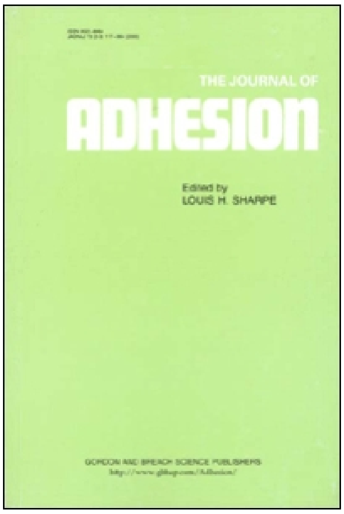
This article was downloaded by:
On: *21 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



The Journal of Adhesion

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Durability of Aluminium Adhesive Joints Bonded with a Homopolymerised Epoxy Resin

Silvia G. Prolongo[a]; Alejandro Ureña[a]
[a] Department of Ciencia e Ingeniería de Materiales, ESCET, Universidad Rey Juan Carlos, Madrid, Spain

To cite this Article Prolongo, Silvia G. and Ureña, Alejandro(2007) 'Durability of Aluminium Adhesive Joints Bonded with a Homopolymerised Epoxy Resin', The Journal of Adhesion, 83: 1, 1 — 14

To link to this Article: DOI: 10.1080/00218460600998490

URL: http://dx.doi.org/10.1080/00218460600998490

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

The Journal of Adhesion, 83:1–14, 2007
Copyright © Taylor & Francis Group, LLC
ISSN: 0021-8464 print/1545-5823 online
DOI: 10.1080/00218460600998490

Durability of Aluminium Adhesive Joints Bonded with a Homopolymerised Epoxy Resin

Silvia G. Prolongo
Alejandro Ureña
Department of Ciencia e Ingeniería de Materiales, ESCET,
Universidad Rey Juan Carlos, Madrid, Spain

The durability of epoxy–aluminium joints that use a homopolymerised epoxy resin was studied, and the effects of relative humidity, temperature, and salt concentration were analysed. The adhesive properties were measured by lap–shear tests, and the water uptake of the epoxy resin was determined by gravimetric measurements. Ageing and degradation effects on the epoxy resin and on the aluminium substrates were also analysed.

The homopolymerised epoxy resin absorbs little water (1.5 wt%) because of its non-polar network structure. The water uptake is enhanced by increasing relative humidity and temperature; however, the joint strength remains constant because of epoxy plasticization. A saline environment is damaging to the adhesive joints, because of metal corrosion, but was not significantly harmful to the epoxy resin, because of a lower diffusion coefficient of salt water. The T_g decrease of the epoxy adhesive due to water absorption depends only on the amount of absorbed water and is independent of the hydrothermal ageing conditions.

Keywords: Durability; Epoxy resin; Homopolymerisation; Hydrothermal ageing; Lap-shear test; Plasticization

1. INTRODUCTION

Epoxy resins dominate the field of structural adhesives because of their high wetting ability, good mechanical properties, and excellent chemical and thermal resistance. However, their main shortcoming is their strong tendency to absorb water in humid environments [1,2]. Water absorption usually weakens the adhesive joints [3–5].

Received 22 March 2006; in final form 4 September 2006.

Address correspondence to Silvia G. Prolongo, Department of Ciencia e Ingeniería de Materiales, ESCET, Universidad Rey Juan Carlos, c/ Tulipán s/n 28933, Madrid, Spain. E-mail: silvia.gonzalez@urjc.es

The reduction in joint strength can be associated with two phenomena: 1) adhesive separation, due to the presence of water on the interface between the substrates, and 2) physicochemical degradation of one of the components, often the adhesive [6,7]. These effects can usually be distinguished by the failure mechanism: interfacial failure when the main cause is adhesive separation and cohesive failure when adhesive degradation occurs [6].

Numerous factors govern the durability of epoxy resin bonds to aluminium substrates, such as the nature of the thermoset adhesive and aluminium alloy, the adherend surface pretreatment, the joint geometry, and the conditions of hydrothermal ageing, among others [3–5]. Some epoxy resins are not very durable because of their tendency to absorb water. The maximum water uptake at saturation varies from 2.5 to 15 wt%, depending on the nature of the hardener used, the ageing conditions, and the pH of the electrolyte [8]. The nature of the aluminium alloy is also important, because its susceptibility to corrosion may vary. On the other hand, the substrate surface pretreatment is the largest influence on joint durability [7]. A durable pretreatment must produce a hydration–resistant oxide on the metal surface. Also, the use of silane coupling agents and suitable primers usually increases bond durability. The joint design can also influence the ageing effect because different designs produce different stress concentrations. Finally, hydrothermal conditions strongly affect joint durability. Numerous variables, such as water quality, exposure time, and salt concentration, influence the behaviour of epoxy–aluminium joints [9].

In previous studies [9,10], several homopolymerised epoxy resins behaved in a manner similar to other commercial epoxy adhesives. The main quality of the homopolymerised epoxy was its low water absorption, which is due to the low concentration of hydroxyl groups in its cross–linked structure. The homopolymerisation process follows an anionic addition mechanism initiated by tertiary amines, often imidazoles [11,12]. This reaction occurs in stages. The initiation stage consists of the formation of anionic reactive species (epoxy/imidazole adducts). Then, these species react with other oxirane rings or hydroxyl groups to generate the epoxy network. Finally, the initiator regeneration occurs by N-alkylation and/or β-elimination. This implies that if the epoxy conversion is high, the epoxy resin will have little or no hydroxyl and oxirane groups, and therefore, it will have nonpolar behaviour, which decreases its capacity to absorb water. In fact, this kind of epoxy resin is widely used in a variety of electrical and electronic applications because of its relative low hygroscopicity, high dielectric capacity, and low thermal expansion coefficient [12].

The main limitations are its relatively low glass-transition temperature (T_g), around 100–140°C, and its high rigidity.

In this article, the joint strength and the durability of a homopolymerised epoxy resin have been studied. The separate and combined influences of temperature, relative humidity (RH), and salt concentration have been analysed.

2. EXPERIMENTAL

2.1. Materials and Specimen Preparation

The epoxy resin is based on diglycidyl ether of bisphenol A (DGEBA), supplied by Ciba (Barcelona, Spain) under the commercial name Araldite F. The equivalent weight was 178 g/eq, measured by chemical titration. The initiator for epoxy homopolymerisation was 2-methylimidazole (2MI), from Sigma-Aldrich (Madrid, Spain). The curing conditions were estimated in previous differential scanning calorimetry (DSC) studies [9]. Two wt% of 2MI were added, and the thermal curing treatment (150°C) was applied for 1 h. The epoxy probes (25 × 12.5 × 1 mm) were manufactured on hot plates using a mould whose walls were previously treated with an anti-adherent demould agent, Marbocote 445 Eco, Araldite, Everberg, Belgium.

The joint strength was determined by a lap-shear test, which followed the UNE-EN-ISO 1465 standard. The metallic substrate was aluminium A1050. Before the adhesive was applied, the adherend surfaces were prepared, following the UNE-EN 13887 standard [10]. They were first wiped with methyl ethyl ketone, and then they were ground at 5000 rpm with silicon carbide paper (grain size 76 μm, 180 mesh). A specific mould was used, according to the UNE-EN-ISO 1465 standard, for the adhesive application. After the surface treatment, aluminium pieces (100 × 25 × 1.4 mm) were assembled into single lap-shear joints with 12.5 mm of overlap length. The adhesive thickness was uniform, 0.22 ± 0.02 mm. Before any test, the prepared probes were stored in a vacuum for 24 h at room temperature.

2.2. Experimental Techniques

Lap-shear joints were tested in air at room temperature before and after ageing in various environments. Hydrothermal ageing was carried out by exposure for 7 days in a climate chamber at different RH, temperature, and salt concentrations, according to the UNE-EN-ISO 29142 standard. The ageing conditions can be divided in several sets of hydrothermal tests: (1) at constant humidity (30% RH) and different temperatures (23, 40, and 80°C); (2) at constant temperature (23°C) and different humidities (30, 45, 80, and 98% RH); (3) at constant temperature (23°C) and humidity (98% RH), with varying salt concentrations—nonsaline environment (distilled water) and saline environment (50 g/L NaCl solution); (4) at varying temperatures (23, 45, and 80°C), humidities (30, 45, 80, and 98% RH) and salt concentrations (nonsaline or saline environments).

The adhesive strength was calculated as the average value of five measurements, determined using a universal tensile machine with a crosshead speed of 1 mm/min.

To determine separately the ageing and degradation effects on each component (epoxy adhesive and aluminium), specimens of both were also tested. The percentage of absorbed water was measured by the gravimetric method, using a high-precision balance (Metter Toledo, New York, NY, USA, ± 0.00001 g).

The glass-transition temperature (T_g) of the epoxy adhesive was measured by DSC (Mettler TA 300) to evaluate the plasticization. The measurements were made in the dynamic mode by applying two thermal scanning cycles, from 30 to 250°C with a heating rate of 10°C/min, under a nitrogen atmosphere.

The fracture surfaces were analysed using scanning electron microscopy (SEM, Philips XL30, Eivdhoven, The Netherlands). SEM observations were made in the environmental mode at 0.4–0.8 torr. The nature of the corrosion products formed on the aluminium adherend surfaces was determined by X-ray emission spectroscopy (dispersive energy, EDS-SEM).

3. RESULTS AND DISCUSSION

3.1. Effect of the Humidity

Popineau and Shanahan [6] recently studied the durability of epoxy–aluminium joints after immersing them in water at room temperature. They observed that both the mechanical properties of the epoxy adhesive and the strength of aluminium–epoxy joints decrease rapidly after short times of water immersion (1 day). For longer times (2 days), the ageing rate decreases. Finally, for a long period of water immersion (7 days), despite the increase of absorbed water in the adhesive, the joint properties remain constant. However, complete immersion in water is not as damaging as exposure in a humid environment because there is less available oxygen in the former case [3,13]. Therefore, to analyse the effect of humidity on the epoxy–aluminium joints, the joints were subjected to atmospheres with different RH, at room temperature, for 7 days in a climate chamber. Seven days is the necessary time for the homopolymerised epoxy resin to reach water saturation in the climate chamber at 98% RH. This was determined using the gravimetric method: weighing the sample each day until it reached a constant weight.

Water absorption was measured by gravimetry on the bulk resin because of the difficulty of precisely detecting differences of weight on the aged adhesive–aluminium joints. This method has been also

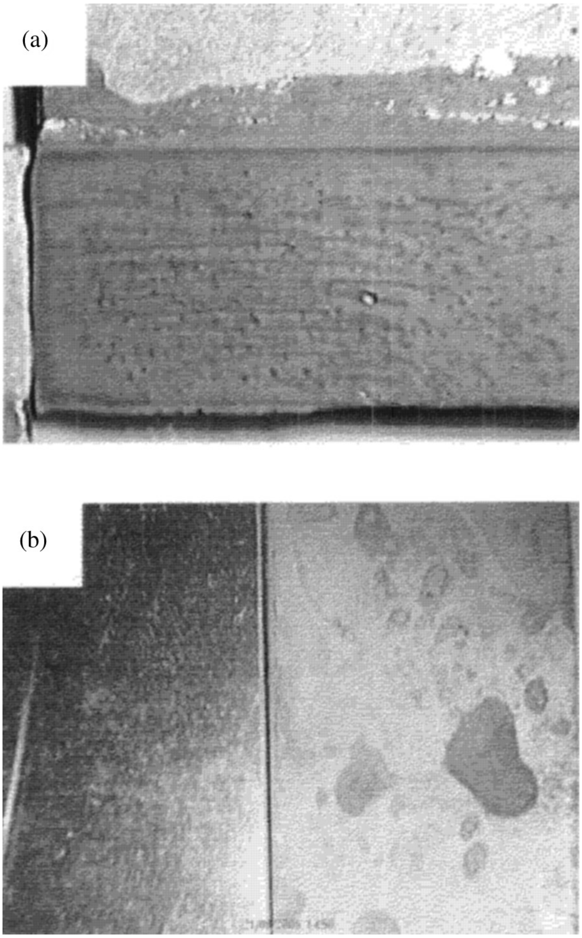


FIGURE 1 Macrographs of (a) the debonded area of aged joint and (b) two aluminium substrates without any treatment (on the left) and after corrosion in a saline environment (on the right).

successfully used by Popineau and Shanahan [6]. They found that there was a direct correlation among the absorbed water content, the decrease of physical properties of the bulk resin, and the joint strength. Figure 1a shows a macrograph of the debonded area of aged aluminium–epoxy joint tested. The high uniformity of the adhesive

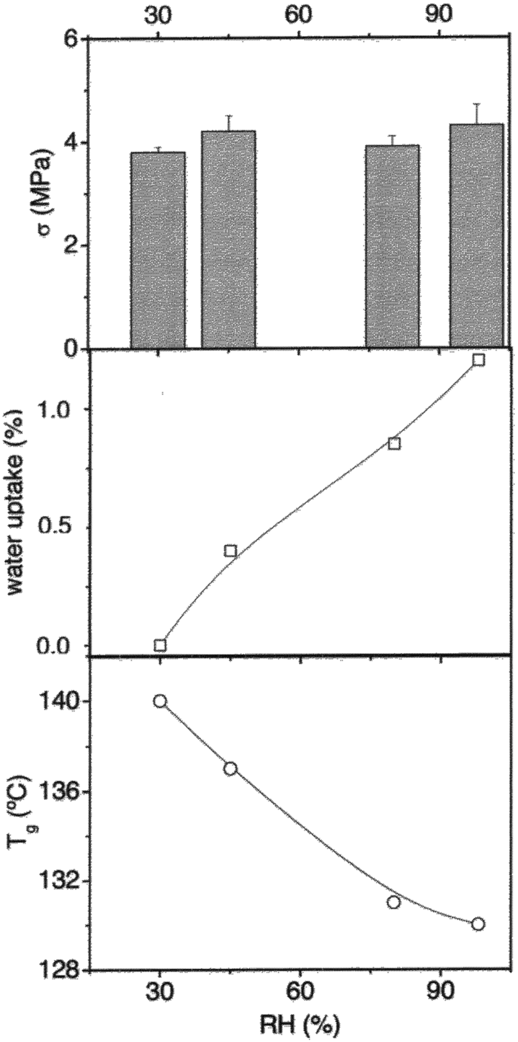


FIGURE 2 Effect of humidity on lap-shear strength (σ) of the aged epoxy–aluminium joints and percentage of absorbed water and T_g of epoxy adhesive.

surface indicates that the water diffusion was uniform through the entire bonded area.

Figure 2 and Table 1 show the lap-shear strength of aged joints at different humid environments. The percentage of water uptake and the T_g value of homopolymerised resin after the hydrothermal ageing are also given. It is worth noting the relatively low amount of absorbed water by the resin compared with other epoxies cured with amine or anhydride hardeners [3,6], which usually absorb between 3 and 15 wt% of water, depending on the hardener and additives. The low water uptake of homopolymerised resins is explained by the low concentration of polar groups in the epoxy network structure. The concentration of hydroxyl groups in the homopolymerised resins is very low. The increase of RH causes an increase of water uptake, although, in any test, water saturation is not reached. The maximum water uptake at saturation of the DGEBA/2MI resin was measured by immersion in distilled water for 1 month at room temperature, and we found that the homopolymerised epoxy resin only absorbs 1.5 wt%. The maximum absorbed water was determined as the water percentage at equilibrium, which is when the sample weight remains constant. Figure 2 shows

TABLE 1 Lap-Shear Strength (σ), Tg, and Water Uptake Percentage of the Aged Epoxy–Aluminium Joints

Ageing conditions			Results		
RH (%)	T (°C)	Atmosphere	σ (MPa)	% wt water	T_g (°C)
Humidity effect					
30	23	Nonsaline	3.8 ± 0.3	0	140
45	23	Nonsaline	4.2 ± 0.3	0.4	137
80	23	Nonsaline	3.9 ± 0.2	0.8	131
98	23	Nonsaline	4.3 ± 0.4	1.2	130
Temperature effect					
30	23	Nonsaline	3.8 ± 0.3	0	140
30	45	Nonsaline	4.0 ± 0.2	0	142
30	80	Nonsaline	3.6 ± 0.3	0	141
Saline effect					
98	23	Nonsaline	4.3 ± 0.4	1.2	130
98	23	Saline	3.2 ± 0.2	1.0	133
Combined effect					
80	80	Nonsaline	3.2 ± 0.2	1.1	128
98	45	Nonsaline	3.5 ± 0.1	1.5	126
98	45	Saline	2.9 ± 0.2	1.4	128

that the water absorption produces a decrease of T_g for the epoxy adhesive. This phenomenon is known as the plasticization effect [14,15].

Despite the changes observed in the adhesive, the joint strength is hardly affected by exposure to humid environments. In principle, the presence of water on joints should cause important damages associated with interfacial disbonding and the swelling of the aged adhesive. This apparent anomaly is explained by epoxy plasticization. The water absorption must cause both adhesive swelling and increase in flexibility, causing the joint strength to remain constant.

Figure 3 shows several SEM micrographs of the adhesive surfaces on the tested joints. The epoxy surface of the joint aged at 30% RH shows a smooth fracture, with a low concentration of fracture lines. Also, these lines are straight, thin, and parallel, which is characteristic of a brittle adhesive. In contrast, the epoxy adhesive aged at 98% RH for 7 days presents a rougher surface, which is characteristic of higher ductility. This change must be associated with absorbed water, which acts a good plasticizier and increases the flexibility of the epoxy adhesive. In summary, at room temperature, the effect of humidity on

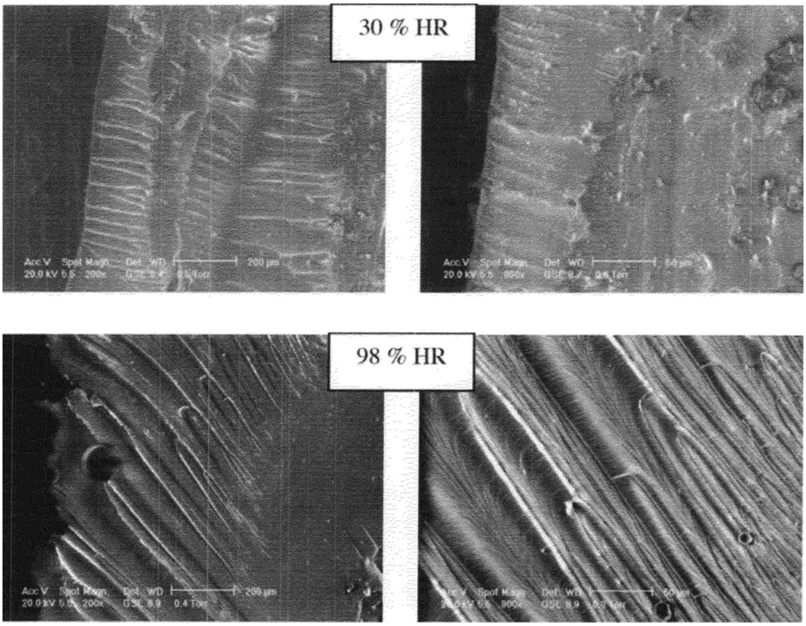


FIGURE 3 SEM micrographs of epoxy surface of joints aged for 7 days at 23°C in air (30% RH) and in a humid atmosphere (98% RH).

the joints is not catastrophic because of both the low absorbed water content and the plasticization of the resin.

3.2. Effect of Temperature

The aluminium–epoxy joints were also aged at different temperatures at room humidity (30% RH). No significant changes, such as weight gain, decrease of T_g, or differences in fractography, were observed on the adhesive joints. This indicates that the absorbed water amount is negligible and that the possible postcuring process does not occur. At low temperatures, 23 and 45°C, the joint strength remained constant, but at high temperature, 80°C, it slightly decreased (Table 1). This decrease could have two origins: the decrease of adhesive–substrate interfacial stress and the residual thermal stresses arising at the joints because of the difference in the thermal expansion coefficient (TEC) of both components [9].

3.3. Effect of the Saline Environment

The joints were aged in atmospheres at 98% RH with different salt concentrations: nonsaline (water vapour) and saline (vapour of a 50-g/L NaCl solution). The results are collected in Table 1. The saline atmosphere is more damaging to the epoxy–aluminium joints than the nonsaline atmosphere. These results contrast with those observed by other authors [3,15], who found that continuous immersion in a 3.5% NaCl solution was less aggressive than immersion in distilled or deionised water. This difference must be associated with the presence of oxygen in the climate chamber, which enhances aluminium corrosion.

The salt concentration seems to present two contrary contributions, acting positively on the adhesive and negatively on the aluminium adherends. The water absorption of the epoxy resin is slightly lower in a saline atmosphere than in a nonsaline one (positive effect). This phenomenon has been already observed by other authors [5], and it could be explained by the lower diffusion coefficient of saltwater relative to distilled water, due to its higher density. In contrast, the aluminium substrates are more affected by a saline atmosphere (negative effect). The surface pretreatment applied is basically the mechanical process of abrasion. Therefore, the aluminium surfaces had no protective layer, only the thin natural aluminium oxide layer. This implies that the susceptibility of untreated A1050-type aluminium alloy to corrosion must be high.

The corrosion phenomenon was directly observed by the appearance of a dark layer on the aluminium substrates (Figure 1b), which

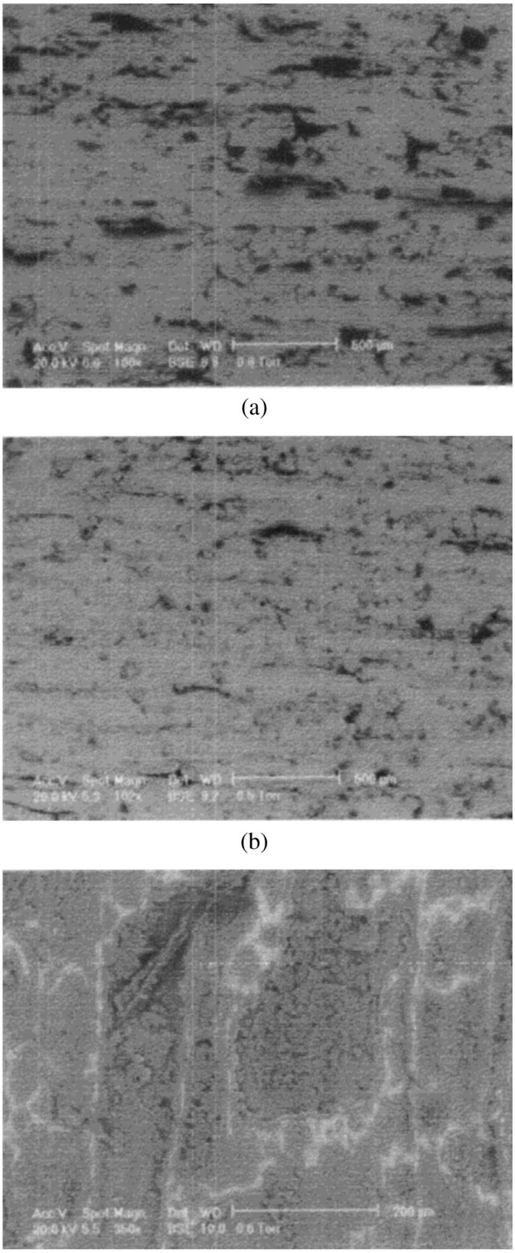
TABLE 2 Elemental Composition of Aluminium Surfaces Before and After Ageing in a Saline and Nonsaline Atmosphere, Measured by EDS-SEM

Atmosphere	Al (wt%)	O (wt%)	Cl (wt%)
Initial	74.4	25.6	—
Nonsaline	67.8	32.2	—
Saline	53.4	46.1	0.5

was analysed by EDS-SEM. Aluminium specimens were subjected to different ageing treatments, at 98% RH and 23°C for 7 days in nonsaline and saline environments, and then they were analysed. The results are shown in Table 2. The composition, supplied by the manufacturer, indicated that A1050 aluminium contains 0.29 wt% Fe, 0.09 wt% Si, and less than 0.01 wt% other elements, such as Mn, Zn, and Ti. The electron beam penetration is approximately 1 μm in SEM; therefore, the EDS analysis is superficial. For this reason, the measured oxygen concentration (25.6 wt%) is high, due to the natural aluminium oxide layer. The theoretical oxygen percentage on pure aluminium oxide is 47 wt%. Both ageing treatments, in nonsaline and saline environments, cause an increase of oxygen concentration, although this effect is more marked in the saline atmosphere. The oxygen concentration on saline-treated aluminium is nearly twice as much as the one on the initial substrate, indicating that the formed oxide layer is considerably higher. Also, the presence of chloride ions on the saline-aged aluminium surface indicates that this atmosphere enhances corrosion.

The analysis of fracture surfaces of the adhesive joints after the lap-shear tests showed that saline humid atmospheres generally corrode the aluminium susbstrates. Figure 4 shows the electron backscattered images of the aluminium side of the adhesive fractures in joints for the different ageing conditions. Both the as-joined specimen and the specimen treated in humidity (98% RH) present similar characterisitics without degradation signs on the fracture surface. Although the failure mechanism is mainly adhesive, remanents of epoxy resin are detected on both surfaces (dark zones). In contrast, adhesive joints treated in the 98% RH saline enviroment showed a thick layer of corrosion products that covered practically all the fracture surface. This corrosion layer has a porous morphology, which is principally responsible for the loss in the strength of the joint.

These two effects could justify the reported results [3]. On adhesive joints whose adherends have a good protective coating, aluminium



(a)

(b)

(c)

FIGURE 4 Electron backscattered images of the aluminium side of the adhesive fractures in joints at different ageing conditions: (a) as joined, (b) 98% RH in deionised water, and (c) 98% RH in a saline atmosphere.

corrosion will be negligible, and therefore, the main effect will be water uptake in the adhesive. In this case, the decrease of the joint strength is mainly caused by those variables that enhance the water absorption. However, the untreated joints could present different behaviour because of a second effect, the aluminium corrosion. The corrosion is enhanced mainly in saline environments at high temperature.

3.4. Combined Effect of Humidity, Temperature, and Saline Environment

As expected, humidity, temperature, and a saline environment create a synergistic effect (Table 1). At the same value of RH (80 and 98% RH), the temperature increase (from 23°C to 45 and 80°C) causes more damage to joints because of the increase in absorbed water by the epoxy adhesive. This is because of the increase of water diffusivity; this behaviour is observed in both nonsaline and saline environments. The damage caused by the combination of temperature and RH can also be explained by the activation of the corrosion mechanisms in aluminium with the temperature. Some authors [3] have even found that, at high temperature, the metal surface catalyses degradation of the adhesive.

The increase of humidity and temperature causes a proportional increase of the percentage of absorbed water, which induces a decrease in T_g. Figure 5 shows the T_g values as a function of absorbed water for

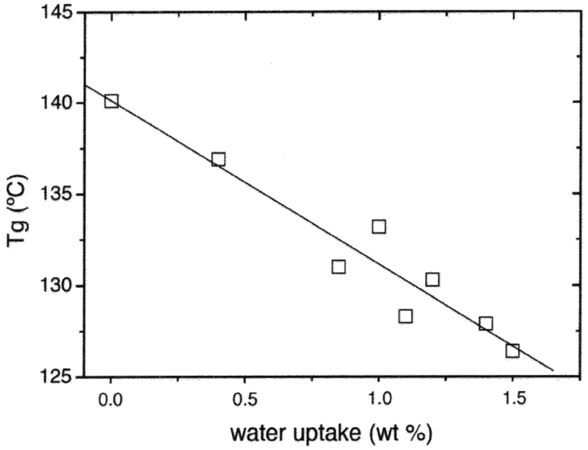


FIGURE 5 T_g values of the epoxy adhesive as a function of the percentage of water uptake.

all tests. There is a linear relationship between the water uptake and the T_g decrease. Also, this linear ratio does not depend on the ageing treatment. This means that the plasticization effect of the epoxy resin is dependent on only the amount of absorbed water and is independent of ageing conditions, such as humidity, temperature, and even salt concentration. Note that the T_g decrease does not depend on salt concentration, which implies that the distilled water has the same plasticization effect as a saline solution. This could be because the plasticization effect originates only when pure water molecules enter into the epoxy network.

The fit of the experimental data (Figure 5) to the straight line was carried out by linear regression of least squares. The ordinate value is $140 \pm 1°C$, coinciding with the T_g value of the neat epoxy resin. The calculated slope $(-9 \pm 1°C)$ indicates the rate of T_g decrease due to the water plasticization. The T_g of the homopolymerised epoxy resin decreases 9°C per each 1 wt% of absorbed water. This value is similar to that reported by other authors for different epoxy resins [16,17]. This means that although the homopolymerised epoxy resin presents a low tendency to absorb water, the effect of water uptake does not depend on the network structure.

Assuming that the T_g decrease caused by the water absorption can be explained by the Fox law $(1/T_g = w_a/T_{ga} + w_r/T_{gr})$ [18], the T_g of the water was determined to be $-144°C$, which is close to $-139°C$, the theoretical value of water T_g. This means that the water absorbed into the homopolymerised resin behaves in a way similar to the ideal miscible mixture. Also, the positive deviation of the Fick law indicates strong interactions between components [19], commonly by hydrogen bonds between the polar groups of the epoxy resin and the water molecules.

4. CONCLUSIONS

The durability of epoxy–aluminium joints that use a homopolymerised epoxy resin as adhesive has been analysed. The effect of several parameters, such as RH, temperature, and salt concentration, has been studied. The homopolymerised DGEBA/2MI resin absorbs only around 1.5 wt% water at saturation because of its nonpolar network structure. The water absorption into the epoxy matrix causes a T_g decrease of 9°C per each 1 wt% absorbed water.

The RH increase causes an increase in the percentage of water absorbed by epoxy adhesive but it scarcely affects the joint strength. The reason is that the water ingress into the epoxy adhesive induces two contrary effects: swelling and plasticization. Also, the effect of the hydrothermal ageing in saline and nonsaline environments is different. In saline environments, the amount of absorbed water is slightly lower because of the lower diffusion coefficient of saltwater into the epoxy adhesive. Also, the aluminium adherends are more susceptible to corrosion in a saline atmosphere. Finally, the T_g decrease associated with water plasticization depends on only the amount of absorbed water, not the hydrothermal aging conditions.

ACKNOWLEDGEMENTS

The authors thank Ministerio de Educación y Ciencia (MAT2004-06018) and Consejería de Educación de la Cominidad de Madrid (S-0505-MAT10077) for the financial support. Useful discussions with Gilberto del Rosario are acknowledged.

REFERENCES

[1] Pascault, J. P., Sautereau, H., Verdu, J., and Williams, R. J. J., *Thermosetting Polymers* (Marcel Dekker, New York, 2002).

[2] Stepto, R. F. T., *Polymer Networks: Principles of Their Formation, Structures and Properties* (Blackie Academic and Professional, London, 1998).

[3] Armstrong, K. B., *I. J. Adhes. Adhes.* **17**, 89–105 (1997).

[4] Kinloch, A. J., *Adhesion and Adhesives Science and Technology* (Chapman and Hall, New York, 1990).

[5] Kinloch, A. J., *Durability of Structural Adhesives* (Applied Science Publishers, London, 1983).

[6] Popineau, S. and Shanahan, M. E. R., *I. J. Adhes. Adhes.* **26**, 363–370 (2006).

[7] Rider, A. and Charkley, P., *I. J. Adhes. Adhes.* **24**, 95–106 (2004).

[8] Patrick, R. L., *Treatise on Adhesive and Adhesives* (Marcel Dekker, New York, 1976), Vol. 4.

[9] Prolongo, S. G., Del Rosario, G., and Ureña, A., *I. J. Adhes. Adhes.* **26**, 125–132 (2006).

[10] Prolongo, S. G., Del Rosario, G., and Ureña, A., *J. Adhes. Sci. Technol.* **20**(5), 457–470 (2006).

[11] Heise, M. S. and Martin, G. C., *Macromolecules* **22**, 99–104 (1989).

[12] Ooi, S. K., Cook, W. D., Simon, G. P., and Such, C. H., *Polymer* **41**, 3639–3649 (2000).

[13] Wylde, J. W. and Spelt, J. K. *I. J. Adhes. Adhes* **18**, 237–246 (1998).

[14] Cabanelas, J. C., Prolongo, S. G., Serrano, B., Bravo, J., and Baselga, J., *J. Mat. Process. Technol.* **143**, 311–315 (2003).

[15] Minford, J. D., *J. Adhes.* **18**, 19–24 (1985).

[16] Musto, P., Mascia, L., Ragosta, G., Scarinzi, G., and Villano, P., *Polymer* **41**, 565–574 (2000).

[17] Xiao, G. Z. and Sanan, M. E. R., *Polymer* **39**, 3253–3260 (1998).

[18] Ellis, T. S. and Karasz, F. E., *Polymer* **25**, 664–669 (1984).

[19] Wang, J., Cheung, M., and Mi, Y., *Polymer* **42**, 2077–2083 (2000); *Polymer* **42**, 3087–3093 (2000).