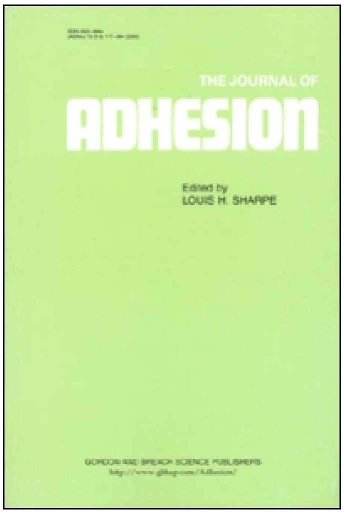

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Strength and Durability of Epoxy-Aluminum Joints

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The adhesive strength and durability of adhesively-bonded aluminum joints in wet environments was analyzed. A2024-T4 alloy was subjected to two different surface treatments based on etching with chromic-sulfuric acid (FPL) and with sulfuric acid-ferric sulfate (P2). Small differences were observed in the lap shear strength as a function of the applied surface treatment. However, durability in humid environments was higher for the joints whose adherends were treated with P2.

Although the amount of water absorbed by the epoxy adhesive is lower in saline environments, the effects on the glass transition temperature of the epoxy adhesive and on the lap shear strength of the joints are more marked than the effects caused by aging with distilled water.

Finally, a new epoxy adhesive with a siloxanic hardener was tested, obtaining good mechanical properties, high glass transition temperature, moderate values of lap shear strength, and high durability in wet environments.

Keywords: Aluminum alloys; Durability; Epoxy adhesive; Surface treatment

1. INTRODUCTION

The importance of lightweight aluminum alloys is reflected in their widespread use in the aerospace, transport, packaging, and general engineering industries. The use of adhesively bonded aluminum joints has several advantages over other traditional joining techniques.

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Adhesively bonded components display good design flexibility, high strength, improved stiffness, and excellent fatigue resistance [1–3]. Also, a high control of tolerances is obtained since distortion resulting from the heat of welding is avoided [4]. Other benefits include improved energy absorption, less vibration, and sound deadening [5]. However, the main limitation of these joints is the deterioration of their mechanical performance as a result of exposure to wet and corrosive environments [6–8]. The degradation of epoxy bonded aluminum joints can occur in alkaline as well as acidic environments. At high humidity, water can diffuse through the adhesive and along the interface between the adherend and adhesive. Water diffusion usually causes a decrease in adhesive strength, promoting adhesive failure due to displacement of the adhesive from the interface. This is caused by the absorption of water or, in certain cases, by the destruction of the oxide layer grown by pre treatment. A moderate increase in temperature, which in the absence of water does not have an adverse effect, leads to a pronounced loss of adhesive strength. Also, the presence of anionic species, like chloride ions, may accelerate this degradation through corrosion of the substrate.

Surface pretreatment of aluminum adherends is usually required to reduce the degradation rate of the joints in hostile environments [3,4,9,10]. The objective of pretreatment is to remove the naturally air-grown oxide/hydroxide surface and to replace it with a more stable oxide film with the highest surface free energy possible. This layer could help to obtain a strong and stable bond between the adherend and the adhesive. Currently, the most successful and widely used treatments in the aircraft and automotive industries are based on etching and anodizing techniques, involving the use of hexavalent chromium [3]. However, in recent years, governmental and environmental associations are applying pressure for the removal of these techniques from industrial processes [11,12].

There are several alternatives to chromic-sulfuric acid pretreatment (FPL etch), such as a sulfuric acid-ferric sulfate based treatment, known as P2 [2]. P2 etch initially provided results comparable with those obtained with FPL treatment.

However, several discrepancies have been found concerning the adhesive strength and durability of the epoxy-bonded aluminum joints treated with both processes [2,13]. In fact, the structure, composition, and thickness of the formed oxide layer depend on processing conditions. There are numerous chromic-sulfuric acid pickling alternatives (FPL, FPL-RT, DEF STAN 03-2, DIN 53 281, etc.) that differ in the concentration of the ionic specimens in the solution and the temperature and time of application of the pretreatment. It seems that

P2 etch provides results comparable with FPL treatment in both lap shear and peel tests, but it behaves worse in wedge tests. In a previous work [14], the authors demonstrated that the success of both pretreatments strongly depends on the nature of epoxy resin and aluminum alloy used as adhesive and adherends, respectively.

The purpose of this work is to study the effect of adhesive type and the applied adherend pretreatment on the adhesive strength and durability of epoxy-bonded aluminum joints. Adherends treated with FPL and P2 etches were tested. Four epoxy adhesives, based on the same epoxy monomer, were used, modifying the cross-linking agent employed. These adhesives were characterized through thermal and mechanical techniques. Joint degradation in hostile environments was assessed by lap shear tests. The effect of water absorption in the epoxy adhesive was also analyzed. Finally, changes in the failure mode and in the fracture surfaces of the aged joints were studied.

2. EXPERIMENTAL

2.1. Materials

The substrates employed were aluminum-copper alloys designed at as A2024-T4. Its composition (submitted by the supplier Fundiciones Gómez, S.A. Madrid, Spain), in weight percentage, is as follows: Cu: 4.67, Mg: 1.34, Mn: 0.63, Fe: 0.25, Si: 0.15; Zn: 0.02, Ti: 0.06; Cr: 0.01, with Al: the balance. The aluminum sheet was manufactured by a lamination process without any cladding.

The adhesives used are based on a diglycidyl ether of bisphenol A (DGEBA), supplied by Huntsman (Fullerton, CA, USA) under the commercial name of Araldite F. Its epoxy equivalent weight was 178 g/eq, which was measured by chemical titration.

Two different curing processes have been carried out for epoxy cross-linking: step-growth polymerization and condensation [15]. The homopolymerized epoxy adhesive, named 2MI in this paper, was obtained using 2-methylimidazole (2MI), from Sigma-Aldrich (St. Louis, MO, USA), as an initiator. The curing conditions, 180°C for 1 h, were estimated from previous differential scanning calorimetric studies. The rest of the epoxy adhesives used were synthesized by additional cross-linking polymerization. Two different amine hardeners were added, 4,4′-diaminediphenylsulfone (DDS, from Aldrich) and poly(3-aminopropyl methylsiloxane) (PAMS). PAMS was synthesized in our laboratory The synthesis and characterization of PAMS were described in a previous article [16]. The curing of the epoxy monomer with a polyaminosiloxane gives a new organic-inorganic network with interesting properties. The behavior of this new resin has been previously studied [16], confirming that it presents a relatively high glass transition temperature and low water uptake.

The stoichiometric mixtures of DGEBA/DDS and DGEBA/PAMS were cured at 210°C for 3 h and 150°C for 1 h, respectively. A commercial adhesive, Araldyt-Epoxy Rapid (Araldyte, from Ceys, Barcelona, Spain) was also tested for comparative proposes. The curing agent of this adhesive contains primary, secondary, and tertiary amines. The curing treatment applied for the Ceys adhesive, room temperature for 2 days, was recommended by the supplier. The molecular structures of the compounds used are shown in Fig. 1, and a summary of their properties and the curing conditions applied is collected in Table 1. From now on, the epoxy adhesives used will be referred to by the name of the cross-linker/catalyzer used (DDS, PAMS, 2MI) or their commercial name (Ceys).

2.2. Joint Preparation

Single lap shear joints represent the most common type of joint geometry employed for comparative studies. The lap shear specimens were prepared following the ISO-EN-UNE 1465 standard. The thickness of the aluminum sheets was 2 mm. The dimensions of the overlapped joints were $25 \times 12.5\,\mathrm{mm}^2$ and the average thickness of the adhesive was close to 0.22 ± 0.05 mm.

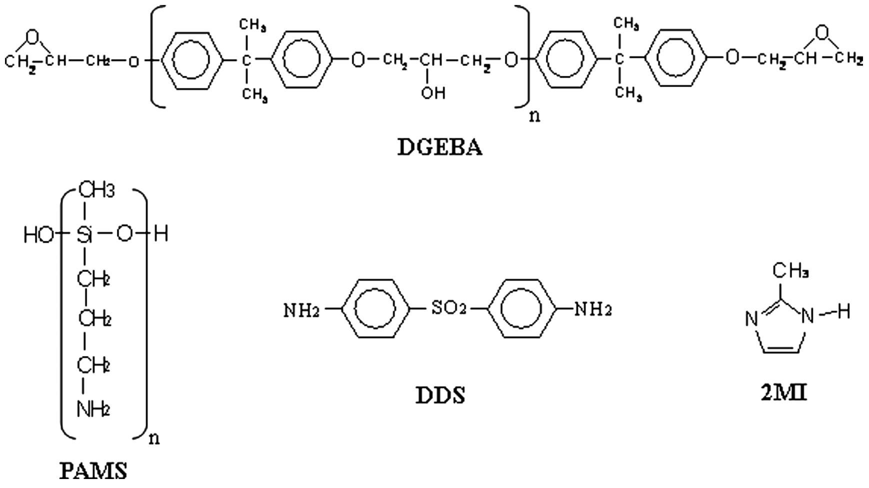


FIGURE 1 Chemical structures of the epoxy monomer (DGEBA), imidazole initiator (2MI), and amine hardeners used (DDS and PAMS).

TABLE 1 Main Properties of the Hardeners and Catalyst Used and Thermal Curing Conditions Applied for the Crosslinking Reaction of Epoxy Adhesives

	M_n^*(g/mol)	P_{eq}^*(g/eq NH)	Purity (%)	T_g (°C)	T_c^* (°C)	t_c^* (min)
PAMS	1419	59.1	89	−69	150	60
DDS	248	62.1	97	–	210	180
2MI	82	–	98	–	180	60

M_n = average molecular weight.
P_{eq} = molecular weight per hydrogen amino equivalent (N-H).
T_g = glass transition temperature.
T_c = curing temperature.
t_c = curing time.

The surface pretreatments [14] employed prior to adhesive bonding consisted of several shared steps: abrasion with P180 sandpaper using a Dremel sanding machine (Dremel from Breda, The Netherlands), degreasing with methylethylketone (MEK) at room temperature, etching in 100 g/L NaOH solution at 60°C for 1 min, and rinsing in tap water. Then, the acid aging treatment (FPL and P2) was applied. FPL treatment consisted of immersion in chromate solution (aqueous solution of 330 mL/L H_2SO_4 and 50 g/L $K_2Cr_2O_7$) for 15 min at 60°C while the P2 treatment was based on immersion for 8 min at 65°C in a equeous solution of 127 g/L $Fe_2(SO_4)_3 \cdot 5H_2O$ and 185 mL/L H_2SO_4. Finally, all the specimens were rinsed in distilled water and dried in the open air.

2.3. Aging and Lap Shear Test

The aging study was carried out by exposing the joints for 1 month (720 h) at 50 ± 2°C and a relative humidity (RH) of 98 ± 2%, in the presence (salt fog chamber, 50 g/L aqueous NaCl) and absence (environmental chamber) of chloride ions, according to the UNE-EN-ISO 29142 standard. The temperature and RH probes were hung vertically inside the chambers. Rectangular samples of epoxy resins used as adhesives, with the same dimensions for the joining area and thickness as the lap shear specimens ($12.5 \times 25 \times 0.2\,mm^3$), were also aged in order to analyze the individual effect of moisture and temperature on the properties of the epoxy resins themselves.

The adhesive strength was determined by a lap shear test following the UNE-EN-ISO 1465 standard. The surface-treated aluminum probes ($100 \times 25 \times 1.5\,mm^3$) were assembled into single lap shear joints with 12.5 mm of overlap length, using a specific steel mould [14–16] to obtain uniform adhesive layers with a thickness of

0.22 ± 0.02 mm. Five specimens were tested for each experimental condition studied and each adhesive system.

The fracture surfaces of broken lap shear specimens were observed by environmental scanning electron microscopy (ESEM, Phillips XL30, Amsterdam, The Netherlands) to analyze the failure micromechanisms.

2.4. Adhesive Characterization

The epoxy adhesives used were characterized by several techniques. The mechanical properties were determined with a tensile test, following the ASTM D638 standard. Type I specimens with $13 \times 57 \times 3\,\mathrm{mm}^3$ in the narrow section were tested on a universal testing machine under displacement control at a crosshead speed of 1 mm/min. After the mechanical test, the fracture surfaces of broken specimens were examined by ESEM.

Thermal properties were analyzed by differential scanning calorimetry (DSC) in order to determine the glass transition temperature (T_g). The measurements were carried out in a Metter Toledo mod 822 apparatus (Metter, Columbus, OH, USA), calibrated with indium. Two scans were done from 30°C to 250°C at a heating rate of 10°C/min under a nitrogen atmosphere (30 mL/min).

3. RESULTS AND DISCUSSION

3.1. Characterization of Epoxy Adhesives

Several epoxy formulations based on DGEBA were tested as adhesives for the aluminum adherends. The difference among them are the curing reaction mechanism and the nature of crosslinker and catalyzer, which significantly change their properties. DDS and PAMS are epoxy resins synthesized by an additional curing reaction using a cross linker agent. The functional groups of both are amine groups, but DDS has aromatic amines while PAMS has aliphatic amines. 2MI was synthesized by a homopolymerization curing process using an imidazole as initiator. Finally, Ceys is a commercial adhesive, whose formulation is complex but is also based on DGEBA.

Table 2 shows the T_g values of the epoxy adhesives used. DDS displays the highest glass transition temperature, indicating the high degree of crosslinking reached, which is associated with the high reactivity of the crosslinker having aromatic amines and the high curing temperature applied. Also, the high T_g of resin cured with DDS indicates the high rigidity and low mobility of the chain segments of the

TABLE 2 T_g Values of Epoxy Resins, Obtained by DSC Measurements in the First and Second Scans, as Synthesised and After Ageing Treatments in Salt Fog and Environmental Chambers

	T_g (°C)							
	PAMS		2MI		DDS		CEYS	
	1th scan	2nd scan	1th scan	2nd scan	1th scan	2nd scan	1th scan	2nd scan
As synthesised	120	137	99	119	181	197	42	34
Environmental	103	139	81	118	173	198	43	33
Salt fog	82	137	80	121	166	197	42	35

formed network. The T_gs of 2MI-and PAMS-Cured resins are around 100°C. *A priori*, the T_g of epoxy resins cured with silanes, which are polymers with high flexibility, should be low. The unexpectedly high T_g of PAMS is explained by the high functionality of the crosslinker used, which has up to 24 reactive groups per molecule (because each siloxane chain contains 12 monomers with one amine group pair at each monomer), increasing the crosslinking degree of the formed network and, therefore, its glass transition temperature. Taking into account the curing temperature applied, 2MI shows a relatively low T_g. The homopolymerized epoxy resin usually reaches a low degree conversion of due to the very high crosslinking rate [15]. Although no residual peak was observed at high temperature, a second scan was done to evaluate the possible post-curing reaction. The T_gs of PAMS, DDS, and 2MI measured in the second scan were increased by around 15–20°C relative to the first measurement, indicating a post-curing reaction due to heating above their curing temperature up to 250°C. Nevertheless, it is possible to conclude that the curing treatment applied in this work is the optimum, since higher curing temperatures scarcely increase the reached conversion. Ceys is the only adhesive studied in which T_g decreases in the second DSC scan. This means that the high temperatures reached during the first DSC scanning caused its degradation. In fact, the supplier indicates that its maximum use temperature is 60°C.

In order to evaluate the isolated effect of moisture in the adhesives, the T_g value was measured after aging treatment (50°C and 98% RH for 1 month in environmental and salt fog chambers). The obtained results are also displayed in Table 2. In order to analyze these results, the amount of water absorbed by each sample was measured through the weight gain of the samples after aging, which is shown in Table 3. For the four epoxy adhesives studied, the percentage of absorbed

TABLE 3 Water Absorption after Ageing Treatments in Salt Fog and Environmental Chambers

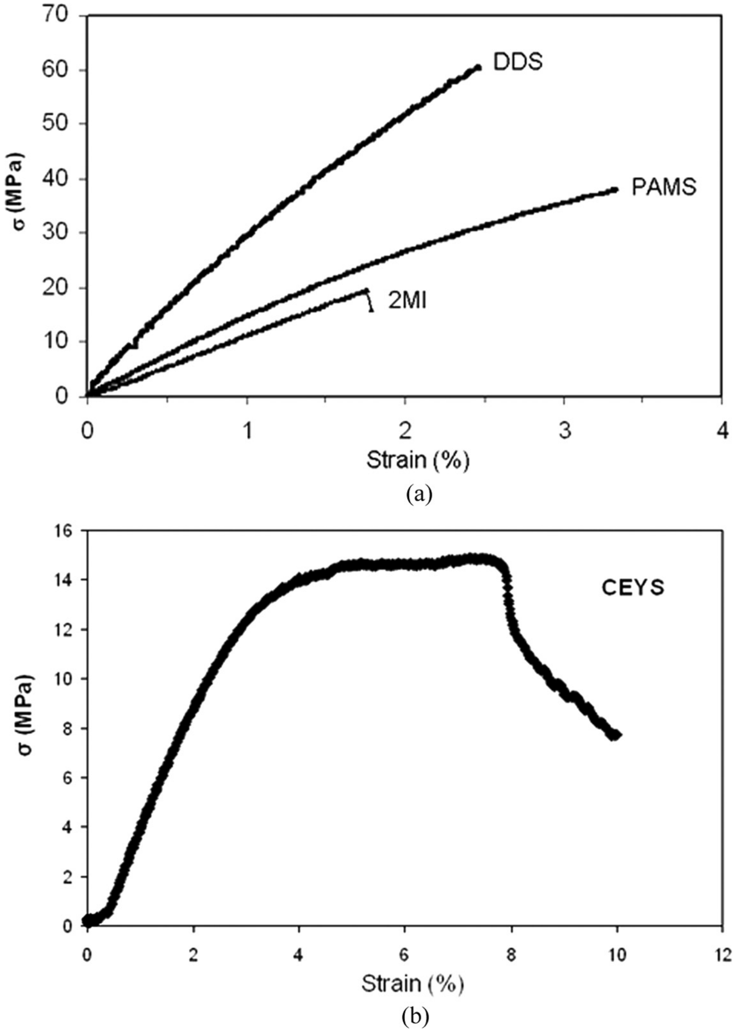
	Water absorption (wt%)			
	PAMS	2MI	DDS	CEYS
Environmental	1.9	1.1	2.1	6.7
Salt fog	1.5	0.9	1.7	4.4

water is higher for the resins aged in the environmental chamber (in the absence of chloride ions) compared with the ones aged in the salt fog chamber. The reason for this could be that the concentration of sodium chloride increases the density of the aqueous solution compared with neat water, decreasing the diffusion coefficient of the solution into the epoxy matrix [17].

Ceys is the studied adhesive that absorbs the highest amount of water. This could be explained by the low epoxy conversion reached during the curing process, which would also justify its low T_g. 2MI and PAMS display the lowest water absorption. The low tendency to absorb water of 2MI could be caused by the structure of the homopolymerized resin, whose hydroxyl concentration is negligible. The presence of OH groups is an important factor governing water uptake due to van der Waals interactions [17]. The low water absorption ability of PAMS is attributed to the high hydrophobicity of the siloxane cross-linker. The low tendency of the silanic polymers to absorb water is well known. It is worth pointing out that the epoxy resin cured with PAMS, which is a new formulation synthesized in our laboratory, presents a relatively high T_g and low water uptake [16].

The entrance of water into the epoxy network usually causes a plasticization effect, among other phenomena, such as swelling, building up of residual stresses, and creation of microcrazes [18–21]. The plasticization of epoxy resins induces a decrease in the glass transition temperature, as can be observed in Table 2. T_g values of the epoxy networks decrease between 4°C and 25°C per 1 wt% absorbed water, depending on the nature of the epoxy and the presence of chloride ions in the water. In fact, although 2MI absorbs a small amount of water, the damage caused, determined by the T_g decrease, is high. In contrast, despite the high water uptake, the T_g of Ceys remains constant, possibly due to commercial additives. Its low initial T_g and high plasticity also have an influence on its low plasticization. For all studied adhesives, the aging treatment in the salt fog chamber caused a higher T_g decrease than aging in the environmental chamber, in spite of lower water absorption. Therefore, it is possible to affirm that the damage to the thermal properties of epoxy resins is higher in a saline environment. The T_g of all samples recovers its initial value during the second DSC, removing the plasticization effect.

The mechanical properties of epoxy adhesives were determined with a tensile test. Figure 2 shows the tensile curves obtained for the four epoxy resins studied, from which elastic modulus, tensile



(a)

(b)

FIGURE 2 Tensile stress *vs* strain curves of epoxy resins: (a) DDS, PAMS, and 2MI and (b) Ceys.

strength, and deformation at break were determined (Table 4). The mechanical behavior of Ceys is radically different from the mechanical behavior of the rest of the epoxy resins. It displays high deformation ability but low tensile strength. This is the only commercial adhesive studied, which should contain several additives and fillers, while the rest are basic formulations (stoichiometric mixtures of DGEBA and crosslinker).

Also, it is a flexible adhesive with a low degree of crosslinking ($T_g = 42°C$). The elastic modulus and tensile strength of DDS are high due to its high crosslinking degree ($T_g = 181°C$). In contrast, 2MI is very weak, displaying a low modulus, low maximum strength, and low elongation. This is associated with the structure of the homopolymerized epoxy network, which is formed exclusively by bonded DGEBA crosslinked molecules and, therefore, has a low molecular weight between crosslinking points. The relatively high elongation at break of PAMS, in spite of its relatively high degree of crosslinking ($T_g = 120°C$), is interesting. This behavior is related to the high flexibility of siloxane chains. The Si-O-Si bonds have high rotational freedom, giving flexibility to the epoxy network.

Figure 3 shows the ESEM images of fracture surfaces of broken epoxy specimens from tensile tests. All the fracture surfaces tested were flat. The fracture surfaces of DDS and 2MI are totally brittle while PAMS, and especially Ceys, show surfaces characteristic of more ductile polymers. The fracture of DDS and 2MI show accentuated river markings and many ridges, pointing to the defect responsible for the failure. This defect is usually air bubbles situated at the edges of the specimen. The fracture surface of PAMS shows some features protruding from the surface, usually called “stacked laminar texture” [22]. These features imply the fortuitous intersection of two fracture planes, indicating localized plastic deformation. Finally, the fracture surface of Ceys is much rougher, and it is not so easy to distinguish the crack initiation. This indicates that this epoxy resin is more flexible.

TABLE 4 Tensile Properties of Epoxy Adhesives

	PAMS	2MI	DDS	CEYS
σ (MPa)	30 ± 6	21 ± 1	60 ± 5	14 ± 7
E (Gpa)	1.4 ± 0.1	2.0 ± 0.5	3.0 ± 0.4	0.50 ± 0.05
ε (%)	3.2 ± 0.1	1.6 ± 0.2	2.9 ± 0.5	10 ± 1

σ = maximum tensile strength.
E=Young’s modulus.
ε = deformation at break.

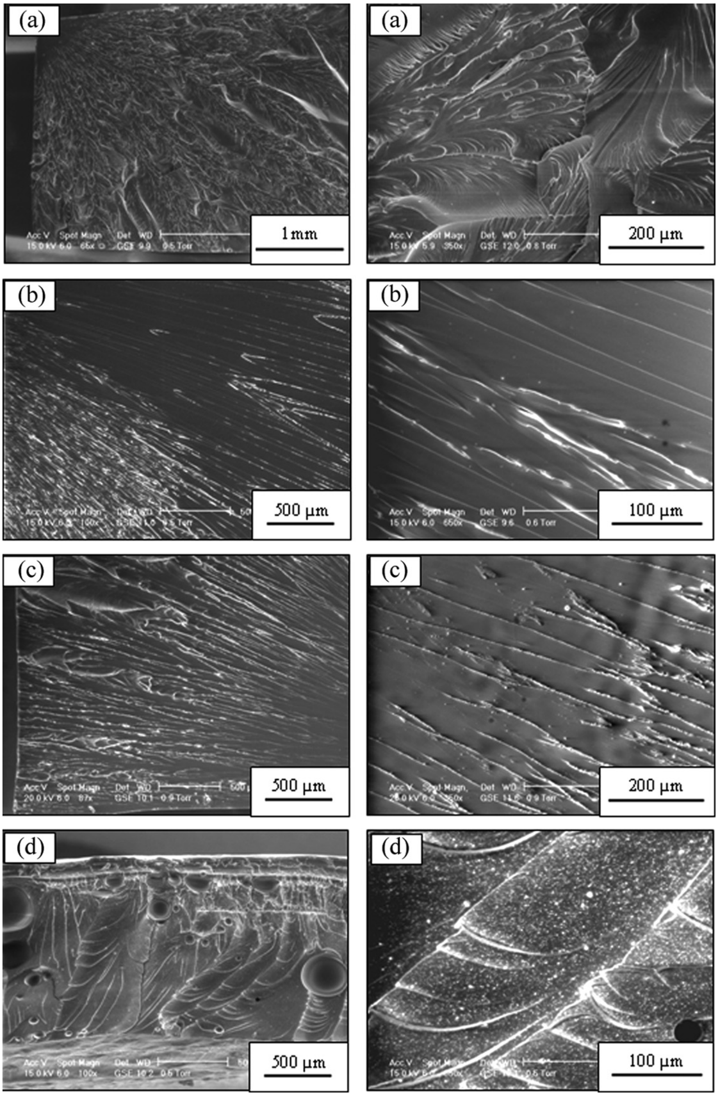


FIGURE 3 ESEM images of fracture surfaces of epoxy resins broken in tensile tests at (left) low and (right) high magnifications: (a) PAMS, (b) 2MI, (c) DDS, (d) Ceys.

This behavior completely agrees with the measured mechanical properties. The Ceys surface shows numerous pores on the upper face due to bubbles of trapped air. These are generated during specimen processing due to the high viscosity of this adhesive and its low curing temperature, which is responsible for its low tensile strength. The surface of this adhesive is covered with white particles, which are formed by the carbonation of non-reacted amine groups, demonstrating the low conversion reached by Ceys.

3.2. Lap Shear Strength of Epoxy-Aluminum Joints

The adhesive strength of epoxy-aluminum joints was measured by a single lap shear test. The obtained results are shown in Fig. 4. In all cases, the failure was partially cohesive.

It is worth noting that during tensile testing of single lap joints, significant peeling (tensile) stresses are generated at the ends of the joint in addition to shear stresses in the adhesive layer [4,10]. Therefore, the true shear strength is not measured.

Both surface treatments, P2 and FPL, give similar results. This means that FPL could be replaced with P2, which is a chromate-free treatment. However, the efficiency of these chemical treatments depends on the nature of the epoxy adhesive [14]. The adhesive strength of Ceys and PAMS scarcely depends on the surface treatment applied. However, the behavior of 2MI is better with FPL treatment and DDS behaves better when the aluminum adherends are previously treated with P2.

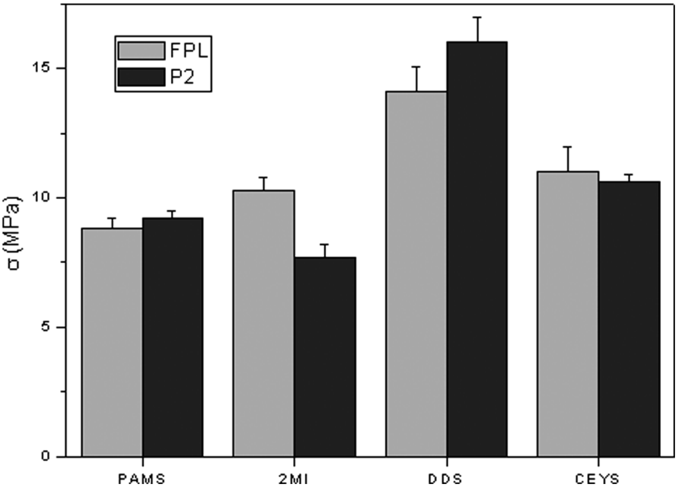


FIGURE 4 Lap shear strength of epoxy-aluminum joints, whose adherends were treated by FPL and P2 surface treatments.

The strength of DDS is the highest, compared with Ceys, 2MI, and PAMS, which display similar values. This could be because DDS is the adhesive with the highest mechanical strength (Table 4) and also because it presents high polarity associated with the formed epoxy–aromatic amine network.

Figure 5 shows the fracture surfaces of the tested epoxy adhesives. As has been already indicated, in all cases the failure mode was partially cohesive. PAMS, 2MI, and DDS display fracture surfaces characteristic of brittle adhesives. The fracture occurred by a delamination mechanism [23]. The surfaces present a closely spaced array of cusp-shaped features, aligned normal to the tensile stress applied. Details of these features, called hackles, show that they consist of a series of river line steps aligned in the general direction of crack propagation. Small particles of aluminum oxide (white and brilliant) were observed on the adhesive surfaces, they have been pulled out of the adherend. The chemical nature of these particles was determined by energy dispersive spectroscopy (EDS) coupled with SEM, confirming its elemental composition (O and Al). PAMS and 2MI show large areas of adhesive failure, which are rough copies of the surface profile of the treated aluminum surface. The fracture surface of Ceys is completely different, showing a relatively ductile fracture. There are numerous micro-crackings oriented at 45° to the tensile stress applied, indicating plastic deformation of the adhesive occurs before fracture. No great differences are observed in the fracture surface as a function of the surface treatment applied, P2 or FPL.

3.3. Durability of Epoxy-Aluminum Joints

The study of the durability of epoxy-aluminum joints, using several epoxy adhesives and different surface adherend treatments, was carried out by aging in environmental and salt fog chambers at 98% relative humidity and 50°C. After the aging treatment, the joint strength was evaluated by the lap shear test, with the results shown in Figs. 6 and 7. While the fracture of all non-aged specimens tested was cohesive, the failure mode after aging treatments changes for some joints. In particular, the fracture of joints bonded with PAMS and aged in the salt fog chamber was partially adhesive, independent of the surface treatment applied, P2 or FPL. Furthermore, the fracture of these same joints aged in the environmental chamber was totally adhesive. The adhesive 2MI also presented partial adhesive failure when it was aged in the environmental camber. The rest of the aged joints mainly presented cohesive failure.

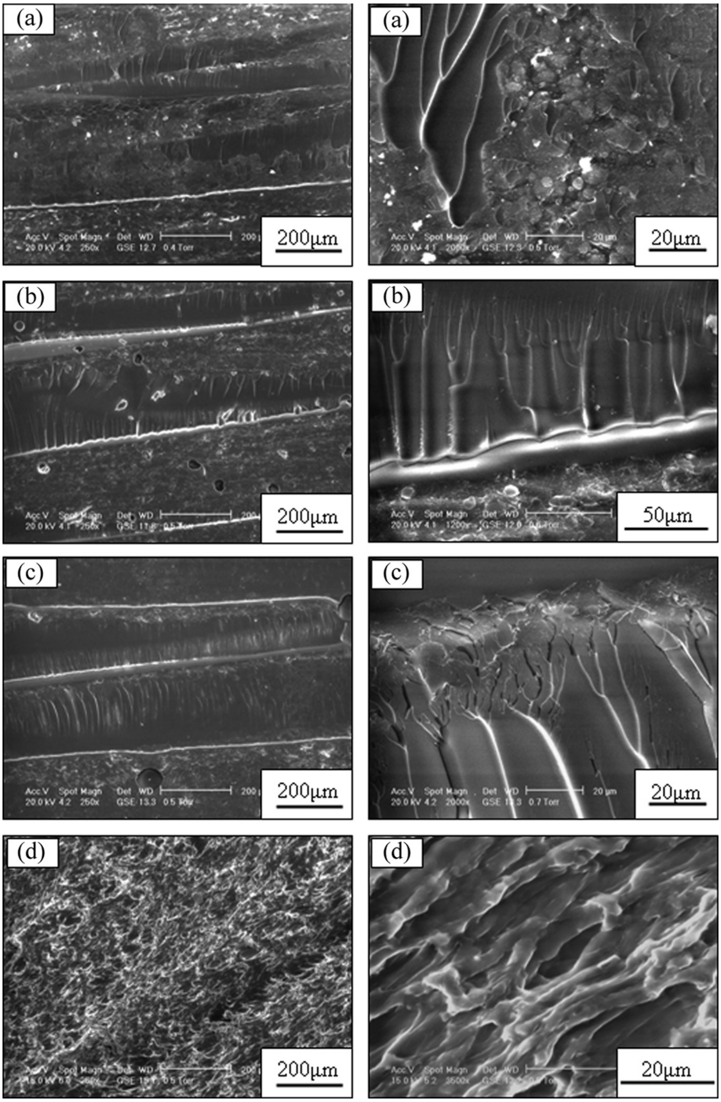


FIGURE 5 ESEM images of fracture surfaces, at (left) low and (right) high magnification, of epoxy adhesives on P2-treated specimens broken in lap shear tests: (a) PAMS, (b) 2MI, (c) DDS, (d) Ceys.

After aging, the strength of the adhesives PAMS and DDS decreases but the strength of 2MI and Ceys increases (Fig. 6). This increase is especially important for the commercial adhesive. It is

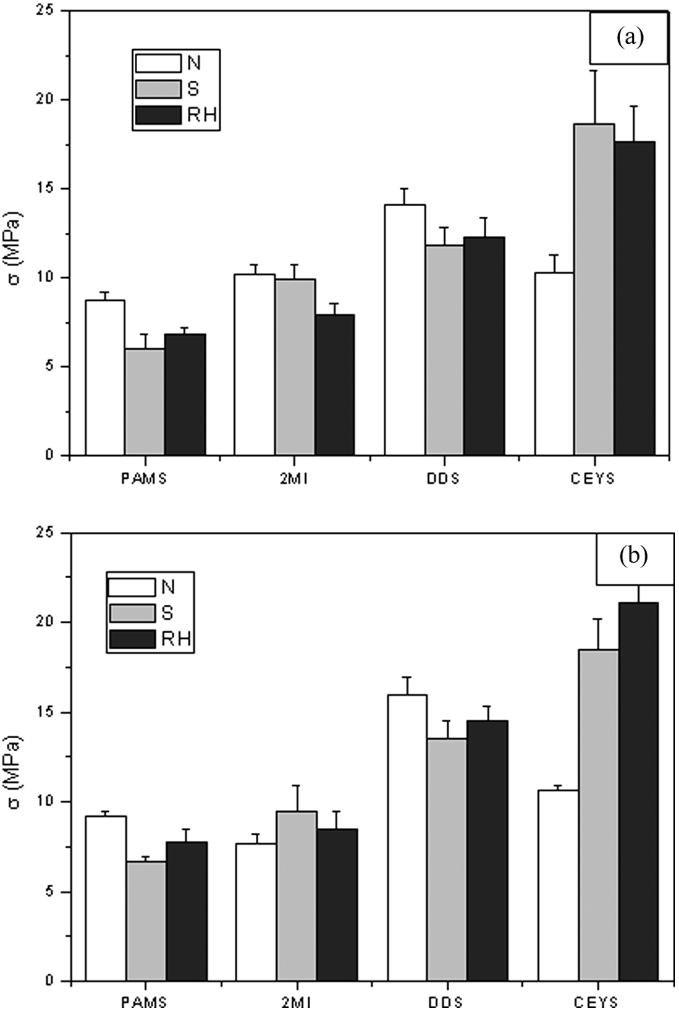


FIGURE 6 Lap shear strength of epoxy-aluminum joints, non-aged (N) and aged in environmental (RH) and salt fog chambers (S), whose adherends were treated by (a) FPL and (b) P2 surface treatments.

known that the absorption of water weakens the joints, breaking the adhesive-adherend interface and promoting adhesive failure [3,4,9]. Therefore, in principle, the expected result is a decrease in adhesive strength. The increase in adhesive strength after aging must be related to the plasticization effect of water, which increases the capacity of the adhesive to deform, increasing its adhesive strength.

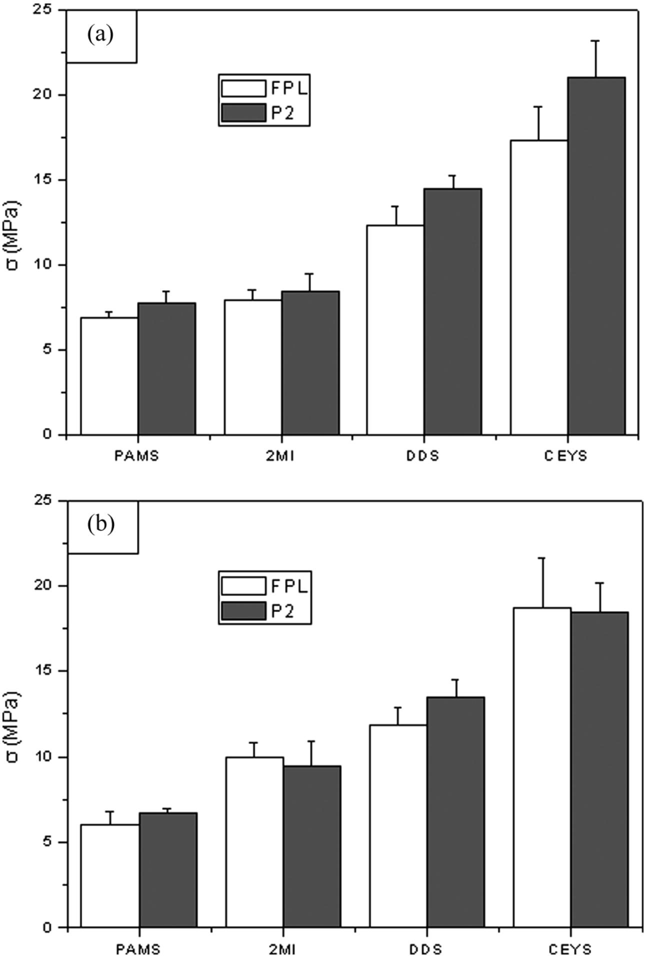


FIGURE 7 Lap shear strength of epoxy-aluminum joints, treated by FPL and P2 surface treatments, that were aged in (a) environmental and (b) salt fog chambers.

A post-curing effect is rejected because the glass transition temperature of this adhesive remains approximately constant after the hydrothermal aging, as demonstrated in Table 5. Also, SEM analysis of fracture surfaces confirms this explanation (Fig. 8). It is worth pointing out that during the characterization of the adhesives it was concluded that Ceys is the studied adhesive that absorbs the highest amount of water (Table 3) and 2MI is the adhesive that is the most

TABLE 5 T_g Values, Obtained by DSC Measurements in the First and Second Scans, of Epoxy Adhesives Bonded to A2024-T4 Aluminium Alloys, that were Treated with FPL and P2 Surface Treatments—the Joints are Non-Aged and Aged in Environmental and Salt Fog Chambers

	T_g(°C)			
	FPL		P2	
	1th scan	2nd scan	1th scan	2nd scan
		PAMS		
Non-aged	100	126	100	133
Environmental	97	115	90	135
Salt fog	99	126	101	108
		2MI		
Non-aged	102	148	98	167
Environmental	85	100	80	105
Salt fog	82	126	90	133
		DDS		
Non-aged	171	190	170	188
Environmental	175	200	175	196
Salt fog	175	201	175	196
		CEYS		
Non-aged	42	34	38	34
Environmental	45	35	46	35
Salt fog	33	34	40	34

affected by water absorption, showing the highest plasticization effect (Table 2).

The decrease in strength observed for PAMS and DDS is marked when the aging treatment is carried out in the salt fog chamber. The explanation for this could be that the presence of the salt spray accelerates the corrosion of the metal adherends. Also, in the initial adhesive characterization, it was demonstrated that the saline environment is more harmful for the studied epoxy adhesives.

Comparing both surface treatments applied to the aluminum adherends (Fig. 7), in most of the studied cases, the chromate-free treatment (P2) seems to give higher durability to the specimens. After aging, the strength of P2-treated joints is usually higher than that of the specimens treated with FPL.

In order to evaluate the effect of aging on the adhesive layer of the joints, their T_g was measured after aging and testing by the lap shear test. The obtained results are collected in Table 5. Comparing the T_g values of the adhesives bonded to the aluminum substrates with the measured T_gs of the same resins as-synthesized, which were not bonded (Table 2), it is confirmed that the glass transition temperature

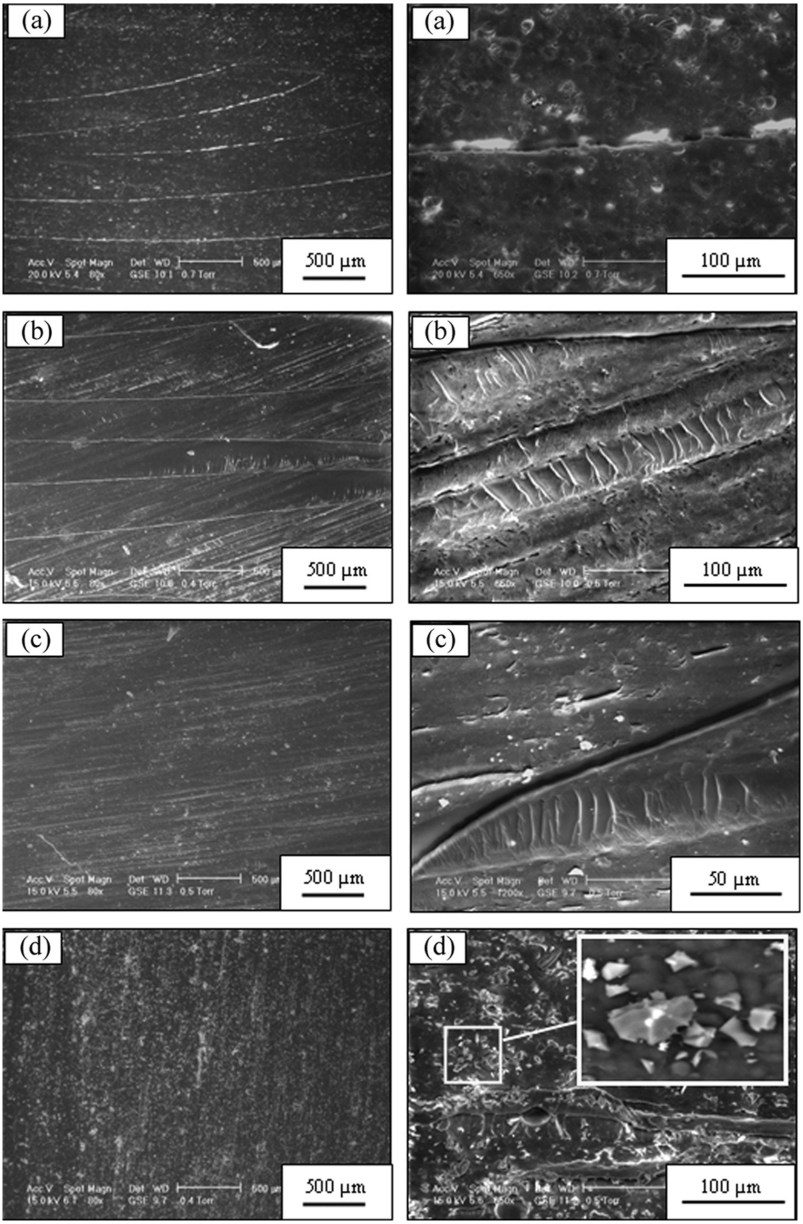


FIGURE 8 ESEM images, at low (left) and high (right) magnifications, of fracture surfaces of epoxy adhesives on P2-treated specimens aged in an environmental chamber and broken in lap shear tests: (a) PAMS, (b) 2MI, (c) DDS, (d) Ceys.

reached by the adhesives in the joints is lower, indicating that the curing was not finished in the lap shear specimens. In spite of the high thermal conductivity of the aluminum, the contact with these adherends shows that the conversion reached by the epoxy adhesives was not so high. In fact, the T_g measured for the bonded adhesives in the second DSC scan (Table 5) is similar to that reported for the non-joined resins (Table 2). This effect is not observed for the Ceys adhesive, whose low T_g remains approximately constant.

The T_g of the DDS, Ceys, and PAMS adhesives are not affected by the aging treatment of the joints. This implies that the decrease of strength of the joints with PAMS and DDS must be mainly related to the entry of water at the interface. However, the adhesive 2MI, which presented higher strength after aging, showed an important plasticization effect, decreasing its T_g by around 10–20°C. It is worthwhile to note that 2MI and Ceys were the adhesives among the studied ones that presented anomalous behavior after aging, both showing an increase in adhesive strength. Although the glass transition temperature of Ceys seems to remain constant, it was confirmed during the initial characterization that it is the adhesive that absorbs a higher amount of water.

After aging, the main difference between specimens treated with different surface treatments was the failure mode. The specimens treated with FPL presented larger areas with adhesive fracture. On the other hand, no great differences were found between the same specimens aged in hydrothermal and salt fog chambers. However, significant singularities were observed between the adhesive surfaces as synthesized (Figure 5) and after aging. Figure 8 shows the fracture surfaces of aged joints obtained by SEM. Aged joints bonded with PAMS showed adhesive failure. In fact, in the micrograph at high magnification, it is confirmed that the roughness of the adhesive is similar to that of the treated aluminum surface. This explains the decrease in strength obtained when the specimens bonded with PAMS were aged in environmental and salt fog chambers. In contrast, the fracture surface of 2MI is rougher, showing fracture rivers which are not directionally sited. This indicates a higher flexibility of the adhesive, which would explain the values obtained for its adhesive strength measured before and after aging treatment. At low magnifications, the fracture surfaces of Ceys are very rough, and at high magnification, SEM micrographs show white particles dispersed through the surface when the sample is subjected to aging. These particles are attributed to carbonation of free amines on epoxy resins ($-NH + H_2O + CO_2 \Leftrightarrow -NH_3^+ + HCO_3^-$). This carbonation is enhanced by the presence of water and, therefore, it only appears in aged specimens. The fracture surface of the non-aged probes bonded with Ceys (SEM micrographs, Fig. 5d) did not show these particles, confirming that this is an effect of the hydrothermal aging. This is the adhesive that presents the highest content of carbonate particles because it is the studied adhesive with the lowest epoxy conversion, as demonstrated by its low T_g, and, therefore, it must have a high content of non-reacted amines in its structure.

4. CONCLUSIONS

The strength and durability of epoxy-aluminum joints have been studied using several epoxy formulations and applying different surface adherend treatments. The surface treatments consisted of the conventional chromic-sulfuric acid pretreatment (FPL etch) and an alternative chromate-free treatment based on sulfuric acid-ferric sulfate (P2). Both give similar results for adhesive strength, but the P2 treatment enhances the durability of the epoxy-aluminum joints. The efficiency of these chemical treatments depends on the nature of the epoxy adhesive used. So, the adhesive strength of Ceys and PAMS scarcely depends on the surface treatment applied while the behavior of 2MI is better with FPL treatment and DDS behaves better when the aluminum adherends were previously treated with P2.

In regards to durability in aggressive environments, all the studied joints show higher durability when they are treated with the P2 etch, showing higher lap shear strength after aging.

The nature of the epoxy adhesive is a critical parameter that determines the strength and durability of the joints. A new formulation based on the use of polyaminosiloxane as a crosslinker has been studied, finding that it presents an interesting combination of mechanical, thermal, and adhesive properties. Its strength and durability are suitable, showing relatively high T_g and good mechanical properties. The homopolymerized epoxy adhesive using an imidazole as initiator presents high strength in wet environments due to its high hydrophobicity associated with the absence of hydroxyl groups. So, although its adhesive strength is not high, it remains constant after aging.

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REFERENCES

[1] Kinloch, A. J., *Adhesion and Adhesives: Science and Technology*, (Chapman and Hall, London, 1987).

[2] Critchlow, G. W. and Brewis, D. M., *Int. J. Adh. Adh.* **16**, 255–275 (1996).

[3] Abel, M. L., Adams, A. N. N., Kinloch, A. J., Shaw, S. J., and Watts, J. F., *Int. J. Adh. Adh.* **26**, 50–61 (2006).

[4] Lunder, O., Olsen, B., and Nisancioglu, K., *Int. J. Adh. Adh.* **22**, 143–150 (2002).

[5] Barnes, T. A. and Pashby, I. R., *J. Mater. Process. Tech.* **99**, 72–79 (2000).

[6] Davis, G. D., Whisnant, P. L., and Venables, J. D., *J. Adh. Sci. Tech.* **9**, 433–442 (1995).

[7] Curley, A. J., Jethwa, J.K., Kinloch, A. J., and Taylor, A. C., *J. Adh.* **66**, 39–59 (1998).

[8] Turner, H. and Boerio, F. J., *J. Adh.* **78**, 495–504 (2002).

[9] Rushforth, M. W., Bowen, P., McAlpine, E., Zhou, X., and Thompson, G. E., *J. Mater. Proces. Tech.* **153–154**, 359–365 (2004).

[10] Luo, Q. and Tong, L., *Int. J. Sol. Struct.* **44**, 2349–2370 (2007).

[11] Directive 2000/53/EC of the European Parliament and of the Council of 18 September 2000 on end-of-life vehicles. EU Off J. Eur. Communities 20.10.2000, L269, p. 34–43.

[12] Lohse, J., Sander, K., and Wirts, M., Heavy metals in vehicles II. Final Report of the Directorate General Environment, Nuclear Safety and Civil Protection of the Commission of the European Communitees, July 2001 www.europa.eu.it/comm./environment/wate/heavy_metals.pdf.

[13] Digby, R. P. and Packham, D. E., *Int. J. Adh. Adh.* **15**, 61–73 (1995).

[14] Prolongo, S. G. and Ureña, A., *Int. J. Adh. Adh.* **29**, 23–31 (2009).

[15] Prolongo, S. G., Rosario, G., and Ureña, A., *Int. J. Adh. Adh.* **26**, 125–132 (2006).

[16] Prolongo, S. G., Cabanelas, J. C., and Baselga, J., *Macromol. Symp.* **198**, 283–293 (2003).

[17] Crank, J. J. and Park, G. S., *Diffusion in Polymers*, (Academic Press, London, 1968).

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

[19] Li, C., Dickie, R. A, and Morman, K. N., *Polym. Eng. Sci.* **30**, 249–255 (1990).

[20] Carter, H. G. and Kibler, K. G., *J. Compos. Mater.* **12**, 118–131 (1978).

[21] Wu, P. and Siesler, H. W., *Chem. Phys. Lett.* **374**, 74–78 (2003).

[22] Robertson, R. E. and Mindroiu, V. E., *Polym. Eng. Sci.* **27**, 55–62 (1985).

[23] Hull, D., *Fractography: Observing, Measuring and Interpreting*, (Cambridge University Press, Cambridge, 1999).

[24] Cabanelas, J. C., Prolongo, S. G., Serrano, B., Bravo, J., and Baselga, J., *J. Mater. Proces. Tech.* **143**, 311–315 (2003).