



## THE EFFECT OF ACCELERATED AGEING ON THE MECHANICAL AND PHYSICAL PROPERTIES OF THERMOSET POLYMERS

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### Abstract

Structural adhesives and composite materials are generally exposed to harsh environmental conditions that lead to their degradation. Saline and moisture environment at high temperatures are some of the common conditions that degrade polymers. A full factorial design was conducted to analyse the effects of accelerated ageing in salt-spray and 100% relative humidity (RH) chambers on the mechanical and physical properties of epoxy and unsaturated polyester (UP) polymers. In saline environment, the epoxy and UP polymers presented 42% and 38% less moisture absorption, respectively, than in 100% RH chamber. The epoxy polymer achieved 99% higher tensile strength than the UP in the condition without ageing, however the overall compressive properties of the UP were slightly higher than the epoxy.

**Keywords:** Thermoset polymers, epoxy properties, unsaturated polyester properties, harsh environment.

### 1. INTRODUCTION

Thermoset polymers can be used as structural adhesives or matrix of composite materials for application in several industries such as automotive and aeronautical. An adhesive may be defined as a material that can join components together and resist separation [1]. Epoxy polymers are the most widely accepted and used as structural adhesives, due to their good mechanical and thermal properties. On the other hand, unsaturated polyester (UP) is the most used polymer as composite matrix, particularly in the marine industry. UP possess low cost compared to the epoxy, good processing characteristics, specific physical properties and the ability to cure under room temperatures and pressures. Thus UP are widely used in materials such as glass fibre reinforced polyester composites [2, 3]. The composite matrix has several important functions, such as: it binds the reinforcements together, maintains the shape of a

component and transfers the applied load to the reinforcing fibres, and also protects the fibres from environmental attack [4].

Structural adhesives and composite materials are generally exposed to harsh environmental conditions that lead to their degradation. Saline and moisture environment at high temperatures are some of the common conditions that degrades polymers. Water molecules diffuse into adhesively-bonded joints and degrade both the interface and the adhesive itself [5]. Some authors [6 – 9] have found that water decreases the tensile strength and elastic modulus of epoxy polymers due to plasticization effect. When the time exposed in ageing is prolonged, an anomaly can occur due to more complex interactions between water molecules and epoxy cross chains forming hydrogen bonds. This effect can led to increased elastic modulus [10].

Quino *et al.* [11] have assessed the changes in the fracture and toughness properties of epoxy polymer when it is exposed to a wet environment. The toughness was affected locally varying moisture absorption over the cracking path. Arrieta *et al.* [12] have studied the thermal oxidative ageing of unsaturated polyester and vinyl ester plates at high temperatures of 120°C to 160°C. The findings revealed the vinyl ester was more oxidisable than the unsaturated polyester. Sugiman *et al.* [10] have analysed the water absorption and tensile properties of epoxy polymers after ageing in distilled and salt water in steady and fluctuating conditions at 50°C. The results showed that in steady and fluctuating conditions, the equilibrium water absorption of epoxy aged in the brine is lower than that of distilled water. The tensile properties of the epoxy polymer were not affected by the ageing conditions.

This paper investigates the effects of artificial ageing in high humidity, temperature and salt-spray fog on the tensile and compressive properties and moisture absorption of epoxy and polyester polymers. A design of experiments (DoE) was conduct in order to verify the effects of individual factors and interactions on the variable responses.

## 2. MATERIALS AND METHODS

### 2.1 Materials

The epoxy polymer used in this study was the low-viscosity Araldite<sup>®</sup> LY 5052 based on diglycidyl ether of bisphenol-A (DGEBA) with the hardener Aradur<sup>®</sup> 5052 which is a mixture of polyamines. This epoxy system is indicated for aeronautical applications and it is qualified by the Luftfahrtbundesamt (German Aircraft Authority) for the production of gliders. Both the epoxy resin and hardener were fabricated by Huntsman<sup>®</sup>. The unsaturated polyester resin used was the orthophthalic PolyLite<sup>®</sup> 10316-10 pre-accelerated with cobalt octoate and the hardener was the methyl ethyl ketone peroxide (MEK-P), both fabricated by Reichhold<sup>®</sup>.

### 2.2 Fabrication and ageing of the specimens

The concentrations of hardeners considered were 38wt.% and 2wt.% for the epoxy and polyester system, respectively according to the manufacturer's recommendations. The resins and hardeners were hand mixed for 5 minutes. The fabrication and mechanical tests of the specimens followed the recommendations of the standards ASTM D638 [13] and ASTM D695 [14] for tensile and compressive properties respectively.

After the mixture, the polymers were poured into silicon moulds. The epoxy samples were left at room temperature for 7 days and the polyester samples for 12 h at room temperature (~22°C and 55% of relative humidity), with additional time of 48 h at 60°C in an oven. After the curing, the specimens were removed from the moulds, as shown in Figure 1. A set of specimens was left for more 7 (168 h) days at room temperature. Another set of specimens was left for 7 days in an accelerated ageing chamber to simulate 100% of relative humidity (RH) at 40°C according to recommendations of ASTM D2247 [15], and other set was left for

7 days in a salt-spray chamber with 5wt.% of NaCl at 35°C following the recommendations of ASTM B117 [16].

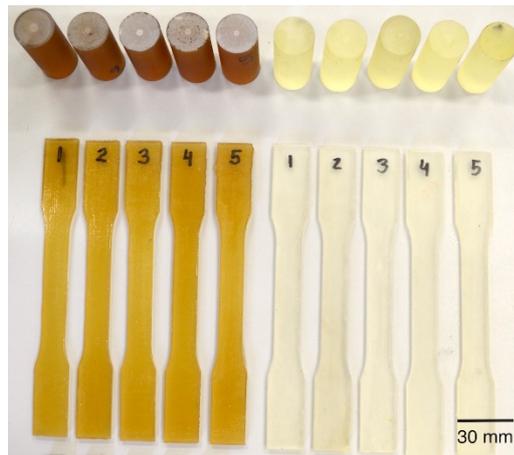


Figure 1: A set of specimens

A full factorial design was considered to analyse the effect of individual factors and their interactions. The design of experiments is shown in Table 1. Five repetitions were performed for each condition and two replicates were evaluated in order to estimate the experimental error of the individual response [17] resulting in a total of 60 specimens for tensile and 60 for compressive tests.

Table 1: Design of experiments 2<sup>1</sup>3<sup>1</sup>

Condition	Factors	
	Type of Polymer	Environmental conditioning
1	Epoxy	No degradation
2	Epoxy	100% R. humidity
3	Epoxy	Salt-spray
4	Polyester	No degradation
5	Polyester	100% R. humidity
6	Polyester	Salt-spray

### 2.3 Mechanical and physical evaluations of the specimens

After the environmental conditioning, the specimens were dried using a blow drier. The mechanical tests were performed using a Shimadzu AG-X Plus testing machine of 100 KN capacity with a testing speed of 2 mm/min. The moisture absorption was calculated considering the mass of the compressive specimens before and after the environmental ageing for 7 days in both harsh environments of 100% of relative humidity at 40°C and salt-spray chamber with 5wt.% of NaCl at 35°C according to the standard ASTM D5229 [18].

### 3. RESULTS AND DISCUSSION

#### 3.1 Moisture absorption

After 7 days in the chambers of 100% RH and salt-spray fog, the epoxy specimens showed mean moisture absorption values of 0.49% and 0.34%, respectively. The polyester specimens presented mean values for moisture absorption of 0.30% in 100% RH and 0.21% in salt-spray fog. The moisture absorption was 42% and 38% lower in the 100% RH than in the salt-spray chambers for the epoxy and polyester polymers, respectively. According to Tan *et al.* [19], this reduction in moisture absorption at saline environment is probably due to the change in the driving force as the chemical potential of water is decreased in salt solution. This phenomenon would effectively generate an osmotic pressure that inhibits the moisture absorption by the polymer. Moreover, Prolongo *et al.* [20] have attributed this effect to the sodium chloride presence, which increases the density of the aqueous solution, consequently decreasing the diffusion coefficient of the solution in the polymer.

#### 3.2 Mechanical testing

Table 2 shows the analyses of variance (ANOVA) for the mean response variables. The statistical software Minitab® v. 17 was used to manipulate the data. P-values lower or equal to 0.05 mean the effect was significant considering a confident interval of 95% [21]. The underlined P-values shown in Table 2 indicate the significant factors identified in this work. F-values evaluate which one of the factors provided a greater influence in the responses. The higher the F-value, the greater the effect of this factor on the response, i.e., the tensile modulus was more affected by the environmental conditioning factor (F-value = 140.46) than by the type of polymer (F-value = 35.88). When one or more interaction effects are significant, the factors that interact can be considered jointly. All interactions were significant and their P and F values are highlighted in bold letters in Table 2. The adjusted R<sup>2</sup> value indicates whether the model behaved properly. R<sup>2</sup> values closer to 1 (100%) indicate a more significant predictive ability of the model. R<sup>2</sup> values varied from 84.17% to 99.01%, indicating acceptable correlations obtained for the response variables analysed. A normality test via Anderson-Darling technique was used to validate the ANOVA. In this case, P-values must be equal or superior to 0.05 to follow a normal distribution configuration. As shown in Table 2, all data followed a normal distribution exhibiting P-values (And. Darling) higher than 0.05.

Figure 2 shows the interaction effect plots between "type of polymer" and "environmental conditioning" factors for the mean tensile modulus (a) and strength (b). The tensile modulus data varied from 2.92 GPa to 3.96 GPa. The letters in the graphs represent the results for the Tukey comparison test; similar letters belong to the same group indicating there is no significant variation between the means. For the condition with no degradation, the polyester presented 25% higher tensile modulus than the epoxy. The ageing decreased the polyester tensile modulus in 40% and 35% at 100% RH and salt-spray levels, respectively. According to Sugiman *et al.* [10], the modulus decreases as moisture content increases due to plasticisation; however, an anomaly might occur, such as the recovery of the tensile properties. Small variations were noted between environmental conditioning levels for the epoxy polymer. Tukey test revealed these means are equivalents, then, the conditioning did not provide any significant change in tensile modulus. The tensile strength data varied from 19.82 MPa to 54.50 MPa. The epoxy achieved 99% higher tensile strength than the UP in the condition without degradation as shown in the interaction plot (Figure 3b). Tukey's comparative test showed that the small variations between all levels of conditioning for the UP and between the level without degradation and chamber of 100% RH for the epoxy did not significantly affect the tensile strength. However, sodium chloride caused a 20% increase in the tensile strength of the epoxy. This was probably due to the positive post-cure effect of

the epoxy leading to an increase in the number of cross-reactions and thus increasing its resistance [22].

Table 2: Analyses of variance for the mechanical tests

<b>P and F values</b>									
<b>Experimental factors</b>		<b>Tensile modulus</b>		<b>Tensile strength</b>		<b>Compressive modulus</b>		<b>Compressive strength</b>	
		P	F	P	F	P	F	P	F
<b>Main factors</b>	Type of Polymer (Pol)	<u>0.001</u>	35.88	<u>0.000</u>	1044.08	<u>0.002</u>	29.99	<u>0.000</u>	118.98
	E. conditioning (E)	<u>0.000</u>	140.46	<u>0.000</u>	12.04	0.060	4.66	0.078	4.03
<b>Interactions</b>	Pol * E	<b><u>0.000</u></b>	<b>182.37</b>	<b><u>0.003</u></b>	<b>18.09</b>	<b><u>0.008</u></b>	<b>12.09</b>	<b><u>0.003</u></b>	<b>18.23</b>
R <sup>2</sup> - adjusted		98.40%		99.01%		84.17%		93.51%	
P-value (And. Darling)		0.158		0.167		0.875		0.709	

The compressive modulus (Figure 2c) for the polymers varied from 2.95 GPa to 3.14 GPa. The epoxy presented a modulus of 6.1% lower than the UP in a 100% RH chamber, probably due to the plasticisation effect [10, 22]. The formation of complementary crosslinks between the polyester chains is activated by raising the temperature through a suitable post cure and may lead to increased mechanical properties as observed for the 100% moisture and salt spray conditions [23]. However, the epoxy had the effect of plastification when conditioned in high humidity and temperature leading to a decrease of its modulus. The compressive strength (Figure 2d) for the polymers ranged from 110.07 MPa to 127.72 MPa. The UP achieved a slight increase of 9.2% in the compressive modulus for the specimens aged at 100% RH, being 13.9% higher than the epoxy at saline environment. This is probably due to the anomaly explained by Sugiman *et al.* [10] which could be due to competition between the plasticisation effect and the effect of additional crosslinking caused by the extended time at elevated temperatures and humidity, wherein the positive effect of an additional crosslinking is more dominant in polyester than the negative effect of plasticisation.

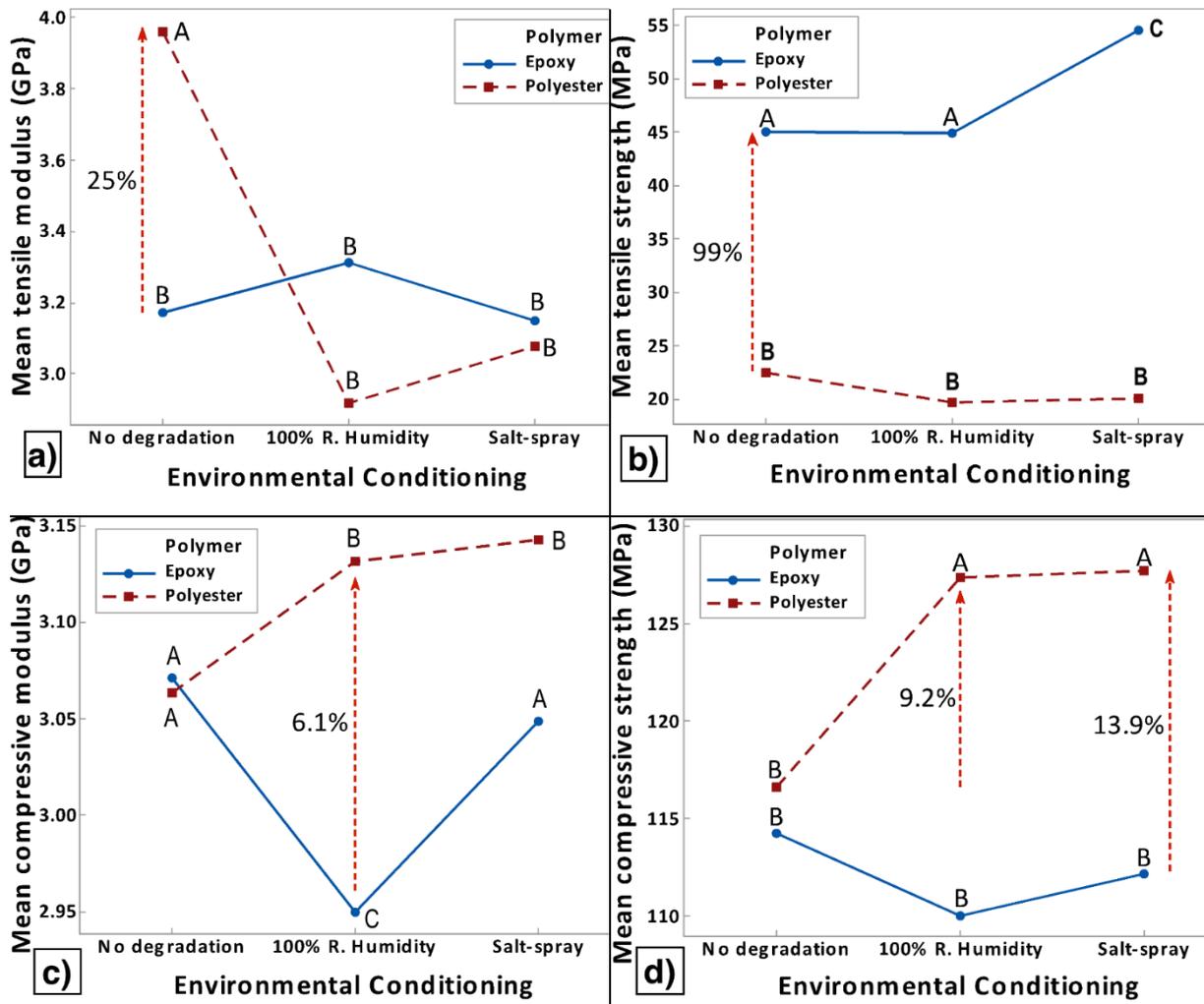


Figure 2: Interaction effect plots for the mean (a) tensile modulus, (b) tensile strength, (c) compressive modulus, (d) compressive strength.

#### 4. CONCLUSION

This paper investigated the effects of environmental ageing in 100% RH and salt-spray chambers on the mechanical and physical properties of epoxy and unsaturated polyester polymers. The moisture absorption in salt-spray chamber was 42% and 38% lower than in 100% RH chamber for epoxy and UP, respectively. The tensile modulus of UP was 25% higher than the epoxy in condition without ageing. After ageing in both high humidity and salt-spray environments, the tensile modulus of UP dropped about 30%, being attributed to the negative effect of plasticisation. The tensile strength of the epoxy polymer was 99% higher than UP for the condition without ageing. The overall compressive properties of UP were slightly higher than epoxy.

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