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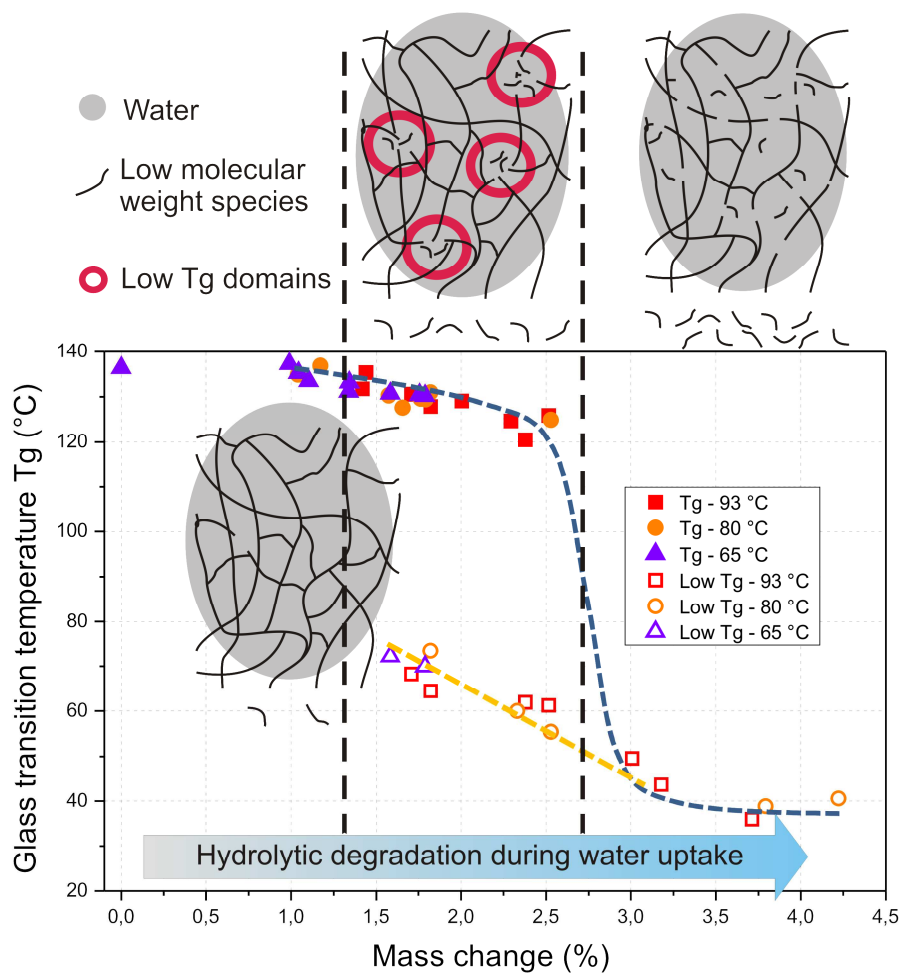
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# DIFFUSION AND HYDROLYSIS EFFECTS DURING WATER AGING ON AN EPOXY-ANHYDRIDE SYSTEM

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**1 Abstract**

2 Hydrothermal aging of an epoxy-anhydride network has been studied by means of gravimetric  
3 analysis, Fourier transform infrared spectroscopy (FTIR) and modulated differential scanning  
4 calorimetry (MDSC). The long-term aging results revealed a fourth stage mechanism in which an  
5 initial short diffusional period is followed by the hydrolysis of the ester groups. Degraded materials  
6 showed two values of glass transition temperature suggesting a heterogeneous process. Hydrolysis  
7 undergoes in preferential sites due to the catalytic effect of the carboxyl acids formed during the  
8 chemical degradation. Domains with low crosslinking density and high mobility are formed. At long  
9 degradation time, samples presented a unique glass transition temperature around 50°C. The  
10 lexiviation of low molecular weight species formed by the hydrolytic scissions was confirmed by  
11 FTIR and pH variations.

12

**13 Key words**

14 Hydrothermal aging; Water absorption; Hydrolysis; Epoxy-anhydride networks.

## 1 **Introduction**

2 The use of fiber reinforced epoxy composites (FRP) in technological applications has been growing  
3 in the last decades due to their outstanding properties such high strength and stiffness to weight ratio  
4 and chemical resistance. However, the poor knowledge about their durability under in-service  
5 conditions limits their reliability especially in certain industrial applications in which a catastrophic  
6 failure could lead to a severe damage not only on the components but also on the environment, as in  
7 the case FRP pipes used in oil industry. Durability issues are directly related to the degradation  
8 processes affecting a component during its service life [1]. Many times, polymer matrix aging due to  
9 water exposure combined with temperature variations is the major responsible for component failure  
10 [2–5]. Therefore, the understanding of the degradation mechanism for hydrothermal aging of epoxy  
11 composite matrices is mandatory in order to establish satisfactory methods to evaluate deterioration  
12 and to achieve accurate in service behavior predictions.

13 Water uptake induces reversible and irreversible changes in physical and chemical properties  
14 affecting the designed material performance [6–11]. Polymer nature and its interaction with water  
15 define the main characteristics of the degradation process. In the case of polymers which chemically  
16 reacts with water, as unsaturated polyesters or anhydride-cured epoxies, swelling and plasticization  
17 caused by water absorption have minor effects, while the hydrolysis of the reactive groups of  
18 polymer structure is the responsible for the main material damage [12]. Hydrolysis is a chain scission  
19 process and therefore decreases the polymer crosslink density. Moreover, the replacement of ester  
20 groups by alcohols and carboxyl acids resulting from the chemical reaction increases the number of  
21 polar groups in the network. These physico-chemical changes affect not only the diffusion process  
22 but also the hydrolysis kinetics. Water absorption in epoxy systems increases non-linearly with the  
23 presence and accessibility of polar groups in the polymer due to the strong water-polymer  
24 interactions (hydrogen bonds) [13–16]. Concerning the chemical reaction, hydrolysis rate could be  
25 affected by the new chemical groups due to catalytic effect of acid products [17]. In addition, when  
26 the chemical scissions caused by the hydrolytic degradation process take place on the same  
27 elastically active chain, produce relatively low molecular weight species that eventually are capable  
28 to leave the polymer network by lexiviation [18–20]. As a result, chemical and structural changes  
29 induced by hydrolysis turn the global degradation process into a complex diffusion-reaction coupled  
30 process.

31 The understanding of water degradation process in polymers with hydrolysable groups in their  
32 backbones is a challenge. Recently, many efforts have been made to approach the study and

1 modeling of the diffusion-reaction coupled processes. Gautier *et al.*[20] studied the hygrothermal  
2 degradation of polyester matrices and proposed that the process involves water uptake, swelling,  
3 ester hydrolysis, osmotic cracking and leaching of small molecules. They also studied the osmotic  
4 cracking nucleation, which is produced by a phase separation between the polymer and water-soluble  
5 organic molecules resulting from hydrolysis. More recently, a phenomenological reaction-diffusion  
6 scheme for an epoxy-anhydride system was proposed by El Yagoubi *et al.* [21]. At short time, water  
7 transport is a competition between diffusion and the reactive process. A more detailed kinetic model  
8 for ester hydrolysis of an almost ideal polyester network based on macrodiols was developed [22]  
9 including the autocatalytic effect of carboxylic acids resulting from the reaction. However, there are  
10 insufficient studies of long-term degradation where high hydrolysis conversions and mass loss are  
11 expected.

12 We studied the long-term behavior of an epoxy-anhydride system exposed to water at four different  
13 temperatures. The main goal is to explain water diffusion and reaction in order to identify composites  
14 durability critical steps.

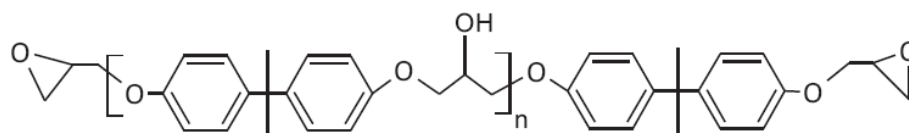
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## 16 **Materials and Experimental methods**

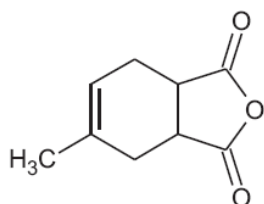
### 17 **Materials preparation**

18 Epoxy-anhydride materials were prepared using a commercially available epoxy resin based  
19 on diglycidyl ether of bisphenol A (DGEBA, DER 383) supplied by Dow Chemical Co. and a methyl  
20 tetrahydrophthalic anhydride (MTHPA, Dicure 319, from Novarchem S.A.) as a curing agent (Fig.  
21 1). Stoichiometric mixtures with a mass ratio of 100:85 (DGEBA:MTHPA) were used. A 3% by  
22 weight of resin of 2,4,6-tris-(dimethyl-aminomethyl)phenol (from Novarchem S.A.) was added as  
23 accelerator. The reactive mixtures were manually homogenized and then poured into an aluminium  
24 mold in order to obtain 1 mm thickness sheets. The curing cycle included three steps of one hour  
25 each: a) 60 °C, b) 90 °C and c) 145 °C. The aim of first step was to decrease the viscosity of the  
26 reactive mixture in order to allow the escape of the air trapped, thus avoiding undesirable air bubbles  
27 in the final material. The second step consisted in an isothermal cure stage where the selected  
28 temperature was lower than  $T_{g\infty}$ . The last step was carried out at a temperature higher than  $T_{g\infty}$  in  
29 order to obtain fully cured materials. Finally, rectangular samples of 55 x 12 x 1 mm<sup>3</sup> were cut from  
30 the obtained sheets.

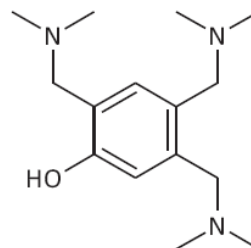
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(a) Diglycidyl ether of bisphenol A (DGEBA)



(b) Methyl tetrahydrophthalic anhydride



(c) Tris(dimethylaminomethyl)phenol

**Figure 1.** Chemical structure of the reactants.

#### Water absorption tests

Rectangular samples previously dried in a vacuum oven at 80 °C for 48 hs, were immersed in distilled water at 22 °C, 65 °C, 80 °C and 93°C. The immersion temperatures selected in this work included the study of water absorption behavior of the epoxy-anhydride system at a moderate temperature (22°C, 65 °C) and at a very high temperature (80°C and 93 °C). The highest temperature was chosen considering the possibility of industrial applications up to 93 °C (200 F).

The samples were placed vertically into a closed glass recipient filled with distilled water to ensure fluid contact on both surfaces. Then the recipients were placed into an oven (San Jor, SL60DB) equipped with an auto-tuning PID temperature control, at the corresponding temperature (22 °C, 65 °C, 80 °C or 93 °C).

In order to record the gravimetric data, they were periodically removed from the water, wiped dried with a tissue paper to remove the surface moisture, weighed in an analytical balance, and immersed again into water. The accuracy of the analytical balance used is  $10^{-4}$  g. The mass change during the absorption tests was determined using the following expression

$$\text{Mass change (\%)} = \frac{m_t - m_i}{m_i} \times 100 \quad \text{Eq. I}$$

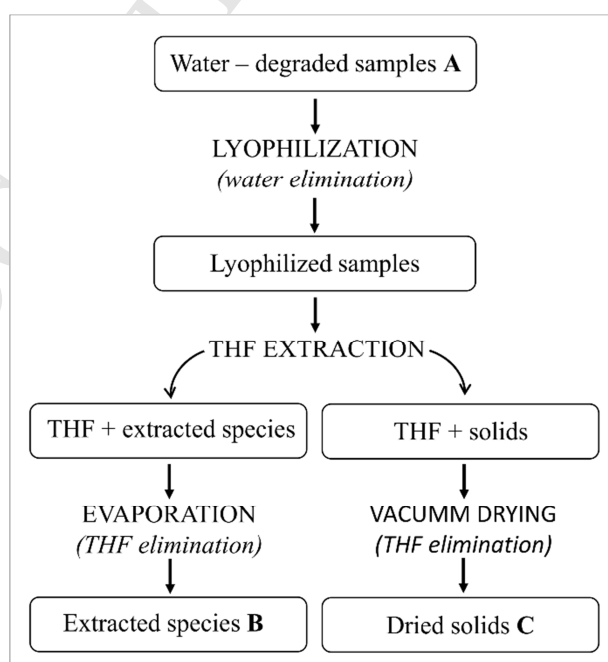
where  $m_t$  is the sample mass at time t, and  $m_i$  is the initial sample mass.

1 The immersion tests for samples degraded at 93 °C and 80 °C were carried out until a drastic mass  
2 loss was detected and the immersion tests for samples degraded at 65 °C and 22 °C, were carried out  
3 for 675 and 500 days respectively. Considering that the initial gravimetric changes occur during the  
4 first days of water immersion, the periods of time between gravimetric measurements were shorter at  
5 the beginning of the of immersion tests than that at long exposure times. Measurements were  
6 performed initially twice a day, then once a day and finally once or twice a week. When gravimetric  
7 curves were close of the drastic mass loss event, the measurements were performed once a day.

8 Only for the immersion test in water at 93 °C, the water-bath pH was recorded. To follow the pH  
9 evolution, when samples were taken off from the oven in order to perform the gravimetric  
10 measurement, a sample of the water-bath was taken. The pH was measured using a pH-meter  
11 (Arcano, PHS-3E) and the water was then returned into the glass recipient containing the solid  
12 samples under gravimetric study.

### 13 **Lyophilization and solvent extraction**

14 Water-degraded samples identified by the absorption time and temperature were submitted to a three  
15 steps treatment in order to remove water and products formed during hydrolytic degradation. Sorbed  
16 water was eliminated by means of lyophilization and then, the hydrolytic degradation products were  
17 removed from the lyophilized samples by extraction with tetrahydrofuran (THF), see Fig. 2.



19  
20 **Figure 2.** Schematic procedure of sample treatment.



1

2 Lyophilization was conducted at -45 °C and 100 mbar during 72 h using a VirTis – Benchtop SLC  
3 lyophilizer. The water-degraded samples were previously frozen at -18 °C for 24 h.

4 The lyophilized samples were then immersed in THF during 24 h at room temperature under  
5 continuous stirring. After that, the remaining solid was withdrawn from the solvent and dried under  
6 vacuum at 45 °C for 48 h and then maintained under vacuum at room temperature. The extract  
7 (named B in Figure 2) was concentrated at room temperature until further use.

#### 8 **Fourier transform infrared spectroscopy (FTIR)**

9 All the infrared spectra were obtained in transmission mode, with 32 scans and 4 cm<sup>-1</sup> resolution in a  
10 Thermo Scientific Nicolet 6700 spectrophotometer.

11 The samples immersed in water at different temperatures were analyzed in the Near-infrared (NIR)  
12 range (8000-4000 cm<sup>-1</sup>) and the extracts in the Mid-infrared (MIR) range (4000-600 cm<sup>-1</sup>). Thin  
13 films were obtained from the extracts by evaporating THF solutions onto NaCl windows.

#### 14 **Modulated differential scanning calorimetry (MDSC)**

15 The calorimetric measurements were performed using a TA Instruments Q2000 differential scanning  
16 calorimeter. The experiments were conducted under nitrogen atmosphere, from room temperature to  
17 220 °C at a heating rate of 3 °C/min, with a modulation amplitude of ± 1 °C/60 seconds.

18 Glass transition temperature (T<sub>g</sub>) of wet samples (named A in Figure 2) and dried extracted samples  
19 (named C in Figure 2) was measured as the mid-point of the inflection in the reversible heat flow vs.  
20 temperature curve. In all cases, the MDSC analysis was carried out using randomly located areas of  
21 the degraded samples but excluding the sample edges.

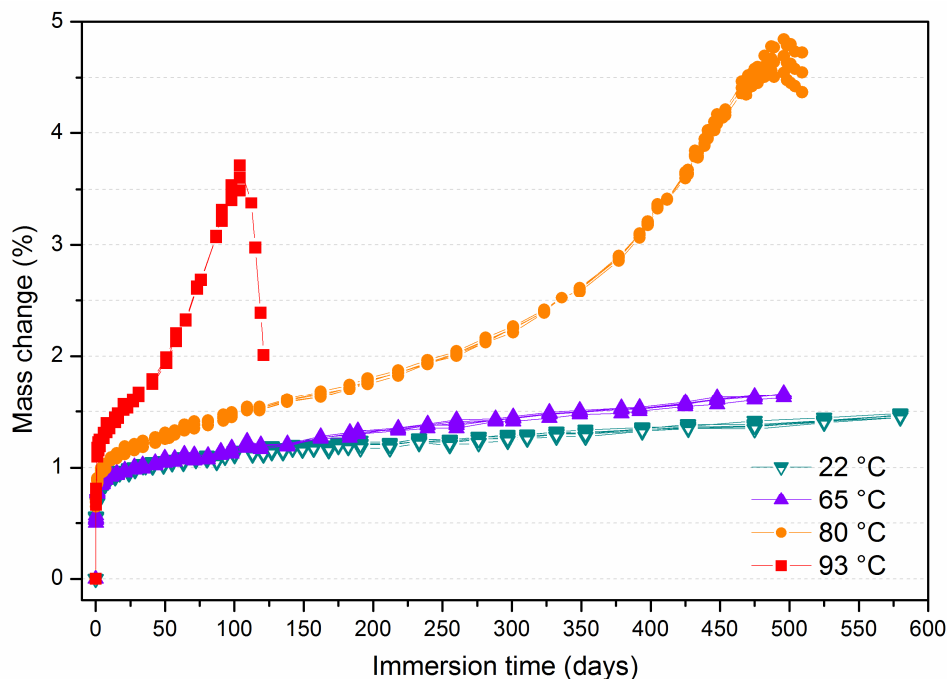
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#### 23 **Results and discussion**

24 Gravimetric data recorded during immersion test at high temperatures (93 °C and 80 °C) show the  
25 characteristic behavior of epoxy polymer matrices containing hydrolysable groups in their structure  
26 [12,20] (Figure 3). Such behavior is characterized by an initial increase of mass mainly associated  
27 with a water diffusion process followed by a second mass increase that reaches a maximum value  
28 and then a drastic mass loss. The hydrolytic degradation process is characterized by crosslinking

1 density decreasing, network hydrophilicity increasing, and low molecular weight products lixiviation  
 2 [12,18,20,22].

3



4

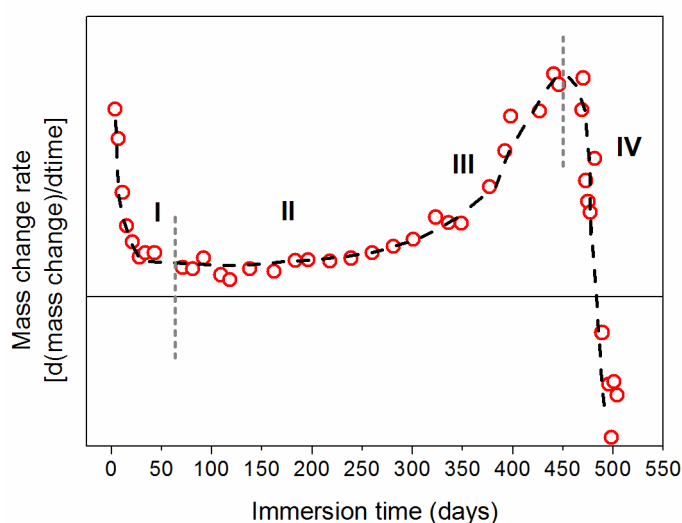
5 **Figure 3.** Gravimetric data for epoxy-anhydride samples immersed in distilled water at 22 °C, 65 °C, 80 °C  
 6 and 93 °C.

7

8 Gravimetric results are widely used to explain the behavior of polymers in contact with water.  
 9 Diffusion, hydrolysis and lixiviation are simultaneous and coupled processes. While water diffuses  
 10 into the polymer network, it is able to react with the ester groups resulting from the epoxy-anhydride  
 11 polymerization. This reaction produces hydrophilic groups and reduces crosslinking density. When  
 12 hydrolysis occurs, small species are free to move out of the original network. In order to identify  
 13 diffusion, hydrolysis and lixiviation processes, Figure 4 shows a schematic representation of the  
 14 mass change rate. As can be clearly seen, the whole processes can be divided in four stages.

- 15 i. Initially, mass change rate decreases continuously until it reaches a plateau  
 16 (approximately 25 days at 93 °C; 100 days at 80 °C; 400 days at 65 °C; not reached at 25  
 17 °C).

- 1 II. During the second stage, mass change rate remains almost constant at a positive value,  
 2 this indicates, that the mass increases linearly with time (approximately 25 to 75 days at  
 3 93 °C; 100 to 325 days at 80 °C).
- 4 III. During the third stage, mass change rate increases from the second stage plateau up to its  
 5 maximum value (approximately 75 to 100 days at 93 °C; 325 to 500 days at 80 °C).
- 6 IV. In the fourth stage, mass change rate continuously decreases from its maximum reaching  
 7 negative values at the end of the process (>100 days approx. at 93 °C; > 500 days at 80  
 8 °C).

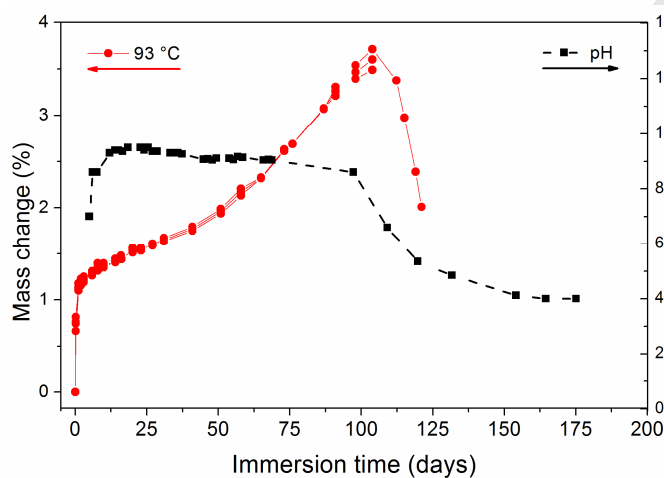


9  
 10 **Figure 4.** Mass change rate schematic representation (at 80 °C).

11  
 12 The first stage seems to be governed by diffusion. The early initial mass increase at high absorption  
 13 rate could be associated with a classical Fickian process [23] characterized by the mass increases up  
 14 to the equilibrium value ( $M_{\infty}$ ) that remains constant in time. Figure 4 shows that mass change rate  
 15 do not falls up to zero. Instead of reaching an equilibrium, gravimetric curve shows a continuous  
 16 mass increase although at a relatively low rate. This lack of equilibrium could be associated with the  
 17 chemical reaction; part of water intake is consumed by hydrolysis [24]. Besides this, the increase in  
 18 network hydrophilicity and the reduction in crosslinking density both induce  $M_{\infty}$  increases. The third  
 19 stage is characterized for an increase in mass change rate from the second stage plateau up to the  
 20 maximum. The network is able to absorb a considerable higher amount of water; this could be due to  
 21 different factors such as an increase in hydrolysis rate caused by the catalytic effect of acid products,  
 22 an increase in network relaxation capability and/or the aforementioned increase in network  
 23 hydrophilicity. After the maximum, mass change rate decreases continuously until it takes negative

1 values. This decrease, indicated as the four stage, suggest that the lixiviation of low molecular weight  
 2 species resulting from chemical degradation is considerably more important. An evidence of this is  
 3 observed in Figure 5 where it can be seen that the evolution of pH of the immersion water (at 93 °C).  
 4 The initial pH increase can be due to the lixiviation of traces of 2,4,6-tris-(dimethyl-  
 5 aminomethyl)phenol added to increase curing reaction rate. Although a slightly decrease in pH is  
 6 registered after the first 20 days, it steeply falls at the same time that the mass change rate reaches its  
 7 maximum.

8



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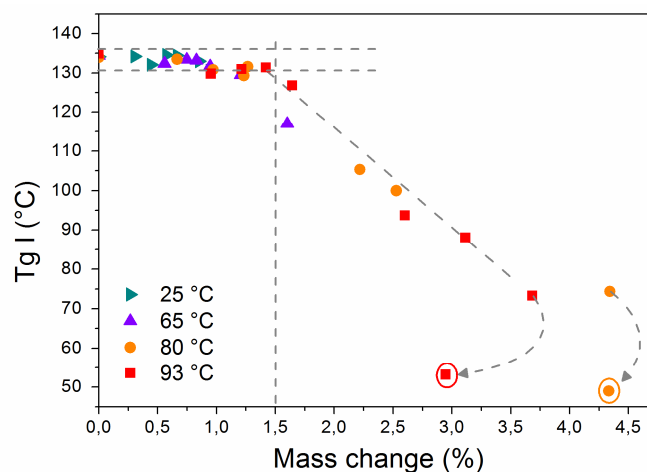
10 **Figure 5.** pH evolution of the water-bath during immersion test at 93 °C.

11

12 Even though gravimetric data gives very valuable information about the in-water behavior of the  
 13 epoxy-anhydride system, it is necessary to find complementary methods that could provide  
 14 information about the significance of diffusion, hydrolysis and lixiviation in each stage in order to  
 15 get better understanding of the global degradation process.

16 Figure 6 shows the glass transition temperature for water-degraded samples at the three different  
 17 temperatures plotted as function of gravimetric mass change. The Tg-I represents the value obtained  
 18 during the first heating cycle. For a gravimetric mass change lower than 1.5% approximately, the Tg-  
 19 I of the samples degraded in water at the three temperatures slightly decrease (less than 5%).  
 20 However, for higher mass change Tg I diminishes considerably reaching values even below the bath  
 21 immersion temperature.

22

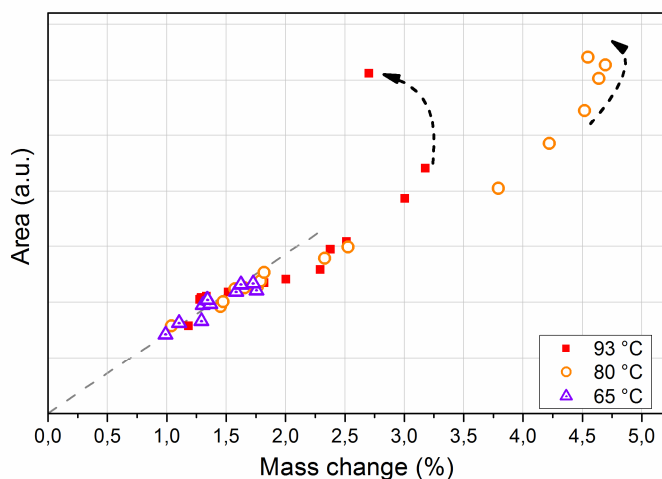


**Figure 6.** Glass transition temperature (°C) of samples immersed in water at 93 °C, 80 °C, 65 °C and 25 °C during different times as a function of percentage mass change. The greatest circles represent data corresponding to the fourth stage in the gravimetric curve and dot arrows represent the sense of increasing time.

### Determination of water content by NIR spectroscopy

Infrared spectroscopy proved to be very useful not only for studying molecular interactions between water and polymeric matrices but also for quantifying the amount of water sorbed [25–28]. NIR spectroscopy has been extensively used for this purpose. A peak located in the region between 5000 and 5350  $\text{cm}^{-1}$  arises from the combination of two vibration bands,  $\nu_{\text{as}}$  and  $\delta$  of the OH bond and its area has been proven to be proportional to water concentration. This peak varies from one polymer to another and is placed at 5250  $\text{cm}^{-1}$  for the epoxy -anhydride network under study.

Figure 7 shows the area of the NIR peak associated with water normalized by the thickness of the samples, plotted against mass change (%) for samples immersed in water at 65, 80 and 93°C.



**Figure 7.** Area of the NIR peak associated with water vs. percentage mass change. The dot arrows represent the sense of increasing time.

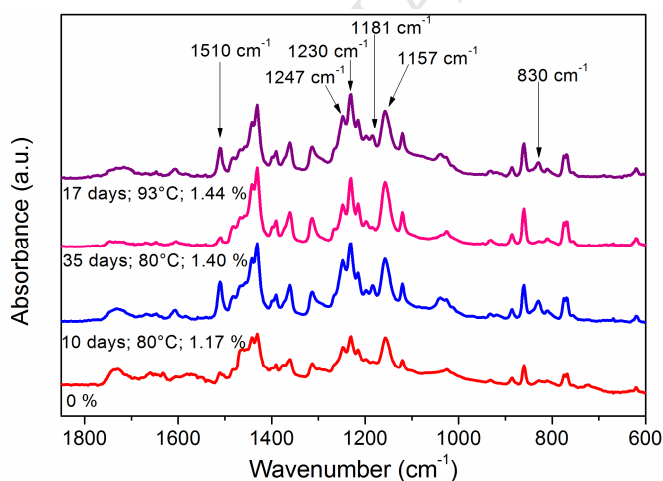
As can be seen in Figure 7, the  $5250\text{ cm}^{-1}$  peak area increases while mass change also does but its behavior varies along the whole range. Three steps can be recognized. The first one extends up to a mass change of about 1.5% and a linear regression passing through zero can be applied to the experimental results. This behavior is in agreement with that reported in the literature for other polymers exposed to water, including several epoxy-based, where diffusion is the sole process that takes place, so that mass change is only related to sorbed water [28]. While gravimetric mass change increases from 1.5 to about 2.3% the  $5250\text{ cm}^{-1}$  peak area also increases but the results do not fit with the first part linear behavior. The difference between the experimental data and the linear regression shows that the  $5250\text{ cm}^{-1}$  peak area is lower than the one expected according the measured gravimetric data. This behavior can be due to that a part of the water is consumed by hydrolysis. Therefore, while the whole water uptake produces an increment in weight; only a part of it, which does not react, is registered by FTIR. After that, the slope of experimental data increases. A plausible explanation is that hydrolysis increases network hydrophilicity and reduces crosslinking density. Both facts increases network infrared absorbance [26] and maximum water uptake ( $M_{\infty}$ ). Eventually, for long periods, the lixiviation of small molecular weight species observed in Figure 4 is responsible of the FTIR signal increment even when the mass decreases.

The experimental design allows also to analyze both low molecular weight free species and the  $T_g$  of the remaining network. In Figure 2 those samples are identified as extracted species and dried solids (named C). The extracted species were evaluated by FTIR and the  $T_g$  of the dried solid were measured by DSC.

## 1 Extracted species infrared spectroscopy characterization

2 All the polymeric networks contain extractable compounds such as impurities, unreacted starting  
3 materials, catalysts, initiators. Besides, when the material is in contact with water and hydrolysis  
4 proceeds, as it is the case, chain scissions generate low molecular weight free fragments. All these  
5 compounds can be extracted and their characterization constitutes an additional tool to get  
6 information about the course of the hydrolytic degradation process. Hydrolysis produces acid species  
7 detectable by FTIR. Procedure specified in Figure 2 allows identifying acid groups once they are  
8 removed from the network, i.e. FTIR characterization of the extracted species will detect the  
9 presence of degradation products once they are not bonded to the network. Figure 8 show the MIR  
10 spectra of extracted species (named B in Figure 2) from samples degraded at different conditions  
11 (immersion temperature and immersion time) but all corresponding to the first stage as it was shown  
12 in Figure 2 (up to 1.5% mass increasing). They were selected and grouped according the degradation  
13 stage. Non-aged sample extracts (indicated as 0%) are also included.

14



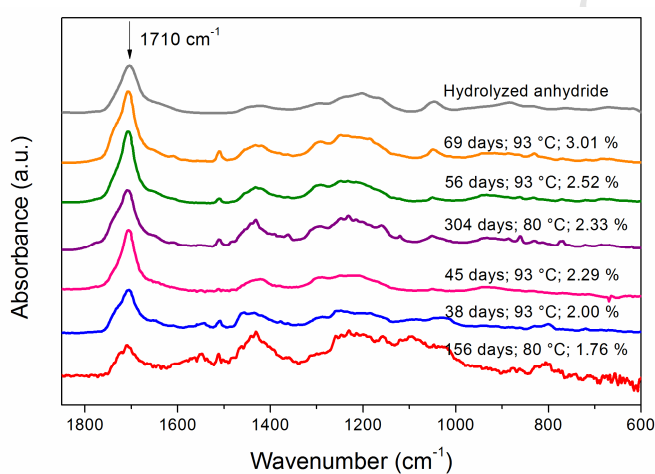
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16 **Figure 8.** MIR spectra of extracts from samples corresponding to the first stage of water degradation: 10 days  
17 of immersion in water at 80 °C with a 1.17% of mass change; 35 days of immersion in water at 80 °C with a  
18 1.40 % of mass change; 17 days of immersion in water at 93 °C with a 1.44 % of mass change. 0% indicates  
19 a sample extracted in THF previous to be aged.

20 The spectra show characteristic signals of carbonyls from aromatic rings (1510, 1181, 830  $\text{cm}^{-1}$ ) and  
21 C-O-C bonds from ethers and esters (1247, 1230, 1157  $\text{cm}^{-1}$ ) that appear in almost every spectra,  
22 though with variable relative intensities. These results suggest that, during the first stage, the extracts  
23 may contain epoxy resin impurities, unreacted compounds and/or products of polymerization not

1 incorporated to the network. Therefore, it can be said that hydrolysis did not progress up to a  
2 significant extent to be detected by this technique.

3 As long as mass change increases (Figure 9) a peak at  $1710\text{ cm}^{-1}$  appears while epoxy resin  
4 characteristic peaks structure are negligible, making the whole spectra looking like that of the  
5 hydrolyzed commercial anhydride. Acid detected in those extracts assure the presence of hydrolysis  
6 products unbounded to the network even after short periods in contact with water. This also indicates  
7 that the degradation begins even before as it was pointed out previously. Spectra of extracts taken  
8 from samples with longer periods and/or higher mass uptake looks similar to the ones presented in  
9 Figure 9 as it was expected.



10

11 **Figure 9.** MIR spectra of extracts from six samples degraded at different conditions but corresponding to the second  
12 stage of degradation: 56 days of immersion in water at  $80\text{ }^{\circ}\text{C}$  with a 1.76 % of mass change; 38 days of immersion in  
13 water at  $93\text{ }^{\circ}\text{C}$  with a 2.00 % of mass change; 45 days of immersion in water at  $93\text{ }^{\circ}\text{C}$  with a 2.29 % of mass change;  
14 304 days of immersion in water at  $80\text{ }^{\circ}\text{C}$  with a 2.33% of mass change; 56 days of immersion in water at  $93\text{ }^{\circ}\text{C}$  with a  
15 2.52 % of mass change; 69 days of immersion in water at  $93\text{ }^{\circ}\text{C}$  with a 3.01 % of mass change; hydrolyzed anhydride.

16

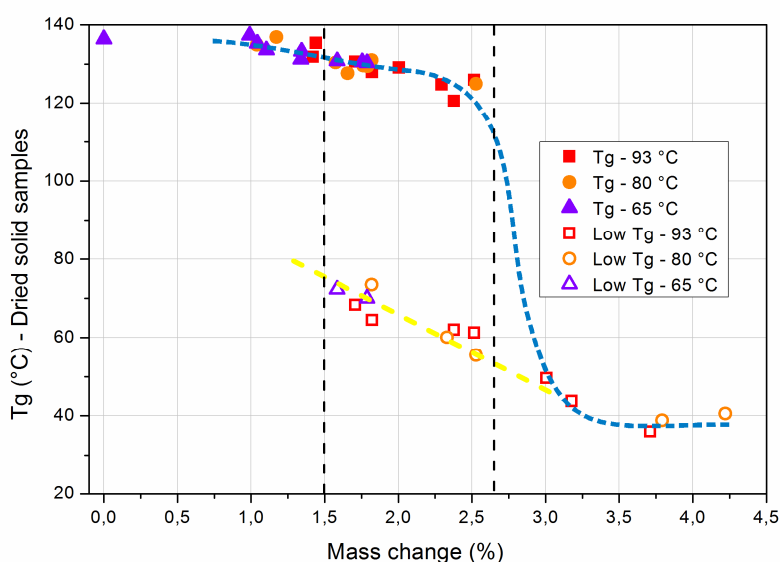
### 17 **Dried solids glass transition**

18 In order to evaluate the structure of the network after degradation the glass transition temperature of  
19 samples lyophilized, extracted and dried were studied. Assuming that water and low molecular  
20 weight degradation products were removed, the glass transition temperature can be related to the  
21 network crosslinking degree. Figure 10 shows the glass transition temperature versus its mass  
22 increasing of samples named C in Figure 2; similar behavior is observed in samples aged at different  
23 temperatures. Three stages can be clearly identified. In the first one the network present only one  $T_g$ ;  
24 up to about 1.5% mass increase,  $T_g$  decreases less than 5%. Around 1.5 % a second stage initiates,



1 this is characterized by the appearance of a second transition at lower temperature. The presence of a  
 2 second Tg allows to infer that the material contains two phases with different crosslinking density.  
 3 The second phase could be related to domains where the hydrolysis rate is higher than it is in the  
 4 bulk. Two main reasons could explain the presence of those domains. Firstly, it is well known  
 5 [17,29] that acids catalyze hydrolysis; secondly the crosslinking density reduction increases chain  
 6 mobility. Both effects could produce highly degraded areas (domains) where Tg drops up to 70 °C.  
 7 During the second stage both Tgs decrease gradually. Between 2.5 – 3.0 % mass uptake the higher  
 8 Tg disappear. The third stage is characterized again by a single Tg; however in this case it can be  
 9 correlated with a homogeneous behavior of a completely degraded network where the glass  
 10 transition is below 60°C. Calorimetry thermograms of samples at different degradation stage are  
 11 shown in the supplementary material file

12



13

14 **Figure 10.** Glass transition temperature (°C) of samples immersed in water at 93 °C, 80 °C and 65 °C during  
 15 different times, after being lyophilized and extracted in THF as a function of mass change (%). Dot lines are  
 16 just a guide for the eyes.

17

## 18 Conclusions

19 Four steps have been identified during the in-water degradation of the epoxy-anhydride system.

20 The first one is mainly characterized by a diffusion behavior. Water uptake reaches a pseudo  
 21 equilibrium up to approximately 1.5 % mass increase. This part mostly occurs during a short period

1 considering possible service life of commercial products. Network plasticization due to water uptake  
2 seems to be the main cause of the slight decrease observed in Tg during this period. Water uptake  
3 can be evaluated by FTIR considering the  $5250\text{ cm}^{-1}$  peak area. Although hydrolysis should exist,  
4 there are no visible signals that it affects the network structure.

5 The second and third parts are governed by hydrolysis. Even though hydrolytic degradation begins at  
6 the first stage, is in this second stage when its consequences affect the network behavior. The main  
7 tip of the second part is the existence of a second phase, highly degraded, with a Tg that varies  
8 between  $70^{\circ}\text{C}$  and  $50^{\circ}\text{C}$ . Water uptake is not univocally related to  $5250\text{ cm}^{-1}$  peak because part of  
9 the water is consumed by hydrolysis, the increase in network mobility and hydrophilicity increases  
10  $M_{\infty}$  that explains the absence of a mass uptake plateau. The third part is identified by the high Tg  
11 disappearance. In this part network mobility strongly grows since diffusion occurs in a rubbery state.  
12 Moreover, acid species acts as hydrolysis catalyst producing a higher hydrophilic network.  
13 Eventually, polymer affinity with water increases during second and third stage.

14 The last stage would be characterized by the mass decrease produced by lixiviation; the material  
15 continues absorbing water while a great number of degradation products leave the matrix. At this  
16 point, the material has lost its designed properties. At first sight, this stage could be considered the  
17 most critic considering operative conditions; however, for structural effects the disappearance of  
18 high Tg phase could be more critical. This part begins before the drastic mass losses and, depending  
19 on temperature, can be long before.

20 This behavior allowed to explain the interaction between diffusion and hydrolysis in epoxy-  
21 anhydride networks which are present in a long list of technological products. Experimental  
22 conditions were chosen in order to avoid the influence of some variables. However, some of them are  
23 important for industrial applications. Some questions like the effect of temperature and pH on the  
24 diffusion coefficient ( $D$ ) and the hydrolysis kinetics ( $k_h$ ), or how both variables affect the process  
25 remain unsolved. However, the four-stage model can be an interesting improvement in order to  
26 estimate residual life, evaluate service performance and develop a more appropriate integrity  
27 management program for composite industrial installations.

28

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9

Highlights

The long-term behavior during water uptake of an epoxy-anhydride network was studied.

A fourth stage mechanism including diffusion and hydrolysis is proposed.

Degraded samples showed two glass transitions suggesting a heterogeneous process.

Hydrolysis undergoes in preferential sites due to presence of acids products.

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