

THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

**QUASI-STATIC AND FATIGUE LIFE ASSESSMENT OF
HYGROTHERMALLY AGED ADHESIVES UNDER MODE I CONDITION**

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ABSTRACT

Adhesive joints used in advanced industries such as those operating in the automotive, railways, and aerospace sectors, usually experience different environmental conditions in service. Humidity can significantly degrade the mechanical properties of the bonded joints and accordingly, the effects of humidity on the performance of bonded structures must be considered in the design stage. Furthermore, real joints often experience a cyclic environmental change, where they are subjected cyclically to a humid stage for a period immediately followed by a drying stage. Therefore, a combination of humidity variations and cyclic loadings is a major factor contributing to the reduction of an adhesive joint properties.

To this end, in this research, experimental investigations were conducted under different moisture absorption levels in order to study the influence of the humidity levels on the mechanical properties of the adhesive joints, loaded under mode I loading condition. To investigate the moisture absorption and desorption mechanisms, hygrothermal ageing experiments were performed. To analyse the water diffusion into the adhesive, standard bulk specimens were used. Two ageing mechanisms were considered in this work, including the single cycle and cyclic ageing, where the single cycle ageing aims to determine the humidity level and saturation level while the aim of the cyclic ageing is to understand the absorption mechanism at different ageing cycles. The diffusion coefficient for single cycle and cyclic ageing were determined based on the Fick's law.

To investigate the effects of the humidity on the mechanical properties of the bulk adhesive, dogbone specimens were manufactured, aged, and tested under mode I static loads. The mechanical properties of the bulk adhesive under the effect of humidity were determined.

By manufacturing, ageing, and testing Arcan joints, the effect of humidity on the tensile performance of adhesive joints was analyzed. Joints were subjected to both the single cycle

and cyclic ageing conditions. Results of the static tests showed that the stress and the stiffness of the aged joints decreased significantly when compared to the unaged joints. By increasing the ageing time, a more significant reduction of the joint strength can be found.

Fatigue tests based on the S-N approach were also conducted for unaged, single cycle aged, and cyclically aged Arcan joints, allowing to better understand the influence of the humidity levels, and cyclic ageing on the fatigue response of the bonded joints. The results of the S-N approach revealed that the presence of moisture within the joints affects the decrease in fatigue life of joints for both single cycle and cyclic ageing, as the joints lose their endurance limit for higher ageing cycles. The results showed that changing the ageing frequency can considerably change the fatigue life of the Arcan joints.

For the numerical simulations, the finite element method was used to reproduce all the experimental tests carried out with the bulk adhesive and the adhesive joints. The simulation of the bulk adhesive aims to determine the moisture uptake levels of the studied adhesive, via the application of the the moisture saturation level and the diffusion coefficient (D) which was obtained from the experimental measurement. Joint simulations aim to predict the moisture uptake in the joints, and the effects of the moisture on the strength degradation for both static and fatigue under mode I loading conditions.

Resumo (Português)

As juntas adesivas utilizadas em indústrias avançadas como a indústria automóvel, os caminhos-de-ferro e o setor aeroespacial estão geralmente sujeitas a diferentes condições ambientais em serviço. A humidade pode degradar significativamente as propriedades mecânicas das juntas coladas e por conseguinte, os efeitos da humidade no desempenho das estruturas coladas devem ser tidos em conta na fase de conceção. Além disso, as juntas reais estão frequentemente sujeitas a um ambiente cíclico onde são submetidas a uma condição húmida durante um determinado período, seguido de um estágio onde existe secagem. Desta forma, a combinação entre variações de humidade e um estado de carga cíclica contribui de forma significativa para a redução do desempenho de juntas adesivas.

Para este efeito, nesta investigação foram realizadas atividades experimentais sob diferentes níveis de humidade absorvida, a fim de estudar a influência desta condição nas propriedades mecânicas das juntas adesivas sujeitas a condições de carregamento do modo I. Para investigar os mecanismos de absorção e dessorção da humidade, foram realizadas experiências de envelhecimento higrotérmico. Para analisar a difusão da água no adesivo, foram utilizados provetes de adesivo maciço. Foram considerados dois mecanismos de envelhecimento distintos, incluindo um ciclo único e um processo de envelhecimento cíclico, onde o envelhecimento em ciclo único visa determinar o nível de humidade e o nível de saturação, enquanto o objetivo do envelhecimento cíclico é de compreender a variação do mecanismo de absorção sob diferentes ciclos de envelhecimento. O coeficiente de difusão para o ciclo único e para o envelhecimento cíclico foram determinados com base na lei de Fick.

Para investigar os efeitos da humidade nas propriedades mecânicas do adesivo, amostras do tipo *dogbone* foram fabricadas, envelhecidas e testadas sob carregamentos estáticos em modo I.

Ao fabricar, envelhecer, e testar juntas do tipo *Arcan*, foi possível analisar o efeito da humidade no desempenho das juntas adesivas à tração. Estas juntas foram submetidas tanto a um ciclo único como a condições de envelhecimento cíclico. Os resultados dos testes estáticos mostraram que a resistência e a rigidez das juntas envelhecidas diminuíram significativamente quando comparadas com as características das juntas não envelhecidas. Ao aumentar o tempo de envelhecimento, uma maior redução da força da junta foi encontrada.

Foram também realizados testes de fadiga com base na abordagem S-N para juntas *Arcan* não envelhecidas, sujeitas a um ciclo único e ou múltiplos ciclos de envelhecimento, permitindo compreender a influência dos níveis de humidade e o envelhecimento cíclico na resposta à fadiga das juntas ligadas. Os resultados da abordagem S-N revelaram que a presença de humidade nas juntas afeta a diminuição da vida de fadiga das juntas tanto para o ciclo único como para o envelhecimento cíclico, com as juntas a perderem o seu limite de resistência para ciclos de envelhecimento mais elevados. Os resultados mostraram também que mudar a frequência de envelhecimento pode alterar consideravelmente a vida de fadiga das juntas *Arcan*.

Para as simulações numéricas, o método dos elementos finitos foi utilizado para reproduzir todos os ensaios experimentais realizados nas juntas adesivas e no adesivo. A simulação do adesivo em maciço visa determinar os níveis de absorção de humidade do adesivo de estudo através da aplicação do nível de saturação da humidade e do coeficiente de difusão (D) obtido a partir da medição experimental. As simulações de juntas visam prever a absorção de humidade nas juntas, e os efeitos da humidade na degradação da resistência tanto para condições estáticas como para a fadiga, sempre para carregamentos em modo I.

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List of publications

International Journal Papers

1. da Costa, J., et al., Cyclic ageing of adhesive materials. The Journal of Adhesion, 2022, Vol. 98, No. 10, 1341-1357.
2. da Costa, J., et al., Effects of cyclic ageing on the tensile properties and diffusion coefficients of an epoxy-based adhesive. Proceedings of the Institution of Mechanical Engineers, Part L: Journal of Materials: Design and Applications, 2021.
3. da Costa, J.A., et al., The influence of interfacial failure on the tensile S–N response of aged Arcan joints. Journal of Applied Polymer Science, 2021.
4. da Costa, J.A., et al., Effects of ageing frequency on the interfacial failure and tensile properties of adhesive bonded joints exposed to cyclic ageing environments. Proceedings of the Institution of Mechanical Engineers, part E: Journal of Process Mechanical Engineering, 2022.
5. da Costa, J.A., et al., The influence of cyclic ageing of the fatigue performance of bonded joints. International Journal of Fatigue, 2022.

1. Introduction

1.1. Background and motivation

Due to the many advantages over conventional joining methods such as welding, bolting, and riveting, adhesive joints are extensively used in different industrial sectors. Adhesive bonding produces a more uniform stress distribution along the bonded area, provides higher stiffness, is relatively cheaper in manufacturing process, is able to bond thinner sheets, lightweight materials, and similar and dissimilar materials.

However, one of the biggest challenges is the effect of moisture attack on the strength of the bonded joints. The real constraint in the application of adhesive joints is in the transportation sectors such as cars, trains, and airplanes, where the joints often work in a humid environment where the adhesive absorbs moisture in its life. Therefore, the effects of moisture on the adhesive joints are very important topic and must be studied before the joint design. Since the real joints are often subjected to a cyclical environment where the humidity level increases and decreases cyclically during the service, consequently considering the effects of cyclic ageing on the fatigue response of bonded joints is also a key parameter in the design of such joints.

Accordingly, the aim of the current study is to investigate the effects of cyclic ageing and ageing frequency on the tensile fatigue life and tensile static strength of Arcan joints bonded with a structural epoxy adhesive. The absorption and desorption mechanisms were analysed based on the Fick's law as presented in paper [1]. The diffusion coefficients (D) of the studied adhesive for both single cycle and cyclic ageing were determined. The saturation level of the tested epoxy-based adhesive was found to be 13.49% and saturation time was 7500 hours. The diffusion coefficients at first stage (D_1) and the second stage (D_2) were obtained as $2.34\text{E-}07$

m^2/s and $3.21\text{E-}08 \text{ m}^2/\text{s}$, respectively. A numerical simulation showed a good agreement with the experimental results.

The effects of the humidity levels of the ageing cycles on the tensile strength of the of the bulk adhesive were determined as presented in paper [2]. The results showed that the mechanical properties of the adhesive decreased significantly at the initial ageing cycle, but less reduction can be found at the subsequent ageing cycles. The tensile strength of the unaged bulk samples was obtained as 23.71 MPa while after a single ageing cycle it reduced to 14.63 MPa, 13.99 MPa, and 13.53 MPa, respectively for 5, 12, and 20 days of ageing. The cyclic ageing of the bulk adhesive was performed for 5 days ageing. The tensile strength of the bulk adhesive after cyclic ageing was obtained as 14.63 MPa, 13.90 MPa and 13.96 MPa, for the first, second, and the third cycles, respectively.

The effects of humidity absorption on static and fatigue response of the adhesive joints under mode I loading condition by using Arcan substrate were investigated and presented in paper [3]. The results showed that both static strength and fatigue life decreased by the increase of the ageing level. Both the static strength and fatigue lives were functions of the ageing time. The static strength of the unaged Arcan joints was found to be 31.3 MPa. After performing single cycle ageing the static strength decreased to 25.8 MPa, 15.9 MPa, and 11.72 MPa for 2, 7, and 14 days ageing, respectively. The percentage of fatigue lives reduction of the aged Arcan joints under single cycle ageing when compared to the unaged conditions was decreased by 30.7%, 50.0% and 67.8%, after 2, 7, and 14 days ageing, respectively.

The effect of the cyclic ageing on the Arcan joints were studied under static loading condition in paper [4]. Based on the results the mechanical properties of the joints decreased by ageing cycles. The reduction of the mechanical properties of the joints was a function of ageing cycles. Three ageing cycles were performed for 2- and 14-days ageing frequencies. The reduction of

the Arcan joint's strength for 2 days cyclic ageing was found to be 17.67%, 35.27%, and 55.01% for the first, second, and third ageing cycles. For the ageing frequency of 14 days, joint's strength for the first, second, and third ageing cycles were reduced by 62.70%, 82.26% and 94.28%, respectively.

The influence of the cyclic ageing on the Arcan joints were studied under fatigue loading condition in paper [5]. The fatigue results presented that the fatigue strength is significantly influenced by the ageing cycles where the fatigue life of the joints become shorter by ageing cycles.

Numerical calculation based on the Fick's law formula was performed to confirm the water absorption phenomenon of the bulk sample and to determine the diffusion coefficient (D) of the studied adhesive and to confirm the moisture absorption characteristic of the adhesive. Finally, a coupled numerical simulation considering the moisture absorption and linear elastic analysis of the Arcan joints was conducted to study the moisture effects on the degradation of the joints strength and also to predict the fatigue life of adhesive joints with different humidity levels under mode I loading condition.

To carry out this thesis the following materials were needed to support the entire research process:

1. Regarding the mutual applications of the material in industries, an aluminium alloy of Al 6082 T651 was selected as the substrate.
2. The selected adhesive in this investigation was a one-part epoxy-based adhesive, which is commonly used as a structural component bonding to support a bearing load.

1.2. Objective and methodology

The objectives and the methodology of the thesis can be defined as follows:

- Select the adhesive which is used to study the absorption and desorption characteristic and possible degradation of the adhesive after ageing.
- Experimentally investigate the moisture uptake characteristics of the adhesive by applying continuous and cyclic ageing, applying Fick's law equation and determine the diffusion coefficient (D) of the studied adhesive.
- Determine the mechanical properties of the aged bulk adhesive by performing static test of dogbone specimens.
- Investigate the degradation of the adhesive joints' properties after moisture absorption for continuous ageing under mode I static and fatigue loadings.
- Investigate the degradation of the adhesive joints subjected to cyclic ageing condition under mode I static and fatigue loadings.
- Perform a numerical simulation based on the diffusion coefficient obtained experimentally to model water uptake levels in the adhesive and adhesive joints.

Figure 1.1 presents the flowchart of this research and shows the experimental procedures.

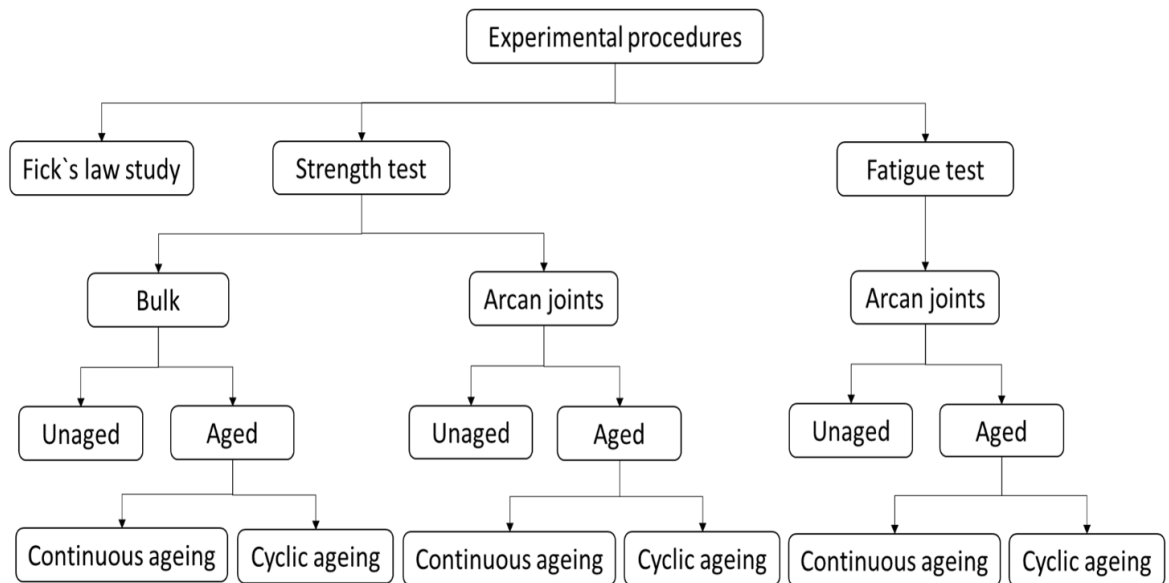


Figure 1.1 Research flow chart

1.3 Thesis outline

The outline of the thesis is as follows:

- Chapter 1: Introduction, which consists of the motivation and research methodology to meet the sets of objectives.
- Chapter 2: Experimental details, which is composed of materials, manufacturing process, hygrothermal ageing, and testing procedures of the samples.
- Chapter 3: Summary of the appended papers which consists of the main objectives and conclusions of each consecutive work.
- Chapter 4: Conclusions are then drawn, and future works are suggested as possible improvements for the present work.

2. Experimental details

In this section the related experimental processes were described in detail to reach the final objectives. The experimental tests consisted of bulk adhesive and adhesive joints. Each of the test has different samples configurations such as bulk plate, dogbone and Arcan joints. The bulk plates were used to study the Fick's law, the dogbone specimens were used to assess the strength of the aged adhesive and the Arcan joints were used to investigate the strength of the joints as a function of the presence of the water under mode I static and fatigue loadings.

2.1. Adhesive and substrates

The adhesive used in this research was a one-part epoxy-based adhesive, solvent free and heat curing. It is a highly viscous and usually provided in a paste form. The adhesive is a tough and structural adhesive which is suitable for bonding load-bearing structures. The mechanical properties of the studied adhesive are summarized in Table 2.1.

The Arcan substrate was manufactured from Al 6082 T651 ($E = 70$ GPa, $\nu = 0.3$), which has high strength and is corrosion resistant. An example of the aluminium Arcan substrate is shown in Figure 2.1.

Table 2.1. Mechanical properties of the tested adhesive (Papers 3 and 5).

Properties	Adhesive
Maximum tensile strength, MPa	31.3±0.6
Maximum tensile strain, %	10.4±0.5
Maximum shear strength, MPa	23.1±0.5
Maximum shear strain, %	43.3±0.9
Young's modulus, MPa	1 159±29.3

Shear modulus, MPa	440±8.7
Poisson's ratio, ν	0.35

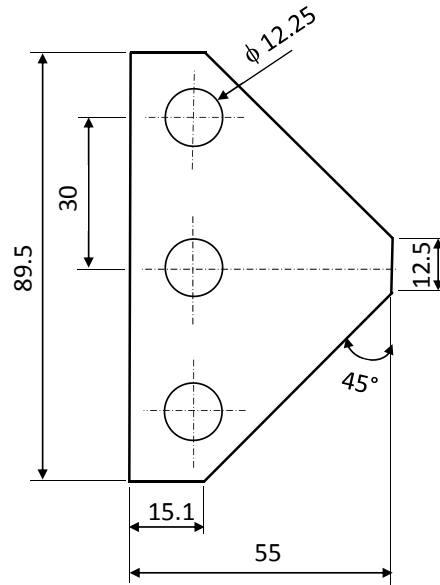


Figure 2.1. Arcan substrate. The thickness of the substrate is 10 mm (**Paper 3, Paper 4 and Paper 5**).

2.2. Hygrothermal ageing

In this research, the ageing processes were performed both in bulk adhesive and in joints.

Bulk specimens: Before the ageing process was conducted, the bulk plates were kept in a silica filled container at 50°C to ensure that the bulk plates were completely dried. This was followed by ageing the bulk plates in distilled water and salt water in a thermally controlled chamber at 50°C. To study the Fick's law, the mass gain of the bulk plates was measured regularly at specific time intervals, using a high precision micro balance (Kern-Toledo, Balingen, Germany) with 0.1 mg of accuracy. At the specific time interval, the weight of the bulk plate was

measured to obtain the amount of water absorbed by the adhesive plate. The weight measurement was performed periodically until the saturation level was attained. The bulk plate ageing of the adhesive was shown in Figure 2.2(a). The desorption process was also performed by drying the ageing specimens. The specimens were kept at a constant temperature 50°C for a specific drying time [Paper 1 and Paper 2].

Joints: After manufacturing, the Arcan joints they were kept in a container with silica for at least 2 days. The objective of this process is to remove the moisture that may have been absorbed by the joints during the manufacturing process. To conduct the hygrothermal ageing, the joints were then moved to a container filled with distilled water. The container was then placed in a controlled temperature chamber, at a temperature of 50°C. The ageing process of Arcan joints is shown in Figure 2.2(b) (Paper 3, Paper 4 and Paper 5).

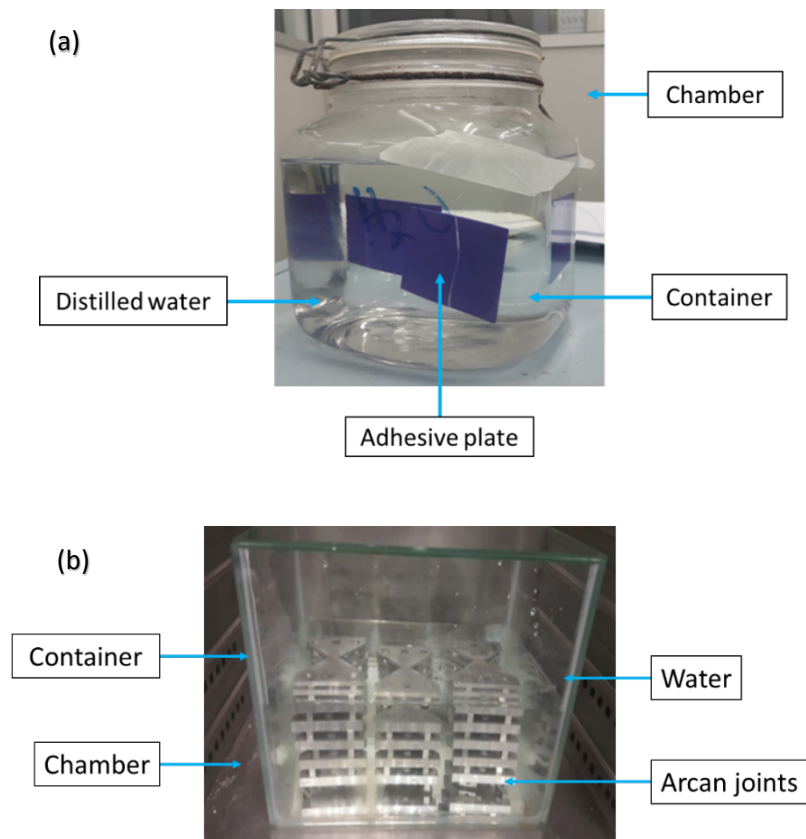


Figure 2.2. Ageing samples. (a) Bulk samples and (b) Joint samples.

2.2.1. Single cycle ageing

A single cycle ageing procedure was followed where the plates were saturated and then completely dried. The weight and the thickness of the plate were measured during the saturation and drying processes. This is a commonly used ageing procedure, well described in the literature. This procedure was applied for both samples, immersed in distilled water and salt water. Four samples for each test condition were tested.

2.2.2. Cyclic ageing

- **Cyclic ageing by controlling the level of water uptake**

In the cyclic ageing process, the duration of each cycle was controlled by the level of water uptake. This means that ageing was carried out until the level of water uptake reached a specific value. In this study, the specific level saturation was chosen as 12.45%. These water absorption and desorption processes were repeated for three cycles (see Figure 2.3(a)). During the ageing and drying process, the weight and thickness of the specimens were measured periodically.

- **Cyclic ageing by controlling the ageing time**

In this process, the cyclic ageing was carried out by controlling the duration of the ageing and drying periods, which were set to last 30 days and 7 days, respectively. The process was repeated for four cycles (see Figure 2.3 (b)). During the ageing and drying process, the weight and the thickness of the plates were measured at specific intervals. These specific intervals mean the time between each measurement which was used in this research (**Paper 1**).

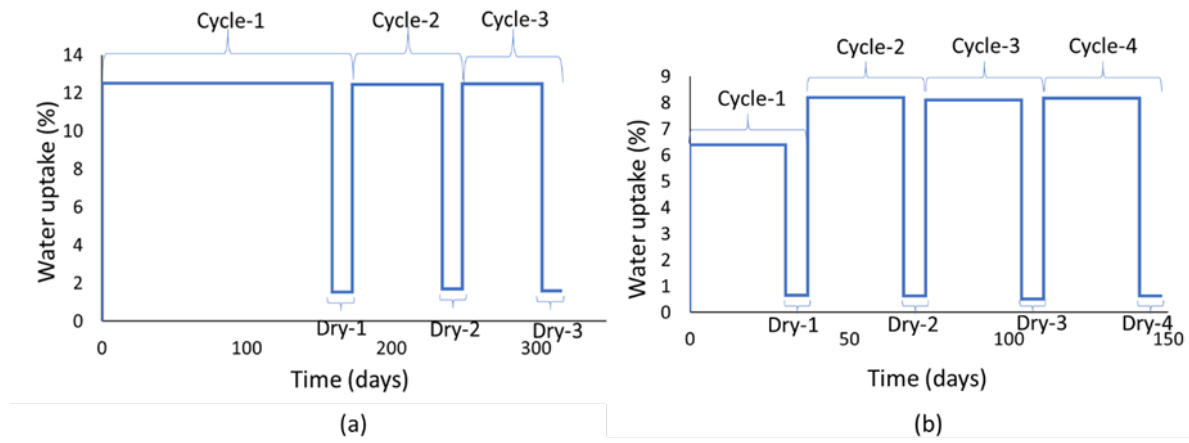


Figure 2.3. Schematic ageing time for each cycle. (a) Cyclic ageing by controlling the level of water uptake and (b) Cyclic ageing by controlling the ageing time (**Paper 1**).

2.3. Glass transition temperature (T_g)

The glass transition temperature (T_g) of the unaged and aged adhesive of the single cycle ageing process were tested and compared. Adhesive samples aged in distilled water and in salt water were considered in this analysis. To analyse the T_g , a dynamic mechanical analysis (DMA) technique was used (**Paper 1**). The representation of the DMA process is schematically shown in Figure 2.4. The T_g was measured by recording the temperature at which the specimen's peak damping occurs.

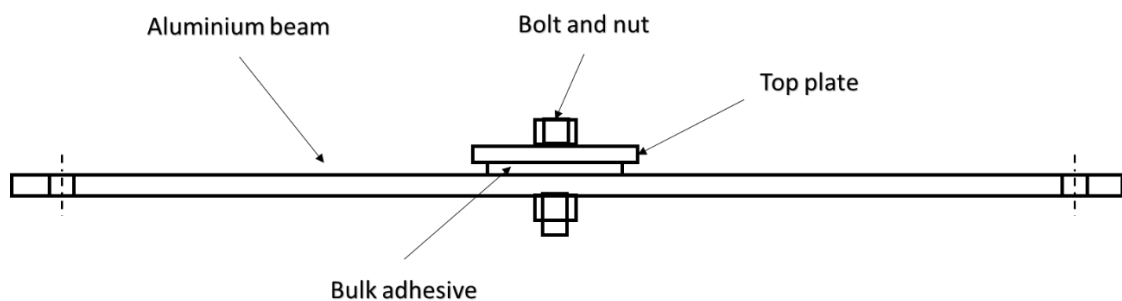


Figure 2.4. Schematic representation of the T_g test specimen.

2.4. Specimen manufacturing

To achieve the research objectives, several testing samples were manufactured before the ageing processes were conducted. The tested samples produced include bulk plate, dogbone, and Arcan joints.

Dogbone: To study the water diffusion process, and the strength of the adhesive under cyclic ageing, bulk plates with a thickness of 1 mm were manufactured. To ensure the accuracy of the plate thickness, a specific mould with a silicone frame of 1 mm thickness was used (see Figure 2.5). The curing time and the curing temperature of the adhesive were 60 minutes and 177°C respectively, based on manufacturer's specification. Mini dogbone specimens, as shown in Figure 2.6(a), were then machined from the manufactured plates using a computer numerical controlled (CNC) milling machine.

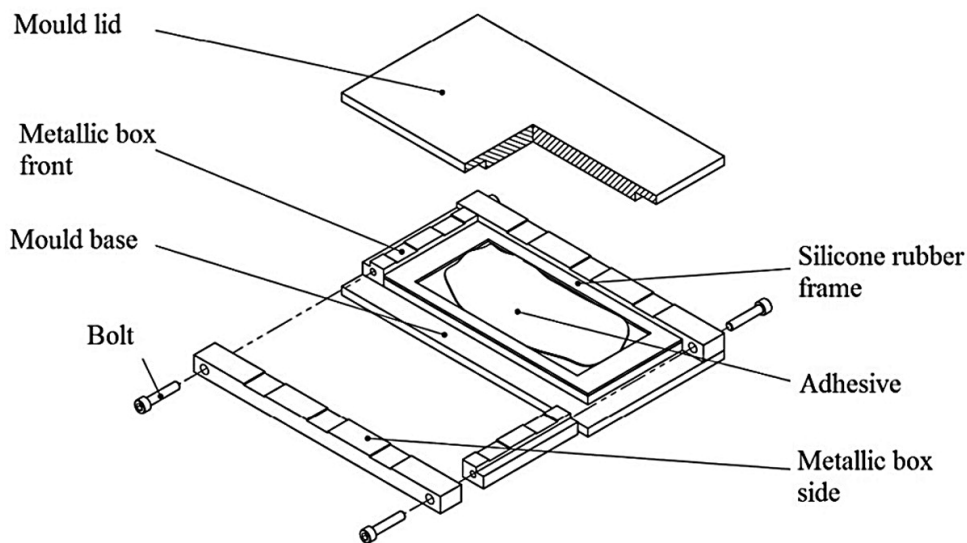


Figure 2.5. Mould used in the manufacture of the adhesive bulk plate (Paper 2).

Bulk plate: To investigate the water diffusion process, 1 mm thick plates of bulk adhesive were manufactured and then immersed in distilled water. To ensure the geometrical accuracy of the plates, a mould with a silicone frame of 1 mm thickness was again used, able to precisely

control the thickness of the bulk plate during manufacture under pressure. The curing time and curing temperature of the adhesive were also of 60 minutes and 177°C respectively, following the recommendations of the adhesive's manufacturer. The bulk plate was then cut machined into 60 by 60 mm plates as shown in Figure 2.6(b) according to ISO/DIS 294-3 (**Paper 1** and **Paper 2**).

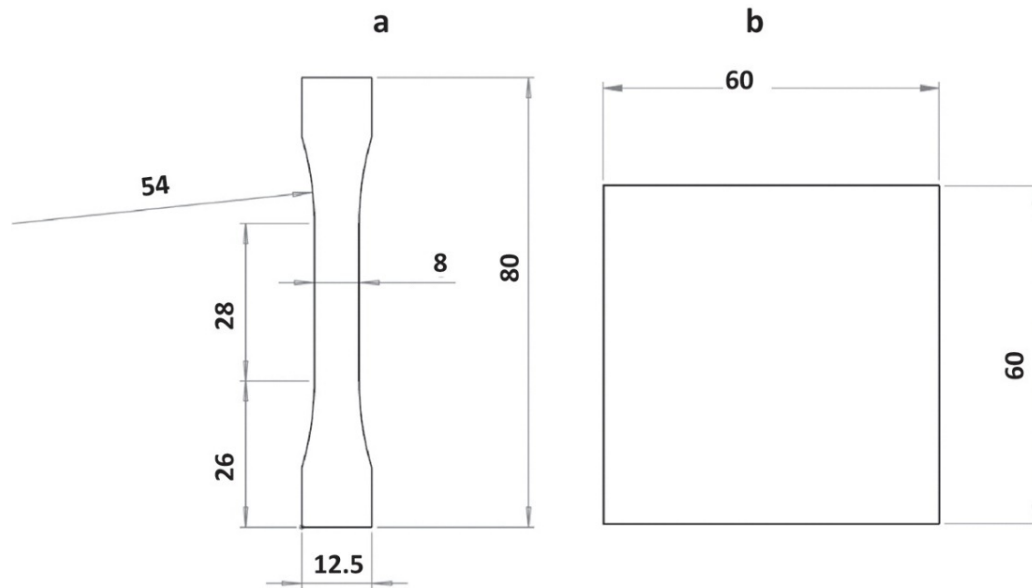
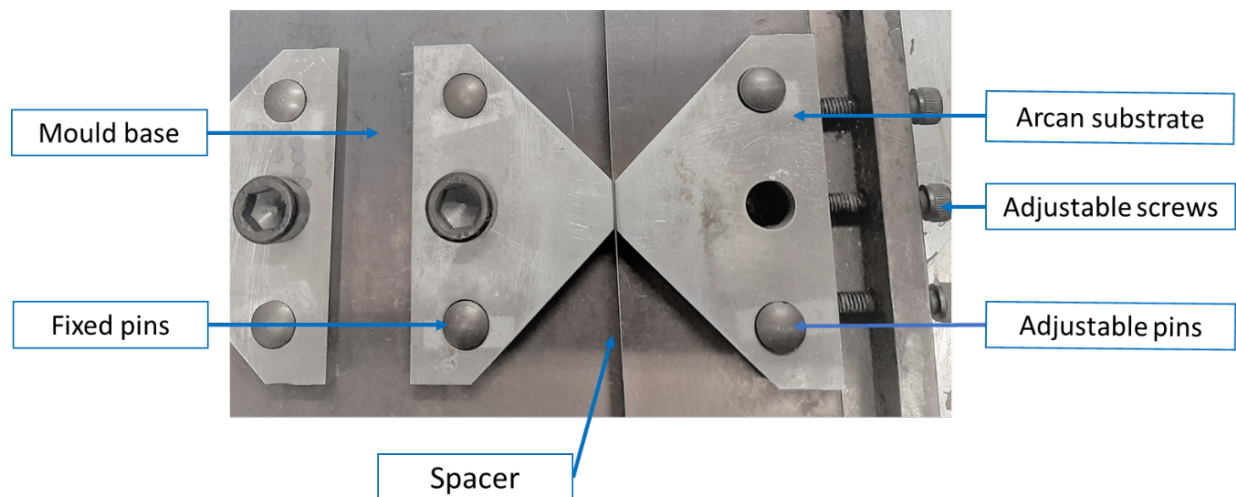


Figure 2.6. (a) Dogbone tensile specimen and (b) square bulk plate. Thickness of the samples is 1 mm. Dimensions in mm (**Paper 2**).

Arcan joints: The Arcan joints were manufactured in a specially designed mould, shown in Figure 2.7. The thickness of the adhesive layer was set to 0.2 mm. To precisely obtain the desired adhesive layer thickness, a 0.2 mm gap between the substrates was imposed by finely adjusting the screws shown Figure 2.7. Before bonding, the surface was prepared with an anodization treatment applied to the aluminium substrate, ensuring good adhesion between the adhesive and the substrate. Aluminium surfaces were first cleaned with acetone to remove any substances that might contaminate the aluminium surfaces during anodizing. Then, the aluminium specimens were immersed in an anodizing solution for 25 minutes. The anodizing

solution consists of 88% by volume of distilled water and 12% by volume of phosphoric acid. The percentage of the anodization solution and the immersion time were set based on the aluminium anodization standard defined in ASTM 3933 (**Paper 3**). After the anodization process was completed, the substrates were removed from the solution and cleaned with distilled water and acetone. The substrates were dried at room temperature for about 30 minutes before bonding took place. The joints were cured at 177 °C for 60 min in a hot plate hydraulic press.



*Figure 2.7. Joints manufacturing (**Paper 3** to **Paper 5**).*

2.5. Testing methods

The mechanical tests of the adhesive and adhesive joints were carried out in three different conditions with different objectives.

2.5.1. Static test-Bulk

To determine the mechanical properties at different ageing times and ageing cycles, tensile tests were carried out using INSTRON 3367 (Norwood, Massachusetts, USA) universal tensile

test machine. The tested samples were the mini dogbone specimens already shown in Figure 2.6(a). The tensile tests were performed at room temperature with a constant cross head displacement rate of 1 mm/min. The tensile test set up is shown Figure 2.8.

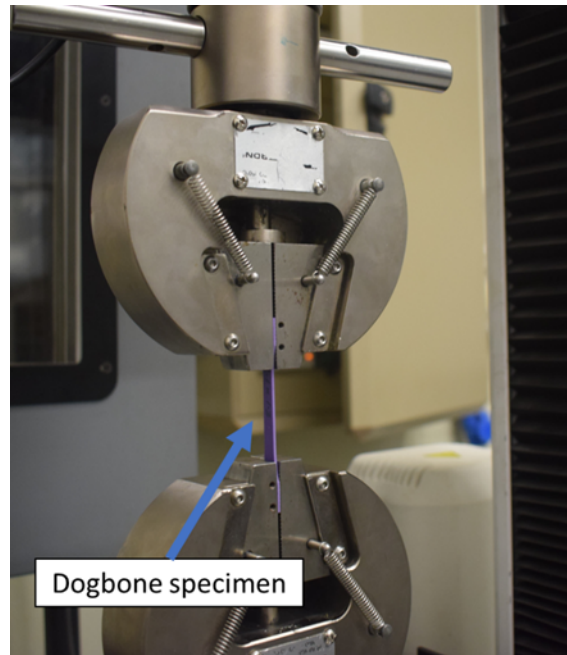


Figure 2.8. Static test of dogbone specimen (Paper 2).

2.5.2. Static tests-Joints

Initially, Arcan joints were statically tested to evaluate the effects of humidity levels on the mode I static performance of the adhesive. The static tests were performed at the end of each ageing level, after 2, 7, and 14 days of ageing. The dried specimens were also tested in order to investigate the rate of the recovery of the adhesive properties. Six joints were tested for each ageing and drying condition.

Static tests of the Arcan joints were conducted at room temperature using an Instron 8801 servo-hydraulic testing machine. The test conditions for continuous ageing of static and fatigue are presented in Table 2.2.

Table 2.2. Static and fatigue test conditions for continuous ageing (*Paper 3*).

Static		Fatigue	
Ageing time (day)	Ageing conditions	Ageing time (day)	Ageing conditions
0	Unaged	0	Unaged
2	Aged	2	Aged
7		7	
14		14	
2	Dried	2	Dried
7	for 2 days	7	for 2 days
14	after ageing	14	after ageing

Besides being used for continuous ageing, the static test procedure was also performed for cyclic ageing conditions. To this end, cyclic aged joints were tested statically to evaluate the effects of humidity levels on mode I static performance of the Arcan joints. Tensile tests were conducted for both the aged and dried samples at different ageing/drying cycles. Six samples were used for each testing condition. The static tests were performed at the end of each ageing cycle after 2 and 14 days. The static tests were conducted in three different cycles (cycle 1, 2, and 3). The dried specimens were also tested in order to compare the performance recovery ability of the adhesive joint. The static tests were conducted using an Instron 8801 servo-hydraulic testing machine at room temperature conditions. The test device and Arcan joint sample are shown in Figure 2.9.

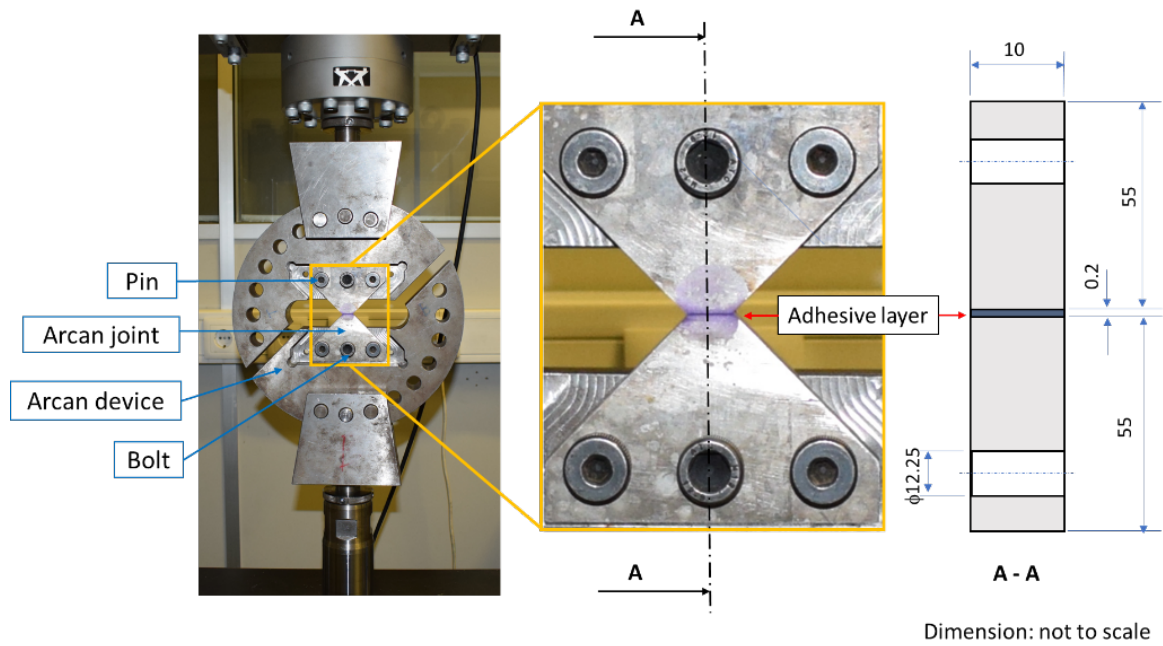


Figure 2.9. Arcan joints setup for static and fatigue tests (**Paper 4**).

2.5.3. Fatigue test

Fatigue tests were conducted using several different load levels for both continuous and cyclic ageing conditions, with these levels being determined using data from the static test results. Fatigue tests were conducted at room temperature using an Instron 8801 servo-hydraulic testing machine. The frequency of loading cycles for fatigue was 10 Hz and the load ratio (the ratio of minimum to maximum load) was set to 0.1. The fatigue tests were also performed for three different ageing and drying conditions for continuous ageing (2, 7, and 14 days) and two different ageing conditions for cyclic ageing (2 and 14 days). The test conditions for cyclic ageing and drying are presented in Table 2.3. The testing device and the sample set up are shown in Figure 2.9.

Table 2.3. Static and fatigue test conditions for cyclic ageing (**Paper 5**).

Ageing time (day)	Ageing conditions	Tested cycles
0	Unaged	0
2	Aged	1
		2
		3
14		1
2		
3		
2	Dried for 2 days after ageing	1
		2
		3
14		1
2		
3		

2.6. Surface failure observation

To understand the water absorption and desorption mechanism in the Arcan joints, the failure surface of the tested Arcan joints should first be visually observed. Figure 2.10 shows a representation of the failure surface of the unaged, aged, and dried samples of the Arcan joints. The fracture surface of the unaged samples tested statically, and under fatigue showed a cohesive failure (see Figure 2.10(a)). The fracture surface for aged and dried specimens under mode I loading conditions showed a mixed failure mode, for both the aged and dried surfaces as shown in Figure 2.10(b) and (c), respectively.

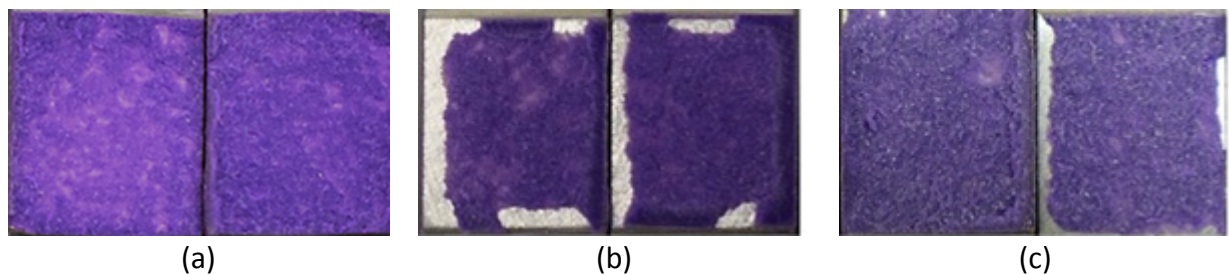


Figure 2.10. Representation of the failure surface of the Arcan joints. (a) Unaged, (b) Aged and (c) Dried (**Papers 3 to Paper 5**).

2.7. FTIR analysis

Fourier transform infrared (FTIR) analysis was employed to determine the effects of moisture on the chemical structures of the tested adhesive. The unaged, aged, and dried samples were considered in this analysis. To this end, the specimens were experimentally aged in water for 2, 7, and 14 days, each followed by 2 days of drying. Unaged, aged, and dried samples then were tested. After joint failure, a small portion of the adhesive layer taken from the failure surface was used for the FTIR analysis. The FTIR analysis was performed using a PerkinElmer Spectrum Two Machine (Waltham, MA). The range of the wavelength was set to 4000–500 cm⁻¹ with a scanning velocity of 0.2 cm⁻¹ (**Paper 3** and **Paper 4**).

2.8. Numerical modelling

A numerical model was developed using Abaqus software in order to predict the average water absorption and water absorption distance in the adhesive layer of an Arcan joint. In this model, an analogy between the heat transfer and fluid flow was explored. The water diffusion into the adhesive layer, the thermal conductivity, thermal diffusivity and heat capacity were set as the permeability, diffusion, and solubility coefficients, respectively, while the nodal temperature of the elements corresponds to the nodal humidity level.

This approach is possible since the mathematical equation of diffusion is based on the equation of heat conduction, which was derived by Fourier in 1822, as shown by Fick in 1855. The diffusion hypothesis is presented mathematically by Equation ((2.1) (**Paper 4**).

$$F = -D \frac{\partial c}{\partial x} \quad (2.1)$$

where F is the flux or rate of transfer per unit area, c is the concentration of diffusing

substance, x is the space coordinate measured normal to the section, D is the diffusion coefficient. The negative sign in Equation ((2.1) is due to the fact that diffusion occurs in the direction opposite to that of the increasing concentration.

The mathematical expression for 1 D diffusion is shown in Equation (2.2). This expression called Fick's second law (**Paper 4**).

$$\frac{\partial c}{\partial t} = \frac{\partial F}{\partial x} = \frac{\partial}{\partial x} \left(D \frac{\partial c}{\partial x} \right) = D \frac{\partial^2 c}{\partial x^2} \quad (2.2)$$

Equation (2.2) can easily be extended to 2 or 3 dimensions. Many classes of problems are governed by an equation of a similar form to Fick's second law, for example, the governing equation for heat transfer is given by:

$$\frac{\partial}{\partial x} \left(k_x \frac{\partial T}{\partial x} \right) + \frac{\partial}{\partial y} \left(k_y \frac{\partial T}{\partial y} \right) + \frac{\partial}{\partial z} \left(k_z \frac{\partial T}{\partial z} \right) + Q = \rho c \frac{\partial T}{\partial t} \quad (2.3)$$

where T is temperature, k_i is conductivity in the i direction, Q is the rate of internal heat generation, c is the specific capacity, and ρ is the density.

Fick's law analysis:

Numerical simulations were conducted to reproduce the experimentally obtained data. Using the finite element method, the ageing process was numerically simulated for both the bulk plates and the mini dogbone specimens.

Abaqus, as a commercial FE program, was used for this analysis. Using the numerical results, the average amount of the water uptake was obtained and compared with the experimental measurements. The water uptake process was measured by the heat transfer analogy as previously mentioned. The water absorption process was modelled both in two-dimensional (for the bulk plates) and three dimensional (for the mini dogbones). For the bulk plates, standard four-node linear heat transfer quadrilateral (DC2D4) elements were employed. Due to the symmetrical geometry of the tested specimens and to optimize the computational time, only a quarter of the specimens was simulated. Uniform mesh size (0.04mm), in both the width and height directions, was employed which produced a total number of 9750 elements for the bulk plate specimens. Figure 2.11(a) shows the square bulk plate and Figure 2.11(b) is the 2-D simulation model.

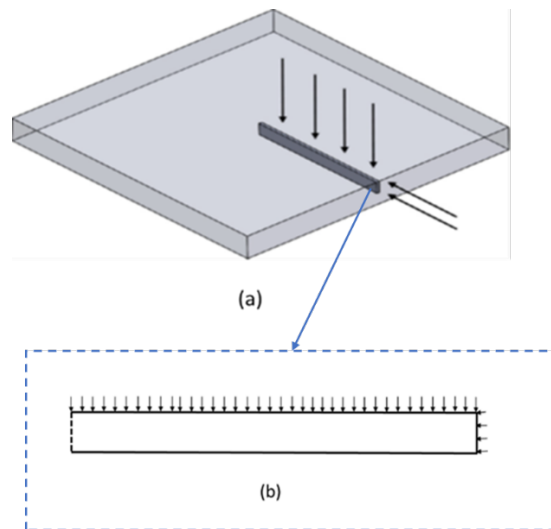


Figure 2.11. Simulation model used for determining water uptake in the bulk. (a) Bulk plate and (b) 2-D simulation model (Paper 1 and Paper 2).

The same strategy was followed to simulate the dogbone shape samples. However, as the dogbone samples were simulated in a 3-D model, the standard eight-node linear heat transfer brick (DC3D8) elements were used. In this case, a total of 5640 elements were used to model

the mini dogbone samples. Figure 2.12(a) is the 3-D mini dogbone and Figure 2.12(b) shows a quarter of the simulation model.

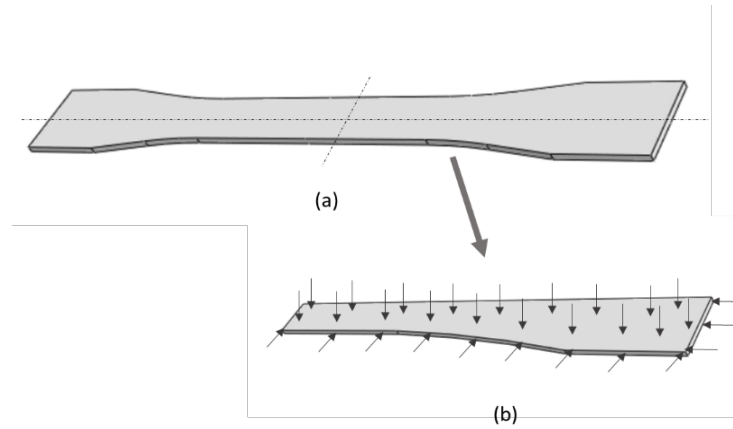


Figure 2.12. 3-D model for determining the water uptake level. (a) 3-D dogbone model and (b) Quarter part of the simulation model. Arrows indicate water directions (Paper 2).

Joint ageing: To investigate the water content in the adhesive layer of the joint, and to calculate the rate of water diffusion through the interface, a numerical analysis was carried out. The objective of the analysis is to predict the average amount of the water content in the adhesive layer during the ageing process. The D value used in this simulation was already obtained in **Paper 1**. The obtained D was used to simulate the water diffusion in a bulk adhesive in order to confirm the water diffusion through the adhesive layer. Figure 2.13 represents the Arcan joint for the analysis. The water absorption of the adhesive layer is shown in Figure 2.13(a) and drying process is shown in Figure 2.13(b), respectively (**Paper 5**).

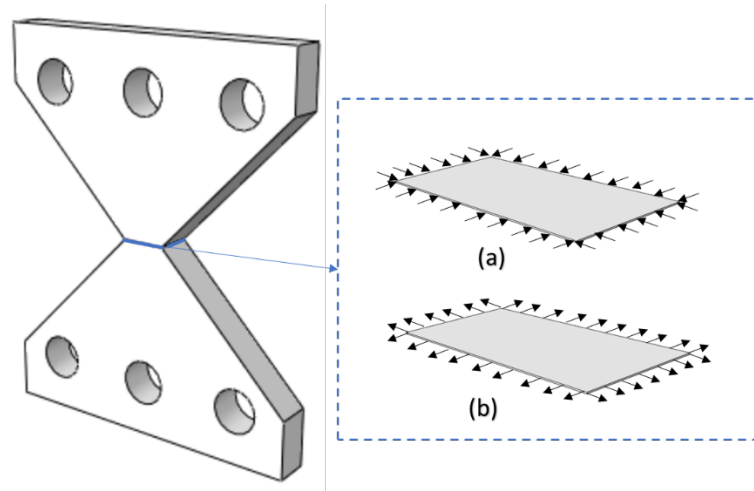


Figure 2.13. 3-D Arcan joint simulation model. (a) Ageing and (b) drying. Arrows indicate the water directions (**Papers 3 to Paper 5**).

3. Summary of appended papers

In this section, the purpose of each appended paper and the main results are explained.

3.1. Paper 1

In this study, hygrothermal ageing of an epoxy-based adhesive has been investigated by performing single cycle and cyclic ageing experiments. Two ageing strategies were followed in this research including a constant ageing time and similar maximum absorbed water. The absorption and desorption processes for each ageing cycle have been investigated experimentally. The diffusion coefficients of the absorption and desorption were analysed by using Fick's law approach. The Fick's law relation is presented as follows:

$$D = \pi \left(\frac{h}{4M_{\infty}} \right)^2 \left(\frac{M_t}{\sqrt{t}} \right)^2 \quad (3.1)$$

where, D is the diffusion coefficient, M_t is the mass uptake, M_{∞} is the final mass uptake, h is the thickness and t is the ageing time. The diffusion coefficient at the first stage and the second stage of the process will be calculated and known as D_1 and D_2 respectively. To calculate the water uptake at time t , Eq. (3.2) was used.

$$M_t = \left(1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} e^{\left(\frac{-D_1(2n+1)^2 \pi^2 t}{4h^2} \right)} \right) \times M_{1\infty} + \emptyset(t - t_d) * \left(1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} e^{\left(\frac{-D_2(2n+2)^2 \pi^2 t}{4h^2} \right)} \right) \times M_{2\infty} \quad (3.2)$$

where $M_{1\infty}$ and $M_{2\infty}$ correspond to the fractional mass uptake in the first and second stages respectively, t_d is the time of transition between the two stages, and $\Phi(t - t_d)$ is the Heaviside step function which is equal to zero for negative values of $t - t_d$ and equal to one for positive values of $t - t_d$. To predict the desorption mechanism during the drying process, the corresponding Fickian model gives M_t based on the following relation.

$$M_t = M_r + \left(\frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp \left(\frac{-D_d(2n+1)^2 \pi^2 t}{4h^2} \right) \right) \times (M_{\infty} - M_r) \quad (3.3)$$

where, M_r is minimum fractional retained water after drying and D_d is the diffusion coefficient of the desorption mechanism. Figure 3.1 shows the water uptake level as a function of time.

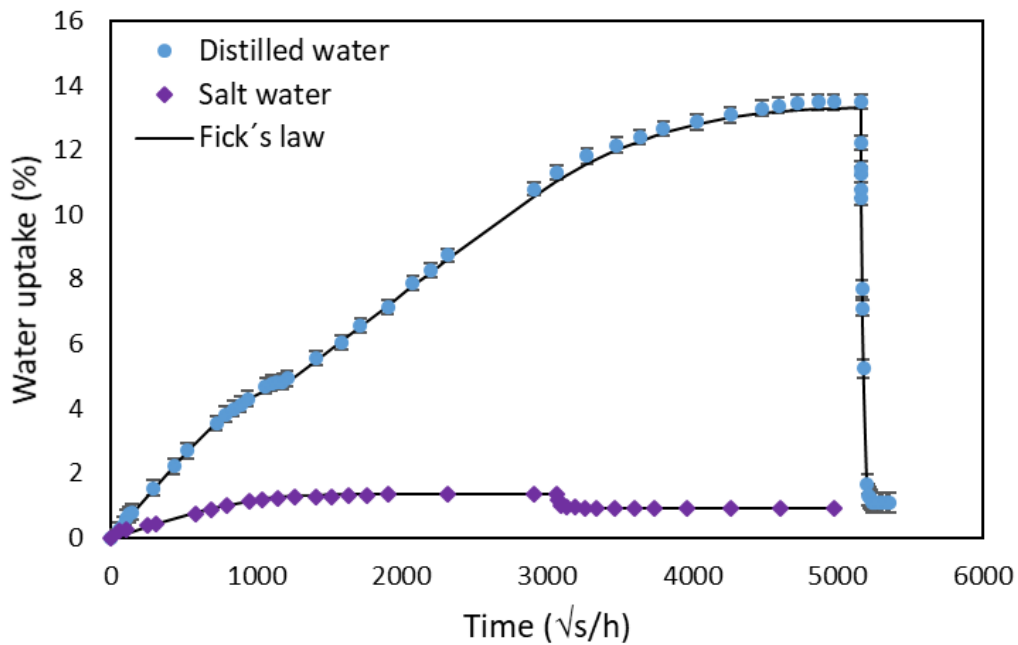


Figure 3.2. Hygrothermal ageing of the adhesive in distilled and salt water. Solid lines show the Fick's law predictions. The points show the average values.

The absorption ability, time to reach saturation level and the glass transition temperature were also studied as a function of the different ageing conditions. The hygrothermal ageing in salt water reached the saturation level at 1009 hours with the water uptake level of 1.34%. In contrast, the hygrothermal ageing in distilled water required around 7500 hours to reach saturation level of 13.49% water uptake. The D for saltwater ageing was found as $1.92\text{E-}07\text{ m}^2/\text{s}$, while for distilled water ageing D_1 and D_2 was obtained as $2.34\text{E-}07\text{ m}^2/\text{s}$ and $3.21\text{E-}08\text{ m}^2/\text{s}$.

The experimental measurements of the cyclic ageing showed that the water diffusion in the adhesive layer changes with the increase of ageing cycles. The diffusion coefficient increases by the increase of the ageing cycles however, the glass transition temperature decreases with ageing cycles. The diffusion coefficient for cyclic ageing was obtained as $2.34\text{E-}07\text{ m}^2/\text{s}$, $2.26\text{E-}07\text{ m}^2/\text{s}$ and $2.29\text{E-}07\text{ m}^2/\text{s}$, for first, second and third cycles. The numerical analysis was performed by using Fick's law constants and good agreement between the experimental and numerical results was obtained.

3.2. Paper 2

The aim of this study is to consider the effect of cyclic ageing on the rate of water uptake and the drying process in an epoxy-based adhesive. Fick's law was considered to estimate the water diffusion coefficients for the ageing and the drying steps at different cycles. Different cyclic ageing times have been considered in the ageing procedure. To this end, the dogbone shape specimens were manufactured and subjected to cyclic ageing to investigate the tensile properties of the tested adhesive as a function of ageing cycles.

The gravimetric results showed that the rate of water uptake and drying is mainly a function of the level of water uptake of the first ageing cycle. Tensile test results (see Figure 3.3) showed that the maximum water content increases with each subsequent ageing cycle. It was also found that the Young's modulus and the tensile strength of the adhesive decreased significantly after the initial ageing cycle, but all subsequent ageing cycles have considerably less influence on the mechanical properties of the adhesive.

The tensile strength of the unaged bulk samples were obtained as 23.71 MPa. The tensile strength of the bulk adhesive of the single cycle ageing was found to be 14.63 MPa, 13.99 MPa and 13.53 MPa for 5, 12 and 20 days of ageing. The cyclic ageing of the bulk adhesive was performed for 5 days ageing and the tensile strength of the bulk adhesive of the cyclic ageing was obtained as 14.63 MPa, 13.90 MPa and 13.96 MPa, respectively.

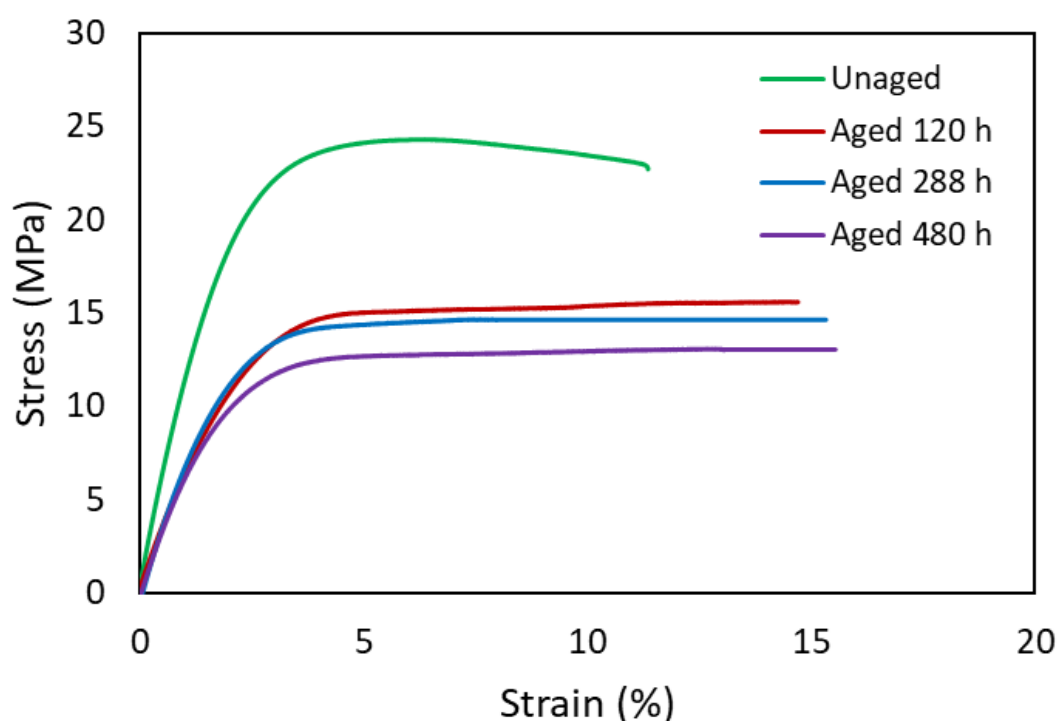


Figure 3.4. Typical stress-strain curves of an epoxy adhesive of unaged and hygrothermal aged specimens (dogbone) as a function of time.

3.3. Paper 3

The humidity absorption and desorption by the adhesive can cause the deleterious effects of the joint's performance and influence the durability and strength of the adhesive joints.

The aim of this study is to investigate the tensile and fatigue properties of an epoxy-based adhesive using Arcan joints subjected to different ageing levels and loading conditions. The ageing and drying samples were tested under static and fatigue loading conditions.

The static results showed that the mechanical properties, such as tensile strength of the joints decreased with an increase of the ageing time. The static strength of the unaged Arcan joints was found to be 31.3 MPa. After performing single cycle ageing the static strength decreased to be 25.8 MPa, 15.9 MPa and 11.72 MPa for 2, 7, and 14 days ageing, respectively

As shown in Figure 3.5 the fatigue strength and the fatigue lifetime were significantly decreased by the increase of ageing levels, mainly due to an interfacial ageing phenomenon. The percentage of fatigue lives reduction of the aged Arcan joints under single cycle ageing when compared to static strength was obtained as 30.7%, 50.0% and 67.8% respectively.

The water diffusion in interfacial ageing is faster than that of the adhesive ageing, which resulted in a premature failure of the joints for both the static and fatigue conditions. Based on the experimental results, the interfacial diffusion coefficient was calculated using an inverse method.

The interfacial diffusion coefficients for three different ageing levels were obtained as $7.30 \times 10^{-6} \text{ m}^2/\text{s}$. According to the results, the rate of water uptake along the interface is more than 30 times higher than that which occurs in the adhesive.

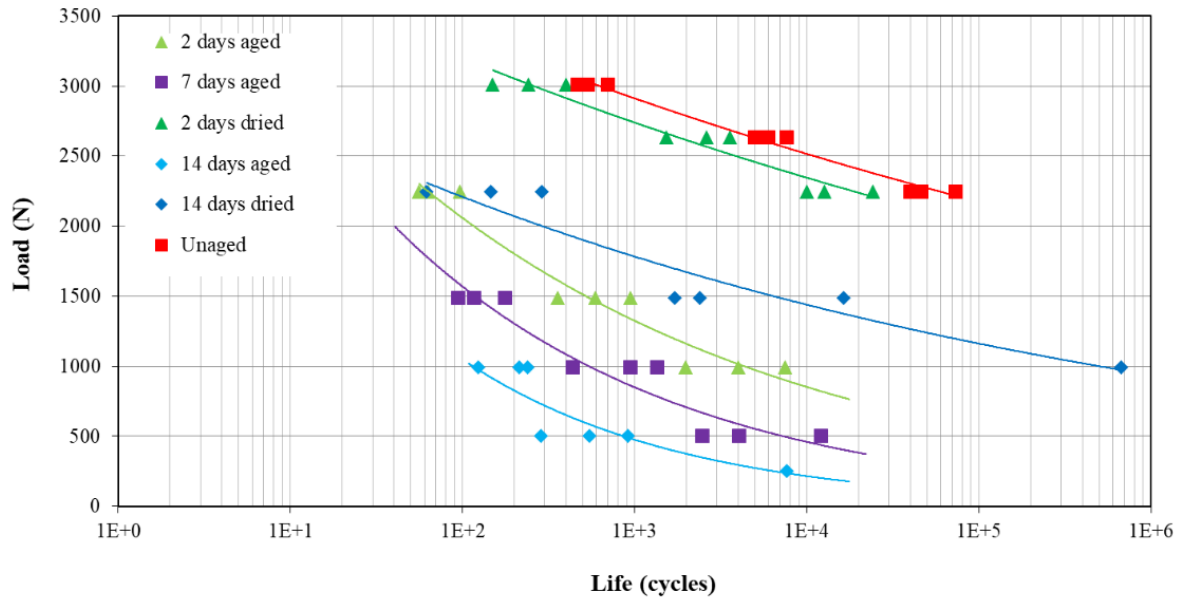


Figure 3.6. Fatigue life of aged, dried and unaged of Arcan joints for tensile loading conditions.

3.4. Paper 4

The adhesive joints tend to absorb moisture which can drastically reduce the mechanical performance of the bonded joints; therefore, the strength and durability of adhesive joints are significantly influenced by environmental conditions. Accordingly, it is necessary to study the ageing behaviour of the adhesive when they are exposed to environments with cyclic humidity conditions. To this purpose, the current study investigates the mechanical properties of the epoxy-based adhesive joints which subjected to the cyclic ageing conditions using Arcan joint specimens. The static tensile tests were performed for both cyclic aged, dried, and unaged Arcan joints. The effect of cyclic ageing and drying conditions, such as absorption and desorption mechanisms, on the mechanical properties of the joints were studied. In the numerical part, an experimentally obtained diffusion coefficient (D) was used to simulate the water diffusion in Arcan joint. The results showed that key mechanical properties, such as tensile strength and displacement of the joints are reduced by the number of ageing cycles. As shown in Figure 3.7 the reduction of the strength of Arcan joints for 2 days cyclic ageing is

17.67%, 35.27%, and 55.01% for the first, second, and third ageing cycles. For 14 days cyclic ageing, the reduction of the joint's strength for first, second, and third ageing cycles were obtained as 62.70%, 82.26% and 94.28%, respectively.

It was also found that the recovery ratio increases with the ageing cycles. The strength recovery for 2 days ageing cycles was obtained as 89%, 74% and 57%, respectively for the first, second and third ageing cycles. For 14 days ageing frequency the rate of recovery was obtained as 82%, 63% and 40% for the first, second and the third ageing cycle. Results showed that the increase in the ageing frequency will decrease the rate of strength recovery after the drying process.

It is shown that a short drying process can significantly recover the mechanical response of the cyclically aged adhesive joints, especially at higher ageing cycles.

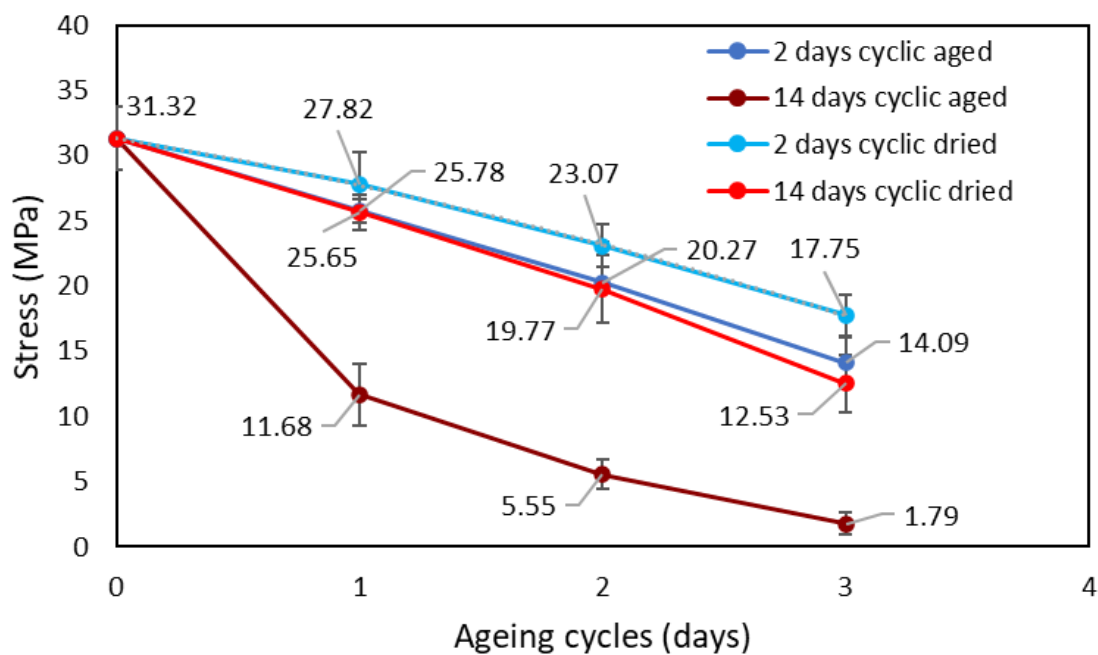


Figure 3.8. Stress reduction as a function of the ageing cycles.

3.5. Paper 5

Although joints in many applications are typically subjected to a combination of cyclical ageing and loads, the durability of joints under these aggressive conditions has not yet been

investigated. Therefore, in this study, the authors investigate the influence of cyclic ageing conditions on the fatigue behaviour of epoxy adhesive joints using Arcan samples. For this purpose, Arcan joints were manufactured and exposed to cyclic ageing environments with different ageing cycles and different ageing frequencies.

The aged samples were then subjected to fatigue loads. Different fatigue stress levels were taken into account in order to create S-N curves for different ageing conditions. The results showed that the fatigue life of the joints was shortened when increasing the number of ageing cycles. It has also been found that the life cycle decreases with the ageing frequency.

The fatigue strength corresponding to the fatigue life of 1000 cycles for all the ageing frequency was determined using the obtained experimental S-N data and shown in Figure 3.9. Based on the results, for the 2-days ageing frequency the life decreases by 54% at the first cycle and by 66% after the third cycle. The fatigue strength reduction for 14 days ageing frequency was found to be 83% and 94% for the first and the third cycles, respectively. The fatigue life recovered by drying the samples. The maximum fatigue life recovery was achieved on the first 2-day ageing cycle.

A combination of adhesive and cohesive failure modes was observed at the fracture surfaces due to the interfacial ageing mechanism. The results showed that the area of adhesive failure increases with the number of ageing cycles, resulting in worsened joint fatigue behaviour.

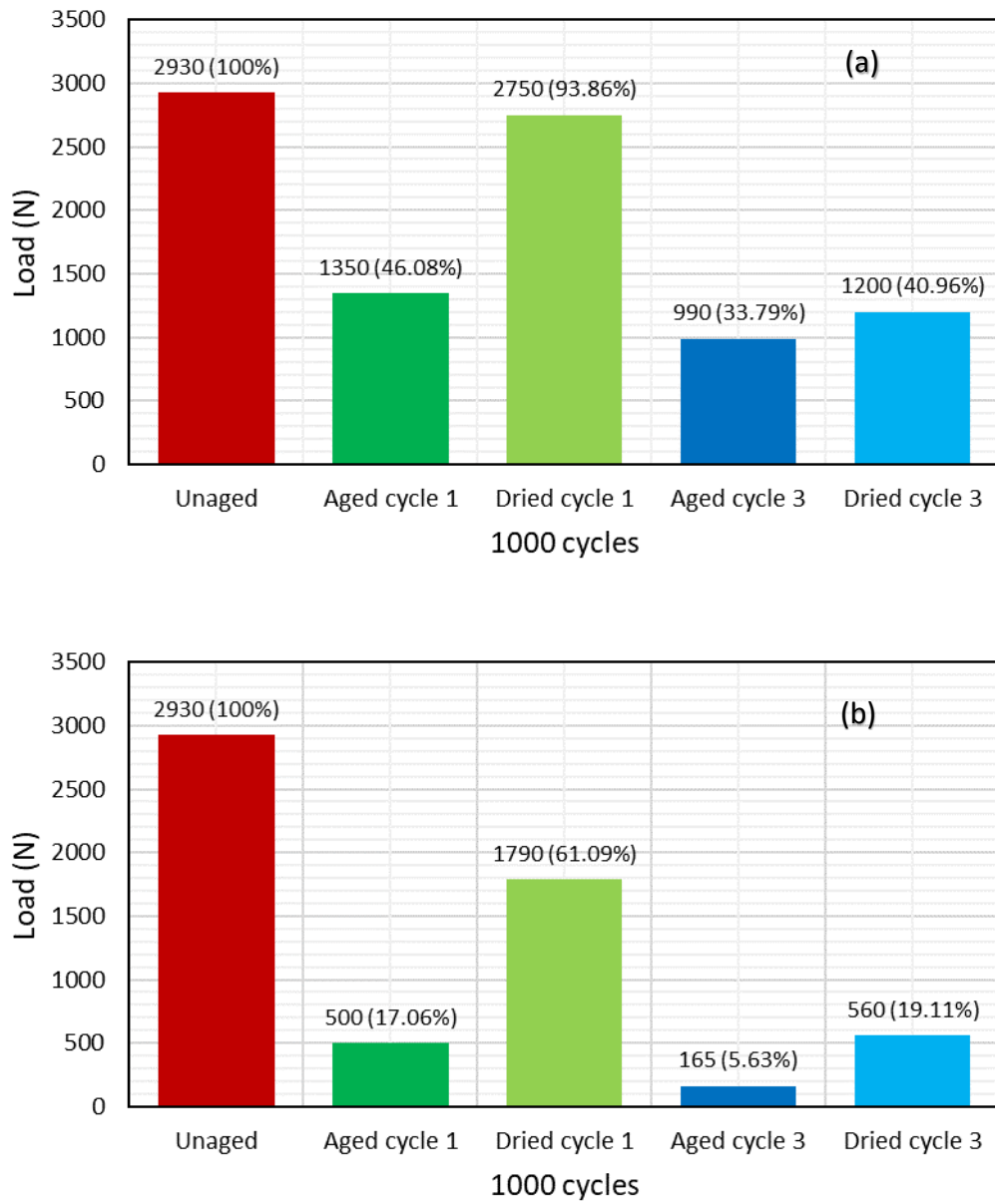


Figure 3.10. The fatigue strength of aged and unaged samples corresponding to 1000 loading cycles for (a) ageing frequency of 2 days, and (b) ageing frequency of 14 days.

4. Conclusions and future works

4.1. Conclusions

The objective of this thesis is to experimentally investigate the effects of cyclic ageing on the fatigue performance of bonded joints subjected to tensile loading conditions. To accomplish this goal, extensive experimental works were carried out to determine the influence of humidity levels on the static properties such as tensile strength, displacement and Young's modulus of adhesive and adhesive joints. The static tests of the adhesive joints were performed by using Arcan joints under mode I loading conditions and various stage of water uptake levels. Following a finite element analysis was performed to verify the water uptake levels in the adhesive and adhesive joints and the effects of the of moisture uptake on the stress distribution along the overlap length.

Furthermore, fatigue tests were performed for Arcan joints under mode I loading conditions at different water uptake levels to determine the influence of humidity levels on the fatigue lives degradation of the adhesive joints. Therefore, the following conclusions can be drawn:

- The water uptake level in the adhesive and adhesive joints greatly affected the performance of the adhesive joint and should be considered in the adhesive joint design.
- Single cycle and cyclic ageing of the adhesive and adhesive joints resulted in the distinct of water diffusion rate in the adhesive and adhesive joints, and affected the mechanical properties of the adhesive and adhesive joints.
- There was a drastically fatigue life reduction of the of the tested adhesive which was affected by the moisture uptake level under mode I loading conditions for both single cycle and cyclic ageing conditions.

- The aged adhesive joints were failed adhesively for both static and fatigue loading conditions.
- Based on the results considering the single cycle ageing conditions to design joints that are subjected to a cyclic ageing condition can overestimate the fatigue performance of the bonded structures.

4.2. Future works

To improve the present works, several studies should be done in the future:

- The present works focus on the influence of the hygrothermal ageing of adhesive on the static strength and fatigue life under mode I loading condition. Although, being critical, it was not fully representing all the joints behaviour and loading conditions in the real applications. Therefore, the work should be continued for mode II and mixed mode using similar specimens and appropriate experimental setup, such that the static and fatigue properties as function of humidity levels can be determined and compared.
- Developing a numerical fatigue model to be able to take into account the effects of cyclic ageing conditions on the fatigue performance of bonded joints can significantly reduce the tests required for characterization of the adhesives.

Appendices

Paper 1



Cyclic ageing of adhesive materials

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Cyclic ageing of adhesive materials

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ABSTRACT

In real-world applications, adhesive joints are often exposed to the environment and can experience cyclic ageing conditions caused. However, the adhesive response under cyclic ageing is still relatively unexplored. In this study, hygrothermal ageing of an epoxy-based adhesive has been investigated by performing single cycle and cyclic ageing experiments. Different cyclic ageing strategies were followed in this research. In the first strategy the ageing time was set to a constant value and in the second approach, the maximum absorbed water content was limited for each ageing cycle. Absorption and desorption processes for each ageing cycle have been analysed using Fick's law. This analysis allowed to determine the diffusion coefficients and assess how they are affected by cyclic ageing. Other parameters, such as the ability to absorb water, saturation time and the glass transition temperature were also studied as a function of the different ageing conditions. The experimental results of the cyclic ageing studies showed that the water diffusion process changes with ageing cycles. It was also found that the glass transition temperature decreases with ageing cycles. Numerical analysis was also conducted using Fick's law constants. Good agreement between the experimental and numerical results was obtained.

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Adhesive; hygrothermal ageing; cyclic ageing; Fick's law; diffusion coefficient

1. Introduction

Although a relatively recent joining technology, adhesive bonding has found extensive use in diverse industrial sectors, being employed in the manufacture of a myriad of product, ranging from simple packaging to more complex and expensive structural applications in the transportation and aerospace industries. This widespread use is driven by the several important advantages that adhesive joints have over the conventional mechanical joining methods, such as welding, riveting and fastening. Adhesive bonding creates a more uniform stress distribution along the bonded area, it is relatively cheap to manufacture, can provide higher stiffness and is appropriate for lightweight structures where it can efficiently join very thin sheets of similar and dissimilar materials.^[1,2] However, one key challenge related to the application of adhesive joints is the

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significant influence of hygrothermal ageing on the performance of the adhesive. Many authors have described how adhesive properties are degraded by aggressive environments.^[3–6]

From these early works, it is now known that adhesives can absorb moisture in two different ways: In the first way, the free space of the adhesive is occupied by water molecules and, in the second way, the water is absorbed as bound water, which forms single or multiple hydrogen bonds with the adhesive's polymer chains. The former is responsible for the plasticization process; the bound water results in swelling of the adhesive, plasticization and consequently decreases the strength and the glass transition temperature (T_g).^[6–8] It's important to note that the water uptake that occurs at low temperature does not greatly affect the adhesive's mechanical properties, as the properties of the adhesive will mostly recover whenever it is dried. However, water uptake at high temperature can severely affect the mechanical properties of the adhesive, especially when the adhesive joint remains at high temperature for a certain amount of time.^[9] In this case, the properties of the adhesive will decrease continuously due to degradation effects.

Generally, a water absorption process can be described and simulated with Fick's law of diffusion, in which the water diffusion of the adhesive is plotted as a function of the square root of time divided by the thickness of the specimen.^[10–12] However, in some cases water diffusion is actually a two-stage procedure where a sequential dual Fickian model (SDF) should be employed.^[13]

However, adhesive joints will in practice experience cyclic ageing conditions, where the adhesive frequently absorbs and desorbs moisture. As stated before, many researchers have investigated the response of polymers exposed to wet/humid environments,^[14,15] but only a limited number of works have been conducted in relation with cyclic hygrothermal ageing of adhesive materials. The mechanical properties of the structural adhesives are significantly influenced by the moisture content,^[16–18] and the strength of the adhesive degrade significantly whenever the adhesive absorb water.

Chiang et al.^[19] investigated 3 M 5042 (an epoxy-based adhesive), at different temperatures (30°C, 35°C, 40°C and 45°C) under cyclic ageing in distilled water. They found that the water diffusion in the adhesive followed the dual Fickian sorption after it reached the saturation level. The diffusion coefficients of a two-part epoxy adhesive (Araldite 420) were investigated under cyclic temperature (20°C and 50°C) by Nguyen et al.^[20] They found that the diffusion coefficients increased with increasing immersion temperature, using sea water. Mubashar et al.,^[21] investigated an epoxy-based adhesive (FM73-M) under cyclic ageing in distilled water. Their work revealed that the diffusion coefficients varied with absorption and desorption cycles. Lin Y. and X. Chen,^[22] investigated the behaviour of DGEBA/DDA (an epoxy system) under cyclic ageing. They found that the moisture diffusion is not only

affected by the ageing conditions, but also is affected by the specimen thickness and ageing history as well. The moisture concentrations and moisture diffusion of the FM73-M structural adhesive were used with cohesive zone modelling to determine damage and failure of the single lap joint of Al2024 T3.^[23] The results showed a decrease in the failure load with increasing conditioning time. Qin et al.^[24] found that the chemical composition, T_g , melting temperature (T_m) and thermal stability of Sikaflex-265 adhesive all changed after cyclic ageing.

Moazzami et al.^[25] investigated an epoxy-based adhesive (AW106/HV953) subjected to cyclic ageing. They found that the elastic modulus and the tensile strength of the epoxy adhesive decreased with increasing of ageing cycles. Furthermore, they revealed that the water diffusion constant and the water content both increased with ageing cycles. CFRP/steel joints bonded with a two-part structural epoxy adhesive, STO®BPE 567, were investigated by Heshmati et al.^[26] The results showed a progressively strength reduction of the joints under cyclic ageing in both distilled and salt water. Tests on UD-GFRP and UD-CFRP composite specimens subjected to cyclic ageing in distilled and salt water were carried out by Gao and Zhou.^[27] The results revealed that the water uptake did not follow Fick's law for second and third cycles of the water absorption. Another research work investigated CFRP/Al bonded and hybrid bonded-riveted joints subjected to cyclic salt mist-dry-wet conditions.^[28] The results of this work indicate that, under cyclic ageing conditions, both bonded and hybrid joint strength significantly decreased. Reductions of up to 40.4% were found with increased ageing cycles.

The objective of the present study is to investigate the behaviour of an epoxy-based adhesive in water absorption, desorption, and resorption processes. Two distinct ageing conditions were considered, including single cycle and cyclic ageing. Single-cycle ageing was used to investigate the absorption and desorption parameters, the saturation time, and the T_g . Cyclic ageing was conducted to investigate the effect of ageing cycles on the diffusion parameters of the adhesive. Using Fick's law, the water diffusion coefficients (D) of the adhesive as a function of different ageing cycles were obtained. The T_g for different ageing conditions was determined using dynamic mechanical analysis (DMA) technique.

2. Experimental

2.1. Material properties

The tested adhesive is a one component epoxy-based adhesive. Its viscosity is high and can be considered as a paste. The tested adhesive is tough and structural which makes it suitable for joining load-bearing structures.^[29]

2.2. Specimens manufacturing

To investigate the water diffusion process, 1 mm thick bulk plates of adhesive were manufactured and then immersed in distilled water. To ensure geometrical accuracy of the plates, a mould with a silicon frame of 1 mm thickness was used, able to precisely control the thickness of the bulk plate during manufacture under pressure. The curing time and temperature of the adhesive were 60 minutes and 177°C, respectively, following the recommendations of the adhesive's manufacturer.

The resulting 1 mm thick plate was cut into smaller 60 mm x 60 mm according to ISO/DIS 294-3.^[30]

2.3. Testing procedure

• Hygrothermal ageing

Before the ageing process was initiated, the bulk plates were kept in a container filled with silica at 50°C, ensuring that all testing starts with the specimens are fully dried. Using high precision scales, the weight of the adhesive plates was measured at specific time intervals. After each time interval the weight of the test plates was measured to obtain the amount of water absorbed by the plate. For hygrothermal ageing of the adhesive, the bulk plates were immersed in distilled water inside a sealed container. The container was kept in a controlled temperature chamber, at a temperature of 50°C. The gravimetric method was used to quantify the amount of water uptake as a function of the ageing time. Weight measurement performed periodically until the saturation was attained. To analyse the effect of salt water on ageing process of the joints, the procedure used was similar to that used for distilled water. The specimens were immersed in salt water, its mass was controlled and after saturation was attained, the desorption process was performed by drying the ageing specimens. The specimens were kept in the controlled temperature chamber at 50°C until completely dry.

Three different ageing processes were conducted in this research, which are described in detail below.

• Single cycle ageing

For a set of samples, a single cycle ageing procedure was followed where the plates were saturated and then completely dried. The weight and the thickness of the plate were measured during the saturation and drying processes. This is a commonly used ageing procedure, well described in the literature. This procedure was applied for both samples immersed in distilled water and salt

water. Four samples for each test condition were tested. However, the cyclic ageing processes explained below were conducted using distilled water only.

- **Cyclic ageing by controlling the level of water uptake**

In this cyclic ageing process, the duration of each cycle was controlled by the level of water uptake. This means that ageing was carried out until the level of water uptake reached a specific value. In this study this specific level was chosen as 12.45%. This water absorption and desorption processes were repeated for three cycles (see Figure 1a).

During the ageing and drying process, the weight and thickness of the specimens were measured periodically.

- **Cyclic ageing by controlling the ageing time**

In this process, cyclic ageing was carried out by controlling the duration of the ageing and drying periods, which were set to last 30 days and 7 days, respectively. The process was repeated for four cycles (see Figure 1b). During the ageing and drying process, weight and the thickness of the plate were measured at specific intervals. Specific intervals mean the time between each measurement which was used in this research.

2.4. Glass transition temperature (T_g)

Another important property of the adhesive is its T_g which is a function of the ageing conditions. To measure the T_g , bulk samples with dimensions of 30 mm×12 mm and a thickness of 1 mm were prepared.

To determine the T_g , a DMA testing equipment was used. An in-house developed apparatus was employed, based on the measurement principle

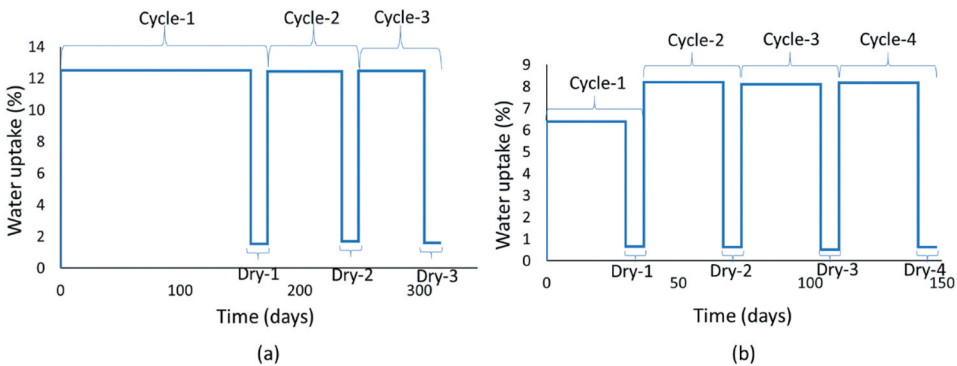


Figure 1. Schematic ageing time for each cycle. (a) Cyclic ageing by controlling the level of water uptake, (b) Cyclic ageing by controlling the ageing time.

described by Zhang et al.^[31] The T_g is determined by recording the peak in the material damping characteristics and the temperature at which it occurs.

3. Measurement procedures and Fick's law relations

Equation (1) was used to calculate the amount of water uptake.

$$M_t = \frac{w_t - w_0}{w_0} \times 100\% \quad (1)$$

where M_t is the fractional mass uptake at time t , w_t is the weight of the bulk plate specimen at time t , and w_0 corresponds to the initial weight of the bulk plate.

The thickness of the bulk plate was also measured periodically during the ageing process using a micrometer. The average thickness of the bulk plate can be calculated using Equation (2).

$$\frac{\Delta V}{V_0} = \frac{V_t - V_0}{V_0} \quad (2)$$

where V_t is the volume of the plates after ageing, and V_0 is the initial volume of the plates. In a typical moisture diffusion process, the increase in weight is first linear with the square root of time, divided by the thickness. However, it then gradually decreases until the saturation mass (M_∞) is reached. The moisture absorption and desorption can be described using Fick's law. Hygrothermal ageing can be approximated by a one-dimensional diffusion process, through an infinite plate of the thickness h , as shown in Equation (3).^[7,10]

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad (3)$$

where, D is the diffusion coefficient, c is the concentration of water, and t is time. Crank^[10] proposed a simplification of Equation (3), pointing out that for the initial stage of the process where $\frac{M_t}{M_\infty} < 0.6$, the resulting relationship can be described as in Equation (4).

$$\frac{M_t}{M_\infty} = \frac{4}{\sqrt{\pi h}} \sqrt{Dt} \quad (4)$$

By rearranging Equations (3) and (4), the D of the moisture absorption can be determined as shown in Equation (5).

$$D = \pi \left(\frac{h}{4M_\infty} \right)^2 \left(\frac{M_t}{\sqrt{t}} \right)^2 \quad (5)$$

Adhesives vary in their moisture absorption characteristics, mainly due to the highly distinct chemical compositions they can exhibit. While some adhesives absorb

moisture in accordance to Fick's law, others absorb moisture faster in the first stage of the absorption process and transition into a less abrupt second stage, with a different diffusion rate, before reaching an equilibrium plateau. For this condition, the SDF model^[13,32] should be used instead. In this condition, the diffusion coefficient during the first stage and the second stage of the process can be calculated separately and are known as D_1 and D_2 respectively. To calculate the water uptake at time t , Equation (6) was used.

$$M_t = \left(1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} e^{\left(\frac{-D_1(2n+1)^2 \pi^2 t}{4h^2} \right)} \right) \times M_{1\infty} + \Phi(t - t_d) \left(1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} e^{\left(\frac{-D_2(2n+1)^2 \pi^2 t}{4h^2} \right)} \right) \times M_{2\infty} \quad (6)$$

where $M_{1\infty}$ and $M_{2\infty}$ correspond to the fractional mass uptake in the first and second stages, respectively, t_d is the time of transition between the two stages, and $\Phi(t - t_d)$ is the Heaviside step function which is equal to zero for negative values of $t - t_d$ and equal to one for positive values of $t - t_d$.

To predict the desorption mechanism during the drying process,^[33] the corresponding Fickian model gives M_t based on the following relation.

$$M_t = M_r + \left(\frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp \left(\frac{-D_d(2n+1)^2 \pi^2 t}{4h^2} \right) \right) \times (M_{\infty} - M_r) \quad (7)$$

where M_r is minimum fractional retained water after drying and D_d is the diffusion coefficient of the desorption mechanism.

4. Results and discussions

4.1. Single cycle ageing

Hygrothermal ageing of the adhesive in distilled water was found to require 7500 hours to reach the saturation point, while hygrothermal ageing of the same adhesive in salt water reached saturation after 1009 hours have passed.

Figure 2 shows the level of water uptake of the adhesive, plotted against the square root of time, normalized by the thickness of the specimen (Π s/h). Based on the data at the saturation point, the maximum increase in sample weight is of 13.49% and 1.34% for hygrothermal ageing in distilled water and salt water, respectively.

Ageing in distilled water followed a dual-stage process, while ageing in salt water exhibited single stage saturation. In order to confirm that the material has been fully saturated, three consecutive measurements were obtained were the amount of water uptake did not exceed a variation of 1%.^[34] The adhesive

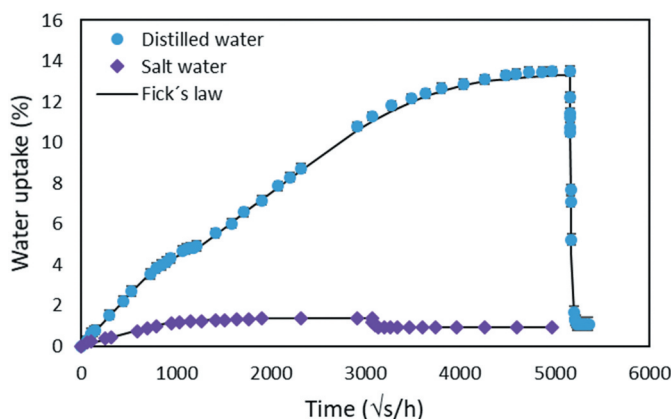


Figure 2. Hygrothermal ageing of the adhesive in distilled and salt water. Solid lines show the Fick's law predictions. The points show the average values.

that aged in salt water absorbs less water because the molecules of salt are not able to diffuse into the crazes and voids of the adhesive. The size of these molecules is greater than the size of microcavities of the adhesive, which inhibits the process of water diffusion into the adhesive. This causes saturation to be reached earlier.

Molecules of distilled water have smaller dimensions than the free volume of microcracks and voids of the adhesive and thus they are able to traverse the polymeric network and occupy the free space throughout the adhesive prior to saturation. The weight of the absorbed water increases linearly with the square root of time at the initial stage. It then slows down gradually until saturation is reached (see Figure 2).

The increase in thickness of the adhesive due to swelling closely follows the increase of mass due to water uptake. The thickness swells linearly with the increase of water uptake as shown in Figure 3. The results show that swelling of the thickness of the adhesive aged in distilled water is higher than that of the adhesive aged in salt water. The swelling of the adhesive aged in distilled water is of 4.77%, which is significantly higher than the value registered for ageing salt water (0.51%). Table 1 shows the Fick's law constant for different ageing and drying conditions.

4.2. Cyclic ageing by controlling the level of water uptake

In this cyclic ageing procedure, the maximum level of water uptake per cycle was limited. In each cycle, the adhesive absorbed water up to a value of 12.49% water uptake and was then subjected to a desorption process. The samples were dried in an oven at 50°C until they reached a constant mass. The resorption process was then performed for the second and third cycles, until reaching the same amount of water uptake as for absorption process.

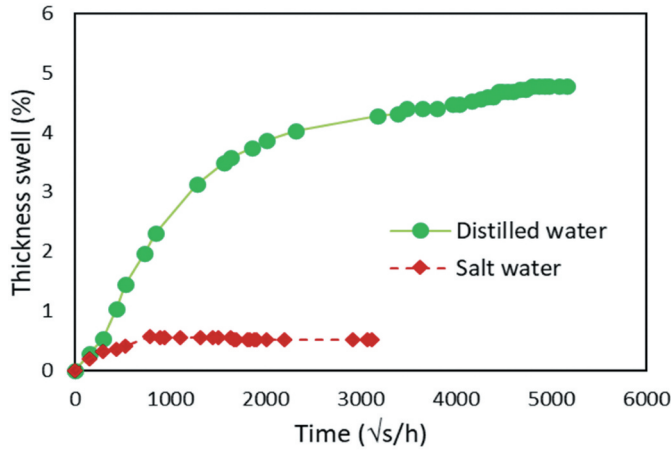


Figure 3. Thickness swelling of the adhesive in distilled and salt water. The points show the average values.

Table 1. General properties of water absorption by the adhesive.

Condition	Stage	Properties	
Distilled water	Absorption	$M_{1\infty}$ (%)	4.94
		D_1 (m^2s^{-1})	2.34E-07
		$M_{2\infty}$ (%)	13.49
		D_2 (m^2s^{-1})	3.21E-08
	Desorption	M_r (%)	1.083
		D_d (m^2s^{-1})	6.69E-07
Salt water	Absorption	M_i (%)	1.34
		D_1 (m^2s^{-1})	1.92E-07
	Desorption	M_r (%)	0.916
		D_d (m^2s^{-1})	8.02E-07

In the first cycle, the adhesive required 3816 h (159 days) to reach a value of 12.49% of water uptake. In the second cycle, it required 1490 h (62 days) to reach 12.44% of water uptake and, in the third cycle, 1322 h (55 days) were necessary to absorb 12.46% of water content. It is important to note that the ageing time necessary for resorption is shorter than that of absorption, the process becoming quicker with each subsequent step.

The ageing process is usually not a fully reversible phenomenon. It means that after drying the properties of the adhesive usually are not fully recovered. For the tested adhesive, 1.6% of water content remained in the adhesive, due to the effect of bound water during the ageing process. The water uptake of three different cycles is shown in Figure 4a.

To clarify the differences between D of the cycles, the D can also be plotted as shown in Figure 5a, showing that the values of D for the second and third cycles are greater than during the first cycle.

The differences between the values of D for the three cycles show that the resorption speed is faster than that of absorption. The water absorption

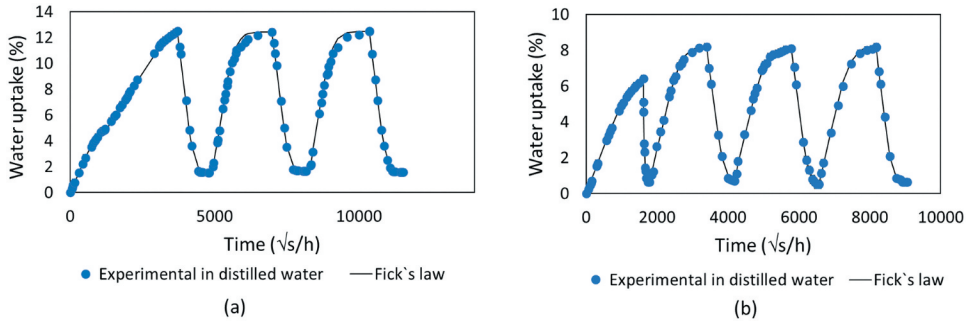


Figure 4. Cyclic ageing of adhesive in distilled water. (a) Cyclic ageing by controlling the level of water, (b) Cyclic ageing by controlling ageing time. Solid lines show Fick's law predictions. The points show the average values.

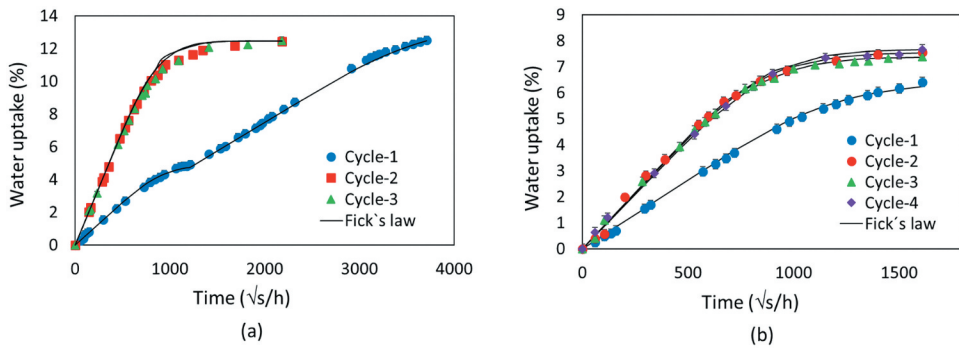


Figure 5. Comparison of the D. (a) Cyclic ageing by controlling the level of water uptake, (b) Cyclic ageing by controlling ageing time. Solid lines show Fick's law predictions. The points show the average values.

parameters of the adhesive after performing cyclic ageing by controlling the level of water uptake have been listed in [Table 2](#).

4.3. Cyclic ageing by controlling the ageing time

As stated above, in this approach, instead of targeting a given absorbed water content, each cycle lasts an equal period of time, which in this case was set to be one month. In the first cycle, the adhesive plate absorbed 6.40 wt% of water. In the second cycle, the adhesive plate absorbed 8.19 wt% of water for the same time period (one month). In the third and fourth cycles the adhesive plate absorbed 8.10 wt% and 8.17 wt%, respectively. In the drying process that occurs between subsequent ageing cycles, the weight and the thickness of the adhesive were again not fully reverted to the initial state. Around 0.6 wt% of water content remained locked in the adhesive due to the bound water phenomenon. The results also show that the absorbed water content for

Table 2. General water absorption parameters of cyclic ageing by controlling the level of water uptake of the adhesive.

Cycle number	Stage	Properties	
1	Absorption	$M_{1\infty}$ (%)	4.92
		D_1 (m^2s^{-1})	2.34E-07
		$M_{2\infty}$ (%)	12.49
	Desorption	D_2 (m^2s^{-1})	3.08E-08
		M_t (%)	1.5324
		D_d (m^2s^{-1})	5.56E-07
2	Resorption	$M_{1\infty}$ (%)	12.4443
		D_1 (m^2s^{-1})	2.26E-07
		M_t (%)	1.6838
	Desorption	D_d (m^2s^{-1})	5.56E-07
		$M_{1\infty}$ (%)	12.4625
		D_1 (m^2s^{-1})	2.29E-07
3	Resorption	M_t (%)	1.5959
		D_d (m^2s^{-1})	5.56E-07
		$M_{1\infty}$ (%)	12.4625
	Desorption	D_1 (m^2s^{-1})	2.29E-07
		M_t (%)	1.5959
		D_d (m^2s^{-1})	5.56E-07

the second to fourth cycles were generally similar but still higher than the value registered during the first cycle (see [Figure 4b](#)).

The most important parameter that can be determined during this cyclic ageing process is the D . It was found that D values for the resorption process are greater than D of the initial absorption process (see [Figure 5b](#)). Accordingly, the water diffusion of the adhesive at the resorption process is faster than that of absorption process.

The D and M_t of the absorption, desorption and resorption processes of the cyclic ageing where the ageing time was controlled per cycle are summarized in [Table 3](#). The results showed that D of the second, third and fourth cycles are almost equal.

The thickness swelling curves for the two different cyclic ageing strategies are plotted and compared in [Figure 6](#). It is observed that the thickness swelling of the adhesive increased significantly as the water uptake increased. It is also clear that once thickness swelling occurs, it cannot be fully reversed to the initial thickness in subsequent drying processes.

Table 3. General water absorption parameters of cyclic ageing by controlling of ageing time.

Cycle number	Stage	Properties	
1	Absorption	$M_{1\infty}$ (%)	6.40
		D_1 (m^2s^{-1})	1.33E-07
	Desorption	M_t (%)	0.6549
		D_d (m^2s^{-1})	8.28E-07
2	Resorption	$M_{1\infty}$ (%)	8.19
		D_1 (m^2s^{-1})	2.51E-07
	Desorption	M_t (%)	0.6198
		D_d (m^2s^{-1})	8.28E-07
3	Resorption	$M_{1\infty}$ (%)	8.09
		D_1 (m^2s^{-1})	2.51E-07
	Desorption	M_t (%)	0.5117
		D_d (m^2s^{-1})	8.28E-07
4	Resorption	$M_{1\infty}$ (%)	8.17
		D_1 (m^2s^{-1})	2.51E-07
	Desorption	M_t (%)	0.6296
		D_d (m^2s^{-1})	8.28E-07

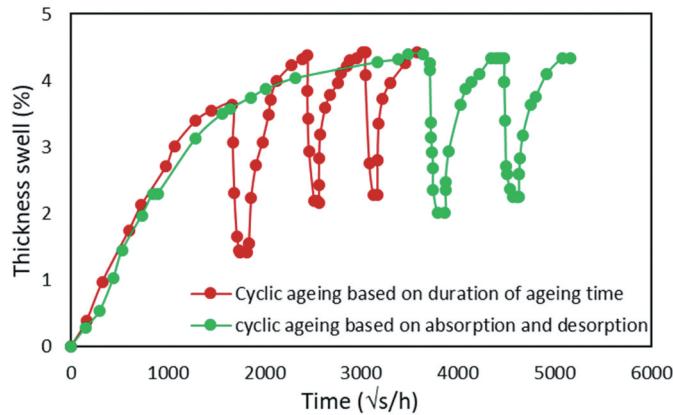


Figure 6. Comparison of the thickness swelling of different cyclic ageing.

4.4. Glass transition temperature (T_g)

The T_g of the samples that experienced single cycle ageing was measured and compared. Adhesive samples that were aged in both distilled water and in salt water were considered in this analysis. The measurement of T_g of the adhesive before and after performing hygrothermal ageing shows a very drastic difference in the value of T_g . The results are shown in Figure 7.

The reduction of the T_g for the samples immersed in distilled water and salt water is highly influenced by the water content in the adhesive. The absorbed water creates a plasticization effect and reduces the T_g of the adhesive. This reduction of the T_g depends on the amount of water in the adhesive. For instance, the reduction of the T_g of the specimens aged in salt water is not significantly affected by ageing, mainly due to the small amount of water diffused through the ageing process in salt water. The results confirm this, as the T_g of the adhesive aged in salt water decreased only by 4°C. For the samples aged in distilled water, where

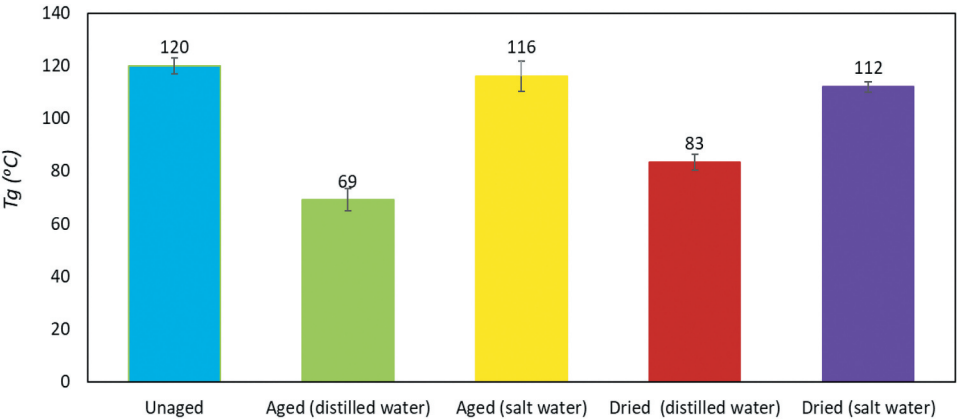


Figure 7. T_g of the adhesive for different ageing conditions.

the water content in the adhesive reached up to 13.49% the T_g of adhesive aged in distilled water decreased by 51°C. Figure 7 shows the T_g of the adhesive for different ageing conditions.

4.5. Simulation of the water absorption

A numerical analysis was carried out in this work with the objective of creating a model that is able to accurately reproduce the experimentally determined ageing behaviour. To construct such model, the equivalence between thermal flow and moisture uptake is exploited, where thermal conductivity, thermal diffusivity and heat capacity are equivalent to the permeability coefficient, diffusion coefficient and solubility coefficient, respectively. In this analysis, the nodal temperature of the model elements is replaced with the humidity level. A schematic representation of the bulk adhesive model used to simulate the water absorption in the adhesive is shown in Figure 8, and the arrows show the directions of the water uptake.

The simulation of water diffusion in the adhesive of bulk plate was carried out using FE analysis. Figure 9 shows the water ingress and the level of humidity of the simulation process. The results present the humidity level for a total of 34 days and the saturation conditions are reached after a period of 289 days.

Using the diffusion parameters obtained with Fick's law, the ageing time of the adhesive can be predicted by this model. The effectiveness of the model can be assess comparing the obtained water uptake results against the experimental measurement and the original Fick's law, as shown in Figure 10.

Hygrothermal ageing at higher temperatures will speed up the absorption rate of the adhesive. Higher temperatures will increase the diffusion coefficient value and will decrease the time to reach the saturation condition. However, it

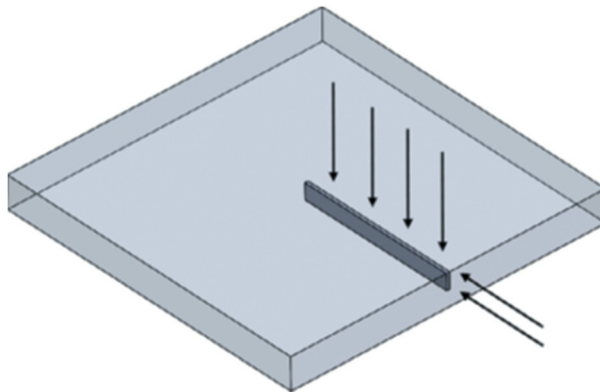


Figure 8. Schematic representation of 2D model used for determining water uptake in the bulk plate. Arrows indicate the water uptake directions.^[34]

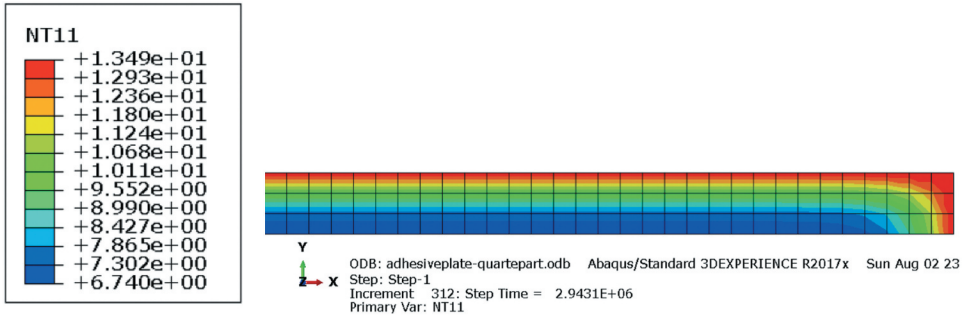


Figure 9. Distribution of the water through the bulk plate after 34 ageing days.

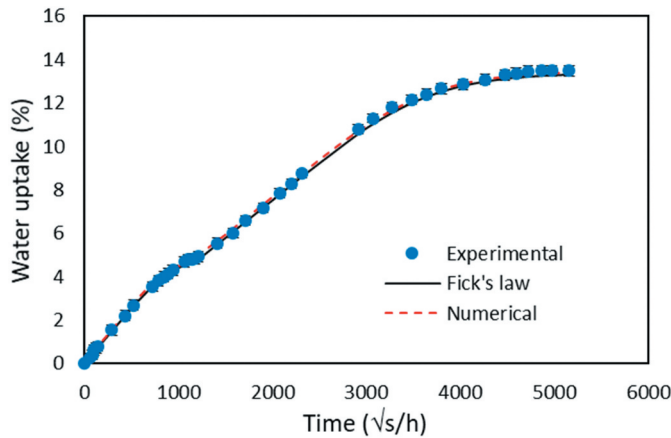


Figure 10. Comparison of measured, Fick's law and numerical simulation of water absorption of the adhesive bulk plate.

should be noted that the considered temperature should be below the T_g of the adhesive. Adhesive thickness in bulk samples can also influence the saturation time. The thicker the adhesive layer the longer the time to reach the saturation level. But it should be taken into account that the considered Fick's law relations are valid for one-dimensional problems where the water is assumed to be absorbed mainly along one direction within the adhesive material. Accordingly, to obtain precise results out of Fick's law analysis, the adhesive thickness should be small enough.

5. Conclusions

According to the results it was found that different hygrothermal ageing conditions have very different diffusion coefficients and saturation levels. Using salt water, the hygrothermal aging process reached the saturation level at 1009 hours with 1.34% of water uptake. In contrast, hygrothermal ageing of the sample in distilled water required around 7500 hours saturate with

a maximum value of 13.49% for the water uptake. The different hygrothermal ageing conditions were found to follow different diffusion stages. Hygrothermal ageing in salt water exhibited only one stage of water absorption, while for the distilled water it was a two stage water absorption that resulted in two diffusion coefficients such as D_1 and D_2 . In cyclic ageing processes, it was found that the D differs between the initial and the subsequent ageing cycles. For the second cycle of ageing the value of D increased but it then remained almost constant for all following cycles. In practice this means that the aging time need to reach the same level of water uptake is shorter for the second cycle than for the first ageing cycle. In a practical application, using the diffusion coefficient of single-cycle ageing for joints which experience cyclic aging represents conservative results. According to the results it was also shown that the thickness swelling of the adhesive increased faster when hygrothermal ageing was performed in distilled water. For saltwater, the increase is more limited. This is because of more moisture is absorbed in distilled water compared to the salt water and, consequently the thickness swelling will also be more significant. Hygrothermal ageing for higher temperature will speed up the absorption rate of the adhesive.

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Paper 2

Effects of cyclic ageing on the tensile properties and diffusion coefficients of an epoxy-based adhesive

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Abstract

In real practice, adhesively bonded structures are usually exposed to cyclic environmental conditions. However, cyclic ageing processes are relatively unexplored. The aim of this study is to consider the effect of cyclic ageing on the rate of water uptake and the drying process in an epoxy-based adhesive. Fick's law was considered to estimate the water diffusion coefficients for the ageing and the drying steps at different cycles. Different cyclic ageing times have been considered in the ageing procedure. Dogbone shape specimens were also manufactured and subjected to cyclic aging to investigate the tensile properties of the tested adhesive as a function of aging cycles. The gravimetric results showed that the rate of water uptake and drying is mainly a function of the level of water uptake of the first ageing cycle. Tensile test results showed that the maximum water content increases with each subsequent ageing cycle. It was also found that the Young's modulus and the tensile strength of the adhesive decreased significantly after the initial ageing cycle, but all subsequent ageing cycles have considerably less influence on the mechanical properties of the adhesive.

Keywords

Epoxy adhesive, cyclic ageing, Fick's law, diffusion coefficient, hygrothermal ageing

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Introduction

Adhesive joints are widely used in industries which manufacture heavy duty equipment, such as transportation, aerospace and naval industries, but they also find use in less severe applications, such as shoe manufacturing and book binding. Adhesive joints have important advantages when compared to conventional joining methods, such as welding, riveting and fastening. Adhesive bonding allows for a more uniform stress distribution of the bonded area, is well suited for joining thin sheets of similar and dissimilar materials which enables light-weight structures and offers higher stiffness.^{1,2}

In real-world applications, adhesive joints usually encounter specific service conditions that lead to the degradation of the adhesives, substrates and interfaces. Perhaps one of the most severe is the degradation of the adhesive in humid environments. Long-term service period in extreme environments causes the adhesive to absorb moisture and even if the loads acting on the joint are constant, the degradation of the joint due to the humidity can eventually lead to the complete failure of the structure. Therefore, it is

important to investigate the mechanical properties of adhesive joints by performing hygrothermal ageing, testing the aged adhesive and using the resultant data to predict joint strength for a long lasting structural design.^{3–6}

Usually, the water diffuses into the adhesive in two ways. The first is the water that diffuses into the adhesive as a free water. In this way, water occupies the free spaces of the adhesive structure. This phenomenon is responsible for adhesive plasticization. In the second way, the water diffuses into the adhesive as bound water which forms single or multiple hydrogen bonds with the adhesive's polymer chains. The bound

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water also creates plasticization and leads to swelling of the adhesive, which results into the degradation of the adhesive mechanical properties.^{6–8}

The rate of water absorption in an adhesive is measured by the moisture diffusion coefficient (D). A higher diffusion coefficient results in faster moisture uptake at a specific ageing time.^{9–12} Simulation of the water diffusion in an adhesive joint is only possible by knowing the correct D value.

However, a single ageing period does not represent actual service conditions in many applications. When in service in extreme environment for long periods of time, adhesives usually repeatedly absorb and desorb moisture. Therefore, to model the long-term service of adhesive joints, cyclic hygrothermal ageing of adhesives should be conducted to predict the moisture diffusion in the adhesive layer under these alternating conditions. Many researchers have investigated the effects of moisture diffusion by conducting hygrothermal ageing of adhesives, but very few investigations have focused on the hygrothermal ageing process in cyclic humidity conditions.

Fibre-reinforced epoxy composites were investigated under cyclic absorption and desorption processes by Gao and Zhou.¹³ They revealed that weight gain due to moisture absorption is no longer well described by Fick's law during the second and the third cycle of the moisture absorption processes. Moisture diffusion coefficients in these two periods are obviously higher and lower than Fick's law predictions during the first and the second halves of the moisture absorption processes. Mubashar et al.¹⁴ investigated an epoxy-based adhesive (FM73-M) under cyclic ageing in distilled water. This work revealed that the diffusion coefficients vary with the absorption and desorption cycles. Lin and Chen¹⁵ investigated the behaviour of an epoxy system under cyclic ageing. They found that the moisture diffusion is not only affected by the ageing conditions, but it is also affected by the specimen thickness and the ageing history as well. Both the tensile elastic modulus and the tensile strength of the studied epoxy system were reduced after hygrothermal ageing.

The moisture concentrations and moisture diffusion of FM73-M epoxy adhesive were associated to a cohesive zone model to determine damage and failure of a single lap joint with Al2024 T3 substrates.¹⁶ The results showed a decrease in failure load with increasing conditioning time. Nguyen et al.¹⁷ investigated the diffusion coefficients of Araldite 420 under cyclic temperature (20 and 50 °C). They showed that the diffusion coefficients increased with higher immersion temperatures in sea water. Mechanical properties of ISR-7008 adhesive under cyclic ageing condition were analysed by Fan et al.¹⁸ They found that the failure strength and stiffness of adhesive joints decrease significantly after hygrothermal ageing. Failure strength was found to decrease with larger numbers of aging cycles. Carbon fiber

reinforced polymer (CFRP)/steel joints, bonded with a two-part structural epoxy adhesive (STO® BPE 567), were investigated by Heshmati et al.¹⁹ The results showed a progressive strength reduction of the joints under cyclic ageing in both distilled and salt water. Moazzami et al.²⁰ investigated an epoxy-based adhesive AW106/HV953 subjected to cyclic ageing. They found that the elastic modulus and the tensile strength of the epoxy adhesive decreased with subsequent ageing cycles. Furthermore, the results also indicate that water diffusion constant and the water content both increase with ageing cycles.

These studies show that limited data are available for cyclic ageing of bonded joints. As bonded joints usually experience a cyclic environmental condition in service, it is crucial to explore more precisely the response of adhesive materials in this condition. The objective of this study is to investigate how the diffusion coefficient (D) of an epoxy-based adhesive and its mechanical properties vary under cyclic ageing conditions. The obtained diffusion coefficients were first used to simulate the water uptake in the numerical analysis. In this case, a finite element model, constructed in Abaqus, was used to perform the numerical analysis process. Three different cyclic ageing conditions were used to investigate the evolution of the D of the adhesive.

In the second part of this study, the effects of cyclic ageing on the tensile properties of the tested adhesive were also investigated. The Young's modulus, tensile strength and tensile elongation of the considered adhesive were determined as a function of the different ageing cycles and ageing times.

Experimental

Material properties

An epoxy-based adhesive was used to analyse the effect of cyclic ageing on the mechanical response and the ageing procedure of the adhesive. It is a one-part epoxy-based adhesive with high viscosity. The adhesive used is a tough, structural adhesive which is mainly used in the construction of load-bearing structures.

Specimen manufacturing

To study the water diffusion process, and the strength of the adhesive under cyclic ageing, 1-mm thick bulk plates were manufactured in a specific mould. To ensure the accuracy of the plate thickness, a specific mould with a 1-mm thick silicon frame was used (see Figure 1). The adhesive curing cycle consisted in a stage of 60 min at 177 °C, as defined in the material datasheet. The bulk plate was then cut into 60 by 60 mm² plates, suitable for water diffusion testing. Mini dogbone specimens (as shown in Figure 2)

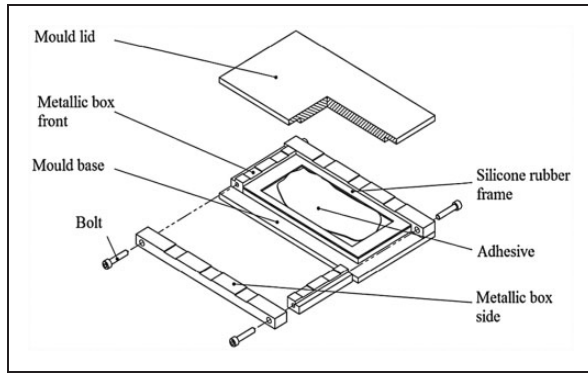


Figure 1. Mould used in the manufacture of the adhesive bulk plate

Source: reproduced with permission from Viana et al., 2017.¹¹

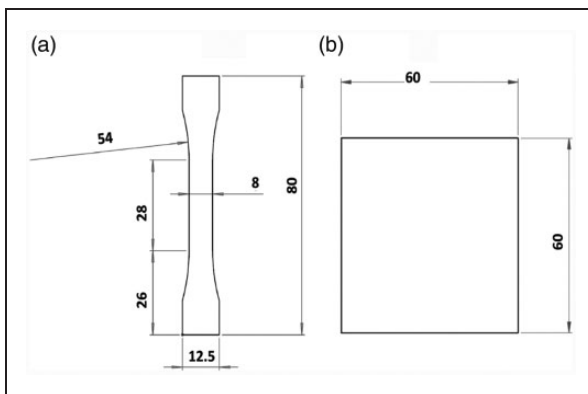


Figure 2. (a) Dogbone tensile specimen and (b) square bulk plate. The thickness of the samples is 1 mm. Dimensions in mm. Source: reproduced with permission from Viana et al., 2017.¹¹

were also cut from the manufactured plates, to be used in mechanical characterization processes.

Testing procedure

Hygrothermal ageing. The bulk plates and dogbone specimens were kept in a container filled with silica at 50 °C to ensure that the specimens are fully dried before the ageing process begins. In this research, a micro balance (Kern-Toledo, Balingen, Germany) with 0.1 mg of accuracy was used to measure the weight of the samples during the ageing process. The weight of the adhesive plates was measured at specific time intervals until the mass stabilized at a minimum value. For hygrothermal ageing of the adhesive, the bulk plates and dogbone specimens were fully immersed in distilled water. The container, including the bulk plates and dogbone specimens, was kept in an oven at 50 °C. To speed up the ageing process, ageing was performed at high temperature. However, the selected temperature should be well below the T_g of the adhesive. Accordingly, 50 °C was chosen. The gravimetric method was used to quantify the amount of water uptake as a function of the ageing time. Weight measurements were

performed periodically during a five-day period. After this five-day period, the desorption process was initiated by drying the ageing specimens. The drying processes were performed by keeping the specimens in a container filled with silica particles. The container was kept in an oven at 50 °C. The drying temperature is the same as the ageing temperature.

The same procedure was also applied to perform long-term cyclic ageing, with one month and six months of ageing time per cycle and in which the drying time was set to one week and two weeks, respectively. Based on the experimental results, the tested specimen reaches the saturation condition after six months ageing. To analyse the effect of different aging levels before the saturation condition, it was necessary to define shorter ageing times. Accordingly, three different ageing times were thus carried out in this study in order to compare the diffusion coefficient of the cycles (6 months, 30 days and 5 days).

Cyclic ageing of bulk plate and dogbone specimens by controlling the ageing time. In this process, the cyclic ageing was carried out by controlling the times of ageing and drying periods. As it was mentioned above, periods of 5 days, one month and six months were considered for the ageing time, matched with periods of two days, one week and two weeks for drying, respectively. For each condition, the process was repeated for three full ageing and drying cycles. During the ageing and drying process, the weight of the plate was measured at specific intervals. The same ageing procedure was followed for the dogbone specimens.

Tensile test. To determine the mechanical properties of the adhesive at different ageing time and ageing cycles, tensile tests were carried out using INSTRON 3367 (Norwood, MA, USA) universal tensile test machine. The tested samples were reduced-scale dogbone specimens as already shown in Figure 2(a). The tensile tests were performed at room temperature with a constant cross head displacement rate of 1 mm/min. The tensile test set up is shown in Figure 3.

Fick's law relationship and the numerical analysis

Fick's law

The amount of water uptake for the bulk plates was calculated using equation (1)

$$M_t = \frac{w_t - w_0}{w_0} \times 100\% \quad (1)$$

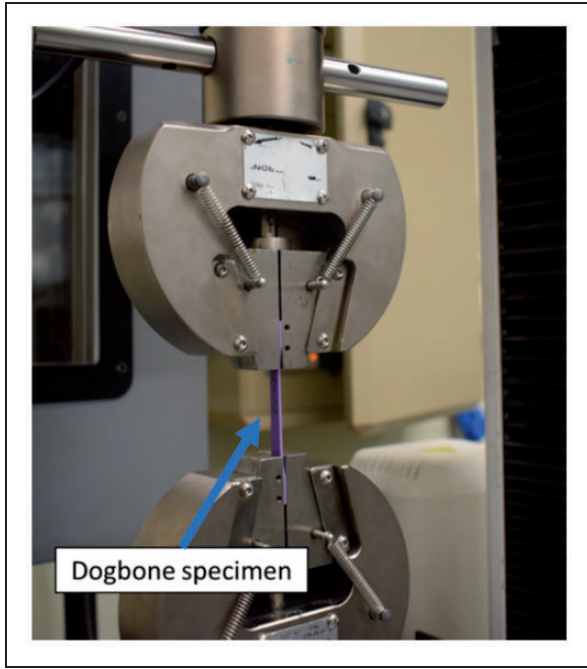


Figure 3. Tensile test set up.

where, M_t is the fractional mass uptake at time t , w_t is the weight of the bulk plate specimen at time t and w_0 corresponds to the initial weight of the bulk plate.

In moisture diffusion, the increase in weight is first linear with the square root of time divided by the specimen thickness. However, it then gradually decreases until the saturation mass (M_∞) is reached. In an hygrothermal ageing process, the moisture absorption and desorption can be described by using Fick's law. Hygrothermal ageing is considered as a one-dimensional diffusion through an infinite plate of the thickness h , as shown in the equation (2)^{21,22}

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

where D is the diffusion coefficient, c is the concentration of water and t is time. Crank²¹ proposed a simplification of equation (2) and pointed out that for the initial stage of the process where $\frac{M_t}{M_\infty} < 0.6$, the resulting relationship can be described as in equation (3)

$$\frac{M_t}{M_\infty} = \frac{4}{\sqrt{\pi h}} \sqrt{Dt} \quad (3)$$

By rearranging equations (2) and (3), the D of the moisture absorption can be determined as shown in the equation (4)

$$D = \pi \left(\frac{h}{4M_\infty} \right)^2 \left(\frac{M_t}{\sqrt{t}} \right)^2 \quad (4)$$

To predict the desorption mechanism during the drying process,²³ the corresponding Fickian model gives M_t based on the following relation

$$M_t = M_r + \left(\frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp \left(\frac{-D_d(2n+1)^2 \pi^2 t}{4h^2} \right) \right) \times (M_\infty - M_r) \quad (5)$$

where, M_r is the minimum fractional retained water after drying and D_d is the diffusion coefficient of the desorption mechanism.

Numerical analysis

Numerical simulations were conducted to prove the obtained experimental data. Using the finite element method, the ageing process was numerically simulated for both the bulk plates and the mini dogbone specimens. Abaqus as a commercial FE program was used for this analysis. Using the numerical results, the average amount of the water uptake was obtained and compared with the experimental measurements. The water uptake process was measured by the heat transfer analogy. Nodal temperature in this case shows the level of water uptake at each material point. In the FE analysis, the conductivity of the adhesive was set as the diffusion coefficient obtained using Fick's law for different ageing cycles.

The water absorption process was modelled both in two-dimensional (for the bulk plates) and three-dimensional (for the mini dogbones). For the bulk plates, standard four-node linear heat transfer quadrilateral (DC2D4) elements were employed. Due to the symmetric geometry of the tested specimens and to optimize the computational time, a quarter part of the specimens was simulated. Uniform mesh size (0.04 mm) in both the width and height directions were employed which produced a total number of 9750 elements for the bulk plate specimens. The same strategy was followed to simulate the dogbone shape samples. However, as the dogbone samples were simulated in 3D condition, standard eight-node linear heat transfer brick (DC3D8) elements were used. In this case, a total number of 5640 elements were used to model the mini dogbone samples.

Results and discussions

Cyclic ageing of bulk plates by controlling the ageing time

Figure 4 shows the water uptake of three different cyclic ageing conditions. The comparisons of the three ageing conditions revealed that for the six

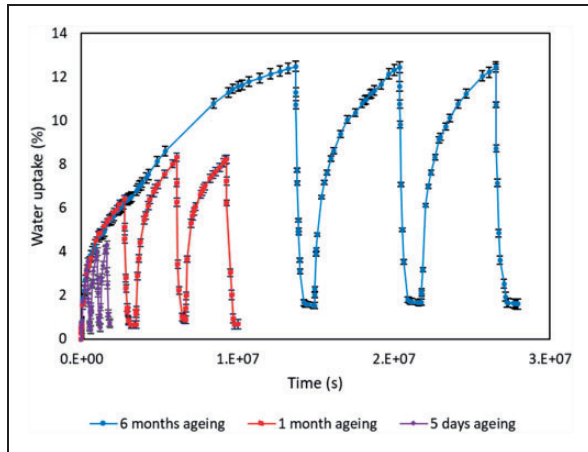


Figure 4. Cyclic ageing of three different ageing conditions.

months ageing, the sample absorbed more water, and consequently there are more bound water compared to the specimens aged for shorter periods. During the drying process, the sample releases part of or all the free water (based on the drying period), but the bound water remains in the adhesive. Consequently, as it is shown in Figure 4, the remained bound water is higher for samples aged for six months than those aged for one month or five days. Based on the results shown in Figure 4, the remaining bound water for samples with one month and six months ageing are 0.72 and 1.60 wt%, respectively. These results are in agreement with the literature,²⁰ which shows that at the end of the drying process of each ageing cycle, a little amount of moisture remains in the specimen.

Based on the results shown in Figure 4, the rate of water uptake for the tested samples is a nonlinear function of time. The total amount of water uptake is the summation of the bound water and the water that occupies the free spaces of the adhesive. As it was mentioned above, after the drying process, the bound water and usually part of the free water remain in the adhesive (based on the drying time). The nonlinear response of the adhesive in terms of the absorbed water for different ageing time results in a nonlinear level of remained water after drying for the different drying times considered in this study. However, changing the drying time may influence the results and cause a different relation between the remained water for the specimens aged for different periods.

Figure 5 shows the respective level of water uptake for each cycle, where the ageing time was set to five days. In the drying process, the weight of the adhesive was not reversed to the initial values. Around 0.4 wt% of water remained in the adhesive due to the effect of bound water during the ageing process. It was found that the water uptake level for the second and the third cycles were higher than that of the first cycle as shown in Figure 5.

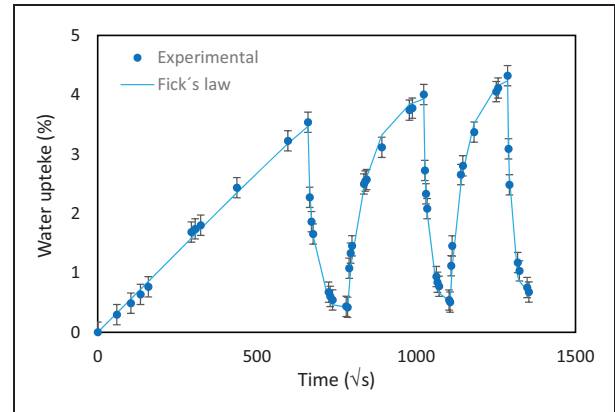


Figure 5. Cyclic ageing of bulk plates. Five days ageing followed by two days drying for each cycle.

Effect of different ageing conditions on water diffusion coefficients

Based on the obtained results, it was found that in cyclic ageing processes, D is a function of water uptake level in the first ageing cycle. The results shown in Figure 6 indicate that D_2 and D_3 (diffusion coefficients of the second and the third ageing cycles) are significantly influenced by the level of water uptake during the first cycle.

Based on the results shown in Figure 6, it was found that the rate of water uptake for the second and the third ageing cycles is a function of the level of water uptake of the first cycle. Based on the results, the higher the level of water uptake for the first cycle, the lower the rate of water uptake for the second and third cycles.

Although each ageing step is followed by a drying process, longer ageing periods will result in a higher amount of bound water that remains within the adhesive even after the drying process. On the other hand, the water that occupies the free spaces of the adhesive usually does not completely evaporate after the drying process (depending on the drying time). Both these phenomena decrease the capacity of the adhesive to absorb more water in the second and third ageing cycles.

However, this influence is reduced if the level of water uptake in the first ageing cycle is more than 50% of the saturation condition. By considering the results shown in Figure 6, it can be concluded that the ageing level in the first cycle can significantly change the rate of water uptake for the second (D_2) and third (D_3) cycles. However, it is shown that D_2 and D_3 are less sensitive to the ageing level when the water uptake of the first cycle is more than 50% of the saturation condition. A possible reason can be the amount of remained water after drying. A higher level of water uptake results in a higher amount of bound water and subsequently a higher amount of remained water after drying. Accordingly, there is less capacity for absorbing more water for the second (or the third) cycles which can result in a lower rate of water uptake for

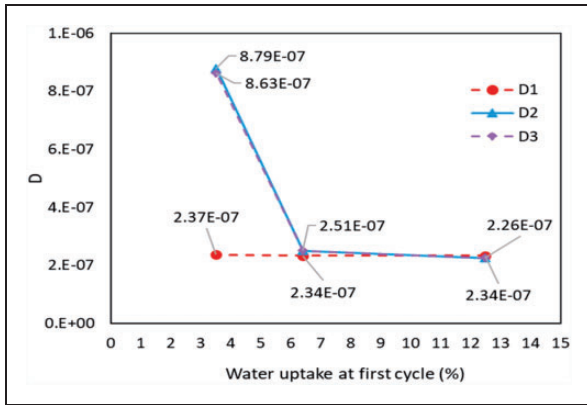


Figure 6. D values for three different levels of water uptake of ageing cycles.

Table 1. D values for three different ageing cycles.

Ageing time	Wt (%)	D_1	D_2	D_3
Six months	12.49	2.34E-07	2.26E-07	2.26E-07
One month	6.40	2.34E-07	2.51E-07	2.51E-07
Five days	3.50	2.374E-07	8.79164E-07	8.63488E-07

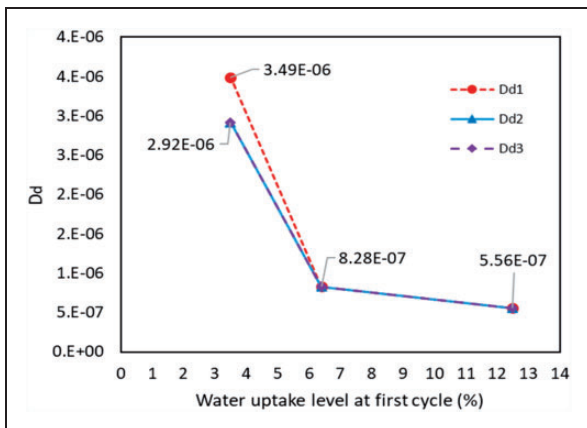


Figure 7. D_d values obtained for three different levels of water uptake of drying process.

Table 2. D_d of the three different drying process.

Ageing time	Wt (%)	D_{d1}	D_{d2}	D_{d3}
Six months	12.49	5.56E-07	5.56E-07	5.56E-07
One month	6.40	8.28E-07	8.28E-07	8.28E-07
Five days	3.50	3.4906E-06	2.92026E-06	2.92026E-06

the second or third cycles. However, the obtained value (50% of the saturation) as a limit is a rough value based on the considered test conditions. More experimental data points and further analysis are needed to determine a precise limit and to explain this phenomenon in more details.

The D values of the three different cyclic ageing conditions are listed in Table 1. It was also found

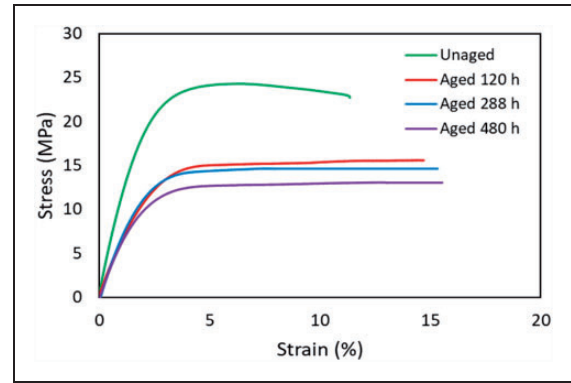


Figure 8. Typical stress–strain curves of an epoxy adhesive specimens (dogbone) of unaged and hygrothermal aged based on ageing time.

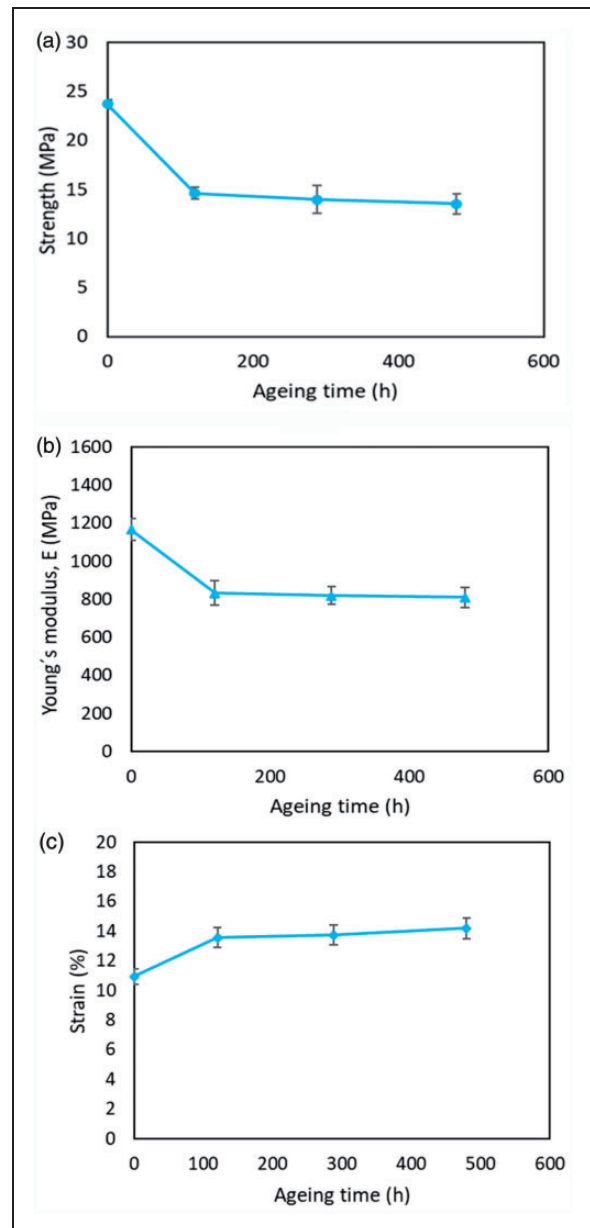


Figure 9. Mechanical properties of epoxy-adhesive after the time-based ageing. (a) Tensile strength, (b) Young's modulus and (c) strain at failure.

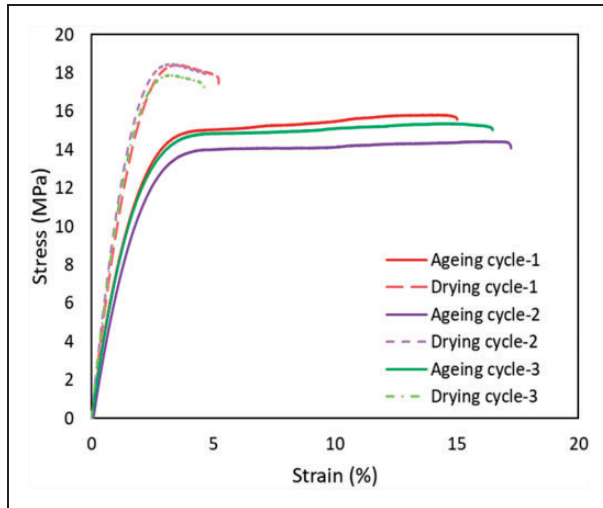


Figure 10. Stress–strain curves of the adhesive for cyclic aged condition.

that the values of D_d at different cycles are a function of the water uptake level attained during the first ageing cycle (see Figure 7). The values of D_{d1} , D_{d2} and D_{d3} for the level of water uptake of 6.40 wt% (one month) were higher than those found for 12.49 wt% (six months). For specimens with a maximum of 3.50 wt% of water uptake, the rate of drying during the first cycle is higher than the second and the third cycles. The results of D_d for different cyclic ageing conditions are listed in Table 2.

Tensile strength

Tensile strength based on ageing time. The typical stress–strain curves for aged specimens tested after different ageing times are shown in Figure 8. Using the tests results, the tensile strength, Young's modulus and strain at failure of the tested samples were obtained and are presented in Figure 9(a) to (c), respectively. The results show that the tensile strength and Young's modulus decrease as a function of the ageing time. By increasing the ageing time, the adhesive absorbs more moisture and becomes more ductile. The ductility of the adhesive affected both the tensile strength and Young's modulus which were found to decrease (see Figure 9(a) and (b)). The degradation of the tensile strength at 120, 288 and 480 h ageing time was of 38.27, 41.00 and 42.95% respectively. The Young's modulus was also degraded by 28.60, 29.71 and 30.57%, respectively. On the other hand, the ductility increases the strain to failure of the samples as shown in Figure 9(c). The increment of the strain to failure was found to be 2.63, 2.81 and 3.27% for the respective ageing time.

Tensile strength based on ageing cycles. The effect of cyclic ageing on the mechanical response of the adhesive was also analysed using dogbone specimens. To achieve this, the ageing time was set to five days,

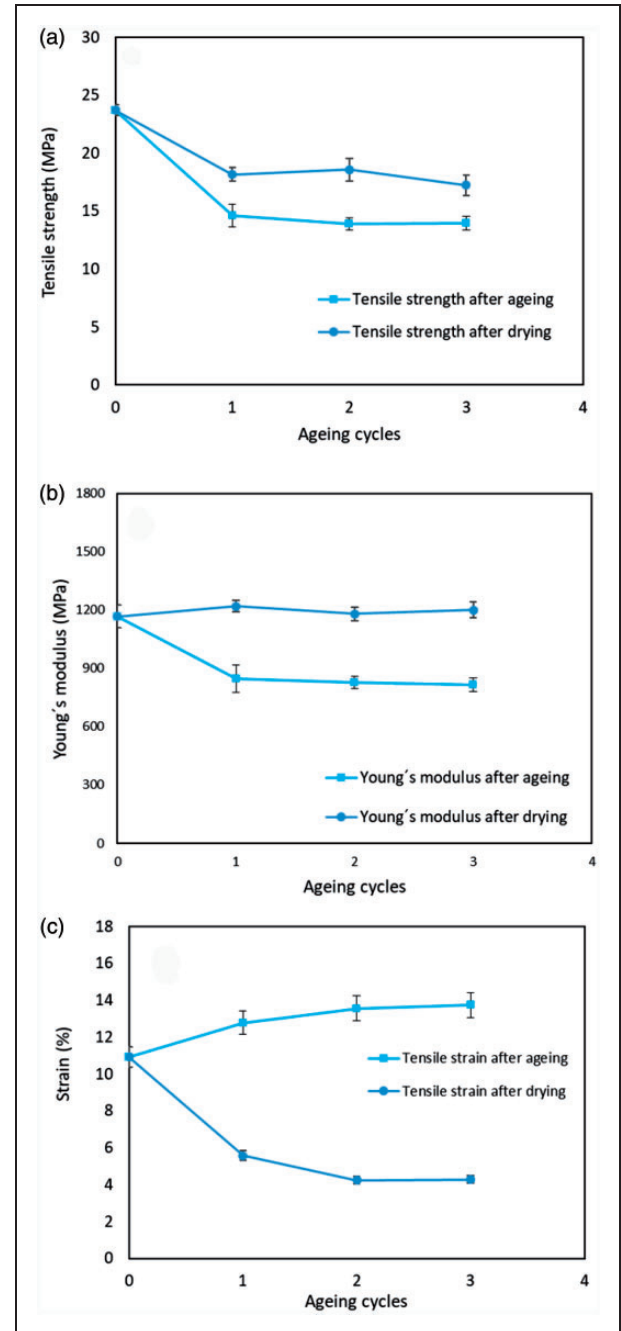


Figure 11. Mechanical properties of epoxy-adhesive after performing cyclic ageing and drying. (a) Tensile strength, (b) Young's modulus and (c) strain at failure.

followed by two days of drying for each cycle. Typical stress–strain curves of the adhesive after cyclic ageing are plotted in Figure 10. The strength, Young's modulus and strain to failure are also shown in Figure 11(a) to (c) respectively. The results of the cyclic ageing showed that the tensile strength and the Young's modulus decrease as the number of cycles increases. The degradation of tensile strength and Young's modulus for the first, second and the third cycles were calculated as 38.28, 41.01 and 42.95%. The Young's modulus degraded by 27.43, 29.07 and 30.14% respectively. The results showed a

non-significant level of degradation between the second and the third cycles for both tensile strength and Young's modulus. In contrast, the strain to failure increases gradually with each subsequent ageing cycle. The increment of the strain to failure was of 1.86, 2.63 and 2.81% for the respective ageing cycles.

Tensile Properties after drying in cyclic ageing. During the drying process, the samples desorb moisture that they have previously absorbed during the ageing process. In this case, the adhesive becomes more brittle and mostly recovers its mechanical properties. Figure 10 shows typical stress–strain curves for drying cycles. The tensile strength, Young's modulus and strain to failure almost entirely recovered for all the three cycles after drying for two days, as shown in Figure 11. Results show that the Young's modulus has increased slightly more than the unaged condition. Based on the results shown in Figure 11, it was

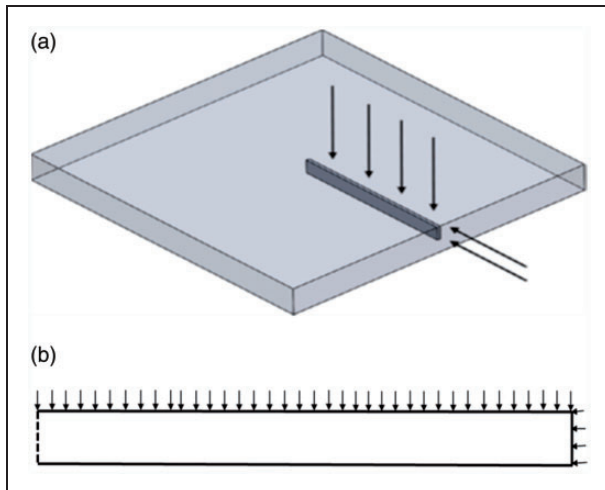


Figure 12. Schematic representation of the 2D model used for determining water uptake in the bulk plate. Arrows indicate the water uptake directions.

found that the strain at failure decreased after the drying process by 5.34, 6.67 and 6.64% for the first, second and the third cycle, respectively, compared to the unaged condition (Figure 11(c)).

Numerical results

Bulk plate. Numerical analysis was conducted on bulk plates and the reduced size dogbone specimens to evaluate the experimentally obtained ageing results and the calculated Fick's law parameters. In the simulation, the D values obtained from the experimental procedures were used. The two-dimensional geometry used for numerical simulation of the bulk plate and the respective boundary conditions are shown in Figure 12. The numerical model and the mesh used are shown in Figure 13.

Figure 14 compares the numerical results with the experimental data, where a good agreement is found. To precisely simulate the ageing process in cyclic ageing conditions, a predefined condition should be defined for the model at each cycle. The predefined value defines the level of water within the sample that remained from the previous cycle. These values are also derived from the experimental data.

Reduced scale dogbone. To determine the ageing level for the sample at each ageing cycle, it is necessary to conduct a numerical simulation based on the data already obtained by ageing the bulk plates. To simulate the dogbone specimens, a 3D model was used (see Figure 15). To reduce the analysis time, only a quarter of the specimen was modelled. The arrows show the directions of water ingress in the adhesive during ageing process, indicated in Figure 15(b).

Figure 16 compares the experiments results, Fick's law predictions and the numerical simulation results. Figure 16 shows that the rate of water absorption increases by ageing cycles. However, no significant difference is observed between the second and third cycles. Based on the results, it can be concluded that for specimens that experience cyclic ageing, a single

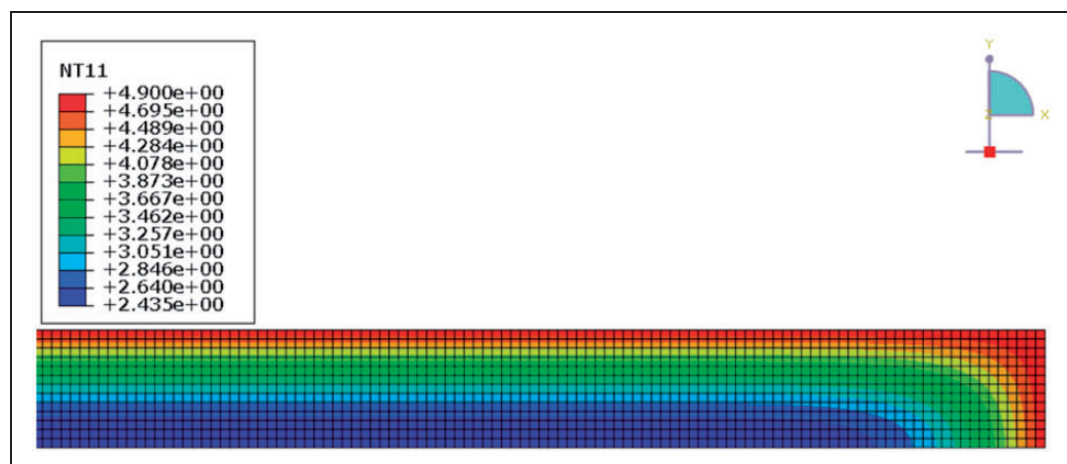


Figure 13. Numerical simulation of bulk plate specimen.

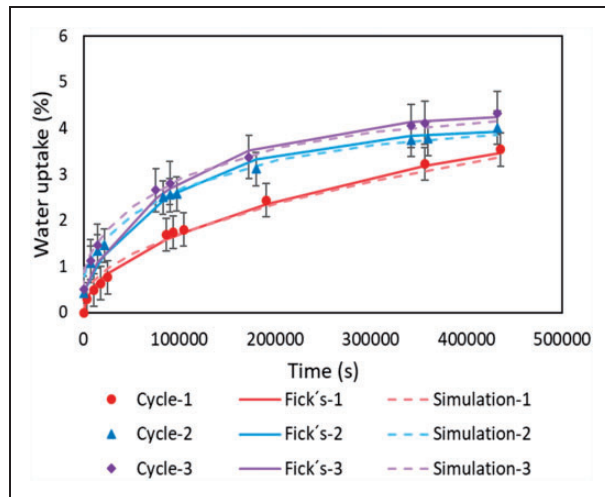


Figure 14. Simulation results of the bulk plate fitted with experimental results.

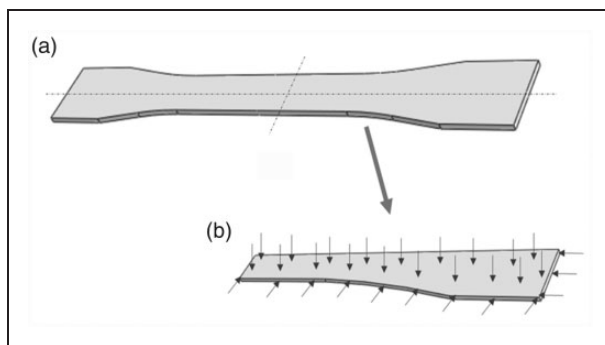


Figure 15. (a) Schematic representation of the 3D model used for determining water uptake in the mini dogbone. (b) Quarter part for simulation. Arrows indicate the water uptake directions.

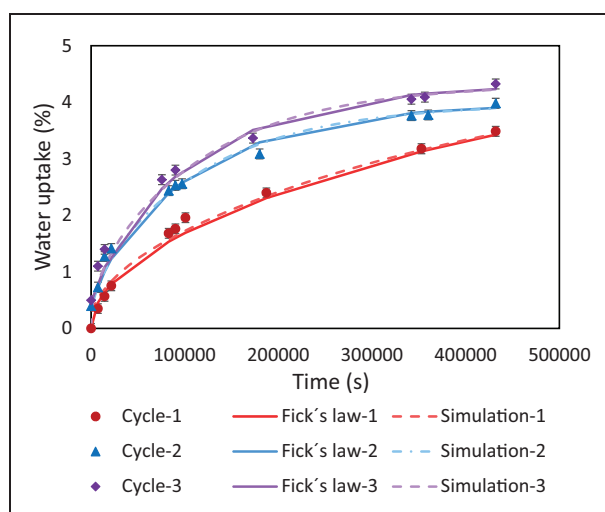


Figure 16. Simulation results of dogbone specimens fitted with experimental results.

cycle ageing analysis will not present a correct estimation of the ageing response of the joint. Based on the results, when the ageing conditions are cyclic, a single cycle analysis of the joint will overestimate the aging life of the specimen.

Conclusions

In this study, the effect of cycling ageing conditions in the diffusion coefficients and the mechanical properties of an epoxy-based adhesive were investigated. To achieve this, bulk plates and dogbone specimens were manufactured. The bulk plates were used to measure the diffusion coefficient for different ageing cycles, while the dogbone specimens were employed to obtain the mechanical properties under cyclic ageing conditions. Based on the obtained results, the following conclusions can be drawn:

- The level of water uptake in the first cycle plays a key role in the rate of water uptake for the subsequent ageing cycles. However, the rates of water uptake for the second and the third cycles were almost similar, regardless of the level of water uptake at the first cycle.
- The tensile test results showed that during the absorption stage, the Young's modulus and the tensile stress decrease significantly.
- The stress–strain results show that during the drying stage, the Young's modulus and the tensile stress are almost fully recovered. However, they do not fully return to their initial conditions.
- Both the Young's modulus and the tensile strength decreased as the number of ageing cycles increased. This was found to be true for all ageing conditions tested.
- The stress–strain results also showed that the strain increases during the absorption process, however, it decreases after the drying process (even less than the initial condition).
- The numerical simulation of bulk plate and dogbone specimens validated the experimentally obtained D values.

Declaration of conflicting interests

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Paper 3

ARTICLE

The influence of interfacial failure on the tensile S–N response of aged Arcan joints

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Abstract

The strength and durability of adhesive joints are significantly influenced by environmental conditions. Humidity absorption can cause deleterious effects on the adhesive joint's performance. The current study investigates the tensile properties of an epoxy-based adhesive using Arcan joints (which is a kind of butt joint) subjected to different aging levels and loading conditions. To this end, joints with different aging times, as well as reference-dried samples, were subjected to both the static and cyclic loading conditions. To construct the S–N curves, different cyclic load levels were applied to the joints. The static results showed that the mechanical properties, such as tensile strength of the joints decreased with an increase of the aging time. The fatigue strength and the fatigue lifetime were significantly decreased by the increase of aging levels, mainly due to an interfacial aging phenomenon. The water diffusion in interfacial aging is faster than that of the adhesive aging, which resulted in a premature failure of the joints for both the static and fatigue conditions. Based on the experimental results, the interfacial diffusion coefficient was calculated using an inverse method. According to the results, the rate of water uptake along the interface is more than 30 times higher than that which occurs in the adhesive.

KEYWORDS

adhesives, ageing, degradation, fatigue, mechanical properties

1 | INTRODUCTION

Adhesive joints are widely used in structural construction in a diverse set of industrial sectors, among which are the aerospace, automotive, railway, marine, electrical, and wind turbine industries. This joining methodology offers many important advantages over the so-called classical joining methods, such as welding, bolting, and riveting. It offers more uniform stress distributions along the bonding area, a low-cost fabrication process, produces higher rigidity, lightweight components, has the ability to bond similar and dissimilar substances, suitable for joining thin sheets.^{1,2} However, one of the crucial weaknesses of

adhesive joints is the sensitivity of the adhesive materials to moisture, leading to a reduction of the joint performance. To analyze the effects of humidity level on adhesive joints, the hygrothermal aging mechanism should be fully understood and replicated under laboratorial conditions. To analyze the degradation of the adhesive's strength induced by absorbed humidity, static tests under mode I and fatigue load condition are usually performed. Both temperature and moisture are known to highly affect the fatigue life and fracture toughness threshold of adhesives with this effect being magnified when exposure to humidity occurs at raised temperatures. Furthermore, the combined effect of hygrothermal aging and fatigue

loading of adhesive joints will cause inevitably premature failure of bonded structures.

In real applications, adhesive joints often encounter several adverse environmental conditions that strongly degrade the adhesives' properties and weaken the adhesive/adherend interface. The following studies show that the reduction of joints strength cannot be avoided when the joints work in the extreme environment for a long period.

An epoxy-based adhesive AW106/HV953 subjected to cyclic aging was investigated by Moazzami et al.³ The results showed that the elastic modulus and the tensile strength of the epoxy adhesive decrease with subsequent aging cycles. Da Costa et al.⁴ investigated the mechanical properties of an epoxy-based adhesive under single cycle and cyclic aging conditions. The authors concluded that the tensile strength and the Young's modulus of the aged adhesive decreases significantly with initial aging cycle, but each subsequent aging cycle was found to have a lower impact on the adhesive properties.

Machado et al.⁵ investigated joints with carbon fiber reinforced polymer (CFRP) and aluminium substrates under hygrothermal aging. The joints tested included similar and dissimilar substrate material combinations. They concluded that the humidity level affects the fatigue performance, driven by a loss of the interfacial strength. The results also showed that the performance of the tested dissimilar joints specimen was better than that of similar substrate materials. Costa et al.⁶ investigated the effects of water on the fatigue behavior by using double cantilever beam of aluminium substrate bonded with XNR 6852-1 and SikaPower 4720 adhesives. They found that the fatigue joint strength and lifetime of adhesive joints decreases by an increase of water content in the joints. Wei et al.⁷ investigated the effect of hygrothermal aging on the Sikaflex[®]-265 adhesive using aluminium alloy butt joints, scarf joints and thick-adherend shear joints. They noticed that the reduction of the joint's strength can be accelerated up by exposing them to humidity at elevated temperatures. The failure mode of the joints was found to change as the aging time increased. The initial shear strength and hygrothermal degradation of adhesive-bonded single lap shear joints were investigated by Zhang et al.⁸ The results showed that at higher temperatures and higher humidity levels the shear strength degraded significantly.

As these works show, the general performance of adhesive joints under-aged conditions has been investigated widely. However, the effects of interfacial aging on the fatigue response of the joints have been poorly studied. Interfacial aging, which can significantly change the fatigue response, cannot be neglected, and needs to be explored. The interfacial failure of bonded joints occurs

with a reduction of the interfacial strength during the aging process. Loh et al.⁹ determined the interfacial strength of epoxy-steel interface, which aged at various moisture uptake levels, finding that the interfacial fracture energy decreases with increasing interfacial moisture levels. Borges et al.¹⁰ reviewed the effects of the moisture and contamination on the interfacial of the adhesive joints. One of the main conclusions of this work is that water absorption can occur through the interface between the adhesive and the substrate or in the cracks and micro voids of the adhesive, which leads to the interfacial failure of the joints.

The aim of this study is to investigate the performance of an epoxy-based adhesive under tensile loading using an Arcan butt joint loaded in pure mode I conditions, considering hygrothermal aging and an interfacial failure mode. The effect of three different aging levels on the mechanical properties of the adhesive was studied. The tensile strength and tensile elongation of the Arcan joint specimens were determined. Fatigue tests at different aging levels for different loading levels were performed using Arcan joints. A numerical analysis was also carried out, considering the diffusion coefficient (D) of the respective adhesive and of the interface. The amount of average water level in the adhesive layer was also accurately determined.

2 | EXPERIMENTAL PROCEDURE

2.1 | Material

A heat curing, solvent free, one component structural epoxy-based adhesive was used to study the effect of aging levels on the mechanical performance of an Arcan joint specimen, loaded under a pure mode I condition. It is a highly viscous paste adhesive of a tough and structural nature, which makes it highly suitable for joining

TABLE 1 Mechanical properties of the adhesive¹¹

Properties	Adhesive
Maximum tensile strength, MPa	31.3 ± 0.6
Maximum tensile strain, %	10.4 ± 0.5
Maximum shear strength, MPa	23.1 ± 0.5
Maximum shear strain, %	43.3 ± 0.9
Young's modulus, MPa	1159 ± 29.3
Shear modulus, MPa	440 ± 8.7
Poisson's ratio, ν	0.35
Viscosity, cps	High, 250 (Pa s)
Density, g/cm ³	1.200

load-bearing structures. The mechanical properties of the adhesive are shown in Table 1.

2.2 | Geometry and manufacturing procedure

Arcan substrates were manufactured from high-strength Al 6082 T651 ($E = 70$ GPa, $\nu = 0.3$). The geometry of the substrates is shown in Figure 1a. The thickness of the substrate is 10 mm.

The Arcan butt joints were manufactured in a specially designed mold, shown in Figure 1b. The thickness of the adhesive layer was set to 0.2 mm. To precisely obtain the desired adhesive layer thickness, a 0.2 mm

thick spacer was used, finely adjusted using the screws shown in Figure 1b. The surface was prepared with an anodization treatment applied to the aluminium substrate before, ensuring good adhesion between the adhesive and the substrate. Aluminium surfaces have been cleaned with acetone to avoid unnecessary substances that contaminate aluminium surfaces during anodizing. Then, the aluminium specimens were immersed in the anodizing solution for 25 min. The anodizing solution consists of 88% by volume of distilled water and 12% by volume of phosphoric acid. The percentage of the anodization solution and the immersion time were set based on the aluminium anodization standard defined in ASTM 3933. After anodization, the substrates were removed from the solution and cleaned with distilled water and

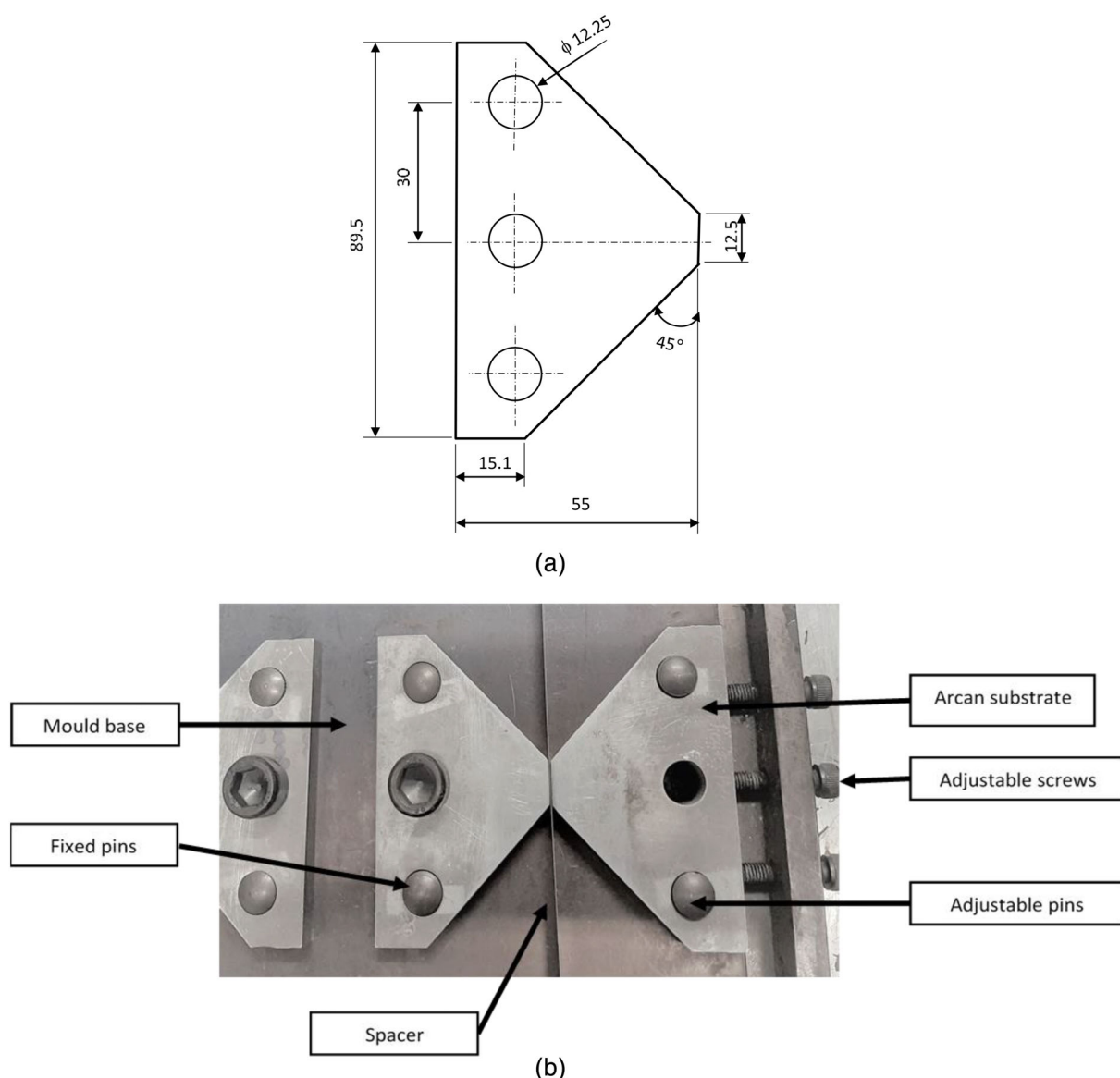


FIGURE 1 Arcan specimen. (a) Arcan substrate (only half is represented) (dimensions in mm), (b) Arcan butt joint manufacturing [Color figure can be viewed at wileyonlinelibrary.com]

acetone. The substrate dried at room temperature about 30 min before joining the samples.

Joints were cured at 177°C for 60 min in a hot plate hydraulic press. Due to the heat curing process, residual stresses will be induced into the adhesive layer. However, since similar substrates were used, the effect of residual strains is negligible.

2.3 | Aging process

After manufacturing the Arcan joints, the samples were kept in a container with silica for at least 2 days. The aim of this process is to remove all moisture that might have been absorbed during the manufacturing process. Subsequently, to conduct the hygrothermal aging procedure, the joints were transferred to a container filled with distilled water. The container was then placed in a controlled temperature chamber, set to 50°C. The absorption rate and the diffusion coefficient of the tested adhesive was already obtained in a previous study, calculated using Fick's law.¹²

2.4 | Testing condition

Initially, Arcan joints were statically tested to evaluate the effects of humidity levels on the Mode I static performance of the adhesive. The static tests were performed at the end of each aging level, after 2, 7, and 14 days passed. The dried specimens were also tested in order to investigate the rate of the recovery of the adhesive properties. Fatigue tests were then conducted using several different load levels, with these levels being determined using data from the static test results. The frequency of loading cycles for fatigue was 10 Hz and the load ratio (the ratio of minimum to maximum load) was set to 0.1. The fatigue tests were also performed for three different aging and drying conditions. Both static and fatigue tests were conducted at room temperature using an Instron 8801

servohydraulic testing machine. The test conditions and the samples for each condition are listed in Table 2.

Using Arcan assembly the load should transfer through several components and connectors to finally reach the adhesive layer. Each part has its stiffness and its elongation during the test. Accordingly, the displacement measured by the machine is not exactly what the adhesive layer experiences during the test. Consequently, strain values obtained using the load line displacement will not be precise. Accordingly, the displacement was reported instead of strain. However, since the load is precisely measured, the average stress can be calculated by dividing the measured load by the bonded area.

The fracture surface of the tested adhesive joints was analyzed to observe the failure mechanism of the unaged, aged, and dried samples. Initially the failure mode of the joints was observed visually. However, for a detailed analysis and to measure the area with adhesive failure mechanism a high-resolution Nikon DX VR (AF-P NIKKOR 18–55 mm 1:3.5–5.6G) camera was used.

2.5 | Fourier transform infrared spectroscopy

Fourier transform infrared (FTIR) analysis was considered to determine the effects of moisture on the chemical structures of the tested adhesive. The unaged, aged, and dried samples were considered in this analysis. To this end, the specimens were experimentally aged in water for 2, 7, and 14 days, following each by a 2 days drying process. Unaged, aged, and dried samples then were tested. After joint failure, a small portion of the adhesive layer taken from the failure surface was used for the FTIR analysis. The FTIR analysis was performed using a PerkinElmer Spectrum Two Machine (Waltham, MA). The range of the wavelength was set to 4000–500 cm^{−1} with a scanning velocity of 0.2 cm^{−1}. These explanations were added to the text (Section 2.6).

Static		Fatigue	
Aging time (day)	Aging conditions	Aging time (day)	Aging conditions
0	Unaged	0	Unaged
2	Aged	2	Aged
7		7	
14		14	
2	Dried	2	Dried
7	For 2 days	7	For 2 days
14	After aging	14	After aging

TABLE 2 Static and fatigue test conditions

2.6 | Numerical simulations

The simulation process was conducted to investigate the average water amount in the adhesive layer and to determine the interfacial water diffusion coefficients using an inverse method. To simulate the water absorption process of the Arcan joint, a 3D Arcan joint model was created using Abaqus. The water diffusion in the adhesive is calculated based on the heat transfer analogy. Accordingly, the nodal temperature was interpreted as the level of water uptake at each node and the conductivity was set to correspond to the diffusion coefficient (D) obtained experimentally in a previous research¹² using the Fick's law. By knowing the area of the interfacial failure region, an interfacial diffusion coefficient was also calculated with the numerical model, based on an inverse approach.

For the diffusion analysis Linear hexahedral elements (DC3D8), that is an eight-node heat transfer brick, was employed to the adhesive layer. Elements with the same width and length sizes of 0.1 mm were considered while along the thickness the element size of 0.05 mm was used. Total nodes and elements were 63,630 and 50,000 for the adhesive layer, respectively. In water diffusion analysis, only the adhesive layer is simulated. A heat transfer analogy with uniform distribution of hygrothermal conductivity was considered where the temperature of 13.49°C that is exactly the level of water uptake at saturation conditions for the bulk sample was set at the boundaries of the joint (see Figure 7). The adhesive material was considered as isotropic. The water uptake level was analyzed by measuring the nodal temperatures.

For the stress analysis simulation, the both the substrates and the adhesive layer were modeled where C3D8T and C3D8R elements were used for the adhesive layer and the for the Arcan substrates, respectively. C3D8T is an eight-node thermally coupled brick, trilinear displacement and temperature element while the C3D8R is an eight-node linear brick reduced integration element. Different material points within the adhesive layer experience different aging levels and consequently different properties should be assigned to each material point. The properties of the adhesive elements as a function of the aging level was already obtained and reported in Reference 12. The same properties were considered in the current study.

3 | RESULTS AND DISCUSSIONS

3.1 | Static strength

Static tests were carried out for both the aged and dried joints. A total of six samples were used for each testing

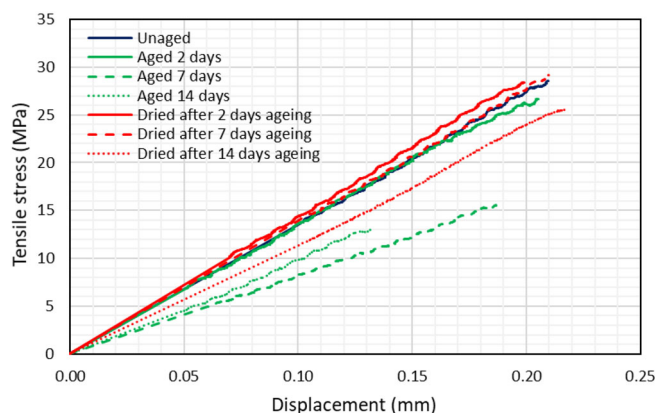


FIGURE 2 Typical stress and displacement curves [Color figure can be viewed at wileyonlinelibrary.com]

condition. The typical stress-displacement curves obtained during these tests are presented in Figure 2. Based on the testing results shown in Figure 2, it was found that the average strength of the unaged samples is 31.3 ± 4.3 MPa, while for the aged samples it decreases to 25.8 ± 0.9 , 15.9 ± 2.9 , and 11.72 ± 4.35 MPa after 2, 7, and 14 days aging, respectively. Accordingly, the percentage of reduction of the strength of the aged samples was found to be 17.67%, 49.61%, and 62.70%, when compared to the unaged samples. The reduction of the joint strength was mainly driven by the occurrence of failure in interfacial bonding during the aging process. The reduction of the bonded area that supports the external load and the stress concentration created at the interface by the aging process also contributed to the degradation of the joint performance. Furthermore, the postdrying results showed that while most of the adhesive strength is recovered in the drying process, there is not a complete recovery. The strength of the dried samples recovered to 27.8 ± 4.4 , 26.7 ± 2.5 , and 25.7 ± 1.4 MPa as shown in Figure 3.

The existence of the water at the interface degrades the adhesion level between the adhesive and the substrate, weakening the joint performance. It can also cause interfacial failure, which can drastically reduce the joint strength. However, during the drying process, the water content at the adhesive layer drained off and the strength of the adhesive was partially recovered as shown in Figure 3. Water is absorbed through two different mechanisms. The first is a physical process where the water occupies free spaces in the adhesive. The second mechanism is a chemical phenomenon in which the water molecules are bound to the polymer chains. In the desorption process, the water which has occupied the free spaces will evaporate. In these conditions, part of the adhesive properties that have been degraded due to the

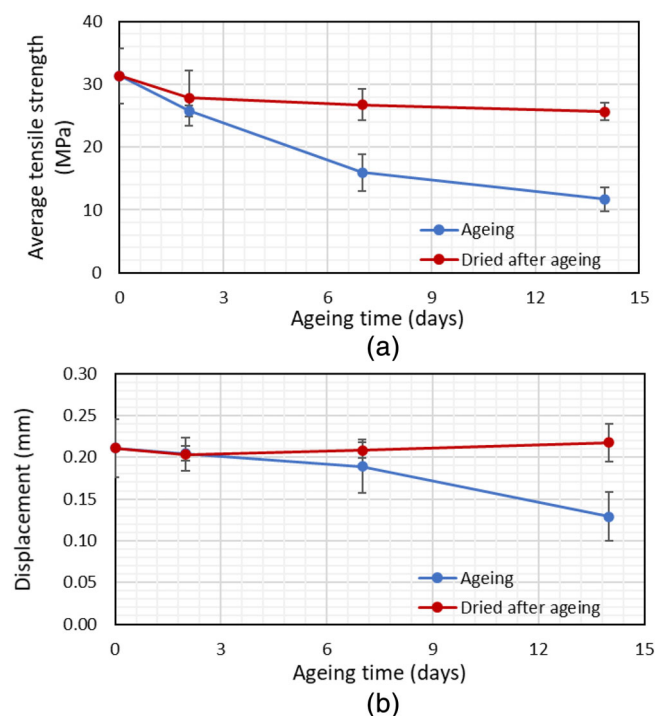


FIGURE 3 Mechanical properties of the Arcan joints as a function of aging time. (a) Tensile strength. (b) Displacement [Color figure can be viewed at wileyonlinelibrary.com]

physical aging will be recovered after drying. However, degradation due to the chemical aging is a permanent phenomenon and will not be recovered after drying.

Figure 3a presents the average tensile strength as a function of the aging time. It can be observed that the joints experience a first a higher rate of degradation in terms of strength followed by a lower degradation rate. The strength again increases after the drying process. According to Figure 3a the effect of drying for joints exposed to aged conditions for a long time is more significant than the joints that have been aged for a shorter time. Figure 3b shows the average tensile displacement against the aging time. For the studied adhesive, aging causes a reduction in the displacement of the adhesive at failure. Based on the results, the higher the aging time the higher the reduction is in the joint displaced. This reduction is more pronounced for longer aging times.

3.2 | Fatigue test results

Fatigue tests were conducted at different load levels for each aging condition, as shown in Table 2. The results of these tests were used to construct the stress-life (S-N) curves as shown in Figure 4. Different aging times resulted in different amounts of water content in the

adhesive layer that ultimately led to the degradation of the fatigue life of the tested adhesive.

The percentage of the reduction in the fatigue strength for 2 days aged was found to be 30.7% of the static load. While the percentage of the reduction of the fatigue strength for 7 and 14 days aging are 50.0% and 67.8%, respectively. These results show that the aging process can drastically reduce the fatigue endurance limit of the tested joints.

The idea behind this study is to experimentally understand the roles of adhesive aging level and interfacial aging mechanisms in the fatigue life of adhesive joints. To this end, different aging times (2, 7, and 14 days) were initially defined. However, according to Figure 4, it was found that after 14 days of aging, the fatigue endurance limit of the joints drops drastically, which in practice means that the aged joint does not support most of the applied fatigue loads. From the industrial point of view, the tested bonded joint must be replaced after 14 days of aging. Consequently, in this study, the aging time was not increased above 14 days.

After the aging process was completed, samples subjected to 2 and 14 days aging were dried. Results showed that the fatigue life of the adhesive after drying is mainly recovered specially for samples aged for a shorter time. To verify if this massive drop in durability was mainly due to aging, a fracture surface analysis was conducted, the results of which are presented in the next section.

3.3 | Fracture surface analysis

Static fracture surfaces

The fracture surface of the unaged samples tested statically showed a cohesive mode of failure (see Figure 5). The fracture surface for aged and dried specimens under static condition showed a mixed failure mode, for both the wet and dried surfaces. The interfacial failure occurred by the degradation of the bonding strength at the interface near the bond edges. The degradation process was affected by the changes in the properties of the adhesive during the water absorption process. However, the center of the joints was less affected by the aging process. Despite the high rate of water uptake at the interface, the aging time is not sufficiently long to cause significant degradation of the adhesion level at the center of the joint. After the drying process is completed, the fracture surface mainly returns to the cohesive failure mode. However, a small region at overlap edges still remains where the failure mode is adhesive in nature. Therefore, the fracture surface of the dried specimens is

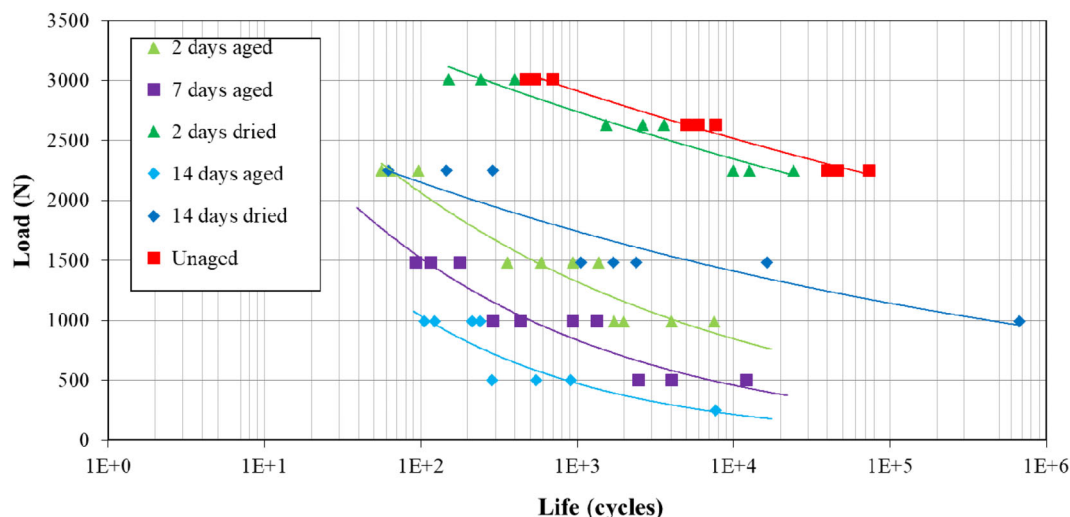


FIGURE 4 Fatigue life of aged, dried, and unaged of Arcan joints for tensile loading conditions [Color figure can be viewed at wileyonlinelibrary.com]

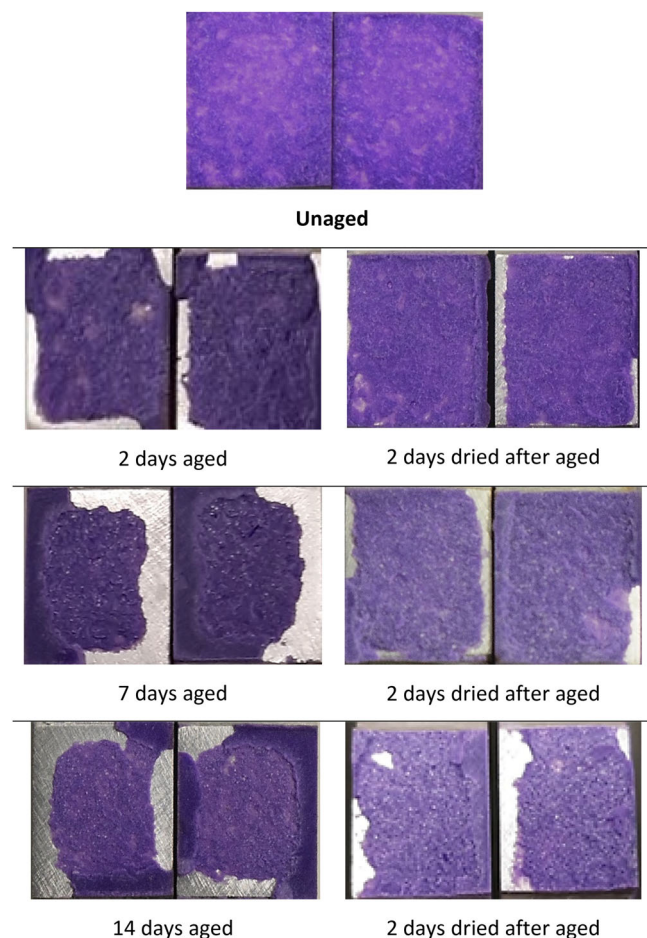


FIGURE 5 Failure surface of statically tested Arcan joints for aged, dried, and unaged conditions [Color figure can be viewed at wileyonlinelibrary.com]

not completely recovered to cohesive failure, as shown in Figure 5, which results in the loss of bonding strength.

Fatigue fracture surfaces

The failure surface of the joints subjected to fatigue loading conditions showed that for the unaged samples, the failure mode is of the cohesive type. However, for the aged samples, mixed failure is found. In the aging process, the water absorption occurs not only through the adhesive, but also through the interface between the adhesive and the substrate. The rate of water ingress at the interface is faster causing a significant adhesion degradation, leading to interfacial failure at the edges of the overlap. After the drying process is fully completed, the area of where cohesive failure occurs increases but there is no full recovery to a complete cohesive failure (see Figure 6).

3.4 | Numerical analysis

Fick's law analysis

To investigate the water content in the adhesive layer of the joint, and to calculate the rate of water diffusion through the interface, a numerical analysis was carried out. A relationship between heat transfer and fluid flow was explored in the simulation, where thermal conductivity, thermal diffusivity, and the heat capacity were set to represent the permeability, diffusion, and solubility coefficients, respectively. The nodal temperature of the elements was interpreted as the nodal humidity level.

The objective of the analysis is to predict the average amount of the water content in the adhesive layer during the aging process. The D value used in this simulation was already obtained in a previous study conducted by the same authors.¹² The obtained D was used to simulate the water diffusion in a bulk adhesive in order to confirm

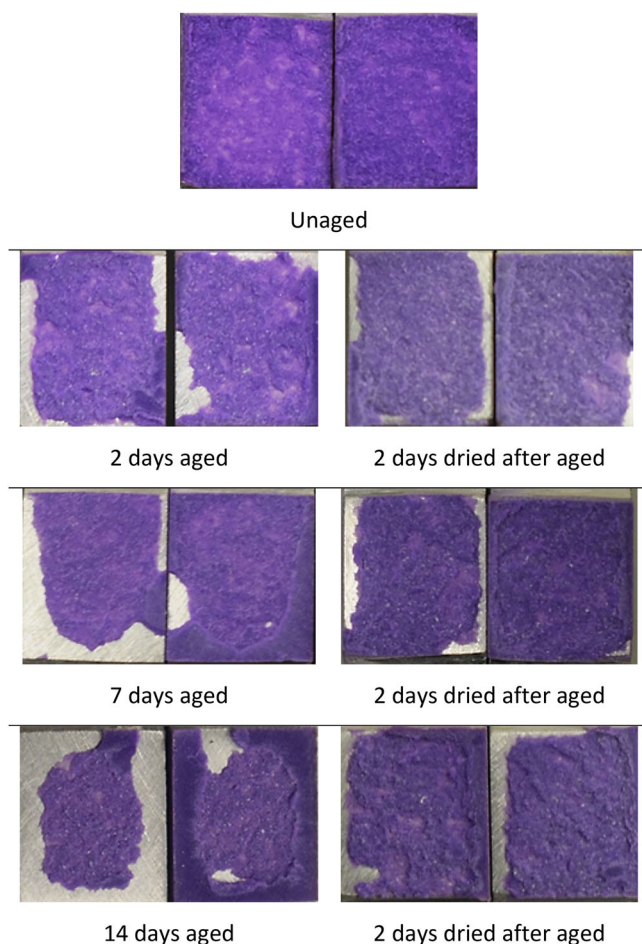


FIGURE 6 Failure surfaces of fatigue tested joints for aged, dried, and unaged Arcan joints [Color figure can be viewed at wileyonlinelibrary.com]

the experimentally obtained D value. The results of the Fick's law and the simulation matched each other, which means that the Fick's law works for the studied adhesive. According to this analysis, the average amount of water uptake for 2, 7, and 14 days of aging of the Arcan joints were 1.32%, 2.18%, and 2.82%, respectively. The boundary condition of the adhesive is shown in Figure 7b. For the bulk plate tested in Reference 12, the average amounts of water uptake at the same aging times were 3.69%, 4.77%, and 5.81%, respectively (see Figure 7a).

The dimension of the adhesive layer is equal to the overlap size shown in Figure 1. As explained in Section 2.6, a heat transfer analogy with uniform distribution of hygrothermal conductivity was conducted where the temperature of 13.49°C was set at the boundary conditions. 13.49°C is exactly the level of water uptake at saturation conditions (13.49 wt%) for the bulk sample. Figure 7c shows the water diffusion in the adhesive layer.

In addition to the prediction of the average amount of water absorbed in the adhesive layer, the progression of

the water diffusion through the adhesive layer was also analyzed. The water uptake distance for different aging levels is shown in Figure 8a,b. The distance of water absorption along the overlap length is listed in the Table 3. However, considering these results will overestimate the joint strength since the rate of water diffusion through the interface is much higher than in the bulk adhesive, as interfacial aging is the main failure mechanism of the tested joints. Interfacial aging is simulated in the next section.

Interfacial aging

Experimental testing has demonstrated that the water absorption at the interface is faster than that of the bulk adhesive layer. In an aging phenomenon, the water absorption can simultaneously weaken the adhesive strength and the level of adhesion at the interface, both of which cause a reduction of the joint strength. An inverse method was followed to calculate the interfacial diffusion coefficient. To this end, a thin layer of elements at the interface of the adhesive and adherend was considered, with an arbitrary D value. The value of D was iteratively adjusted until a level of interfacial aging matching the experiments was obtained. This procedure was followed for joints with different aging levels (2, 7, and 14 days aging). Almost similar interfacial D values were obtained for these three different aging conditions, and the reported interfacial D is the average of the obtained interfacial D values (see Table 3). A comparison of the water ingress through the adhesive and along the interface is shown in Figure 8. These results show that the rate of water uptake through the interface is more than 30 times higher than that which occurs through the bulk adhesive layer. The average interfacial D value was then used to simulate the aging process at the interface of Arcan joints (see Figure 9). As shown in Figure 10, a good agreement between the experimental and numerical results was observed.

A visual comparison of the progress of adhesive and interfacial aging is shown in Figure 9, where the blue color represents no absorbed water content, and the red color represents a fully saturated adhesive or interface.

The reduction of the bonded area with respective aging time is presented in Figure 10a. It is observed that the bonded area of the joint greatly decreases, causing a serious degradation of the joint performance. To calculate the effective bonded area, the following equation was used:

$$A_{\text{eff}} = A_I - A_f, \quad (1)$$

where, A_{eff} is the effective area, A_I is the initial area, and A_f is the interfacial failure area of the Arcan joint. The interfacial failure area (A_f) is the area of adhesive failure

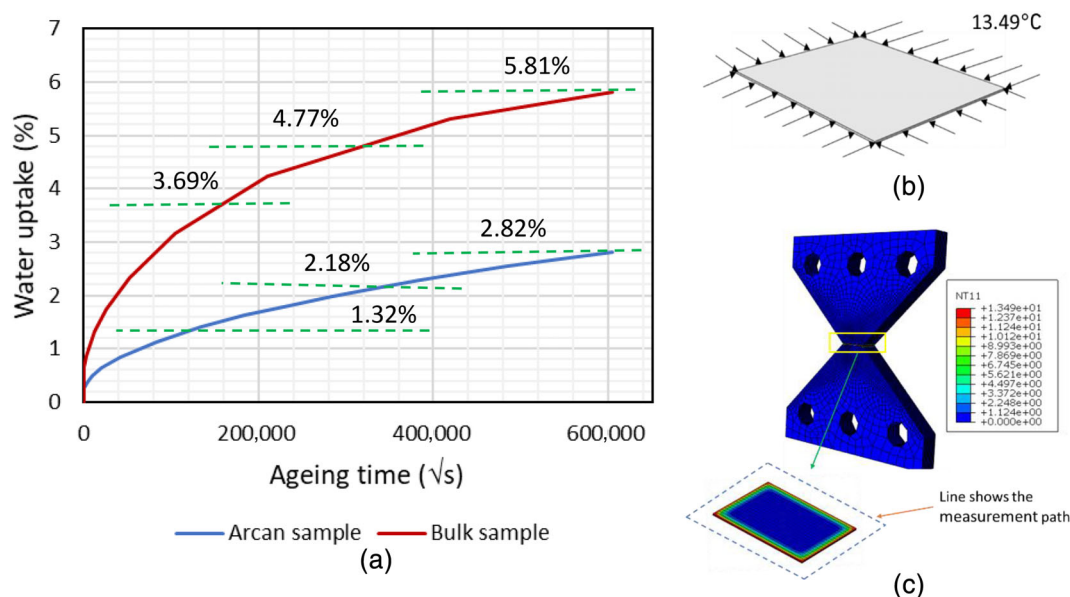


FIGURE 7 Average of the water uptake in the bulk plate¹² and the Arcan joint for 14 days aging. (a) Water uptake level, (b) boundary conditions, and (c) aging diffusion model [Color figure can be viewed at wileyonlinelibrary.com]

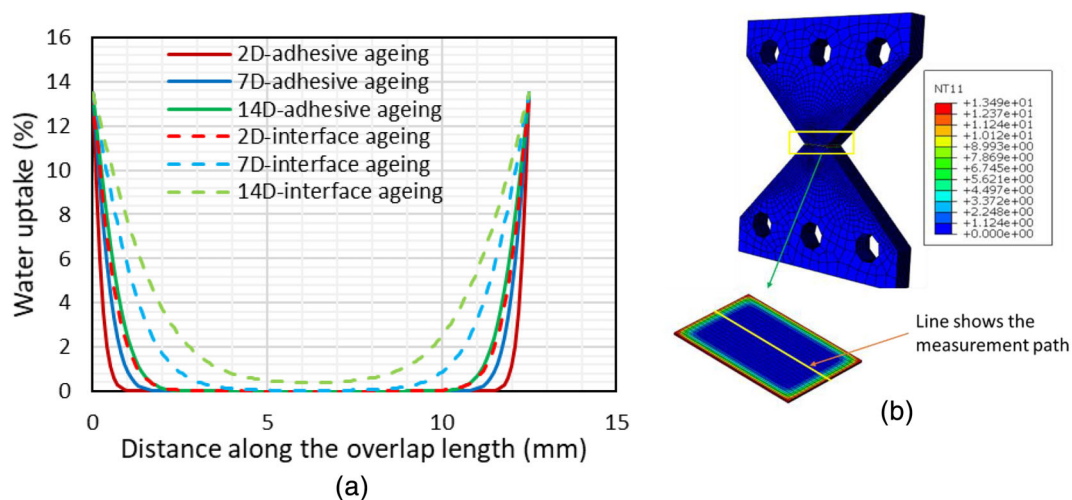


FIGURE 8 Water absorption along the overlap length. (a) Comparison of adhesive and interfacial aging. (b) Aging model [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 3 The aged distance along the overlap length of adhesive and interfacial aging

Distance along the overlap length (mm)					
Aging time	Adhesive simulation (mm)	Experimental (mm)	Interfacial simulation (mm)	D (adhesive) (m^2s^{-1})	D (interfacial) (m^2s^{-1})
2 days	0.5	1.2	1.24	2.34E-07	7.30E-06
7 days	0.9	2.3	2.33		
14 days	1.3	3.3	3.65		

on fracture surfaces. As shown in Figures 5 and 6 and by considering the numerical results shown in Figure 9, the effective area (considered to be the area with cohesive

failure at the center of the overlap) can be simplified as a rectangle. It is noted that the edges of the cohesive failure rectangle at the center of the overlap are not regular,

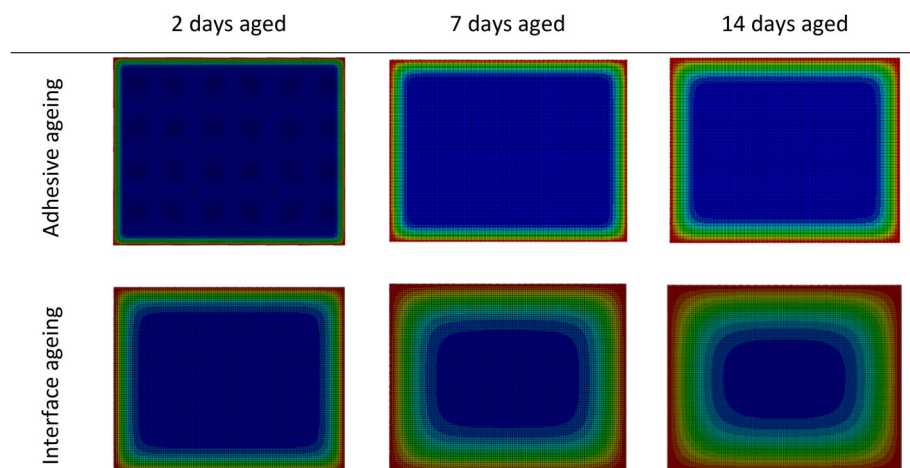


FIGURE 9 Comparison of the adhesive and interface aging surface [Color figure can be viewed at wileyonlinelibrary.com]

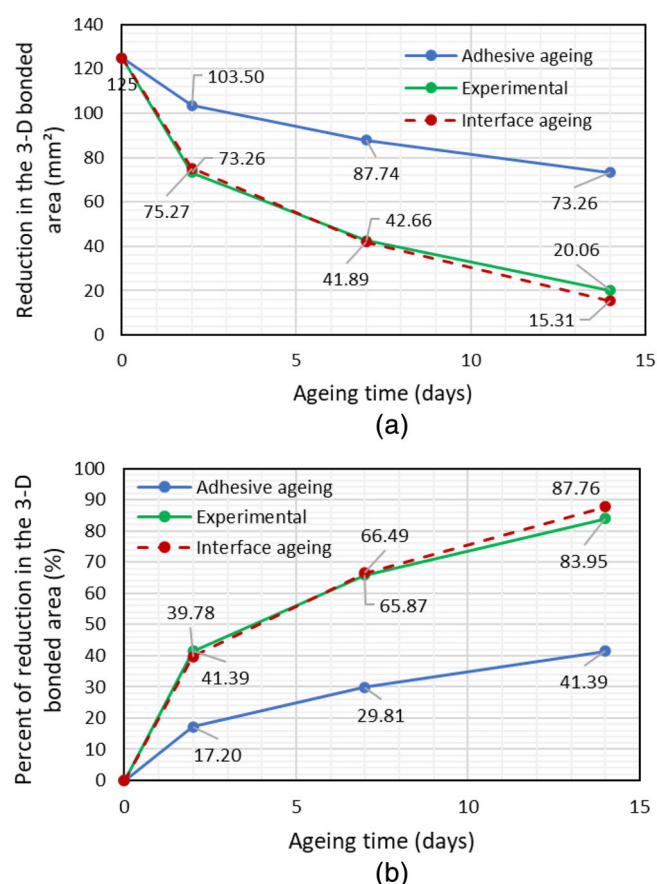


FIGURE 10 The reduction of the bonded area as a function of aging time. (a) Reduction of the bonded area. (b) Percentage of the reduction of bonded area [Color figure can be viewed at wileyonlinelibrary.com]

therefore a precise measurement is difficult to attain. Accordingly, the adhesive surface region can be obtained by measuring the distance between the overlap edges and the edged of this rectangle using calipers.

The percentage reduction in the bonded area is presented in Figure 10b, calculated using the equation shown below.

$$\text{Percent of reduction} = \frac{A_I - A_{\text{eff}}}{A_I} \times 100\%. \quad (2)$$

Stress distributions of the Arcan joints

For further assessment of the effect of moisture on the joint performance, a stress analysis was conducted on the aged and unaged samples. This analysis concerns not only the degradation of the properties of the adhesive but also the reduction in the bonded area, the cause of a significant drop in the endurance limit of the aged adhesive joints. Accordingly, stress analysis was conducted on 3D Arcan models for different aging conditions and the stress distribution along the overlap was analyzed. It is a rough stress analysis just to give an idea about the stress levels in aged and unaged joints to show that the adhesive layer will be subjected to a higher stress level and consequently will experience a lower fatigue life due to the interfacial aging. However, for a more precise analysis, the properties of the material at a nodal level should be defined as a function of the aging level.

As shown in Figure 11, the stress level significantly increases in aged joints due the aforementioned reduction in bonded area, which creates a stress concentration in the corner shown in Figure 11a. It can be observed that the stress concentration at the corner increases for longer aging times. This increase in stress level can drastically reduce the durability of the bonded joints subjected to cyclic loading.

Stress intensity factors at the interface

The degradation of the adhesive in the Arcan joints can be affected by three distinct phenomena. Two of these reasons (the loss of adhesive properties and degradation of the interface) were already discussed in detail in the previous section. The third reason, much less discussed in the literature, is the increase in the bimaterial stress

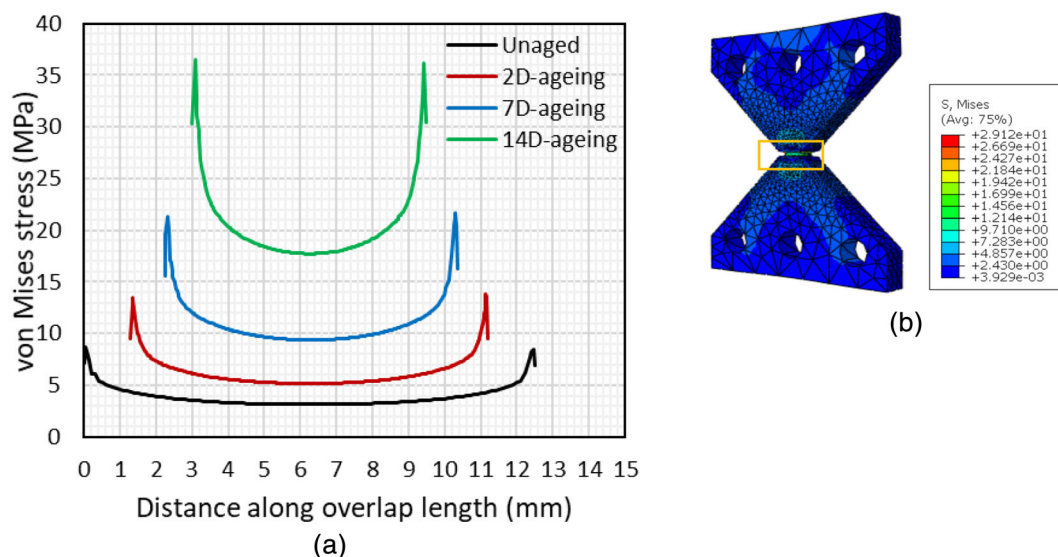


FIGURE 11 Stress distribution along the overlap length. (a) Stress distribution of different aging time. (b) 3-D Arcan joint model [Color figure can be viewed at wileyonlinelibrary.com]

intensity factor. Due to the interfacial aging and reduction in bonded area, the interfacial bonding angle after aging reduces as shown in Figure 12. The bimaterial bonded angle before aging is 135° as shown in Figure 12a. However, it decreases to 90° after interfacial aging is completed as shown in Figure 12b. On a microscopic scale, some deviations might be found from the considered angles, but even with considering these deviations, the bimaterial angle after aging decreases. A decrease in the bimaterial angle can significantly alter the stress intensity factor at the interface,^{13,14} and consequently, alter the stress gradient within the adhesive layer. This phenomenon was considered as the third reason for the significant drop in fatigue life of aged samples.

3.5 | Fourier transform infrared spectroscopy

The presence of the water in the adhesive joint affected considerably the performance of the tested samples. After drying, some samples were able to fully recover their performance to the initial unaged condition but for the joints aged for 14 days the drying process was not that helpful. To better understand the reasons behind these results, the chemical structure of the unaged, aged and dried samples was analyzed using FTIR.

The range of the FTIR spectrum under analysis was between 4000 and 500 wavenumber cm^{-1} as shown in Figure 13. The key aspect of this analysis is identifying the single band area, which contains hydrogen bonds. In fact, the absorption band in the range of 3650 and

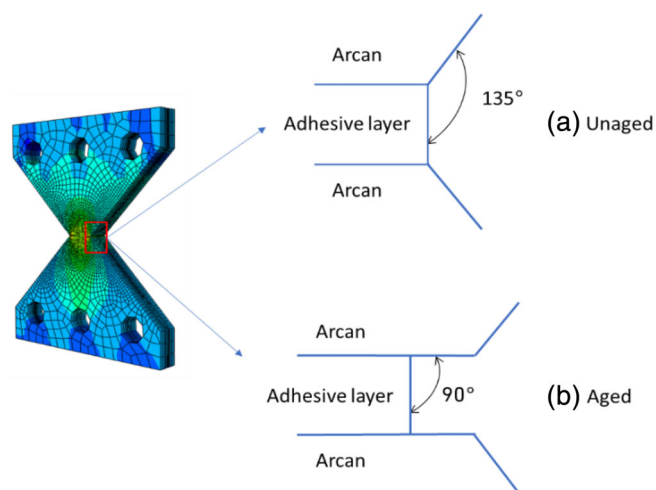


FIGURE 12 The comparison of the joint angle of the sample. (a) Unaged. (b) Aged [Color figure can be viewed at wileyonlinelibrary.com]

3250 cm^{-1} indicates a hydrogen bond, representing the existence of water (H_2O), Hydroxyl ($-\text{OH}$), and ammonium or amine in the analyzed adhesive. Figure 13a, compare the FTIR results of the aged, unaged, and dried samples. Since the level of water uptake at the edges of the overlap is generally different from that verified at the center of the joint, two different samples were analyzed. One was picked from the corner formed at the edge (see Figure 13b) of the overlap of the joints and the other one was extracted from the center of the overlap (see Figure 13d).

An extensive analysis of the results indicated that the spectra are almost similar, showing no significant

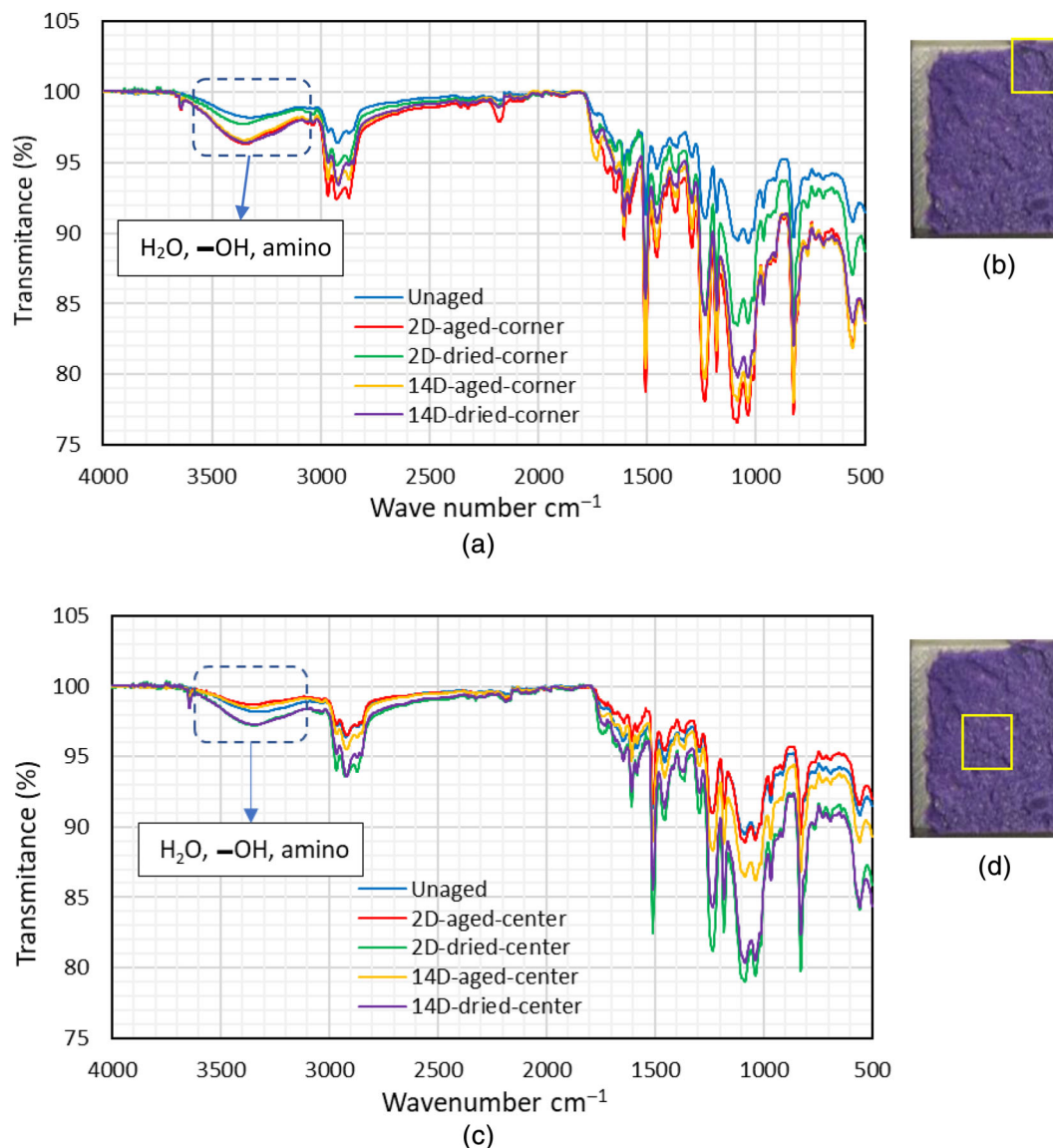


FIGURE 13 FTIR spectrum in the range of the wave numbers of 4000–500 cm^{-1} for unaged, aged, and dried samples. (a) and (b) at the corner, (c) and (d) at the center [Color figure can be viewed at wileyonlinelibrary.com]

changes in the chemical structure of the adhesive caused by the hygrothermal aging processes.^{15–17} However, some differences can still be found for the spectrum of H_2O , $-\text{OH}$, and amine absorption groups. This group decreases due to the drying of the samples and increases for the aged conditions. For the dried group, the spectrum is almost similar to the unaged condition, however the spectrum for the joints aged for 14 days and then dried for 2 days, is still higher than the other dried samples. This can be explained by the fact that H_2O and $-\text{OH}$ still exist in the adhesive in this sample, which is in accordance with the fatigue results shown in Figure 4 where the drying process could not fully recover the fatigue properties of the joints aged for 14 days.

As discussed in the introduction, there are only a few studies on the influence of aging on the S–N behavior of adhesive joints. All published results confirm that the aging conditions can significantly reduce the fatigue behavior of the bonded joints even for a short exposure time as also shown in the current work. However, the results of the current study show that the fatigue life deterioration rate of the tested Arcan joints is much higher than that obtained by other authors. Mu et al.¹⁸ investigated the influence of humidity on the fatigue behavior of CFRP/aluminium butt joints. Cohesive failure mode was observed in the compounds tested by them. Their results showed that aging for 15 days can reduce the fatigue life of the tested specimens almost by a factor of 10. However, for the current study, the fatigue

results shown in Figure 4 showed that 14 days of aging reduced the infinite life of the Arcan samples to around 100 cycles life where the fatigue load was 1000 N. This is a drastic reduction in the durability of the considered adhesive joints compared to other studies. Another study was done by Machado et al.⁵ They carried out cyclic load tests on aged, unaged, and dried single lap bonded joints. Based on their reported S–N results, the lifespan of the tested SLJ was again reduced by a factor of almost 10.

There are several reasons for the difference in the fatigue results obtained in this study and what has been reported in the mentioned works. Taking the failure mechanisms into account, it turns out that interfacial aging is the main cause of the deterioration in the durability of the Arcan samples tested. A severe interfacial aging is much worse than the adhesive aging. Severe interfacial aging can lead to an adhesive failure especially at overlapping edges. As mentioned earlier, interfacial aging reduces the quality of adhesion between adhesive and substrate, can lead to adhesive failure leading to a reduction in the effective bonding area which results in an increase in the stress level within the adhesive layer. It also increases the stress intensity factor at the interface region. All these parameters cause a big reduction in durability of the bonded joints. Another possible reason is the materials. The aging behavior of different adhesives is different. Using an adhesive less sensitive to the aging can increase the durability of the bonded joints against the wet environments. Some parameters, such as surface treatment, can also influence the results especially for the interfacial aging condition. Another possible reason behind the different degradation rates is the loading mode. A pure mode I loading condition was considered in this study while for example for the work of Machado et al.⁵ SLJs with complex mixed mode loading conditions were tested. However, the effects of the interaction of the stress mode and the aging level on the fatigue life of adhesive joints requires further studies.

4 | CONCLUSIONS

The effects of adhesive and interfacial aging on the tensile S–N behavior of a structural epoxy-based adhesive were analyzed using Arcan butt joints subjected to tensile cyclic loads. Fatigue tests were conducted on unaged samples, aged joints (at different aging levels) and dried specimens (dried after aging). Fatigue tests were conducted at different load levels in order to construct the S–N curves. Fracture surface assessments and FTIR analysis were also performed to support the fatigue results.

The presence of the moisture in the adhesive significantly affected the mechanical properties of the joints. Although to reach a full saturation condition the joint needs to be aged for more than 312 days, however, results showed that a much shorter aging time can significantly reduce the durability of the bonded joints. One main reason behind this phenomenon is the water diffusion through the interface. The experimental results and the numerical model showed that the rate of water diffusion along the interface is more than 30 times higher than that of the bulk adhesive layer. The FTIR results showed that although the drying process reduces the level of water uptake, the adhesive layer of joints aged for 14 days still contains some amounts of water, which causes a significant degradation in the tensile S–N response of Arcan joints. According to the results, it was also shown that a short-term drying process (2 days in this study) can lead to a significant recovery in the mechanical properties of the joint specially for joints that are aged for a long time.

It was found that a short aging time can drastically reduce the fatigue life of the joints. There are several factors that contribute to the durability degradation of the aged joints. First, water absorption degrades the adhesive properties, a common mechanism reported by several authors. This process results in the degradation of the static strength and consequently reduces the fatigue life of the aged joints. Second, the interfacial strength of the tested specimens is significantly reduced. This phenomenon results in a significant reduction in the effective overlap area, increases the stress level and consequently decreases the fatigue life of the aged samples. Importantly, the effective area did not completely recover even after drying the samples. Lastly, it was found that the reduction in the bimaterial angle caused by the reduction of the effective overlap increases the stress concentration at the interface, representing a third strength damaging mechanism.

DATA AVAILABILITY STATEMENT

No. Research data are not shared.

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Paper 4

Effects of ageing frequency on the interfacial failure and tensile properties of adhesively bonded Arcan joints exposed to cyclic ageing environments

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Abstract

The strength and durability of adhesive joints are significantly influenced by environmental conditions. When working in a humid environment, the adhesive tends to absorb moisture and this phenomenon can drastically reduce the mechanical performance of the adhesive joints. In practice, joints are usually subjected to cyclic ageing due to moisture absorption and desorption. Accordingly, it is necessary to study the ageing behaviour of the adhesives when they are exposed to environments with cyclic humidity conditions. Accordingly, the current study investigates the mechanical properties of adhesive joints with an epoxy-based adhesive subjected to cyclic ageing conditions using Arcan joint specimens. To this aim, static tensile tests were performed for both cyclic aged, dried, and unaged Arcan joints. The effect of cyclic ageing and drying conditions, such as absorption and desorption mechanisms, on the mechanical properties of the joints were studied. In the numerical part, an experimentally obtained diffusion coefficient (D) was used to simulate the water diffusion in Arcan joint. The results showed that key mechanical properties, such as tensile strength and displacement of the joints are reduced by the number of ageing cycles. The maximum strength degradation of the aged joints compared to the unaged condition was 94% for the third ageing cycle. For the dried condition, the strength of the joints was recovered although it was not fully returned to the initial stage. It was also found that the recovery ratio increases with the ageing cycles. It is shown that a short drying process can significantly recover the mechanical response of the cyclically aged adhesive joints, especially at higher ageing cycles.

Keywords

Adhesive, Arcan joints, cyclic ageing, interfacial, diffusion coefficient

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Introduction

Adhesive bonding has many advantages over conventional joining techniques such as welding, fastening, and riveting. It offers more uniform stress distributions along the bonded area, and generally a lower manufacturing cost (although a long curing time may increase the total expenses). Adhesive joining technique is also able to bond similar and dissimilar materials and able to joint thinner sheets, facilitating the development of lightweight components. Adhesive joints are widely used in aerospace, automotive, railway, marine, and electrical industries, allowing to create multi-material structures with excellent strength to weight-ratios.^{1,2} Although adhesive joints offer many advantages, their usage is also beset with some drawbacks. One of these limitations is related to the water absorption of the adhesives in wet environments and its negative effect on joint strength, a problem that is still not completely explored and

addressed. To investigate the effects of humidity level on adhesive joints, a hygrothermal ageing process should be carried out.^{3–7} To study the effects of humidity on the degradation of an adhesive joint's strength, some authors have conducted static tests on aged samples.^{8–10} Hygrothermal ageing can drastically affect the quality of the joints and lead to a failure.¹¹ By increasing the ageing time the strength of the joints decreased

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significantly from 31.32 MPa for unaged joints to about 11.72 MPa after 14 days ageing.¹² Furthermore, susceptibility to delamination failure is also increased with water absorption in composites and adhesives.¹³ However, other studies have shown that the degradation of the joint's performance is actually negligible when the joint is working in extreme environment conditions for long periods of time.^{14,15} To investigate the reduction in joint's properties, diverse works have been carried out hygrothermal ageing processes on joint level specimens. The durability of the single lap joints (SLJ), scarf joints (SJ), and butt joints (BJ), bonded with Sikaflex -265, was studied under cyclic hydrothermal conditions experimentally by Qin et al.¹⁶ They found that the composition, glass transition (T_g), melting temperature (T_m), and thermal stability of adhesive undergo changes after cyclic hydrothermal ageing. The water diffusion coefficient, the strength and stiffness of nanocomposite adhesives under water absorption, desorption and resorption using bulk samples were experimentally studied by Khoramishad et al.¹⁷ They revealed that by desorption of the aged samples, part of the reduction in strength can be recovered. Furthermore, rewetting of the specimens resulted in additional water absorption and material degradation at a much higher rate. The absorption and desorption effects in single lap adhesive joints using single part epoxide adhesive FM73 and Al 2024T3 aluminium substrate were studied by Mubashar et al.¹⁸ The results of this work showed that while the strength of the joint drastically decreased when aged in water at temperature 50°C, it is almost completely recovered when the water is desorbed.

The effects of cyclic ageing on different parameters such as the rate of moisture absorption and desorption, the stress and strain curve, and glass transition temperature (T_g) have been studied using an epoxy based adhesive (AW106/HV953) in bulk form by Moazzami et al.¹⁹ Their results suggest that key mechanical properties such as tensile strength and elastic modulus at the saturation level decrease with an increasing number of ageing cycles. The hygrothermal ageing cycles effects were studied under single lap joint (SLJ) using ISR 70-08. It is a polyurethane adhesive which is commonly used in automotive glazing works.²⁰ They concluded that the hygrothermal ageing drastically changes the failure strength of the adhesive joints. However, the failure displacement increases with the number of ageing cycles. Moreover, the hygrothermal ageing process changes the failure surface from cohesive failure in the unaged adhesive layer to an interfacial failure for aged adhesive joints.

The effect of cyclic moisture absorption and desorption on the strength of epoxy adhesive joints at the ageing temperature 23°C was investigated by Houjou et al.²¹ leading to the conclusion that the strength of the lap joint was not significantly damaged by the respective ageing conditions.

The effects of the cyclic ageing on the tensile properties of an epoxy based adhesive under temperature 50°C

were investigated by da Costa et al.,²² finding that Young's modulus and the tensile strength of the adhesive both decrease significantly after the first cycle. All subsequent ageing cycles have considerably less influence on the mechanical properties of the adhesive. The influence of hygrothermal cyclic ageing of the tensile properties of single lap adhesive joints was studied using ductile and brittle adhesives and aluminium 6082-T6 substrates by Hirulkar et al.²³ They reported that the failure load and the ultimate strain drastically reduced at the higher hygrothermal ageing temperature.

As shown in the literature discussed above, although the effect of water absorption and cyclic ageing conditions have already been considered by a limited set of authors, the influence of cyclic ageing on the interface of adhesive and substrates has not yet been the target of study. Accordingly, the aim of this study is to investigate the interfacial performance of aluminium substrates bonded with an epoxy-based adhesive under tensile static loading and cyclic ageing conditions. To achieve this Arcan specimens were used and the effect of three different ageing cycles on the mechanical properties of the adhesive was analysed. The tensile strength and tensile elongation of the Arcan joint specimens were determined under mode I loading conditions. It should be noted that in real practise (e.g. automotive and marine industries), bonded joints are usually exposed to cyclical environments where they experience cyclic water absorption and desorption phenomenon. Based on the results already shown by da Costa et al.²² the rate of water uptake changes as a function of the ageing cycle and is different from the typical continuous ageing procedure. Accordingly, it is important to consider the cyclic ageing conditions in experiments to estimate the mechanical response of such bonded joints more precisely.

A numerical analysis was also performed, considering the D of the respective adhesive and of the interface. The rate of water absorption in adhesives is shown by D (the diffusion coefficient parameter). D is determined by measuring the amount of water absorbed by the adhesive bulk plate of a given size, using the gravimetric approach and based on the Fick's law. A higher D value means a faster moisture uptake for a given ageing time. The average water content in the adhesive layer was also precisely determined. The mechanical property degradation of the tested adhesive is a function of the amount of water it absorbs. Accordingly, it is important to know how much water the adhesive has absorbed after a certain ageing time.

Experimental method

Material

A one-component structural epoxy-based adhesive was used in this study. The adhesive is heat curing, solvent free with high viscosity that can be considered as a paste. It is a tough and structural adhesive which is

suitable for the manufacture of load-bearing structures. The tensile strength and Young's modulus of the epoxy-based adhesive are 31.3 MPa and 1159 MPa, respectively.²⁴ The substrates were machined from the high strength Al 6082T651 ($E = 70$ GPa, $\nu = 0.3$) alloy. The geometry of the Arcan specimen is shown in Figure 1(a). The thickness of the substrate is 10 mm.

Joint manufacturing

To manufacture an Arcan joint, a special mould was designed and used, as shown in Figure 1(b). A metal shim with 0.2 mm thickness was used to accurately control the adhesive thickness, ensuring that is constantly set to 0.2 mm. The spacer was adjusted using the positioning screws shown in Figure 1(b). The aluminium substrates were pre-treated using fine sandpaper followed by an acetone cleaning to remove the residues. A phosphoric acid anodising (PAA) process was used as a surface treatment, applied to the bonding surface of the aluminium substrates before bonding. After adhesive application, the joints were cured at 177°C for 60 min in a hot plate press.

Ageing plan

Before the ageing process was performed, the Arcan joints were kept in a container with silica for at least 2 days, allowing to remove any moisture that may have been absorbed during the manufacturing process.

The ageing process of the Arcan joints was carried out in a container placed in an environmental chamber, set to a temperature of 50°C (see Figure 2(a)). The diffusion coefficients of the adhesive were obtained in the previous study,²⁵ dispensing the need to study the diffusion in the bulk adhesive. To study the effects of the humidity level of the aged adhesive, Joints were subjected to two different ageing frequencies (2- and 14-days), and each for three ageing cycles.

The ageing cycles diagram for 2 and 14 days are shown in Figure 2(b) and (c) respectively. At the end of each ageing cycle, the samples were tested under static load. For some samples, the drying process was also performed after the ageing (see Figure 2) to investigate the characteristics of the adhesive when the water is drained off the adhesive layer. The dried samples were also tested in parallel with the aged samples at the end of the cycles. According to the previously published

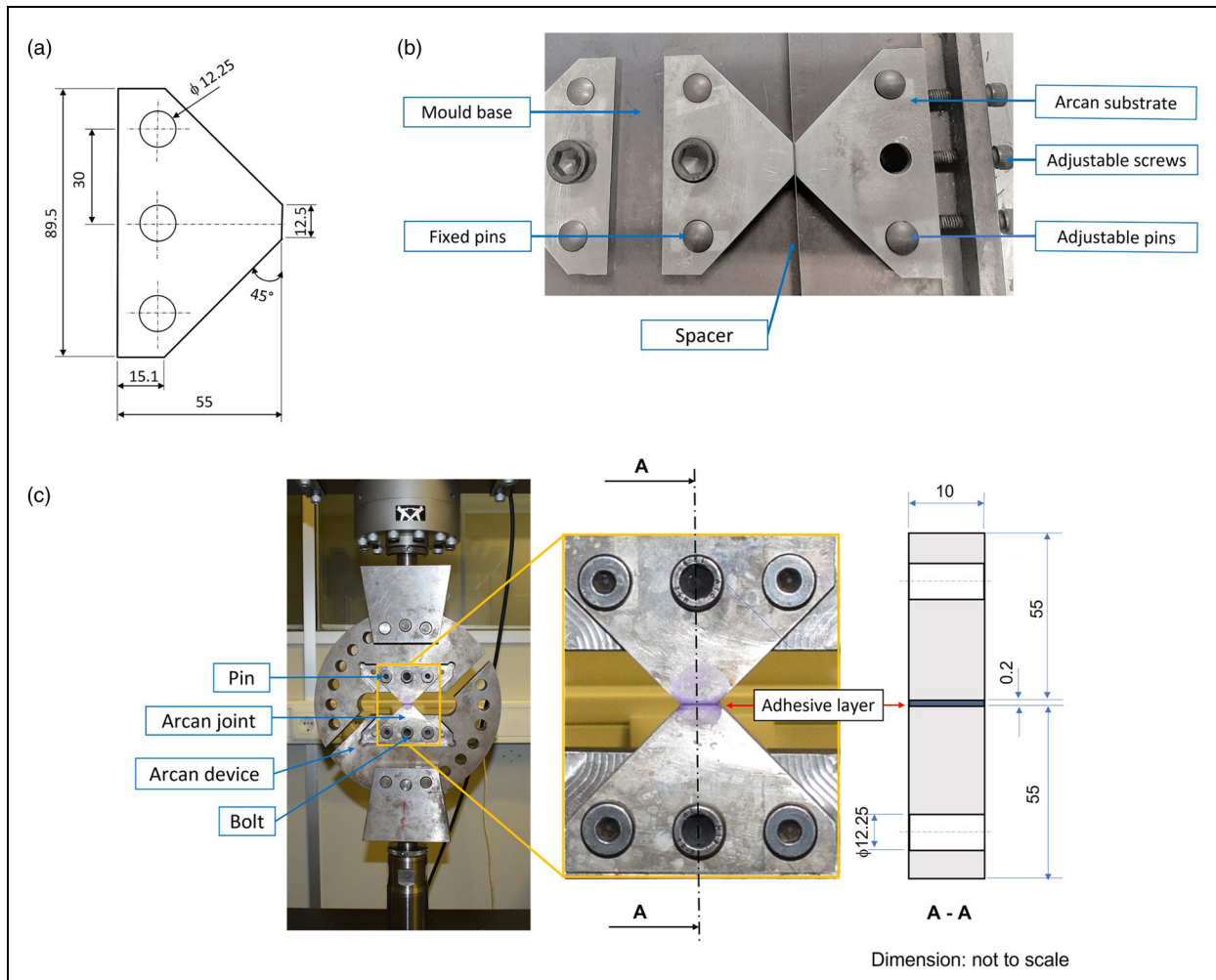


Figure 1. Arcan specimen. (a) Arcan substrate (dimensions in mm), (b) Arcan joint manufacturing, and (c) Arcan joint testing device.

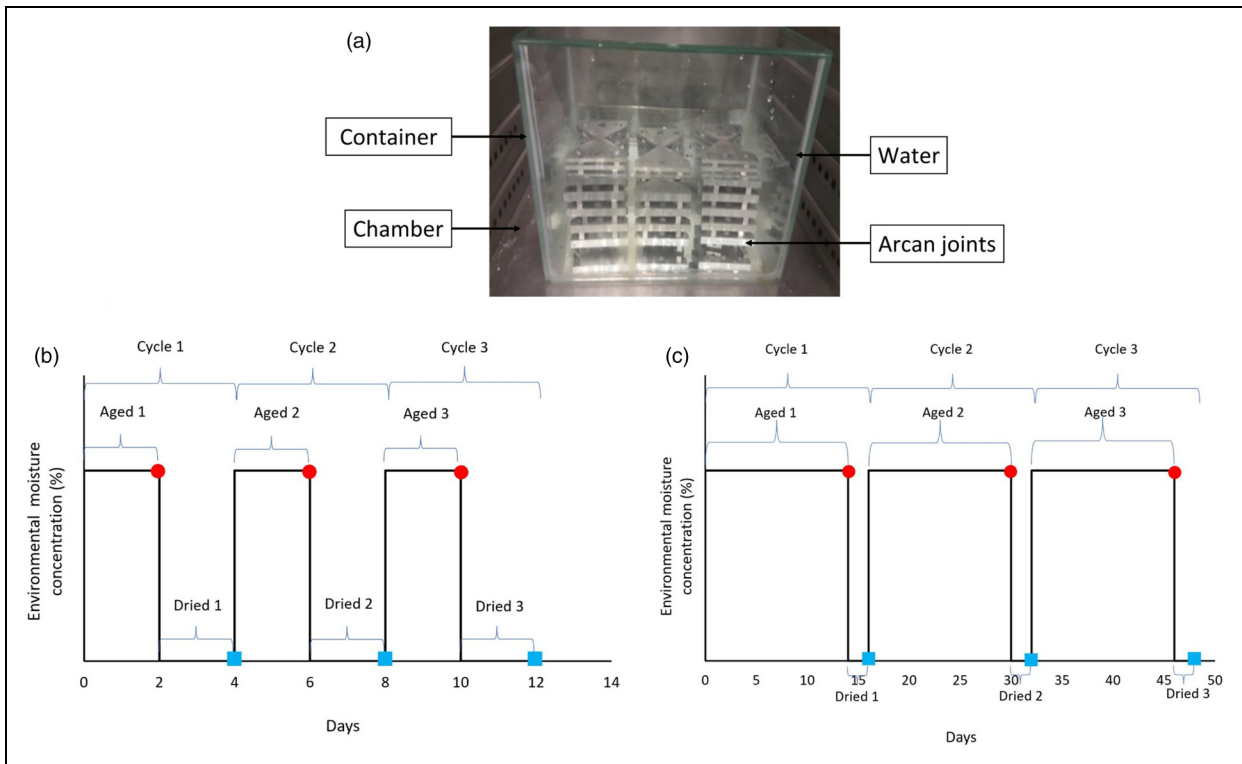


Figure 2. Ageing. (a) Arcan joint ageing, (b) 2 days ageing cycles, and (c) 14 days ageing cycles.

results,¹² it can be shown that the hygrothermal ageing of the joints for 14 days can significantly change the failure mode from cohesive failure (for unaged condition) to the mainly adhesive failure mode (after 14 days ageing). Based on the results after 14 days ageing, the joint can be considered as a dead joint due to the significant drop in its mechanical properties. Accordingly, in the current study, the ageing frequency was ranged from unaged to 14 days ageing.

Test procedure

The Arcan joints were statically tested to evaluate the effects of humidity levels on the mode I static performance of the Arcan joints. Tensile tests were conducted for both the aged and dried samples at different ageing/drying cycles. Six samples were tested for each condition. Static tests were performed at the end of each ageing cycle, after 2 and 14 days. The static tests were conducted in three different cycles (cycle 1, 2, and 3) for both the aged and dried samples. The term “aged” here means that the joint was tested immediately after it was taken out of the water. “Dried” here means that after taking the samples out of the water the joints were exposed to a dried condition for two days and then they were tested. The term “unaged” in this study corresponds to the reference joints that have not experienced any ageing condition.

The dried specimens were also tested in order to compare the recoverability of the adhesive joint behaviour. Static tests were conducted using an Instron 8801

servo-hydraulic testing machine, operating at room temperature conditions. The test device and an Arcan joint sample are shown in Figure 1(c). The test conditions and the samples for each condition are shown in Table 1.

Numerical simulation

To investigate the amount of average water uptake in the adhesive layer of Arcan joints, a 3D Arcan joint simulation process was conducted using Abaqus software. Since the water uptake can be predicted using the diffusion coefficient of the respective adhesive, the interfacial water diffusion coefficient can be isolated and determined. In this simulation, a heat transfer analogy was used to calculate the water diffusion in the adhesive joint. The water uptake level at each node corresponds to the nodal temperature. In this analysis, the conductivity is replaced by the value of D which was obtained experimentally in a previous research work,²⁵ using the Fick’s law.

Based on the interfacial failure area observed from the experimental results, the interfacial diffusion coefficient was also calculated following the finite element method (FEM) by using an inverse approach.

To analyse water diffusion in Arcan joints, linear hexahedral (DC3D8) elements were used which are eight-node heat transfer brick elements. The elements have a uniform mesh size of 0.1 mm in length and width directions, while the thickness of the element was set to 0.05 mm. The applied boundary conditions

Table 1. Static test conditions.

Ageing condition	Ageing frequency (days)	Cycle No.	Total ageing time (days)
Unaged	0	0	0
Aged samples	2	1	2
		2	4
		3	6
	14	1	14
		2	28
		3	42
Dried samples	2	1	2
		2	4
		3	6
	14	1	14
		2	28
		3	42

were based on the heat transfer analogy with a uniform distribution of hygrothermal conductivity and with a magnitude of 13.49% which is equal to the saturation level of water uptake. For the stress analysis simulation, both the substrate and the adhesive layer were modelled with C3D8T and C3D8R elements, respectively. C3D8T is an eight-node thermally coupled brick, trilinear displacement, and temperature element while the C3D8R is an eight-node linear brick reduced integration element. The material properties at different water uptake levels were defined in the material properties section in Abaqus as temperature dependent data. The degradation of the material properties as a function of the water uptake level was already obtained in.¹² To couple the diffusion analysis and the static analysis, the elements were defined by using the couple temperature-displacement elements.

Results and discussions

Stress-displacement curves of joints after cyclic ageing

It can be observed that the mechanical properties of the joints decreased at each ageing cycle. Based on the load-displacement curve, it was found that the average failure load of the unaged joints is 31.32 ± 4.4 MPa. The results showed that this value decreases by around 55% and 94% after 3 ageing cycles for 2 days and 14 days ageing cycles, respectively. It can be observed that the degradation of the mechanical properties is not only based on the number of cycles, but it also depends strongly on the ageing frequency. Critical degradation of the mechanical properties occurred at the second and third cycles of 14 days ageing, a finding which can have important applications when designing joints that will operate in cycling ageing conditions.

Comparisons of the stress and displacement of the respective cyclic ageing are presented in Figure 3. During the drying process, the water drains off the

interface after a sufficient drying time has passed and the water absorption path created in the previous ageing cycle remains free. Thus, when the specimen is exposed to the following ageing cycle, the water can more rapidly occupy this empty space created at the interface. The water level at the interface significantly affects the adhesion quality between the adhesive and the substrate, resulting in a reduction in the joint strength.

The results presented in Figure 3, show that the strength of the joints is mostly recovered after a drying process. However, according to the results, the strength recovery is in fact a function of the ageing cycles. For example, the maximum strength recovery after drying was around 89% (compared to the strength of the unaged joint) at the first ageing cycle for the joints subjected to the 2-days ageing frequency process while for the second and third drying cycles strength was recovered up to 74% and 57%, respectively. The results of the drying process for joints subjected to 14-days ageing frequency showed a smaller amount of strength recovery after drying. The strength of the dried samples after 14 days ageing, was recovered to 82% at the first cycle, and to 63%, and 40% for the second and third cycles, respectively. Accordingly, it was found that the rate of strength recovery significantly decreases by the ageing cycle and also by increasing the ageing frequency.

The reduction of the strength was affected by the moisture in the adhesive layer and at the interface. The existence of moisture in the joints contributed to the deterioration of the interfacial bonding during the cyclic ageing process.

Joint stiffness, defined as the ratio of the applied load to the obtained displacement, also decreased in relation to the ageing cycles. However, as shown in Figure 3(c) it actually increases when the drying process is applied. The maximum stiffness reduction of the joints compared to the unaged joints, was found to be 84.93% at the third cycle of 14 days ageing plan.

The effects of cyclic ageing on the fracture surface of the joints

Hygrothermal cyclic ageing significantly affected the bonding strength of the adhesive joint. While the fracture surface of the unaged specimens showed cohesive failure, after cyclic ageing conditions, the failure surface starts to exhibit mixed failure (both the cohesive and interfacial) for the 2 days cyclic ageing and full interfacial failure for the 14 days cyclic ageing conditions. There are three distinct failure mechanisms present in the Arcan joints subjected to tensile loadings and exposed to 2- and 14-days cyclic ageing conditions. The first failure mode is a cohesive failure, observed in unaged joints. The second failure mechanism is the mixed adhesive/cohesive failure, observed for the joints subjected to ageing cycles. In these joints the overlap edges experienced mostly interfacial failure while cohesive failure was observed at the centre of the bonded area. However, by increasing the

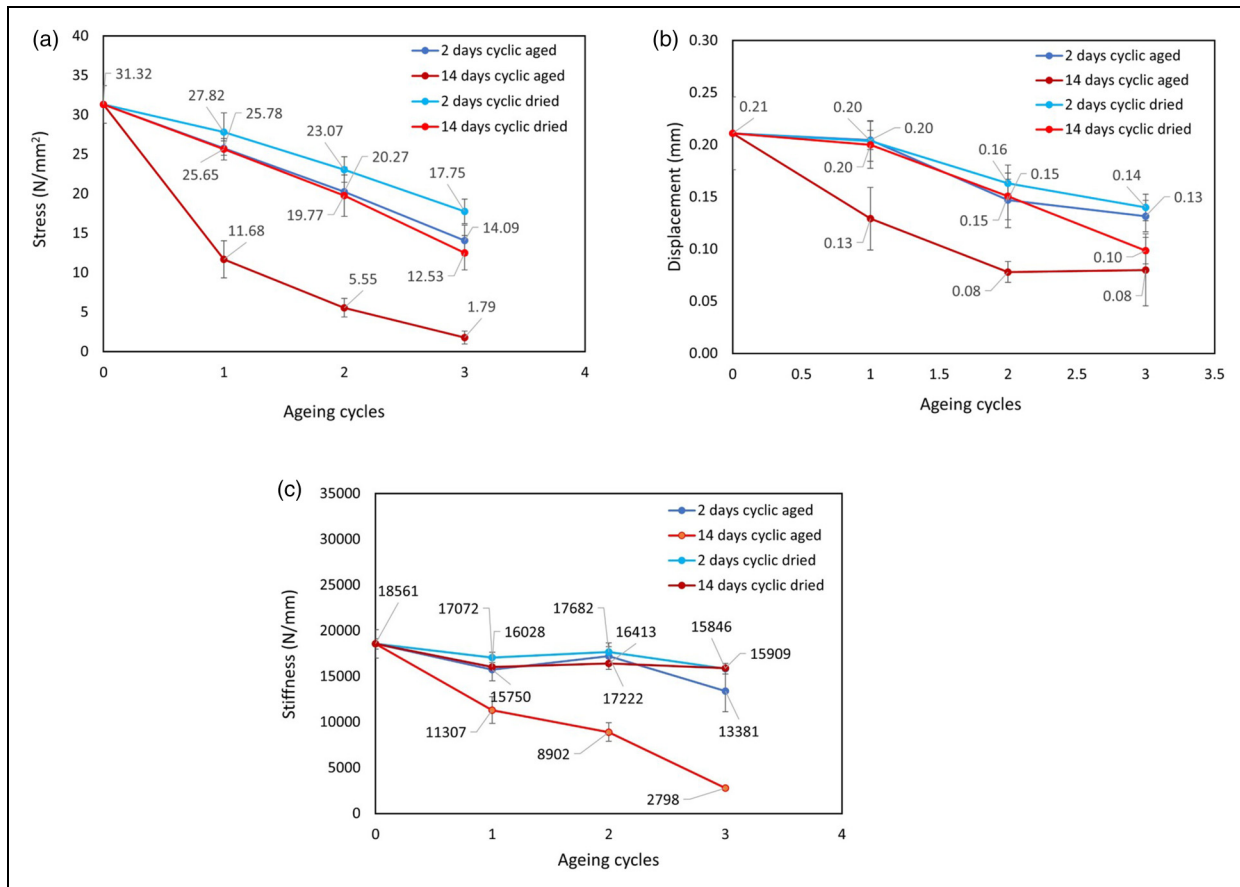


Figure 3. The reduction of the mechanical properties of the adhesive joints as a function of ageing cycles. (a) Stress, (b) Displacement and (c) Stiffness.

ageing cycle and ageing frequency the joint experienced a complete adhesive failure. For joints subjected to three ageing cycles, with an ageing frequency of 14 days, full adhesive failure was observed. Examples of the different failure mechanisms are shown in Figure 4.

Figure 4 shows that the effective bonded area of the joint decreases with ageing cycles for both the 2- and 14-days ageing frequency. The effective bonded area for 2 days of cyclic ageing was found to be approximately 73 mm² and 40 mm² and 18 mm² for the second and third cycle. The approximation of the effective bonded area for 14 days of ageing was found to be as low as 20 mm² for the first cycle and 2 mm² and 0 (zero) for the second and the third cycles, respectively. For the third cycle of the 14 days aged joints, the effective bonded area was reduced to zero because at this stage, the interface was fully saturated and led to full adhesive failure. It was noted that the adhesive failure on the interface was measured as a reference to determine the diffusion coefficient of the interfacial ageing.

Fourier-transform infrared spectroscopy (FTIR) analysis

In the drying process, joints subjected to 2 days ageing mostly recovered to the initial condition. However, for

14 days of ageing this did not occur. To better understand this discrepancy, FTIR analysis was conducted to precisely characterise the influence of the water on the chemical structure of the joints. The range of the considered FTIR spectra was between 4000–500 wavenumber cm⁻¹, as shown in Figure 5. Hydrogen bonds can be found in the wavenumber range of 3650 and 3250 cm⁻¹, indicating the presence of water (H₂O, Hydroxyl (-OH)) and ammonium or amine in the adhesive layer.

According to the FTIR results, no significant chemical change was found in the tested joints. The differences found in the H₂O, -OH and amine absorption group, mostly reflect the variation of the level of water uptake during the absorption and desorption processes. Based on the results, one can conclude that water still exists in the adhesive layer after the drying process, especially for joints subjected to the higher ageing cycle frequencies.

Numerical results

A numerical model was developed using Abaqus software in order to predict the average water absorption and water absorption distance in the adhesive layer of an Arcan joint. In this model, an analogy between heat transfer and fluid flow was explored. The water diffusion into the adhesive layer, the thermal conductivity, thermal diffusivity, and heat capacity were set as permeability,

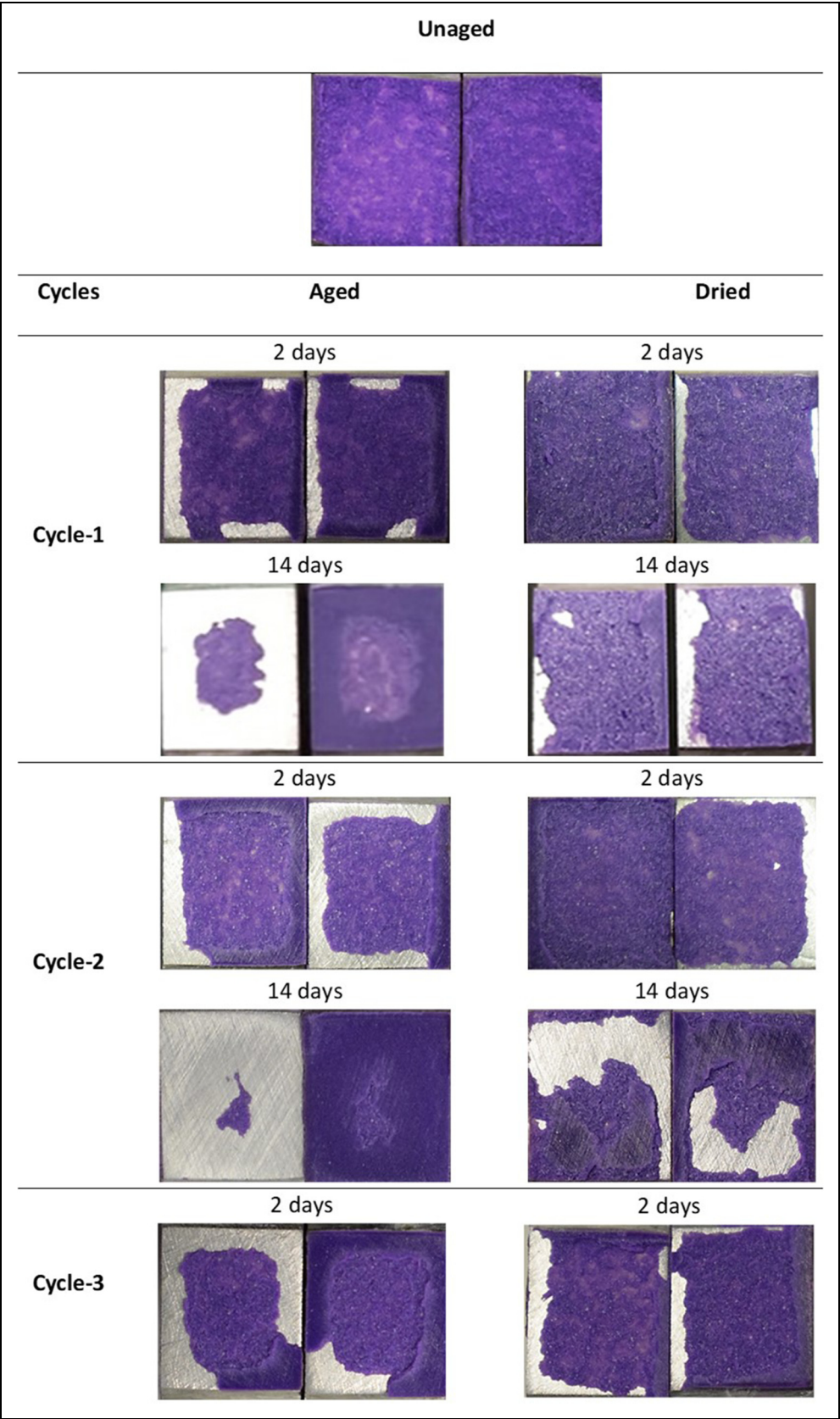


Figure 4. Tensile test failure surface of cyclic hygrothermal aged.

diffusion, and solubility coefficients, respectively, while the nodal temperature of the elements corresponds to the nodal humidity level.

The mathematical equation of diffusion is based on the equation of heat conduction which was derived by Fourier in 1822, as shown by Fick in 1855. The

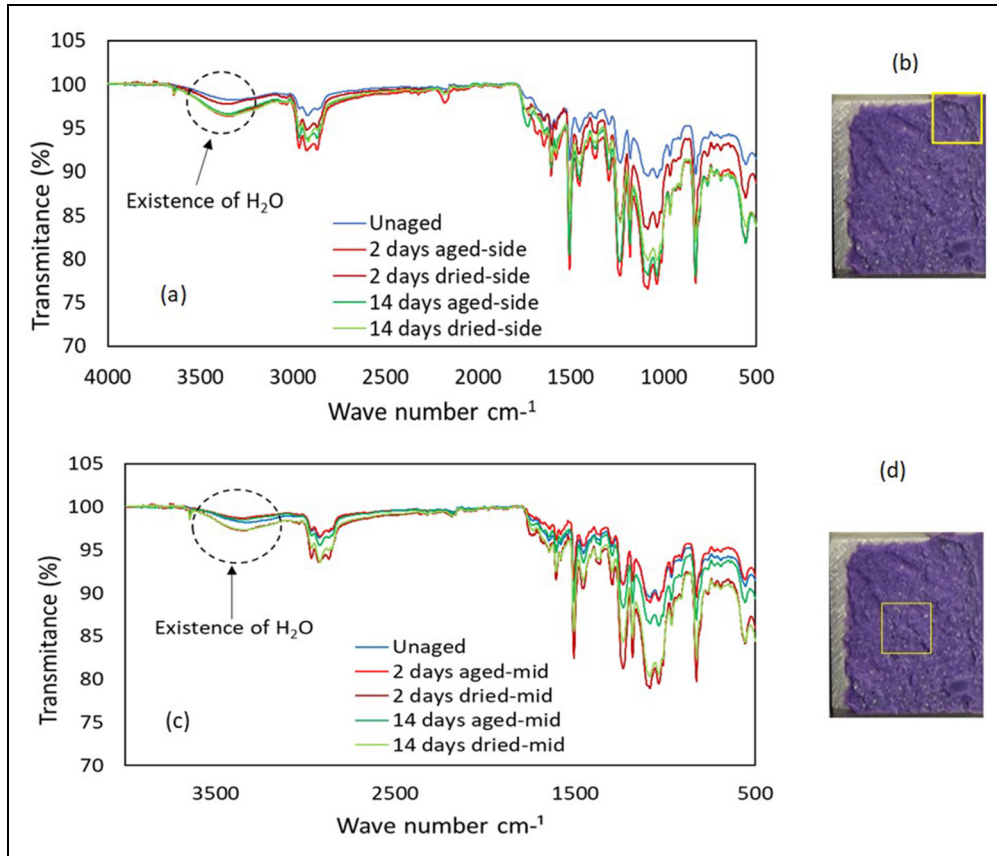


Figure 5. FTIR analysis of the aged and dried samples. (a) FTIR spectrum measurement on the side, (b) Measurement location on the side, (c) FTIR measurement in the middle, and (d) Measurement location in the middle.

diffusion hypothesis is presented mathematically by Equation 1.²⁶

$$F = -D \frac{\partial c}{\partial x} \quad (1)$$

where F is the flux or rate of transfer per unit area, c is the concentration of diffusing substance, x is the space coordinate measured normal to the section, D is the diffusion coefficient. The negative sign in Equation 1 is due to the fact that diffusion occurs in the direction opposite to that of the increasing concentration.

The mathematical expression for 1 D diffusion is shown in Equation 2. This expression called Fick's second law.²⁶

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

Equation 2 can easily be extended to 2 or 3 dimensions. Many classes of problems are governed by an equation of a similar form to Fick's second law, for example, the governing equation for heat transfer is given by 2:7

$$\begin{aligned} \frac{\partial}{\partial x} \left(k_x \frac{\partial T}{\partial x} \right) + \frac{\partial}{\partial y} \left(k_y \frac{\partial T}{\partial y} \right) + \frac{\partial}{\partial z} \left(k_z \frac{\partial T}{\partial z} \right) + Q \\ = \rho c \frac{\partial T}{\partial t} \end{aligned} \quad (3)$$

where T is temperature, k_i is conductivity in the i direction, Q is the rate of internal heat generation, c is the specific capacity, and ρ is the density.

Based on the analysis results shown in Figure 6, the average amount of water uptake for the 2-days ageing frequency it was found as 1.15% for the first cycle, while for the second and the third cycles it is higher and equal to 2.07%. For joints subjected to 14-days ageing frequency the adhesive layer absorbs more water. For the first cycle the level of water uptake is 2.93% while for the second and the third cycle the level of water uptake increases up to 5.07%. It should be noted that the second and third ageing cycles have almost the same D values, which resulted in a similar level of water uptake for both cycles. The water content on the interface was higher than that in the adhesive layer, caused by the higher D of the interface. To determine the D of the interface, an inverse method was applied. The average water uptake of adhesive and interface, for 2 days cyclic ageing, was determined as being 2.78% for the first cycle and 4.59% and 5.86% for the second and third cycles, respectively. The average water uptake of adhesive and interface for 14 days cyclic ageing was found to be 6.10% for the first cycle and the second and third cycle was calculated to correspond to 6.72% and 7.41%, respectively. Figure 6(a) shows the average water uptake level for 2 days ageing, while the average water uptake level

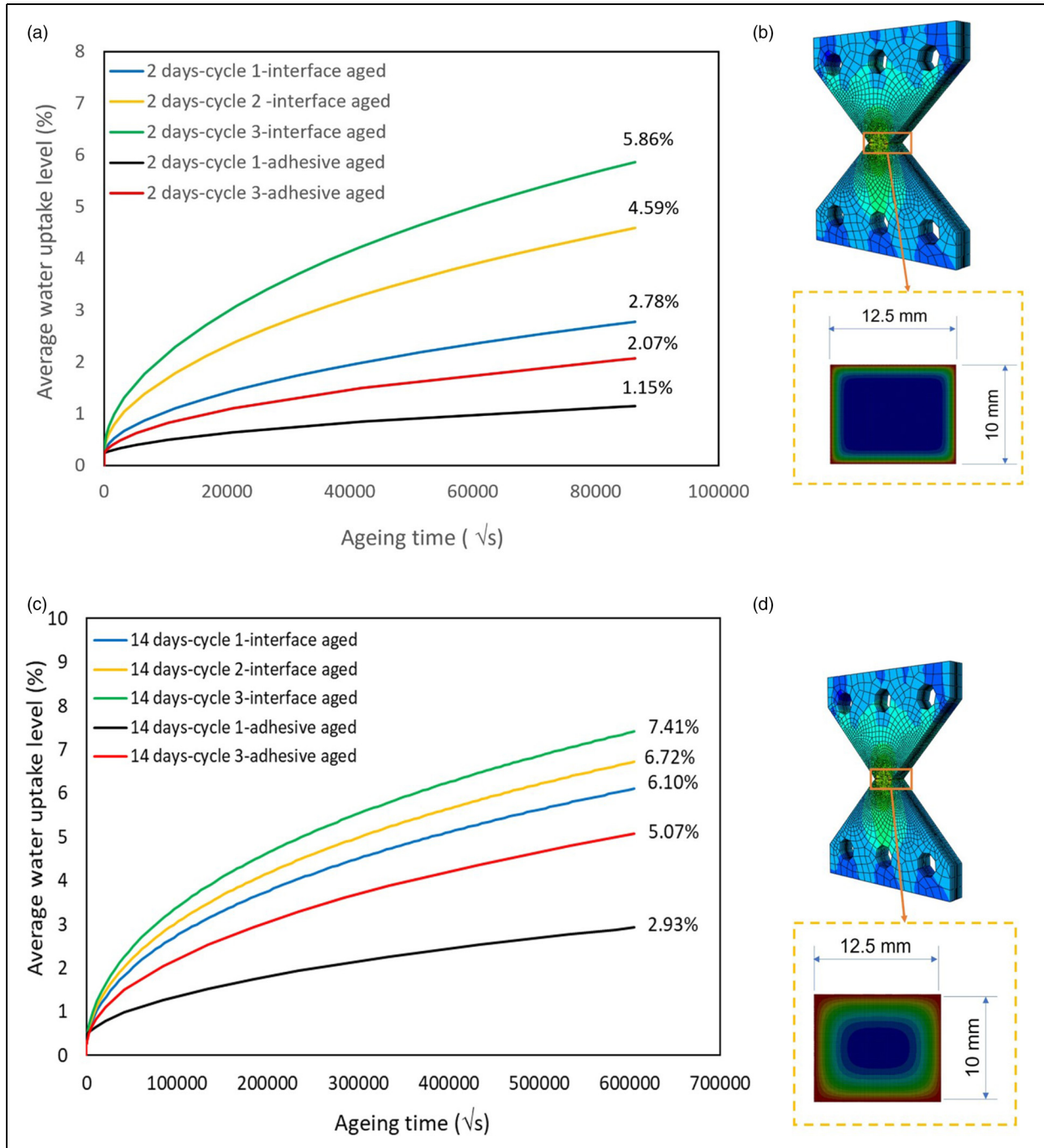


Figure 6. Simulation of average water uptake level for adhesive and interface cyclic ageing. (a) 2 days ageing, (b) 2 days ageing model, (c) 14 days ageing, and (d) 14 days ageing model.

for 14 days ageing is shown in Figure 6(c). The numerical models used, and a cross section of the adhesive layer are also shown in Figure 6(b) and (d), respectively.

It can be observed in Figure 6(a) and (c) that the level of water uptake of the adhesive and the interface are different for every cycle. It should be noted that the D value for the adhesive layer is similar for both the second and the third cycles. Therefore, no significant difference in the water uptake at these levels was observed. During the drying process, after the first cycle, the free water is

removed from the adhesive, but the bound water still remains locked in place. Based on the FTIR results, there is still water in the adhesive after the drying process. During the drying process in the first cycle, part of the free water in the adhesive layer is desorbed and evaporated. When the second aging cycle begins, the free water is reabsorbed by the adhesive, resulting in the second level of water uptake. The same procedure is followed for the water uptake process through the interface. During the first cycle, most of the water is absorbed by the interface and occupied the interface region. When

Table 2. Water absorption distance along the overlap length of cyclic ageing.

	Cycles	Experiment* (mm)	Adhesive (mm)	Interface (mm)	Ratio interface/ adhesive	$D \text{ (m}^2\text{s}^{-1}\text{)}$	
						D_{adh}	D_{int}
2 days aged	1	1.3	0.5	1.35	2.70	2.34E-7	8.40E-6
	2	2.4	0.95	2.45	2.74	8.79E-6	2.84E-5
	3	3.4	0.95	3.42	3.58		4.84E-5
14 days aged	1	3.3	1.3	3.36	2.62	2.34E-7	6.84E-6
	2	4.7	2.65	4.75	1.81	8.79E-6	8.84E-6
	3	6.25	2.65	6.25	2.36		1.24E-5

*The experiment data here is measured based on the adhesive failure area obtained after the experimental tensile tests conducted on the joints. The real distance of the interfacial water diffusion can be greater than the experimental values reported in this table.

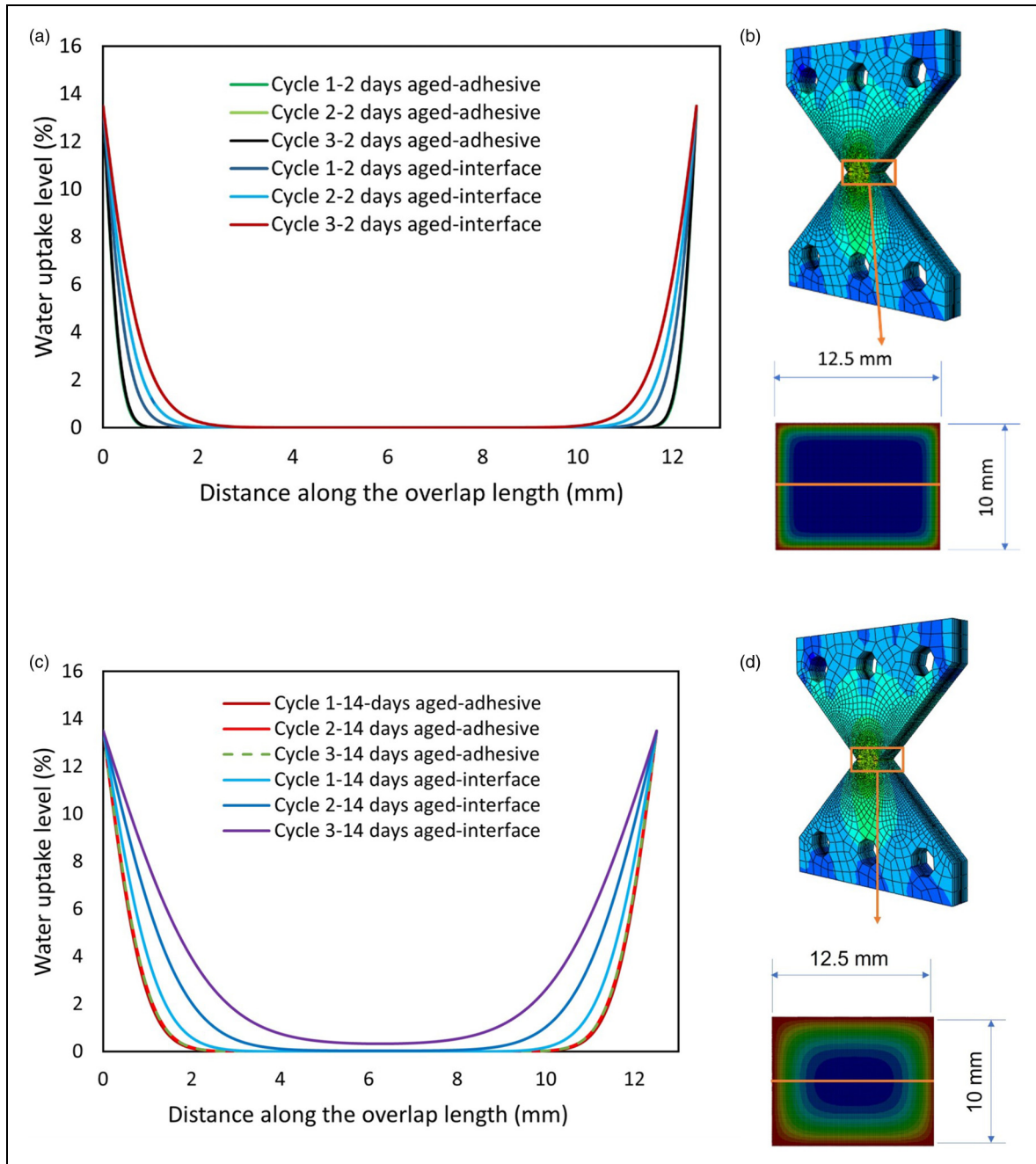


Figure 7. Simulation of water uptake distance along the overlap length for adhesive and interface cyclic ageing. (a) 2 days ageing, (b) 2 days ageing model, (c) 14 days ageing, and (d) 14 days ageing model.

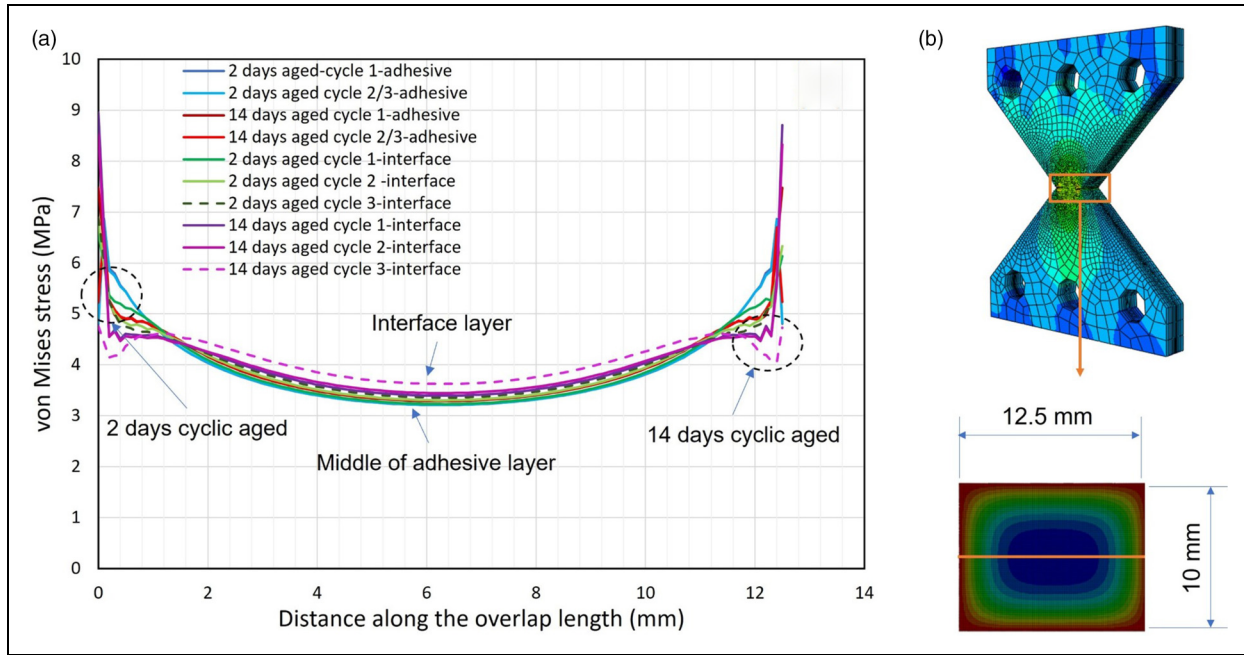


Figure 8. Stress distributions on the adhesive layer and interface of the cyclic ageing. (a) Stress distributions and (b) Analysis model.

the drying process takes place, the water is removed from the interface and the absorption path used is released. Therefore, when the second ageing cycle is applied, the water can occupy the empty spaces faster and continue to diffuse into the interface at a higher rate. Based on the results, it can be seen that D for the adhesive material is much lower than that of the interface.

Water uptake distance along the overlap length of each ageing cycle

To predict the water uptake distance along the overlap length for each ageing cycle, a path plot of the adhesive layer was obtained. Two distinct distance measurements were elaborated, including adhesive and interface overlap length. The water absorption distance of the adhesive layer for 2 days ageing was found to be 0.5 mm for the first cycle and 0.95 mm for the following two cycles. The water absorption distance of the adhesive layer for 14 days ageing was determined to be 1.3 mm for first cycle and 2.65 mm for the remaining 2 cycles.

Moreover, the water absorption distance on the interface was measured. To this end, an inverse method was used to calculate the interfacial D value. A thin layer of elements at the interface of the adhesive and substrate was created, with an arbitrary D value. The D value was iteratively adjusted until a level of interfacial ageing matching the experimental value was obtained. A similar procedure was followed for samples with different ageing times (2- and 14-days ageing) and cycles (1, 2, and 3). It was noted that the experimental value corresponds to adhesive failure on the interface and not the measurement of the water uptake distance on the interface. Therefore, the interface D value was based on the adhesive failure

on the interface. The D of the adhesive and interface ageing are in shown in Table 2.

The interface distance for 2 days cyclic ageing was found to be 1.35 mm, 2.45 mm, and 3.42 mm for the first, second, and third cycles, respectively.

The interface distance for 14 days cyclic ageing was obtained as 3.36 mm, 4.75 mm, and 6.25 mm, for all three cycles, respectively. It can be observed in Figure 7 that the most affected part of the joints is the interface of the 14 days cyclic aged specimens. The water absorption distance along the overlap length of the simulation and the adhesive failure on the interface can be found summarised in Table 2.

The stress distributions on the adhesive layer of each ageing cycle

The presence of water in the joints has a strong effect on the joint performance. However, degradation of the joint strength is not due to changes in the adhesive properties but mostly the result of changes at the interface between the adhesive and the substrate. To simulate the interface degradation a model created in Abaqus software was employed. To create this model, the mechanical properties of the adhesive are set as a function of the ageing cycles. The elements used are of the coupled temperature-displacement type, available in the element library. The results of these simulations showed that joint strength is degraded due to the existence of the water in the adhesive and the interface of the Arcan joints (see Figure 8). It can be observed in Figure 8, that the von Mises stress distribution is also affected by the number of ageing cycle as well as the ageing cycle frequency. More stress reduction was found for joints subjected to 14-days cycles ageing after three

ageing cycle. Figure 8(a) shows the von Mises stress distributions on the overlap length of the adhesive layer, and Figure 8(b) provides an example of the Arcan joint model and of the water distribution in the interface layer.

Conclusions

The performance of Arcan joints exposed to a cyclic water absorption condition under tensile loads was analysed in detail in this work. The obtained results allowed to conclude that water absorption significantly contributed to the degradation of the joint's mechanical performance. Both the tensile strength and the stiffness of the Arcan joints decreased significantly by increasing the ageing cycles. Therefore, cyclic ageing conditions should be avoided in adhesive bonding applications or, if cyclic ageing conditions cannot be avoided in service, the effects of the cyclic ageing on the joint's strength should be studied and accounted for. Relying on a typical ageing analysis where the joints are subjected to a continuous ageing process (that is often considered in literature) usually overestimates the strength of the joints. This type of ageing was already conducted in a previous research work²⁵ using the same adhesive which resulted in a very different rate of water uptake compared to the cyclic ageing conditions.

Regarding the numerical modelling and study of the failure modes, it was shown that the ratio of water diffusion at the interface to the adhesive is more than 35. This fast water uptake diffusion through the adhesive layer leads to a significant degradation in the adhesion strength at the interface of the tested joints. The maximum reduction of the joint strength was found to be 55% and 94% for 2- and 14-days ageing obtained for the third ageing cycle, respectively.

Finally, an FTIR analysis of the aged joint showed that water remains locked in the adhesive layer even after the joints were dried, especially for higher cycle numbers in cyclic ageing conditions.

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Abbreviations

Al: Aluminium
BJ: Butt joint
c: Specific capacity ($\text{Jkg}^{-1}\text{K}^{-1}$)

C3D8R: Eight-node linear brick reduced integration element
C3D8T: Eight-node thermally coupled brick trilinear displacement and temperature element
D: Diffusion coefficient (m^2s^{-1})
DC3D8: Linear hexahedral of eight-node heat transfer brick
E: Young's modulus (MPa)
F: Flux (Wm^{-2})
FEM: Finite element method
FTIR: Fourier transform infrared spectroscopy
H: Hydrogen
K: Conductivity ($\text{Wm}^{-1}\text{K}^{-1}$)
O: Oxygen
PAA: Phosphoric acid anodising
Q: Internal heat (J)
SJ: Scarf joint
SLJ: Single lap joint
T: Temperature
T_g: Glass transition
T_m: Melting temperature
ρ: Density (Kg/m^3)
ν: Poisson's ratio

Paper 5



The influence of cyclic ageing on the fatigue performance of bonded joints

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ABSTRACT

Although the cyclical environment can significantly influence the fatigue performance of the bonded joints, however, the interactions of cyclic ageing and fatigue loading on the mechanical performance of bonded joints have not been studied yet. Accordingly, the aim of the current study is to investigate the influence of cyclic ageing on the fatigue behaviour of epoxy adhesive joints using Arcan samples. Accordingly, different ageing frequencies, different ageing and drying cycles, and different loading conditions are analysed. As a result, performing a single ageing analysis overestimates the life of adhesive joints if they are exposed to cyclic environments. Results also showed that the life cycle decreases with the ageing frequency.

1. Introduction

The application of adhesive joints is growing extensively in diverse industrial applications. It is mainly used in the manufacture of advanced structures, such as aircraft, road vehicles, rolling stock, ships, and electronic products and appliances. In these applications, adhesives are used to replace conventional joining techniques such as bolting, riveting, and welding. Adhesive joints offer more uniform stress distributions along the bonded area, lower manufacturing costs, are able to join a wide range of materials and enable the design of lightweight components [1,2]. The fatigue performance of adhesive joints has been considered by several researchers [3,4]. By testing real joints, some authors [5] found that the fatigue performance of bonded assembly is higher than welded joints.

Although adhesive joints have important advantages over conventional joints, they also bring significant drawbacks. One of the crucial weaknesses is the fact that the adhesives absorb moisture in humid environments, leading to reduced mechanical performance. This ageing phenomenon is often neglected in many practical applications and still needs further exploration, since some aspects of it are not yet fully understood.

The effects of hygrothermal ageing on the tensile strength of adhesives have already been studied by diverse several authors. The degradation of the fatigue life was affected by the temperature and moisture [6–8] and fatigue strength of the joints under cyclic hygrothermal ageing conditions has also been investigated [9–11]. The literature shows that the combination of temperature, moisture and fatigue leads

to premature and unpredictable failure of bonded joints.

In practical applications of bonded joints, exposed to the environment, a cyclic hygrothermal ageing process is impossible to avoid, therefore effects of the cyclic ageing on adhesive joints should be considered in the joint design.

Da Costa et al. [12] investigated the effect of cyclic hygrothermal ageing conditions on the mechanical response of bulk specimens of an epoxy-based adhesive. The authors found that the tensile mechanical properties of the adhesive decreased as the number of ageing cycles increased. The effect of cyclic hygrothermal ageing of epoxy-based adhesive using bulk samples was also investigated by Moazzami et al. [13]. They reported that the mechanical performance of the tested epoxy adhesive decreased with the number of ageing cycles. The effect of cyclic moisture absorption and desorption on the strength of an epoxy adhesive was analysed using open lap joints by Houjou et al. [14], where no significant decrease in the lap joint strength by the moisture absorption was detected. The effects of hygrothermal cyclic ageing on bonded aluminium specimens were analysed by Fan et al. [15]. This work revealed that hygrothermal ageing significantly decreases the ultimate failure strength and the stiffness of adhesive joints. Wei et al. [16] investigated the influence of hygrothermal ageing on the mechanical properties of Sikaflex®-265 adhesive in butt joints with aluminium substrates. They found that, under high-temperature conditions, the rate of decrease in the failure strength of the adhesive joints could be accelerated with the presence of moisture. Under increased ageing times, the proportion of interfacial failure also increased. The influence of hygrothermal cyclic ageing on the tensile properties of single-lap

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Table 1
Mechanical properties of the epoxy-based adhesive [23].

Properties	Adhesive
Maximum tensile strength, MPa	31.3
Maximum tensile strain, %	10.4
Maximum shear strength, MPa	23.1
Maximum shear strain, %	43.3
Young's modulus, MPa	1 159
Shear modulus, MPa	440
Poisson's ratio, ν	0.35

adhesive joints was studied using a ductile (Araldite® 2015) and a brittle (Araldite® AV138/HV998) epoxy adhesive joint with aluminium 6082-T6 substrates by Hirulkar et al. [17]. They reported that both the failure load and the ultimate strain drastically reduced under a higher hygrothermal ageing temperature. Hygrothermal ageing of joints with fibre reinforced polymer (CFRP) and aluminium substrates, bonded using XNR6852 E-3 adhesive was conducted by Machado et al. [18]. The authors concluded that the water absorption of the adhesive can affect the fatigue performance of the adhesive joints and reduces the interfacial strength of the joint. The effects of the temperature and humidity on the static and fatigue behaviour of two-component epoxy Araldite® 2015 adhesive bonded CFRP/aluminium alloy butt joints were carried out experimentally by Mu et al. [19]. This work has shown that by increasing the test temperature, the fatigue performance of the adhesive joints decreases significantly, especially when the temperature is close to or higher than the T_g of the adhesive.

Although usually, the rate of water uptake through the interface is usually higher than the adhesive, however, this phenomenon has attracted less attention. On the other hand, measuring the interfacial properties has some difficulties. The interfacial toughness of an epoxy adhesive bonded with aluminium was investigated by Reedy and Stavig [20]. They reported that the interfacial toughness is a function of the surface roughness and the test temperature of the bonded aluminium and epoxy adhesive. Dionísio et al. [21] study the stress singularity at the adhesive and adherend interface corners of the single lap joint (SLJ) using aluminium substrate bonded with Araldite® AV138 adhesive. The results of the study were to determine the singularity's exponent and intensity of the stress singularity field (ISSF) of the bonded joint. Effects of interfacial cracks on the residual strength of adhesive joints were analysed by Akhavan-Safar et al. [22]. Using fracture mechanics-based approaches they could predict the strength of adhesive joints weekend with an interfacial flaw.

Although there are some studies on the cyclic aging analysis of bonded joints, the effects of the interaction of cyclic aging and cyclic loading conditions on the mechanical performance of adhesive joints have not yet been investigated. Since in practice the joints are subjected to both cyclic environment and fatigue loads, consideration of these aggressive conditions in the design of bonded structures is crucial. On the other hand, due to the interface ageing, the failure mechanism can change from cohesive failure for the unaged condition to adhesive failure after a sufficient number of ageing cycles. This means that not only the effects of cyclic ageing, the interfacial failure mechanism should also be considered in the fatigue performance analysis of adhesive joints. Accordingly, the objective of the present study is to determine how the fatigue strength of epoxy-based adhesive joints changes after cyclic hygrothermal ageing and also to investigate the failure mechanisms of the joints under cyclic hygrothermal ageing and cyclic tensile loading conditions. The hygrothermal cyclic ageing procedure was conducted in two different conditions (two ageing frequencies including 2 and 14 days) and three different ageing cycles. The results obtained led to the conclusion that the fatigue strength of the adhesive decreased linearly with an increase in the number of ageing cycles. All testing conditions were conducted at room temperature and the fatigue tests were performed after the first and the third ageing cycles.

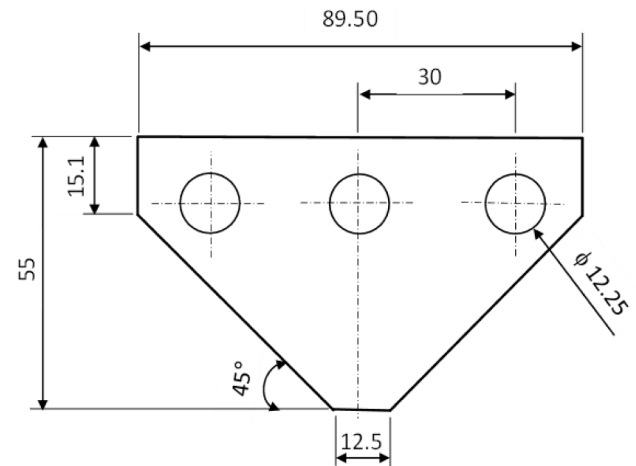


Fig. 1. Arcan substrate (dimensions in mm).

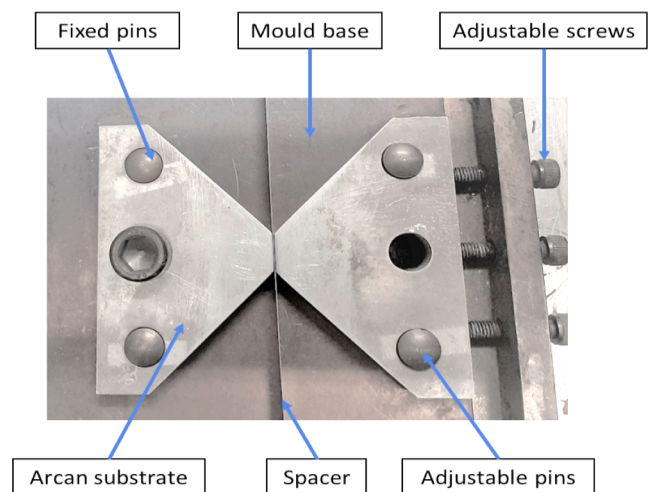


Fig. 2. Arcan joint manufacturing.

2. Experimental procedures

2.1. Materials

A one component, heat curing, solvent-free epoxy-based adhesive was used to investigate the effects of cyclic ageing on the fatigue life performance of the bonded joints loaded under mode I. To achieve this, Arcan joints were manufactured and tested under tensile fatigue loading conditions. This is a tough and highly viscous paste adhesive which is suitable for joining load-bearing structures. The mechanical properties of the adhesive are shown in Table 1. The Arcan substrates were manufactured using a high strength aluminium alloy, of the type Al 6082 T651 ($E = 70$ GPa, $\nu = 0.3$). Fig. 1 shows the dimensions of the Arcan substrate. The thickness of the substrate is 10 mm.

2.2. Joint manufacturing

To manufacture the Arcan joints, a special mould was used (see Fig. 2). Furthermore, to accurately set the adhesive layer thickness to 0.2 mm, a calibrated metal strip was used, and adjustable screws were set as shown in Fig. 2. Metal spacers, pins, and adjustable screws were used to precisely control the thickness of the adhesive layer in Arcan joints. First, the metal strip with a high precision thickness of 0.2 mm was placed between the two substrates. One substrate is fixed with the fixed pins and using the adjustable screws the other substrates can be

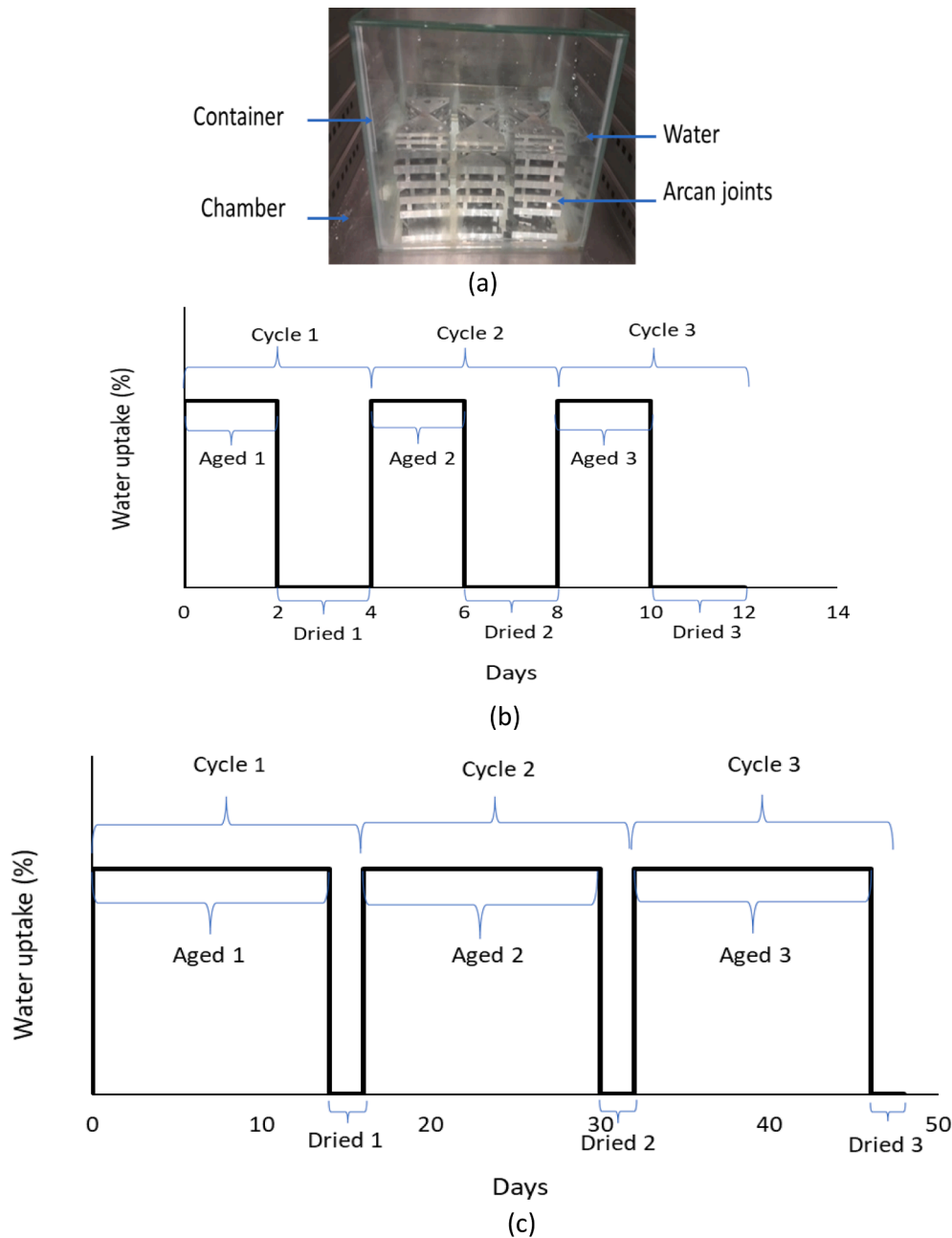


Fig. 3. Arcan joint ageing. (a) Arcan joints in the chamber, (b) Ageing and drying diagram for 2 days ageing, and (c) Ageing and drying diagram for 14 days ageing.

pushed forward until it touches the metal spacer. Using the pin and screws both substrates can be fixed in the right position. Then the spacer is taken out before adhesive application. Fig. 2 shows the details.

To ensure good adhesion between the adhesive and the substrate the bonding surfaces were anodized for 25 min, followed by a cleaning and degreasing process using distilled water and acetone. The anodized layer was created to resist corrosion, wear, and increase the surface adhesion capability. The anodizing solution employed in this work consisted of 88 vol% deionized water and 12 vol% phosphoric acid, prepared according to the ASTM 3933 standard. After the anodization and cleaning process was completed, the substrates were dried at room temperature at least 30 min before the application of the adhesive.

Bonded joints were cured at 177 °C for 60 min in a hot plate press machine.

2.3. Ageing

Before any ageing process or cycle was carried out, Arcan joints were kept in a container filled with silica for at least 2 days. The purpose of this stage is to remove all moisture that might have been absorbed by the adhesive during the manufacturing process.

Afterward, the dried samples were exposed to an ageing environment by immersing them in a container filled with distilled water. The container was then transferred to a temperature-controlled chamber set to 50 °C. The diffusion coefficient (D) and the absorption rate for the tested adhesive joint were already determined in previous work using Fick's law [24]. Fig. 3 (a) shows the Arcan joints ageing in the chamber at a temperature of 50 °C. Two different ageing frequencies were considered in this study. Fig. 3 (b) details the ageing and drying cycles for the case where the ageing stages are 2 days long and (c) represents the ageing and drying cycles for the case where the ageing stages are 14 days

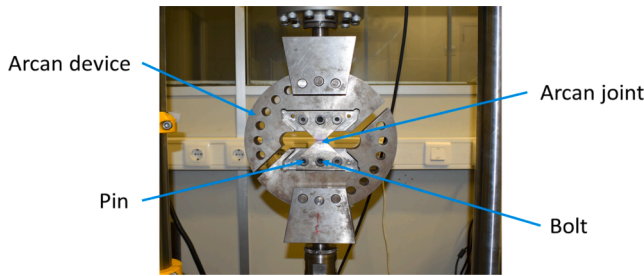


Fig. 4. Arcan joint testing device.

Table 2

Fatigue testing condition.

Ageing time (day)	Ageing conditions	Tested ageing samples	
		Static	Fatigue
0	Unaged	0	0
2	Aged	1	1
		3	3
14		1	1
		3	3
2	Dried	1	1
		3	3
14	for 2 days after ageing	1	1
		3	3

long. The ageing cycles are shown in Fig. 3(b) and (c). For both ageing frequencies (2-days and 14-days) the same drying period (2-days) was considered as the drying cycle.

2.4. Testing procedure

Static tests were performed before conducting fatigue experiments. The results of the static tests were used as a benchmark to conduct the fatigue loading of the cyclically aged specimens. Load (stress) controlled fatigue tests at different loading levels were also carried out on Arcan samples exposed to different ageing conditions shown in Fig. 4. The frequency for fatigue tests was 10 Hz and the load ratio (minimum to maximum load) was set to 0.1. An Instron 8801 servo-hydraulic testing machine was used to conduct the static and fatigue tests, both of which were performed at room temperature. The test conditions and the samples for each condition are listed in Table 2. The testing sample and the device are shown in Fig. 4.

2.5. Numerical simulation

The average level of water content in the adhesive layer was numerically determined. This was achieved using a 3D Arcan joint model, created using Abaqus. Due to the interfacial failure mode of the joints, an interfacial diffusion coefficient (D_{int}) of the joints can be determined using an inverse method.

The water diffusion process within the adhesive was modelled using a heat transfer analogy. The analogy between fluid/mass and heat transfer process allows for the conversation of mass transfer into the heat transfer process. This process arises from the similarity of the equations governing the mass and heat transport process. Since the boundary conditions are the same for a given geometrical, these equations have the same solutions and give the same results [25]. The mathematical equation of diffusion is based on the equation of heat conduction, which was derived by Fourier in 1822, as shown by Fick in 1855. The diffusion hypothesis is presented mathematically by equation (1) [26].

$$F = -D \frac{\partial c}{\partial x} \quad (1)$$

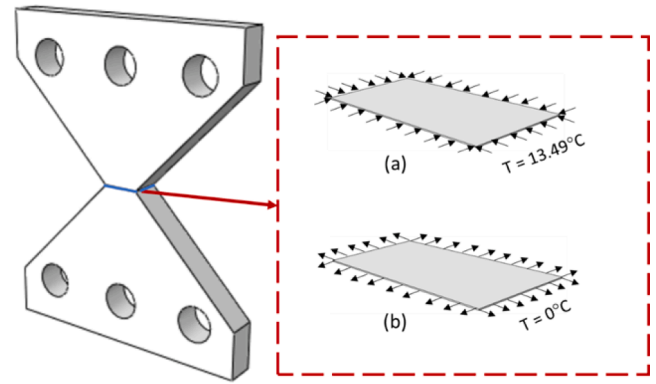


Fig. 5. Boundary condition of ageing and drying of Arcan joints. (a) The ageing process, and (b) the drying process. The arrows show the water direction.

where F is the flux or rate of transfer per unit area, c is the concentration of diffusing substance, x is the space coordinate measured normal to the section, and D is the diffusion coefficient. The negative sign in Equation (1) is due to the fact that diffusion occurs in the direction opposite to that of the increasing concentration.

The mathematical expression for 1D diffusion is shown in Equation (2). This expression is called Fick's second law. [26].

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

Equation (2) can easily be extended to 2 or 3 dimensions. Many classes of problems are governed by an equation of a similar form to Fick's second law, for example, the governing equation for heat transfer is given by [27].

$$\frac{\partial}{\partial x} \left(k_x \frac{\partial T}{\partial x} \right) + \frac{\partial}{\partial y} \left(k_y \frac{\partial T}{\partial y} \right) + \frac{\partial}{\partial z} \left(k_z \frac{\partial T}{\partial z} \right) + Q = \rho c \frac{\partial T}{\partial t} \quad (3)$$

where T is temperature, k_i is conductivity in the i direction, Q is the rate of internal heat generation, c is the specific capacity, and ρ is the density.

Afterward, the nodal temperature was set to correspond to the water uptake level at each node and the conductivity was set as the D of the adhesive. Based on the interfacial failure distance observed in the experimental results, a D_{int} value was also calculated with a numerical model, by using an inverse approach.

For the diffusion analysis, linear hexahedral elements (DC3D8) were employed, being an eight-node heat transfer brick. The boundary conditions follow the heat transfer analogy with uniform distributions of hygrothermal conductivity and the applied magnitude was 13.49% of water uptake level until saturation. Elements were considered to have a uniform mesh size of 0.1 mm with similar width and length, while the thickness of the element was set to 0.05 mm.

For the stress analysis simulation, both the substrate and the adhesive layer were modelled with C3D8T and C3D8R elements. C3D8T is an eight-node thermally coupled brick, trilinear displacement and temperature element while the C3D8R is an eight-node linear brick reduced integration element. The boundary condition of the ageing and drying process is shown in Fig. 5.

3. Results and discussions

3.1. Fatigue results

Fatigue test results for cyclic ageing and drying conditions were used to construct the stress-life (S-N) curves for different ageing cycles, as shown in Fig. 6. The stress in S-N curves is the average tensile stress obtained by dividing the maximum fatigue load to the total bonded area. Fig. 6 (a) shows the fatigue results after the 2 days cyclic ageing

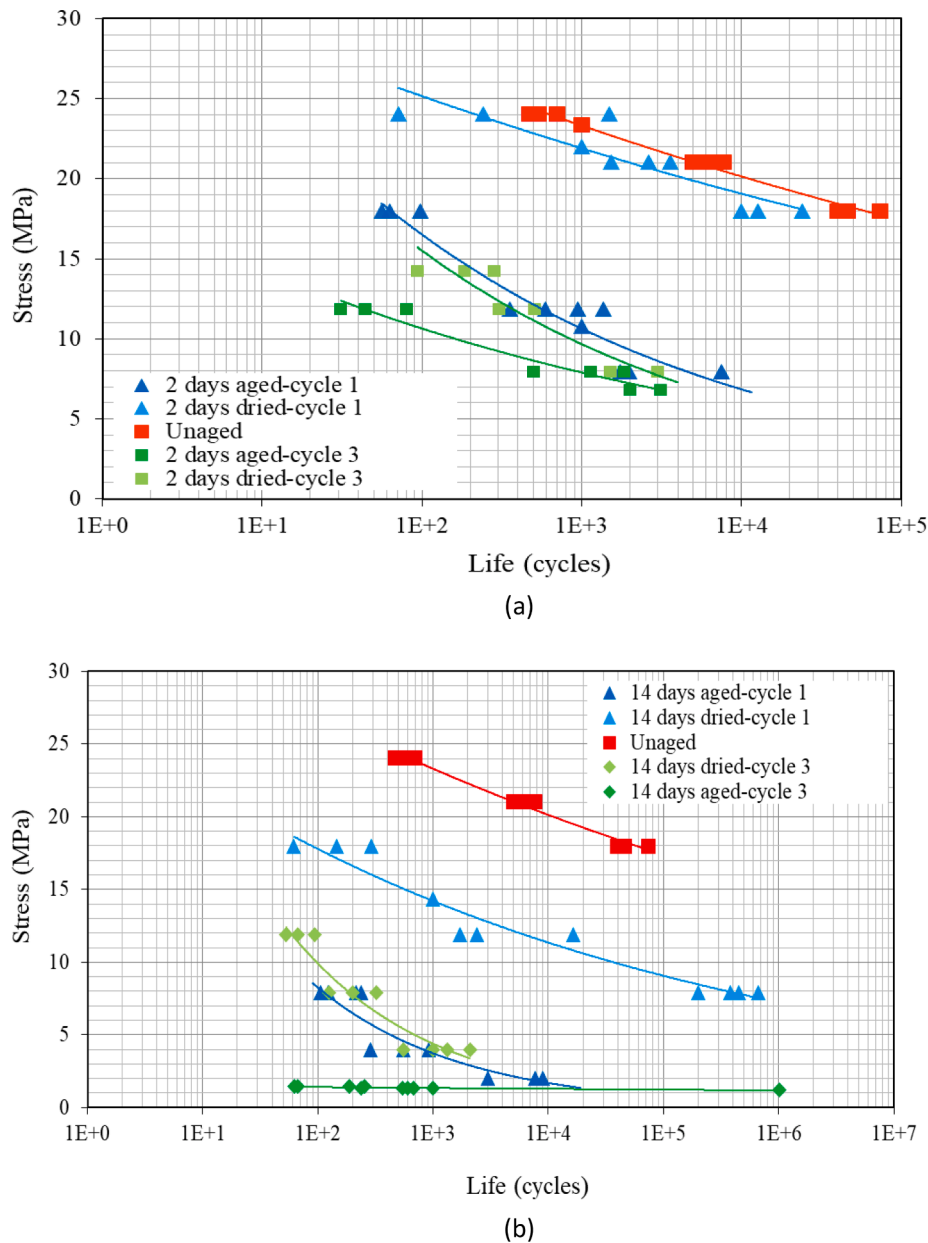


Fig. 6. Stress-life (S-N) curves. (a) 2 days cyclic ageing and drying and (b) 14 days cyclic ageing and drying.

procedure and the fatigue response after drying the joints. Fig. 6 (b) presents the fatigue strength after 14 days of the cyclic ageing procedure and drying of the joints. The results showed that cyclic ageing can significantly reduce the fatigue strength of the bonded structures. Based on the results shown in Fig. 6, it can be observed that the fatigue endurance limit of the joints decreases drastically with an increase in the ageing time and ageing cycles, indicating that the aged adhesive joints in practice will not be able to support significant fatigue loads. From the industrial point of view, an aged joint must be removed from service after the first ageing cycle when the ageing period is set to 14 days since it loses most of its fatigue endurance.

Nonetheless, it is also found that the drying process can partially recover the fatigue resistance of the tested joints. Based on the results fatigue strength of cycle 1 recovered higher than that of cycle 3 as shown in Fig. 7. During the drying process, the aged joints release free water from the adhesive and the interface, which results in some recovery of the joint strength. However, bound water still remains in the adhesive layer during the drying process and the strength is thus not fully

recovered to the initial condition. It should be noted that in an ageing process, the water molecules in an epoxy adhesive can be absorbed as free water and bound water. Free water occupies the free spaces and bound water makes a chemical connection with the polymer chains. During the drying process, the free water often leaves the adhesive, but the bound water usually remains. There might be also free water trapped in the adhesive layer even after drying. On the other hand, there is a probability that a free water molecule gets bound, or a bound water molecule is released. Accordingly, it is very difficult to distinguish the free water and bound water.

The results of the drying process showed that the fatigue strength after drying was partially recovered and for shorter ageing times it returned nearly to the unaged conditions.

Fig. 7 shows the fatigue strength of the tested joints, corresponding to around 1000 fatigue cycles. According to the data shown in Fig. 7, the fatigue strength of the joints after the first ageing cycles for 2 days of ageing was obtained as 46% of the fatigue strength of the unaged joints (see Fig. 7 (a)). However, this value reduces to around 34% after the

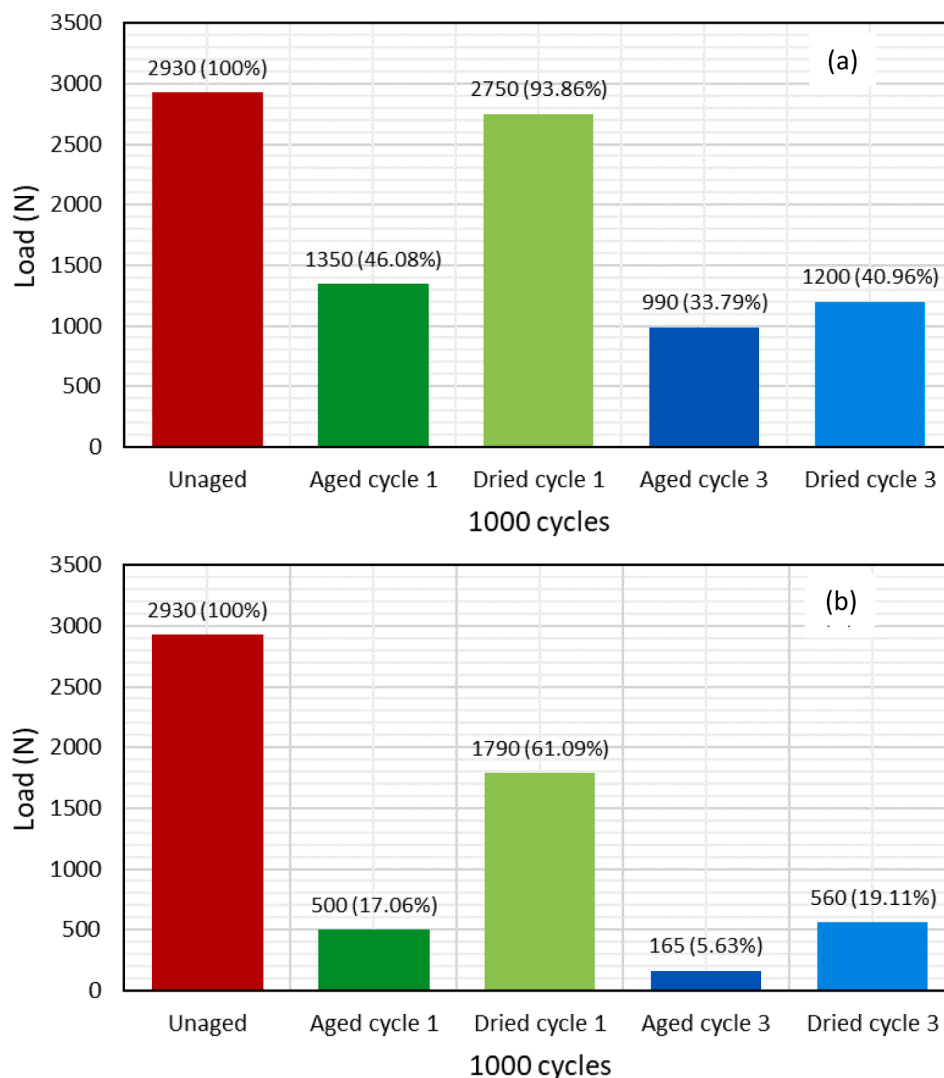


Fig. 7. The fatigue strength of aged and unaged samples corresponds to 1000 loading cycles for (a) ageing frequency of 2 days, and (b) ageing frequency of 14 days.

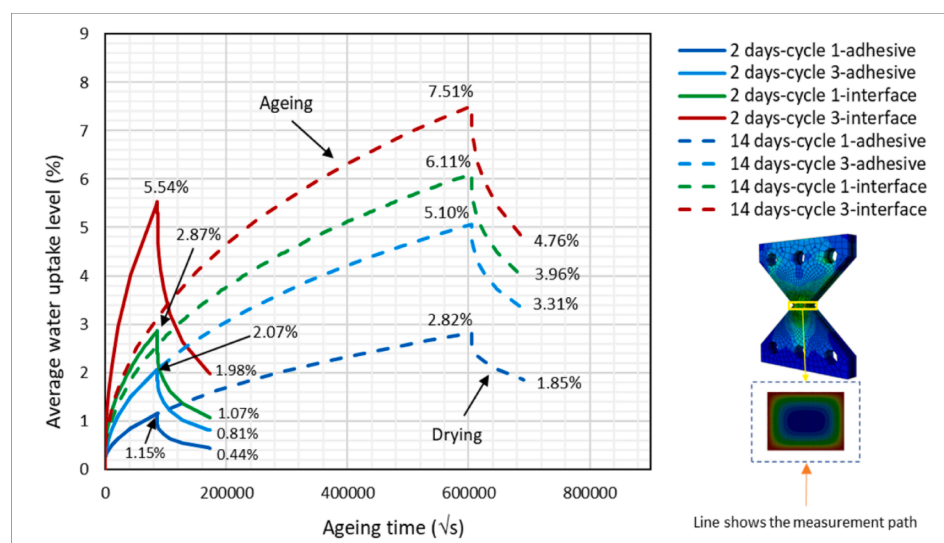


Fig. 8. Simulation of water uptake level for 2 and 14 days cyclic ageing conditions.

Table 3

The failure distance and the diffusion coefficients for the adhesive and the interface.

Ageing	Cycles	Experiment *	Adhesive	Interface	D	
		(mm)	(mm)	(mm)	D_{adh}	D_{int}
2 days aged	1	1.3	0.5	1.35	2.34E-7	8.40E-6
	3	3.4	0.95	3.42	8.79E-7	4.84E-5
14 days aged	1	3.3	1.3	3.36	2.34E-7	6.84E-6
	3	6.25	2.65	6.25	8.79E-7	1.24E-5

* The experiment data here is measured based on the adhesive failure area obtained after the experimental fatigue tests conducted on the joints. The real distance of the interfacial water diffusion can be greater than the experimental values reported in this table.

third ageing cycle. The same trend is observed for joints tested after 14 days of ageing (see Fig. 7 (b)). On the other hand, it was found that the rate of recovery also decreases as a function of the ageing cycles. This means that the drying process after the third cycle will not significantly recover the fatigue strength of the aged joints.

To further shed light on the effects of ageing on the fatigue strength of joints, fracture surfaces were also analysed, with the results being presented in the following section.

3.2. Water uptake level in the adhesive joints

Abaqus software was used to simulate the water uptake levels in Arcan joints. A heat transfer analogy was again considered to represent the water diffusion. Accordingly, the permeability, diffusion coefficient, and solubility were replaced with thermal conductivity, thermal diffusivity, and heat capacity, respectively. The humidity level was set to the applied boundary conditions. The water uptake level was measured at two different zones, including the bulk adhesive layer and the adhesive/substrate interface and the results are shown in Fig. 8. To calculate the average water uptake through the interface, an inverse method was used, considering different interface diffusion coefficients for different ageing conditions. To achieve this, the size of the zone with adhesive failure obtained in experiments was measured and considered in this analysis. The obtained results are summarized in Table 3.

It should be noted that to simulate the drying process, a procedure

similar to the water uptake analysis should be followed. The boundary conditions of the water uptake and drying process are shown in Fig. 5. The water uptake and drying simulation processes were performed in a single job submission in Abaqus. The results are shown in Fig. 8.

It can be observed in the failure surface of the bonded joints that by increasing the water uptake level, the size of the area with interfacial failure increases. Therefore, the bonding strength decreases mainly due to the reduction in the effective bonded area caused by the cyclic ageing process. The results of the analysis are shown in Fig. 9. The average bonding strength of the Arcan joints was obtained by the current authors in the previous study [28].

3.3. Failure mechanisms

The presence of water significantly affected the fatigue strength of the tested joints. Surface analysis was conducted for both the aged and unaged samples. The results showed cohesive failure for the unaged joints while a mixed failure mode was for after the 2 days cyclic ageing procedure. After the third cycle of ageing, where the ageing duration was set to 14 days, full interfacial failure was obtained.

Accordingly, three different failure modes exist in the Arcan joints subjected to fatigue loadings for 2 and 14 days cyclic ageing conditions. By increasing the duration of the ageing cycles, the failure mode changed from cohesive to adhesive failure. The failure modes of aged samples subjected to fatigue loading are shown in Fig. 10.

The effective bonded area of the unaged joints is 125 mm² (total bonded area) but it becomes significantly reduced after interfacial ageing. This reduction can be easily observed in Fig. 10.

The reduction in the bonded area increases the stress level within the adhesive layer and thus leads to a decrease in the fatigue life of the joint. Using fracture surface analysis, it was found that around 52 mm² of the bonded area experiences adhesive failure after the first cycle, while this value increases to around 107 mm² in the third ageing cycle. Increasing the ageing period to 14 days causes a further increase in the area where adhesive failure has occurred. After the third cycle for the ageing period of 14 days, 100% adhesive failure was observed. It was found that the fatigue loading and the fatigue life of the tested adhesive joints do not significantly change the failure mode. However, additional experiments on very high cycle fatigue loading conditions are needed to further understand the effects of fatigue loading on the failure mode in aged adhesive joints.

The dried samples at cycle 3, for joints subjected to the ageing frequency of 14 days, showed that the cohesive failure mechanism initiates

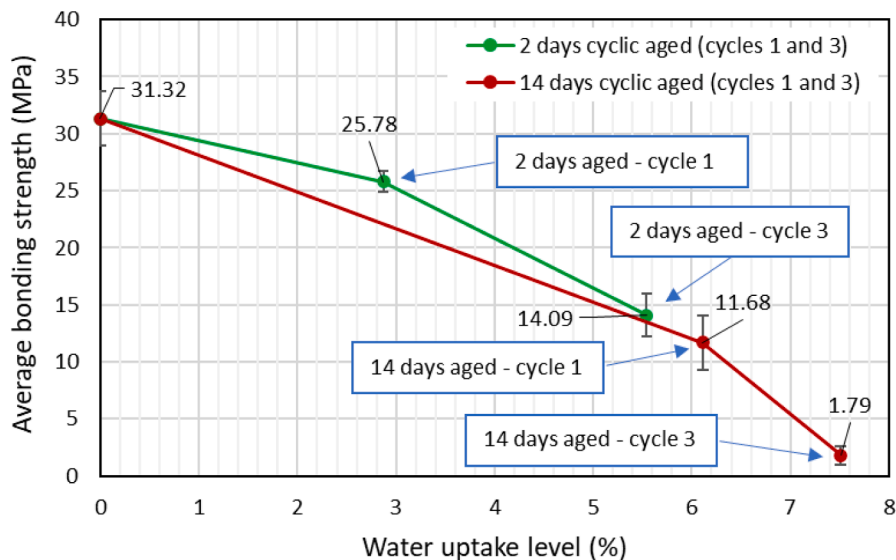


Fig. 9. The relationship between the bonding strength and the water uptake level of the cyclic Arcan joints.

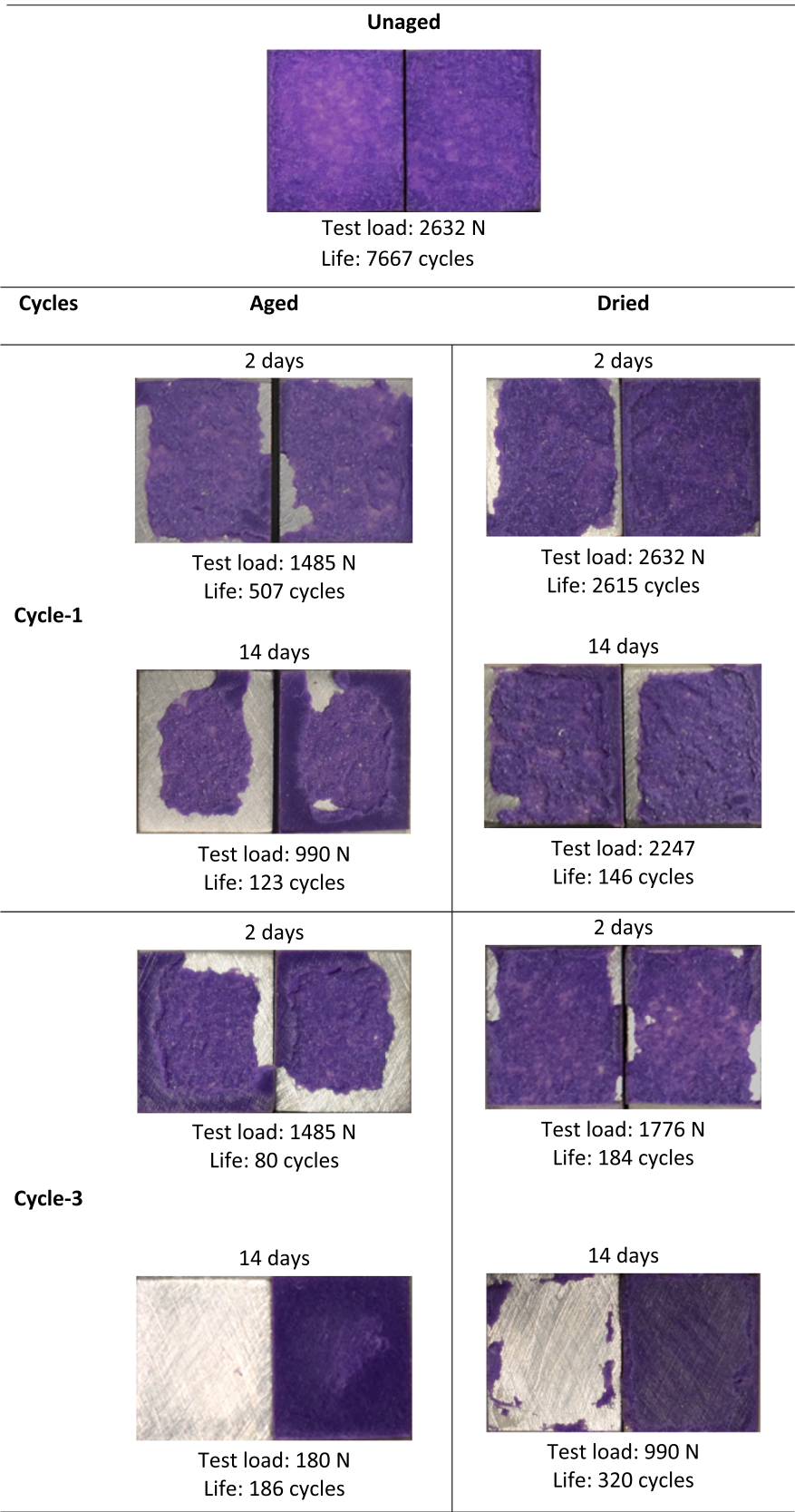


Fig. 10. Surface failure mechanism of the cyclic hygrothermal ageing of the Arcan joints under cyclic loading condition.

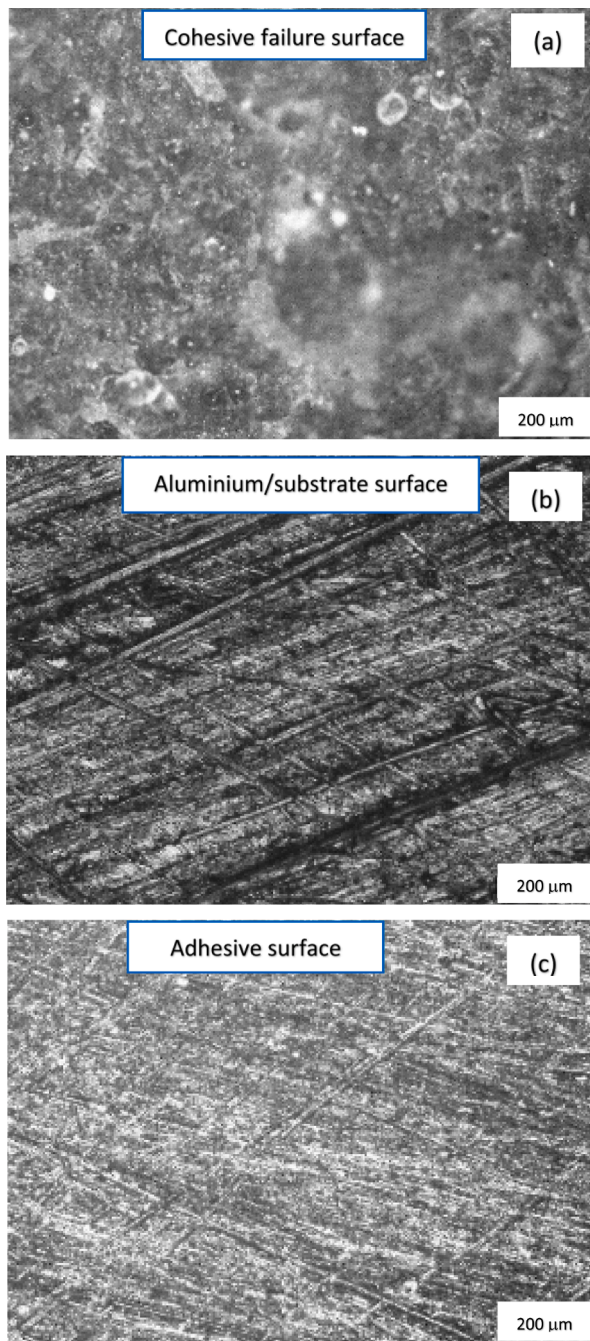


Fig. 11. Microscopic observation of the surface failure of aged Arcan joints. (a) Cohesive failure surface, (b) Substrate surface and (c) Adhesive surface.

at the edges of the joint (see Fig. 10). This is due to the fact that the drying process is faster at the edge of the joints, where water is quickly drained off. At the centre of the joint, the water is drained off at a much slower rate. Therefore, after 2 days of drying, cohesive failure returned to the edges of the joint while the centre of the overlap still experienced adhesive failure.

The effective bonding area was calculated based on the interfacial failure mechanisms imposed by the ageing phenomenon. Although this is not a very precise approach, it gives an estimation of the effective load-bearing bonded area after ageing. Results show that due to the interfacial ageing process the adhesion quality at the aged area significantly drops. In these regions, there is almost no considerable resistance against the applied load (dead regions) and consequently, adhesive failure takes place in these zones. Accordingly, the effective bonded area

was considered as the difference between the total bonded area and the area of the dead regions (zones with interfacial failure). The static strength of the unaged and cyclically aged joints has been already carried out by the current authors [28].

The failure mode of the unaged and aged Arcan joints was analysed for all cases. Generally, the observation was done visually and with the help of a high-resolution Nikon DX VR (AF-P NIKKOR 18–55 mm 1:3.5–5.6G) digital camera. However, the fracture surfaces for different failure modes including adhesive and cohesive failure mechanisms were also examined using a microscope. The results are shown in Fig. 11. Based on the microscopic images, no specific and distinct markings were observed in this microscopic examination. However, for further analysis, the crack path for joints with adhesive failure and also for joints with mixed adhesive/cohesive failure mechanisms was analysed. (See Fig. 12.).

The total bonding strength is a combination of the interfacial strength and the adhesive strength. In unaged bonded joints a complete cohesive failure was observed. It means that the interfacial strength for unaged conditions is more than the adhesive strength. Consequently, the bonding strength is limited by the strength of the adhesive. However, after ageing, a combination of adhesion failure through the interface and cohesive failure through the adhesive layer was observed. It means that the ageing process is more aggressive for the interface than the adhesive layer causing a faster and higher reduction in the strength of the interface than the adhesive. Finally, after a sufficient number of ageing cycles, a complete interfacial failure was observed. The obtained strength corresponds to the joints with a complete interfacial bonding gives a rough estimation of the interfacial strength after ageing. More details can be found in a previous study conducted by the current authors [4].

3.4. Effective bonded area (experiment vs. numerical)

The failure surface of the aged joints showed that the adhesive failure occurs at the edges and cohesive failure takes place in the middle of the joints. Failure was fully cohesive for the unaged joints while for the aged samples interfacial failure at the edges was observed. That means that the ageing process can significantly reduce the interfacial strength of the studied joints. Accordingly, it was assumed that the interface has experienced significant ageing at these points. The size of the area with adhesive failure was measured experimentally. Considering these data, in the numerical analysis, the interfacial diffusion coefficient was changed until the same interfacial areas with aged conditions were obtained numerically. The corresponding diffusion coefficient was considered as the D_{int} . It should be noted that for the numerical analysis, a very thin interfacial layer was created between the substrate and the adhesive layer. Two different diffusion coefficients were defined one for the adhesive and one for the interface (D_{int}). The obtained D_{int} was used to simulate the interfacial ageing in other joints aged for different ageing times. Good agreements were obtained as shown in Fig. 13 (in the revised paper). It means that the assumptions based on the inverse method are precise enough to estimate the interfacial diffusion coefficient. Similar calculations were carried out by the authors in previous studies [23,28].

Using the information provided in Table 3, the effective bonded area was numerically estimated. To achieve this, a very thin interfacial layer was created between the substrate and the adhesive layer. Two different diffusion coefficients were defined one for the adhesive and one for the interface D_{int} . The value of D_{int} should reproduce the same ageing area at the interface as the interfacial failure area obtained experimentally. Accordingly, using an inverse approach, D_{int} should be changed until a good agreement between the numerical results and the experimental observations is obtained. Using the obtained D_{int} the effective bonded area of joints with different ageing conditions were numerically obtained. As shown in Fig. 13, good agreements between the numerical and experimental analysis were obtained. It means that the inverse method is precise enough to estimate the effective bonded area. Similar

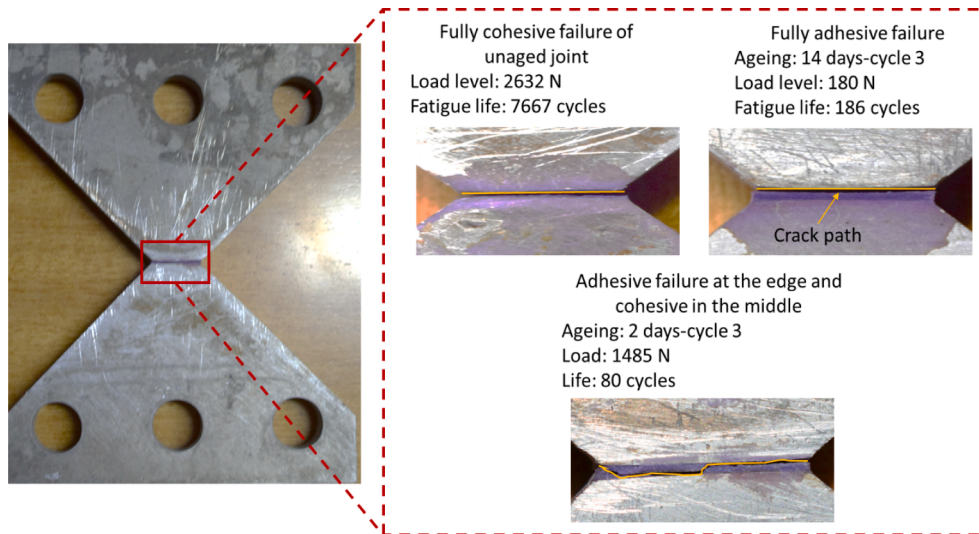


Fig. 12. The failure mechanism of aged Arcan joints.

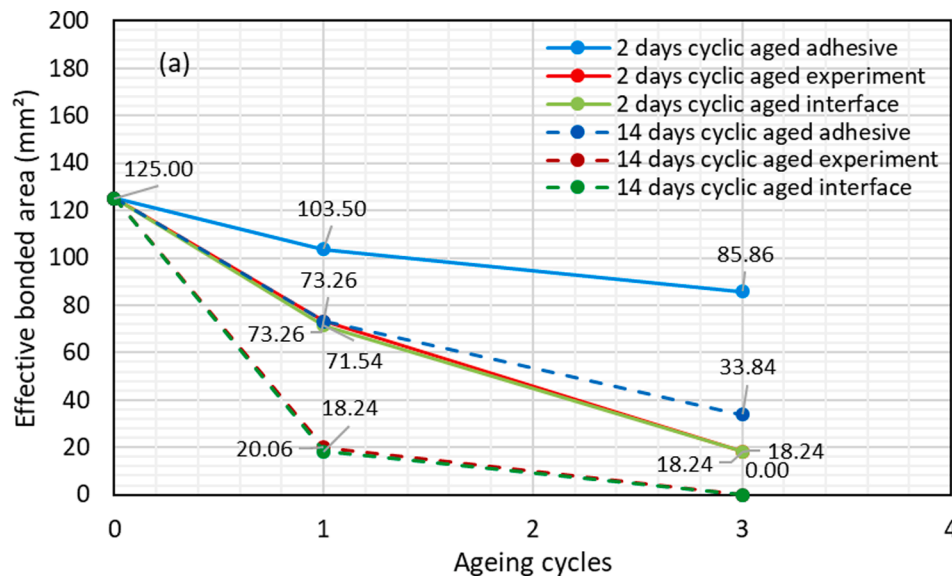


Fig. 13. The effective bonded area as a function of ageing conditions.

calculations were carried out by the authors in previous studies [23,28]. Fig. 13 compares the estimated effective bonded area with the experimental data. It was found that the effective bonded area decreases cycle by cycle during a cyclic ageing process. Based on the ageing analysis results, the effective bonded area was calculated using the following equations where A_{eff} is the effective bonded area, A_I is the initial bonded area and A_f shows the area with elements hydrothermally aged.

$$A_{eff} = A_I - A_f \quad (4)$$

Using the interfacial diffusion coefficient, D_{int} , the aged elements at the interface were obtained after a defined ageing time and the size of the effective bonded area (zones with no aged elements) was calculated accordingly. The same procedure was followed with the adhesive diffusion coefficient which is much lower than the D_{int} .

4. Conclusions

The fatigue performance of the Arcan joints subjected to cyclic ageing conditions was investigated experimentally and numerically. Arcan joints were exposed to water and both the interface, and the bulk

adhesive were affected by moisture ingress. Based on the experimental observations and the numerical analysis results, it was found that the water diffusion rate at the interface is around 35 times faster than that of the adhesive layer for the tested joints. The water diffusion through the interface deteriorates the bonding strength between the adhesive layer and the substrate, which leads to the degradation of the interfacial strength and adhesive failure.

It was also found that water absorption through the interface can drastically reduce the fatigue performance of bonded joints. Furthermore, increasing the ageing cycle can significantly decrease the fatigue strength of adhesive joints. The fatigue strength could be partially recovered after drying the aged joints. However, the recovery mainly occurred in the first ageing cycle, with the rate of recovery decreasing with each subsequent ageing cycle.

In sum, if adhesive joints are to be exposed to a cyclical ageing environment in a practical application, a cyclical ageing analysis is necessary to assess the fatigue performance of these joints. In this case, the service life could be grossly overestimated if only the results of the first ageing cycle are taken into account.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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