scanning electron micrograph (1500x) of periphery of 0.25(RT) MS-B-E32 cohesive failure surface
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Figure 6-25 Scanning electron micrograph (4000x) of periphery of 0.25(RT) MS-B-E32 cohesive failure surface

Figure 6-26 Scanning electron micrograph (1500x) of periphery of 0.125(RT) MS-B-E32 cohesive failure surface
Figure 6-27 Scanning electron micrograph (1500x) of periphery of 0.125(Hot) MS-B-E32 cohesive failure surface

Figure 6-28 Scanning electron micrograph (1500x) of dry MS-B-AV119 cohesive failure surface
Figure 6-29 Scanning electron micrograph (1500x) of periphery of 0.25(Hot) MS-B-AV119 cohesive failure surface

Figure 6-30 Scanning electron micrograph (1500x) of periphery of 0.125(Hot) MS-B-AV119 interfacial failure surface (substrate side)
6.12 Conclusions

- results show that residual joint strength is generally reduced by absorbed moisture. Typical reductions at a fractional uptake level of 0.25 were found to be between 20% and 40% for most systems studied (see Table 6-3)

- the results from tests at the above moisture level confirm that only an outer border of degraded material is required for these levels of joint strength degradation

- especially for E32 butt joints, the locus of failure remains centrally cohesive throughout the absorption range studied. The aluminium E32 lap-shear joints also display cohesive failure. This supports the suggested need for cohesive durability models

- the use of residual strength data from hot-absorbed joints appears largely consistent with room temperature-absorbed results. Thus, as with bulk adhesive properties, absorption temperature does not affect residual joint strengths (at least, up to 55 °C.)
7. Durability modelling of a butt joint

This chapter brings together the work described in the previous chapters and presents a stress analysis approach to the prediction of the cohesive environmental durability of bonded joints. PATRAN/ABAQUS finite element software running on a Sun computer was used for this work. Previous models in the literature usually focus on interfacial environmental degradation and failure, Gledhill et al.'s model [2] being one of the most popular. In consideration of cohesive durability aspects, Roy [55] and Roy and Reddy [56, 57] used a finite element stress analysis approach to model the cohesive environmental performance of adhesive joints. However, they modelled the adhesive as failing in creep, using a viscoelastic constitutive model. In contrast, the current research proposes that creep is not a significant failure mechanism for a well-designed adhesive joint, and instead considers a quasi-static response.

Other cohesive durability models are not well represented in the literature, no one author appearing to have offered a complete model from uptake of moisture through to the prediction of residual strength. Therefore, this research aims to do just that and predicts the quasi-static failure of an adhesive joint which is first environmentally exposed and subsequently subjected to load. The basis of this durability modelling technique is the direct linking of moisture content to the degradation of the adhesive by incorporation of moisture-dependent elastic-plastic material properties into the finite element model.

The finite element work described in this chapter focuses on the mild steel E32 butt joint ("MS-B-E32"), primarily because this joint type retained a cohesive failure mode throughout the environmental ageing range used in the experimental joint programme. Also, this type of joint was tested dry as well as aged to nominal fractional uptake levels of 0.125 and 0.25, thus giving the maximum three conditions against which to test the proposed finite element durability model. As no thickness-dependent uptake models have been developed for hot absorption, only room temperature-absorbed joints were modelled here. The finite element work presented in this chapter is divided into moisture uptake modelling and structural analysis. The uptake modelling takes account of the important finding of Chapter 4 that moisture uptake is not simple Fickian, as suggested by much of
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the literature. Thus, the improved diffusion model described in §4.3.3 is used here. Consisting of standard diffusion (or thermal) components, this model could be directly implemented in ABAQUS. Using the best-fit uptake parameters for E32 given in Table 4-8 of Chapter 4, it was thus possible to determine the nodal concentration values for the joints at the required immersion times. These moisture profiles were then used as input to the sequential quasi-static structural analyses, where appropriate.

The structural analysis part of the finite element work was more complex, the key points being the choice of material model and failure criterion. Although it had already been concluded that a static analysis with elastic-plastic constitutive properties would be used - and although a method of implementing their moisture-dependence had been established - the yield model and flow rule remained to be selected. Within the structural part of the analysis work, preliminary analyses were carried out on a dry joint using 2-dimensional models with linear material properties. Then, as the work progressed, 3-dimensional models and nonlinear adhesive properties were introduced, finishing with the durability modelling of wet joints.

### 7.1 Finite element uptake modelling

The two-stage diffusion model used for the uptake modelling here consisted of a simple Fickian with an instantaneous boundary equilibration stage superposed on a second simple Fickian bulk diffusion with an evaporative boundary condition stage. Each of these Fickian bulk diffusion processes is equivalent to heat conduction with constant conductivity (or diffusion coefficient). Then, the evaporative boundary condition is equivalent to a convective surface heat transfer process. Thus, using the best-fit parameters for E32, as given in Table 4-8 in §4.3.3 of Chapter 4, the two-stage model was directly implemented in ABAQUS using standard thermal processes. Each of the two stages was implemented separately and the moisture concentration values simply added together node by node using a FORTRAN programme. Thus, the output from the diffusion modelling of the MS-B-E32 adhesive layer gave the required nodal moisture profiles for the experimentally tested nominally $U=0.125$ and $U=0.25$ joints. These were then used in the later 3-dimensional analyses of wet joints, providing the link to the definition of moisture-dependent mechanical properties. As discussed in Chapter 6, the target $U=0.125$ and
\( U=0.25 \) conditions in the experimental joints were estimated based on non-thickness-dependent diffusion parameters determined from early uptake experiments. Later experimental uptake work identified a non-simple Fickian thickness effect, resulting in more accurate estimates of the moisture absorbed. However, the notation "\( U=0.125 \)" and "\( U=0.25 \)" is retained for identification purposes.

Noting the equivalence of thermal and diffusion analyses, local temperature becomes concentration, conductivity becomes diffusion coefficient, ambient temperature becomes equilibrium concentration and surface convective heat transfer coefficient becomes \( \alpha \) (as defined in § 4.2.3.1).

### 7.1.1 Material definition

The material definition required for a Fickian diffusion analysis of bulk adhesive is simply that of the diffusion coefficient value. Boundary conditions, required to specify instantaneously equilibrating surface concentration or to specify an evaporative surface effect, act independently of the diffusion behaviour of the bulk material and are discussed later. Therefore, as both stages of the final proposed uptake model from Chapter 4 use a simple Fickian diffusion process within the bulk adhesive, a standard constant diffusion coefficient is all that is required. Table 4-8 in Chapter 4 gives the optimised two-stage model parameters for room-temperature-absorbed E32. Referring to this table, a diffusion coefficient of 6.07 x 10^{-14}.m^2.s^{-1} was specified for the stage with the instantaneous boundary equilibration. Then, for the stage with the evaporative boundary condition, a diffusion coefficient of 13.75 x 10^{-14}.m^2.s^{-1} was specified. This was achieved in each case by the use of the *CONDUCTIVITY option within the material definition section of the ABAQUS input data deck, with the appropriate constant diffusion coefficient value specified on the following line

### 7.1.2 Mesh design

To ensure easy mapping of nodal moisture profiles onto the later 3-dimensional structural finite element models of wet MS-B-E32 joints, it was expedient to make use of an identical mesh for the uptake modelling - although the element type would change from
stress/displacement to heat transfer. As finite element mesh refinement is more critical in the case of structural analyses, mesh design was carried out at that stage. Thus, reference should be made to §7.2.2.1, later in this chapter, where this is discussed.

However, to summarise some points here, symmetry suggested that only an eighth of the full 10.0 x 2.90 x 0.48 mm average MS-B-E32 adhesive layer needed to be modelled, two of those faces being exposed to the environment. Of course, at this uptake modelling stage, there was no requirement to model any substrate material. The resulting 3-dimensional rectangular slab was meshed in its entirety with 20-noded quadratic brick heat transfer elements (DC3D20), these having exactly the same node topography as the C3D20 structural stress/displacement elements used later. The total number of elements and nodes used for the model were approximately 1830 and 9300, respectively.

Figure 7-1 shows the mesh used, also indicating planes of symmetry and exposed faces. Note that, although the model is 3-dimensional, the diffusion behaviour in the modelled portion of the adhesive layer is only 2-dimensional.

![Figure 7-1 Schematic of 3-dimensional finite element mesh used for uptake (and later structural) analyses. One eighth of the full adhesive layer modelled](image)

### 7.1.3 Boundary conditions for uptake model

With regard to uptake modelling, the boundary conditions correspond to the definition of equilibrium moisture concentration and the behaviour of the diffusion flux on the planes of symmetry. In the case of this model of one eighth of the full MS-B-E32 adhesive layer, the diffusion conditions on the two planes of symmetry parallel and opposite to the two
exposed faces are simply the default condition of zero normal flux. Therefore, it was not necessary separately to specify a condition on those model faces. Nor did the third plane of symmetry, parallel to imagined substrate surfaces, require any boundary condition, as the diffusion process is purely 2-dimensional with no flux normal to that plane.

Moving onto the definition of equilibrium concentration "loading", this is different for the two stages of the uptake model. In the case of the stage with instantaneous boundary equilibration, an appropriate concentration value was simply applied as a boundary condition to all exposed surface nodes of the finite element model. Because of the convenient linear scaling properties of concentration values throughout the uptake analysis, a system of normalised concentrations, \( c/c_0 \), was used. In the case of the other stage, the evaporative boundary condition was achieved by applying the equivalent of a convective heat transfer film condition to the outside faces of all exposed elements. Here, the concentration equilibration of the surface is constrained to occur gradually. To control this process, it was necessary to specify a remote equilibrium concentration value in addition to the equivalent of a surface heat transfer coefficient, this corresponding to the \( \alpha \) parameter in Equation (28). Note again that concentration profiles are simply linearly scalable with equilibrium concentration. Therefore, it is only ever necessary to specify an equilibrium value of unity. Then, the required profile can be generated later simply by factoring all nodal concentration values by the actual equilibrium value. Also, as the adhesive is assumed always to be initially dry, all internal nodes were left at zero concentration.

Later, during benchmarking of the 20-noded diffusion elements, there was found to be a problem with the direct stepped application of the instantaneous equilibrium concentration. There appeared in practice to be an inability of this element type to cope with an abrupt change in concentration. However, this problem was solved and is discussed in the following benchmarking section.

### 7.1.4 Benchmarking of finite elements and selection of numerical parameters

Prior to running full uptake analyses on the model, it was important to run a simpler benchmark test to check the correct behaviour of the intended finite element types and to confirm numerical controls. Using DC3D20 elements, a simple linear strip of 10 cube
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elements of realistic characteristic half-length of 2 mm was constructed with a view to checking both stages of the chosen uptake model. Using this number of elements gave enough integration points for the model to give reasonable resolution of spatial concentration results, whilst remaining computationally trivial. Also, as this benchmark model would give 1-dimensional concentration values in position and time, analytical solutions were available against which to test the finite element model. For evaluation of the analytical solutions, 50 terms each of Equations (7) and (30) were summed using a spreadsheet as before.

An equilibrium concentration of unity was applied to one end of the strip, with or without an intermediate evaporative process. No specific boundary conditions were applied to the other faces of the model. Thus, this model represented a symmetric half of a 1-dimensional diffusion situation in a plane sheet exposed to moist conditions. For the benchmarking of the stage with evaporative boundary condition, a value of \( \alpha = 5.0 \times 10^{-11} \text{ms}^{-1} \) was used. Then, for both models, a realistic diffusion coefficient value of \( 10 \times 10^{-14} \text{m}^2\text{s}^{-1} \) was applied to the bulk material, as described earlier in the material definition section. With regard to numerical controls, it was necessary only to specify a maximum allowable concentration change for each increment (or timestep), as well as initial suggested timestep size, total time analysed, and minimum and maximum allowable timestep sizes. A maximum change of 0.05 in concentration per increment was allowed. Making use of automatic timestep selection, the suggested size of the first increment (100 seconds) was not critical, ABAQUS optimising the final value used. For all subsequent finite element uptake analyses, minimum and maximum timestep size values were chosen to be \( 1.0 \times 10^{-6} \) seconds and 0.1 of the total analysed time, respectively. For the above values, and in order to achieve a good spread of concentration values for both stages, a total time of \( 2.5 \times 10^7 \) seconds was selected.

At the first attempt to run the stage with the instantaneous boundary equilibration, the model refused to run properly. Contrary to the software documentation, it appeared that the 20-noded brick diffusion element could not be used with such a stepped boundary concentration condition. However, needing to retain this type of element for later structural modelling continuity purposes, an alternative method of applying the boundary condition was used. Thus, for this stage of the uptake model, a very short initial ramped boundary
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condition step was inserted before the main step. This initial step was given a duration of one thousandth of the total analysed time and served simply to allow ABAQUS to attain numerical stability whilst not significantly affecting the overall results. For the stage with the evaporative boundary condition, ABAQUS coped better with the less abrupt boundary equilibration and an initial ramped step was not required.

Figure 7-2 shows a comparison of analytically calculated results and results output by ABAQUS for both stages of the model set-up described above at the end-of-analysis time. The results show the variation of concentration along the length of the strip and demonstrate that ABAQUS produces adequate accuracy for both uptake model stages. Note that this benchmark suggests that no significant accuracy is lost by the insertion of an initial ramped step in the simple Fickian stage. Also, note that the stage with boundary resistance shows a surface concentration which has not equilibrated.

![Figure 7-2 Benchmarking of ABAQUS 20-noded DC3D20 diffusion elements (zero distance corresponds to the initially dry centre of the modelled linear strip). Results shown for 2.5 x 10^7 seconds](image-url)
7.1.5 Modelled moisture profile in the adhesive layer

After benchmarking the DC3D20 diffusion elements, ABAQUS was then used to model the uptake of moisture into the MS-B-E32 adhesive layer. The two stages were run independently, using the two-stage uptake parameters given in Table 4-8 in Chapter 4 and each for a total analysed time of the 75 days used to age the 0.25(RT) MS-B-E32 joints (see again Table 6-2 in Chapter 6). Results were requested to be output after every increment of the finite element analyses. Both stages were run with an equilibrium concentration value of unity, ensuring that the results would be consistent with fractional bulk uptake, i.e. fractional concentration would be equivalent to fractional uptake. Resulting nodal concentration profiles were then combined in accordance with the ratio of bulk uptake equilibrium values for E32. To calculate the moisture profile for the 0.25(RT) joints, the two sets of nodal concentrations from the end of the analysis were combined. Then, for the 0.125(RT) joints, which took 18.7 days to absorb, the results cases for both analyses were inspected, linear interpolation being used between nearest lower and higher times to determine the moisture profile of the adhesive layer. This interpolation and nodal addition of concentration results was carried out using a simple FORTRAN programme. This programme produced the required overall moisture profiles for the 0.125(RT) and 0.25(RT) cases in a format which could simply be inserted into the later structural finite element analysis input decks.

Using automatic timestep control together with limits similar to those used for the previous benchmark test, both model stages ran stably. In both cases, the initially suggested timestep values were accepted by ABAQUS, these being automatically steadily increased as each analysis progressed in time. For the two-step stage with the instantaneous boundary equilibration, both steps were given a smaller initial suggested timestep of 10 seconds (as opposed to the usual 100 seconds). This resulted in 17 increments being required for the starter ramped step and an exaggerated 106 steps for the main stepped step. For the stage with the evaporative boundary condition, the usual 100 second initial timestep was suggested, this giving an analysis-total of 30 increments.

Figure 7-3 shows the overall moisture in one symmetric eighth of the MS-B-E32 adhesive layer for both the nominal 0.125(RT) and 0.25(RT) ageing conditions.
Figure 7-3 Fringe plots showing overall 2-dimensional moisture profile in quarter of MS-B-E32 adhesive layer. Upper plot for 0.125 condition and lower plot for 0.25 condition. Legend gives fractional concentration values.

The figure shows the expected radial variation of concentration across the cross-section. In each case, the convective boundary condition contribution has prevented the maximum local concentration (always in the bottom-left corner of the quarter cross-sections shown) from reaching its unity equilibrium value at the time shown. Noting that the minimum concentration is always in the middle of the full section, Table 7-1 shows the extreme values for each ageing condition.

<table>
<thead>
<tr>
<th></th>
<th>Minimum concentration</th>
<th>Maximum concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.125(RT)</td>
<td>0.0045</td>
<td>0.6738</td>
</tr>
<tr>
<td>0.25(RT)</td>
<td>0.1611</td>
<td>0.7679</td>
</tr>
</tbody>
</table>

Table 7-1 Finite element prediction of minimum and maximum local fractional concentration in MS-B-E32 adhesive layer after 18.7 days (0.125(RT)) and 75 days (0.25(RT)) exposure.

Although no formal integration of the above moisture profiles was carried out, a quick visual inspection confirms that actual bulk uptake levels are in excess of the nominal target values of 0.125 and 0.25. By definition, this is consistent with the thickness effect identified in the more recent experimental uptake work and as included in the current finite...
element model. Thus, the above finite element uptake modelling work has produced a more accurate estimation of moisture profiles in the joint than would have been obtained by the use of a simple, single-stage Fickian model. Therefore, the profiles shown in Figure 7-3 will be carried forward into the final structural modelling stages, the refined uptake model providing a sound basis for full durability prediction.

7.2 Finite element structural modelling of a dry joint

The previous sections of this chapter have described the finite element implementation of the two-stage uptake model chosen in Chapter 4. The resulting moisture concentration profiles after 18.7 days and 75 days of room temperature immersion in water were then shown. Previously, Chapter 5 discussed moisture-dependent mechanical properties of adhesives. In choosing how to implement this moisture-dependence of mechanical properties within the structural part of the finite element durability model, it was concluded that complete experimental uniaxial stress-strain curves at the various available uptake levels would be used as the basis of a properties definition within ABAQUS, together with other material model components still to be discussed.

The structural modelling presented in this chapter looks at the dry MS-B-E32 joint and initially carries out some investigative 2-dimensional plane stress analyses with linear material properties. Using the findings of this initial work, 3-dimensional models are then introduced, particularly so that the full moisture profile in the adhesive layer can obtained. As the modelling becomes more refined, appropriate failure criterion are investigated in conjunction with introducing nonlinearity and moisture-dependence into the adhesive's properties.

7.2.1 Preliminary 2-dimensional analyses

The linear 2-dimensional analysis work investigates the dry MS-B-E32 joint with a cracked and an uncracked adhesive layer and attempts to justify the experimentally observed stable central cohesive failure locus and to establish possible failure criteria. As adhesives tend to fail in tension, major principal stress was used as an indicator of failure and locus.
The J-integral was also used with some analyses of cracked joints in order to investigate the use of critical flaw size as a failure criterion. All 2-dimensional models made the assumption of plane stress, this being most appropriate for the thin butt geometry.

7.2.1.1 Linear elastic material definition

In defining mechanical properties for the steel and dry E32 in the butt joint model, elastic modulus and Poisson's ratio values were required for both materials. For steel, values of 205 GPa and 0.3, respectively, were chosen. Then, for dry E32, the experimentally measured elastic modulus value of 2008 MPa (see Table 5-2 in Chapter 5) was used. For Poisson's ratio, the value for E32 of 0.406 quoted by Bysh et al. [110] was used.

7.2.1.2 Mesh designs for 2-dimensional models

The meshes for all 2-dimensional models were very similar, representing a realistic adhesive layer thickness of 0.48 mm together with a nominal height of substrate material (1.0 mm) to give the required rigidity of the steel and to distribute the effects of loading. Differences between meshes were limited to model width, to the occasional use of different element types, to the introduction of a crack and to the use of a half-model instead of the usual quarter-model. Reduced symmetry required the use of a half-model when a single adhesive layer quarter-plane crack was investigated. All models were meshed mainly with CPS8 8-noded plane stress biquadratic quadrilateral elements. In cases where a rounded fillet was required on the substrate at the end of the adhesive layer, a number of CPS6 6-noded plane stress quadratic triangle elements were introduced to improve element proportions. Figure 7-4 shows the mesh of a typical reduced-width 2-dimensional quarter-model. Individual variations to the mesh shown will be mentioned where necessary in later sections of this chapter. However, all 2-dimensional meshes shown have a similar distribution of characteristic element sizes.

In some cases, the effect of an initial cohesive crack was investigated. Such a crack was modelled simply by constructing adjacent meshed geometry segments and leaving appropriate nodes "un-equivalenced". In the final cracked joint analysis, where the J-Integral was used to determine fracture energy against crack length, a full-width model was
employed with a centreline crack. For such a crack, this effect was achieved by modifying
the boundary conditions by leaving appropriate nodes along the bottom edge of the model
unconstrained in the vertical direction. Cracks were always introduced on the right-hand
side of the appropriate model.

Figure 7-4 Typical 2-dimensional mesh for the MS-B-E32 butt joint

7.2.1.3 Loading and boundary conditions

For uncracked analyses or for cases where an adhesive layer centreline crack was required,
a quarter-model was sufficient. The bottom edge of the model corresponded with the
adhesive layer centreline and all nodes were fixed in the vertical direction (except for
centreline crack-front nodes, where appropriate). For the single quarter-plane crack half-
model case, the mesh is reflected about the line PQ in Figure 7-4. The base of this model (substrate) was also constrained in the vertical direction. As symmetry about the vertical centreline of the joint was always present, both half and quarter-models were constrained along their left-hand vertical edge in the horizontal direction.

Loading for all models was applied at 50.6 MPa in the form of distributed nodal loads acting vertically upwards along the top horizontal edge of the portion of substrate represented. In order to distribute the total required load as evenly as possible, one sixth of each equal elemental load was applied to each end node and two-thirds to the mid-edge node of each element. Although these analyses were linear, the total applied load was still based on the average experimental dry MS-B-E32 nominal failure stress value of 50.6 MPa given in Table 6-3 in Chapter 6.

7.2.1.4 Major principal stress as a failure criterion

Suggesting that adhesive materials fail in tension, two quarter-model variations were investigated here and major principal stress fields in the adhesive layer inspected. Both models were uncracked, the difference between the two being the introduction or otherwise of a rounded fillet on the outboard end of the substrate, as shown before in Figure 7-4. This fillet was introduced in order to reduce predicted stress singularities at the substrate-adhesive interface. Although the length of an actual steel butt joint was 10.0 mm, the models here were of reduced width in order to carry out a comparative study and to focus mainly on orientation of the major principal stresses near the end of the adhesive layer. These two model variations are summarised below:

- "B200" - uncracked adhesive layer; no fillet
- "B201" - uncracked adhesive layer; fillet at outer edge of substrate

Set up as described above, these models were run and then the major principal stress fields inspected.
Discussion of results

Figure 7-5 shows major principal stress colour fringe plots for both B200 and B201 models. Immediately it can be seen that the provision of a fillet in Model B201 has tended to reduce the predicted magnitude of the stress in the adhesive layer near the interface at the free-edge. However, the results suggest that maximum major principal stress is always found near this point - independent of fillet. Then, taking a broader view of the whole adhesive layer, the two fringe plots predict similar patterns, although the distribution of major principal stress magnitude remains slightly modified by the fillet towards the free edge.

Figure 7-5 Colour fringe plots showing major principal stresses in the adhesive layer for Models B200 (top) and B201 (bottom) (MPa)
Looking now for support of the experimentally observed central cohesive failure for this joint type, the major principal stress fringe plots appear not to conclusively support adhesive layer centreline failure starting from the free edge - as would seem most physically realistic. Indeed, both models suggest a decrease in magnitude of major principal stress in this area. However, ignoring the maximum predicted in the vicinity of the free edge at the interface, both models suggest a fairly uniform distribution of stress throughout the bulk of the adhesive layer. Again, though, this distribution would not appear specifically to favour centreline failure.

Major principal stress vector plots were also inspected (not shown). Neither did they tend specifically to support adhesive layer centreline failure. Expecting failure to initiate in a direction normal to the maximum principal stress vector, both models appeared to favour stable interfacial failure.

The above two models have consistently favoured interfacial locus of failure and have thus gone against experimental observations of central cohesive failure for the MS-B-E32 joint type. At best, the models suggest that exactly centreline crack propagation is perhaps just feasible. However, the models suggest that any deviation of the propagating crack tip from the centreline would be reinforced and interfacial failure would ensue. Thus, even if a centreline crack were to initiate, propagation along that locus would not be stable. These initial linear analyses suggest, therefore, that major principal stress may not provide a realistic justification of experimentally observed central cohesive failure locus.

7.2.1.5 J-Integral as a failure criterion

The linear 2-dimensional stress analysis work was developed further in order to consider other possible fracture mechanics failure criteria. Noting the previous work which looked at the stress field around various uncracked and cracked butt joint adhesive layers, this J-Integral work attempted to quantify crack tip fracture energy. In the case of linear material properties, the fracture energy associated with a crack can be approximated using the J-Integral, and thus the stability of the crack can be estimated. The work was carried out in two parts, the first attempting to justify the experimentally observed centrally cohesive failure locus and the second predicting the critical centreline flaw size needed for crack
propagation. In all cases, four crack-tip J-Integral estimates (or paths) were requested from ABAQUS. Although ideally identical, estimates tended to increase slightly, stabilising by the third or fourth value. Therefore, the fourth estimate was used as the final value. Checking of the J-Integral calculation procedure implemented in ABAQUS was carried out on one of the later models (B208) by comparing values to those obtained using a virtual crack closure technique [112].

Justification of observed adhesive centreline failure

This investigation made use of further reduced-width models of a dry MS-B-E32 joint, using an identical mesh to that used for the previous 2-dimensional models. Substrate fillets were not introduced for these models. Two model variations were investigated with a view to quantifying the relative stability of cracks in two different positions within the adhesive layer. Thus, J-Integral estimates of fracture energy for cases of a centreline crack (using a quarter-model) and a single quarter-plane crack (using a half-model) were compared. Both cracks were one tenth of the length of the adhesive layer of the reduced-width model. Apart from the positioning of the adhesive layer crack, both models represented identical situations. These models are summarised below:

- "B205" - quarter-model with adhesive layer centreline crack
- "B206" - half-model with single adhesive layer quarter-plane crack

With regard to loading, this was identical to that used for the previous 2-dimensional models, distributing the equivalent of the 50.6 MPa experimental dry MS-B-E32 stress evenly between the nodes along the top edge of each model.

- Discussion of results

At the specified loading conditions, the B205 centreline crack model gave a J-Integral estimate of 220.0 Jm$^{-2}$ for the fracture energy and the similar B206 quarter-plane crack model gave an estimated of 220.4 Jm$^{-2}$. These values being very nearly identical, the immediate suggestion was that neither locus showed preference for the propagation of a flaw. However, taking a more detailed view, it is possible to argue that a centreline crack
would be more likely to propagate than an equal-length quarter-plane crack with the same associated fracture energy.

It is generally accepted for a butt joint remotely loaded in pure tension that the stress field on the adhesive layer centreline is pure Mode I. On the adhesive layer quarter-plane, however, the stress field consists of a mixture of Modes I and II. Now, given a fixed amount of available fracture energy, a Mode I crack is easier to propagate than one of Mode II. Therefore, for the quarter-plane crack situation with Mode II stresses becoming a factor, such a crack is less likely to propagate. This can be visualised as a partially Mode II crack being less efficient to propagate than a Mode I crack under remote pure tension. Taking this point of view, the apparently equivalent fracture energy results of models B205 and B206 could favour a stable centreline cohesive locus of failure. Thus, the experimental observation of consistent centrally cohesive failure of MS-B-E32 joints (both dry and wet) is supported by this study.

**Estimation of critical centreline flaw size**

Building on the experimentally observed observation of centreline failure and accepting the support offered by the B205 and B206 finite element models, a new full-width quarter-model was drawn up in order to predict the critical length of a centreline crack. This investigation was carried out as a final test of the validity of a fracture mechanics-based failure criterion. Although models B200, B201, B205 and B206 represented a butt joint of width much less than the 10.0 mm length of an actual joint, those studies were only comparative in nature and did not seek to provide data for a joint of dimensions studied experimentally. However, the current model was required to represent an experimental joint more accurately. Therefore, a joint with the full 10.0 mm adhesive layer length was modelled.

Loading was again similar to all previous 2-dimensional models, 50.6 MPa being uniformly distributed along the elements on the top edge. Unlike the previous 2-dimensional models, however, this model was run several times. Each time, the bottom edge boundary condition was adjusted in order to vary the length of the adhesive layer centreline crack, the J-Integral being evaluated around the respective crack-tip node. To remain realistic, crack length ranged from nearly 10 µm to 2 mm. In order to obtain this
level of refinement, the finite element mesh used for this model made use of layers of smaller elements than used before near the centreline. Figure 7-6 shows the details of the mesh used.

![Mesh Diagram]

**Figure 7-6** Detail of adhesive mesh used for variable crack length Model B208

J-Integral fracture energy estimates were then plotted against crack length. A previously obtained value of fracture toughness was then used to estimate the critical flaw size for this type of joint subjected to the experimental failure load. The model used for this investigation is summarised below:

- "B208" - full-width quarter-model with variable-length adhesive layer centreline crack

Also, in order to check function of the J-Integral calculation, model B208 was used with virtual crack closure. This is described in the following section, before the main results section.

- Validation of the J-Integral calculation

A technique of "virtual crack closure" was used on the results from one run of Model B208 in order to validate the J-Integral calculation procedure used by ABAQUS. This technique provides an approximate estimate of fracture energy for a crack from internal or reaction
forces and crack separation displacements, which can then be compared to the J-Integral value given for the same crack. Noting that Model B208 is a quarter model and thus its lower edge corresponds to the adhesive layer's major centreline, Figure 7-7 shows a sketch of the deformed finite elements near the centreline crack tip.

\[ RF = \text{reaction forces} \]
\[ \delta = \text{displacements from centreline} \]

**Figure 7-7** Schematic of distorted bottom row of elements around crack tip for loaded Model B208

The results of a single finite element analysis, represented by the figure, can be used to estimate fracture energy by visualising an initial centreline crack to have propagated from Node B to Node D. This then causes the six-noded Element A to lift and for Node B and Node C to displace from the centreline. To estimate the energy associated with the formation of this new portion of crack, reaction forces and displacements can be combined. For a more accurate estimate of fracture energy, the model could be run twice. For the first analysis, the crack tip (defined by the start of the vertically fixed nodal boundary conditions) would be set to Node B, and the reaction forces at undisplaced Nodes B and C noted. For the second run, the crack tip would be defined as in the figure and the displacements of Nodes B and C noted. Then, bearing in mind the use of linear elastic material properties as well as model symmetry, the energy associated with the new crack BD could be estimated by combining the appropriate values from the two analyses as follows:
\[ \text{Energy} = \frac{1}{2} RF_B \cdot (2\delta_B) + \frac{1}{2} RF_C \cdot (2\delta_C) \] (59)

However, using a single analysis, a satisfactory estimate can still be obtained using the following alternative (as long as the crack tip mesh is sufficiently refined):

\[ \text{Energy} = \frac{1}{2} RF_D \cdot (2\delta_B) + \frac{1}{2} RF_E \cdot (2\delta_C) \] (60)

Then, dividing by the newly formed crack area, the fracture energy of the crack can be determined and compared with the J-Integral value also output by the analysis for the loading level and crack length concerned. Table 7-2 summarises reaction force, vertical displacement, J-Integral and elemental side length values for a crack length of 0.3906 mm used in this check.

<table>
<thead>
<tr>
<th>Reaction force, ( RF_D ) (N/mm)</th>
<th>1.1268</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reaction force, ( RF_E ) (N/mm)</td>
<td>0.8617</td>
</tr>
<tr>
<td>Displacement, ( \delta_B ) (mm)</td>
<td>0.001831</td>
</tr>
<tr>
<td>Displacement, ( \delta_C ) (mm)</td>
<td>0.001195</td>
</tr>
<tr>
<td>Elemental bottom edge length (mm)</td>
<td>0.007813</td>
</tr>
<tr>
<td>J-Integral output (Jm(^2))</td>
<td>396.0</td>
</tr>
</tbody>
</table>

Table 7-2 Model B208 analysis (crack length 0.3906 mm) output for validation of J-Integral results

Implementing Equation (60) gave an estimate of 395.9 Jm\(^2\) for the model set-up considered. Given the tabulated J-Integral value of 396.0 Jm\(^2\), this confirms the function of ABAQUS's contour integral calculation procedure with the element type used in the vicinity of the crack plane.
• Discussion of results

Model B208 was run nine times, each time with a different crack length. From each of the data output files, the J-Integral estimate was extracted and then the nine values plotted against crack length. Figure 7-8 shows this graph.

![J-Integral or fracture energy, $G_f$ against crack length for Model B208](image)

**Figure 7-8** J-Integral (or fracture energy) against crack length for Model B208

In order to estimate the critical crack length for a dry MS-B-E32 joint, a value of fracture energy, $G_{lc}$, for dry E32 was required. This was calculated from a previously obtained value of fracture toughness, $K_{lc}$, for dry E32 of 38.0 Nmm$^{3/2}$ [113]. As with all 2-dimensional finite element modelling presented here, plane stress was assumed. Thus, the calculation of fracture energy was achieved using the following relationship:

$$G_{lc} = \frac{K_{lc}^2}{E}$$

(61)

Noting the dry E32 elastic modulus given in §7.2.1.1 of 2008 MPa, this gave a fracture energy value of 719 Jm$^{-2}$. Referring back to Figure 7-8, this value has been superposed and gives a critical crack length of 0.91 mm. This represents an unrealistically large flaw size and thus suggests fracture mechanics is unsuitable to predict failure load.
7.2.1.6 Conclusions on the preliminary 2-dimensional analysis work

- inspection of major principal stress magnitude and vector plots does not support centreline cohesive failure for the steel-E32 butt joint
- evaluation of the J-integral over-estimated the critical flaw size but supported centreline failure. Thus, centreline stress and strain fields can be used to investigate failure in the later 3-dimensional analyses

7.2.2 3-dimensional analyses

The 3-dimensional modelling work starts here by analysing a dry MS-B-E32 joint, using linear elastic material properties as described previously in §7.2.1.1. On the basis of these initial linear static 3-dimensional analyses, mesh refinement is justified. Also, and in an additional attempt to reduce model size, these analyses were used to investigate the viability of an adhesive layer-only model (achieved by replacing the substrate-adhesive interface by a suitable boundary condition applied to the top surface of the adhesive). After these linear mesh-rationalisation analyses, nonlinear elastic-plastic material properties (based on material data shown in Figure 5-7 in Chapter 5) were introduced in order to consider the choice of yield model and failure criterion. Still working only with the dry joint, analyses were carried out using a choice of von Mises and linear Drücker-Prager yield surface. Finally, by considering both local stress and strain fields and global collapse, yield model and failure criteria were evaluated.

7.2.2.1 Linear analyses

Although the final 3-dimensional adhesive layer finite element mesh was shown earlier in the uptake modelling section of this chapter, it was on the basis of the current structural analysis work that the mesh design was chosen. Using initial analyses with linear, dry adhesive properties and comparing results for different mesh variations, an adequately refined yet computationally reasonable model was justified. The linear elastic properties for the steel substrate and dry E32 adhesive were those used in the previous 2-dimensional work (as described in §7.2.1.1).
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Initial mesh design

Symmetry of the butt joint adhesive layer allowed only one eighth of the full 10.0 x 2.90 x 0.48 mm layer to be modelled, as in the earlier finite element uptake modelling work. Especially for the 3-dimensional structural analyses, this very much reduced the total number of degrees of freedom and thus cut down on the computational effort required. After reducing the model requirements in this way, it was concluded that computational resources would allow the use of the more accurate ABAQUS biquadratic C3D20 20-noded brick elements, as opposed to the basic 8-noded pattern. Thus, a 5.0 x 1.45 x 0.24 mm rectangular corner block of adhesive, with or without a portion of attached steel substrate material was meshed with 20-noded brick stress-displacement elements. Although final mesh refinement is discussed later, the meshing process was organised such that there was increased detail at the outer corner of the model.

Loading and boundary conditions

As with the linear 2-dimensional work, loading for these initial mesh-rationalisation linear 3-dimensional analyses was applied at a level equivalent to the 50.6 MPa average experimental failure stress of the dry MS-B-E32 joint. The method of application of the load was dependent upon whether a portion of substrate was modelled or whether the adhesive layer only was represented. In the first case, a uniform upwards pressure was applied to the top surface of the model (substrate). In the second case, and as discussed more fully later, a single equivalent load was applied to one of the top surface nodes of the adhesive-only model.

Boundary conditions for all linear and nonlinear 3-dimensional analyses were identical and simply defined the symmetry conditions in the joint. Nodes in the surfaces of the eighth-model corresponding to the three orthogonal planes of symmetry of the full joint were constrained in their respective normal directions.

Choice of adhesive-substrate or adhesive-only model

As the use of a 3-dimensional finite element model greatly increases the number of degrees of freedom compared to that needed for an equivalent 2-dimensional model, it was important to reduce the mesh complexity wherever possible. In addition to controlling the
refinement of the mesh, the possibility of modelling only the adhesive layer was considered. Bearing in mind the much larger elastic modulus value for the steel substrate material, it was investigated whether the substrate could be replaced by a rigid boundary condition applied to the top surface of an adhesive layer-only model. Therefore, two models, named B4 and B9 were prepared using PATRAN. Both using an identical adhesive layer mesh, B4 modelled the adhesive layer with a 2.0 mm depth of mild steel substrate attached. With an appropriate extra boundary condition, B9 modelled the adhesive layer only.

Model B9 achieved the effect of completely rigid substrate material bonded to the adhesive layer by means of a multi-point constraint applied to the top surface of the adhesive layer-only model. Such a condition was chosen that each top surface node in turn was rigidly linked to a master node. Together with the normal symmetry boundary conditions, the use of this particular type of multi-point constraint forced the top surface of the model to move only vertically and undistorted as a whole. Thus, the top surface of the adhesive layer was forced to move as if bonded to an infinitely rigid substrate. Loading for this adhesive layer-only model was applied as a vertical point force applied to the master node.

The choice of level of refinement chosen for the adhesive layer was based upon previous experience within the Research Group. Another consideration was the compromise between increased detail and computational effort requirements to analyse the model. With the intention of making a good first estimate of refinement, the eight-model of the adhesive layer was divided into four equal horizontal slices. Then, working from the outer, free corner of the model, one-way biasing was used in the application of mesh seeds to gradually reduce the refinement in the x and z directions. This process gave a smallest element size in the critical outer corner of approximately 0.06 mm all round. Then, for the portion of substrate material included in Model B4, meshing was arranged so that adhesive layer refinement was matched near the interface. Again, moving further away from the interface and into regions of the substrate which would experience lower predicted stress levels, mesh refinement was reduced. Figures 7-9 and 7-10 show the meshes used for Models B4 and B9.
The B4 and B9 models (both with identical adhesive layer meshes) were run with linear elastic material properties and with loading and boundary conditions as described earlier. With regard to the relative computational effort required for these models, the adhesive-only model took 15 minutes to analyse and the adhesive-substrate model took nearly 3 hours. Note that the differences would be orders of magnitude greater if using nonlinear
material properties. For both models, the von Mises effective stress fields on the adhesive layer centre-plane were compared. The centre-plane was chosen for analysis of stress and strain results because both the experimental joint testing work and the previous 2-dimensional modelling had confirmed the importance of that locus when determining failure. Admittedly, both models predicted relatively high stress values at the interface, but this was expected by virtue of the junction of two dissimilar materials alone.

Figure 7-11 shows a colour fringe plot of von Mises effective stress for the two models. Looking at this figure, only small differences in centre-plane von Mises stress field can be seen between the two models. Both models predict the von Mises stress to form a general peak of between 31 and 32 MPa with a locus which runs approximately 0.15 mm inside the outer periphery of the adhesive layer. The absolute von Mises peak is predicted just inside the outer corner of the adhesive layer for both models. In the case of the B4, substrate-adhesive model, this local maximum is slightly higher and has a value of between 32 and 34 MPa. Inspecting the von Mises stress distribution towards the centre of the adhesive layer centre-plane, very similar minimum values are predicted. Again, the adhesive-substrate model tends towards predicting slightly higher stress values across the section in general. In addition to the slightly increased local maximum towards the outer corner, the spread of the similar minimum value area is smaller than for the adhesive-only B9 model. Thus, Model B9 predicts a slightly more uniform distribution, which one would expect as a result of infinitely rigid modelling of substrate.

Ideally, in deciding whether the far less computationally demanding B9 adhesive-only model has sufficient accuracy, the final choice of failure criterion should be taken into consideration. As shall be seen in the later nonlinear 3-dimensional modelling work, both local and global failure criteria are considered. Depending on the type of criterion used, differences in stress or strain fields between models may have a greater or lesser effect. However, at this stage in the durability modelling procedure, the B9 adhesive-only model compares well enough with the adhesive-substrate model and thus provides a sufficient basis for further modelling investigations. Note also that, as the adhesive layer within the joint becomes degraded by absorption of moisture, the differential between adhesive and substrate stiffnesses will become very much increased, rendering the adhesive-only model even more faithful to the real joint situation.
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Figure 7-11 Fringe plots showing the von Mises stress distribution on the adhesive layer centre-plane for Models B4 (top) and B9 (bottom)

Adhesive layer mesh refinement

To support the level of mesh refinement used for the adhesive layer in Model B9, another similar adhesive-only model was created with approximately double the mesh refinement. Again, the multi-point constraint condition was used to link the nodes on the top surface of the model in order to represent the effectively rigid substrate material. Whereas a typical smallest element in the outer corner of the B9 model was approximately a cube of side length 0.06 mm, the equivalent element size used for the B8 model was a cube of side length 0.03 mm. Similar rates of reduction in refinement away from the corner were used for both models.

Again using linear dry adhesive properties, as above, the adhesive layer centre-plane von Mises stress distributions were compared in order to justify the original level of mesh refinement chosen (Model B9). Thus, it was hoped that the finer mesh of Model B8 would not give significantly different stress results in the important centre-plane region of the adhesive layer. Figure 7-12 shows a single colour fringe plot of the centre-plane von Mises stress distribution, as predicted by the more detailed Model B8.
Figure 7-12 Fringe plot showing the von Mises stress distribution on the adhesive layer centre-plane for Model B8

Figure 7-12 shows that Models B8 and B9 produce virtually identical von Mises stress distributions. Thus, the added refinement of Model B8 offers no advantage in accuracy on the adhesive layer centre-plane and therefore suggests that the B9 mesh is sufficient.

7.2.2.2 Evaluation of yield models and failure criteria

The previous linear structural 3-dimensional finite element modelling of the dry MS-B-E32 joint served to justify the mesh design of the proposed B9 model. In the current section, however, nonlinear elastic-plastic adhesive properties are introduced in order to start investigating appropriate choice of yield surface and failure criterion. Still retaining the unexposed joint at this stage, the curve representing dry E32 uniaxial tensile properties from Figure 5-7 in Chapter 5 was discretised (in 10 steps) and used as the basis for hardening definition within the following finite element analyses. With regard to yield model, both the conventional von Mises and a linear version of the hydrostatically-sensitive Drucker-Prager model were investigated. Then, considering choice of failure criterion, two approaches were again investigated. Firstly, local stress and strain parameters on the adhesive layer centre-plane were inspected and correlated against the experimental failure load of the dry joint. Then, a global limit state approach was also evaluated. This involves loading a joint until such a point that the load path becomes completely cut by a stream of fully yielded adhesive. Thus, the joint can support no further load and failure occurs by global collapse of the adhesive layer.
In the following sections, the yield models are first outlined and then local and global approaches to failure prediction are evaluated. Finally, at the end of this nonlinear analysis work on the dry joint, provisional conclusions are made as to the chosen yield model and failure criterion combination.

**Yield models and their definition**

In addition to hardening defined using experimental uniaxial properties for dry E32, the triaxial yield surface and plastic flow have to be defined. For the purposes of this work, two models were investigated. Firstly, the conventional von Mises model was implemented. This is a popular model and is traditionally used to represent metals and, as such, is insensitive to hydrostatic stress. However, failure in polymers is typically aggravated by hydrostatic tension. Thus, an appropriate alternative model was investigated, this being a linear variety of the Drucker-Prager model.

As software limitations required hardening to be defined in uniaxial compression, the dry E32 tensile stress-strain curve of Figure 5-7 had to be converted. Using a ratio of compressive to tensile yield strength for dry E32 of 1.4 [114], with no change in plastic strain, Figure 7-13 shows the mapping procedure used.

![Figure 7-13 Schematic showing mapping of tensile to compressive uniaxial properties for (dry) E32](image-url)
Next, the definition of the Drücker-Prager yield model itself was considered. With its hydrostatic sensitivity, this model predicts earlier yielding with increasing tensile hydrostatic stress. Of the various Drücker-Prager yield surfaces offered by the current release of ABAQUS, a linear form (in the hydrostatic-von Mises stress plane) was chosen for investigation. This yield surface is shown in Figure 7-14.

![Figure 7-14 Linear Drücker-Prager yield surface](image)

The yield surface shown in the figure can be expressed in terms of the stress state \( (t_\sigma, p) \), material friction angle \( (\theta) \) and cohesion \( (d) \) as follows:

\[
F = t_\sigma - p \tan \theta - d = 0, \quad \text{where:}
\]

\[
t_\sigma = \frac{1}{2} q \left[ 1 + \frac{1}{R} \left( 1 - \frac{1}{R} \left( \frac{r}{q} \right)^3 \right) \right], \quad \text{and}
\]

\[
d = \left( 1 + \frac{\tan \theta}{3} \right) \sigma_t, \quad \text{and}
\]
Additionally, the plastic flow properties of this model in relation to the yield surface are defined in terms of the dilation angle:

$$\tan \psi = \frac{3(1-2v)}{2(1+v)}$$

(65)

For the purposes of the current research, $R$, the ratio of the yield stress in triaxial tension to the yield stress in triaxial compression, was assumed to be unity. In any case $R$ must lie between 0.778 and 1.0. However, using a unity value results in the following simplification:

$$t_0 = q$$

(66)

Having made this simplification, the previously-found ratio of yield stresses in uniaxial compression to uniaxial tension of 1.4 for (dry) E32 was incorporated. By applying the yield surface expressions to cases of uniaxial tension and uniaxial compression, the material cohesion term was eliminated and the values for friction and dilation angles determined, as shown in Table 7-3. Note that, for later analysis of environmentally exposed joints, these values were retained in the absence of evidence to the contrary.

<table>
<thead>
<tr>
<th>Friction angle, $\theta$</th>
<th>26.56°</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dilation angle, $\psi$</td>
<td>12.72°</td>
</tr>
</tbody>
</table>

Table 7-3 Friction and dilation angles for E32

The fact that friction and dilation angles are not equal indicates a case of non-associated flow, as is usually assumed for polymeric materials. Together with the assumed unity $R$ value, the above parameters were sufficient to define the Drücker-Prager yield surface and plastic flow behaviour.

**Benchmarking of Drücker-Prager yield model**

Especially for the Drücker-Prager model, where original tensile properties data required converting to compressive, it was felt important to run a simple benchmark test. Bearing in mind that the stress state in the butt joint is predominantly (triaxial) tensile, such a
benchmark test would provide confidence that the uniaxial tensile-compressive conversion method described in §7.2.2.2 was working correctly in combination with the friction angle calculation described in the same section. Thus, a single 8-noded, 2-dimensional, plane stress element, using the previously-described dry E32 compressive hardening and Drücker-Prager yield definition, was loaded in uniaxial tension using ABAQUS. The incremental load and displacement results were then inspected and a tensile uniaxial stress-strain curve reconstituted. This was overlaid onto the original hardening definition to check the model operation. Figure 7-15 shows this superposition of input and finite element output and suggests a good reproduction of uniaxial tensile properties. Thus, accurate operation of the various parts of the material model within the finite element analysis was confirmed.

![Stress-Strain Curve](image)

**Figure 7-15** Benchmarking of FE model with Drücker-Prager yield model. Reproduction of uniaxial tensile stress-strain curve modelled

**Evaluation of local failure criteria**

The finite element model was solved first with the von Mises and then with the Drücker-Prager yield model. Loading was applied at the experimental dry joint failure load of 50.6 MPa (see Table 6-3 in Chapter 6). Then, the centre-plane stress and strain fields were inspected in an attempt to correlate the peak value of a representative parameter with an appropriate bulk material property (either UTS or uniaxial ultimate strain, shown in Figure
Chapter 7: Durability modelling of butt joint

5-7 and Table 5-2 in Chapter 5). Noting that stress reaches an asymptote near ultimate load and is thus perhaps less useful as a local failure criterion, results from both the von Mises and Drücke-Prager are compared and discussed in the following paragraphs.

A selection of key stress and strain quantities were inspected for each of the two analyses. In particular, hydrostatic, von Mises and major principal stresses and major principal and equivalent plastic strains were chosen. Figures 7-16 to 7-20 show contour plots of these quantities. In comparing local stress and strain results for the two models, it was intended to plot distributions at the experimental dry joint failure load of 50.6 MPa. However, it was not possible to do this for the Drücke-Prager model. Although the analysis using the von Mises yield surface sustained considerably in excess of 50.6 MPa, the Drücke-Prager model predicted the adhesive layer to collapse globally a little under this load. Therefore, whilst the von Mises model results were inspected at the required load level, it was possible to inspect the Drücke-Prager results at a maximum of only 45.9 MPa. Despite this inconsistency between results cases, it was still possible to make useful comparisons.

Figure 7-16 Contour plot of hydrostatic stress distribution on dry MS-B-E32 adhesive centre-plane for both von Mises (top) and Drücke-Prager (bottom) yield models (legend in units of MPa)
Chapter 7: Durability modelling of butt joint

Figure 7-17 Contour plot of major principal stress distribution on dry MS-B-E32 adhesive centre-plane for both von Mises (top) and Drücker-Prager (bottom) yield models (legend in units of MPa)

Figure 7-18 Contour plot of von Mises stress distribution on dry MS-B-E32 adhesive centre-plane for both von Mises (top) and Drücker-Prager (bottom) yield models (legend in units of MPa)
Figure 7-19 Contour plot of major principal strain distribution on dry MS-B-E32 adhesive centre-plane for both von Mises (top) and Drücke-Prager (bottom) yield models (legend in units of %)

Figure 7-20 Contour plot of equivalent plastic strain distribution on dry MS-B-E32 adhesive centre-plane for both von Mises (top) and Drücke-Prager (bottom) yield models (legend in units of %)
Figures 7-16 and 7-17 show that both the von Mises and the Drucker-Prager models predict tensile hydrostatic and major principal stress components to be maximum in the centre of the adhesive layer and to decrease as the periphery is approached. This was as expected, as conditions change from plane strain at the centre to plane stress at the periphery of the layer. The choice of yield surface also significantly affects the detailed stress distribution. In the case of the von Mises model, there is a relatively broad central plateau of maximum stress, which then decreases ever more rapidly as the periphery of the adhesive layer is approached. The Drucker-Prager yield surface, on the other hand, still produces a maximum stress value in the centre of the layer but does not give such a wide plateau; stress values decrease almost linearly from the centre to the periphery, the central maximum thus appearing more focused. Another feature of the hydrostatic and major principal stress distributions predicted using the Drucker-Prager model is that the central area of general peak values produces a maximum on the major centreline at points 1.33 mm from each end of the adhesive layer, whereas von Mises yielding predicts a central peak.

Moving onto the von Mises stress distributions, however, Figure 7-18 shows that both models predicted a central medium value leading into a band of high stress approximately 0.25 mm inside the extreme outer periphery of the adhesive layer - followed by an almost complete drop-off at the periphery. In each case, this band peaked just inside the outer corner of the adhesive layer. Also, Figures 7-19 and 7-20 show that major principal and equivalent plastic strains for the von Mises model follow a similar inboard peak pattern. This predicted maximum appears genuine and is not purely a mesh artefact, refinement being such that the area of interest is covered by a square grid of perhaps 16 element faces. Remember also that the characteristic element length in the outer corner of the model is approximately 0.06 mm.

Having now described the distributions of the predicted stress field patterns on the adhesive layer centre-plane, magnitudes are discussed in more detail in order to justify the behaviour of the two models. Taking into account the reduced loading situation and generally increased hydrostatic tension for the Drucker-Prager case, the von Mises stress plots, shown in Figure 7-18, for both models are consistent with expectations. The sensitivity of the Drucker-Prager model to hydrostatic stress suggests that an increase in hydrostatic tension should result in a decreased von Mises stress. Inspecting the hydrostatic
and von Mises stress plots for both model cases (see again Figures 7-16 and 7-18), and concentrating on the centre of the adhesive layer, it can be seen that von Mises stress is lower in the Drücker-Prager case. The rest of the adhesive layer centre-plane follows this pattern, as expected.

Now investigating the generally higher tensile hydrostatic stress levels predicted using the Drücker-Prager model, the major principal (predominantly yy stresses) shown in Figure 7-17 suggest similar magnitudes for both yield surfaces. The central peak major principal stress values for both cases are similar, at approximately 62 MPa. Therefore, it is suspected that the Drucker-Prager model generates increased intermediate and minor principal stress values across the centre-plane, resulting in a lower von Mises stress in this region. Inspecting the results (not shown) shows this to be the case. Thus, it would appear that the two models produce sensible and mutually consistent results.

Moving on to consider more critically possible failure criteria, both local stress and strain parameters and a limit state concept were considered. Of the many variations of stress and strain available, the von Mises and major principal stresses and the equivalent plastic and major principal strains were selected as possible local criteria. Not only do these quantities represent the triaxiality of the stress and strain fields but the major principal quantities represent the preferred tensile failure mode of polymeric adhesives.

Firstly discussing detailed results for the von Mises model at the experimental failure load of 50.6 MPa, the equivalent plastic strain plot shown in Figure 7-20 suggests that virtually all of the material on the centre-plane has yielded to a certain extent. At the very most, only a very narrow outer border of adhesive has not deformed plastically. Furthermore, the plot suggests that the maximum strain occurs at a point just inside (approximately 0.25 mm) the exposed corner of the adhesive layer. Again, this appears to be a genuine effect and is not simply a mesh artefact. Moving on to inspect the major principal strain plot for the same model (see Figure 7-19), the peak value just inside the corner of the adhesive layer was predicted to be 1.86%, whilst the value at the centre was approximately 1.4%. Thus, Major principal strain provides a realistic failure initiation locus, i.e. just inside the outer corner of the adhesive layer. However, the peak value correlates badly with the 4.08% experimental ultimate strain value. Furthermore, as it is difficult to achieve full and meaningful ultimate strain values from experiments, this 4.08% value is likely to be an
under-estimation. Thus, major principal strain, too, appears to offer little promise as a basis for a local failure criterion.

Inspecting the von Mises stress field (shown in Figure 7-18) for the von Mises yield surface case, this is again consistent with the predicted large-scale yielding, only an extreme border experiencing stress levels less than the 15.1 MPa tensile yield stress. Again, von Mises stress followed the inboard peak border pattern, giving a central medium value of approximately 20 MPa. Then, considering the peak value 0.25 mm inside the adhesive layer outer corner, 27.5 MPa was predicted. This is still below the 31.7 MPa uniaxial UTS value input and confirms the operation of the finite element analysis. Note also that the difference between the nominal applied 50.6 MPa and the centre-plane 27.5 MPa von Mises stress maximum confirms the triaxiality of the stress field within the adhesive layer. Von Mises stress also offers a possible local failure criterion. The peak value of 27.5 MPa correlates reasonably well with the 31.7 MPa experimental UTS value (which approximates to the von Mises value in uniaxial tension). However, effective stress is never very discriminating with plasticity. For this reason, therefore, it is perhaps not feasible as a potential basis for a local failure criterion.

Remaining with the von Mises model and now looking at the major principal stress field shown in Figure 7-17, the central peak value was predicted to be 61.8 MPa. Taking the above observations of peak values for the von Mises model, major principal stress would not appear to form a good basis for failure prediction. The central peak value of 61.8 MPa neither correlates well with the experimental uniaxial UTS for dry E32 of 31.7 MPa nor suggests a realistic locus of failure initiation.

Moving on to discuss detailed results for the Drucker-Prager model at the maximum sustained load of 45.9 MPa (4.7 MPa below the desired experimental value), peak major principal stress and strain as well as von Mises effective stress were inspected. Starting with major principal stress, Figure 7-17 shows that the central peak value of 62.5 MPa is similar to the peak value predicted using the von Mises model (61.8 MPa). Thus, as concluded earlier, this does not provide a good correlation to the experimental UTS value of 31.7 MPa. Then, considering major principal strain, Figure 7-19 shows that the twin peak loci produce a value of 4.3%. Bearing in mind the shortfall in applied load, this value
correlates well with the experimental uniaxial ultimate strain value of 4.08%. However, as the joint is on the point of collapse, predicted strains become arbitrary.

Finally considering von Mises stress, Figure 7-18 shows that the peak value 0.25 mm inside the outer corner of the layer is predicted to be 30.7 MPa. This again correlates well with the experimental UTS value for dry E32 of 31.7 MPa, and also suggests a sensible locus of failure initiation. However, as before, von Mises stress is perhaps not a mechanistically suitable parameter to use as a failure criterion.

Evaluation of global limit state failure criterion

Having discussed the possibility of a local failure criterion, it now remains to consider the use of the von Mises and Drücker-Prager yield models in combination with a global limit state failure criterion. In identifying the limit state for both models, excessive load was applied and the finite element analyses allowed to run until no further load could be supported. Then, inspecting the incremental results output, sustained load was plotted against displacement of the rigid top surface of the adhesive layer. Thus, an indication of the gross yielding of the adhesive layer could be visualised. Figure 7-21 shows this plot.

![Graph showing sustained stress against displacement for von Mises and Drücker-Prager yield models.](image)

**Figure 7-21** Sustained stress against displacement of adhesive layer for limit state investigations of von Mises and Drücker-Prager yield surface
At low loads, the gross displacement of the top surface increased linearly, correctly suggesting that the adhesive material was not yielding. However, with increasing applied load, both models began to suffer a gradual reduction in their capacity to sustain further load. Thus, the adhesive layer began to deform at a high rate, sustaining little further load and suggesting a continuous path of collapse crossing the load path. To confirm this, the local collapse condition in the 3-dimensional adhesive layer was inspected for each yield model. Figure 7-22 shows this surface of collapsed material for the more complex Drücker-Prager case, where the surface plotted corresponds to the residual component of the effective stress after subtracting the von Mises and hydrostatic stress (see Equation (62)). Thus, for this snapshot of ultimate sustainable load, not only should such a continuous surface of collapse exist, but this surface should describe a locus of stress equal to the cohesion value defined in Equation (64). As Figure 7-22 shows, this plane is indeed effectively continuous and cuts the load path, as required.

Figure 7-22 Surface plot showing continuous locus of collapsed material across adhesive layer. One eighth of the full layer shown, distances being from the three orthogonal centre-planes

Considering ultimate sustained loading predicted by the two yield models, the Figure 7-21 shows that the von Mises model gives a limit nominal applied stress of 84.2 MPa, whilst the Drücker-Prager model gives the 45.9 MPa already mentioned. Thus, compared to the
experimental dry MS-B-E32 nominal failure stress of 50.6 MPa, the von Mises model fails to provide a useful limit state failure criterion, over-predicting by 67%. However, the Drücker-Prager model gives a more reasonable prediction at 9.3% below the experimental value. In criticism, a limit state approach is generally expected to over-predict failure. However, within the context of experimental adhesives work, an error of 9.3% still represents reasonable consistency.

7.2.3 Conclusions from the 3-dimensional dry joint analyses

- a vastly less computationally demanding adhesive layer-only mesh with rigid top surface boundary condition gives sufficient accuracy of results
- the use of von Mises yielding did not result in accurate failure prediction using either local stress and strain or global limit state criteria, where failure load was greatly over-predicted
- substitution of a hydrostatically sensitive linear Drücker-Prager yield model gave good failure prediction. Besides fair correlations of peak centre-plane effective stress and major principal strain to experimental uniaxial data for the dry steel-E32 joint, the limit state approach predicted a failure stress of 45.9 MPa (a 9.3% under-estimation). As local stress is perhaps unsound to use because of its nonlinear, asymptotic characteristics, and as experimental ultimate strain is hard to measure reliably, the combination of Drücker-Prager yielding and a global limit state failure criterion is the chosen modelling package
7.3 Finite element modelling of exposed joint durability

The final sections of this chapter investigate the application of the Drücker-Prager yield model in conjunction with a limit state failure criterion to wet joints. In order to run the finite element model for the steel-E32 butt joints exposed for 18.7 and 75 days, the only necessary adjustments were the definition of moisture-dependent constitutive data and the definition of moisture profiles within the model.

7.3.1 Extension of material properties definition to wet adhesive

Retaining the linear Drücker-Prager yield and plastic flow model, as described in §7.2.2.2, it was required to extend the uniaxial hardening definition for absorbed E32. The 4.53%(RT) and 9.14%(RT) uniaxial tensile stress-strain curves from Figure 5-7 of Chapter 5 were converted to compressive data using the same mapping procedure as shown in Figure 7-13. Although the tensile to compressive uniaxial stress ratio of 1.4 for dry E32 had not been experimentally confirmed for exposed adhesive, this value was retained for the purposes of this research. For the same reason, the values of material friction and dilation angles in the Drucker-Prager yield model definition were also retained.

Furthermore, noting that the wettest bulk E32 test fell slightly short of the room temperature equilibrium value (9.70%), a stress-strain curve corresponding to saturation was estimated using the curve-fitting parameters presented in Chapter 5 (see §5.2 et seq.). The moisture dependence of the four hardening curves was defined in ABAQUS by using the option of field (concentration) dependent material data.

7.3.2 Definition of the moisture profiles in the structural analyses

Unlike the previous dry analyses, the exposed joint models required the definition of the moisture profiles, as described in §7.1.5. These nodal concentration profiles were included by way of appropriate node-concentration lists into the input decks. In terms of the ABAQUS software, this moisture profile definition took the form of an initial conditions (type = temperature) definition in the model part of the data deck.
7.3.3 Results and discussion of exposed joint analyses

Running the model for the two cases, limit loads were determined similarly to the previous dry analysis. As before, in each of the two environmentally exposed cases, the limit condition was checked by confirming the existence of a continuous surface of collapsed adhesive cutting the load path. Although not shown here, this was indeed the case. Figure 7-23 shows the load-displacement profile of the limit state analyses. The limit loads for all three cases are then summarised in Table 7-4. The table also includes the corresponding experimental nominal applied failure stresses together with errors in the predicted values.

![Load-displacement profiles](image)

**Figure 7-23** Load-displacement profiles of the dry and two wet limit state analyses

<table>
<thead>
<tr>
<th>Time to absorb in water at room temperature (days)</th>
<th>Predicted limit stress (MPa)</th>
<th>Experimental failure stress (MPa)</th>
<th>Error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>45.9</td>
<td>50.6</td>
<td>9.3</td>
</tr>
<tr>
<td>18.7</td>
<td>36.6</td>
<td>39.8</td>
<td>8.0</td>
</tr>
<tr>
<td>75</td>
<td>27.4</td>
<td>29.9</td>
<td>8.4</td>
</tr>
</tbody>
</table>

**Table 7-4** Predicted and experimental limit loads for the dry and two exposed MS-B-E32 joints

Firstly, Figure 7-23 confirms that all three analyses have reached a load asymptote. Moreover, the two wet analyses produce very similar levels of slight under-prediction to the dry analysis. Thus, the model reproduces very well the decreasing trend in
experimental residual strength with environmental exposure. Inspecting the three sets of results in more detail, centre-plane yy stress distributions were plotted and are shown in Figure 7-24.

![Centre-plane yy stress distributions at the limit state for the dry (top), 18.7-day (centre) and 75-day (bottom) cases](image)

**Figure 7-24** Centre-plane yy stress distributions at the limit state for the dry (top), 18.7-day (centre) and 75-day (bottom) cases

Referring to the dry joint, the top part of Figure 7-24 shows that most of the load at failure is transferred by the adhesive material towards the centre of the adhesive layer. Then, moving outwards, the load transfer through the layer decreases steadily. Now looking at the environmentally exposed joints, two things are immediately obvious. Firstly, the general level of sustained stress across the whole section reduces with moisture content. Secondly, the shape of the bands changes with exposure. In the dry case, there is a tendency for the centre-plane stress contours to focus into the outer corner of the adhesive
layer, whilst the wettest joint shows contours which seem focused on the centre of the layer. The fact that the corner of the adhesive layer is degraded by the cumulative effects of moisture diffusing from both the $x$ and $z$ directions supports this.

On closer inspection, a third observation becomes apparent. That is that the stress distribution seems not actually to decrease steadily from the centre of the adhesive layer outwards. The centre plot in Figure 7-24 shows this most clearly. Moving across the width of the adhesive layer centre-plane in the middle of the layer (corresponding to the right-hand side of the diagram), it can just be seen that an initial decrease in stress is followed by a partial recovery before decreasing again. Furthermore, upon detailed results inspection, there is evidence of a similar load transfer pattern for all three exposure cases. The graphs in Figure 7-25 show this more clearly.

![Figure 7-25](image-url)

**Figure 7-25** $yy$ stress against distance across adhesive layer at limit conditions for the three exposure conditions

Considering the stress levels at the centre and periphery of the adhesive layer, Figure 7-25 is consistent with expectations. Firstly considering the centre of the adhesive layer, Figure 7-3, shown earlier, suggests that the adhesive of the 18.7-day layer is essentially still dry, whereas the adhesive of the 75-day layer is significantly wet (up to 0.2 fractional uptake). This moisture variation is consistent with the central load transfer properties of Figure 7-
25. At this point, the results suggest that the dry and 18.7-day joints both transfer a similar stress of about 60 MPa, whilst the 75-day layer transfers only approximately 50 MPa at the centre. Then, considering the periphery of the adhesive layer, the grouping of results follows a similar wetness-controlled pattern. Referring again to Figure 7-3, it can be seen that the 18.7-day and 75-day layers shows approximately the same level of absorbed moisture at the periphery. And again, Figure 7-25 mirrors this grouping in terms of peripheral transferred load, i.e. the wet joints transfer approximately 10 MPa at the periphery, while the dry joint transfers nearly 20 MPa.

7.3.4 Conclusions from the exposed joint analyses

- major principal stress does not lead to prediction of centre-plane failure of the steel-E32 joint
- the use of major principal strain does correlate well to experimental bulk adhesive ultimate strain, but the latter is hard to determine reliably
- the use of Drücker-Prager yielding with a limit state failure criterion continues to give good prediction of environmental residual strength for exposed joints, right across the wetness range investigated

Thus, the overall conclusion of this chapter is that the moisture-dependent residual strength of the steel-E32 butt joint was modelled well using a quasi-static nonlinear 3-dimensional finite element stress analysis approach. Experimental moisture-dependent elastic-plastic constitutive material data were used in conjunction with a hydrostatic stress-sensitive linear Drücker-Prager yield model. Failure was then indicated by the use of a limit state approach. This modelling procedure accurately predicted residual strength, with a consistent error of between 8.0% and 9.3%, from the dry condition and up to an approximate adhesive layer fractional uptake level of 0.25 (taking 75 days to expose in distilled water at room temperature).
8. Conclusions and further work

During the course of this work, significant advances have been made in the development of a cohesive durability model, thus satisfying the main aims of the research. Results from bulk adhesive water uptake and mechanical properties programmes have been used as a basis for the development of mathematical models, thus enabling the profile of environmentally degraded properties in an adhesive layer of a joint to be predicted as a function of environmental exposure time. The use of the finite element technique then provided an overall framework for the complete durability model. First modelling the moisture profile in the layer of an exposed steel-E32 butt joint and then the resulting stresses, the latter were used to predict the residual strength of the joint. A linear Drucker-Prager yield model was used together with a limit state failure criterion, the ultimate load results being in good agreement with experimental data over a reasonable range of adhesive layer moisture saturation. The rest of this chapter outlines the main conclusions, discusses problems encountered and suggests possible future continuation work.

8.1 Conclusions

- Water uptake by bulk adhesives was found not to be simple Fickian, but a two-stage process

- There was a pronounced thickness effect which questions the application of thin specimen uptake data to adhesive layers of considerably larger dimensions

- Increasing the temperature of the water in which the specimen is immersed increases rate of uptake as well as equilibrium value

- It has been shown that applied tensile stress mainly increases the equilibrium uptake of adhesives
• A variable, concentration-dependent diffusion coefficient cannot simulate the uptake curves obtained from experiments

• Taking into account the non-Fickian general uptake behaviour and thickness response, the final proposed two-stage uptake model with boundary effect successfully predicts moisture absorbed into adhesive layers of realistic dimensions

• Bulk adhesive properties were found to degrade substantially with absorbed water for both adhesives studied. Table 8-1 shows the degradation measured over almost complete absorption ranges

<table>
<thead>
<tr>
<th>Adhesive</th>
<th>E32</th>
<th>AV119</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reduction in elastic modulus (%)</td>
<td>83</td>
<td>34</td>
</tr>
<tr>
<td>Reduction in UTS (%)</td>
<td>58</td>
<td>55</td>
</tr>
</tbody>
</table>

Table 8-1 Environmental degradation of E32 and AV119 over their almost complete respective absorption ranges

• Elastic modulus was successfully modelled for both adhesives using a mixture law with dry and fully-wet portions of bulk adhesive

• Whilst E32 showed a large increase in ductility with absorbed moisture, AV119 showed an opposite trend

• Experimental results on bulk adhesives show that absorption temperature does not significantly influence mechanical properties, moisture content being confirmed to be the critical parameter. Thus, the use of accelerated uptake tests can be used for room temperature durability prediction

• Absorbed moisture has been shown to degrade ultimate static strength of bonded joints. Typical strength reductions measured in this research have been between 20% and 40% of initial dry strength for joints with adhesive layers absorbed to approximately 0.25 of equilibrium uptake
• E32, in both butt and aluminium lap-shear geometries, has been shown to retain cohesive failure up to the maximum uptake level tested. This further confirms the validity of the current cohesive durability work.

• As with the bulk adhesive work, the evidence from the experimental adhesive joints programme generally suggests that absorption temperature does not affect residual strength. This again supports the use of accelerated uptake tests in durability prediction.

• Sequentially-coupled diffusion-stress analysis has been successfully undertaken.

• Initial modelling work suggests that fracture mechanics cannot provide a useful failure criterion for the steel-E32 butt joint studied.

• Strain-based failure criteria were of limited use, predicting failure at the wrong location.

• The von Mises yield model in combination with a limit state failure criterion over-estimated residual strength.

• The substitution of a Drucker-Prager yield model provides excellent limit state strength prediction for a range of absorbed moisture content.
8.2 Problems and further work

- Although the Drücker-Prager yield model gives good finite element prediction of residual joint strength, its slight but consistent tendency to under-predict suggests further work to more accurately determine model parameters. A programme of mechanical tests on dry and environmentally exposed adhesives is suggested, in order more closely to evaluate the Drücker-Prager model and to optimise its parameters.

- If uniaxial bulk adhesive stress-strain data could be measured at more frequent moisture content levels than studied here, then the interpolation requirements between nearest existing data points would be minimised. Currently, although finite element elastic-plastic input data is supplied at reasonable intervals in the stress-strain plane, only three or four moisture levels are represented. Thus, a wider range of moisture-dependent mechanical tests, using saturated vapours, is suggested.

- Some recent testing of thicker dry bulk E32 dogbone specimens gave consistently much higher elastic modulus and UTS values than the equivalent thin specimens. This leads to the conclusion that mechanical properties may be dependent on specimen thickness for E32. Therefore, a series of tensile tests on dry E32 specimens of varying thickness is proposed, perhaps then followed by further moisture-dependent tests. However, it would still be necessary to address how to apply thickness-dependent mechanical properties within finite element models.

- The above proposal for further thickness-dependent tensile testing perhaps warrants an investigation of non-contact extensometry. As mentioned earlier, conventional contact extensometry of thin adhesive specimens requires considerable skill and time to set up. Although, in this work, possible errors in recorded strain were checked and eliminated, a system of non-contact extensometry would be very useful. Thus, it is suggested that the purchase of a commercial non-contact strain measurement system is considered, or that an in-house system is developed.
The work on water uptake of bulk adhesives suggested that experimentally measured characteristics deviated considerably from the simple Fickian diffusion model. For the purposes of this work, two-stage diffusion models and a relaxation effect were considered, as was the substitution of the conventional instantaneous boundary equilibration condition of the basic Fickian model. However, although these models characterised the non-Fickian thickness scaling and the general two-stage uptake behaviour with good, practical, workable effect, there is an obvious need to understand diffusion mechanisms more fully.

Stress-enhanced diffusion studies should be continued, a fresh experimental programme investigating the effects of a wider range of applied stresses, perhaps at different temperatures.

Fully-coupled (as opposed to sequential) diffusion-stress modelling should be undertaken. Bringing in the above stress-dependency of diffusion, the modelling of simultaneously stressed and exposed joints can be developed. Thus, available durability models will be broadened in their applicability.

Extending the exposed joint testing programme to provide further experimental base data, an interfacial durability model should be developed. Together with full diffusion-stress coupling, the combination of cohesive and interfacial models would broaden the applicability of the current predictive package and allow the treatment of adhesive systems which are prone to interfacial failure.

Following Zanni-Deffarges and Shanahan's [19, 24] observations of increased diffusion rates through interphase regions of adhesive joints, non-uniform water uptake effects should be considered within future integrated interfacial-cohesive durability models.
References

References

53. Comyn, J., Abstracts of Papers of the American Chemical Society, 185 (March 1983), 55-POLY.
References


Appendix A

Linear and exponential variable diffusion finite difference FORTRAN 77 code
This model does Fickian uptake with linear or exponential $D(c)$. It has been tested in const $D$ mode and results match analytical solution.

It runs with $VD$, although very negatively steep $D(c)$ functions at $c=0$ cause instability problems.

LIST OF ESSENTIAL PARAMETERS

- $a$: constant in $D(c)$ definition
- $b$: constant in $D(c)$ definition
- $c$: constant in $D(c)$ definition
- $t$: current time
- $dt$: timestep
- $ttot$: total time
- $u$: integrated bulk mass uptake
- $cmax$: equilibrium concentration
- $minf$: equilibrium bulk mass uptake
- $hlen$: half-length or half-thickness
- $nel$: number of equal-sized elements across half-length
- $nnodes$: number of equi-spaced nodes across half-length
- $elen$: elemental length
- $x_nodal()$: node positions
- $c_nodal()$: nodal concentrations
- $d_nodal()$: nodal diffusion coefficient values
- $dcdx_nodal()$: nodal $dc/dx$
- $dcdx2_nodal()$: nodal $dc/dx$ all squared
- $d2cdx2_nodal()$: nodal second derivative $d2c/dx2$
- $dddc_nodal()$: nodal $dD/dc$
- $dcdt_nodal()$: nodal $dc/dt$
- $dc_nodal()$: nodal concentration change in current timestep
- $dcdx_inter()$: $dc/dx$ between adjacent nodes

Implicit double precision (a-h, o-z)

dimension $x_nodal(0:200)$
dimension $c_nodal(0:200)$
dimension $d_nodal(0:200)$
dimension $dcdx_nodal(0:200)$
dimension $dcdx2_nodal(0:200)$
dimension $d2cdx2_nodal(0:200)$
dimension $dddc_nodal(0:200)$
dimension $dcdt_nodal(0:200)$
dimension $dc_nodal(0:200)$
dimension $dcdx_inter(0:200)$

256
Appendix A: Linear and exponential variable diffusion finite difference FORTRAN 77 code

real minf
real mt
real mtbblast
real mtblast
real mtlast
real mtnow

Do an intro and input stuff

c
print*, 'This uptake model carries out Fickian diffusion with'
print*, 'either a constant or linear or exponentially variable'
print*, 'diffusion coeffient'
print*, 'Two output files will be produced and saved to the'
print*, 'working directory. File zzl will contain concentration'
print*, 'against x position values, file zz4 will contain'
print*, 'fractional uptake, U, against time values.'
print*, 'Note that Diffusion coefficient, D=A+B.exp(-C. (c/cmax))'
print*, 'Lets start ***************'
print*, 'For diffusion coefficient function, enter the constant'
print*, 'A in 10^-14.m2s-1'
read*, a
print*, 'For diffusion coefficient function, enter the factor,'
print*, 'B, also in 10^-14m2/s'
read*, b
print*, 'For diffusion coefficient function, enter the'
print*, 'exponent factor, C (dimensionless)'
read*, c
print*, 'Enter maximum mass uptake as a percentage'
read*, minf
print*, 'Enter half-length in mm of one-dimensional film'
read*, hlen
print*, 'Enter number of spatial elements over half-length'
print*, '(maximum 200)'
read*, nel
print*, 'Enter total time for diffusion analysis in seconds'
read*, ttot

c scale stuff to micrometres and seconds units for all calcs

a = a*0.01
b = b*0.01
hlen = hlen*1000.0

we're now in micrometres and seconds, etc

calc cmax from minf and hlen inputs

mmax = minf/hlen
calc number of nodes (excluding extra one) and elemental length

nnodes = nel + 1
enel = hlen/(real(nel))

c
zero all arrays right along half-length

do 50 i=0, nnodes
   x_nodal(i) = 0.0
   c_nodal(i) = 0.0
   d_nodal(i) = 0.0
   dcdx_nodal(i) = 0.0
   dcdx2_nodal(i) = 0.0
   d2cdx2nodal(i) = 0.0
   dddc_nodal(i) = 0.0
   dcdt_nodal(i) = 0.0
   dc_nodal(i) = 0.0
   dcdx_inter(i) = 0.0
50 continue

c
assign once and for all real nodal positions

do 100 i=1, nnodes
   x_nodal(i) = (real(i-1))*elen
100 continue

set up output files for c(x, t) and U v. 10^5. roott/1

open(10, file='zzl', status='new')
open(13, file='zz4', status='new')

Write top line of c(x, t) file

write(10,777)0.0, ((0.001*x_nodal(i)), i=1, nnodes)
777 format(202F9.5)

assign initial nodal concentration conditions

c_nodal(1)=cmax
do 110 i=2, nnodes
   c_nodal(i) = 0.0
110 continue

set initial zero times

t = 0.0
iout=1
thing=100.0
mtbblast=0.0
mtblast=0.0
mtlast=0.0
mtnow=0.0

This is where we loop back to at each step. For
the first ever step, we have set up the initial concentration
values. For subsequent steps, concentrations will have been
updated already

So, we've got concentrations, whatever the step we've just
started.
Appendix A: Linear and exponential variable diffusion finite difference FORTRAN 77 code

For results, let's integrate concentrations to get mt. Use equi-spaced trapezium rule.

\[
c_{\text{cum}} = 0.0 \\
\text{do } i = 2, (\text{nnodes}-1) \\
\quad c_{\text{cum}} = c_{\text{cum}} + c_{\text{nodal}(i)} + c_{\text{nodal}(i)} \\
\text{continue} \\
\text{mt} = \text{elen} * c_{\text{cum}} / 2.0 \\
u = \text{mt} / \text{minf}
\]

\[
\text{mtbblast} = \text{mtblast} \\
\text{mtblast} = \text{mtlast} \\
\text{mtlast} = \text{mtnow} \\
\text{mtnow} = \text{mt}
\]

if((mtbblast > mtblast). and. (mtblast > mtlast). and. (mtlast > mtnow)) then
    print*, 'Stopped because mt consistently reduced' \\
    print*, 'for 4 steps in a row' \\
    stop
endif

c As output always consists of only concentration and bulk mass data, we can test for it now. This programme works out when the next output should be made each time, so that there are always about 100 data points written to file and so that they are fairly equally spaced on a root time basis.

\[
\text{if}(t > \text{thing}) \text{then} \\
\quad \text{write}(10, 775) t, (c_{\text{nodal}(i)}, i = 1, \text{nnodes}) \\
\quad \text{format}(F9.0, 201F9.5) \\
\quad \text{write}(13, 335) (10.0 * (\text{sqrt}(t)) / \text{hlen}), u \\
\quad \text{format}(F9.5, F9.5) \\
\quad \text{iout} = \text{iout} + 1 \\
\quad \text{abc} = \text{real}(\text{iout}) \\
\quad \text{thing} = \text{thing} + (100.0 * \text{abc}^2 \text{abc})
\]

endif

c Only bother calculating all the finite difference stepping stuff if we still have time left

\[
\text{if}(t \leq \text{ttot}) \text{then} \\
\quad \text{assign nodal D values for 1 to nnodes using D(c/cmax) info} \\
\quad \text{do } i = 1, \text{nnodes} \\
\quad \quad d_{\text{nodal}(i)} = a + (b * \exp(-c * c_{\text{nodal}(i)}/cmax)) \\
\quad \text{continue} \\
\quad \text{using D(c/cmax) function info, determine nodal dD/dc values for 1 to nnodes} \\
\quad \text{do } i = 1, \text{nnodes} \\
\quad \quad ddddc_{\text{nodal}(i)} = -(b * c / \text{cmax}) * \exp(-c * c_{\text{nodal}(i)}/\text{cmax}) \\
\quad \text{continue}
\]

\[
\text{Now work on nodes 2 to nnodes using bulk diffusion model}
\]

259
Appendix A: Linear and exponential variable diffusion finite difference FORTRAN 77 code

```fortran
appendix a: linear and exponential variable diffusion finite difference FORTRAN 77 code

c assign inter-node dcdx values using nodal c values and elen
do 130 i=1,(nnodes-1)
dcdx_inter(i) = (c_nodal(i+1)-c_nodal(i))/elen
continue
c using inter-node dcdx values, determine nodal dcdx values
do 150 i=2,(nnodes-1)
dcdx_nodal(i) = (dcdx_inter(i-1)+dcdx_inter(i))/2.0
continue
dcdx_nodal(nnodes) = 0.0
c square nodal dcdx values
do 160 i=2,(nnodes)
dcdx2_nodal(i) = dcdx_nodal(i)*dcdx_nodal(i)
continue
c using inter-node dcdx values, determine nodal d2cdx2 values
do 140 i=2,(nnodes-1)
d2cdx2_nodal(i) = (dcdx_inter(i)-dcdx_inter(i-1))/elen
continue
d2cdx2_nodal(nnodes) = -2.0*dcdx_inter(nnodes-1)/elen

c using basic equation, calculate nodal dcdt values
do 180 i=2,nnodes
   dcdt_nodal(i) = (dddc_nodal(i)*dcdx2_nodal(i))+
                  (d_nodal(i)*d2cdx2_nodal(i))
continue

Now got dc/dt for nodes 2 to nnodes (node 1 doesn't move)

Now calculate dt
Use this dt <= (dx)^2/2D thing for now

Find biggest D across nodes

biggestd=0.0
do 821 i=1,nnodes
   if(d_nodal(i).gt.biggestd)then
      biggestd=d_nodal(i)
   endif
continue

Put timestep size inside limiting case by double
dt=0.5*0.5*elen*elen/bigestd

calculate nodal dc values from nodal dcdt and dt values
do 200 i=2,nnodes
   dc_nodal(i) = dcdt_nodal(i)*dt
continue
```

260
Now use all the last lot of stuff to update the nodal concentration values

\begin{verbatim}
  do 210 i=2,nnodes
    c_nodal(i) = c_nodal(i) + dc_nodal(i)
  210 continue

  Let's just check for convergence, making sure we're actually somewhere
  
  if(t.gt.0.0) then
    if(u.gt.0.999) then
      goto 784
    endif
  endif

  Lastly, before looping around for next step, update time and output time gap counter
  
  t = t + dt

  goto 999
  endif
  
  Ah, we must have exceeded ttot, so we must close the output file and go home.

  784 close(10)
close(13)
stop
end
\end{verbatim}

********************************************************************************
********************************************************************************
********** **********
********** END OF MAIN (THE ONLY) PROGRAM **********
********** **********
********************************************************************************
********************************************************************************
Appendix B

Individual adhesive joint failure loads and glueline thicknesses
### MS-B-E32

<table>
<thead>
<tr>
<th>Condition</th>
<th>Joint ID</th>
<th>Failure load (N)</th>
<th>Nominal average failure stress (MPa)</th>
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</table>

*Result ignored

**Table B-1 Individual MS-B-E32 joint failure loads**

### AL-B-E32

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**Table B-2 Individual AL-B-E32 joint failure loads**
Appendix B: Individual adhesive joint failure loads and glueline thicknesses

### MS-B-AV119

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Table B-3 Individual MS-B-AV119 joint failure loads

### AL-B-AV119

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Table B-4 Individual AL-B-AV119 joint failure loads
## Appendix B: Individual adhesive joint failure loads and glueline thicknesses

### MS-LS-E32

<table>
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<th>Condition</th>
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**Table B-5 Individual MS-LS-E32 joint failure loads**

### AL-LS-E32

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**Table B-6 Individual AL-LS-E32 joint failure loads**
### MS-LS-AV119

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Table B-7 Individual MS-LS-AV119 joint failure loads

### AL-LS-AV119

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<td>6987</td>
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Table B-8 Individual AL-LS-AV119 joint failure loads
Appendix B: Individual adhesive joint failure loads and glueline thicknesses

Figure B-1 Average adhesive layer thickness for all MS-B joints

Figure B-2 Average adhesive layer thickness for all AL-B joints
Appendix B: Individual adhesive joint failure loads and glueline thicknesses

Figure B-3 Average adhesive layer thickness for all MS-LS joints

Figure B-4 Average adhesive layer thickness for all AL-LS joints
Publications


- Crocombe AD, Hambly HO and Pan J, "Measurement and prediction of the strength of bonded structures exposed to moisture", accepted for the World Congress on Adhesion and Related Phenomena, Inst. of Materials, Garmisch-Partenkirchen, Germany, 1998