



The influence of water when bonding with heat-curing epoxy adhesives on sealed sulphuric acid-anodised aluminium

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ABSTRACT

In this paper, it is demonstrated how the formation of blisters or foaming in a heat-curing epoxy adhesive can be avoided during bonding to sealed sulphuric acid-anodised aluminium. The crucial points to control are the release of water from the anodic film and the total amount of water in the joint. The cure cycle will affect the rate of water release, while the total amount to a large degree depends on the relative humidity in the area of bonding before joint assembly. Besides the adhesive, also the anodic film absorbs water within a short time scale. This behaviour is caused by aluminium sulphate, which is always present in the anodic film after sulphuric acid anodisation. At room temperature the aluminium sulphate is in equilibrium with water vapour at about 30% r.h. It has been experimentally demonstrated that the amount of water stored in the anodic film has a dramatic step change between 30% and 40% r.h. at room temperature. Outside this range up to condensing conditions differences are relatively small. The release of water during the curing of the adhesive can in addition to blistering or gassing also cause a boundary layer with changed properties in between the adhesive and the anodic film.

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1. Introduction

Sulphuric acid anodising (SAA) is the most widely used anodising procedure for aluminium, due to esthetic appearance and excellent corrosion resistance together with the use of rather low cost and benign chemicals. Especially, architectural products have taken advantage of the good weathering resistance and the decorative colouring options the thick and porous oxide offer.

In addition, it is desirable to use SAA as surface pre-treatment for adhesive bonding. In the aircraft industry it was early discovered that bonded joints with SAA could fracture in the oxide at high-peel loading, resulting in lower joint strength [1,2]. Thick films and low temperatures promote this behaviour. Thinner anodic films with better behaviour had been found earlier with chromic acid as anodising electrolyte; later it was followed by phosphoric acid (PAA). These anodic films have a more open pore structure allowing penetration of high molecular primers/adhesives resulting in superior adhesion and durability [3]. They have therefore become the preferred choice for advanced structural adhesive bonding applications in the aircraft industry.

Minford [4] has shown that thinner SAA films can perform with adequate durability in long-term exposures; the joint strength

retention in more aggressive water exposures like soak/freeze/thaw and corrosive salt spray conditions is superb. The morphology of the SAA oxide provides excellent resistance to both pitting corrosion and degradation by harsh-wet environments. This fact has often been foreseen when the initial strength is not amongst the highest ones. Many papers have however reported difficulties in bonding SAA, results with intermediate performance, concerns about poor adhesion, weak boundary layers and glue line defects as voids or blistering in the adhesive, especially in comparison with PAA [5].

Hydro Aluminium did start manufacturing of bonded body structures for Lotus sports cars in 1995, the Elise model; also several Aston Martin models has followed later. Adhesive bonding is the primary joining method, even if mono bolts, self-piercing rivets and E-jot screws are used for mechanical fixation before cure. The bond system in use is a heat-curing epoxy adhesive on sealed SAA anodising with a film thickness of <10 μm. The robustness of the bonding process has been successfully proven. A key is to control the water in the system.

It is known that a lot of water will be left in the SAA film after the sealing process. Also reaction products and residuals from the electrolyte will remain in the oxide and the film will roughly contain about 13% sulphate [6]. This paper will show how the content of these reaction products strongly affects how the water is bound in the anodic film. The aims of this study were to gain knowledge on how the water is bound to the SAA oxide film, the

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dynamics of water transportation and also a better understanding of how water will interact with the adhesive during the bonding process.

Although the work done and the results generated are of quantitative value only to users of the specific system employed, the generic implications are of importance also to other adhesive bonding systems involving sealed sulphuric acid-anodised aluminium.

Details on materials and equipment are given in Appendix A.

2. Dynamics of water transport out of and into sealed anodised films on aluminium

2.1. Experimental determination of the amount of water in sealed anodised films

Anodised films on aluminium are porous and therefore prone to contain water. In addition, the film will contain some impurities and aluminium compounds like sulphate that also might bind water as hydrate.

In an attempt to determine the state of the water in the films, reflection infrared molecular spectroscopy was applied. There are distinct differences between such absorption spectra from aluminium oxide, aluminium hydroxide and water. However, no differences were observed between the spectra from the surface of 'as-anodised' samples and from 'as-anodised' samples a short time after they had been heated to 100 °C in air to degas the films. Both spectra clearly show the presence of water on the surface of the samples, while indications of hydroxide were not seen. This observation was interpreted as an indication that the water was present as bound or adsorbed water, and that it was either never completely removed from the film during the degassing or that it was very quickly re-adsorbed on the surface of the anodised films. A limitation to this technique is that it does not directly allow for quantification of the amount of water on the surface, but only its presence above a certain detection limit.

In an attempt to get further information on the dynamics of the removal and re-adsorption of water, the electric leakage current through the anodised film was measured with an electrode area of about 10 cm² with varying applied voltage up to 45 V, both polarities. The aluminium substrate formed one electrode and the other electrode was made of electrically conductive porous polymer as used for packing electronic components. This technique allows measurement of the leakage current in real time under varying environmental conditions. The basic assumption behind these measurements is that the leakage current increases with increasing water content. It was found that the leakage current was not dependant on polarity of applied voltage and that the measurements were reversible and reproducible under stationary conditions. It was further demonstrated that the leakage current was reduced by more than a decade by degassing the anodic film at temperatures above 140 °C, but when exposed to room conditions after the degassing the current increased again in a short time to a new fixed level. These measurements indicated that the water content of the anodised films adapts to the environment within less than 1 h, but the technique does not allow for quantification of the amount of water.

In an attempt to quantify the amount of water released on heating of the anodised aluminium sample, a vacuum condensation procedure was applied. These experiments showed that a large fraction of the water is released during the first hour of degassing at 180 °C. The experiments further showed that after about an hour at room temperature and humidity an appreciable fraction of the water was reabsorbed and that after a couple of days at room temperature and humidity the water released on

repeated heating is just the same as before the first degassing. To get an indication on how the degassing temperature influences the degassing rate, a set of data were collected, where the temperature was increased stepwise after some time at selected temperatures. The results from these experiments indicated that the amount of water that was released increased with increasing temperature. These results further demonstrated that the amount of water released and re-adsorbed was in the order of 50 µg/cm², or equivalent to a continuous water layer of about 0.5 µm thickness.

The amount of water transported into and out of the anodised films was found to be so large that a simple gravimetric technique could be applied for further investigations. The samples used were anodised panels of size 125 × 80 × 2 mm³. Before the investigation started, all samples were heated to 180 °C for 70 h in an oven to condition the samples. After this conditioning, the samples were rapidly transferred to containers with controlled humidity. The wanted humidities were obtained according to ASTM E104-85, Standard Practice for Maintaining Constant Humidity by Means of Aqueous Solutions. Salt slush of LiCl and KCl were applied to represent low and high humidities (11% r.h. for LiCl and 84% r.h. for KCl, respectively, at 25 °C). A separate measuring instrument regularly controlled the humidity in the containers during the experiments. To expose the samples to intermediate humidity, they were left open in the laboratory and the humidity registered.

After the exposure, the samples were transferred back to the degassing oven and weighted at different times while being degassed. Since the change in weight (a few mg) is small compared to the sample weight (~50 g for the aluminium samples), the samples were handled with lint-free gloves and the samples were not marked with ink etc., but by scribing. During degassing, the samples were weighted by hanging them by a thin metal string that went through the top of the oven and were attached to a sensitive laboratory scale with a resolution of 0.1 mg. When weighting the samples at elevated temperatures, the weight change must be corrected for the change with temperature of buoyancy in air.

In the following measurements of weight changes at exposure and degassing, it is assumed that this is due to water transport in and out of anodised films. This assumption is based on general knowledge to the systems involved.

The weight change from degassing and exposure at 84% r.h. (oversaturated solution of KCl) and ~40% r.h. (open in the laboratory) is shown in Table 1.

The same samples were then re-exposed, some to 11% r.h. (oversaturated solution of LiCl) and some to ~47% r.h. The results are shown in Table 2.

All these data are shown graphically in Fig. 1.

Samples 1A, 2A and 3A are repeated tests as are samples 4B, 5B and 6B. This indicates that the repeatability of the measurements is within ~10 µg/cm² and significantly smaller than the difference between these two groups of samples after re-exposure at 11% r.h. and 85% r.h., respectively, which is ~40 µg/cm². When comparing parallels in Fig. 1 it should be kept in mind that the change in weight is small compared to the total weight of the samples. The spread in data is therefore probably solely due to random weighting errors. The data in Fig. 1 do not give reason to other conclusions than that all the water released during conditioning is re-adsorbed during exposure to ~40% r.h. and 84% r.h. and released again on degassing, while exposure to 11% r.h. gives only about 1/3 re-adsorption.

It might also be concluded that the samples exposed to controlled humidity after repeated cycles end up somewhat lighter than the samples exposed only to open laboratory air. Before taking this observation further, it should be remembered that the difference is only a few mg on 50 g samples.

Table 1
Change in weight for anodised material after different exposures to humidity

Step Sample	1 Weight loss when conditioned at 180 °C for 70 h ($\mu\text{g}/\text{cm}^2$)	2a Weight increase after exposure to 84% r.h. for 24 h ($\mu\text{g}/\text{cm}^2$)	2b Weight increase after exposure to 40% r.h. for 24 h ($\mu\text{g}/\text{cm}^2$)	3 Weight loss when degassed at 180 °C for 20 min ($\mu\text{g}/\text{cm}^2$)	Net change after conditioning ($\mu\text{g}/\text{cm}^2$)
1A	55	41		51	-10
2A	64	43		63	-20
3A	69	52		68	-16
4B	46		39	48	-9
5B	51		49	52	-3
6B	79		57	66	-9

Table 2
Change in weight for anodised material after different exposures to humidity

Step Sample	1 Weight loss when conditioned at 180 °C for 70 h ($\mu\text{g}/\text{cm}^2$)	4a Weight increase after exposure to 11% r.h. for 24 h ($\mu\text{g}/\text{cm}^2$)	4b Weight increase after exposure to 47% r.h. for 24 h ($\mu\text{g}/\text{cm}^2$)	5 Weight loss when degassed at 180 °C for 20 min ($\mu\text{g}/\text{cm}^2$)	Net change after first conditioning ($\mu\text{g}/\text{cm}^2$)
1A	55	16		27	-11
2A	64	16		37	-21
3A	69	16		29	-13
4B	46		48	43	5
5B	51		58	50	8
6B	79		66	61	5

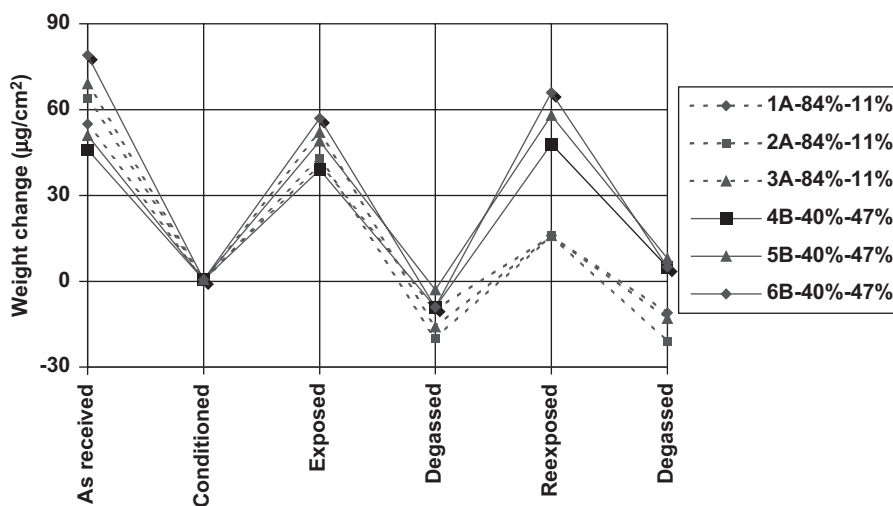


Fig. 1. Weight change referred to conditioned state for anodised aluminium after different exposures to humidity and degassing. The first digit in the labels refers to the sample numbers as used in Tables 1 and 2 and the percentage values in the labels refer to the relative humidities the samples have been exposed to.

2.2. Rate of release and re-absorption of water in anodised films

The weight increase during exposure at room temperature and ~40% r.h. has also been followed as a function of time. These results are shown in Fig. 2.

Fig. 2 shows that water is quickly reabsorbed, mostly within 1 h at room temperature. At 180 °C the release of water is even quicker. Experiments have shown that degassing is almost complete within 5 min at this temperature.

2.3. The influence of relative humidity on the water content of anodised films

In Fig. 3 the water content in anodised films is shown after exposure at different relative humidities. The rapid and marked

increase in water content at 30–40% r.h. is remarkable and will be further discussed in the following sections.

2.4. The role of aluminium sulphate for the dynamics of water transport out of and into anodised films

The anodised film will always contain some sulphate, and typical values that are found for the sulphur content are about 0.1 mg/cm². X-ray fluorescence spectroscopy has shown by line shift that the sulphur is present as sulphate. Depth profiles of the elemental composition of anodised films by glow discharge optical emission spectroscopy (GD-OES) have shown the sulphur content to be slightly increasing from the surface and inwards.

Aluminium sulphate binds water as Al₂(SO₄)₃·nH₂O, with *n* between 27 (below 10 °C) and 3 (200 °C) (see Fig. 4). The ratio by

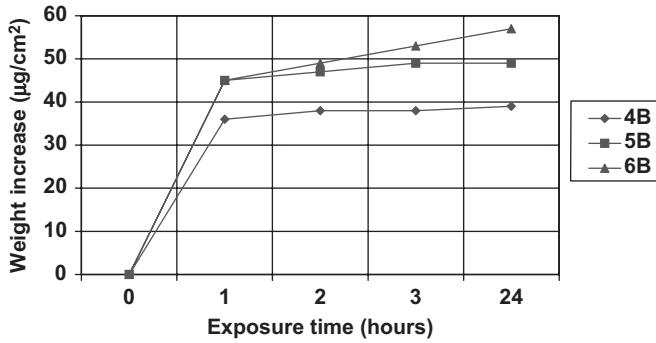


Fig. 2. Weight increase during exposure of anodised aluminium at room temperature and 40% r.h.

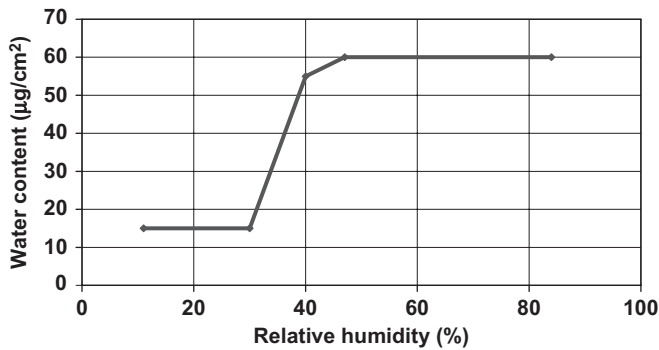


Fig. 3. Water content in anodised films after exposure at room temperature to different relative humidities.

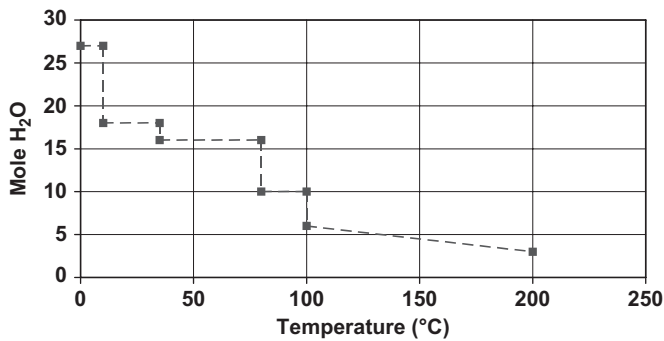


Fig. 4. Water of hydration for aluminium sulphate as a function of temperature [7].

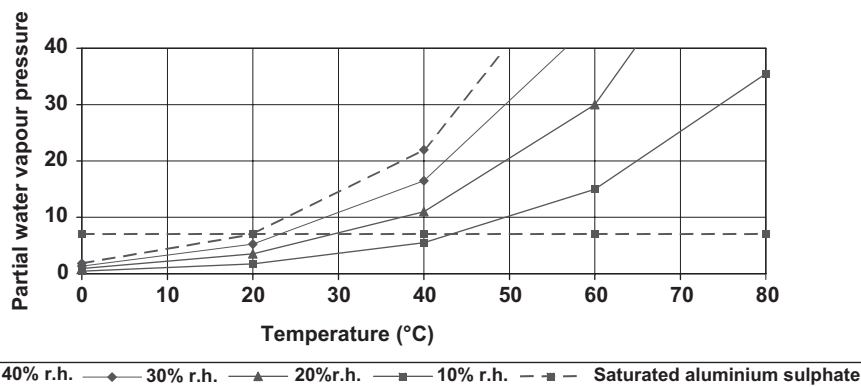


Fig. 5. Partial water vapour pressure in air, measured in mm of Hg [8] together with the equilibrium water vapour pressure above aluminium sulphate [7] as a function of temperature.

weight between S (mol weight 32) and H₂O (mol weight 18) in these compounds is $3 \times 32/n \times 18$. This implies that 0.10 mg/cm² sulphur might bind 0.019 mg/cm² of water for each unit of *n*. An observed release of water of 0.10 mg/cm² at 180 °C therefore corresponds to $\Delta n \sim 5$. This shows that the amount of sulphur is plenty to account for the observed release of water. The saturation water vapour pressure for this compound is between 5 and 7 mmHg for temperatures up to at least 100 °C. This vapour pressure corresponds to about 30% r.h. at room temperature and accordingly it corresponds to the step in water content shown at this humidity in Fig. 3. It is interesting to compare this with the results previously described where it has been observed that there is no difference in water uptake between exposure at ~40% r.h. and 84% r.h., but an appreciable difference between exposure at ~40% r.h. and 11% r.h.

In Fig. 5 the partial water vapour pressure in air for some temperatures is shown together with the equilibrium water vapour pressure above aluminium sulphate. Note that the curves for 30–40% r.h. cross the saturation pressure for aluminium sulphate at room temperature.

To summarize these findings:

- Above 40% r.h. the amount of water stored in the sealed anodised films is ~55 µg/cm² and does not increase with further increase in r.h.
- At 30% r.h. and below the amount of water stored in these anodised films is ~15 µg/cm².
- The time constant for reaching equilibrium with the environment is at room temperature about 1 h for the anodic film.
- The aluminium sulphate acts like a water pump being switched on at ~30% r.h. and above.
- The limitation to the amount of water being absorbed is however the porosity of the sealed anodising film.

2.5. The influence of film thickness on water transport out of and into anodised films

In Fig. 6 the weight changes associated with repeated heating and reconditioning are shown for two films of, respectively, 2 and 9 µm thickness.

The general response is very much the same, and, as is to be expected, much smaller for the thinner film. The reduction is not however as large as to be expected from the ratio in film thickness. This might be explained by the relatively larger influence of adsorbed water on or at the surface for the thinner film.

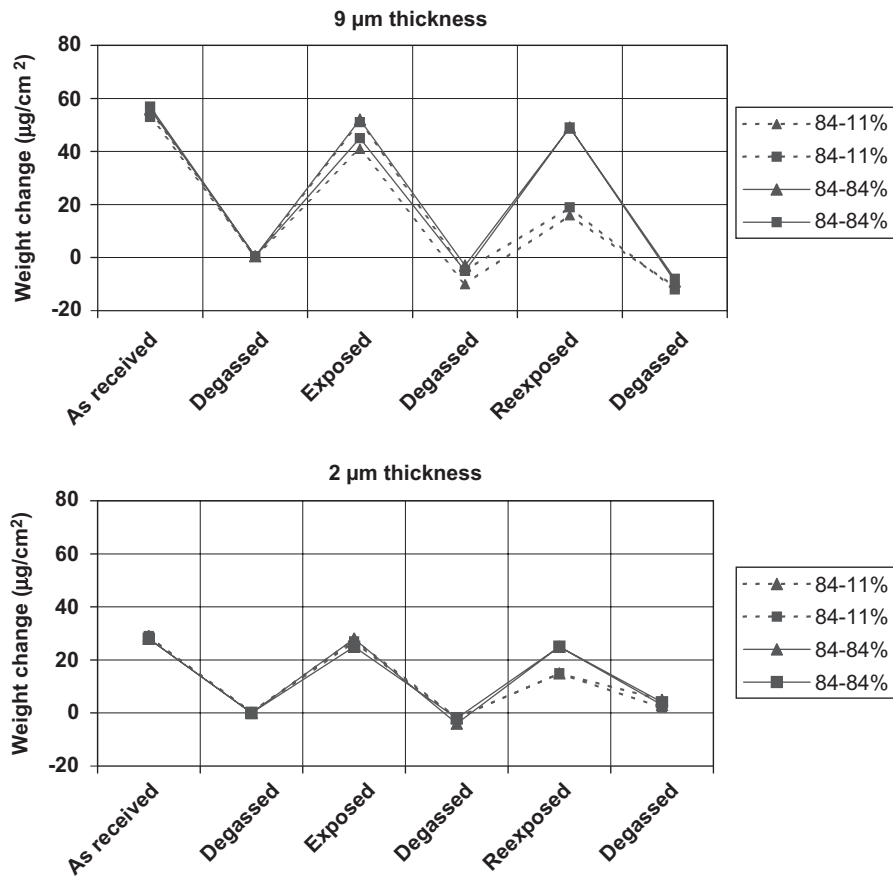


Fig. 6. Weight change for anodised aluminium after degassing and repeated exposures for two different film thicknesses. The numbers in the labels refer to the relative humidities the samples were exposed and re-exposed to, respectively.

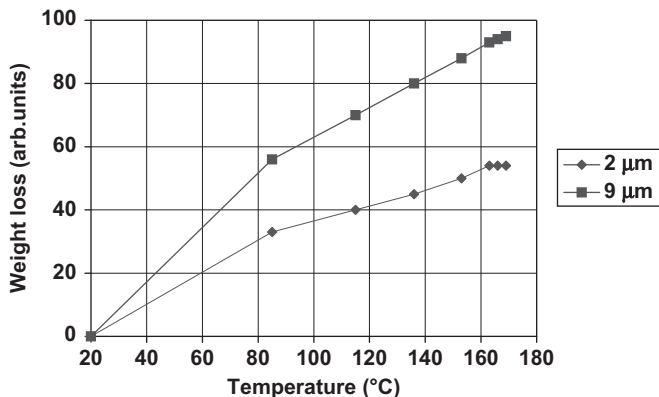


Fig. 7. Response of anodised aluminium with two different film thicknesses to heating.

In Fig. 7 the response to heating for samples with different film thicknesses is shown. This is done to measure the amount of water that would be released from the film into an epoxy adhesive during curing.

For both film thicknesses an almost linear relationship is shown between water release and temperature. Again the ratio between the two curves is close to two and not four, as the ratio between film thicknesses.

In Fig. 8 a comparison is given between degassed and not degassed material with respect to response to heating on curing and repeated exposure to high humidity. Again the material with

thin films reacts in the same way, but to a less degree than the material with thicker films.

In Fig. 9 the dynamics in the response to rapidly varying humidity is shown. Samples with two different film thicknesses were weighted while exposed to increasing humidity.

As is to be expected, the thinner film reacts much quicker to varying humidity than the thicker films. For the thin film, the response is so quick that the step at ~35% r.h. can be clearly observed.

3. Dynamics of water transport out of and into beads of epoxy adhesive

3.1. Experimental determination of the amount of water in beads of uncured epoxy adhesive

The same gravimetric procedures as for the determination of water transport out of and into anodised films were applied to study the water transport out of and into adhesive beads applied on aluminium foils. The adhesive was applied with a dispenser giving about 4 mm wide beads (equivalent to ~16 g/m). This rather small bead size was chosen to give a large surface to volume ratio. Still the beads are representative for what is used in production. The foil substrate was non-anodised to avoid interference from water transport related to the anodic films. For all experiments, the XD 4600 adhesive was used unless otherwise stated.

The weight loss at 115 °C was measured as a function of time just after application. This 'drying' temperature was selected to be

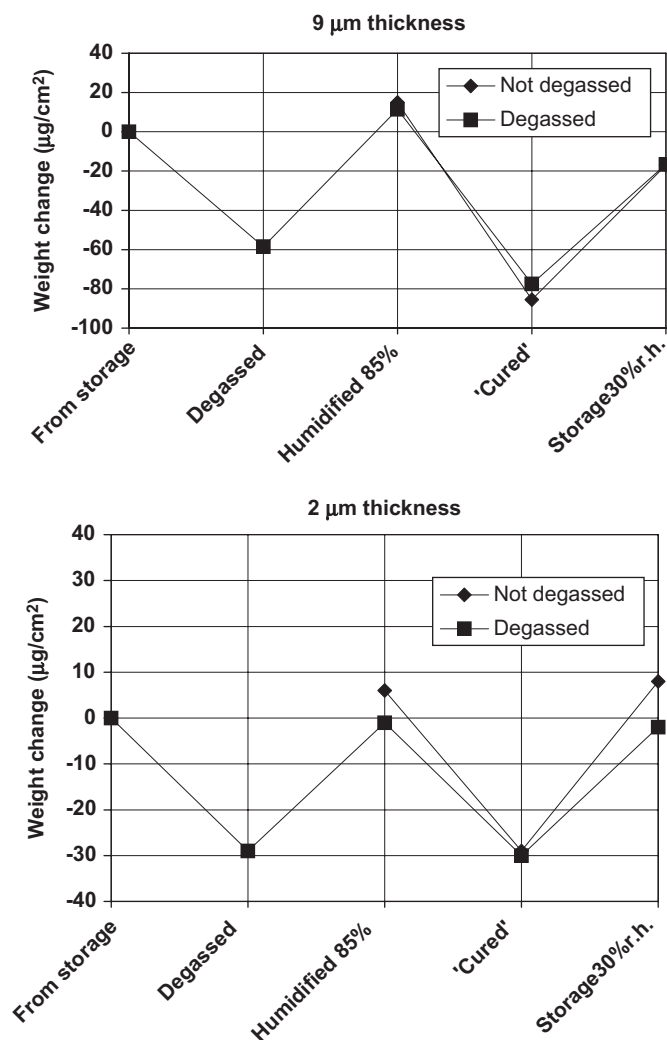


Fig. 8. Response of degassed and not degassed anodised aluminium with two different film thicknesses.

below the temperature required to start the main cross-linking reactions in the epoxy. Degassing measurements were also made on adhesive beads after exposure to controlled humidity for different times. The results from exposure to 84% r.h. are shown in Fig. 10 and from exposure to 11% r.h. in Fig. 11.

Fig. 10 shows that the weight loss on degassing/drying varies from about 0.4% just after application to about 1% after several hours at 84% r.h. and does not increase further for a couple of days. After about 90 min at 115 °C, the beads of adhesive have ridged themselves of most of the water absorbed during exposure to high humidity.

Fig. 11 shows that the weight loss from the epoxy beads on heating is somewhat lower if exposed to low humidity (11% r.h.) for 9 h than if tested as applied. The losses have in both cases stabilised after about 1 h.

Fig. 12 shows the weight change during exposure to 84% r.h. The second graph shows the weight loss for each exposure time after a subsequent heating to 115 °C for 90 min. Fig. 13 shows the corresponding result for an exposure at 11% r.h.

The total water content could possibly be as high as 1% by weight. Part of the weight loss could come from other volatiles than water. Nevertheless, these figures show that the relative humidity affects the uptake and release of water and the change in weight by at least ~0.5%, and already after a few hours the uptake is decisive.

These experiments were made to simulate the behaviour of epoxy beads left open for some time during production before closing the bond and squeezing the epoxy into a thin layer, typically 0.2 mm thick. For a joint with adhesive thickness 0.2 mm, 0.5% water by weight corresponds to ~65 µg/cm² (adhesive density 1.3 g/cm³ and two interfaces in a joint).

Fig. 14 shows the response of adhesive beads of two different types of epoxy adhesives, XD 4600 and Henkel 5075, to varying humidity. The main difference between the two runs is that for run 1 the humidity was allowed to drop instantly while run 2 was kept at high level for some time. The experimental procedures were as in the previous section. These data clearly demonstrate that epoxy 5075 takes up about 50% more water than epoxy 4600.

Fig. 15 shows the response of adhesive beads to repeated humidity cycling. These data verify the results shown in Fig. 14 and demonstrate great repeatability. The weight loss on curing is shown to be the same after repeated humidity cycles as if cured immediately after application from the cartridge.

4. Factors influencing foaming during curing

4.1. Blistering tests

If much water is present in the adhesive joint at curing it might result in blister formation. Beforehand it was known that blistering was suppressed if the anodised substrates were preheated in a simulated cure cycle, reaching the cure temperatures, i.e. a 'degassing' prior to the application of the adhesive.

Bonding samples were made of 2 mm thick extruded aluminium. The samples were 40 mm wide and 120 mm long and the bonding overlap was 20 mm. The samples had 0.25 mm high ridges lengthwise to ensure even thickness of the glue line in the adhesive joint. All samples had an anodic layer of 9 µm unless stated otherwise. The aluminium samples were first conditioned (degassed) at 180 °C. After applying the adhesive beads, the samples were kept at controlled humidity for at least 1 h before closing the joint. After curing, the bonded samples were tensile tested. The bonded area after testing is shown in Fig. 16.

In Fig. 16 it can clearly be seen that if the adhesive beads were conditioned at 10% and 20% r.h. very little blistering was developed in the adhesive joint. At 50% and 70% r.h. a lot of blisters have developed in the adhesive joint. Only massive blistering affects the lap shear strength because it is more controlled by strain than stress for this joint configuration.

To study the effect of the curing cycle, a parallel set of samples was made, half of them cured by quickly heating directly to curing temperature (180 °C), while for the other half the curing was held at 140 °C for 1/2 h, before ramping up to final cure at 180 °C. The results are shown in Fig. 17.

From the lower row of images in Fig. 17 it can be seen that holding the curing at 140 °C prevents foaming even if the adhesive has been exposed up to 40% r.h., whereas on heating directly to curing temperature blisters are formed at 40% r.h. If the adhesive has been exposed to 50% r.h., blistering and possible cracking occurs; the amount will depend on the curing cycle.

To further study the effect of the curing cycle, a series of experiments were conducted and a summary of the results is described in the following paragraphs.

To test the influence of temperature ramping rate, two different cure cycles were tested. This parameter was found to be important for the control of blistering. The qualitative tests indicate that the rate of ramping during the setting of the adhesive is a very important parameter with slow ramping rates to be preferred.

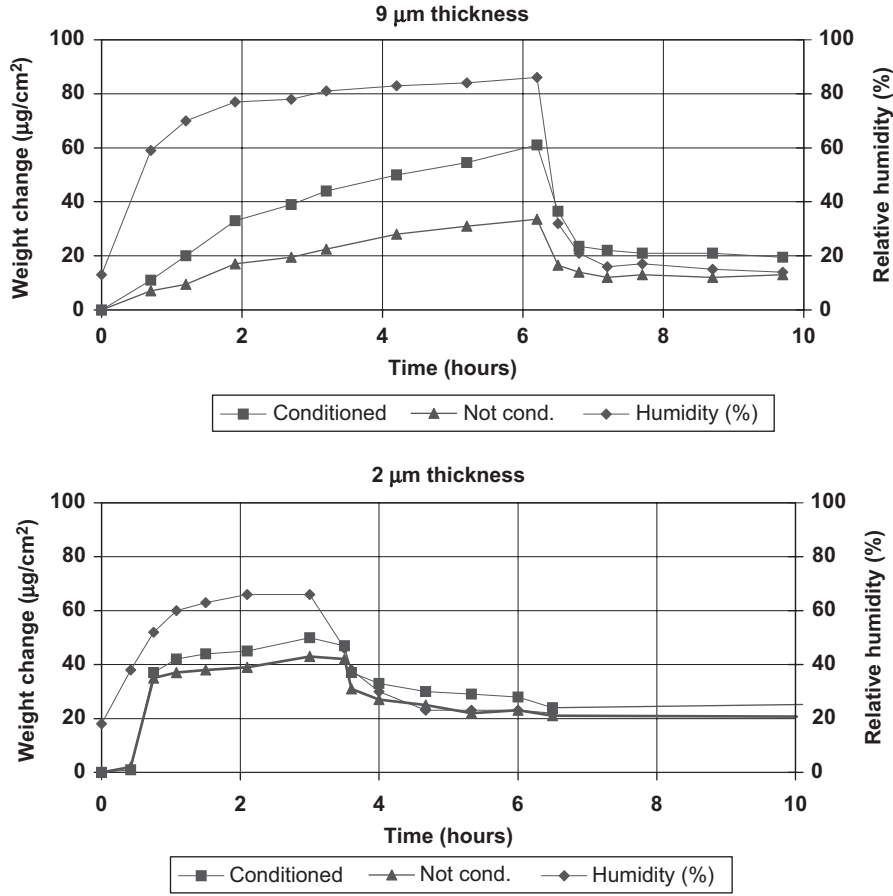


Fig. 9. Response to rapid changes in humidity for two different thicknesses of anodised films.

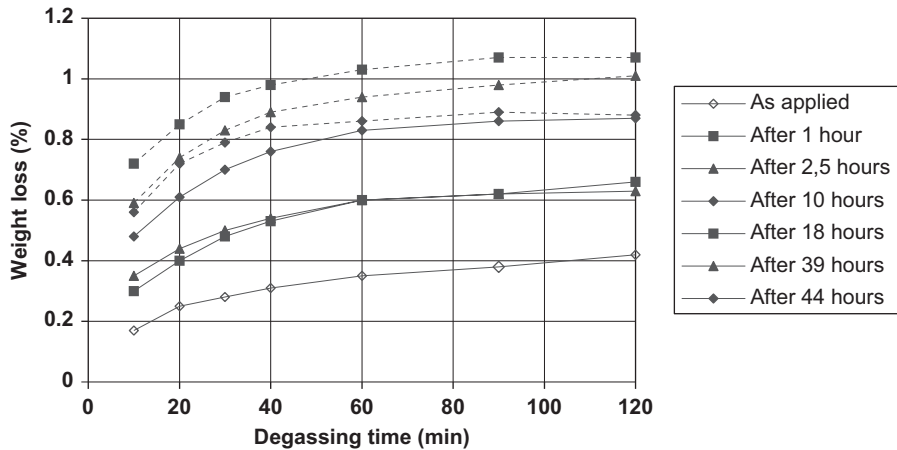


Fig. 10. Weight losses from beads of adhesive XD 4600 by time at 115 °C. Tested just after application and after exposure to 84% r.h. for different times.

To test the influence of the thickness of the anodic film on blistering, tests were run that showed the blistering to be more severe for 9 μm thick films than for 2 μm films under otherwise identical curing conditions.

To test the influence of the thickness of the adhesive in the joint, samples were made with glue lines of 0.25 and 1.0 mm, respectively. These experiments showed that foaming is less pronounced with a thicker glue line under otherwise identical conditions.

To test the influence of the humidity of the environment during the open time of the adhesive bead, from applying the

bead to closing the bond, samples were exposed to different humidities for 2 h before closing the bond and curing. In order to see the effect on the epoxy separate from the effect on the anodic film, these experiments were done with glass plates. A few blisters were observed after exposure at 45% r.h. and a fast ramping cure to 180 °C, while extensive blistering was found after 83% r.h. exposure. Introduction of an intermediate hold of the temperature at 140 °C before completing the cure resulted in a cracked pattern with clear visibility through cracks in the adhesive layer. No blisters were observed if the adhesive was cured on an open plate.

The alternative adhesive, 5075, showed much less blistering than XD 4600, even after being kept at 85% r.h. for 2 h before closing the bond and curing of samples with a 9 μm anodised film.

4.2. Local heating within the glue line during curing

The curing of the epoxy is an exothermic reaction. It is therefore conceivable that the reaction heat can influence the

curing rate to an extent that might influence the formation of blisters or foaming. The temperature inside the adhesive joint has therefore been measured with a very thin thermocouple inserted into the adhesive during curing. In Fig. 18 comparisons are made between two thicknesses of the glue line (0.2 and 2.0 mm) and two heating rates. To find the contribution to the heating from the reaction heat of the epoxy, the same samples were reheated once again after the first curing and cooling down to room temperature.

The tests were repeated with the 5075 adhesive. Any heating effect of the exothermic curing reaction could hardly be observed for this adhesive. Differential scanning calorimetric (DSC) measurements were carried out to see the difference in reaction heats and critical temperatures for the two adhesives. The results are shown in Fig. 19. Here it can be seen that the curing starts at a lower temperature and ends at higher for the 5075 adhesive than for XD 4600, and that the maximum heat output is lower. The total heat of curing has been determined to be ~350 J/g for 4600 and ~235 J/g for 5075. All together, these differences explain why no excess temperature could be observed inside the joint for 5075 during curing. The heat has time to dissipate from the bond, when less energy is to be released over a longer time.

4.3. Curing behaviour

Fondeur and Koenig [9] studied the curing behaviour of epoxy in situ with nuclear magnetic resonance (NMR) imaging of anodised and untreated aluminium joints. For anodised substrates

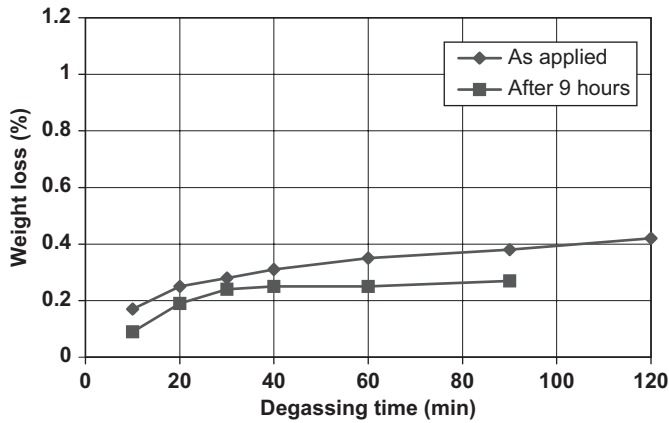


Fig. 11. Weight losses from beads of adhesive XD 4600 by time at 115 °C. Tested just after application and after exposure to 11% r.h. for 9 h.

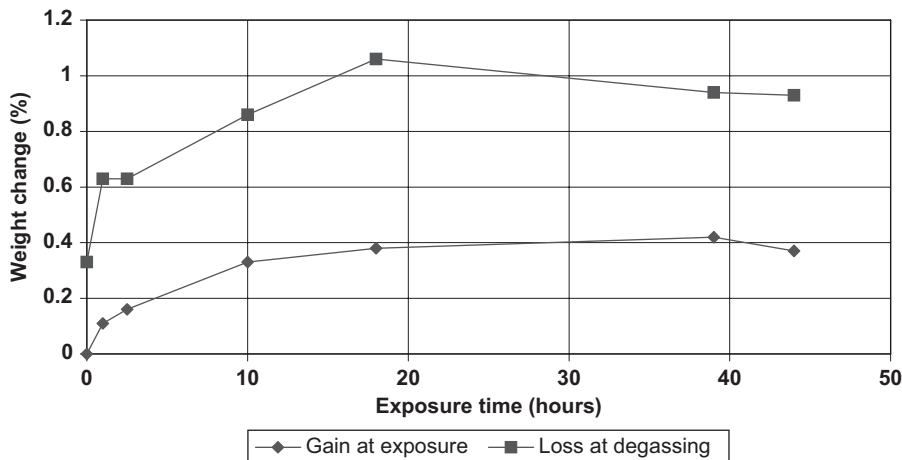


Fig. 12. The weight gain for beads of adhesive XD 4600 during exposure to 84% r.h. and the weight loss when the exposure is followed by a 90 min degassing at 115 °C.

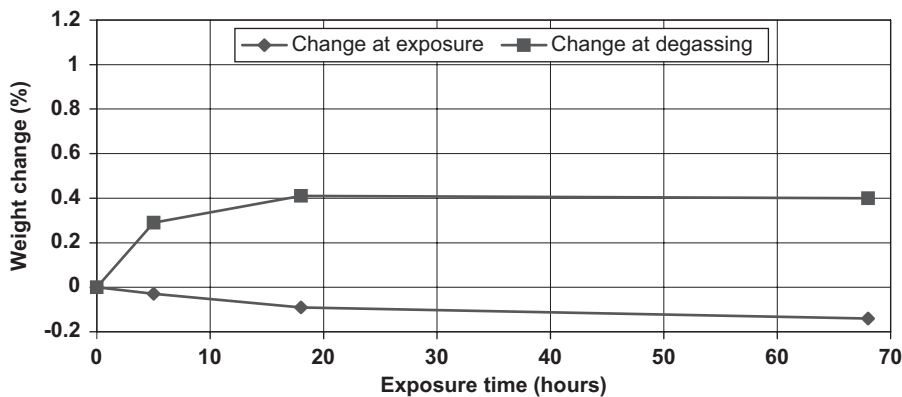


Fig. 13. The weight change for beads of adhesive XD 4600 during exposure to 11% r.h. and the weight loss when the exposure is followed by a 90 min degassing at 115 °C.

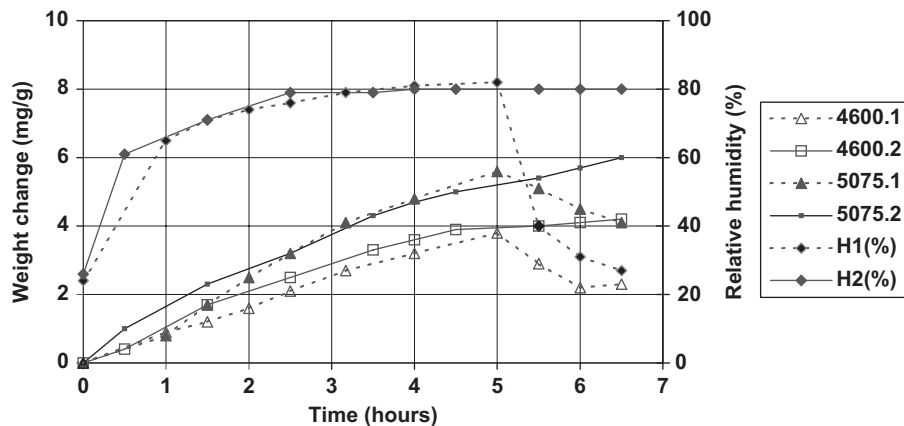


Fig. 14. Response to rapid changes in humidity for two different epoxy adhesives, XD 4600 and 5075. H1 and H2 refer to the relative humidity as registered at the time of the weight change measurements and should be read off the right-hand ordinate axis.

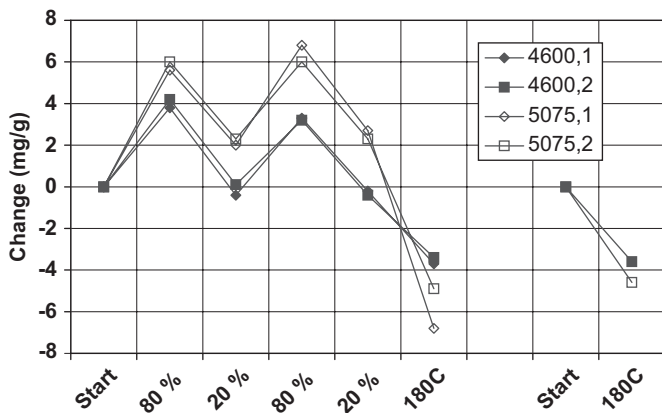


Fig. 15. Weight change for beads of the two different adhesives XD 4600 and 5075 after repeated exposure to different humidities and final curing. The values marked 180 °C on the abscissa axis indicate weight change after curing.

they found the adhesive bulk to solidify earlier than the adhesive close to the surface. For untreated substrates, the adhesive in the bulk did cure last. They also found that the overall cure did happen somewhat faster on anodised substrates.

It has been confirmed that the investigated bond system (sulphuric acid-anodised aluminium and XD 4600 adhesive) behaves in the same way. Lap shear specimens were removed from a laboratory oven after different times. To immediately stop the curing process, the samples were dipped in water or liquid nitrogen and then broken apart. After about half an hour in an oven temperature of 140 °C a viscous uncured layer was found close to the anodised surface at the same time as the bulk of the adhesive already was in a gelled state. Additional sampling gave a rough estimation that the viscous layer exists together with a gelled/solidified bulk for a time period of about 2–4 min (Fig. 20). Temperature measurements also confirmed somewhat faster temperature rise in anodised aluminium joints compared to joints made of as extruded aluminium.

Transmission electron microscopy (TEM) was used to study the interphase region of a specimen bonded at standard laboratory conditions with an anodic film thickness of 6 µm. The anodic film is hard and brittle compared to the adhesive and the aluminium and therefore the anodic film tends to break at sample preparation when cut to 1 µm slices with an ultra microtome. However, it can

be seen from the micrographs in Fig. 21 that the thixotropic agent, fused silica, is lacking in a layer adjacent to the anodic film. This phenomenon has been further investigated and has been reported separately [10].

5. Discussion

The humidity in the working area a few hours in advance of closing the joint controls the total amount of water trapped in the joint, both in the anodic film and in the adhesive. Water will continuously be released from the anodic film during the increase in temperature at curing. Depending on joint geometry, the water contribution from the anodic film can easily be in the same order of magnitude as the water content in the adhesive.

There is a certain total amount of water in the joint area not to be exceeded if blisters in the adhesive are to be avoided. The water release and the adhesive properties interact in many ways during the cure. Several different mechanisms that affect the result have been observed.

The cure cycle utilized is of critical importance. The rate of temperature rise from the onset of reaction up to the maximum cure temperature will strongly affect the cure rate. At heating the metal in the bond area will reach the onset temperature for curing slightly before the adhesive bulk. The XD 4600 adhesive starts its exothermic cross-linking reactions at about 140 °C. The curing will therefore start at the metal/adhesive interface. However, the adhesive is rather reactive and the release of curing energy will further raise the temperature. At rapid temperature increase considerable over temperatures has been measured in the centre of the adhesive joints, especially for thicker glue lines. Such overheating will speed the cross-linking reaction rate and shorten the time for cure. At the interface, the temperature will remain closer to the metal temperature.

The release of water from the anodic film will locally cause high concentrations in the adhesive close to the interface. The fast overheating triggers more release of water in a short time. Released water needs time to diffuse and spread in the adhesive and out from the joint. Dissipation is prevented by the limitation in the rate of diffusion and possibly by saturation. A thicker adhesive layer will increase the water buffering capacity of the adhesive joint. However, the diffusion rate will be reduced with the increasing state of cross-linking.

The large amount of water in the interphase region can reduce viscosity and possibly also delay the cross-linking rate

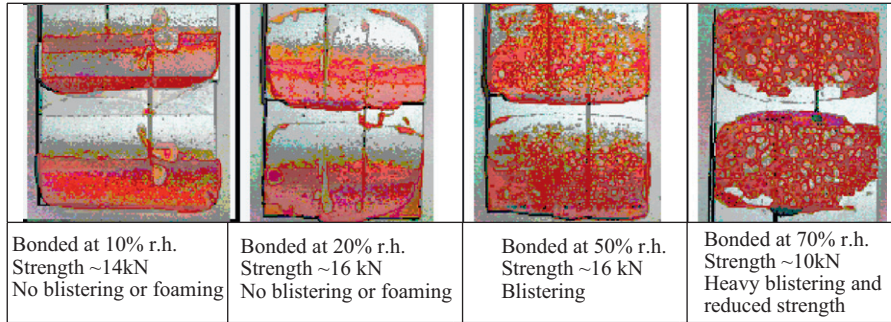


Fig. 16. Effect of bonding conditions on foaming. The anodised aluminium samples were conditioned at 180 °C before application of the adhesive.

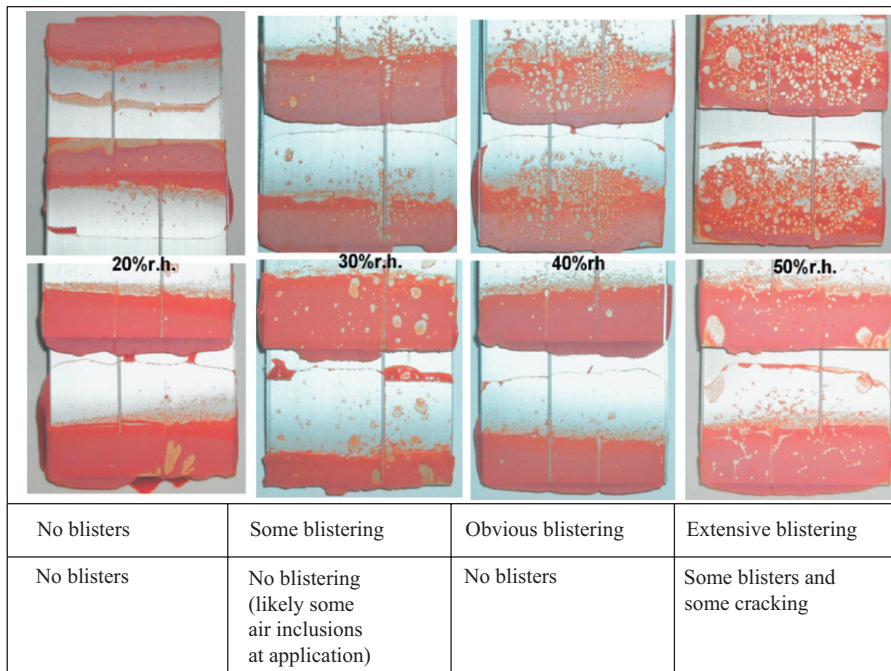


Fig. 17. Effect of exposure to different relative humidities before closing of joint made on not degassed anodised samples before the adhesive application. The samples at the upper row are heated directly to 180 °C. The lower row is heated to and held at 140 °C for 1/2 h and then heated to 180 °C.

locally. These effects contribute to maintain the water concentration high.

After the main bulk has started its gellification, it has been shown that a viscous layer is still present at the aluminium interface during a short period of time in the cure cycle.

The release of the water will require energy and this will cause some local cooling of the interphase region. The poor thermal conductivity of the anodic film contributes by delaying the levelling out of temperature differences. Blisters can reduce conductivity as well.

The introduction of an intermediate hold of the curing temperature at 140 °C before ramping to 180 °C reduces the amount of blisters, but introduces a new failure mode with cracks visible in the bond failure surface. During the period when the viscous layer is present, the hydrostatic pressure from the water vapour is able to crack and move blocks of gelled bulk adhesive, leaving large cracks in the joint with a very thin adhesive layer left on the substrate. Also external forces can cause the movement of the gelled adhesive, e.g. residual and thermal stresses and shrinkage constrains. With

the holding times chosen in this investigation, the setting/gelling of the adhesive bulk happens when the ramping-up to final cure temperature already has started. The adhesive is then strong enough to withstand further blistering.

Another effect to consider is vitrification, which can happen at isothermal curing [11]. If the glass transition temperature, T_g , of the adhesive lies above the actual temperature, this could possibly explain the low strength of the partially cross-linked and brittle epoxy.

Some comparison tests with another batch of the same adhesive with slightly modified flow properties suggest that adhesive rheology is a parameter to take into account for the understanding of blister/crack formation, as well. Less blistering was observed in the adhesive with higher thixotropy, the same trend applied also for other adhesives of similar type.

The observation made by TEM is that the released water seems to cause the hydrophobic thixotropic agent (fused silica) in the adhesive to be displaced from the interphase region. The lack of thixotropic agent close to the anodic surface suggests a distinct reduction in flow resistance in this adhesive layer. The depletion

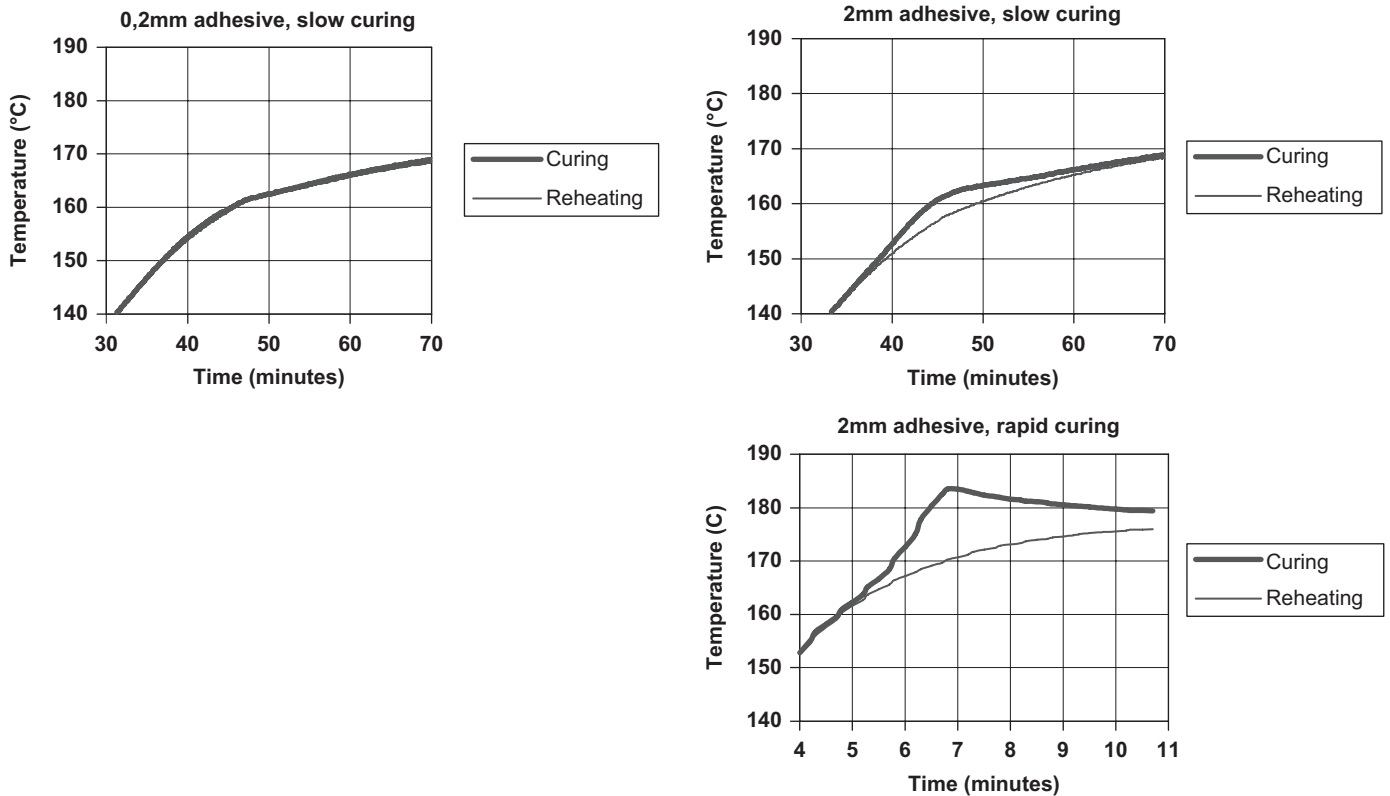


Fig. 18. Temperatures in the glue line on curing compared to temperatures on the same sample reheated after curing for the adhesive XD 4600 with 9 µm oxide thickness.

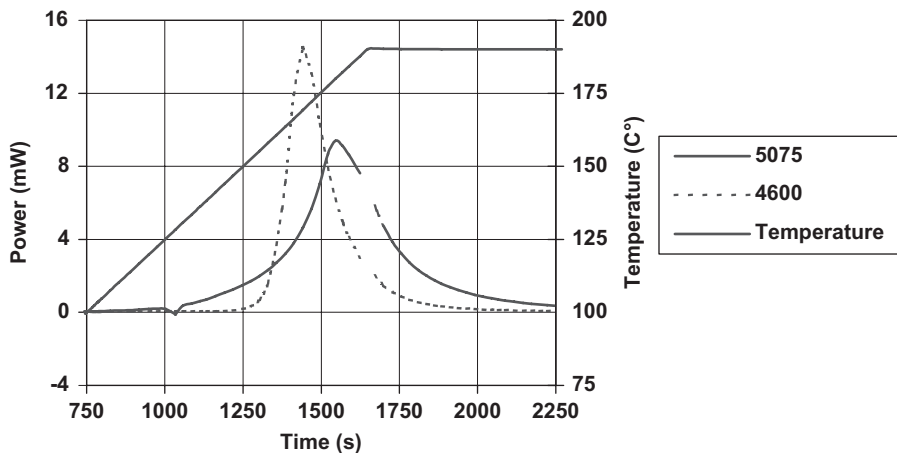


Fig. 19. Differential scanning (DSC) measurements of adhesives XD 4600 and 5075. Heating rate 6 °C/min in N₂ atmosphere.

of thixotropic agent close to the surface does also change the mechanical properties of the layer after cure. The effect can be a boundary layer with reduced strength and by that a possible path for the crack in static wedge tests, fatigue tests or in simple lap shear tests, which also very easy can be misjudged as an adhesion failure.

The other adhesive, 5075, in the investigation gave less blistering even if it can absorb much more water. The main reason seems to be a slower reaction rate. Less energy is released and it has clearly a broader DSC curve; as a consequence, the curing starts earlier and stops later. This will give a more homogeneous and even temperature profile during the cure with less blistering than for the XD 4600 adhesive.

6. Conclusions

The water contents in the adhesive and the sealed (SAA) anodic film are both governed by the relative humidity in the ambient air before closing the joint. At room temperature, a steep increase in the amount of water in the film has been found at 30–40% relative humidity. This is attributed to the affinity to sulphate residuals in the anodic film. At curing, the water in the system may cause blisters in the joint. Besides the joint geometry and the total amount of water in the system, the main controlling parameter is found to be rate of heating at curing. The anodic films will incessantly release water when the temperature is raised. The water released at the setting of the adhesive is most detrimental.

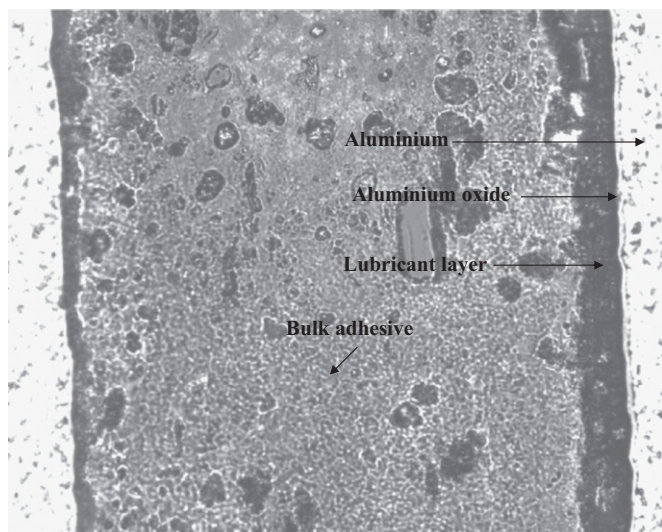


Fig. 20. Cross-section photo of a joint quenched at setting, postcured and polished, magnification ca 300 \times . The anodic film is about 5 μm and the viscous layer is in the order of 15–20 μm .

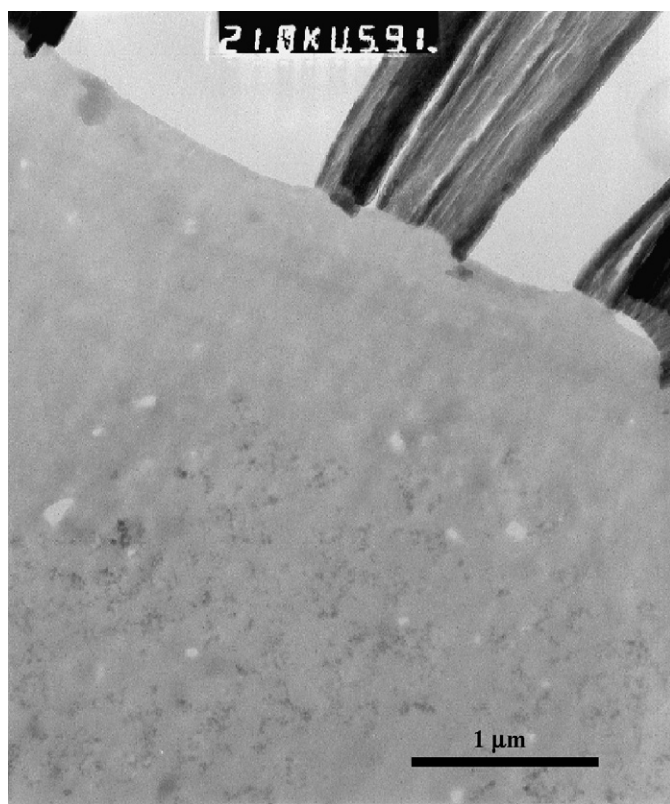


Fig. 21. TEM picture of the interphase region of adhesive and the anodic film. Some anodic film filaments are still attached to the adhesive. The darker particles in the bulk of the adhesive are fused silica (thixotropy agent).

There are also strong indications that the local accumulation of water at the interface between the epoxy and the anodic film might evict the thixotropic agent from the interphase region, which may result in a boundary layer with reduced mechanical properties.

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Appendix A. Materials and equipments

Alloy: 6060.35 AlMgSi: content, Si (0.40–0.45%), Mg (0.45–0.50%), Fe (0.18–0.22%), and maximum 0.02% of (Cu), (Mn), (Zn), (Ti) (Cr).

Anodising procedure: Cleaning, caustic etch, rinse, desmutting (H_2SO_4), rinse, anodising (H_2SO_4 160–210 g/l, temp. 15–20 $^\circ\text{C}$, voltage max 21 V, current density 1.5 A/dm 2), rinse, sealing (boiling water with anti-blooming additive, temp. 96–100 $^\circ\text{C}$).

Anodising film: Thickness 2–10 μm , most characterization and experiments are made on 7–10 μm film thickness. Thickness was measured by eddy current technique. Degassing before bonding (adhesive curing temperature, 180 $^\circ\text{C}$ for 5–15 min).

Adhesives: Betamate XD 4600, from Dow Automotive. A high-strength and impact-resistant one-component heat-curing epoxy adhesive especially developed for automotive body in white applications. The curing agent is dicyandiamide. A normal cure cycle is 180 $^\circ\text{C}$ with a hold time of 20–30 min.

Terokal-5075DC-25, from Henkel Teroson. A development product, intended for similar applications as XD 4600. The 5075 adhesive is less reactive and more flexible.

Humidity control: According to ASTM E104-85, Standard Practice for Maintaining Constant Relative Humidity by Means of Aqueous Solutions.

Humidity measurement: Tinytag, View 2 TV-4501.

Weight measurements: Mettler, PM-400. Any electronic lab scale with resolution 0.1 mg and possibility of hanging samples underneath the scale by a thin metallic wire may be used.

Heating chamber: Heraeus UT6060. The oven must have a hole in the top through which a thin metallic wire supporting the samples may be passed. The scale must be placed on top of the oven just above the hole.

X-ray spectrometer: Philips PW-2400.

IR-spectrometer: Perkin-Elmer FTIR-System 2000 with Auto-image IR-microscope.

GD-OES measurements: Tests were made by a supplier of GD-OES equipments, HORIBA Jobin Yvon in France.

DSC-equipment: Mettler Toledo DSC 820.

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