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Controlled reduced-strength epoxy-aluminium joints validated by ultrasonic and mechanical measurements

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Abstract

In this study a series of joint systems, consisting of aluminium substrates bonded using an epoxy adhesive, were produced. Several levels of adhesion were achieved by altering the substrate surface treatment and the curing cycle of the adhesive. The goal of this study was to produce reduced-strength epoxy-aluminium joints that could be used as reference samples for ultrasonic non-destructive testing (NDT) studies. There is clearly a continuing challenge to improve the quality of the adhesively-bonded joint inspection to ensure the durability of the bonds, to monitor repairs, and to evaluate the strength of the bonds. However, developing and qualifying innovative or advanced non-destructive testing requires an essential preliminary step: a method for repeatedly producing reduced-strength bonded test specimens must be developed. In this study, in addition to a rigorous protocol to produce bonded joints, complementary ultrasonic CSCAN were realised to validate the homogeneity of the joints and to ensure that samples met all requirements so as to be considered as reference samples. Mechanical tests were performed to evaluate the mechanical strength of each joint and Acoustic Emission (AE) was used during the tests in order to confirm the expected fracture mechanisms.

Keywords: epoxy, adhesive bonding, surface treatment, lap shear, reduced-strength bond

1. Introduction

The use of adhesive bonding offers many advantages over traditional mechanical assembly and welding, and it is used in many applications where weight is critical, such as the transport industry. Adhesive bonding improves the stress distribution in joined structures and allows the bonding of dissimilar materials and composite structures. The performance of the bond in terms of mechanical strength and durability is determined by the following main factors: adhesion between substrates and adhesive, cohesion and structural inhomogeneities of the adhesive, defects in the bondline (e.g. delaminations, unbonds, kissing bonds, pores, etc.), bondline thickness, adhesive edges, and also ductility of the adhesive or the adherent. Three classical defects are searched for [1, 2]: i. complete voids, disbonds, or porosity, ii. poor adhesion, iii. poor cohesive strength.

In this study we investigate the second type of defect: poor adhesion. This defect is still extremely difficult to detect non-destructively and this difficulty reduces the use of bonding techniques in loaded structures. Poor adhesion is a reduction in the strength of the bond between the adhesive and the adherent. When the adhesion is null, this defect is known as the Kissing Bond. The Kissing Bond is itself a specific topic [3, 4] and will not be considered in this paper as we are studying a more general case of reduced-strength adhesion and not only the zero adhesion defect. The development of weak bond specimen sets to be provided to the NDT community was recently recommended to the Federal Aviation Administration (FAA). More precisely, it was recommended to generate weak bonds on aluminium substrates with epoxy adhesives and to focus on variations in the surface preparation method of a standard full-strength bonding recipe? [5]. This study anticipated this recommendation to produce reduced-strength bonded assemblies to qualify non-destructive methods.

In addition, the present study aims to show how the combination of mechanical testing and ultrasonic testing can provide complementary information in view of a better qualification of bonded

specimens to be considered fully as reference samples. Even if the main objective is to consider the strength of the adhesion between adherent and adhesive, it is necessary to make the epoxy bond cohesive strength vary so as to propose a complete set of various specimens for NDT testing.

Two critical factors affecting the joint performance in an aluminium–epoxy–aluminium joint are investigated. The factors considered are representative of scenarios that can happen during manufacturing, namely:

i) the epoxy conversion, related to the curing cycle, known as a critical issue as it can compromise the integrity of the bonded joint. The epoxy conversion has a strong influence on the mechanical behaviour of the material: a partially cured epoxy-amine network has many unreacted chain ends, it is more brittle than a fully cured network, it has a higher Young's modulus at room temperature, and a lower elongation and strain at break [6]. It can be assumed that these differences will influence the strength of the joint [7].

ii) the treatment of the substrate, also known as one of the most important factors governing the adhesive strength of epoxy resins bonded to aluminium alloys. The benefits of surface preparation are widely known, but it is not always done properly. For many decades, chromate-based treatments have been reported as the most efficient, used as anti-corrosive and adhesion promoters on aluminium substrates [8]. Such treatments are expensive and use aggressive and toxic chemicals that will be prohibited by REACH regulation from manufacturing processes. Indeed a number of Cr(VI) compounds currently used for surface treatment, such as chromium trioxide and sodium dichromate, have been included in the List of Substances subject to Authorisation (Annex XIV). This means that they shall in principle not be used or placed on the market in the European Economic Area for use any longer after the "sunset date" on 21 September 2017, unless an authorisation for the specific use has been granted by the European Commission [9]. Surface treatments based on organo-functional silanes have evolved as a promising alternative to the chromate-based treatments [10]. One of the most commonly used silanes as adhesion promoter is (3-glycidyloxypropyl)trimethoxysilane (γ -GPS, or GLYMO). On the one hand, after the hydrolysis reaction of the methoxy groups, the silane can

enable the formation of strong Al-O-Si bonds between the hydroxyl groups on the aluminium surface and the hydrolysed groups of the silane. On the other hand, the epoxy group of the γ -GPS will react with the amino groups of the curing agent; indeed amines are by far the most common curing agent used with epoxy-based adhesives. The treatment of aluminium substrates with aqueous solution of γ -GPS has been shown to improve bond durability if done in good conditions [11]. Moreover, the silane treatment leads to a strength of adhesion that is similar to that obtained by sulfo-chromate treatment [12, 13].

In this work a series of model joint systems were produced, consisting of aluminium substrates bonded using an epoxy adhesive in a single lap shear configuration. Specimens were designed to promote different levels of adhesion by altering the substrate surface treatment and the curing cycle of the adhesive, as explained previously. Ultrasonic CSCAN imaging and mechanical tests associated with acoustic emission were performed to evaluate the quality of the sample and the mechanical strength of each joint. In addition, fracture surfaces were examined. The results will allow the design of specific specimens for the qualification of new NDT methods aiming at evaluating the reduced strength of bondings.

2. Experimental

2.1. Materials

The epoxy adhesive used in this investigation was a two-component model system. The epoxy resin was a classical diglycidyl ether of bisphenol A DGEBA, (DER331, Dow Chemicals) with an epoxy equivalent weight of 182-192 g/eq. The curing agent was a polyetheramine (Jeffamine D230, Huntsman) with an amine equivalent weight equal to 60 g/eq. The epoxy resin and the diamine curing agent were mixed mechanically at room temperature at the stoichiometric ratio of amino hydrogen / epoxy equal to one; the mixture was carefully degassed in an ultrasonic bath (VWR, France) for 5 minutes to avoid the formation of air bubbles in the adhesive joint. An adhesion promoter, (3-glycidyloxypropyl)trimethoxysilane (γ -GPS), was also used for the surface treatment of

the substrates. It is known as one of the most efficient adhesion promoters for epoxy networks [10, 11]. The structures of the components are shown in Table 1. All chemicals were used as received. The experiments were conducted using an aerospace grade aluminium alloy T2024. The thickness was $1.64 \text{ mm} \pm 0.017 \text{ mm}$.

2.2. Surface preparation of the aluminium substrates

The following three procedures were used for the surface treatment of the aluminium adherents before adhesively joining them.

i – substrates were degreased by wiping with a tissue soaked in isopropyl alcohol.

ii – after degreasing, the substrates were sand-blasted with corundum particles having a size of $40 \mu\text{m}$ to create a surface roughness, degreased again and blown using clean N_2 to remove residual particles.

iii – afterwards, the substrates were treated with a silane solution. First, a γ -GPS solution in distilled water at a concentration of 1 wt% was prepared, the pH of the solution was adjusted to 4.5 and the solution was stirred for 1 hour at room temperature for the hydrolysis of the methoxy groups.

Secondly, the aluminium substrates were immersed in the hydrolysed silane solution for 10 min.

Finally the treated substrates were heated for 1 h at $93 \text{ }^\circ\text{C}$ to allow condensation reactions between the hydrolysed silane and the aluminium substrate.

The nomenclature adopted for these surface treatments i, ii and iii is D, DS, and DSSi respectively.

2.3. Preparation of single lap shear test samples

Single lap joints (SLJ) were produced by first machining the metal substrates to $100 * 25 \text{ mm}^2$ pieces; then the substrates were treated according to the three procedures described above and assembled together with a 12.5 mm overlap following EN 2243-1 Standard. A specifically machined mould was designed allowing the simultaneous preparation of seven specimens. The fourteen aluminium plates were firstly waterjet cutted and the seven specimens were separated, no cutting was needed after the bonding process. The mean value of the adhesive thickness was 0.26 mm. The mould was placed under a press (2.2 bars) and two curing cycles were done. To assess the effect of poor crosslinking on

the bond quality, a first curing cycle of one week at room temperature throughout the curing process was applied. The second curing cycle was 48 hours at room temperature, followed by three hours at 160 °C, leading to a fully cured adhesive [14]. Two specimens of bulk epoxy networks were cured under the same conditions to determine their glass transition temperature, T_g . For clarity, the letter and number in the nomenclature of the sample refer to the surface treatment and to the epoxy conversion, respectively. The list of samples studied is given in Table 2.

2.4. Characterization techniques

Four characterization techniques were used for chemical, NDT and mechanical qualification, and for gathering multidisciplinary data about our samples.

The glass transition temperature, T_g , of the adhesive was determined by using differential scanning calorimetry (DSC Q20, TA Instruments, France) under inert atmosphere, the scan rate being 10 °C/min and the temperature range 25 – 200 °C. T_g was determined from the midpoint of the heat capacity change. The value of T_g was used to calculate the epoxy conversion, x , through the Di Benedetto empirical model modified by Pascault and Williams [15].

$$\frac{T_g - T_{g_0}}{T_{g_\infty} - T_{g_0}} = \frac{\lambda x}{1 - (1 - \lambda)x} \quad (1)$$

where T_{g_0} and T_{g_∞} are the glass transition temperatures of the unreacted initial system and of the fully cured network respectively; λ is the ratio of the change in heat capacity at the glass transition temperature, for the fully cured and uncured states: $\Delta C_{p_\infty} / \Delta C_{p_0}$. All these values were taken from DSC runs.

A surface profilometer (Dektak 150, Veeco Instruments Inc., Germany) with a tip of 1.5 μm was used to measure the roughness of the substrate. R_q , the root mean square of the average departure from

the mean plane, is defined by:

$$R_q = \sqrt{\frac{1}{l} \int_0^l Z^2(x) dx} \quad (2)$$

In this study, the most complete description of the bond was searched for. Bond homogeneity was tested but a thickness measurement was also required. From the ultrasonic point of view, the difficulty of thickness evaluation was due to the thinness of the bond. Classical ultrasonic testing, with the transducer frequencies around 1 to 10 MHz, was not sufficient to measure epoxy thicknesses below 1 mm. In a previous study, we used focused ultrasonic transducers [16] to test bond homogeneity, but these transducers also produced a spurious echo attributed to a diffracted effect from the edge of the transducer. In this study, this echo interfered with various interfaces echoes. A better configuration was designed with non-focused transducers. High frequency and heavily damped transducers (Panametrics V317-N-SU) were chosen with a tiny 0.25" diameter to keep a very thin beam diameter. The theoretical central frequency was 20 MHz. The focal zone was then about 0.0625" (1.59 mm). The ultrasonic testing setting was a through-transmission setting with two identical transducers. Transducers were positioned perpendicularly to the aluminium plate (normal incidence or 0° incidence). Their ultrasonic beams were carefully aligned using the maximum transmitted energy and the distance to the plates was adjusted to maximise the amplitude of the first transmitted signal. As ultrasounds were both transmitted and reflected at each interface, numerous paths were possible, as shown in Figure 4. This figure represents the three echoes of interest. The first echo (t_0 time) corresponds to the direct ultrasonic path through water, aluminium, epoxy, aluminium, water. The second one (t_2 time) is the addition of two ultrasonic paths in the medium: the ultrasonic wave was reflected at the aluminium–epoxy interface and did a second round trip in the aluminium. The same round trip travel was done after the wave reflection at the aluminium–water interface. Both of these ultrasonic waves combined to give a higher amplitude signal. The third signal corresponds to a round trip in the epoxy bond (t_1 time). This signal should be the most interesting one to analyse the quality of the interface. An amplitude map is constructed using an XY table (CSCAN image analysis) to evaluate the bond homogeneity, and signal analysis (time of flight measurements) is used to evaluate precisely the local thickness.

Mechanical testing of our adhesive joints was done following EN 2243-1 Standard specifications. This test method provides a standard method for obtaining adhesive shear data for quality control. The length, width and thickness dimensions of the adhesive were measured at several points using a digital vernier caliper and the average values were calculated.

Experimental tests were carried out on an electromechanical universal testing machine (MTS systems, France) of 100 kN. The machine is interfaced with a dedicated computer for controlling and data acquisition. The specimens were tested in static tests, loaded at a constant rate of 0.1 mm/min. An extensometer was used to monitor the single lap joint deformation. End tabs were bonded to the substrates for the alignment in the load fixture.

Average bond strengths were calculated using the following formula: $\tau = \frac{P_{\max}}{A}$ where τ is the adhesive strength in MPa, P_{\max} is the maximum load at failure in N, and A is the adhesive lap area in mm^2 . Five or six specimens of each set were tested to ensure repeatability of the sensing response and failure mechanism.

The acoustic emission (AE) technique is essentially destructive as high loads are used but enables to identify fracture mechanisms. Consequently acoustic emission occupies a special position among NDT methods used to evaluate bonded structures. This method is also well known for having the potential to obtain information related to the bond strength [16-17]. A number of investigations are currently being performed, using this technique to characterise metal-composite single lap joints. In this study we want to investigate additional information about fracture mechanisms. The acoustic emission (AE) measurement system (Physical Acoustics Corporation, Princeton Junction, USA) supplied two channels with a sampling rate of 5 MHz. A 40 dB pre-amplification was used to record AE data. AE measurements were achieved by using two resonant Micro-80 sensors with a frequency band 100 kHz – 1 MHz and a peak of resonance at 300 kHz, coupled on the faces of the specimens with a coupling agent (Sofranel, Sartrouville, France), as illustrated in Figure 2 with an example of signal. An amplitude threshold of 35 dB was used to detect the arrival time and the end of any AE

signal. The amplitude distribution covered the range 0–100 dB (0 dB corresponds to 1 μ V for the transducer output).

Several temporal features were calculated by the acquisition system for each AE event: amplitude, energy, duration, rise time, counts, etc. [18]. Only the amplitude of the signal was measured in real time by the data acquisition system. All the other parameters were calculated from the waveforms and they were dependent on the amplitude threshold. These collected parameters were used as input descriptors in the proposed classification method.

3. Results and discussion

3.1. Adhesive conversion

The glass transition temperature, T_g , of the room temperature cured network was found to be equal to 48 °C, while the T_g of the high temperature cured network was found to be 93 °C. This latter value is the maximum that can be obtained on the DER331-D230 network [14]. This network is fully cured and its epoxy conversion is 100 %. Using the Di Benedetto relation, the conversion of the partially cured network was found to be 80 %.

3.2. Ultrasonic measurements

The produced bonds were characterised non-destructively by means of through transmission ultrasonic inspection. The CSCAN (XZ) graphs of three specimens are illustrated in Figure 3, the three specimens being tested during the same acquisition. The amplitude represented in this CSCAN image corresponds to the epoxy signal (time t_1). The transducer displacement step is 0.5 mm in each axis. In this figure, the bond homogeneity is confirmed by the homogeneous amplitudes of the CSCAN: no bubbles or lack of bonding are visible. There are usual variations in signal amplitude close to the sample edges due to the width of the focal zone and the choice of temporal windows. A more precise analysis such as the study of variations in the shape of the bond edges was not planned in this work. It would have required a thinner spatial step. In the other area, the amplitude varies slightly according to the epoxy thickness, as epoxy strongly attenuates ultrasounds. For a thinner bond, the

amplitudes are higher. In this figure, the respective thicknesses of DSSi100-4, DSSi-100-5 and DSSi-100-7 are 289 μm , 300 μm and 167 μm . This thickness variation is the greatest among all the samples. The value 167 μm is the thinnest one ((less than 2% occurrence) and it is due to epoxy glue leakage. Knowledge of the precise ultrasound velocities in the materials allows one to identify echoes with time of flight calculations. These velocities were measured at the I2M laboratory (Bordeaux, France) which characterised the elasticity constants for aluminium and epoxy [19]. The longitudinal wave velocity is 6370 $\text{m}\cdot\text{s}^{-1}$ in the aluminium and 2512 $\text{m}\cdot\text{s}^{-1}$ in the epoxy. Thickness evaluation could be done with separated echoes. That required a very short signal, so we chose in our experimental setting a large band transducer with a delay line. The effective measured frequency of the transmitted signal was 12 MHz due to the low pass filter effect of the epoxy layer and due to the low pass filter of the complete measurement system.

Figure 4 demonstrates that, as expected, we obtain clearly separated echoes that allow precise thickness measurements. These values are in perfect agreement with those obtained via the digital vernier caliper : the maximum observed differences are about 4% . Based on the NDT results, it is concluded that a satisfactory bonding quality has been achieved, along with a constant thickness for a given sample.

3.3 Lap shear results

Typical load-displacement plots for the single lap shear test are illustrated in Figure 5 for the five types of sample: S80, DSSi80, D100, DS100 and DSSi100. The measured adhesive strengths are presented in Figure 5. In the given series, our samples were not exactly identical to each other because of the manufacturing process; the adhesive may present a different profile on the free edge of the overlap. This has an impact on the values obtained and explains the dispersion of data [20] . Indeed, it is known that in the tensile mode, peak stresses are produced at the ends of the overlap due to the absence of equilibrating shear stress on the free surfaces of the adhesive layer at the overlap ends, as well as because of the bending of the joint due to the eccentricity in the load path

resulting from the presence of the overlap. In our study eccentricity was minimised using end tabs. These peak stresses may be several times the average failure stresses [21]. We tried to have a reproducible shape of the free edge to avoid mechanical dispersion [20, 22]. The Tensile Yield Strength of the A2024-T3 adherent was about 345 MPa. All adherents in this study were the same, so no variation in strength could be due to variations in the metal properties (ductility or yield strength) [23, 24]. Nevertheless, a clear trend can be seen in the respective influence of the surface treatment and the adhesive conversion on the adhesive strengths. These values are commented upon in the following paragraphs. Fracture specimens were visually examined to determine the failure mode: adhesive fracture (i.e., apparent interfacial debonding), cohesive fracture, delamination fracture and special substrate-near cohesive fracture are possible according to DIN EN ISO 10365.

3.3.1 Effect of the aluminium surface treatment

We first examine the three series of samples in which the adhesive was fully cured, namely D100, DS100 and DSSi100. As expected, the lowest strength was measured for sample D100, where the substrate was only degreased with isopropyl alcohol. It was close to 7.7 MPa. The measured surface roughness of the aluminium substrate is equal to $R_q \sim 0.6 \mu\text{m}$, which is too low and does not allow sufficient mechanical anchoring of the adhesive. This is the reason why the strength has a low value. However, this value is in the range found for model epoxy adhesive and degreased aluminium substrates [25]. It can be seen that the fracture surface indicated clearly an interfacial fracture mode: adhesive layers on one side of the joint surfaces are clearly shown in Figure 7.

The obtained value of adhesive strength for the DS100 is higher than for the D100 sample. It is close to 13.5 MPa; this value is in the same range as the published data on epoxy-aluminium joints treated with mechanical abrasion [26]. Obviously, the adherent roughness is increased due to the sanding treatment. The roughness, R_q , as measured using a profilometer, was found to be $14.5 \mu\text{m}$. This high value gives a larger effective surface area for the bond. Here the main bonding forces are physical or mechanical forces and their magnitudes mainly depend on the contact area. Most of the time,

however, the roughness values are not reported in the literature, making it impossible to establish a clear correlation with the adhesive strength. Recent studies about metal-composite adhesion have carefully observed the roughness parameter [27]. Another related factor is the wettability of the substrate. In general, smoother grit-blasted surfaces display higher surface energy [27]. This variation is attributable to changes in surface composition, and not only to a geometric effect of the surface.

The mechanical (abrasive) treatment removes the natural surface oxide.

The adhesive strength is increased in average with the silane treatment (sample DSSi100); a value close to 14.3 MPa is reached, which represents an increase of 100 % as compared to the basic degreasing treatment. The roughness of the substrate is not modified by the silane layer. Therefore, this increase is associated with the strong Al-O-Si covalent bond created between the aluminium rough substrate and the epoxy adhesive via the hydrolysed (3-glycidyloxypropyl)trimethoxysilane.

The existence of covalent bonds is also known to improve the durability of bonded joints [28, 29].

Organosilanes such as γ -GPS are very efficient adhesion promoters and can replace chromium-based treatment of aluminium alloys.

The DS100 and DSSi100 joints failed almost in adhesive mixed failure mode: fracture for every specimen was found to occur only on interfaces between the adhesive and the adherent, and the adhesives remained on either surface of the adherent (Figure 7), contrary to D100, where the adhesive remained on only one substrate.

3.3.2 Effect of the adhesive conversion

A large difference (close to 50 %) in the adhesive strengths of sample DS80 and sample DS100 is observed (see figure 5): the poor curing cycle leads to a value equal to 8.7 MPa, while the optimised cycle leads to 13.5 MPa. This highlights the importance of the curing procedure. The fracture surfaces are not the same: the adhesive remained mainly on one face of the substrate for sample DS80 (similarly to sample D100), while the adhesive was observed on both faces of the substrate for sample DS100 (Figure 7).

Brett et al. [30] studied the effect of the conversion of the adhesive on bond strengths. The adhesive was based on DGEBA crosslinked by 4, 4'-diaminodiphenylmethane and the substrate was aluminium. The results of single-lap and double-lap tests show an increase in the bond strength with an increase in conversion. Similar conclusions were also reached by Markatos et al. [7], who studied the effect of the curing cycle of an epoxy adhesive in composite bonded joints by investigating mode I-fracture toughness. A 95 % decrease in the G_{Ic} value was observed on the sample that was partially cured.

However, the influence of the epoxy conversion is considerably reduced when the silane pretreatment is applied to the aluminium substrate. The values obtained are much closer: 13.8 MPa for DSSi80 vs. 14.3 MPa for DSSi100. The silane treatment allows one to compensate the effect of a poor curing of the adhesive. There is no difference in the failure mode: the visual observation of the surface reveals the adhesive on either surface of the aluminium (Figure 7). Despite the higher value of adhesive strength reached, interfacial failure occurs in both samples. Surface treatment does not modify the failure mode of the joint.

3.4. Acoustic emission

The aim of this analysis is to identify the acoustic signals emitted by different types of damage, and also to compare the evolution of these various mechanisms in adhesive materials during tests. The five selected descriptors extracted from signals were the energy, the amplitude, the rise time, the counts and the duration of the signals. The AE signals were classified by the K-means method using the Noesis software (Advanced Data Analysis Pattern Recognition and Neural Networks Software for Acoustic Emission Applications) [31]. The number of classes is optimised by taking the minimum value of the Davies and Bouldin factor [32] by scanning a number of classes in a range from 1 to 4. The K-means method is an unsupervised pattern recognition analysis providing a multi-dimensional data classification. The aim of this method is to minimise the sum of squared distances between all the vectors of a cluster and its centre. The K-means algorithm is described in [33].

According to the Davies and Bouldin factor, the optimal clustering was obtained with two classes. After that, the acoustic signals collected during tests were classified by the K-means method. Figure 8 shows the classification of AE signals during loading tests for two specimens representative of the D100 serial and the DSSI80 series. These figures give a distribution of amplitude versus time (Figure 8 a), the Principal Component Analysis (PCA) (Figure 8 b) and time dependency of the identified damage mechanisms (Figure 8 c). For both specimens, the amplitude threshold is 35 dB. The PCA is achieved in order to visualise the signals of each class grouped after classification in a two-dimensional sub-space. In order to associate each class obtained from the output of the classification algorithm with the damage mechanisms, the characteristic forms of each class are considered. For the set of materials studied, the classification of AE signals reveals the presence of two classes. The first class includes signals whose amplitudes are between 35 and 60 dB. These signals can be attributed to the interfacial (aluminium/epoxy) debonding (class 0). There are highly predominant when adhesion is very low, as for D100 specimens (Fig 8a). The second class contains signals with amplitudes between 50 and 75 dB, which appear just after the interfacial debonding damage, and probably result from the resin cracking (class 1). The observation of these signals is correlated with the visual observation of the surface, revealing the adhesive on either surface of the aluminium. In addition, most of the acoustic events are concentrated, but some events are mixed with each other. In the monotonic tests, the load was increased to failure, so the progression of damage was dependent on the increasing level of applied stress. It is worth noting that the acoustic activity depends on the adhesive quality. The distribution of amplitude versus time (Figure 8 a) shows that the interfacial debonding damage (class 0) is the most dominant damage mechanism in D100 specimen and the resin cracking (class 1) is the most dominant damage mechanism when the cure process is not optimum, as for the DSSI80 specimen in Figure 8. These results were confirmed by fracture surface observations. The event amplitude for the D100 specimen is higher than those observed for the DS and DSSI specimens.

4. Conclusions

The aim of the present study was to investigate a rigorous protocol to produce reduced-strength samples for NDT qualification. To produce a complete set of reference samples, chemical defects such as a partially crosslinked adhesive and/or a bad substrate treatment were produced. High frequency through transmission ultrasonic tests were conducted in order to assess the quality of the bondline - bond homogeneity and constant bondline thickness. This quality will enable measurement variations due to bondline dissimilarities to be eliminated and ensure that variations in ultrasonic measurements could be correlated with variations in surface treatments and corresponding reduced-strength.

Considering the adhesion properties of our reference samples, poor curing, i.e., a low epoxy conversion of the adhesive, was found to have a strong negative effect on the bond quality in the case where the substrate was only mechanically abraded. As soon as an adhesion promoter such as (3-glycidyloxypropyl) trimethoxysilane was used on the sanded substrate, the effect of the epoxy conversion of the adhesive was minimised. Very close values of adhesive strength were obtained on joints made with silane-treated substrates, whatever the curing of the adhesive. The silane treatment will be suitable to ensure better adhesion. In addition, such pretreatment is suitable for industrial large-scale applications because it is waterborne with no critical release of volatiles, is compatible with epoxy adhesives and easily applied to metal sheets. Reference levels of adhesion were obtained with curing variations or surface treatments. Acoustic-emission confirmed the quality of these samples since only two classes of signals were identified and correlated with the two expected fracture mechanisms : interfacial debonding and adhesive cracking. Using the conclusion of this study, it is now possible to design reference samples of various sizes for the qualification of NDT methods. New developments in ultrasonic non-destructive techniques are currently being studied for the evaluation of the adhesion level in the frame of a national scientific programme in progress. In this programme the main concern being addressed is the development of advanced NDT methods for a reliable quality assurance concept for adhesive bonding [34].

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Fig 1 Ultrasonic paths in the bonded Al-epoxy-Al specimens, using the through transmission method

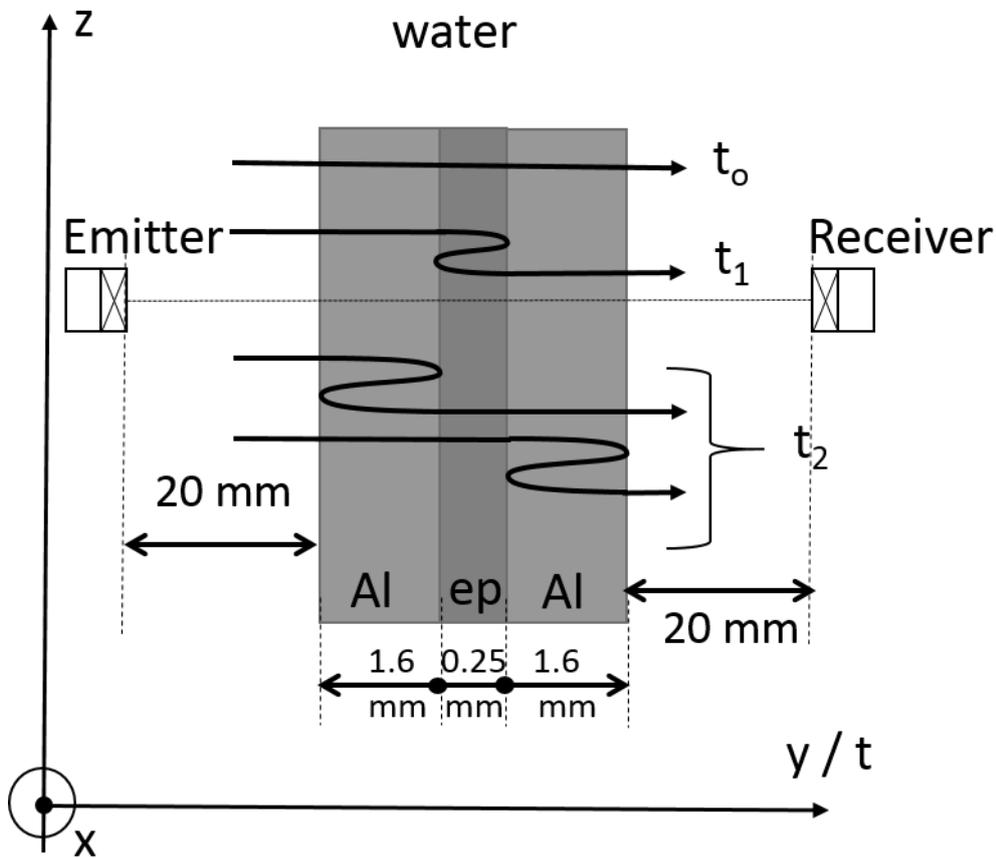


Fig 2 A snapshot of the testing procedure with AE sensors and example of signal (DSSi80-3)

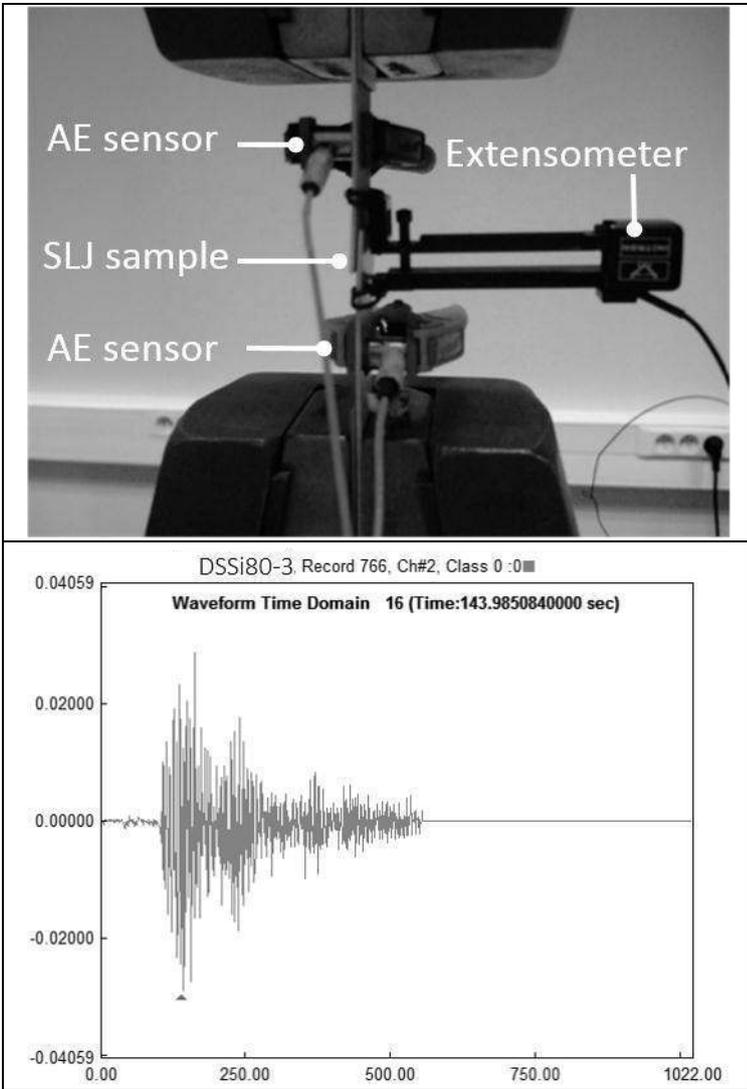


Fig 3 CSCAN images for bond quality evaluation (3 samples (4, 5 and 7) in DSSi100 series)

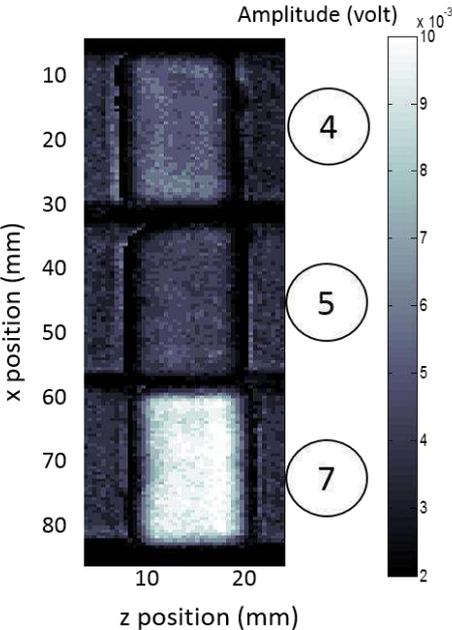


Fig 4 Ultrasonic signals for three samples of DSSi specimens

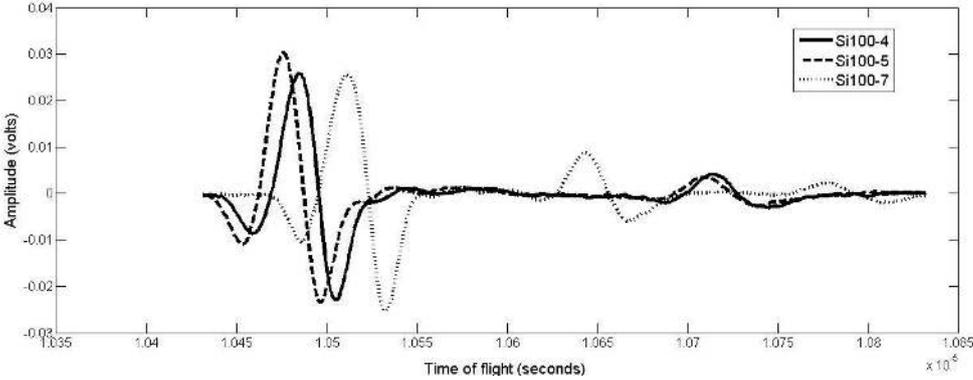


Fig 5 Typical load–displacement curve for the five scenarii

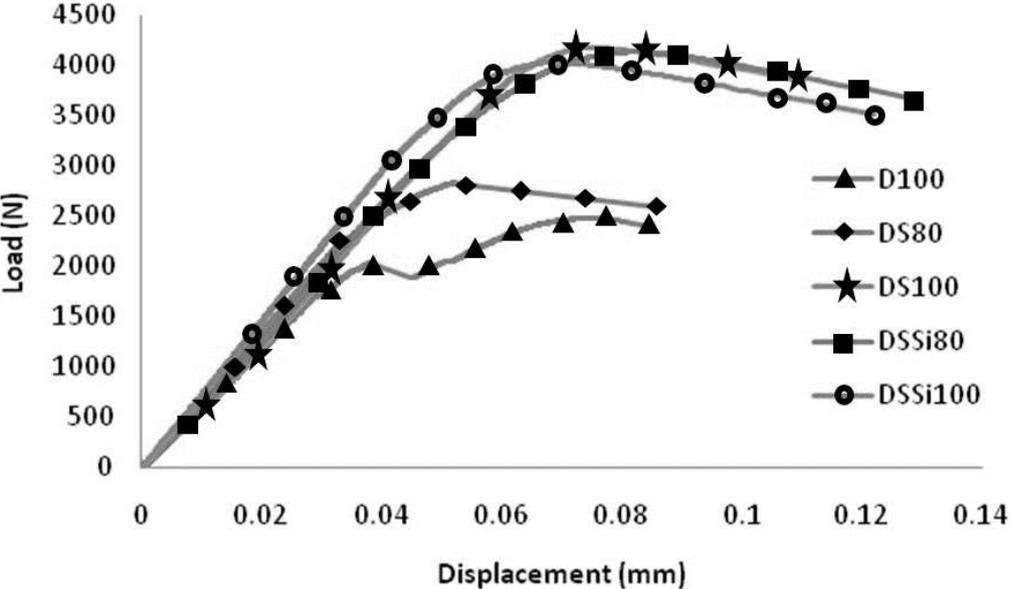


Fig 6 Adhesive strengths of the different joints (x= conversion)

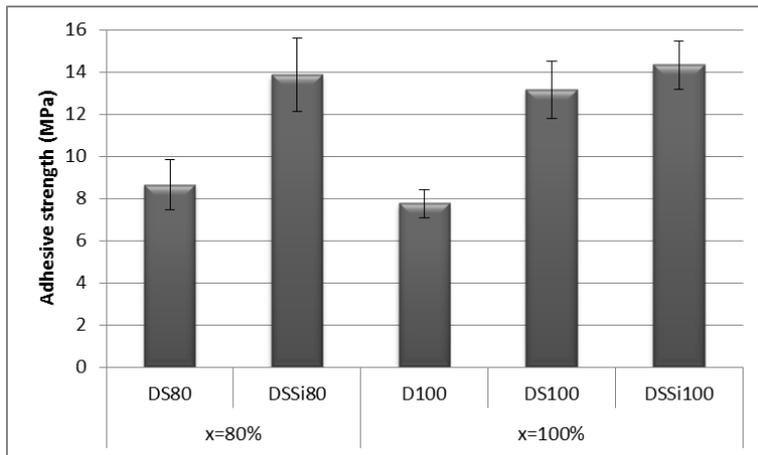


Fig 7 Fracture surfaces of aluminium joint bonded by epoxy: D100, DS100, DSSi100, DS80, DSSi80

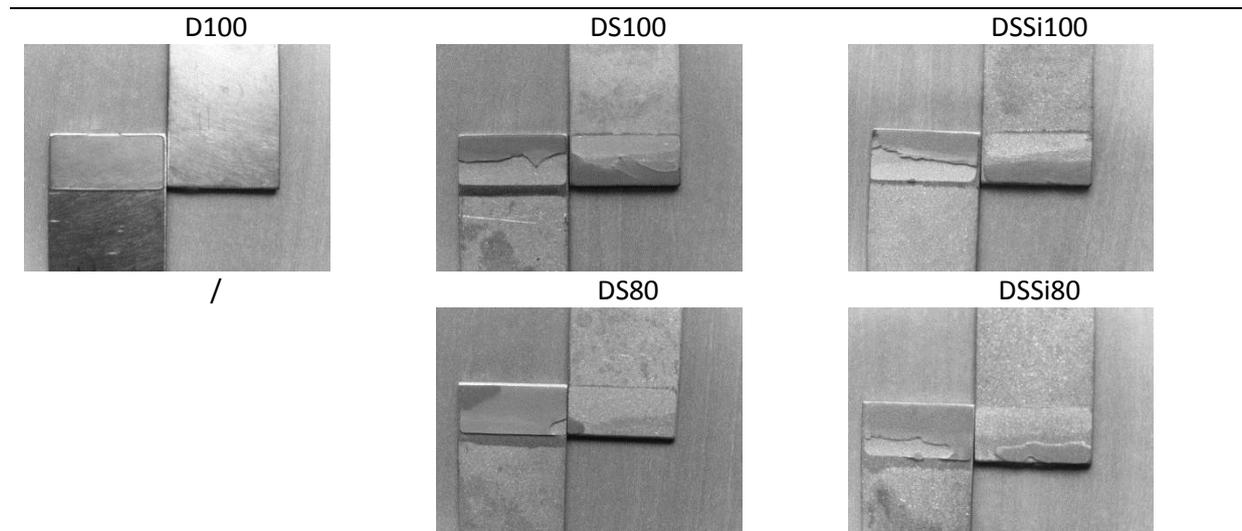
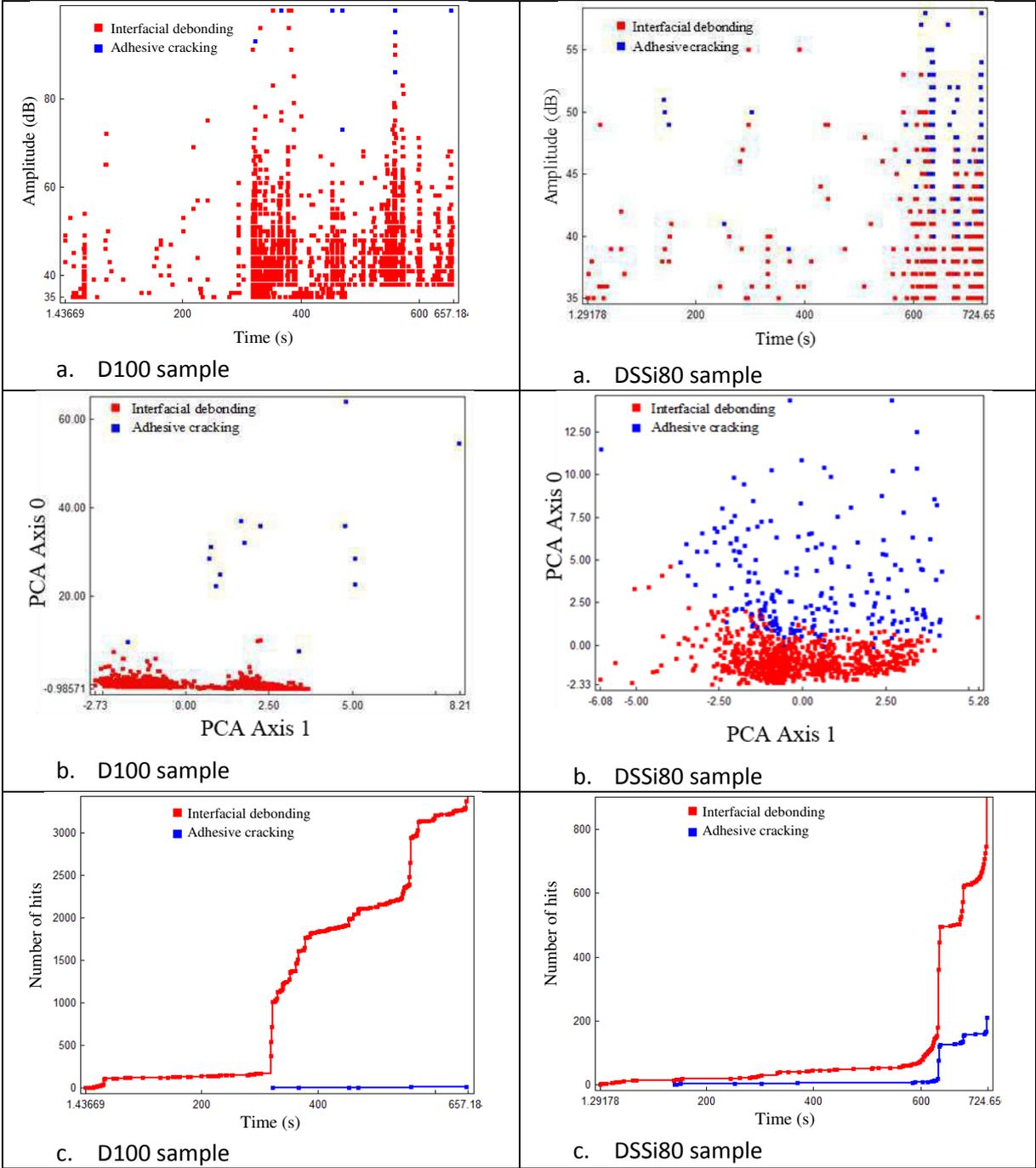


Fig 8 Examples of acoustic emission response of the two types of samples D100 and DSSi80: a) Distribution of amplitude versus time, b) PCA visualization of the AE signals clustering and c) Time dependency of the identified damage.



(NOTE : this figure 8 should be in colour in the printed version)

Table 1 Chemical structures of components

Name	Chemical structure	Molar mass (g/mol)
Diglycidyl ether of Bisphenol A: DGEBA		374
Polyetheramine: D230		230
3-(glycidyloxypropyl)trimethoxysilane: γ -GPS		236

Table 2 Set of samples used for NDT and mechanical tests

Reference	Al surface treatment	Curing cycle / conversion
DS80	Degreased + sanded	
DSSi80	Degreased + sanded + silanisation	1 week at RT / partial
D100	Degreased	
DS100	Degreased + sanded	48 h at RT + 3 h at 160°C / full
DSSi100	Degreased + sanded + silanisation	