THE EFFECTS OF PROCESSING PARAMETERS ON REACTIVE EPOXY ADHESIVES

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Abstract

Adhesives are now widely used in the automotive industry. This paper presents some of the aspects related to the processing of a single component (1K) hot cure epoxy adhesive. Results presented within this paper demonstrate that both the substrate and the epoxy adhesive are sensitive to moisture exposure. The moisture absorbed in the adhesive system (adhesive + substrate) evaporates during the cure cycle and causes defects such as voids within the joint. The effect of voids on the mechanical properties of the bonded assembly was evaluated using single lap shear and T-Peel tests. Results showed that extensive void formation could result in a significant drop of the mechanical properties with a maximum loss of 18.3 % and 50 % of the lap shear strength and peel load respectively for samples. The effect of the curing kinetics on the final amount of voids was investigated and it appeared that fast curing rates led to extensive void formation. The experimental work suggested that both the shape and the quantity of voids within the adhesive joint were dependent on the initial amount of moisture present in the system and on the extent of cure of the adhesive when the moisture is released.

1 Introduction

The automotive industry is continually facing conflicting challenges regarding fuel consumption and safety regulations. These demands have led to the increased use of lighter materials and new joining technologies to save weight. Adhesives have been used at different levels to bond car components such as windscreens, rear view mirrors and body panels. Recent progress in the adhesive sciences has enabled engineers to design structural adhesively bonded assemblies [1]. Low investment and improved design flexibility make adhesive bonding technology particularly suitable for the low volume vehicle industry (< 10K units per annum).

These vehicles are often manufactured using aluminium rather than steel and more conventional joining technology such as spot-welding has been replaced with adhesive bonding. This has led to a number of structural improvements such as increased body stiffness, better stress distribution leading to better durability, improved corrosion properties, improved fatigue performance and noise, vibration and harshness (NVH) while saving weight [2]. Aluminium components generally are anodised using a direct current sulphuric acid (SAA-DC) anodising process and bonded together with a hot cure epoxy adhesive. These automotive structures do not rely solely on mechanical fasteners such as rivets or spot welds for their structural integrity.

The integrity of the final bonded assembly relies on the intrinsic properties of the constitutive materials and also the interface properties between the substrate and the adhesive. When considering adhesive bonding for automotive applications, various factors are likely to affect the final joint properties. This paper focuses on the effects of the processing parameters for an adhesive system made from aluminium anodised substrates (6060-T6 alloy) and a single component hot cure epoxy adhesive (Dow Betamate XD4600).

The first stage of the bonding process consists of applying a heat-treatment on the anodised parts to remove any surface contaminants (dust, moisture or oil residues). The adhesive then is applied to the part using a robot to ensure consistent geometry and bead placement. The structure is built in several sub-assemblies and the parts are assembled using various fixtures. Standard rivets, self-piercing rivets and monobolts are used to hold the structure in

shape until the adhesive has been thermally cured within an oven.

On a plant scale, it is often difficult to control the relative humidity and the ambient temperature, thus large seasonal variations can be expected throughout the year.

Once the adhesive has been applied on the parts, the joints are left open during the assembly of the structure. Both the assembly time and the cure cycle of the adhesive are required to be compatible with the rest of the manufacturing process.

It was reported [3] that pre-bond humidity exposure and the cure rate could affect the formation of voids within adhesive joints. The Fig. 1 below shows the effect of different pre-bond humidity exposure on the final amount of voidage.

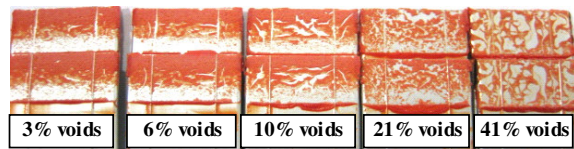| 3% voids | 6% voids | 10% voids | 21% voids | 41% voids |

Fig. 1: Conditioning and void formation (plan view showing the through thickness defects)

More specifically, this paper aims to investigate the sensitivity to moisture of the adhesive system and to understand the mechanisms of void formation during the cure cycle. The effect of voids on the initial mechanical properties was evaluated using the single lap shear and T-Peel tests. Identifying the root causes for void formation and understanding their effects on the integrity of the bonded assembly will help in improving the overall bonding process.

2 Experimental procedures

2.1 Materials

All substrates were prepared from an extruded 6060-T6 alloy and the adhesive Betamate XD4600 was provided by Dow Automotive, Switzerland.

2.2 Surface pre-treatment

The 6060-T6 aluminium substrates were anodised using SAA-DC with parameters listed in Table 1. The average oxide layer thickness

produced during the anodising process was measured at 7 μm.

H$_2$SO$_4$ Conc. (wt%)	Current density (A/m^2)	Time (min)	Bath Temperature (°C)
18.5	140	10	18

Table 1: Anodising parameters for samples pre-treatment

2.3 Relative Humidity exposure

A 75% relative humidity (RH) environment was created by using a NaCl saturated salt solution [5]. The saturated salt solution was placed at the bottom of a sealed plastic box and the substrates were placed on a polyethylene rack during conditioning. The box was maintained at ambient temperature (20°C) during all the experiments.

2.4 Samples preparation

Lap shear and T-Peel specimens were prepared according to the relevant standards [10, 11]. The Fig. 2 below shows the geometry used for the lap shear specimens.
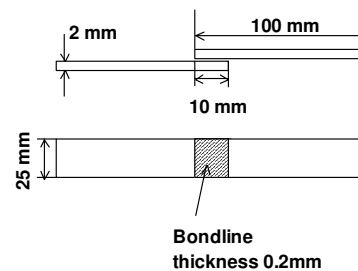

Fig. 2: Geometry of the LS specimen

The Fig. 3 below shows the geometry for the T-Peel specimens. The jaws set on the universal tensile test machine were fixed and no rotation was allowed at the front end of the sample.
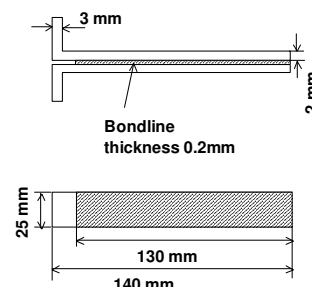

Fig. 3: Geometry of the T-Peel specimen

Different levels of voids were created within the adhesive bondline by applying different heat-treatments and conditionings on both the substrate and the adhesive. Five samples were bonded for each set of parameters. The parameters used to prepare the lap shear and T-Peel samples are listed in Table 2 below.

Amount of voids	Heat Treatment (HT)	RH Conditioning
No voids	190°C / 30min	No conditioning
Low	No HT	No conditioning
Medium	190°C / 30min	4h @ 75% RH on substrate
High	No HT	4h @ 75% RH on substrate + adhesive
Very High	No HT	16h @ 75% RH on substrate + adhesive

Table 2: Conditioning parameters for the lap shear and T-Peel samples

Alternative samples were prepared by bonding a glass microscope slide onto an anodised aluminium substrate to investigate the effects of the reaction rate on the final void area. The 100x25x2 mm aluminium substrates were anodised with the parameters listed in Table 1. The aluminium plates were heat-treated (190°C for 30 min) and the conditioning and cure parameters listed in the Table 3 below were applied to the samples.

Sample	RH conditioning	Cure Cycle
1-A	No Conditioning	Slow
1-B	No Conditioning	Standard
1-C	No Conditioning	Fast
2-A	4h @ 75% RH	Slow
2-B	4h @ 75% RH	Standard
2-C	4h @ 75% RH	Fast

Table 3: Conditioning and cure parameters for the "glass slide" samples

The temperature ramp rates used for the fast, standard and slow cure cycles were $21°C.min^{-1}$, $5.5°C.min^{-1}$ and $2°C.min^{-1}$ respectively.

2.5 Equipment

2.5.1 Analytical microbalance

Gravimetric analyses were performed using an Oertling analytical microbalance with a resolution of 0.01 mg. Under-bench measurements were performed on 125x80x2 mm aluminium plates anodised with the parameters listed in Table 1. A heat-treatment (190°C for 30 min) was applied to the samples prior to humidity exposure. The substrates were then placed in the humidity chamber underneath the microbalance as shown in Fig. 4 below. The mass uptake was measured at different time intervals.
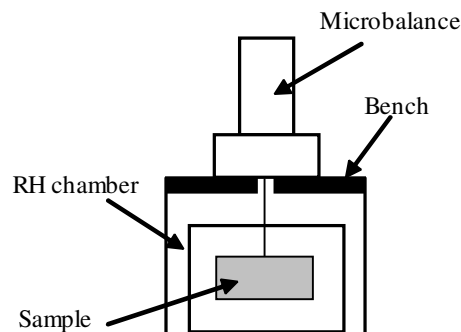

Fig. 4: Gravimetric analyses using under-bench measurement technique

2.5.2 Moisture analyser

The moisture content in the anodised layer was measured using a LECO RC412 carbon/moisture analyser. The LECO RC412 depicted in Fig. 5 consisted of an oven where a thermal cycle was applied to the sample. A gas flow (nitrogen for moisture analysis) was applied to the oven for the duration of the experiment. An infrared cell analysed the waste gas composition downstream of the oven and provided a direct measurement of the water content.
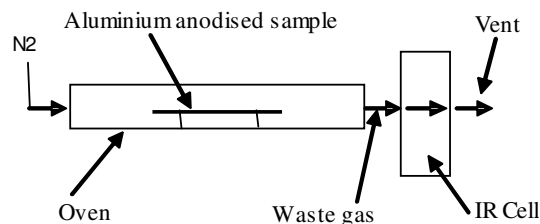

Fig. 5: The LECO RC412 carbon/moisture analyser

LECO analyses were performed on a 100x25x2 mm aluminium substrate anodised using the parameters listed in Table 1.

2.5.3 Tensile test machine

The lap shear and T-Peel tests were performed using an Instron Series 3300 universal tensile test machine with a 30 kN load cell. The crosshead displacement was set at 10 mm/min and 254.5 mm/min for the lap shear and T-Peel specimens respectively.

2.5.4 Void measurement

The percentage area of voids within the adhesive joint was measured using a digital camera and the Adobe Photoshop [13] software. A representative picture of the bonded area was converted into black and white and the amount of voids was determined by measuring the ratio between black and white pixels.

3 Results

3.1 Lap shear tests

The maximum lap shear strength at break was recorded. The results presented in Fig. 6 below show that this lap shear strength was affected by the presence of voids within the adhesive. The lap shear strength showed a linear decrease with a maximum loss of 18.3 % when the void content was increased from 2 % to 41 %.
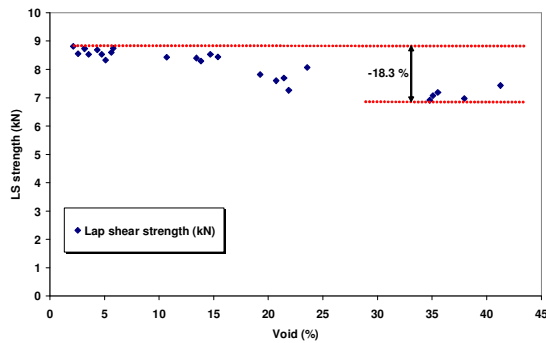
Fig. 6: Lap shear strength versus void area

3.2 T-Peel tests

The peak load, the plateau load, and the elongation at break were recorded. Fig. 7 below shows the main output variables from the T-Peel results. The peak load showed a linear decrease

with increasing levels of voids. Increasing the void content within the adhesive from 3 % to 44 % resulted in a drop of 65 % of the peak load. The results presented in Fig. 8 show that the peak load could vary significantly for specimens with similar void areas.
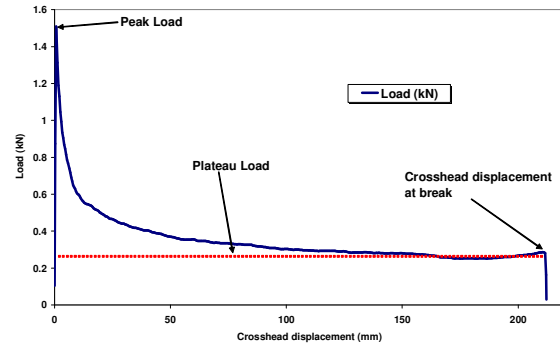
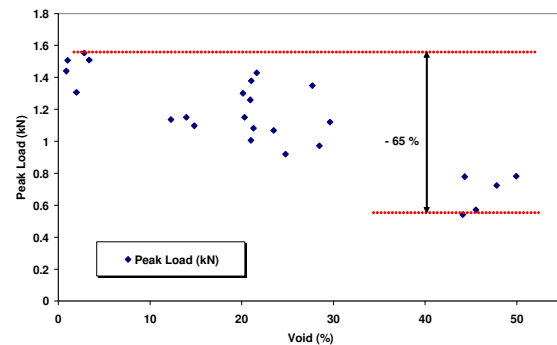Fig. 7: Output variables from the T-Peel test

Fig. 8: Peak load versus void content

The crosshead displacement at break reflects the amount of plastic deformation that the substrate experienced before it broke. Fig. 9 below presents the plastic deformation of the T-Peel specimens with different levels of void.
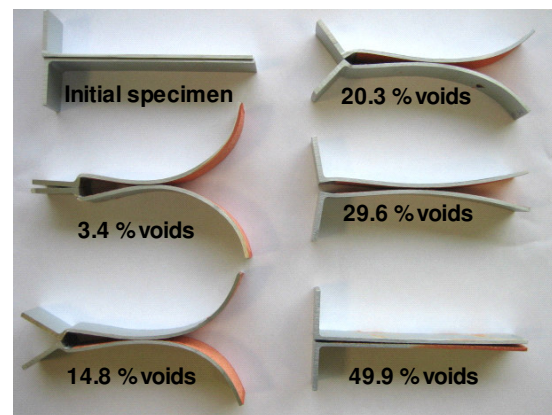
Fig. 9: Plastic deformation versus void area

The presence of voids within the bond area affected significantly the plastic deformation of the different samples. The large plastic deformation for the specimen with a void area of 3.4 % indicated a strong peel resistance between the adhesive and the two substrates. A voidage of 49.9 % within the bondline resulted in almost no plastic deformation of the substrate. The amount of voids did not change the failure mode and a cohesive failure was observed for all the samples. Fig. 10 below shows the maximum crosshead displacement versus the void area.
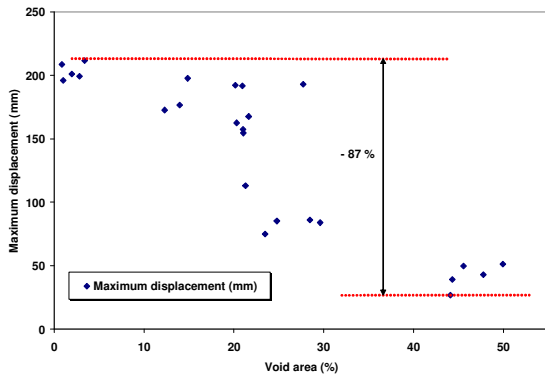
Fig. 10: Maximum crosshead displacement versus void content

Increasing the void content in the samples resulted in lower crosshead displacements and thus lower plastic deformation of the substrate. The maximum displacement was reduced by 87 % when the void area increased from 4.3 to 41.3 %.

The plateau load presented in Fig. 11 below shows a linear decrease for a void content up to 20 % and remains stable afterwards. Increasing the void area from 2.1 % to 41.3 % resulted in a 50 % drop of the plateau load.
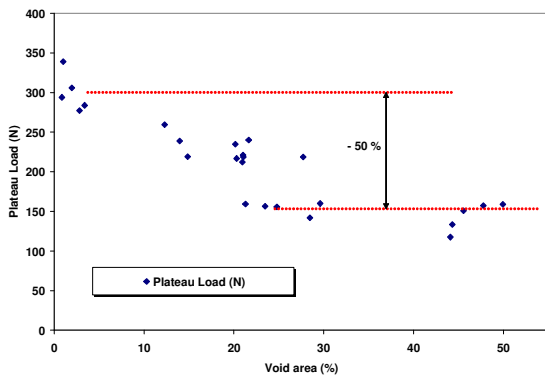
Fig. 11: Plateau load versus void area

3.3 Gravimetric analyses

3.3.1 Moisture uptake in the anodised layer

The anodising process consists of growing an oxide layer at the surface of the aluminium substrate [4]. Both the presence of aluminium sulphate and the resulting porous columnar structure of the oxide film make it particularly sensitive to moisture [3]. Fig. 12 below shows the under-bench measurement results for anodised samples exposed to ambient and 75 % RH.
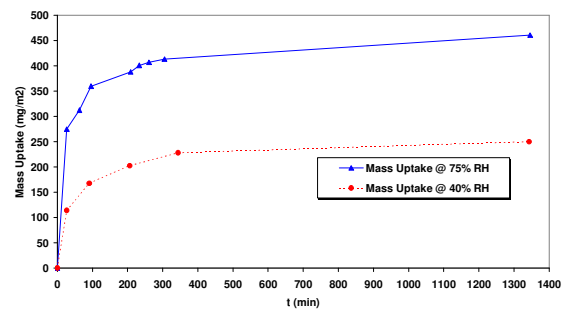
Fig. 12: Mass uptake in the aluminium

The results show a sharp increase of the mass uptake within the first 30 minutes of exposure, followed by a gradual uptake to form a plateau. The sample exchanges moisture with the environment up to an equilibrium dictated by the relative humidity level. The normalised plot of the mass uptake at time t (M_t) over the equilibrium mass (M_e), presented in Fig. 13 below, shows that the sorption kinetics is essentially independent of the relative humidity.
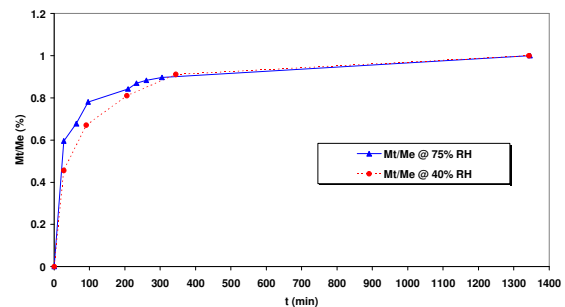
Fig. 13: Sorption kinetics of the anodised aluminium substrate

Further analyses were performed using the LECO RC412 moisture/carbon analyser [6]. The

aluminium anodised samples were not heat-treated but stored for 4h at 75 % RH prior to the analysis. The results presented in Fig. 14 below show the presence of two water peaks. The main peak, located between 50°C and 150°C is attributed to the free water absorbed on the surface and in the upper part of the oxide layer. The second peak at 200°C suggests that there is water being released by an alternative mechanism.
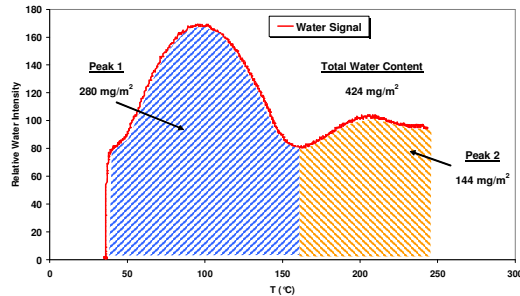

Fig. 14: Two types of water in the oxide layer

3.3.2 Moisture uptake in the epoxy adhesive

The second source of moisture uptake in the system was the epoxy adhesive. Gravimetric analyses on uncured XD4600 adhesive [9] presented in Fig. 15 revealed that when exposed to humid environments the adhesive also absorbed moisture. It can be seen that this process is reversible and moisture desorption occurs when the adhesive is exposed to lower humidity levels.
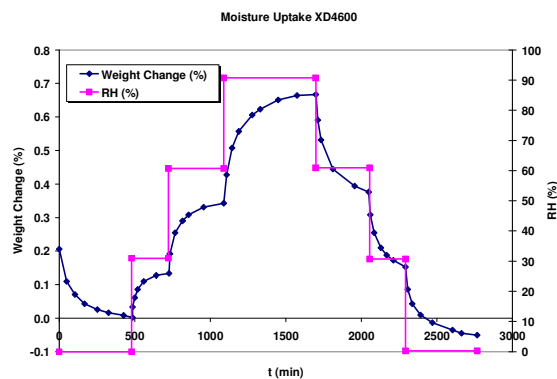

Fig. 15: Moisture uptake in the epoxy adhesive

Both the assembly time and the relative humidity in the plant during production will affect the final amount of moisture in the system (adhesive + substrate) and thus the total amount of voids within the joints.

3.4 Cure rate and void formation

The effect of the reaction rate on the final amount of voids was investigated by applying different conditioning to the aluminium anodised substrate and curing the samples using the different cure cycles presented in Fig. 16 below. The cure kinetics for the epoxy adhesive was calculated using the following model based on the general autocatalytic equation (1):

$$\frac{dX}{dt} = A \exp\left(\frac{-Ea}{RT}\right) X^m (1-X)^n \qquad (1)$$

Where: X = the degree of cure at time t (%)
t = the reaction time (min)
T = the temperature (K)
Ea = the activation energy (J.mol^{-1})
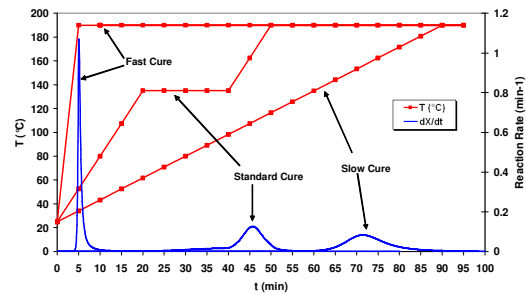R = Universal gas constant 8.314 J.K^{-1}.mol^{-1}
A, m, n = constants

Fig. 16: Cure cycles and cure kinetics

As expected, heat-treated samples with no pre-bond conditioning did not show any voids. Samples exposed for 4 hours at 75 % RH showed different levels of voids when cured with the different cycles, as shown in Fig. 17.
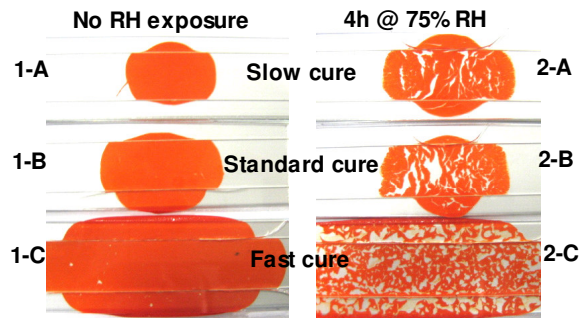

Fig. 17: Conditioning, cure cycles and void content

The thermal profile applied during the cure cycle of the adhesive was shown to affect both the shape and the amount of voids for samples containing an initial amount of moisture. The total amount of voids for samples exposed to pre-bond humidity was 9.7 %, 16 % and 28.5 % for samples 2-A, 2-B and 2-C respectively. Sample 2-A and 2-B show voids with sharp geometries (Fig. 18) suggesting the diffusion of moisture from the centre of the bondline towards the edges of the joint. The voids in sample 2-C, as shown in Fig. 19, do not indicate the same diffusion paths.
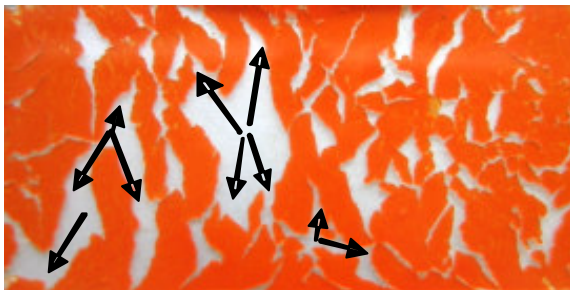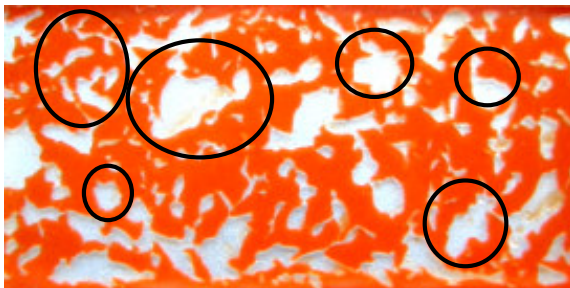

Fig. 18: Voids geometry in sample 2-B

Fig. 19: Voids geometry in sample 2-C

4. Discussion

Moisture uptake in both the epoxy adhesive and the anodised substrate could result in the formation of voids within the adhesive joints and affect the structural integrity of the aluminium-bonded structure. The results highlighted that a void content of 41.3 % could reduce the lap shear strength by 18.3 %. The lap shear test specimens are easy to prepare and therefore represent a convenient quality control tool. However, the geometry of the sample and the stress distribution in the bonded area can cause some variability in the results. As illustrated on Fig. 20, the high stress concentration at the edges of the bonded area [12, 14], the shape and

the size of the spew filet are the key parameters likely to affect the initial maximum lap shear strength.
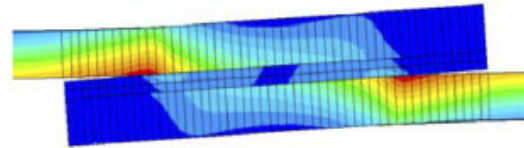

Fig. 20: Deformation of the lap shear joint [14]

The T-Peel test, initially intended to evaluate the adhesive-substrate interface properties, was more affected by the presence of voids within the adhesive bondline. The amount of plastic deformation was significantly lower for samples presenting a large void area. The formation of voids within the joint resulted in a lowered bonded surface and thus a lower plateau load to peel the two substrates apart. The peak load showed a variability of up to 40 % for some of the samples presenting a similar amount of voids. Even if special care was taken during the T-Peel specimens preparation, the shape of the front-end adhesive tip and the distribution of the voids is likely to affect the crack initiation mechanisms and create some variability in the peak load.

The gravimetric analyses highlighted that when exposed to humid environments, both the anodised substrate and the epoxy adhesive tended to reach equilibrium mainly dependent on the relative humidity of the environment. The sorption kinetics in the aluminium oxide were essentially independent of the relative humidity and it is expected [7, 8] that the structure of the porous layer such as the thickness and the pore diameters are likely to control the mechanisms of moisture uptake. The LECO analyses confirmed the presence of two types of water within the oxide film with a second peak observed at 200°C. Johnsen et Al. [3] suggested that the aluminium hydroxide precipitated in the porous oxide layer during the anodising process was transformed into oxide at high temperatures as described in (2):

$$2 \ Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O \qquad (2)$$
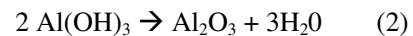
The results also showed that the moisture absorption process was reversible for the epoxy adhesive and that when exposed to lower humidity levels the polymer could reach a new equilibrium by releasing moisture.

Although the initial amount of moisture in the system (adhesive + substrate) is a key parameter

controlling the final amount of voids, the reaction rate affected both the final amount and the shape of these voids. It is speculated that the viscosity of the adhesive increases with the crosslinking of the adhesive. The results from the kinetic model plotted in Fig. 16 show that the cure cycle (temperature ramp rate) affects the beginning of the cure process and that the crosslinking starts after 3 min for the fast cure cycle while it is delayed after 60 min when curing the sample with the slow cycle. Fig. 14 shows that the moisture is released from the anodised layer at temperatures above 50°C therefore, the extent of cure and the viscosity of the adhesive when the moisture is released from the anodic film might explain the differences regarding the final amount and the shape of the voids. Further work is required to characterise the viscosity of the adhesive during the cure cycle, however moisture diffusion is expected to be easier in a low viscosity adhesive which might explain the shape of the voids seen in the sample 2-A and 2-B. As the viscosity increases, the diffusion of moisture may be more difficult which might prevent the moisture from moving towards the edges of the bondline and affect the shape of the voids.

5. Conclusion

The assembly time and relative humidity can be critical during the manufacturing process of aluminium bonded structures. Pre-bond exposure at high humidity levels on both the substrate and the adhesive can lead to the formation of voids within the adhesive joints and alter the integrity of the structure. Controlling the relative humidity in a production environment is a difficult and expensive alternative. It is therefore important to understand the impact of all the process parameters on void formation and on the final properties of a joint. Fast cure cycles resulted in an increased number of voids when curing samples that had been exposed to humidity. The shape of the defects for samples cured with a fast and a standard or low ramp rate suggested that the moisture released from the film do not follow the same diffusion paths, which might be explained by a different adhesive viscosity.

This work demonstrated that both the aluminium anodised substrate and the epoxy adhesive were sensitive to moisture uptake when exposed to humid environments. Thermal analyses revealed the presence of two types of water within the oxide layer. This observation might be explained by the transformation from the aluminium hydroxide into the aluminium oxide already highlighted in previous work [3]. A better understanding of the moisture uptake kinetics in both the substrate and the adhesive could help in improving the initial heat-treatment process. Understanding the factors that affect void formation within a bonded structure can lead to improved manufacturing robustness.

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