Effects of Water in the Fatigue Behaviour of an Adhesive for the Automotive Industry

A dissertation submitted for the degree of Master in Mechanical Engineering

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Abstract

More and more interest has been shown recently regarding adhesion technology. It has a lot of advantages that makes it competitive with the traditional methods, especially in the automotive and aerospace industries where lightness, strength and durability of a joint is increasingly sought. Toughened, high performance adhesives can provide exceptional strength while producing lighter structures and, therefore, improve vehicle safety and efficiency. But, like any technology, it has some disadvantages, in particular water degradation that substantially decreases the strength, the rigidity and the durability of a joint. At the moment, it is difficult to predict the failure load under static or dynamic conditions after humidity exposure.

The presented work studies the effect of water on fatigue behaviour of an adhesive, which also requires the study of how water degrades the adhesive properties as well as the joint strength. The objective of this study is to measure the fatigue crack growth rate of aged joints in order to accurately predict water's toll on the fatigue properties of the adhesive. Static tests were also needed to correctly obtain the fatigue test parameters and the evolution of the fracture toughness as a function of humidity. The properties of the aluminium were obtained by conducting tensile tests. Bulk adhesive specimens were also tested in unaged and aged conditions in order to understand the influence of humidity on the adhesive properties.

It was found that humidity makes the fatigue crack growth rate to be slightly lower, the threshold region is much harder to determine and the Paris law curve to shift to the left which means the crack propagation will start at lower values of the $G_{\text{max}}/G_{\text{Ic}}$ ratio. Also, the adhesive properties such as strength, rigidity and fracture toughness all decreased due to water degradation with the exception of the strain that increased, concluding that water reduces the joint strength and lifespan.
Resumo

Existe cada vez mais interesse na tecnologia adesiva. Esta tecnologia tem variadas vantagens que a faz ser competitiva com os métodos tradicionais, especialmente nas indústrias automóveis e aeroespaciais onde a força, a leveza e a durabilidade de uma junta são cada vez mais importantes. Adesivos endurecidos e de alto desempenho podem proporcionar resistência excepcional ao produzir estruturas mais leves e, portanto, melhorar a segurança e eficiência do veículo. Mas, como qualquer tecnologia também existem desvantagens, em particular o efeito degradante da água que reduz substancialmente a resistência, a rigidez e a durabilidade de uma junta. Neste momento, é difícil prever a carga de fratura em condições estáticas ou dinâmicas após exposição à humidade.

O trabalho apresentado estuda o efeito da água no comportamento à fadiga de um adesivo, que também requer o estudo de como as propriedades adesivas e a resistência de uma junta são influenciadas pela água. O objetivo deste estudo é medir a velocidade de propagação da fenda na fadiga de juntas envelhecidas a fim de prever com precisão como é que a água afecta as propriedades à fadiga do adesivo. Testes estáticos foram também realizados para obter os parâmetros dos ensaios de fadiga e a tenacidade do adesivo em função da humidade. As propriedades do alumínio foram obtidas através da realização de testes de tração e, os adesivos foram testados sem e com envelhecimento a fim de compreender a influência da humidade sobre as propriedades adesivas.

Conclui-se que a presença da humidade faz com que a velocidade de propagação da fenda diminua ligeiramente, a região inicial da curva de fadiga seja mais difícil de se ver e a curva da lei de Paris se desloque para a esquerda, o que significa que a fratura começa a valores mais baixos do rácio $G_{max}/G_{Ic}$. Devido à degradação do adesivo provocada pela água, as propriedades do adesivo como a resistência, rigidez e tenacidade diminuíram com a excepção da deformação que aumentou, concluindo que a água reduz a resistência e a durabilidade da junta adesiva.
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<th>Description</th>
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<tbody>
<tr>
<td>ADCB</td>
<td>Asymmetric double cantilever beam</td>
</tr>
<tr>
<td>BEFM</td>
<td>Beam on elastic foundation model</td>
</tr>
<tr>
<td>BEM</td>
<td>Boundary element method</td>
</tr>
<tr>
<td>CBT</td>
<td>Corrected beam theory</td>
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<td>CBBM</td>
<td>Compliance-based beam method</td>
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<td>CCM</td>
<td>Compliance calibration method</td>
</tr>
<tr>
<td>DCB</td>
<td>Double cantilever Beam</td>
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<tr>
<td>ENF</td>
<td>End notched flexure</td>
</tr>
<tr>
<td>FCG</td>
<td>Fatigue crack growth</td>
</tr>
<tr>
<td>FDM</td>
<td>Finite difference method</td>
</tr>
<tr>
<td>FEM</td>
<td>Finite element method</td>
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<tr>
<td>FPZ</td>
<td>Fracture process zone</td>
</tr>
<tr>
<td>PAA</td>
<td>Phosphoric acid anodisation</td>
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<td>RH</td>
<td>Relative humidity</td>
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## Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
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<tbody>
<tr>
<td>$F_x$</td>
<td>Flux in x-direction</td>
</tr>
<tr>
<td>$D$</td>
<td>Diffusion coefficient</td>
</tr>
<tr>
<td>$\frac{dC}{dx}$</td>
<td>Concentration gradient</td>
</tr>
<tr>
<td>$c$</td>
<td>Concentration</td>
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<tr>
<td>$t$</td>
<td>Time</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>$M_t$</td>
<td>Mass absorbed as function of time</td>
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<td>$M_\infty$</td>
<td>Equilibrium mass</td>
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<td>Thickness</td>
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<tr>
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<td>Energy release rate</td>
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<tr>
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<td>$G_{lc}$</td>
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<tr>
<td>$\sigma_c$</td>
<td>Tensile strength</td>
</tr>
<tr>
<td>$\sigma_{el}$</td>
<td>Yield strength</td>
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<td>$\sigma_r$</td>
<td>Ultimate strength</td>
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<td>$\epsilon$</td>
<td>Strain</td>
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<td>$E$</td>
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<td>$a$</td>
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<td>$C_0$</td>
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<td>$k$</td>
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<tr>
<td>$E_{xy}$</td>
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<tr>
<td>$\alpha$</td>
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<td>Coefficient of the CBBM formulation</td>
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<tr>
<td>$\gamma$</td>
<td>Coefficient of the CBBM formulation</td>
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<tr>
<td>$N$</td>
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<td>$\frac{da}{dN}$</td>
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<tr>
<td>$C$</td>
<td>Paris law constant</td>
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<td>$m$</td>
<td>Paris law constant for the slope</td>
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<td>$G_{\text{max}}$</td>
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<tr>
<td>$R$</td>
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<td>$f$</td>
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Chapter 1

Introduction

1.1 Background and motivation

Adhesion technology is increasingly more studied and implemented in the automotive industry in order to solve some problems related to the traditional methods of bonding (bolting, riveting, welding, and others). The growing availability of a variety of new materials and significant advances in bonding technology have allowed engineers to trust adhesive joints as a viable alternative to other joining techniques. Because of this, the study and understanding of adhesives has never been more pertinent.

Nowadays more attention is required to study the durability of a joint under ageing conditions such as humidity, since it is difficult to predict the failure load after ageing effects. Humidity degrades the bond between the adhesive and the adherends causing the reduction of the joint’s lifespan. The fatigue study under humidity condition will allow a deeper understanding of how the lifespan of a joint will be reduced as well as to create a proper simulation model that can be generalised.

1.2 Objectives

The main objective of this thesis is to study the effect of humidity on the fatigue behaviour of an adhesive, learn and compare how the crack propagates throughout the joint under unaged and moisture aged conditions. To accomplish this, properties like the diffusion coefficient, fracture toughness, Young’s modulus and tensile strength for both aged and unaged state are required.
Specifically, the objectives are:

- Obtain the mechanical properties for the two adhesives studied (SikaPower® 4720 and Nagase® XNR 6852-1) for both aged and unaged conditions;
- Test DCB joints from both adhesives through static and fatigue tests in mode I;
- Obtain the value of the fracture toughness for both adhesives through CBBM method to every aged scenarios;
- Obtain the diffusion coefficients for both adhesives;
- Obtain the Paris law constants;
- Compare how the Paris law constants, the fracture toughness and the mechanical properties of an adhesive are influenced by the ageing effect of water.

1.3 Research methodology

A methodology had to be defined to accomplish the objectives above. The methodology is the following:

1. A bibliographic research about the topic of adhesives and its emerging use in the automotive industry;
2. Understand the formulation behind the CBBM method for the calculation of the fracture toughness as well as the fracture mechanics;
3. Study the Paris law formulation to understand the crack propagation;
4. Research about phosphoric acid anodisation and manufacture all the DCB joints required;
5. Obtain the diffusion coefficient, fracture toughness and fatigue constants for the two adhesives using the formulation presented in the literature review for each one of them;
6. Develop a numerical model and compare it to the experimental results;

1.4 Thesis outline

The outline of this thesis is the following:
Chapter 2: An introductory literature review of adhesives in general is made, focusing on their historical development, some important definitions, advantages, disadvantages, analysis methods and formulations required to obtain the experimental results;

Chapter 3: The experimental details where all the procedure is described for the various tests performed.

Chapter 4: The experimental results are described in detail for both adhesives, including the process to obtain adherends and adhesives mechanical properties, the fracture toughness and fatigue tests for the two adhesives;

Chapter 5: A numerical model is described and compared to the experimental work, validating the results;

Chapter 6 & 7: Conclusions and ideas for future work are presented.
Chapter 2

Literature review

2.1 Adhesives in the automotive industry

Adhesive bonding in the automotive industry has increased substantially in recent years as adhesives have advantages over traditional methods of fastening. Adhesion technology is increasingly more studied and improved to achieve more demanding requirements imposed by the industry. They are used both in the assembly of supplementary elements (windows, wind screens, rubber joints and inside cladding) as in structural applications [1].

2.1.1 Applications

There are many applications of adhesive bonding in the automotive industry, ranging from flexible car body adhesives with low mechanical properties of components of little importance to high performance structural adhesives that must satisfy a wide range of requirements. The use of adhesives in the automotive industry requires the study of the material characteristics such as adhesion properties, ageing resistance, hydrolytic stability, flexibility at high/low temperatures, curing time and others. For all ranges of application the adhesives should not only meet the structural requirements but also hold them under a wide variety of conditions during its life time such as: climate conditions, extreme changes in temperature, impacts, vibrations, corrosion and so on [1].

One example of the use of adhesives in the automotive industry is in the production of sports model Lotus Elise [2, 3]. The aluminium frame is fixed together using a combination of adhesive and rivets to provide the best of the two fastening technologies. Figures 2.1 and 2.2 show some applications of adhesive bonding in the automotive industry.
Figure 2.1: Adhesives applications in cars [2].

Figure 2.2: Adhesives applications in trucks [2].
2.2 Adhesive joints

An adhesive joint is formed by the union of two or more structural members through an adhesive. The structural members are generally described as adherends. The adhesive is the element responsible for the union of the adherends through adhesion forces and cohesion. The adhesion strength is based on the attractive forces between the adhesive molecules and the surfaces of the materials to be joined. Cohesion refers to the internal resistance of the adhesive molecules when subjected to loads. The higher the intermolecular bond of the adhesive, the greater the cohesion and thus greater the adhesive strength is [4].

![Example of a adhesive joint][5]

When a substantial stress (around 7 MPa [6]) is required to separate the connected elements of a joint, the adhesive is generally designated as a structural adhesive because it contributes to an increase of strength and rigidity of the structure. These are normally used to bond high strength materials such as metals or composites. According to Gauthier [7], a structural adhesive is defined by any material capable of transferring loads applied to the joint without the occurrence of failure even though subjected to significant loads for a long period of time.

2.2.1 Advantages

Adhesive bonds are particularly interesting as an alternative to traditional joining techniques such as riveting, bolting and welding, and others. An increasing use of adhesive bonding is due to the fact that it has the following main advantages [4, 8, 9, 10, 11]:

- Allows a more uniform distribution of the static and dynamic loads over the bonded area of the joint, granting a greater rigidity and load transmission. Having a more uniform stress distribution will result in an absence of stress concentration effect and therefore will allow the joint to have a better fatigue resistance;
Figure 2.4: Stress distribution in adhesive bonding, bolted/riveted and welding [4].

- Creates a continuous contact between the bonded surfaces ensuring a continuous fixation with good sealing capacity, thermal insulation and damping vibrations due to viscoelastic behavior of the adhesive, thus improving the fatigue resistance of the joint components;
- Allows the manufacture of joints with high mechanical strength as well as being able to obtain significant reductions in the cost of manufacture since this technique tends to be milder and more economic;
- Enables the manufacture of complex shapes and can achieve good aesthetic appearance of the product, producing structures with regular contours because they avoid holes and welding marks;
- Facilitates the connection between different materials, which are not necessarily metallic, like composites where adhesives are the only viable option because in traditional methods it would interfere with the fibres of the composite;
- Since adhesives have a polymeric nature, they have a low density that allows weight reduction of the target structure and can also reduce the structural number of parts, making the adhesives technology appealing for the aerospace and automotive industry;
- Minimizes corrosion problems in the union area. The material properties of the adherends are not affected by the temperature related to the curing process of the adhesive;
- The process can be automated and it is a more convenient and effective method for joining two materials.
2.2.2 Disadvantages

Even though this process has a lot of advantages compared with other methods of fastening, it also has its limitations or drawbacks which are the following [4, 8, 9, 10, 11]:

- In order to achieve good results it is required a surface preparation that sometimes is complex, time consuming and expensive and can be made by sanding, chemical treatment, degreasing, and others. This treatments ensures a good adhesion and durability of the joint;

- When subjected to extreme working conditions such as heat and humidity, the joint degrades and the bond has a decreased resistant and durability;

- Sometimes the curing time of the adhesives is relatively long and may require high temperatures during the curing process which does not allow the bond to be made instantly, thus requiring the use of clamping tools to fix the parts and it could be an economic disadvantage;

- When compared with other fastening processes the quality control and inspection of the product is more difficult, although there have been recently developed non-destructive techniques;
2.3 Humidity effects

Adhesive joints are, in many situations, exposed to severe environment conditions during their life time that will weaken the adhesive properties as well as the bond strength, thus losing the ability to maintain a good adhesion [12]. For automotive applications, the majority of adhesive-bonded components are exposed to moist air. When the relative humidity is high over a period of time, the strength and fatigue performance of the joint will gradually decline [13]. The water diffusion on to an adhesive joint can be through the adhesive, the adhesive-adherend interface and by cracks or flaws in the adhesive. There are some phenomena responsible for the water degradation of a joint which are:

- Plasticisation of the adhesive;
- Swelling;
- Hydrolysis or cracking of the adhesive;
- Degradation or change of the interface resulting in loss of adhesion;
- Corrosion of the substrate.

Even though water can negatively affect the adhesive properties, the main factor in the weakening of joints is the water attack on the interface, which causes the most damage and leads to degradation and loss of adhesion between the adhesive and the adherends. Some of the water effects are reversible up to a certain point, such as swelling, but others are not (plasticization, cracking and hydrolysis), and as such permanently degrade the adhesive properties [14].

2.3.1 Fickian model

The water diffusion on to adhesives and adhesive joints can be modelled using Fick’s law which can then be used to easily predict the mass of water absorbed or desorbed as a function of time [15]. Fick’s first law states that the flux in x-direction \( \left( F_x \right) \) is proportional to the concentration gradient \( \frac{dC}{dx} \):

\[
F_x = -D \frac{dC}{dx}
\]  \hspace{1cm} (2.1)
Where $F_x$ is the diffusion flux, $D$ is the diffusion coefficient and $\frac{dC}{dx}$ is the concentration gradient. Fick’s second law account the non-steady state of diffusion in cartesian coordinates where there will occur diffusion onto all axis.

\[
\frac{dC}{dt} = D \left( \frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2} \right) \quad (2.2)
\]

Eq. 2.2 is commonly arranged to analyse only one direction, so it simplifies to:

\[
\frac{dC}{dt} = D \frac{\partial^2 C}{\partial x^2} \quad (2.3)
\]

The solution for Eq. 2.3 for a film of polymer immersed in an infinite bath gives us the following equation.

\[
\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{(2n-1)^2} \exp \left[ - \frac{(2n-1)^2 D \pi^2}{h^2} t \right] \quad (2.4)
\]

Where $M_t$ is the total mass absorbed by the sample at a time $t$, $M_\infty$ is the equilibrium mass of the absorbed substance and $h$ is the thickness of the sample. Figure 2.5 represents the fickian sorption and and desorption of a sample as function of time.

![Figure 2.5: Fickian sorption and desorption plot [15.]](image-url)
Crank proposed that sorption is linear up to $\frac{M_t}{M_\infty} \approx 0.6$, and a simplification of the equation can be made, valid only for the initial stage of the process where $\frac{M_t}{M_\infty} < 0.6$ [16]:

$$\frac{M_t}{M_\infty} = \frac{4}{\sqrt{\pi h}} \sqrt{D t}$$  \hspace{1cm} (2.5)

When an adhesive sample is submerged to water or moisture environments, the weight of the specimen can be periodically measured and posteriorly plotted in conformity with Eq. 2.5. The initial slope, related to the initial linear behaviour, can be used to determine the diffusion coefficient. As it is defined that the initial behavior is linear until $\frac{M_t}{M_\infty} \approx 0.6$, then $D$ can be calculated through the next expression.

$$D = \pi \left( \frac{h}{4M_\infty} \right)^2 \left( \frac{M_t}{\sqrt{t}} \right)^2$$  \hspace{1cm} (2.6)
2.4 Mechanical approach

2.4.1 Fracture mechanics

Fracture mechanics allows the study of structures that contain a crack or a flaw. It predicts if the material will cause a catastrophic failure of the structure or if it can withstand the stresses throughout the service life of the component [17].

One definition states that “the energy of a crack tip must remain finite, suggesting that an energy-based criterion on a critical stress state at which a continuum material would yield or fail is measurable. The fracture mechanics theory recognizes that a material’s resistance to crack propagation is related to the energy required to separate adjoining material”[18]. It means that when a direct stress is applied to a plate, the growth of a crack occurs when the absorbed energy reaches the limit value to form a new fracture surface. The crack propagation takes place when the energy release rate ($G$) reaches the initial value characteristic of the material ($G_c$) [19].

This method evaluates if the size of each defect does not exceed the critical fracture size leading to structural failure. There are two types of basic criteria: stress intensity factor and energetic concepts [18]. Figure 2.6 shows the three different loading modes. Mode I is the opening mode that is done by applying traction. Mode II is characterised by a shear loading perpendicular to the crack front and mode III by shear loading parallel to the crack front.

![Figure 2.6: Three crack propagation modes [9].](image-url)
2.4.1.1 Energy criterion

The energy approach was first proposed by Griffith and states that fracture will occur when the energy available for the crack growth is sufficient to overcome the resistance of the material. The material resistance may include the surface energy, plastic work or other types of energy dissipation associated with a propagating crack [17].

The energy release rate \( G \) which is defined as the rate of change in potential energy with the crack area for a linear elastic material was primarily developed by Irwin. As an example, for a crack of length \( 2a \) in an infinite plate subject to a remote tensile stress (Figure 2.7), the energy release rate is given by:

\[
G = \frac{\pi \sigma^2 a}{E} \tag{2.7}
\]

where \( E \) is Young’s modulus, \( \sigma \) is the remotely applied stress and \( a \) is the half-crack length.

![Figure 2.7: Through-thickness crack in an infinite plate subject to a remote tensile stress.](image)

2.4.1.2 Stress-intensity approach

Assuming that the material will fail locally at some critical combination of stress and strain, then it follows that fracture must occur at a critical stress intensity \( K_{Ic} \) [20]. For the plate illustrated at Figure 2.7, the stress-intensity factor is given by:

\[
K_I = \sigma \sqrt{\pi a} \tag{2.8}
\]
Combining equations 2.7 and 2.8 yields a relationship between $K_I$ and $G$.

$$G = \frac{K_I^2}{E}$$

(2.9)

Thus the energy and stress-intensity approaches to fracture mechanics are essentially equivalent for linear elastic materials.

### 2.4.1.3 Mode I

The Double Cantilever Beam (DCB) is the most common method used for the characterisation of mode I failure (Figure 2.8). It is already normalized in ASTM D3433-99 [21] and ISO 25217 [22] standards. It is based on a specimen with a pre-crack loaded in mode I. During the test, the displacement and load are recorded as well as the evolution of the crack length, which is useful to calculate the fracture toughness [17].

There are several methods to measure the fracture toughness: Compliance Calibration Method (CCM), Corrected beam Theory (CBT), Beam on Elastic Foundation Model (BEFM) and Compliance-Based Beam Method (CBBM). Only the CBBM method was used in this thesis because it is the only method that does not require the measurement of the crack length throughout the test. This method is only dependent on the specimen’s compliance during the test [23].

![Figure 2.8: Mode I DCB [17.](image)]
2.4.1.4 Compliance-based beam method (CBBM)

This methodology is based on the beam theory, specimen compliance and crack equivalent concept and allows obtaining the fracture toughness $G_{IC}$ and $G_{IIC}$ using only the $P - \delta$ curve. In this method it is not required to measure the crack length throughout the crack propagation because it uses an equivalent crack length in its formulation. Represented in Figure 2.9, this type of formulation has another advantage related to $a_{eq}$ that includes the effect of the fracture process zone (FPZ) [24].

![Diagram of FPZ and crack equivalent concept](image)

**Figure 2.9:** Schematic representation of the FPZ and crack equivalent concept. [23]

The equation to calculate $G_{IC}$ is [23, 24]:

$$G_{IC} = \frac{6P^2}{b^2h} \left( \frac{2a_{eq}^2}{h^2E_f} + \frac{1}{5G_{xy}} \right)$$  \hspace{1cm} (2.10)

where $a_{eq}$ is an equivalent crack length, $P$ is the load obtained from the $P - \delta$ curve, $b$ and $h$ are the width and thickness respectively, $G_{xy}$ is the shear modulus of the adherends and $E_f$ is a corrected flexural modulus used to take account for all the phenomena influencing the $P - \delta$ curve like stress concentrations at the crack tip and stiffness variability between specimens. The flexural modulus can be obtained through the expression:

$$E_f = \left( C_0 - \frac{12(a_0 + |\Delta|)}{5bhG_{xy}} \right)^{-1} \frac{8(a_0 + |\Delta|)^3}{bh^3}$$  \hspace{1cm} (2.11)

where $\Delta$ is a correction for crack tip rotation and deflection, $a_0$ is the initial crack length and $C_0$ is the initial compliance. The compliance throughout the crack propagation can be obtained by:

$$C = \frac{\delta}{P}$$  \hspace{1cm} (2.12)
The correction for crack tip rotation can be obtained by:

$$\Delta = h \sqrt{\frac{1}{13k} \left( \frac{E_x}{G_{xy}} \right) \left( 3 - 2 \left( \frac{\Gamma}{1 + \Gamma} \right)^2 \right)}$$

(2.13)

$$\Gamma = \sqrt{\frac{E_x E_y}{k G_{xy}}}$$

(2.14)

where $k$ is the shear stress distribution constant for correcting the deflection caused by shear load (derived as 0.85 for DCB specimen) [17].
The crack equivalent concept is:

\[ a_{eq} = \frac{1}{6\alpha} A - \frac{2\beta}{A} \]  \hspace{1cm} (2.15)

where the coefficients are:

\[ \alpha = \frac{8}{bh^3E_f}; \beta = \frac{12}{5bhG_{xy}}; \gamma = -C \]  \hspace{1cm} (2.16)

\[ A = \left( 1 - 108\gamma + 12 \sqrt[3]{\frac{4 \beta^3 + 27 \gamma^2 \alpha}{\alpha}} \right)^{1/3} \]  \hspace{1cm} (2.17)
2.4.2 Fatigue

In engineering, fatigue is a loss of properties over time due to oscillation of stresses [18]. It is an important aspect for any structural joint and it is necessary to determinate the fatigue life and resistance. There are two approaches for fatigue damage: stress-life (S-N) and fatigue crack growth (FCG). Taking interest in the second approach, FCG is a fracture mechanics based method [25]. Fracture mechanics tests have been used to identify the function relating one fracture parameter (stress intensity factor ($K$) or strain energy release rate ($G$) [26]) with the fatigue crack growth rate. Indeed the damaging effects that cyclic-fatigue loading may have on adhesively bonded joints have been quantitatively established [27, 28]. The FCG method is the correlation between the rate of fatigue crack growth per cycle ($da/dN$ that represents the crack growth rate at a certain number of cycles) and the change of one fracture parameter over time. The plotted expression of the obtained function has a sigmoidal shape that has been previously observed in studies of FCG in metals and polymers [27, 26], and for a significant range it follows a power law. The typical propagation curve can be seen in Figure 2.12 which characterises the fatigue behaviour above the threshold value and below the fracture toughness of the adhesive [27].

![Figure 2.12: Plot of the fatigue crack growth rate per cycle versus the maximum strain energy release rate [26].](image-url)
Three regions can be easily identified in the plotted expression:

- Threshold region: below the fatigue threshold \( (G_{th}) \) where the crack growth tends to zero. (represented in Figure 2.12 - threshold region);

- Linear region: where a linear growth is noticed and it is in this stage that the Paris relation or an adaptation of it (Eq. 2.18) normally fits well;

\[
\frac{da}{dN} = C \left( \frac{G_{\text{max}}}{G_{Ic}} \right)^m
\]  

2.18

- The third region starts when the crack becomes unstable and it is characterised by its fast and catastrophic growth.

The second stage of the plot is the most studied to characterise the crack propagation. Then, the Paris power law is applied to the linear region in order to obtain the values of \( C \) and \( m \) which are the parameters that depend on the material, environment, temperature and stress ratio. The environment, such as humidity, will affect negatively the adhesive joint, which will translate into a change of the FCG parameters. According to [13], humidity exposure will significantly decrease the FCG resistances in the low and medium crack growth rate regimes but will have relatively very small effect upon high crack growth rate regimes, as showed in Figure 2.13.

![Figure 2.13: Effect of humidity at 40 °C on the FCG rate of the adhesive-bonded aluminium A356 SENB joints under a load ratio of \( R = 0.1 \) [13].](image)
In [29], the effects of hygrothermal ageing on the fatigue behaviour were studied using open-faced ADCB specimens and the variation of the FCG rate curves can be seen in Figure 2.14, which shows a behaviour similar to that in Figure 2.13 with the exception of the high crack growth rate regime which in this case is also affected by humidity exposure.

Figure 2.14: FCG rate curves at 60 °C for different moisture exposure times of open-faced ADCB specimens under a load ratio of $R = 0.1$ [29].
2.5 Numerical approach

There are a few numerical methods which can accurately predict with small margin of error the behaviour of the adhesives. They are the finite element method (FEM), boundary element method (BEM) and finite difference method (FDM). The finite element method was used in this thesis due to easy access to the program Simulia Abaqus® (Providence, Rhode Island, USA), and because it has a few advantages like having a numerous amount of approaches for the failure criterion and it can also analyse the diffusion of water by using an analogy with heat analysis.

2.5.1 Cohesive damage model

In order to predict the failure, a suitable failure criterion needs to be applied. The use of cohesive damage models in fracture problems has become frequent in recent years. This approach has many advantages like their capacity to simulate onset and non-self-similar growth of damage [30]. For a cohesive damage analysis, no initial crack is needed and the damage propagation occurs without user intervention.

In many materials, fracture involves a process zone ahead of the crack where initiation and growth of micro-cracks or voids occur, called FPZ (see Figure 2.15) [15].

![Figure 2.15: Fracture Process Zone (FPZ) as function of adhesive thickness [24].](image)

There are two experimental tests (DCB and ENF) that can characterise the fracture toughness so an accurate numerical analysis can be made. It is a method that, if well implemented, yields results that allow an engineer to predict with accuracy the behaviour of adhesive joints. The effect of the shape of the traction-separation law is dependent on the nature of the problem, including material behaviour and specimen geometry [30]. Numerically, the shape of the traction-separation law influences the performance of the solution and difficulties can be observed when
using the trapezoidal law rather than bilinear in finite elements analysis [30]. The selection of the cohesive zone law should be based on all the above factors. Usually a trapezoidal law is acceptable for adhesives with ductile behaviour and the bilinear law is used in brittle adhesives [15].

Several forms of traction separation law have been proposed (Figure 2.16) but they all exhibit the same general behaviour. The traction-separation law gives the information of when the material is in the linear-elastic region, for damage propagation and finally when material failure is reached (Figure 2.17). As the cohesive surfaces start to separate, the traction increases until a critical value is reached ($t_c$) which corresponds to a critical opening displacement ($v_c$). After this point, the traction progressively decreases to zero, at which point there is a complete loss of (local) load carrying capacity and complete (local) separation occurs [15]. Considering the bilinear law the constitutive equation can be defined in two ways.
Damage initiation, propagation and failure:

\[
\sigma = \frac{\sigma_0 w}{w_0} \quad \text{if} \quad 0 \leq w \leq w_0
\]

\[
\sigma = \frac{\sigma_0 (w_c - w)}{(w_c - w_0)} \quad \text{if} \quad w_0 \leq w \leq w_c
\]

\[
\sigma = 0 \quad \text{if} \quad w > w_c
\]

(2.19)

Damage parameter \( D \) is calculated in:

\[
D = \frac{w_c (w_{max} - w_0)}{w_{max} (w_c - w_0)}
\]

(2.20)

The tensile stress is related to the initial displacement linearly:

\[
\sigma = (1 - D) k_n w
\]

(2.21)

As function of the initial \( (w_0) \) and critical \( (w_c) \) displacement:

\[
\sigma = \sigma_0 \frac{w_c - w}{w_c - w_0}
\]

(2.22)

From Eq. 2.21 and Eq. 2.22 it is noticed that the stress decreases linearly with the displacement and when \( w \geq w_c \rightarrow D = 0 \) and \( \sigma = 0 \) which indicates that the traction-separation element is fully fractured. The energy release rate is the area under the traction-separation curve.
Chapter 3

Experimental details

To accurately predict the performance of adhesives for dynamic tests and understand how they are influenced by humidity, a characterisation of its physical properties is indispensable. Although the analytical models are getting more accurate over time, there is always the need to test the adhesives so real results can be provided and can account for some unexpected or unpredictable behaviours that would never be possible using analytical model. The effects of humidity in the adhesive mechanical properties is also a reason to perform testing of bulk specimens. There are different behaviours for different kinds of adhesives regarding the mechanical properties [31]. To accomplish the objectives in this study, there is the need to perform a phosphoric acid anodisation of the adherends for the surface treatment and to perform different test methods such as diffusion tests, bulk tensile tests for the adhesive and the aluminium, DCB static and fatigue tests.

3.1 Diffusion tests

In order to calculate the rate at which water diffuses in an adhesive, diffusion tests need to be performed. Through this tests, the diffusion coefficient can be calculated using Eq. 2.6 from the fickian model.

3.1.1 Geometry

According to standard ISO 294-3 [15], the geometry used was a square with 60 mm length and a 2 mm thickness. The geometry is represented in Figure 3.1.
3.1.2 Test procedure

After having the specimens ready, they are submerged in water and, carefully, periodically weighted so that through Fick’s law, the diffusion coefficient can be calculated. Some typical curves for water absorption are represented in Figure 3.2.
3.2 Quasi-static tests of aluminium bulk specimens

This test is exactly the same as for the adhesives but its for the aluminium and uses a different geometry. This test is needed to determine the properties of the aluminium such as yield strength ($\sigma_{yd}$), the ultimate strength ($\sigma_r$), the strain ($\varepsilon$) and the Young’s modulus ($E$).

3.2.1 Geometry

The geometry is according to standard ASTM E8 [33] and it is represented in 3.3.

![Figure 3.3: Standard bulk specimen geometry for the aluminium (dimensions in mm).](image)

3.2.2 Test procedure

It uses the same test type as the adhesive where a load is applied at the extremities of the bulk specimen, applying a traction load at a speed of 1 mm/min until it fails, but for the aluminium it results in a slightly different typical curve. For this test, the optical method that consists on using a camera taking pictures with a 5 seconds interval and then using a routine in MATLAB that analysed the displacement between two marks that were drawn on each specimen. The typical stress-strain curve for the aluminium is represented in Figure 3.4.

![Figure 3.4: Typical stress-strain curve for the aluminium: 1-ultimate strength, 2-yield strength, 3-proportional limit stress, 4-fracture, 5-offset strain of 0.2 %.](image)
3.3 Quasi-static tests of adhesive bulk specimens

This test is needed to determinate the strength properties of an adhesive. It consists on applying and uni-axial and uniform load that will traction the bulk specimen, obtaining as result of the test the properties of an adhesive, such as the tensile strength ($\sigma_e$), the strain ($\varepsilon$) and the Young’s modulus ($E$).

3.3.1 Geometry

There is a wide range of geometries for the bulk specimen according to the standards but in order to study the water absorption and toll on the mechanical properties of the adhesive [32], a small specimen geometry was chosen due to its various advantages like the ability to be tested in the temperature chamber, a greater number of samples can be manufactured and reduces the probability of having any defect [17, 34]. The geometry used is represented in Figure 3.5.

![Figure 3.5: Standard and small bulk specimen geometries for the adhesives (dimensions in mm).](image)

3.3.2 Bulk specimen manufacture

The bulk tensile specimens were produced by curing the adhesive in a mould between the steel plates with a silicone rubber frame according to the French standard NF T 76-142 [35]. The silicone rubber frame was used to avoid the adhesive from flowing out. The dimensions of the adhesive plate were defined from the dimensions of the silicone rubber. To manufacture the bulk
specimens, the plates needed to be machined. The geometry of the bulk specimen is represented in Figure 3.6 and the mould in Figure 3.7.

![Bulk specimens geometry (dimensions in mm).](image1)

Figure 3.6: Bulk specimens geometry (dimensions in mm).

![Exploded view of the mould to produce the adhesive plate.](image2)

Figure 3.7: Exploded view of the mould to produce the adhesive plate.

Similarly to the adherends dog-bone specimens, the adhesive bulks were tested using the universal test machine INSTRON® model 3367 at a speed of 1 mm/min. To measure the displacement two marks were drawn on each specimen and a camera was taking pictures with 5 seconds interval. Then a software (MATLAB) was used to analyse the pictures and convert them into strain data, making each value correspond to its respective stress value obtain by the machine. In the following sections it is possible to see the evolution of the mechanical properties of both adhesives as function of water degradation.
3.3.3 Test procedure

In the tensile test a load is applied at the extremities of the bulk specimen, applying a traction load at a speed of 1 mm/min until it fails. The parameters measured are the load and the displacement. As the used specimens were smaller due to the reasons mentioned before, it was not possible to use a strain gauge. The stress-strain curves where obtained by an optical method [31, 36]. A typical stress-strain curve is represented in Figure 3.8.

![Figure 3.8: Typical stress-strain curve for adhesives [36].](image)

3.4 Surface treatment

Because adhesives must function by surface bonding, the nature and condition of the adherend surfaces is critical to the success of any bonding venture. The preparation of the adherends is a critical step because a proper bond that needs to withstand the degradation from water to the joint is required. Prior to the surface treatment the aluminium must be sanded to remove any particles and smooth the surface from some irregularities. The method of surface preparation used is the phosphoric acid anodising (PAA) and its use in a material such as aluminium creates a porous surface that will allow the adhesive, especially a low-viscosity adhesive, to reach a depth of several hundred nanometers or more, and for that reason, PAA is one of the most widely used anodising process today in the aerospace industry and provides an excellent base for
pre-bond primer applications [37]. Figure 3.9 shows how the aluminium surface transforms after the phosphoric acid anodisation.

Some advantages for the use of phosphoric acid anodisation are the following [5]:

- Develop a protective oxide layer that is resistant to corrosion;
- Remove the weak boundary layer or alternately modify the boundary layer to provide a cohesively strong layer that is well bonded to the bulk, stable, and receptive to common adhesives;
- Improve the surface topography to enable the capillary action of the adhesive to maximize joint strength.
- Protect the surface or provide a new surface that is more resistant to environmental influences once the joint is in service. An example is represented in Figure 3.10 for SikaPower 4720 with and without PAA.
- Has a lower toxicity and easier disposal comparing to other methods of surface treatment.
3.4.1 Procedure

According to standard ATSM D3933-98 [38] regarding the phosphoric acid anodising and taking into account that the adherends were the small DCB specimen, a procedure was made in order to achieve the best adhesion between adherends and adhesive.

1. After the sanding process, to remove all irregularities from the adherend surface, the adherends shall be washed to remove any dust.

2. A group of 10 adherends are placed in an apparatus that applies vibrations in an acetone solvent solution for about 8 to 10 minutes that degrease and clean the adherends.

3. After 10 minutes, remove the adherends from the solvent solution and wait until they are dry before submerging them into the phosphoric acid solution.

4. The phosphoric acid solution was done with a 10 % phosphoric acid and 90 % distilled water, which means that for a 500 g of distilled water it has a 50 g of phosphoric acid. After the combination the solution must be stirred so it becomes homogeneous.

5. An aluminium waste must be inserted to the solution and be connected to the negative pole of the power supply and the adherends to the positive pole.

6. The power supply must be tension controlled and the voltage used was 16 V. The adherends stayed for 25 minutes in the solution.

7. After 25 minutes, turn off the power supply and do a quick wash to remove the phosphoric acid solution.

8. The adherends must dry and then be stored in a limited contamination environment.
After the anodisation treatment the adherends must be bonded with the adhesive as soon as possible to minimize the possibility of inadvertent contamination. An anodized adherend has approximately 72 hours before bonding with an adhesive in order to maintain the properties that the surface treatment conferred to them. Some images of the procedure described can be seen in Figure 3.11.

Figure 3.11: Procedure: a) sanding machine, b) solvent cleaning machine, c) submersion of the aluminium adherends, d) oxide layer formation around the aluminium adherends and e) final result ready to use.

3.5 Quasi-static tests of DCB

Like the bulk specimen test, in the static test, the use of double cantilever beams is required in order to evaluate the evolution of the mechanical properties of the adhesive under mode I, particularly the load \( P \) for the load-displacement \( (P - \delta) \) curves and the fracture toughness \( (G_{fc}) \). A study was previously made [34] where a geometry of \((9 \times 10)\) adherends with steel was defined. Because diffusion takes longer in geometries with higher widths, a new reduction study was performed for 5 mm width, and the use of aluminium adherends was also considered (see Section 4.1 for details).

3.5.1 Geometry study

A previously performed analysis for the 5 mm width determined that a geometry of \((5 \times 5)\) would be viable for a fracture toughness of 2 N/mm, a value typical of high strength epoxy
adhesives. But Nagase XNR 6852-1 was later found to have a fracture toughness of 4 N/mm, and as such the stresses in the adherends would be higher than previously thought and cause plasticity of the aluminium. For this reason a new study was elaborated using the software Abaqus®. A simulation was made using a constant value of 4 N/mm for the fracture toughness and changing the geometry from 5 to 15 mm of the thickness of the adherend. The change in the adherends stress for the different geometries is represented in Figure 3.12.

![Figure 3.12: Geometry study for Nagase XNR 6852-1.](image)

As shown in Figure 3.12, the 5×5 geometry has a maximum stress of 310 MPa which is superior to the 284.1 MPa yield strength of the aluminium and for that reason the adherend would plastically deform. So for this version, Nagase XNR 6852-1, the geometry chosen was the 10×5, which has a maximum stress of 210 MPa, meaning it will not deform the aluminium (which also provides a slight safety factor), and also it is able to fit in the mould for the DCB manufacture, making it possible to produce more specimens with each mould.

### 3.5.2 Geometry

As well as the bulk specimen, a smaller DCB specimen is required to study the effect of humidity over time because to get a fully saturated standard DCB it takes a few years [34]. It consists in two symmetrical beams bonded together with an adhesive layer that commonly have a 0.2 mm thickness. The parameters such as initial crack length ($a_0$), width and thickness of the
adherends or adhesive significantly affect the strength of the bond. There was a necessity to use two DCB geometries that are represented in Figure 3.13.

![Figure 3.13: Standard DCB geometry (Top), Small DCB (10×5) geometry (middle) and Small DCB (5×5) geometry (bottom) (dimensions in mm).](image)

### 3.5.3 DCB manufacture

The DCB geometries used for each adhesive were different (Figure 3.13). For SikaPower 4720 the small geometry (5×5) was used and for the Nagase XNR 6852-1 the (10×5). If a (5×5) geometry was used for Nagase because as it has a higher $G_{IC}$, it would plastically deform the aluminium and interfere with the results, so the initial geometry was maintained for SikaPower and the (10×5) geometry applied to Nagase XNR 6852-1 (more on section 3.5.1). Both geometries were submitted to the surface treatment described previously. After the aluminium mould (Figure 3.14) was cleaned, adhesive was applied in both adherends before assembly and set in the mould for a correct alignment while curing. Before bonding the two adherends, spacers were inserted between the adherends on both ends in order to guarantee the adhesive bondline thickness of 0.2 mm. The mould was placed in a hydraulic press and submitted to 20 bars of pressure and at room temperature for 24 hours in case of SikaPower. For Nagase the same 20 bars were applied but for 3 hours at 150 °C.
The specimens were tested according to standard ASTM D3433 in static and machine at room temperature with a constant speed of 1 mm/min. The specimens were loaded to measure the behaviour of the adhesive to fracture in mode I. Only the CBBM method was used so there was no need to measure the crack length during its growth. A pre-crack was done to the adhesive in the DCB so a cohesive failure can be assured. Like in the tensile test, it is required to test the DCB joint at an unaged state for both adhesives in order to compare the evolution of the static properties.

### 3.5.4 Test procedure

The DCB is loaded in one of the pin holes with a tensile load, usually at a speed of 1 mm/min. Throughout a load cell we are able to obtain the load as a function of the displacement in order to obtain the load-displacement ($P - \delta$) curve. These results can vary due to many factors like materials, geometries or testing conditions. Throughout the load-displacement curve and using the CBBM formulation, the fracture toughness can be calculated and studied as function of humidity. A typical $P - \delta$ curve is represented in Figure 3.15.

---

**Figure 3.14:** Schematic representation of the mould used to cure the DCB specimens [17].
3.6 Fatigue tests of DCB

To characterise the crack growth propagation, a fatigue test with constant amplitude loading was performed. The fatigue test uses the same DCB joint geometry as the static test. A typical configuration of the fatigue test is represented in Figure 3.16.
3.6.1 Test procedure

The principle of this test is to load a DCB specimen with constant amplitude loading. The key parameters (Figure 3.17) used are defined by: maximum load ($P_{\text{max}}$), load ratio ($R = P_{\text{min}}/P_{\text{max}}$) and frequency ($f = 1/$cycle$)$ in Hz [18]. The maximum load is a fraction of the maximum load registered in the static test and the minimum load is obtained using the load ratio. For this test, the value of fracture toughness from static test is also required in order to plot the experimental curve using Eq. 2.18. The frequency is chosen to best fit the speed of the test and still assure a stable crack growth. For every aged condition it is imperative to maintain the amplitude relationship with the static tests (example $P = 0.6P_{\text{max}}$), so that results may be compared for different stages of humidity.

Figure 3.17: Stress parameters used to define constant amplitude loading.
Chapter 4

Experimental results

In this chapter all the experimental details are addressed, including the materials used, the manufacture of the bulk specimens and the tensile tests performed, the manufacture of the DCB joints as well as all the static and fatigue tests performed in order to obtain the fracture toughness and the Paris law curves used to study the crack propagation as function of humidity ageing and the durability of the joints. Afterwards a comparison is made between the evolution of the mechanical properties of the adhesives, between the fracture toughness values and Paris law constants for unaged and several ageing conditions for humidity.

4.1 Adherends

The adherends material to manufacture the DCB was aluminium 6082-T6 due to its strong presence in the automotive industry like control arms, knuckles, wheels hydraulic systems components and others [40]. In order to know the exact properties of this aluminium a tensile test was conducted (explained in Section 4.4.1).

4.2 Adhesives

The objective of this thesis is to study the behaviour of an adhesive regarding the fatigue as a function of humidity. As there are many types of different adhesives, ones very ductile and others very brittle, two adhesives were used in order to cover a wider range of behaviours. The adhesives are the epoxy SikaPower 4720, supplied by SIKA® (Portugal, Vila Nova de Gaia) and the epoxy XNR 6852-1, supplied by NAGASE CHEMTEX® (Osaka, Japan).
4.2.1 SikaPower 4720

SikaPower 4720 is a one component epoxy adhesive (Figure 4.1) with high resistance and excellent adhesion properties to a wide variety of adherends. It is a soft material and presents a brittle fracture. The cure is done at room temperature ($\approx 20 ^\circ C$) for 24 hours.

![Figure 4.1: Package of SikaPower 4720](image)

4.2.2 Nagase XNR 6852-1

This adhesive is a one part system stored at low temperatures (Figure 4.2). It is a ductile adhesive and the cure is done at 150 $^\circ C$ for 3 hours.

![Figure 4.2: Package of Nagase XNR 6852-1.](image)
4.3 Diffusion

There is a need to understand how quickly water penetrates into an adhesive so that the diffusion coefficient can be calculated, and an accurate prediction can be made to know how much time either tensile dogbone specimens or DCB joints must stay in water. For the diffusion coefficient to be calculated, bulk specimens were made. The diffusion coefficient vary for different materials but in adhesive joints it takes quite a long time for water to ingress. There are some accelerated factors that can increase the diffusion such as temperature. The tests were performed in a controlled environment at 32 °C.

4.3.1 SikaPower 4720

This adhesive showed a standard Fick’s diffusion where the maximum mass uptake is 32.54 % and applying Eq. 2.6 from Fickian model, the diffusion coefficient is $8.94 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}$. For the $x$ axis, a time function expression was used so that the diffusion curve is independent of the adhesive thickness and so this data is always correct to apply. The water sorption curve for SikaPower 4720 is represented in Figure 4.3.

![Figure 4.3: Experimental diffusion data for SikaPower 4720.](image-url)
4.3.2 Nagase XNR 6852-1

For Nagase XNR 6852-1 there already was diffusion data previously obtained but for a 1 mm thick specimen. Even though it is the same adhesive, varying the thickness of the specimen will give different results for the diffusion. This happens because for a 1 mm thick specimen, this adhesive behaves like a dual stage Fickian diffusion but for a 2 mm thick specimen it behaves similarly to a standard Fickian diffusion [32]. A reason for this behaviour could be that the moisture diffusion in a thin specimen occurs in a shorter time period than a thick one and it occupies the existing voids in the material which leads to a mass gain. Because a DCB joint have a 5 mm width, the diffusion behaviour will be similar to standard Fickian, and for that reason a minimum of 2 mm thick specimens for the diffusion study is required.

Figure 4.4: The variation of mid-plane moisture concentration with fractional mass uptake for different thicknesses [32].
The maximum mass increase for Nagase XNR 6852-1 is 1.307 % and applying Eq. 2.6 from Fickian model, the diffusion coefficient is $5.02 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$. The water sorption curve for Nagase XNR 6852-1 is represented in Figure 4.5.

![Figure 4.5: Experimental diffusion data for 1 and 2 mm thick specimens for Nagase XNR 6852-1.](image)

A comparison between 1 and 2 mm thickness of the specimen is represented in Figure 4.5. Even with the curves being independent of the thickness due to the $x$ axis function, the diffusion behaviour is different, where the 2 mm specimen has a faster diffusion and behaves more similarly to a standard Fickian diffusion.
4.3.3 Analytical method

Using Eq. 2.4 of the Fickian model and the values of diffusion coefficient and maximum mass uptake previously calculated, it is possible to make an analytical prediction of the diffusion curve for each adhesive. Figure 4.6 and 4.7 shows the comparison between the analytical curves and the experimental curves for both adhesives.

**Figure 4.6:** Comparison between analytical and experimental diffusion data for SikaPower 4720.

**Figure 4.7:** Comparison between analytical and experimental diffusion data for Nagase XNR 6852-1.
4.4 Tensile tests

An optical method was used to obtain the stress-strain curves from the tensile tests. This method was developed for ADFEUP (adhesives group) by Marcelo Costa. It was developed to analyse the strain in smaller specimens because a strain gauge was not possible to use. The optical method consists in a series of images that are then processed on to a routine in MATLAB®. The routine analyses the displacement using the images taken during the test, and with the excel file exported by the machine where the test was performed, which has the information regarding the load applied, the stress-strain curve can be compiled. Figure 4.8 shows the interface of the routine.

![Figure 4.8: Interface of the routine used in MATLAB software.](image)

The space between the vertical lines represent the area that is analysed by the routine concerning the displacement, where the routine identifies the black lines, manually made, and calculates the space between them. The horizontal line represent what part of the bulk specimen is analysed. Several parameters are inserted as the area, the length between the lines, time between images and the column and row where the load starts in excel.
4.4.1 Aluminium 6082-T6

In order to exactly know the properties of the material used for the adherends, tensile tests were done to characterise the aluminium. Even though the properties were already provided from the manufacturer, in some static tests there were some behaviours that led to doubt about the aluminium properties. For this reason, tensile tests for the aluminium were performed so that the real properties could be obtained.

4.4.1.1 Results

Three specimens were tested and their stress-strain curve are represented in Figure 4.9 and the aluminium properties can be seen in Table 4.1.

![Stress-strain curve](image)

**Figure 4.9:** Stress-strain curve obtained from the tensile test of the aluminium.

<table>
<thead>
<tr>
<th></th>
<th>Yield strength (MPa)</th>
<th>Ultimate strength (MPa)</th>
<th>Strain to failure (%)</th>
<th>Young’s modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminium 6082-T6</td>
<td>284.1 ± 6.8</td>
<td>322.1 ± 4.8</td>
<td>15.5 ± 0.7</td>
<td>69</td>
</tr>
</tbody>
</table>

The Young’s modulus is close to the catalogued one although it is difficult to accurately calculate it from the stress-strain curve using an optical method, and therefore it has a big deviation. The three specimens tested showed a ductile fracture and the deformation was essentially uniform until the appearance of necking. Figure 4.10 shows the specimens after they were tested.
4.4.2 Bulk specimens

For the evolution of the mechanical properties as function of water to be obtained, certain points in the diffusion curve were selected to be tested. Those points were selected as function of relative humidity. The tests were performed for unaged condition, 25 %, 40 % and 75 % relative humidity for SikaPower 4720 and for unaged condition, 15 %, 25 %, 35 %, 50 %, 80 % and 90 % relative humidity for Nagase XNR 6852-1, because more specimens were done to confirm the diffusion coefficient and it was decided to take advantage of the situation and gather more points. The specimens were submerged in distilled water at 32 °C. Figure 4.11 shows how both adhesives absorb different amounts of water and SikaPower 4720 swells more than Nagase XNR 6852-1.
4.4.2.1 Results

As expected, the mechanical properties have changed as a function of moisture uptake. While SikaPower has a large mass uptake, its properties are more influenced and can be seen in Figure 4.12, where the evolution of the Nagase properties is not that pronounced, and it is represented in Figure 4.13. More details about the experimental results for the individual points selected of the diffusion curve are presented in Appendix A.

![Figure 4.12: Evolution of the stress-strain curves for SikaPower 4720 as function of moisture uptake.](image1)

![Figure 4.13: Evolution of the stress-strain curves for Nagase XNR 6852-1 as function of moisture uptake.](image2)
Figure 4.14: Representation of the points analysed of the diffusion curve for both adhesives.

Figure 4.14 shows the points analysed of the analytical diffusion curves for both adhesives. For SikaPower 4720, it is possible to see that there is a big loss on the mechanical properties after being submerged for 92 hours. After that, the degradation occurs ever more slowly until it reaches saturation. Nagase XNR 6852-1 behaves in a similar way but less pronounced, where after 42 hours there is some degradation of the tensile strength and an increase of the strain, because it is in the linear region of the diffusion curve where degradation occurs linearly. From 42 to 308 hours (35% to 80% of relative humidity), there is a plateau where the adhesive is able to maintain its properties. When it reaches 506 hours (90% relative humidity), it is almost fully saturated and there is a loss of the mechanical properties, possibly due to hydrolysis that irreversibly degrades the adhesive.
4.4.3 Prediction of the mechanical properties

Using a program called Eureqa (Somerville, MA, USA), a equation was defined in order to predict the evolution of the mechanical properties of the adhesives. The equation only needs to know the initial properties and the final and using an empirical constant \( K \) it is able to draft a evolution curve for every adhesive.

\[
y_{RH} = - (y_{\infty} - y_0) e^{-\frac{RH}{K}} + y_{\infty}
\] (4.1)

Where \( y_{RH} \) is the value obtained as function of relative humidity, \( y_{\infty} \) is the value at 100 % relative humidity, \( y_0 \) is the unaged value or with 0 % relative humidity, \( RH \) represents the relative humidity itself from 0 to 100 % and \( K \) is an empirical value that can be modified so that it has a steeper or gradual evolution of the curve.

The application of Eq. 4.1 to the properties of SikaPower 4720 and Nagase XNR 6852-1 can be seen in Figures 4.15, 4.16 and 4.17. The empirical constant \( K \) used was 0.2 for SikaPower 4720 and 0.25 for Nagase XNR 6852-1.

Figure 4.15: Evolution of the SikaPower 4720 and Nagase XNR 6852-1 tensile strength and comparison with Eq. 4.1.
Figure 4.16: Evolution of the SikaPower 4720 and Nagase XNR 6852-1 strain and comparison with Eq. 4.1.

Figure 4.17: Evolution of the SikaPower 4720 and Nagase XNR 6852-1 Young’s modulus and comparison with Eq. 4.1.
4.5 Fracture tests

Before starting to do the fatigue tests, static test is required in order to know the maximum load for the fatigue parameters. For any state of ageing that has been tested, a static test is necessary because the water degradation will affect the adhesive and also the interface of the joint.

4.5.1 SikaPower 4720

4.5.1.1 Unaged state

Three specimen were tested but only two had a cohesive failure. Figure 4.18 shows an example of the cohesive fracture surface obtained in a specimen tested for unaged state. Figure 4.19 represents the $P-\delta$ curve for unaged state of the DCB with a pre-crack of about 2 mm to ensure a cohesive failure. For each specimen an R-curve was calculated using the CBBM method and they are represented in Figure 4.20.

![Figure 4.18: Cohesive fracture surface obtained in the static test for a unaged DCB.](image)

![Figure 4.19: P-\delta curve for unaged DCB SikaPower 4720.](image)
Figure 4.20: R-curve for unaged DCB SikaPower 4720.

Table 4.2: SikaPower 4720 DCB static properties at unaged condition.

<table>
<thead>
<tr>
<th>Load (N)</th>
<th>$G_{Ic}$ (N/mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SikaPower 4720</td>
<td>190.53 ± 7.35 1.6 ± 0.07</td>
</tr>
</tbody>
</table>

The value of the load can change as function of the specimen geometry but the fracture toughness ($G_{Ic}$) is a property of the adhesive and should not vary with the geometry of the specimen [17]. Previous tests were made and have reached the value of 1.63 N/mm for the $G_{Ic}$ [17] which compare reasonably well with the value obtained here of 1.6 N/mm.

4.5.1.2 Aged (670 hours)

Three specimens were submerged in distilled water for about 670 hours so it would reach an average saturation of 25 % of relative humidity. Only two specimens have translated into acceptable results because even with the surface treatment, the water was able to penetrate the interface in one specimen due to some manufacturing defect, and cause the fracture not to be cohesive but to be an adhesive fracture. A decrease is expected for the maximum load for the $P - \delta$ curve. The $P - \delta$ is represented in Figure 4.21 and the R-curve in Figure 4.22. Figure 4.23 shows how water degraded the joint interface by infiltrating the adhesive and deteriorating it which resulted in a loss of bond strength.
Figure 4.21: $P - \delta$ curve for (25 % RH) aged DCB SikaPower 4720.

Figure 4.22: $R$-curve for (25 % RH) aged DCB SikaPower 4720.

Figure 4.23: Water degraded DCB joint where the attack on the interface is visible.
Table 4.3: DCB static properties for (25 % RH) aged SikaPower 4720.

<table>
<thead>
<tr>
<th>Load (N)</th>
<th>$G_{IC}$ (N/mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SikaPower 4720</td>
<td>173.14 ± 18.13</td>
</tr>
</tbody>
</table>

Table 4.3 shows that the maximum load has decreased and the fracture toughness has a very slight decrease comparing with the unaged value.

4.5.1.3 Aged (1848 hours)

After being submerged for 1848 hours, one specimen had a totally cohesive failure and two others had a partially cohesive failure, where its possible to obtain the fracture toughness. A saturation of about 40 % of relative humidity was reached, and for this saturation it is expected that the middle of the joint’s width already has some water as it is possible to see in Figure 5.13. The $P - \delta$ curve is represented in Figure 4.24 and the R-curve in Figure 4.25. Even though the start of the test for specimens 2 and 3 was not what was expected, after 3.5 mm of displacement they behave in the same way (cohesive) and it is possible to obtain the fracture toughness. The dashed line represents the average of the fracture toughness for the three specimens.

![Figure 4.24: P - \delta curve for (40 % RH) aged DCB SikaPower 4720.](image-url)
Figure 4.25: R-curve for (40 % RH) aged DCB SikaPower 4720.

Table 4.4 shows that the maximum load has decreased and the fracture toughness had a substantially decrease comparing with the previous value. Figure 4.26 shows the specimens tested and its fracture.

Table 4.4: DCB static properties for (40 % RH) aged SikaPower 4720.

<table>
<thead>
<tr>
<th>Load (N)</th>
<th>$G_{Ic}$ (N/mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SikaPower 4720</td>
<td>135.34</td>
</tr>
</tbody>
</table>

Figure 4.26: Fracture of the tested DCB joints for 40 % relative humidity.
4.5.1.4 Evolution of the fracture toughness

For SikaPower 4720, the fracture toughness has decreased as function of humidity, and it is represented in Figure 4.27.

![Figure 4.27: Evolution of the fracture toughness as function of humidity for SikaPower 4720.](image)

After 670 hours, the water is only concentrated in the outer edges of the adhesive, and for that reason it does not have a significant impact on the fracture toughness. After 1848 hours submerged, it is possible to see in Figure 5.13 that water has already reached the middle of the adhesive, and as represented in Figure 4.27, it began to affect the fracture toughness by decreasing it. Figure 4.28 represents the trend of $G_{Ic}$ for SikaPower 4720 as function of humidity.

![Figure 4.28: Trend of the fracture toughness as function of humidity for SikaPower 4720.](image)
4.6 Fatigue tests

After having all the values from the static test, the fatigue tests in mode I can be performed. The fatigue tests were at constant amplitude loading where the maximum load was $60\%$ of the value obtained in the equivalent static test. A ratio ($R$) of 0.1 was used between the maximum and minimum load for all the tests performed.

4.6.1 SikaPower 4720

4.6.1.1 Unaged State

Seven specimens were tested but only three of them presented a cohesive failure due to some manufacturing defects. In this three cases an adequate characterisation of the bonded joint fatigue behaviour was allowed because the crack propagation occurred within the adhesive. Figure 4.29 shows for a specimen with cohesive failure, that there is a relation between the compliance $C$ and the actual damage of the specimen or equivalent crack length $a_{eq}$ and that both present a similar trend as a function of the number of cycles. It should be noted that $a_{eq}$ is a parameter that evaluates the evolution of damage and not the real crack already opened. Figure 4.29 also shows where the joint broke at approximately 6500 cycles.

![Figure 4.29: Variation of the compliance (C) and the equivalent crack length (a_{eq}) as a function of the number of cycles (N) for one unaged specimen.](image-url)
**Maximum energy release rate**

The evolution of $G_{\text{max}}$ as a function of the crack length $a_{eq}$ can be seen in Figure 4.30. It can be observed that $G_{\text{max}}$ tends to the $G_{Ic}$ value, and once $G_{\text{max}}$ is close to reaching the $G_{Ic}$ value, in this case 1.6 N/mm obtained in the static test, it begins to fracture in a unstable way. $a_{eq}$ can be obtained from the CBBM method by solving Eq. 2.11.

![Figure 4.30: Plot of $G_{\text{max}}$ as function of $a_{eq}$ for anaged specimen.](image1)

**Fatigue threshold**

![Figure 4.31: Complete FCG rate curve for anaged specimen identifying the threshold value.](image2)
Figure 4.31 shows the full FCG rate curve where it is possible to observe the 3 regions of crack propagation. The fatigue threshold is an important parameter to define when the initiation stage occurs. It corresponds to a change of the slope in the crack propagation rate and also the beginning of the linear part of $\frac{da}{dN}$ versus $\frac{G_{max}}{G_{Ic}}$ in a logarithmic scale. The corresponding value can normally be defined in the complete fatigue test plot. Even though only three specimens presented a stable crack propagation in the linear region, seven presented a good threshold region where the energy release rate corresponding to the fatigue crack growth threshold ($G_{Ith}$) was estimated for all specimens. Some literature values of $G_{Ith}$ vary from 0.08 to 0.13 N/mm [41, 42] and when compared with the results in Table 4.5 it presents similar values.

**Table 4.5:** Energy fatigue threshold for unaged DCB tests.

<table>
<thead>
<tr>
<th>Specimens</th>
<th>$G_{Ith}$ (N/mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.112</td>
</tr>
<tr>
<td>2</td>
<td>0.304</td>
</tr>
<tr>
<td>3</td>
<td>0.1408</td>
</tr>
<tr>
<td>4</td>
<td>0.144</td>
</tr>
<tr>
<td>5</td>
<td>0.1232</td>
</tr>
<tr>
<td>6</td>
<td>0.1328</td>
</tr>
<tr>
<td>7</td>
<td>0.1456</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td><strong>0.1575</strong></td>
</tr>
<tr>
<td><strong>Standard Deviation</strong></td>
<td><strong>0.0657</strong></td>
</tr>
</tbody>
</table>

**Fatigue crack growth**

Using the CBBM method has prevented problems like crack bowing and tilting and reading errors for the crack length monitoring required for other methods. To determine the fatigue crack growth rate ($\frac{da}{dN}$), the secant method recommended in ASTM E647 standard was used. This method consists in evaluating the variation of the crack as a function of the number of cycles considering a discrete number of measurements ($n$) during the fatigue test. The crack growth rate between two consecutive measurements ($i$ and $i + 1$) including at least 100 cycles is then evaluated with the relation given by Equation 4.2. Figure 4.32 shows the FCG rate curves for all the DCB tested without the ageing effects.

$$\left( \frac{da}{dN} \right) = \frac{(a_{i+1} - a_i)}{(N_{i+1} - N_i)} \quad (4.2)$$
Figure 4.32: FCG rate curves as function of energy ratio \((G_{\text{max}}/G_{\text{ic}})\) for three unaged DCB specimen separately.

Table 4.6: Paris law constants

<table>
<thead>
<tr>
<th>Specimen</th>
<th>(C)</th>
<th>(m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>0.1132</td>
<td>2.0005</td>
</tr>
<tr>
<td>5</td>
<td>0.1823</td>
<td>2.3539</td>
</tr>
<tr>
<td>6</td>
<td>0.1334</td>
<td>2.1963</td>
</tr>
<tr>
<td>Average</td>
<td>0.143</td>
<td>2.1836</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>0.0355</td>
<td>0.177</td>
</tr>
</tbody>
</table>
Figure 4.33: Grouped FCG rate curves as function of energy ratio ($G_{\text{max}}/G_{\text{fc}}$) for three unaged DCB specimen.

4.6.1.2 Aged (670 hours)

After 670 hours submerged in distilled water, it was expected to be at an average saturation of 25 % relative humidity. Only two specimens presented a good crack growth under fatigue. The compliance and the equivalent crack length can be seen in Figure 4.34. In comparison with the unaged state, the lifespan of the joint decreased from an average of 4500 cycles to about 2000 cycles under the load ratio and frequency.

Figure 4.34: Variation of the compliance ($C$) and the equivalent crack length ($a_{\text{eq}}$) as a function of the number of cycles ($N$) for (25 % RH) aged DCB.
Because water had degraded the properties in the outer edges of the adhesive in the DCB joint, once the load is applied the initial fracture occurs in a faster and more unstable way than in the unaged specimens. Due to this effect, the threshold region could not be seen because it become extremely more difficult to be observed.

**Fatigue crack growth**

Using the same secant method as in the first tests, the fatigue crack growth rate curves were obtained and are shown in Figure 4.35.

![Figure 4.35: FCG rate curves as function of energy ratio \( (G_{\text{max}}/G_{\text{fc}}) \) for two (25 % RH) aged DCB specimen separately.](image)

<table>
<thead>
<tr>
<th>Specimen</th>
<th>( C )</th>
<th>( m )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.3718</td>
<td>2.185</td>
</tr>
<tr>
<td>2</td>
<td>0.3397</td>
<td>2.3862</td>
</tr>
<tr>
<td>Average</td>
<td>0.3558</td>
<td>2.2856</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>0.0227</td>
<td>0.1423</td>
</tr>
</tbody>
</table>

Table 4.7: Paris law constants for (25 % RH) aged SikaPower
Figure 4.36: Grouped FCG rate curves as function of energy ratio ($G_{max}/G_{Ic}$) for two (25 % RH) aged DCB specimen.

4.6.1.3 Aged (1848 hours)

After 1848 hours submerged in distilled water, it was expected that the specimens presented an average saturation of 40 % relative humidity. The compliance and the equivalent crack length can be seen in Figure 4.37. In comparison with the previous state, the lifespan of the joint have approximately maintained the average value of 2000 cycles under the load ratio and frequency.

Figure 4.37: Variation of the compliance ($C$) and the equivalent crack length ($a_{eq}$) as a function of the number of cycles (N) for (40 % RH) aged DCB.
Fatigue crack growth

Using the same secant method as in the first tests, the fatigue crack growth rate curves were obtained and are shown in Figure 4.38.

**Figure 4.38:** FCG rate curves as function of energy ratio \((G_{\text{max}}/G_{\text{Ic}})\) for two (40 \% RH) aged DCB specimen separately.

**Table 4.8:** Paris law constants for (40 \% RH) aged SikaPower

<table>
<thead>
<tr>
<th>Specimen</th>
<th>(C)</th>
<th>(m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.631</td>
<td>1.7914</td>
</tr>
<tr>
<td>2</td>
<td>0.5207</td>
<td>1.6832</td>
</tr>
<tr>
<td>Average</td>
<td>0.5759</td>
<td>1.7373</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>0.078</td>
<td>0.077</td>
</tr>
</tbody>
</table>
Table 4.8 shows the Paris law constants for the adhesive after 1848 hours submerged in water. Unlike the previous aged test, the $C$ continued to increase but the slope ($m$) had decreased. Figure 4.39 shows the linear part of the Paris law curve for the two specimens.

![Figure 4.39: Grouped FCG rate curves as function of energy ratio ($G_{max}/G_{Ic}$) for two (40 % RH) aged DCB specimen.](image)

**4.6.1.4 Evolution of the fatigue crack growth**

It is already possible to see a trend for the behaviour of the fatigue crack growth in SikaPower 4720. The Paris law constants, $C$ and $m$, for the DCB joints that were submerged for 670 and 1848 hours to reach a 25 and 40 % relative humidity saturation, respectively. After 670 hours, the constants have slightly been affected by the water penetration and degradation of the adhesive. Those values have gone up which translates into a faster and more unstable crack propagation, especially in the linear region of the FCG rate curve. After 1848 hours, the constant $C$ continued to increase but the slope $m$ has decreased. Also the linear part of the Paris law curve has shifted to the left, which means that the initial crack will occur at lower values of the $G_{max}/G_{Ic}$ ratio. A comparison of the FCG rate curves can be observed in Figure 4.40. The slope ($m$) change is not very perceptible but the change in constant $C$ and the translation to the left is noticeable.
Figure 4.40: Comparison between unaged, 25 and 40 % RH aged states for the FCG rate.
Chapter 5

Numerical analysis

An analysis was performed in software Abaqus® to study the diffusion curves of the adhesives. Also, the numerical analysis of the $P - \delta$ curves from static tests was made for both unaged and aged conditions of the DCB specimen.

5.1 Diffusion analysis

Moisture diffusion is analogous to heat transfer (Eq. 5.1), since both are caused by random molecular motions. Fick adopted Fourier’s mathematical expression for heat conduction to quantify the diffusion [43]. Using the diffusion coefficients experimentally obtained for both adhesives, it is possible to numerically simulate the diffusion analysis.

\[
Q = -k\Delta T
\]

\[
F_x = -D\frac{dC}{dx}
\]  

(5.1)

Where $Q$ (W m$^{-2}$) is the heat flux, $k$ (W m$^{-1}$K$^{-1}$) is the conductivity and $\Delta T$ (K m$^{-1}$) is the temperature gradient. Using the same geometry as in the experimental work, the diffusion analysis was performed and Figure 5.1 represents the diffusion across the adhesive section. Only one axis was considered because the saturation in one axis is much faster than the others, so the analysis is only focusing the critical axis. A 2D model using heat transfer analysis, due to its resemblance to diffusion analysis, was used considering one quarter of the cross section at the middle of the bulk specimen that can be seen in Figure 3.6 in order to perform a faster and practical analysis. Figure 5.1 represents the model used to numerically analyse diffusion, which has a 0.025 mesh discretisation and is modelled with heat transfer that simulates the diffusion (DC2D4: a 4-node linear heat transfer quadrilateral). As was said in the experimental work, the
x axis uses a time function expression to make the diffusion curve independent of the adhesive thickness and be able to compare with other adhesives as well.

![Figure 5.1](image_url)

**Figure 5.1:** Diffusion for one quarter of the bulk section.

<table>
<thead>
<tr>
<th></th>
<th>$D$ $(m^2/s)$</th>
<th>Mass uptake (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SikaPower 4720</td>
<td>8.94e-14</td>
<td>32.538</td>
</tr>
<tr>
<td>Nagase XNR 6852-1</td>
<td>5.02e-13</td>
<td>1.307</td>
</tr>
</tbody>
</table>

**Table 5.1:** Diffusion values for SikaPower 4720.

The comparison between the numerical, analytical and experimental curves for the water diffusion in the adhesive is represented in Figure 5.2 for SikaPower 4720 and in Figure 5.3 for Nagase XNR 6852-1. The prediction of the diffusion curve is acceptable on the grounds that the three methods are very close to each other with a very small margin of error.

![Figure 5.2](image_url)

**Figure 5.2:** Numerical, analytical and experimental diffusion curve for SikaPower 4720.
A comparison can be made between the two adhesives so that the differences between them become more perceptible. This is represented in Figure 5.4. SikaPower has a much slower diffusion rate than the Nagase, but on the other hand, it absorbs a lot more water in comparison which will decrease substantially its mechanical properties.
As Figure 5.4 represent the diffusion curve for the two adhesives, a representation is required to compare the time necessary to saturate the adhesive in both bulk specimens with 2 mm thick and DCB specimens with 5 mm thick. It is represented in Figure 5.5 and 5.6 for both SikaPower 4720 and Nagase XNR 6852-1, respectively. Using the analytical curves (Section 4.3.3) and using a 5 mm thickness, a DCB analytical diffusion was obtained.

Figure 5.5: Diffusion differences between bulk specimen (2 mm thick) and DCB specimen (5 mm thick) for SikaPower 4720.

Figure 5.6: Diffusion differences between bulk specimen (2 mm thick) and DCB specimen (5 mm thick) for Nagase XNR 6852-1.
5.2 Static analysis

To do a quasi-static analysis, a DCB model was created using the geometry \((5 \times 5)\) for SikaPower 4720 and \((10 \times 5)\) for Nagase XNR 6852-1 represented in Figure 3.13. Nagase XNR 6852-1 is a stronger adhesive and requires a bigger adherend thickness so that plastic deformation of the adherend does not occur. The properties used are the same as the properties obtained in the experimental work for each adhesive.

5.2.1 Unaged state

For the unaged state without any degradation of the adhesive due to water penetration, a 2D model is sufficient to accurately predict the \(P - \delta\) curve for both adhesives. The model uses a 0.2 mm mesh size, having approximately 30000 nodes. The adherends were modelled with plane-strain 4-node quadrilateral solid (CPE4R: a 4-node bilinear plane strain quadrilateral, reduced integration, hourglass control) and the adhesive with a cohesive model (COH2D4: a 4-node two-dimensional cohesive element). The predefined cohesive damage model was a bilinear traction-separation law (Figure 2.17). Figure 5.7 shows the 2D model for the DCB \((5 \times 5)\) geometry and Figure 5.8 for the DCB \((10 \times 5)\) geometry.

\[\text{Figure 5.7: 2D model of DCB specimen with finite element mesh, a) cohesive zone (blue), b) view of the all specimen (5 x 5) geometry, c) boundary conditions.}\]

\[\text{Figure 5.8: Modelled DCB specimen with finite element mesh with (10 x 5) geometry.}\]
5.2.1.1 Results

To study the effect of the variation of the crack length, three different lengths were analysed, 10, 20 and 40 mm and the results show that with the increase of the crack length there is a decrease in the rigidity and load of the specimen. Figure 5.9 shows the influence of the crack length on the rigidity of the specimen. The crack length is one of the most important features required to accurately predict the strength of the joint because it is the parameter that has the most effect on the shape of the $P - \delta$ curve [17].

![Figure 5.9: Variation of the $P - \delta$ curve with the crack length.](image)

In Figure 5.10 the comparison between the experimental and numerical $P - \delta$ curve is made. The Young’s modulus and fracture toughness are the same as the experimentally obtained. The crack length considered was the $a_{eq}$ obtained from the CBBM method instead of the crack length measured during the test. This notion applied in the numerical method accurately compare the two results.

![Figure 5.10: Comparison between the numerical and experimental $P - \delta$ curves for SikaPower 4720.](image)
The two methods do not perfectly match but rigidity is very close and the displacement is accurately predicted. The numerical load is a little bit higher but in numerical calculation there is no errors associated with the materials or the manufacturing which could be responsible for the difference. In Figure 5.11 the Nagase $P - \delta$ curve is predicted using the $(10 \times 5)$ DCB geometry. The Young’s modulus used is the one obtained experimentally but for the fracture toughness, static tests were not performed so the value of 4 N/mm was used from other works previously made.

![Figure 5.11: Numerical prediction $P - \delta$ curve for Nagase XNR 6852-1.](image)

5.2.2 Aged state

For any aged state, a 3D model is better to answer the non-uniform degradation along the width of the adherend. But because a 3D model requires a tremendous computational power which increases the computational time necessary to run the analysis, a simple solution was arranged: use of the same 2D model applied in the unaged state but modifying the adhesive properties with an average of the properties along the width. The steps necessary are described as the following:

1. First, taking advantage of the already done diffusion analysis for the DCB specimen, the data is taken for every point along the axis of the diffusion in order to establish the saturation along the width. Figure 5.12 shows the diffusion path for the saturation curve along the width, where the saturation values for every red point was taken. An important note is that the discretization of the mesh needs to be well refined. The path saturation values vary as function of time.
2. For any average value of relative humidity, the saturation along the width will vary, as shown in Figure 5.12. Using Eq. 4.1 it was possible to obtain the degradation of the mechanical properties of the adhesive as function of the width for any average value relative humidity. Figure 5.13 shows the degradation of the mechanical properties as function of the width for some average value of relative humidity.

Figure 5.12: Path for half width of the DCB specimen - water diffusion along the adhesive.

Figure 5.13: Variation of the mass uptake (top), tensile strength (middle) and Young’s modulus (bottom) along the width and their evolution as function of diffusion for SikaPower 4720 (left) and Nagase XNR 6852-1 (right).
3. After having the properties for each point, there are two ways of analysis: Doing a 3D model and inserting every point’s properties individually for every slice of the adhesive in the model or doing a 2D analysis and using the average values from the properties as if it was one piece.

5.2.2.1 670 hours

Figure 5.14 shows the result using the 2D method enumerated for the 25 \% relative humidity test as well as for the 3D model and it gives satisfying results. The 3D model gives a more accurate prediction of the displacement where as the 2D model gives a better maximum load prediction. The fracture toughness used was the same obtained in the static tests for 25 \% relative humidity.

![Comparison between numerical 2D, 3D and experimental P-δ curves (25 \% RH) aged SikaPower 4720.](image)

**Figure 5.14:** Comparison between the numerical 2D, 3D and experimental $P - \delta$ curves for (25 \% RH) aged SikaPower 4720.

5.2.2.2 1848 hours

Figure 5.15 shows the result using the 2D method enumerated for the 40 \% relative humidity test as well as for the 3D model. The results are close but the numerical models, because there are no errors associated with the materials or the manufacturing, it gives a slightly higher load. The 3D model is very close to the 2D with the exception of the displacement that is a little higher.
Figure 5.15: Comparison between the numerical 2D, 3D and experimental $P - \delta$ curves for (40 % RH) aged SikaPower 4720.
Chapter 6

Conclusions

The main objective of this thesis was to characterise the fatigue behaviour of an adhesive as function of water. The analysis of the humidity effect on the adhesives have successfully been characterised with the tensile tests in both adhesives, the static and fatigue tests for SikaPower 4720. For a characterisation of the fatigue behaviour, first tensile and static tests were performed so that it is possible to characterise the fatigue behaviour of an adhesive. Even though both adhesives have completely different behaviours at the unaged state, after water submersion they proportionally behave in the same way, where SikaPower has a stronger decrease in the mechanical properties because it absorbs substantially more water when compared with Nagase. The formulation for the prediction of the mechanical properties is a breakthrough because not only it predicts successfully the evolution of the mechanical properties as a function of humidity for both adhesives, but also it can be implemented for any immersion time of any adhesive. Furthermore, it can be concluded that:

- Nagase XNR 6852-1 has a ductile behaviour and SikaPower 4720 a brittle behaviour;

- Humidity has almost doubled the strain for Nagase XNR 6852-1 (from 16 % to 29 %), and for SikaPower 4720 the strain was more than doubled (from 3.4 % to 7.7 %);

- SikaPower 4720 absorbs 32.5 % of its initial mass, around 25 times more water than the 1.3 % of Nagase XNR 6852-1, a difference that will affect the mechanical properties greatly. SikaPower 4720 has lost 64 % of the tensile strength and 76 % of the Young’s modulus from the initial properties for 75 % relative humidity, where Nagase XNR 6852-1 for the same point has lost about 13 % for tensile strength and 6.6 % for Young’s modulus.
Unfortunately, in the static and fatigue tests, only the SikaPower 4720 adhesive was characterised because although the Nagase XNR 6852-1 adhesive was used with the same DCB geometry (5 × 5) it was found that it would plastically deform the adherend (because Nagase XNR 6852-1 has a much higher fracture toughness than expected when the 5 × 5 geometry was designed and studied), which in turn would affect the results, making them unreliable. For a good characterisation of Nagase XNR 6852-1 a (10 × 5) geometry for the DCB joint should be used (like it was shown on section 3.5.1). SikaPower 4720 in both static and fatigue tests was successfully characterised, but it did not have any more points for more humidity stages because it has a slow diffusion coefficient and it takes a long time to saturate. The results of the static tests are the following:

- For the unaged condition, SikaPower 4720 has a fracture toughness of 1.6 N/mm, which comparing with other works with the same adhesive, is an acceptable result.

- For 25 % of relative humidity, water had very little effect of the fracture toughness (from 1.6 to 1.57 N/mm) because only the outer edges have water saturation where as the inner part of the specimen still remains very close to 0 % of relative humidity, therefore being able to maintain the fracture toughness to a similar value as for the unaged state. Some problems began to appear because in some joints water started to infiltrate the interface of the joint.

- For 40 % of relative humidity, water had already reached the middle of the joint and started to degrade the adhesive. The fracture toughness has then decrease to a value of 1.25 N/mm.

The fatigue tests have demonstrated that water has a negative effect on the properties of a joint, reducing the joint lifespan and changing the behaviour of the fatigue crack growth rate. Water is one of the most destructive environment for a joint because even with the PAA treatment applied to the adherends, it can penetrate the interface and degrade the bond strength. The results of the fatigue tests are the following:

- For 25 % of relative humidity, a change in the Paris law constant is seen, where both of them has slightly increased, meaning that for durability purposes, it reduces the lifespan to some extent because the fatigue crack growth rate has increased. Because the constants have increased, the linear part of the Paris law curve have also raised in comparison with the unaged state.

- For 40 % of relative humidity, the $C$ constant continued to increase but the $m$ constant had decreased, a reduction consistent with the literature. Besides that, the FCG resistance of
the joints were lower due to the Paris law curves being shifted to the left, where the joint will start to crack at earlier values of the $G_{max}/G_{lc}$ ratio.
Chapter 7

Future work

Due to the wide range of possibilities available to study the fatigue behaviour, some ideas are listed here to improve the results obtained and draw more conclusions:

- Because diffusion takes a long time, especially with adhesives that have a small diffusion coefficient, a solution is to study the fatigue behaviour as function of humidity at 50 °C or more, as long as it remains below the glass temperature \(T_g\);

- Complete the static and fatigue tests for SikaPower 4720 to make a fully envelope of the fatigue behaviour as function of humidity;

- Do the same for Nagase XNR 6852-1, but this time for the corrected DCB geometry;

- Study the effects of water in the fatigue behaviour in mode II and mixed mode of an adhesive.
References


Appendix A

Tensile tests

A.1 Unaged state

A characterisation of the mechanical properties as function of water degradation is required. To do that, first the tensile test at an unaged condition was performed in order to evaluate the initial properties. The stress-strain curves are showed in Figures A.1 and A.2 for SikaPower 4720 and Nagase XNR 6852-1, respectively.

![Stress-strain curve for SikaPower 4720 at unaged condition.](image)

**Figure A.1:** Stress-strain curve for SikaPower 4720 at unaged condition.
Figure A.2: Stress-strain curve for Nagase XNR 6852-1 at unaged condition.

Table A.1: SikaPower 4720 and Nagase XNR 6852-1 properties at unaged condition.

<table>
<thead>
<tr>
<th></th>
<th>Tensile strength (MPa)</th>
<th>Strain to failure (%)</th>
<th>Young's modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SikaPower 4720</td>
<td>31.4 ± 1.4</td>
<td>3.4 ± 0.6</td>
<td>2030.9 ± 86.7</td>
</tr>
<tr>
<td>Nagase XNR 6852-1</td>
<td>61.9 ± 1.6</td>
<td>16 ± 6.8</td>
<td>2095 ± 121</td>
</tr>
</tbody>
</table>

The results confirm that SikaPower 4720 has a brittle behaviour and that Nagase XNR 6852-1 has a ductile behaviour. The data obtained have a low dispersion in terms of tensile strength. The strain has a big dispersion due to microscopic defects that lead to uncertainty of the adhesive rupture. The Young's modulus has an acceptable dispersion.
A.2 SikaPower 4720

A.2.1 Aged (92 hours)

For this test it is expected that the tensile strength and the Young’s modulus of the adhesive decreases and the strain increases. The results are shown in Figure A.3 and corroborate the expectations. The specimens were submerged for 92 hours. The mechanical properties for 25 % RH are represented in Table A.2 and Figure A.4 present the rupture of the specimens.

![Stress-strain curve for (25 % RH) aged SikaPower 4720.](image)

**Figure A.3:** Stress-strain curve for (25 % RH) aged SikaPower 4720.

**Table A.2:** SikaPower 4720 properties for (25 % RH) aged condition.

<table>
<thead>
<tr>
<th></th>
<th>Tensile strength (MPa)</th>
<th>Strain to failure (%)</th>
<th>Young’s modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SikaPower 4720</td>
<td>16.9 ± 0.4</td>
<td>9.8 ± 2.5</td>
<td>809 ± 95</td>
</tr>
</tbody>
</table>

![Bulk tensile specimens after the tests (25 % RH).](image)

**Figure A.4:** Bulk tensile specimens after the tests (25 % RH).
A.2.2 Aged (308 hours)

As expected, and represented in Figure A.5, the tensile strength and Young’s modulus continue to decrease but the strain has also decreased in this test. This behaviour can be explained by the water molecules starting to interfere with the adhesive molecules and reducing their bond strength, which will translate into worst mechanical properties. The specimens were submerged for 308 hours. The mechanical properties for 40 % RH are represented in Table A.3 and Figure A.6 present the rupture of the specimens.

![Stress-strain curve for (40 % RH) aged SikaPower 4720.](image)

**Figure A.5:** Stress-strain curve for (40 % RH) aged SikaPower 4720.

<table>
<thead>
<tr>
<th>Tensile strength (MPa)</th>
<th>Strain to failure (%)</th>
<th>Young’s modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SikaPower 4720</td>
<td>14.2 ± 0.9</td>
<td>7.7 ± 1.2</td>
</tr>
</tbody>
</table>

**Table A.3:** SikaPower 4720 properties for (40 % RH) aged condition.

![Bulk tensile specimens after the tests (40 % RH).](image)

**Figure A.6:** Bulk tensile specimens after the tests (40 % RH).
A.2.3  Aged (1248 hours)

As expected, and represented in Figure A.7, the tensile strength and Young’s modulus continue to decrease and the strain rate stabilized. The specimens were submerged for 1248 hours. The mechanical properties for 75 % RH are represented in Table A.4 and Figure A.8 present the rupture of the specimens. The water degradation has reduced the adhesive strength by about 64 %. The analysis did not continue closer to the saturation point because it has a slow diffusion and there was not enough time.

![Stress-strain curve](image)

**Figure A.7:** Stress-strain curve for (75 % RH) aged SikaPower 4720.

**Table A.4:** SikaPower 4720 properties for (75 % RH) aged condition.

<table>
<thead>
<tr>
<th></th>
<th>Tensile strength (MPa)</th>
<th>Strain to failure (%)</th>
<th>Young’s modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SikaPower 4720</td>
<td>11.4 ± 0.2</td>
<td>7.7 ± 1.1</td>
<td>486 ± 9</td>
</tr>
</tbody>
</table>

![Bulk tensile specimens](image)

**Figure A.8:** Bulk tensile specimens after the tests (75 % RH).
A.3 Nagase XNR 6852-1

A.3.1 Aged (8.5 hours)

Due to water exposure, the tensile strength and the Young’s modulus of the adhesive have the tendency to decrease and the strain to increase. Figure A.9 shows the stress-strain curve for 15 % RH and corroborate the expectations, even though the evolution in Young’s modulus is very low, but that is understandable because the adhesive absorbs very few quantity of water (1.307 %). The specimens were submerged for 8 hours and 30 minutes. The mechanical properties for 15 % RH are represented in Table A.5 and Figure A.10 present the rupture of the specimens.

![Stress-strain curve for (15 % RH) aged Nagase XNR 6852-1.](image)

**Figure A.9:** Stress-strain curve for (15 % RH) aged Nagase XNR 6852-1.

**Table A.5:** Nagase XNR 6852-1 properties for (15 % RH) aged condition.

<table>
<thead>
<tr>
<th></th>
<th>Tensile strength (MPa)</th>
<th>Strain to failure (%)</th>
<th>Young’s modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nagase XNR 6852-1</td>
<td>56.3 ± 1.1</td>
<td>21.1 ± 9.8</td>
<td>2060 ± 102</td>
</tr>
</tbody>
</table>

![Bulk tensile specimens after the tests (15 % RH).](image)

**Figure A.10:** Bulk tensile specimens after the tests (15 % RH).
A.3.2 Aged (25.5 hours)

Figure A.11 shows the stress-strain curve for 25 % RH and for the tensile strength and Young’s modulus, they continue to decrease but only just a bit and the strain continues to increase. The effect of necking (reduction of the section area due to tensile loads) can be seen in the Figure A.12. The specimens were submerged for 25 hours and 30 minutes. The mechanical properties for 25 % RH are represented in Table A.6 and Figure A.12 present the rupture of the specimens.

![Stress-strain curve](image)

**Figure A.11:** Stress-strain curve for (25 % RH) aged Nagase XNR 6852-1.

**Table A.6:** Nagase XNR 6852-1 properties for (25 % RH) aged condition.

<table>
<thead>
<tr>
<th></th>
<th>Tensile strength (MPa)</th>
<th>Strain to failure (%)</th>
<th>Young’s modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nagase XNR 6852-1</td>
<td>55.7 ± 1.9</td>
<td>26.5 ± 12.9</td>
<td>2044 ± 48</td>
</tr>
</tbody>
</table>

![Tensile specimens](image)

**Figure A.12:** Bulk tensile specimens after the tests (25 % RH).
A.3.3 Aged (42 hours)

Figure A.13 show the stress-strain curve for 35 % RH. The properties have a very little change with the exception of the strain that have increased. The specimen BN8 have not been considerate due to its fracture that was outside the lines and probably had some defect like bubbles of air in the middle of the adhesive. The specimens were submerged for 42 hours. The mechanical properties for 35 % RH are represented in Table A.7 and Figure A.14 present the rupture of the specimens.

![Stress-strain curve for 35% RH aged Nagase XNR 6852-1.](image1)

**Figure A.13:** Stress-strain curve for (35 % RH) aged Nagase XNR 6852-1.

**Table A.7:** Nagase XNR 6852-1 properties for (35 % RH) aged condition.

<table>
<thead>
<tr>
<th></th>
<th>Tensile strength (MPa)</th>
<th>Strain to failure (%)</th>
<th>Young’s modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nagase XNR 6852-1</td>
<td>55.5 ± 0.2</td>
<td>29.4 ± 0.3</td>
<td>2020 ± 21</td>
</tr>
</tbody>
</table>

![Bulk tensile specimens after the tests (35 % RH).](image2)

**Figure A.14:** Bulk tensile specimens after the tests (35 % RH).
A.3.4 Aged (92 hours)

The tensile strength and Young’s modulus continue to gradually stabilise and the strain has decreased. As BN8, the BN15 was not considered because it broke outside the lines on the grip zone. The stress-strain curve for 50 % RH is shown in Figure A.15. The specimens were submerged for 92 hours. The mechanical properties for 50 % RH are represented in Table A.8 and Figure A.16 present the rupture of the specimens.

![Stress-strain curve for (50 % RH) aged Nagase XNR 6852-1.](image)

**Figure A.15:** Stress-strain curve for (50 % RH) aged Nagase XNR 6852-1.

<table>
<thead>
<tr>
<th>Tensile strength (MPa)</th>
<th>Strain to failure (%)</th>
<th>Young’s modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nagase XNR 6852-1</td>
<td>55.6 ± 0.9</td>
<td>22.6 ± 0.2</td>
</tr>
</tbody>
</table>

**Table A.8:** Nagase XNR 6852-1 properties for (50 % RH) aged condition.

![Bulk tensile specimens after the tests (50 % RH).](image)

**Figure A.16:** Bulk tensile specimens after the tests (50 % RH).
A.3.5 Aged (308 hours)

Figure A.17 represent the stress-strain curve for 80 % RH. The tensile strength and Young’s modulus continue to decrease and the strain it started again to increase. It has reached a point where it is close to saturation, even though it absorbs very little water. The specimens were submerged for 308 hours. The mechanical properties for 80 % RH are represented in Table A.9 and Figure A.18 present the rupture of the specimens.

![Stress-strain curve for (80 % RH) aged Nagase XNR 6852-1.](image)

**Figure A.17:** Stress-strain curve for (80 % RH) aged Nagase XNR 6852-1.

<table>
<thead>
<tr>
<th>Tensile strength (MPa)</th>
<th>Strain to failure (%)</th>
<th>Young’s modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>53.9 ± 1</td>
<td>26.5 ± 5.1</td>
<td>1956 ± 14</td>
</tr>
</tbody>
</table>

**Table A.9:** Nagase XNR 6852-1 properties for (80 % RH) aged condition.

![Bulk tensile specimens after the tests (80 % RH).](image)

**Figure A.18:** Bulk tensile specimens after the tests (80 % RH).
A.3.6 Aged (506 hours)

In the final point that was analysed, every property has decreased. The specimens were submerged for 506 hours. The water degradation have reduce the adhesive strength by about 17%. Figure A.19 represents the stress-strain curve for 90 % RH which is close to saturation. The mechanical properties for 90 % RH are represented in Table A.10 and Figure A.20 present the rupture of the specimens.

![Stress-strain curve for (90 % RH) aged Nagase XNR 6852-1.](image)

**Figure A.19:** Stress-strain curve for (90 % RH) aged Nagase XNR 6852-1.

<table>
<thead>
<tr>
<th>Tensile strength (MPa)</th>
<th>Strain to failure (%)</th>
<th>Young’s modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nagase XNR 6852-1</td>
<td>51.4 ± 1.2</td>
<td>23.7 ± 1.9</td>
</tr>
</tbody>
</table>

![Bulk tensile specimens after the tests (90 % RH).](image)

**Figure A.20:** Bulk tensile specimens after the tests (90 % RH).