Latin American Journal of Solids and Structures
www.lajss.org

Water Diffusion in Double Cantilever Beam Adhesive Joints

Abstract

Structural adhesives are increasingly being used in the aerospace and automotive industries. They allow for light weight vehicles, fuel savings and reduced emissions. However, the environmental degradation of adhesive joints is a major setback in its wide implementation. Moisture degradation of adhesive joints includes plasticization, attacking of the interface, swelling of the adhesive and consequent creation of residual stresses. This may lead to reversible and irreversible damage.

In this work double cantilever beam (DCB) specimens using two different adhesives for the automotive industry were subjected to two different ageing environments. They were tested periodically until the toughness of the adhesives stabilized, which means that they were fully degraded. An association was made between the toughness of the adhesive and the amount of water that it had absorbed. This way it was possible to indirectly measure the water uptake in an adhesive joint taking into account the water uptake properties of the adhesives studied, which had been determined in another study.

It was found that diffusion of water into the studied adhesive joints was faster than diffusion through the bulk adhesive alone. A model that takes into account diffusion through the interface between the adhesive and the adherends was proposed.

Keywords

Hygrothermal ageing,adhesive joints; moisture degradation, double cantilever beam, diffusion

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http://dx.doi.org/10.1590/1679-78253040

Received 02.05.2016
Accepted 16.11.2016
Available online 29.11.2016

1 INTRODUCTION

Structural adhesives are increasingly being used in the transport industries. They allow for light weight vehicles, energy savings and reduced emissions. The main advantages include more uniform load distribution, higher fatigue resistance than other traditional joining methods and the ability to

join dissimilar materials (Banea et al. 2014). Also, due to their high vulnerability to stress concentration, the only viable way to join composite materials, such as fiber reinforced plastic, is with a structural adhesive (Banea and da Silva 2009). However, the environmental degradation of adhesive joints is a major setback in their wide implementation (Costa et al. 2016d).

Moisture degradation of adhesives include reduction of their mechanical properties, inducing plasticization (Costa et al. 2016a, Costa et al. 2016b, Costa et al. 2016c, Sugiman, Crocombe and Aschroft 2013, Wylde and Spelt 1998). The deleterious effects are greater in adhesive joints as the degradation of the adhesive-adherend interface may cause interfacial failure.

The water diffusion in adhesives is frequently controlled by the Fick's laws. Fickian sorption happens when the diffusion is much slower than relaxation. In this situation, the uptake will be proportional to the square root of exposure time. When the opposite occurs, one is in the presence of case II diffusion, in which the water uptake is directly proportional to the exposure time. In this case, a fully saturated and swollen front advances against the unpenetrated polymer (2013).

Although fickian diffusion is the most common uptake behavior in adhesives, non-fickian diffusion is not uncommon. Other models have been developed, such as the dual fickian diffusion (Loh et al. 2005), delayed dual fickian (Mubashar et al. 2009) and the Langmuir model (Ameli et al. 2010). In many cases the water uptake may be fickian under certain environmental situations and non-fickian under others. Generally non fickian behaviour is more prone to happen at higher temperatures (Zhou and Lucas 1995), higher relative humidity (Ameli et al. 2010, Loh et al. 2005) and smaller thicknesses of the bulk adhesive specimen (Loh et al. 2005). There is also evidence that while a bulk adhesive may have a fickian diffusion behaviour, the same adhesive in a joint may have a case II diffusion behaviour (Liljedahl et al. 2009).

The rate at which the water is absorbed and the maximum water uptake depend on environmental factors, such as the relative humidity and temperature and on the thickness (Loh et al. 2005, Y.C. Lin 2005) and the stress state of the adhesive (X. Han 2014).

As the water diffuses into the adhesive, some of this moisture becomes bound water. Bound water generally increases with exposure time and temperature (Zhou and Lucas 1999a, Zhou and Lucas 1999b). Unlike the free water that occupies the free space of the adhesive, this bound water is responsible for the volumetric changes that are observed in adhesives under high humidity environments, which may cause residual stresses in adhesive joints (Adamson 1980). Zhou and Lucas (Zhou and Lucas 1999a, Zhou and Lucas 1999b) have found two types of bound water: Type I involves water molecules forming a single hydrogen bond while type II results from water forming multiple hydrogen bonds. Type I bound water acts as a plasticizer, increasing the chains segment mobility. It is responsible for decreasing the glass transition temperature (Tg) (Barbosa, da Silva and Ochsner 2015, Zhang, Adams and da Silva 2014, Zhou and Lucas 1999b). If the temperature is high and the exposure time is long, type II bound water may also occur. This type of bound water is responsible for creating secondary cross-linking (Zhou and Lucas 1999a), which lessens the extent of Tg depression (Zhou and Lucas 1999b). While type I bound water can be removed at low temperature, in order to remove type II bound water, the adhesive must be subjected to relatively high temperatures (Zhou and Lucas 1999b).

Gravimetric methods are usually used in order to measure the water uptake of an adhesive (2012). This consists simply in subjecting a plate of bulk adhesive to an ageing environment, such

as distilled water, a salt solution, air with a particular relative humidity, or other environments compatible with what the adhesive will be subjected in its service life, such as toluene (Zhang et al. 2014), and measuring the weight change over time with a precision scale. This method is, however, very difficult to use in an adhesive joint, which usually uses a very low amount of adhesive, whose weight change cannot be measured with common precision scales. In order to overcome this difficulty and determine the average water uptake or the moisture profile in an adhesive joint, other techniques have been used. Among these techniques is the FTIR (Fourier transform infrared spectroscopy) -transmission spectroscopy (Wapner and Grundmeier 2004) and nuclear reaction analysis (Liljedahl et al. 2009).

(Zannideffarges and Shanahan 1995) have tested torsional joints and bulk tensile and compressive specimens after ageing them for different amounts of time. The modulus of both the bulk specimens and the torsional joints were monitored as a function of the ageing time. Taking the evolution of the Young's modulus into account, approximations to the diffusion coefficients of the joints and the bulk specimens were computed and it was found that the diffusion coefficient of the joints was much higher than the bulk specimens'.

(Kinloch, Little and Watts 2000) have concluded that relatively viscous adhesives may have difficulty penetrating in the pores and gaps of substrates, which may lead to premature rupture of adhesive joints, which are subjected to moist environments, either due to the hydration of the uppermost regions of the oxide layer or due to weakening of the adhesive-adherend interface. If a low viscosity primer is applied prior to bonding on a phosphoric acid anodized surface, the results are much improved because the primer will fill in the gaps which would be otherwise filled with water.

In this study, the toughness of two epoxy adhesives that were subjected to two different ageing environments: distilled water and a saturated water solution of NaCl (referred throughout this paper as "salt water" and is equivalent to subjecting the specimens to a 75% RH environment (Winston and Bates 1960)). The specimens were tested periodically until no change in the fracture toughness was perceptible. At this point it was considered that the specimens were fully saturated. It was found that the time it took for the specimens to saturate was shorter than if only the properties of the bulk adhesive were considered. Based on this information, the approximate diffusion coefficients of the interfaces were computed. This allows a more accurate prediction of the water diffusion in complex adhesive joints, which leads to more accurate predictions of the strength of aged adhesive joints.

2 MATERIALS

2.1 Adhesives

The adhesives, which were developed for the automotive industry and were recommended by Sika® and Nagase® for this durability study are the following:

- The epoxy adhesive XNR 6852-1, supplied by NAGASE CHEMTEX® (Osaka, Japan). This adhesive is a one-part system that cures at 150°C for 3 h. It has a high strength and high displacement to failure;

- The epoxy adhesive SikaPower 4720, supplied by SIKA® (Portugal, Vila Nova de Gaia). This adhesive is a two-part system that has the advantage of curing at room temperature for 24 hours.

The stress-displacement curves of bulk tensile specimens of these adhesives obtained in a previous study (Viana et al. 2016) are shown in Figure 1.

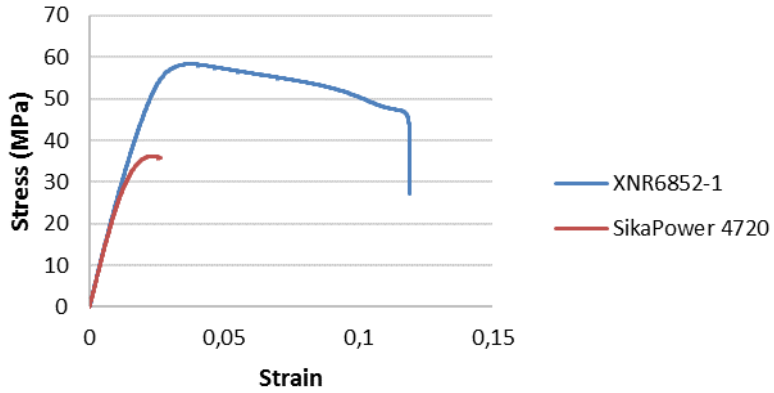


Figure 1: Stress-displacement curves of both adhesives used.

2.1 Substrates

In order to measure the toughness of adhesive joints, DCB specimens were used. To avoid plastic deformation while testing, the substrates were made of the high strength aluminium alloy 6082-T6. In a standard DCB specimen, whose length is much greater than the width, water sorption occurs almost entirely along the width direction (Hua et al. 2006). However, they take very long time to reach saturation. Instead of using this standard specimen geometry, a smaller geometry (shown in Figure 2) was used.

Some studies about the effect of DCB specimen geometry on the fracture energy (G_{IC}) of the adhesive layer have been undertaken (Campilho et al. 2014, Costa et al. 2015). Results show that the geometry of the substrates may have influence on the measured toughness of the adhesive. This suggests that G_{IC} may not be a material parameter, but a geometry-dependent quantity instead. In this study, in order to allow for a fast ingress of water into the adhesive layer, small DCB specimens were used. The results obtained should be compared only between specimens of the same geometry.

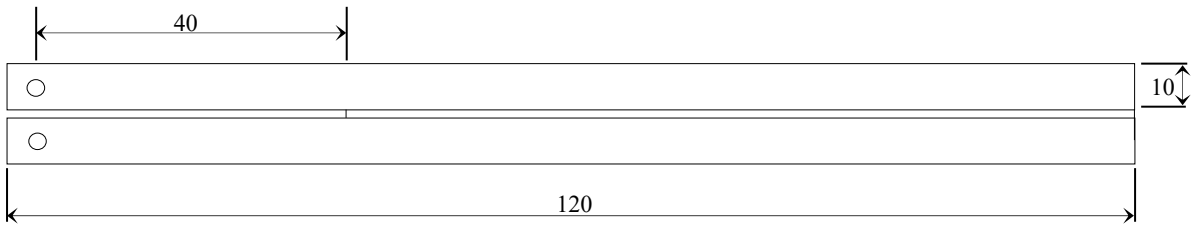


Figure 2: Geometry of the DCB specimens (dimensions in mm).

3 EXPERIMENTAL PROCEDURE

3.1 Specimen Fabrication

Prior to bonding, the surfaces of the DCB substrates were abraded with a 80 grit CSi sandpaper, cleaned in an ultrasonic acetone bath and received a phosphoric acid anodisation. Less than a day after being anodized, the specimens were bonded and left to cure for 3h at 150°C or for 24h at room temperature, according to the indication of the manufacturer of each adhesive used. After the cure cycle the excess adhesive was removed and the specimens were left to dry for at least 3 weeks in a dry desicator. After this time, the specimens of each adhesive were divided into three groups:

- Dry specimens, which were ready to be tested;
- Specimens to be aged in a saturated solution of NaCl at 32.5°C (refered throughout this paper as "salt water"), which is equivalent to ageing them in a 75% RH environment (Winston and Bates 1960);
- Specimens to be aged in distilled water at 32.5°C.

In this study, specimens with reduced dimensions were used. This allowed time efficient production and ageing.

3.2 Test Procedure

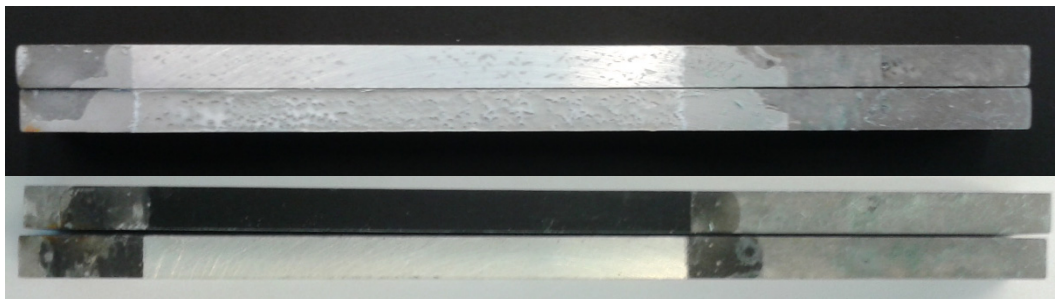
After all specimens had been produced and dried in a dry desicator, they were separated into the three different groups mentioned in the previous section. The dry specimens were immediately tested while the specimens to be aged were placed in their respective ageing environment and tested periodically at a displacement rate of 0.5 mm/min until their toughness stabilized, meaning that they were fully degraded by the absorbed water.

The effect of moisture uptake in the adhesives studied tends to be more pronounced at 80°C than at room or lower temperatures (Viana et al. 2016). For this reason, it was decided that the tests should be made at 80°C, as it would be possible to better associate the toughness of the adhesive to the moisture that the joint has absorbed. A climatic chamber coupled with an universal test machine (INSTRON® model 3367) allowed to test the specimens at 80°C. Right before testing, the specimens were left inside the climatic chamber at 80°C for 10 minutes to make sure that the temperature was exactly 80°C in the entire specimen.

4 EXPERIMENTAL RESULTS

After testing, the fracture surfaces were observed visually. As can be seen in Figure 3, the failure modes were interfacial for every case.

The toughness of the aged specimens was measured regularly. The results were plotted as a function of the ageing time, as can be seen in Figure 4. The longer the specimens were kept immersed in water (either distilled water or salt water), the greater the drop in their toughness was, until it starts to level off.



a. XNR 6852-1
b. SikaPower 4720

Figure 3: Fracture surfaces of both adhesives used.

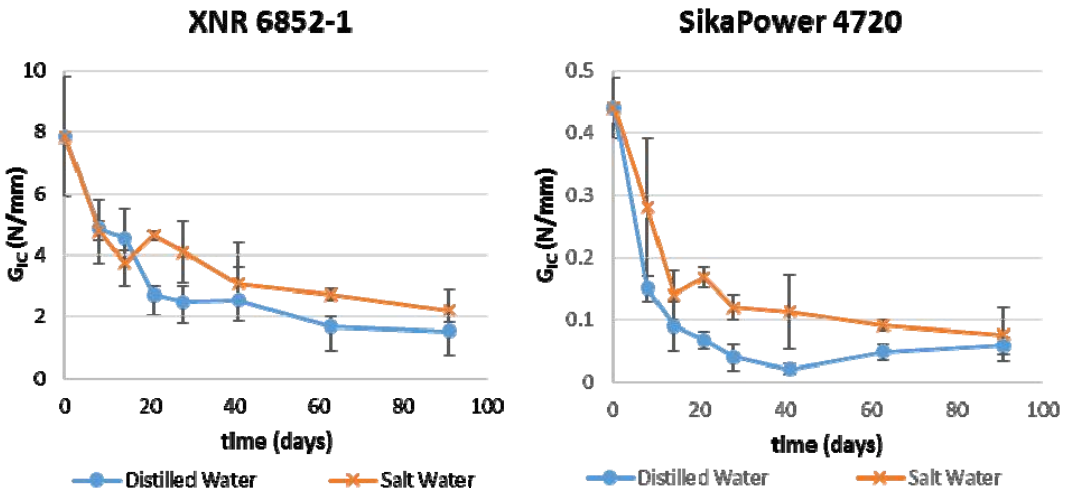
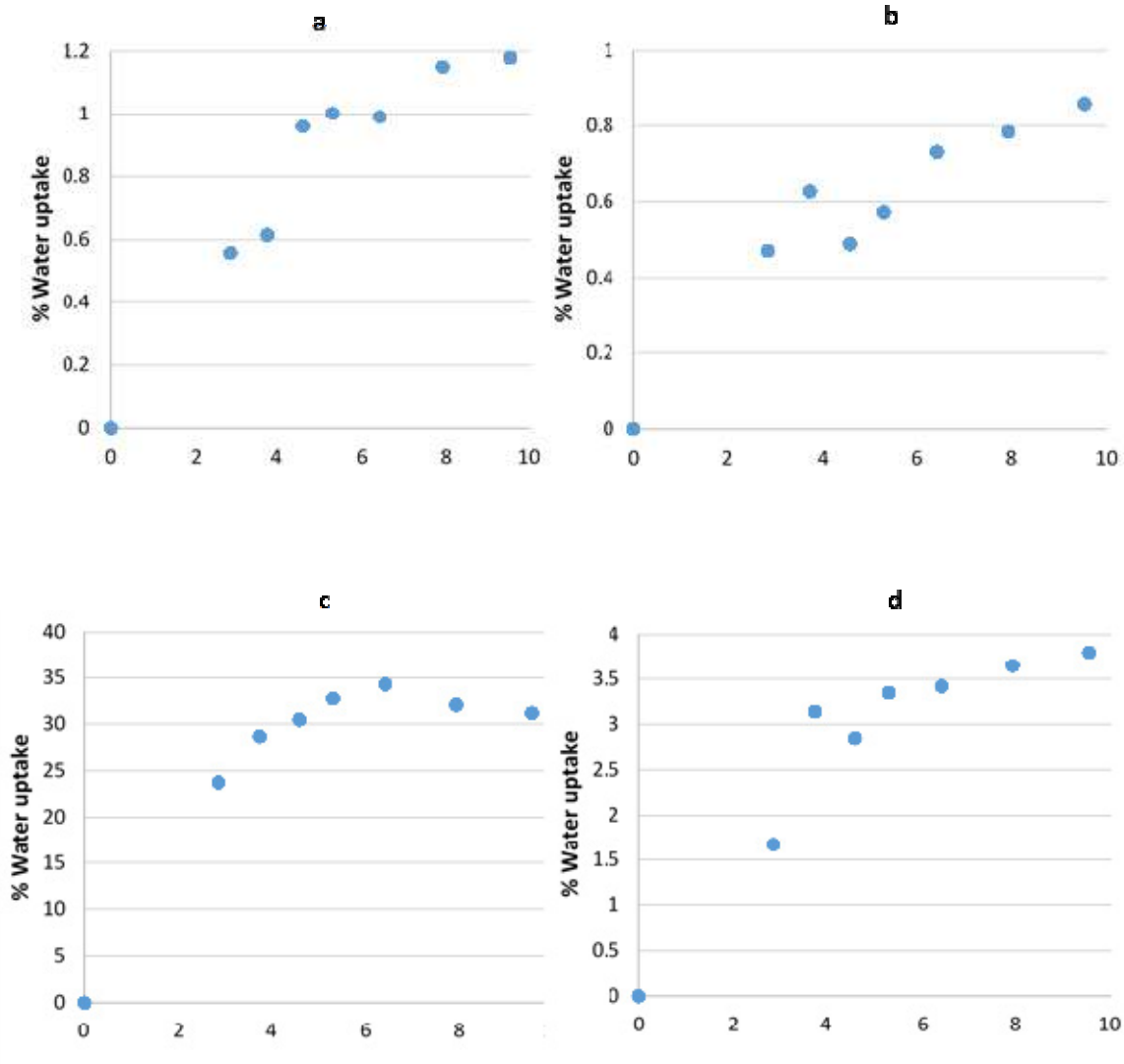


Figure 4: Fracture energy of both adhesives studied as a function of ageing time and ageing environment.

The rate of toughness loss was maximum at the beginning of the exposure and kept diminishing until equilibrium was attained. As it would be expectable, the final toughness of the specimens that were kept in salt water was higher than that of the specimens immersed in distilled water.

Once the toughness reached a plateau, it was considered that the specimens were fully saturated. This way, it is possible to make a correlation between the measured toughness and the water content of the specimen, taking also into account the equilibrium water uptake of the bulk adhesive measured in a previous study (Viana et al. 2016). Although some specimens did not reach a clear plateau, it is perceptible that the toughness of the specimens would not decrease significantly further, meaning that they were almost fully saturated.

It was considered that these specimens were dry when they were first tested and fully saturated at the time of the last toughness measurement. Considering that the G_{IC} that was measured changes linearly with the moisture concentration of the adhesive, using linear interpolation, the moisture concentration as a function of the ageing time was calculated. Figure 5 shows the calculated water uptake of both adhesives as a function of the square root of time.



a. XNR 6852-1 aged in distilled water
b. XNR 6852-1 aged in salt water
c. SikaPower 4720 aged in distilled water
d. SikaPower 4720 aged in salt water

Figure 5: Water uptake of both adhesives used as a function of ageing time and ageing environment.

5 NUMERICAL MODELLING

The water uptake in the adhesive joint was modeled using the Finite element method (FEM). As the bondline is very long, diffusion only in the width direction is enough to predict the water absorption of the adhesive joint (Hua et al. 2006). The adhesive joints reached their maximum moisture uptake sooner than expected if only sorption in the bulk adhesive was considered, taking into account the adhesive diffusion properties determined in a previous study (Viana et al. 2016). This is

thought to be due to interfacial diffusion of water. In order to model this phenomenon, two types of model were adopted:

1. A **one dimensional model**, in which the overall water uptake of the joint was modeled. The diffusion along the width of the joint was modeled using unidimensional beam elements. The diffusion coefficient attributed to these elements were fitted so that the numerical prediction would match the moisture uptake that was calculated, taking into account the experimentally measured toughness. This way it was possible to compute the overall diffusion coefficient ($D_{average}$) of the joint through an inverse method;
2. A **two dimensional model**, in which the water uptake of the bulk adhesive and the water uptake in the adhesive-adherend interface were modeled separately. In this model, the increase in the diffusion speed is attributed to capillary diffusion happening at the interface between the adhesive and the adherends. In order to model this phenomenon, two layers were considered (see Figure 6):
   a. A layer of adhesive, whose diffusion properties were determined in a previous study (Viana et al. 2016) (see Table 1). Depending on the ageing environment, these adhesives may present Fickian or dual Fickian behavior. For this reason, two diffusion coefficients and two equilibrium moisture uptakes are presented;
   b. A very thin layer that represents the interface. The diffusion coefficient of this layer was fitted so that the water uptake of the adhesive would match the water uptake that was calculated from the experimentally measured toughness.

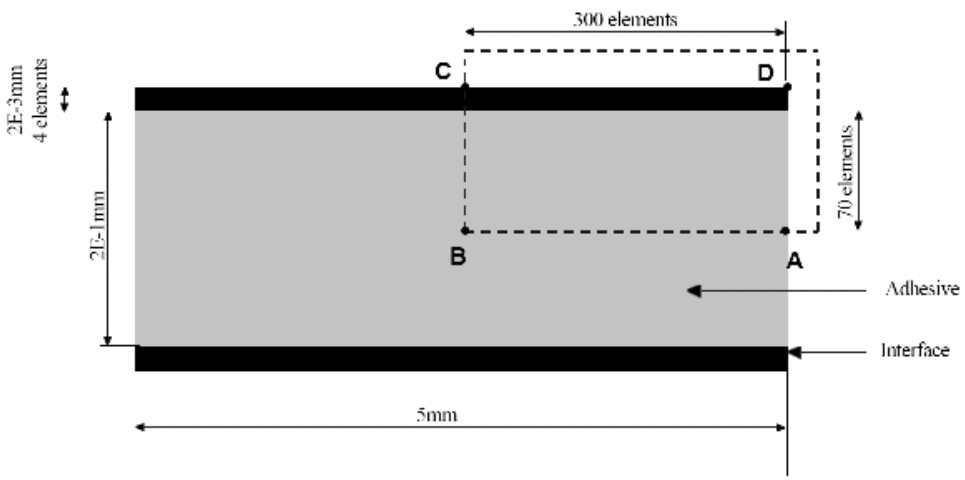


Figure 6: Geometry of the model used to predict interfacial moisture uptake.
Due to the symetry, only the dotted rectangle was modeled.

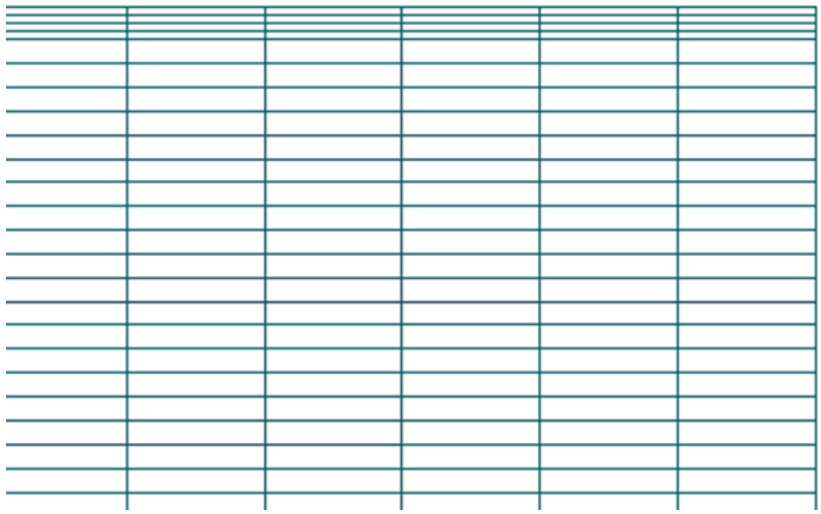


Figure 7: Detail of the mesh used used in the two dimensional model (area contoured in Figure 6).

		D_1 (m^2/s)	mwt_1	D_2 (m^2/s)	mwt_2
XNR 6852-1	Distilled Water	6.0E-13	0.0095	8E-14	0.0023
	Salt Water	6.0E-13	0.0080	8E-14	0.0006
SikaPower 4720	Distilled Water	1.2E-13	0.325	-	-
	Salt Water	2.6E-13	0.020	2.5E-14	0.018

mwt1- Equilibrium moisture content 1
mwt2- Equilibrium moisture content 2

Table 1: Moisture diffusion parameters of both adhesives studied.

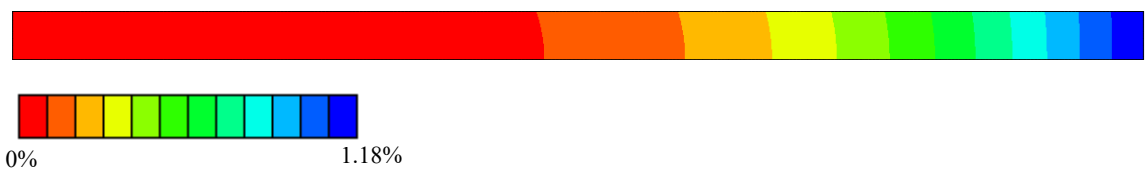
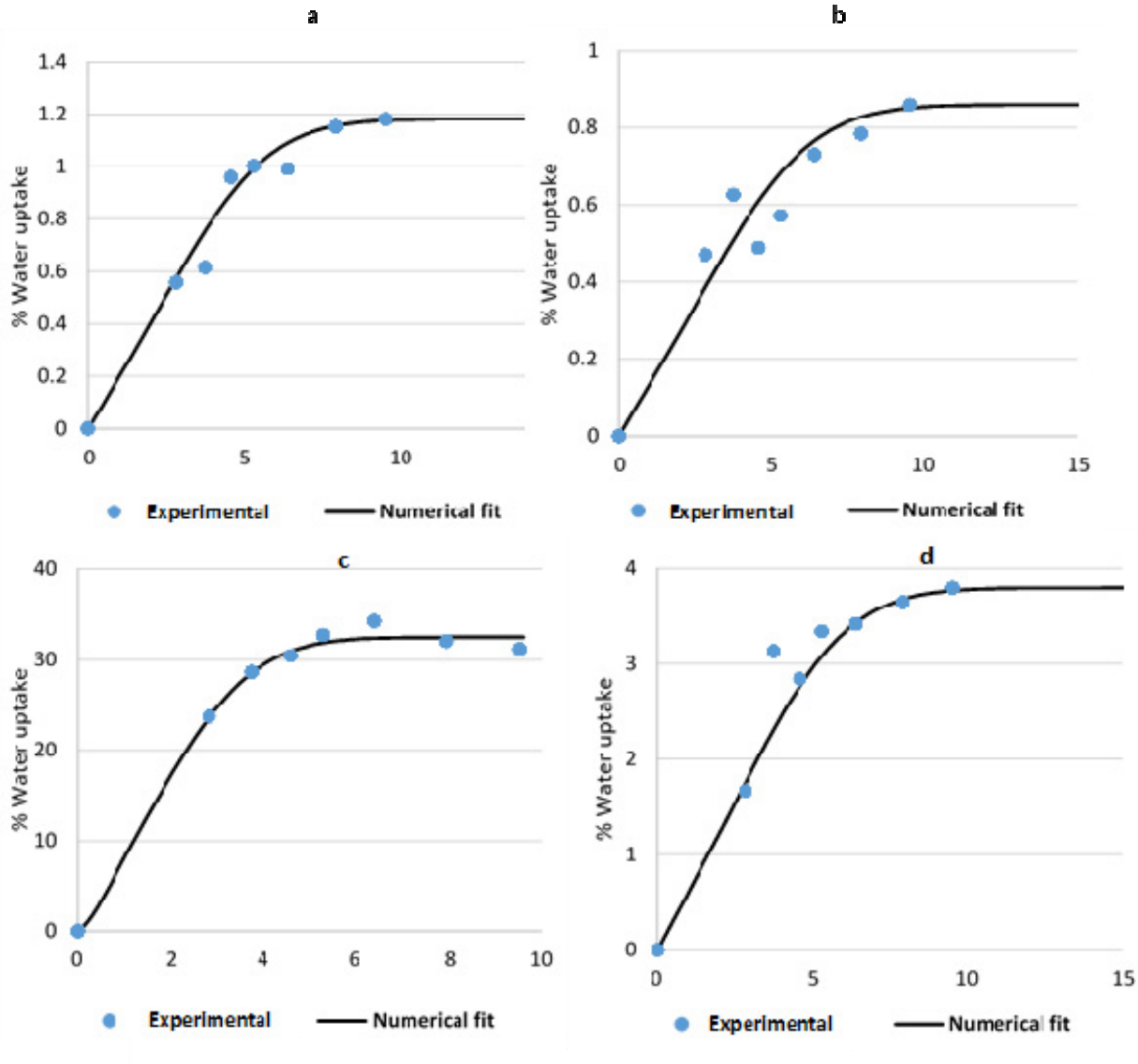


Figure 8: Numerical prediction of the moisture profile of XNR 6852-1 after 24 hours of ageing. The upper bar represents one quarter of the adhesive layer and the lower bar indicates, through a code of colours, its prediction of moisture uptake.

	Ageing environment	$D_{average}(m^2/s)$ (Obtained with the 1D model)	$D_{interface}(m^2/s)$ (Obtained with the 2D model)
XNR 6852-1	Distilled water	1.8E-12	5.5E-11
	Salt water	1.5E-12	5.0E-11
SikaPower 4720	Distilled water	4.5E-12	2.2E-10
	Salt water	1.6E-12	6.2E-11

Table 2: Moisture diffusion parameters of the joints bonded with both adhesives studied.



a. XNR 6852-1 aged in distilled water
b. XNR 6852-1 aged in salt water
c. SikaPower 4720 aged in distilled water
d. SikaPower 4720 aged in salt water

Figure 9: Experimental and numerical prediction of the adhesive joints studied.

This way it was possible to compute the diffusion coefficient of the interface ($D_{interface}$) through an inverse method.

As the coefficient of diffusion was set to be higher at the interface, diffusion of water occurs preferentially in this region, which is then responsible for bringing moisture deeper into the adhesive layer. This moisture is quickly absorbed by the adhesive. Figure 8 shows the computed moisture uptake of XNR 6852-1 adhesive after 24 hours of immersion.

The phenomenon of diffusion shares mathematics with the phenomenon of heat conduction and it is possible to model the moisture uptake of the adhesive simply as a heat transfer problem. The equivalent parameters to permeability coefficient, diffusion coefficient and solubility coefficient are thermal conductivity, thermal diffusivity and heat capacity respectively. In both the one dimensional model and the two dimensional model the heat transfer elements available at the Abaqus® library DC1D2 and DC2D4 for the 1D and 2D analyses, respectively, were used.

Due to the symmetry of the problem, in order to reduce the computation effort and to increase the speed of the analysis only one quarter of the section of the specimens was modelled (see Figure 6). A detail of the mesh is shown in Figure 7. Across line segments [AB], [BC] and [CD], represented in Figure 6, no mass transfer was allowed. In the line segment [AD] equilibrium moisture uptake is attained instantly because it is in contact with the ageing environment.

Using this methodology, both the average diffusion coefficient and the diffusion coefficient of the interface were determined. They are shown in Table 2. The comparison between the experimental diffusion and the numerical predictions are shown in Figure 9. Although there is some dispersion in the results, which is expected given the method used, the numerical prediction fits the experimental results well.

6 DISCUSSION

Experimental results show that the water diffusion in bonded joints was faster than in the bulk adhesive. Other authors have obtained similar results, using different methods (Liljedahl et al. 2009, Wapner and Grundmeier 2004, Zannideffarges and Shanahan 1995). The comparison between the diffusion coefficients obtained in these studies are summarized in Table 3. From the analysis of this table, it is possible to conclude that when in an adhesive joint, the adhesive usually absorbs water faster than when in bulk.

Reference	Method		D (m^2/s)	Ageing temperature
(Zannideffarges and Shanahan 1995)	Mechanical loading (change in adhesive's modulus)		5.3E-12	70°C
	Gravimetric measurement		1.4E-12	
(Wapner and Grundmeier 2004)	FTIR-transmission microscopy		1.13E-13	21°C
(Frantzis 1998)	Gravimetric measurement		1.0E-13	
Present study	Mechanical loading (change in adhesive's toughness)	SikaPower 4720	[1.5-4.6]E-12*	32.5°C
		XNR 6852-1	[1.5-1.8]E-12*	
	Gravimetric measurement	SikaPower 4720	[1.2-2.6]E-13*	
		XNR 6852-1	6E-13	

*These values vary if the adhesive is aged in salt water or distilled water.

Table 3: Comparison between the average diffusion coefficients determined in this work and those found in other studies.

This behaviour might be explained by the fact that in an adhesive joint, as the adhesive is constrained by metallic adherends, the shrinkage due to curing could lead to a less dense structure near the interface and facilitate local water uptake. The orientation of the polymer closer to the substrates could be different and enhance diffusion in that region. Water can diffuse at the interface by capillary diffusion through voids that exist between the adhesive and the adherends(Zannideffarges and Shanahan 1995). On the other hand, the presence of these voids allow the rapid ingress of water and enable pockets of water to be developed along the interface, which may promote diffusion in this region (Kinloch et al. 2000). Another possibility has to do with the creation of stresses due to the swelling of the adhesive. This residual stress may enhance the diffusion and promote case II diffusion, as suggested by Liljedahl et al. (Liljedahl et al. 2009).

The speed of interfacial moisture diffusion depends on the roughness of the substrate and on the capacity of the adhesive to fill in the gaps of the adherends. In order to avoid this problem, maybe if a low viscosity primer capable of filling in the small gaps that exist in the adhesive surface is applied, adsorption of water by the substrates would be reduced (Kinloch et al. 2000) and the water uptake would be slower.

7 CONCLUSION

This work focused on the measurement of the toughness of aged DCB adhesive joints. Tests were made after different ageing times and a strong reduction in the toughness of the adhesive was found. From the variation of toughness of the specimens, the moisture uptake of the adhesive was calculated. The speed of moisture ingress into the adhesive was higher than expected if only the moisture uptake through the bulk adhesive was considered. It is thought that this is due to capillary diffusion enhanced by voids that exist at the interface between the adhesive and the adherends. A finite element model was proposed in order to predict the average diffusion coefficient and the diffusion coefficient of the interface. The numerical prediction fits the experimental results well. This information can help predict the moisture uptake of more complex joints.

In order to predict the mechanical behaviour of adhesive joints, it is very important to be able to predict the moisture uptake in each point of the adhesive layer. This study sheds some light on this subject and allows a better prediction of the water uptake in adhesive joints. However, more work is needed in order to assess the influence of the roughness of the substrates and the capability of the adhesive to fill the voids of the substrates on the interfacial diffusion coefficient.

Aknowledgements

The authors would like to thank Sika for supplying SikaPower 4720 adhesive and Nagase Chemtex for supplying XNR 6852-1 adhesive. This study was financed by the Fundação para a Ciência e Tecnologia through grant EXCL/EMS-PRO/0084/2012.

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