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Comparative study on the adhesive properties of different epoxy resins

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Abstract

Adhesive properties of different epoxy resins have been evaluated in terms of the lap shear strength using aluminium adherends. Its durability in various humid environments has also been analysed. The fracture mechanisms were determined by ESEM observations. Despite fact that fracture seems macroscopically adhesive, it was found that there is an important participation of cohesive fracture mechanisms. Also, it has been demonstrated that the extension of these micro-cohesive mechanisms is directly correlated with the adhesive strength. Studied epoxy formulations are based on the two different crosslinking mechanisms, addition reaction and homopolymerisation. Curing behaviour and T_g reached were studied by DSC. Conventional curing process was carried out with different amine hardeners, while the homopolymerisation reaction was initiated by imidazoles. The results indicate that epoxy/amine systems present a higher adhesive strength than homopolymerised resins. Nevertheless, the hydrothermal ageing causes more damage to epoxy/amine networks. This observation has been associated with the lower water uptake tendency of homopolymerised resins due to its lower hydroxyl group concentration. A new epoxy formulation based on the use of polyaminesiloxane as a hardener has been analysed. This system presents relatively good adhesive resistance, high value of T_g and low water absorption compared with other aliphatic amine/epoxy resins.

Keywords: Epoxy; Lap shear; Cohesive fracture; Durability

1. Introduction

The significance of adhesive bonding as structure-joining technology is increasing because of its numerous advantages compared with other joining methods, being used in many industries like automotive and aircraft structure construction [1,2]. Among other reasons, adhesive joints present a homogeneous stresses distribution, high corrosion resistance, easy application, low weight and low cost. Nevertheless, the adhesion durability depends on many and opposite parameters, such as mechanical, thermodynamical and chemical adhesion [3–11]. Therefore, it is necessary to study the effect of the nature of adhesive and adherend [3,4], the roughness [5], superficial characteristics and geometry of the joining parts [6–9], the environmental conditions [10,11], etc.

Epoxies dominate the field of structural adhesives due to their better wetting ability, excellent mechanical properties and high chemical and thermal resistance. However, fully cured epoxy resins present high brittleness and high capacity of water uptake, which limits their applications in humid environments. Numerous researches have been carried out to determine the most important factors governing the durability of epoxy resin bonds to aluminium [10,12]. It has been found that the distilled water is more damaging to the environment than salt water, that an increase in temperature causes a

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growth in the rate of strength loss, and the presence of stable oxides on aluminium substrate surface provides that the damages are too severe, etc [12]. But, all researchers agree that behaviour of an adhesive joint depends on many different factors and therefore each adhesive–adherend system has to be specifically studied. In this article, we have studied the effect of the humidity and temperature for different epoxy adhesives using the same pre-treated aluminium substrate. The main objective is to determine the influence of adhesive nature on the durability and strength of joints.

The crosslinking of epoxy resins can be achieved through two different reaction mechanisms, polymerisation by addition and by steps [13,14]. The most common curing process is based on the addition reaction of a hardener. Depending on the crosslinker agent, the final properties of epoxy network are different [13]. When the curing agent is an aliphatic amine, the curing process frequently occurs at room temperature, but it is slow and incomplete. Therefore the obtained networks present low glass-transition temperature (T_g) and a high ability to carbonate and to absorb water. On the other hand, epoxy resins cured with aromatic amines generally present good thermal and chemical resistance, while the advantages of anhydride hardeners are their low contraction, viscosity and excellent thermal resistance. But epoxy-anhydride networks present high water uptake capacity. The homopolymerisation is another epoxy curing procedure, which consists of polymerisation by steps initiated through tertiary amines [15–18]. Although the reaction mechanism is still a controversy, it is believed that the initiator forms adducts with oxirane groups (initiation). Then these adducts react with themselves and other epoxy rings (propagation). At the end, the initiator regeneration occurs by N-alkylation or Hoffman elimination (termination). The adhesive capacity of these homopolymerised epoxy resins is still unknown.

In this work, different epoxy formulations have been studied, analysing the curing reaction, its adhesive ability and the joint durability in humid environments. The main difference between studied resins is the kind of curing reaction and the nature of the used hardener. Some studied resins have been synthesised by homopolymerisation, using different imidazole as initiators and other epoxy adhesives were obtained by adding different curing agents. Among them, a new hardener has been investigated, poly (3-aminopropylmethylsilane) (PAMS) [19]. Because of its silane nature, the obtained epoxy network must present low water absorption [20].

On the other hand, it is known that the surface finish of the joining parts is very important for securing good adhesion [5–9]. Sophisticated superficial treatments have been developed to enhance the adhesive joint, like anodising [6,7], sol–gel coating, plasma treatments [9], etc., some of which are already being applied in aerospace industry. Nevertheless, for many other applications, the required superficial treatments must be easier and more inexpensive. In the present article, the applied surface treatment is very easy, which is based on a single abrasion and subsequent degreasing.

2. Experimental

2.1. Materials

Diglycidyl ether of bisphenol A (DGEBA), supplied by Aldrich, whose epoxy equivalent weight is 174 g/epoxy equivalent, was used as an epoxy precursor in all the studied formulations. Two different curing processes have been carried out for epoxy crosslinking, by addition or polymerisation by steps. The used initiators of epoxy homopolymerisation were 2-methylimidazol (2MI) and 2-phenylimidazol (2PI), from Aldrich. For the curing process, two different amine hardeners were added, 4,4′-diaminediphenylsulfone (DDS) from Aldrich and PAMS, which were synthesised in the lab. The synthesis and characterisation of PAMS have already been described in prior articles [19,20]. The average molar mass of synthesised PAMS is 1419 g/mol ($n = 12$), the average amine equivalent weight is 59.1 g/NH equivalent and the glass transition temperature (T_g) is $-69\,^{\circ}\mathrm{C}$. The chemical structure of these products is shown in Fig. 1. A commercial adhesive, Araldyt-Epoxy Rapid from Ceys, has also been tested for comparative purposes.

The curing conditions were estimated by previous DSC studies. DGEBA homopolymerisation process was carried out by addition of 2 and 5 wt% of the initiator (2MI or 2PI), while for the curing with the amine hardeners all studied samples were stoichiometrics. The applied curing conditions were 150 °C during 1 h for the homopolymerisation, 210 °C during 3 h for the DGEBA/DDS curing and 150 °C (1 h) and 180 °C (20 min) for the crosslinking process with PAMS. The curing treatment of the commercial Ceys adhesive was recommended by the supplier, at room temperature for two days.

2.2. Calorimetric study

The curing processes were optimised by a calorimetric study of the polymerisation reactions. The total enthalpy (ΔH) was measured by differential scanning calorimetry (DSC, Mettler TA 300) in dynamic mode. All the measurements were made from 30 to 250 °C with a heating rate of 10 °C/min under nitrogen atmosphere. This measurement was followed by rapid cooling and a second scan was made on the same sample immediately at the same heating rate. In this way, the reached T_g of the network can be obtained.

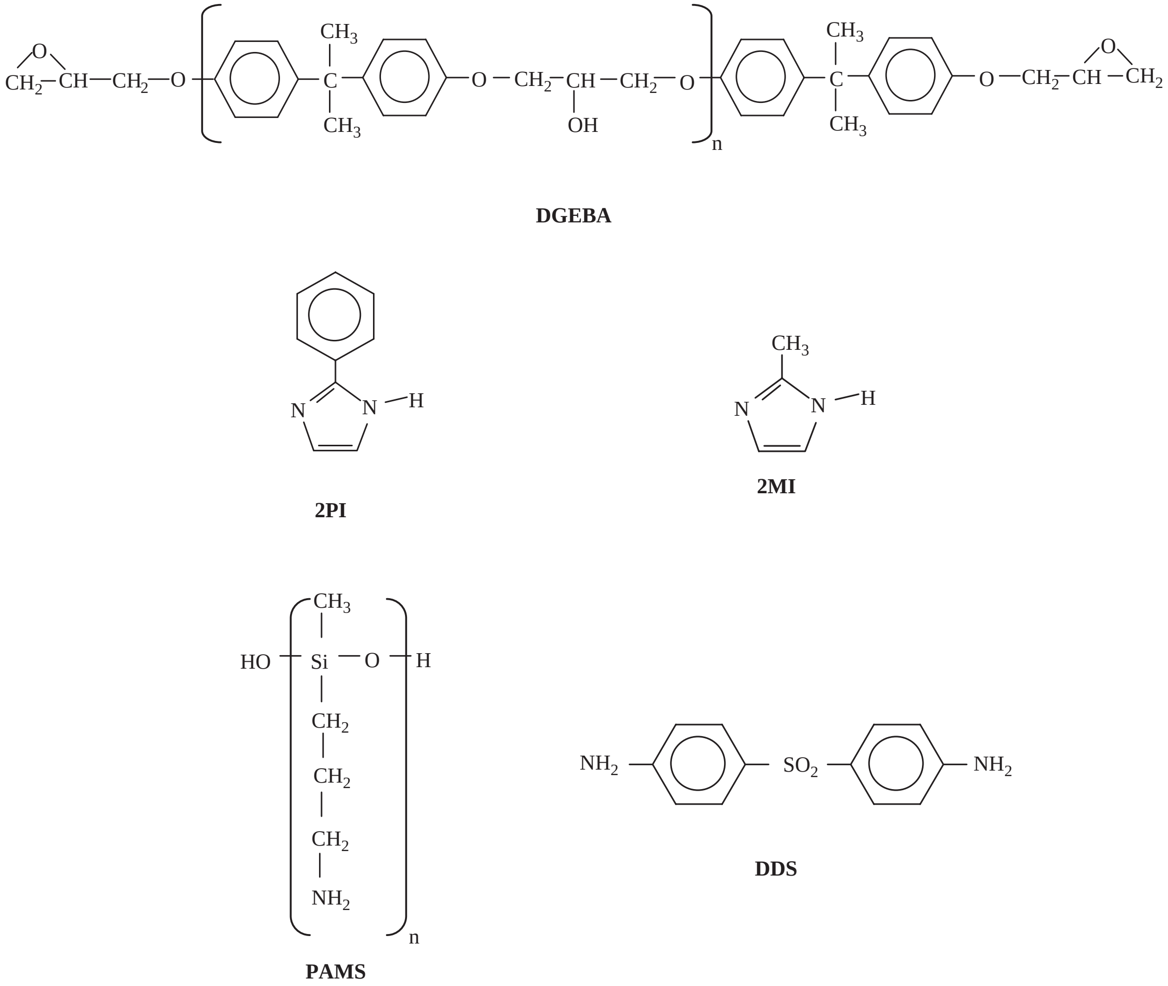

Fig. 1. Chemical structures of epoxy monomer (DGEBA), imidazole initiators (2PI and 2MI) and used amine hardeners (DDS and PAMS).

For cured samples, the reached T_g was measured by two DSC scans at 10 °C/min with a nitrogen flow of 30 ml/min.

2.3. Specimen preparation and mechanical testing

The adhesive behaviour was studied by the lap shear test following UNE-EN-ISO 1465. The used metallic substrate was aluminium A1050. Before application of adhesive materials, the adherend surfaces were prepared. The applied surface treatment consisted of the following steps (UNE-EN 13887). (1) *Solvent wiping*: single wiping of the aluminium surface used methyl ethyl ketone (MEK) soaked lanolina and lint-free tissues. (2) *SiC grinding paper abrasion*: following the solvent wiping, the surface was abraded with silicon carbide paper at 5000 rpm. First, the abrasion direction was perpendicular to the tensile test direction, then at 90° relative to the initial direction and at the end again at the initial direction. The grains size of used SiC abrasive was 76 μm. (3) *Drying*: At the end, the surface was cleared with dry air.

For the adhesive application, a specific mould was used according to UNE-EN-ISO 1465. After surface treatment, aluminium pieces (100 × 25 × 1.4 mm) were assembled into single lap shear joints with 12.5 mm of overlap length. The applied contact pressure was always the same, which allows obtaining probes with the same uniform adhesive thickness, 0.22 ± 0.02 mm. Before any test, the prepared probes were stored at vacuum during 24 h.

The adhesive strength was tested in a universal tensile mechanical machine at a crosshead speed of 1 mm/min. Each result was obtained by the test repetition with five probes.

2.4. Wedge test

Lap shear joints were tested as cured and after ageing in various environments. Ageing was carried out by exposure for 48 h in a climate chamber at different relative humidity (RH) and temperature, according to UNE-EN-ISO 29142. The applied wedge tests were

23 °C/30% RH, 23 °C/80% RH, 80 °C/30% RH and 80 °C/80% RH.

2.5. Surface analysis

The adhesive fracture was analysed at two different scales, macro- and microscopic scale. The used nomenclature for the fracture is according to UNE-EN-ISO10365. For the microscopic observation a scanning electron microscopy was used in environmental mode (ESEM Phillips XL30). The quantification of the ESEM images was performed by quantitative image analysis using public domain software, Digital micrograph (TM) 3.65, designed by *Gatan Software Team*. The analysed image size was 712 × 484 pixels with a lateral resolution of 3.4 μm/pixel. The image segmentation was carried out with *threshold* filter.

3. Results and discussion

3.1. Calorimetric study

Kinetic study of the curing reaction was carried out by dynamic DSC for all studied epoxy formulations. The obtained thermograms are shown in the Fig. 2. The measured values of reaction enthalpy are recorded in Table 1, together with the T_g values reached by the cured network. The curing of neat DGEBA with 2 and 5 wt% of the different imidazoles, 2MI and 2PI, was analysed. The obtained thermograms that correspond on epoxy homopolymerisation processes were constituted by three exothermic peaks (Fig. 1). The mean peak, whose maximum temperature is reported in Table 1, corresponds to epoxy etherification. The small peaks around 100 and 170 °C have been associated to adduct formation and initiator regeneration, respectively [15,16]. Only one isothermal peak was observed for epoxy/amine curing reaction. The epoxy homopolymerisation enthalpy is lower than that measured for the epoxy/amine curing reaction. The reason is that the epoxy/epoxy reaction enthalpy is around 90 kJ/mol [15–17], lower than the reported for amine/epoxy reaction, which value is approximately 100–105 kJ/mol [13,14].

Table 1
DSC results ($^{*}r$ = epoxy/NH equivalent ratio)

Homopolymerisation				
Initiator	wt%	T_{peak}(°C)	ΔH (kJ/eq.epoxy)	T_g (°C)
2PI	2	110	72.1	135
	5	128	75.5	138
2MI	2	108	76.3	138
	5	126	78.2	142
Epoxy-amine reaction				
Crosslinker	r^{*}	T_{peak}(°C)	ΔH (kJ/eq.epoxy)	T_g (°C)
PAMS	1	120	105.0	155
DDS	1	222	107.2	185

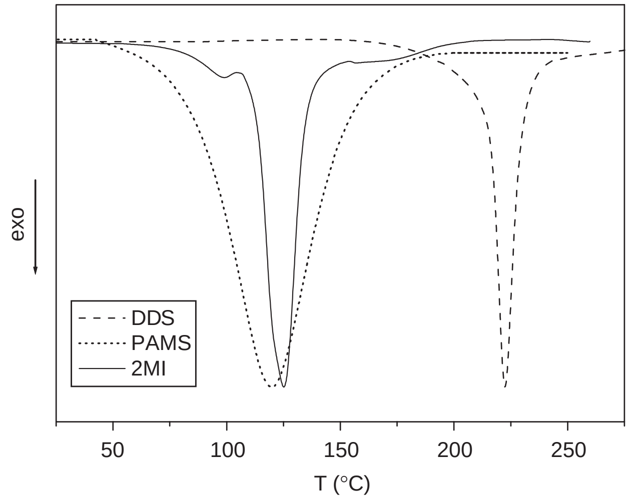

Fig. 2. Thermograms obtained by dynamic DSC for the curing process of DGEBA with DDS and PAMS and for epoxy homopolymerisation reaction with 5 wt% 2MI.

When the added initiator concentration increases, the homopolymerisation enthalpy increases which means a higher reached conversion. This conclusion is corroborated with the higher T_g of the network cured with 5 wt% imidazole. But, in all cases, the measured reaction enthalpy is lower than 90 kJ/mol, attributed value for complete epoxy cure, which is only obtained with 1-methylimidazole [15]. This effect has been observed by other authors and it is attributed to the fact that the network exhibits a less reaction degree when 2MI and 2PI are used as initiators [15,16]. No great differences are observed between the homopolymerisation was initiated with 2MI or 2PI. The exothermic peak temperature and measured enthalpy are very similar, indicating the participation of a similar reaction mechanism. The coincidence of reached T_gs values implies that the final structure of the network and the reached crosslinking degree must be very similar.

The obtained value of the enthalpy for epoxy/amine reactions around 105 KJ/mol indicates a high curing degree, near to 100% [13,14]. The epoxy/amine enthalpy does not depend on the nature of amine groups, aliphatic or aromatic amines. Nevertheless the peak temperature is different in function of the used amine-curing agent. The great shift at lower temperatures of the thermogram peak corresponding to the DGEBA/PAMS cure is indicating that the reaction is faster. Also, despite the PAMS being an aliphatic amine, the reached T_g of DGEBA/PAMS system is very high due to the multi-functional nature of this hardener. These good characteristics of the DGEBA/PAMS system support the study of this new epoxy formulation.

3.2. Effect of the epoxy adhesive on lap shear strength

The obtained results of lap shear test are presented in terms of maximum strength or failure stress, assuming that the stresses generated in the adhesive layer are uniform, although it is known that the eccentricity of the tensile axis results in transverse and peel stresses [7]. To reduce the deviation of the adhesive layer respect to the tensile axis, chocks in the extremes of the probes were used. Fig. 3 presents the measured adhesive strengths for the different studied epoxy formulations: epoxy resin homopolymerised using 5 wt% 2MI as initiator, DGEBA cured with PAMS and DDS in stoichiometric amounts, and the commercial adhesive supplied by Ceys. The obtained values of lap shear strength are lower than that reported actually for epoxy-aluminium joints [7,12]. The reason is the applied superficial pretreatment at the aluminium adherends. In fact, in a first visual observation, all the tested probes presented adhesive fracture (AF mode, according to UNE-EN-ISO 10365). It is well known that an adequate superficial treatment of the join parts produces an increase in the adhesive strength [5–9]. The increase in the adherend roughness largely enhances the adhesive joints, due to a larger effective surface area for the bond [5]. On the other hand, the application of suitable primers causes stronger adhesive-aluminium joint [12]. For these reasons, most of published works are actually based on sophisticated substrate superficial treatments [7,9]. But, in this paper, the objective is to determine the effectiveness of the different epoxy adhesives in single joints, as in common applications like manufacturing.

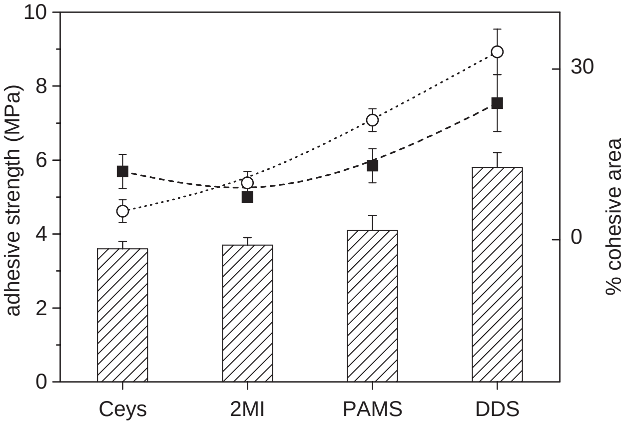

Fig. 3. Adhesive strength of different epoxy resins: commercial adhesive (Ceys), homopolymerised epoxy resin (2MI), DGEBA/PAMS (PAMS) and DGEBA/DDS resin (DDS). Cohesive area percentages measured in the adherent area (■) and in the adhesive area (○). (The abscise origin of the right axis is displaced to avoid overlaps.)

As expected, the epoxy resin that presents the highest adhesive strength is cured with an aromatic amine hardener. This behaviour together with its high T_g reached allows to affirm that this resin is the best of the studied adhesives here, although its high curing temperature is an important limitation. The epoxy resin cured with PAMS also presents a high adhesive capacity compared to the commercial adhesive, although both resins are based on DGEBA cured with aliphatic amines. It means that the presence of a polyaminesiloxane enhances the adhesive joint due to probably its bipolar nature. The homopolymerised resin presents a low adhesive ability that can be explained due to the low hydroxyl group concentration. Several authors have affirmed that the phenolic adhesives present good wetting, high durability and good strength due to the high OH group concentration in its structure respect to epoxy resins [20]. Epoxy homopolymerisation consists of OH-etherification. Therefore, a totally homopolymerised resin would not enclose any hydroxyl group.

The fractured surfaces were observed by ESEM using the back-scattering detector (BSE), whose main utility is the detection of zones with different chemical composition. Fig. 4 shows micrographs of the fracture surfaces corresponding on the aluminium substrate (4A) and the adhered resin (4B) after the lap shear test. Brilliant areas are associated to the aluminium, which is the heaviest element, while the dark zones correspond to resin, which is constituted by light elements. Although the fracture would seem macroscopically adhesive, there are rests of

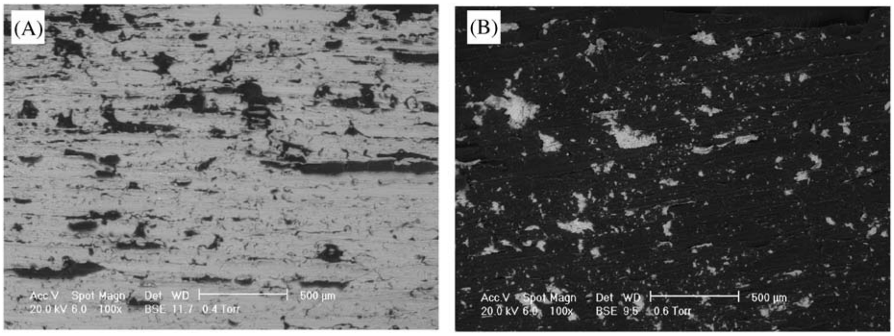

Fig. 4. ESEM micrographs of the fracture surface corresponding to aluminium substrate with rests of adhered resin (A) and adhered resin with rests of pulled aluminium (B) for DGEBA/PAMS system.

trapped adhesives in the substrate surface, indicating a microscopic cohesive fracture. Also, the micrograph 4B surprisingly shows that there exists rests of aluminium in the adhesive surface, which must have been pulled away during the breakage of the tested specimen.

The macroscopic adhesive fracture means that the breakage occurs in the adhesive–adherend interface. Therefore the main cause of fault resides on weak bonding forces. The opposite situation is a macroscopic cohesive fracture, where the rupture is normally caused by the lack of mechanical resistance of the adhesive. In our case, the weak aluminium–epoxy bond could be caused by the wettability fault of an adhesive or a problem of the adherent. The microscopic observation of aluminium pulled away and adhered to the resin seems indicate that the premature fracture of studied joints may be caused by the absence of substrate superficial treatment.

A deeper study of the observed microscopic cohesive fracture was carried out measuring the percentage of area occupied by resin adhered to the substrate and the aluminium pulled away, which we have named cohesive area percentages. For this estimation, three micrographs per probe were analysed at the same magnification (100 ×) in two different regions. One of analysed regions was the aluminium substrate after the breakage that was named as adherend area. The other studied region was the resin that remained adhered to the broken probe and was named adhesive area. The obtained results are represented in the Fig. 3. No great differences are observed between both areas. Nevertheless, it has been found that there exists a linear relation between the percentage of micro-cohesive area and the adhesive strength. Similar conclusions were obtained by other authors, when they analysed the percentage of macroscopic cohesive fracture in other systems.

3.3. Effect of humid environments on lap shear strength

The durability of studied epoxy adhesives under different humid environments has been analysed. The reference conditions of the wedge tests were 23 °C and 30% relative humidity (RH). The extreme applied conditions were 80 °C and 80% RH. But, to study the effect of temperature and the humidity separately, two different ageing treatments were applied, 23 °C and 80% RH and 80 °C and 30% RH. In all cases, the wedge time was 48 h. The obtained results are shown in the Fig. 5. The effect of the environmental conditions in the studied adhesives was analysed by DSC. T_g measurements were carried out after and before wedge test. Also, in all experiences, a witness probe was aged together to the lap shear specimens. These witnesses were prepared applying the same curing treatment that the applied for the shear tensile specimens but using hot plates. The dimensions of the witness were 25 × 12.5 × 0.2 mm, which correspond with the adhesive dimensions in the used lap shear probes. With them, it has been possible to measure the amount of absorbed water by the cured resin without the aluminium substrates, using the gravimetric technique. The summary of the obtained results are collected in Table 2. It is observed the humidity causes higher damage when the temperature is high. Nevertheless at room humidity, the temperature affects scarcely the adhesive strength.

The single effect of the temperature has been analysed comparing the ageing at 23 °C and 80% RH with the reference wedge test (23 °C and 30% RH). A light decreasing of the adhesive strength is observed when the temperature increases. On the other hand, T_g values of the epoxy resins remained constant and the possible little amount of absorbed water was not appreciable by gravimetry. Therefore the little observed changes in the

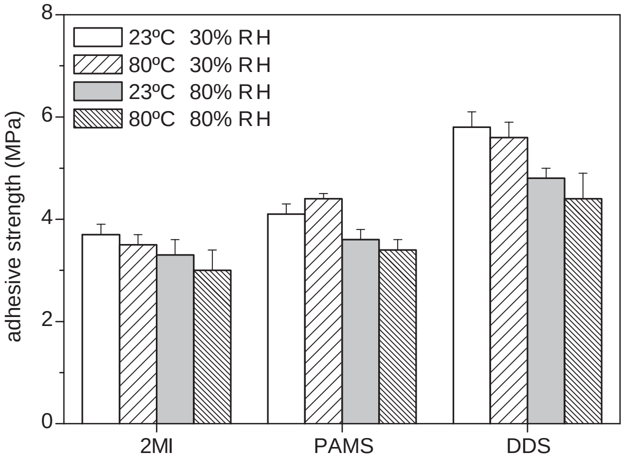

Fig. 5. Adhesive strength of different epoxy adhesive: homopolymerised epoxy resin (2MI), DGEBA/PAMS (PAMS) and DGEBA/DDS resin (DDS) after different wedge tests, at different temperatures (23, 80 °C) and relative humidity (30, 80% RH).

Table 2
Adhesive strength, T_g and the water uptake percentage ($\Delta W/W_0$) of the aged samples at different temperatures and relative humidity

	T(°C)	RH (%)	2MI	PAMS	DDS
Adhesive strength (MPa)	23	30	3.7 ± 0.2	4.1 ± 0.2	5.8 ± 0.3
	23	80	3.5 ± 0.2	4.4 ± 0.1	5.6 ± 0.3
	80	30	3.3 ± 0.3	3.6 ± 0.2	4.8 ± 0.2
	80	80	3.0 ± 0.4	3.4 ± 0.2	4.4 ± 0.5
T_g (°C)	23	30	140	101	207
	23	80	141	91	200
	80	30	141	100	204
	80	80	133	72	115
$\Delta W/W_0$(%)	23	80	0.9	1.2	1.5
	80	80	1.2	1.4	1.9

tensile strength due to the temperature have been associated with the different thermal dilatation behaviour between the aluminium substrates and epoxy resin, whose lineal expansion coefficients are 24.3×10^{-6} and around $40 \times 10^{-6}\,^{\circ}C^{-1}$, respectively.

In all cases, the humidity causes a decrease in the adhesive resistance but the magnitude of damage depends on used epoxy adhesive. It is observed that at higher amount of absorbed water by the adhesive witness, the produced damage is a higher. Nevertheless, it is known that the water diffusion along the interface can be many times faster than water permeation through the adhesive [10]. But, it seems reasonable to suppose that if the ageing time is enough, the uptake water by the lap shear probe must be proportional to the absorbed water by the witness resin. This hypothesis is corroborated with the obtained results. There exists a clear relation between the decreasing of the adhesive strength of the lap shear probes and the amount of absorbed water by the witness.

The decrease in the adhesive strength due to the hydrothermal ageing is lower for the homopolymerised epoxy resin due to its low tendency to absorb water. This behaviour can be explained by the structure of the epoxy network, whose hydroxyl concentration is negligible. The presence of OH groups is an important factor governing the water uptake and the subsequent damage due to van der Walls interactions. Comparing the studied epoxy/amine systems, DGEBA/PAMS resin presents low water uptake ability. In fact, the measured percentage of absorbed water by this system is very low in comparison to other epoxy resin. This behaviour is explained by the hydrophobic nature of the polyaminosiloxane [19].

The decrease in the adhesive resistance can be caused by several different water uptake effects. One of them is the adhesive plasticisation. The water penetration inside the epoxy network produces the rupture of interchain interactions, which causes the stresses relaxation. This relaxation gives rise to decrease in T_g of the network named commonly plasticisation effect [21–23]. In this work, this effect has been analysed through the T_g measurements before and after wedge test. It is observed that the T_g decreasing is not linearly proportional to the absorbed water amount. The T_g decreasing seems to depend on the absorbed water amount, the nature of the epoxy resin and on the ageing temperature. It is observed that the water entering into the epoxy network causes a higher T_g decrease when the ageing temperature increasing. On the other hand, the T_g decrease caused by the water entrance is different depending on the studied epoxy network. The reason can be the different interactions between the absorbed water and epoxy network. In the literature, it has been demonstrated that the absorbed water is found in the network as two different water states: bound and free water [21–23]. In the network, there is some free volume, including voids, which can be occupied by absorbed water (free water). On the other hand, some molecules of water can interact with the resin, since many functional groups are present (bonded water). As the epoxy network is held together by hydrogen bonds and other secondary valence forces between adjacent polymer chains, these interactions will break by forming hydrogen bound with water absorbed. The rupture of interchain interaction causes the T_g to decrease. Therefore the water plasticisation effect is mainly caused by the bonded water, which is enhanced in epoxy networks with high polar group concentration, like hydroxyl, amine, etc., and with little free volume. This reasoning is confirmed by the obtained results. It is observed that the plasticisation effect is lower for the homopolymerised resin, which has neither hydroxyl nor any amines groups.

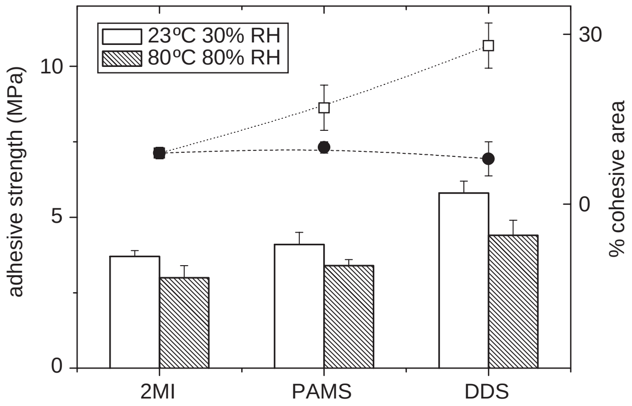

Fig. 6. Adhesive strength of different epoxy resins: homopolymerised epoxy resin (2MI), DGEBA/PAMS (PAMS) and DGEBA/DDS resin (DDS). Cohesive area percentages measured at reference conditions (23 °C and 30% RH) (☐) and after wedge test (80 °C and 80% RH) (●). (The abscise origin of the right axis is displaced to avoid overlaps.)

Before and after the hydrothermal ageing, all the studied samples present macroscopic adhesive fracture. The aged probes were observed by ESEM, finding a micro-cohesive fracture mechanism. The Fig. 6 shows the decreasing of micro-cohesive area percentage associated with the decreasing of adhesive strength due to the wedge test. Therefore, it is confirmed that the microscopic mechanism of cohesive fracture is directly proportional to the adhesive resistance.

4. Conclusions

Adhesive behaviour of different epoxy resins has been investigated by lap shear test using aluminium substrates. It has been found that the epoxy cured with aromatic amine present high adhesive strength and high T_g. But the high necessary curing temperature and the high water uptake capacity limits its utility. On the other hand, it was found that the homopolymerised epoxy resins present a low tendency for the water to absorb, due to the low concentration of polar groups, like amine and hydroxyl groups. Also, a new epoxy formulation based on the use of polyaminosiloxane as hardener has been investigated. This resin presents relatively high adhesive strength and low water absorption due to the hydrophobic nature of PAMS.

Due to the simple adherend superficial treatment, the observed fracture was macroscopically adhesive. However, a micro-cohesive fracture mechanism was found by ESEM. There were traces of trapped adhesive in the substrate surface and traces of aluminium in the adhesive surface, which were pulled away during the breakage of the probe. It has been demonstrated that the percentage of cohesive area is proportional to the adhesive strength.

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