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

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Abstract

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

Key words

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

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

Water uptake induces reversible and irreversible changes in physical and chemical properties affecting the designed material performance [6–11]. Polymer nature and its interaction with water define the main characteristics of the degradation process. In the case of polymers which chemically reacts with water, as unsaturated polyesters or anhydride-cured epoxies, swelling and plasticization caused by water absorption have minor effects, while the hydrolysis of the reactive groups of polymer structure is the responsible for the main material damage [12]. Hydrolysis is a chain scission process and therefore decreases the polymer crosslink density. Moreover, the replacement of ester groups by alcohols and carboxyl acids resulting from the chemical reaction increases the number of polar groups in the network. These physico-chemical changes affect not only the diffusion process but also the hydrolysis kinetics. Water absorption in epoxy systems increases no-linearly with the presence and accessibility of polar groups in the polymer due to the strong water-polymer interactions (hydrogen bonds) [13–16]. Concerning the chemical reaction, hydrolysis rate could be affected by the new chemical groups due to catalytic effect of acid products [17]. In addition, when the chemical scissions caused by the hydrolytic degradation process take place on the same elastically active chain, produce relatively low molecular weight species that eventually are capable to leave the polymer network by lixiviation [18–20]. As a result, chemical and structural changes induced by hydrolysis turn the global degradation process into a complex diffusion-reaction coupled process.

The understanding of water degradation process in polymers with hydrolysable groups in their backbones is a challenge. Recently, many efforts have been made to approach the study and
modeling of the diffusion-reaction coupled processes. Gautier et al. [20] studied the hygrothermal
degradation of polyester matrices and proposed that the process involves water uptake, swelling,
ester hydrolysis, osmotic cracking and leaching of small molecules. They also studied the osmotic
cracking nucleation, which is produced by a phase separation between the polymer and water-soluble
organic molecules resulting from hydrolysis. More recently, a phenomenological reaction-diffusion
scheme for an epoxy-anhydride system was proposed by El Yagoubi et al. [21]. At short time, water
transport is a competition between diffusion and the reactive process. A more detailed kinetic model
for ester hydrolysis of an almost ideal polyester network based on macrodiols was developed [22]
including the autocatalytic effect of carboxylic acids resulting from the reaction. However, there are
insufficient studies of long-term degradation where high hydrolysis conversions and mass loss are
expected.

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

Materials and Experimental methods

Materials preparation

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

(a) Diglycidyl ether of bisphenol A (DGEBA)

(b) Methyl tetrahydrophthalic anhydride  (c) Tris(dimethylaminomethyl)phenol

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

$$\text{Mass change} \, (\%) = \frac{m_t - m_i}{m_i} \times 100$$

Eq. I

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

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

**Lyophilization and solvent extraction**

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

![Figure 2. Schematic procedure of sample treatment.](image-url)
Lyophilization was conducted at -45 °C and 100 mbar during 72 h using a VirTis – Benchtop SLC lyophilizer. The water-degraded samples were previously frozen at -18 °C for 24 h.

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

**Fourier transform infrared spectroscopy (FTIR)**

All the infrared spectra were obtained in transmission mode, with 32 scans and 4 cm$^{-1}$ resolution in a Thermo Scientific Nicolet 6700 spectrophotometer.

The samples immersed in water at different temperatures were analyzed in the Near-infrared (NIR) range (8000-4000 cm$^{-1}$) and the extracts in the Mid-infrared (MIR) range (4000-600 cm$^{-1}$). Thin films were obtained from the extracts by evaporating THF solutions onto NaCl windows.

**Modulated differential scanning calorimetry (MDSC)**

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

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

**Results and discussion**

Gravimetric data recorded during immersion test at high temperatures (93 °C and 80 °C) show the characteristic behavior of epoxy polymer matrices containing hydrolysable groups in their structure [12,20] (Figure 3). Such behavior is characterized by an initial increase of mass mainly associated with a water diffusion process followed by a second mass increase that reaches a maximum value and then a drastic mass loss. The hydrolytic degradation process is characterized by crosslinking...
density decreasing, network hydrophilicity increasing, and low molecular weight products lixiviation [12,18,20,22].

![Figure 3. Gravimetric data for epoxy-anhydride samples immersed in distilled water at 22 °C, 65 °C, 80 °C and 93 °C.](image)

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

I. Initially, mass change rate decreases continuously until it reaches a plateau (approximately 25 days at 93 °C; 100 days at 80 °C; 400 days at 65 °C; not reached at 25 °C).
II. During the second stage, mass change rate remains almost constant at a positive value, this indicates, that the mass increases linearly with time (approximately 25 to 75 days at 93 °C; 100 to 325 days at 80 °C).

III. During the third stage, mass change rate increases from the second stage plateau up to its maximum value (approximately 75 to 100 days at 93 °C; 325 to 500 days at 80 °C).

IV. In the fourth stage, mass change rate continuously decreases from its maximum reaching negative values at the end of the process (>100 days approx. at 93 °C; > 500 days at 80 °C).

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

The first stage seems to be governed by diffusion. The early initial mass increase at high absorption rate could be associated with a classical Fickian process [23] characterized by the mass increases up to the equilibrium value \( M_\infty \) that remains constant in time. Figure 4 shows that mass change rate do not falls up to zero. Instead of reaching an equilibrium, gravimetric curve shows a continuous mass increase although at a relatively low rate. This lack of equilibrium could be associated with the chemical reaction; part of water intake is consumed by hydrolysis [24]. Besides this, the increase in network hydrophilicity and the reduction in crosslinking density both induce \( M_\infty \) increases. The third stage is characterized for an increase in mass change rate from the second stage plateau up to the maximum. The network is able to absorb a considerable higher amount of water; this could be due to different factors such as an increase in hydrolysis rate caused by the catalytic effect of acid products, an increase in network relaxation capability and/or the aforementioned increase in network hydrophilicity. After the maximum, mass change rate decreases continuously until it takes negative
values. This decrease, indicated as the four stage, suggest that the lixiviation of low molecular weight species resulting from chemical degradation is considerably more important. An evidence of this is observed in Figure 5 where it can be seen that the evolution of pH of the immersion water (at 93 °C). The initial pH increase can be due to the lixiviation of traces of 2,4,6-tris-(dimethyl-aminomethyl)phenol added to increase curing reaction rate. Although a slightly decrease in pH is registered after the first 20 days, it steeply falls at the same time that the mass change rate reaches its maximum.

![Figure 5. pH evolution of the water-bath during immersion test at 93 °C.](image)

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

Figure 6 shows the glass transition temperature for water-degraded samples at the three different temperatures plotted as function of gravimetric mass change. The Tg-I represents the value obtained during the first heating cycle. For a gravimetric mass change lower than 1.5% approximately, the Tg-I of the samples degraded in water at the three temperatures slightly decrease (less than 5%). However, for higher mass change Tg I diminishes considerably reaching values even below the bath immersion temperature.
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 cm$^{-1}$ arises from the combination of two vibration bands, $\nu_{as}$ 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 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.
As can be seen in Figure 7, the 5250 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 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 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 Tg 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 Tg of the dried solid were measured by DSC.
Extracted species infrared spectroscopy characterization

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

![MIR spectra of extracts from samples corresponding to the first stage of water degradation](image)

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

The spectra show characteristic signals of carbonyls from aromatic rings (1510, 1181, 830 cm⁻¹) and C-O-C bonds from ethers and esters (1247, 1230, 1157 cm⁻¹) that appear in almost every spectra, though with variable relative intensities. These results suggest that, during the first stage, the extracts may contain epoxy resin impurities, unreacted compounds and/or products of polymerization not
incorporated to the network. Therefore, it can be said that hydrolysis did not progress up to a significant extent to be detected by this technique.

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

**Figure 9.** MIR spectra of extracts from six samples degraded at different conditions but corresponding to the second stage of degradation: 56 days of immersion in water at 80 °C with a 1.76 % of mass change; 38 days of immersion in water at 93 °C with a 2.00 % of mass change; 45 days of immersion in water at 93 °C with a 2.29 % of mass change; 304 days of immersion in water at 80 °C with a 2.33 % of mass change; 56 days of immersion in water at 93 °C with a 2.52 % of mass change; 69 days of immersion in water at 93 °C with a 3.01 % of mass change; hydrolyzed anhydride.

**Dried solids glass transition**

In order to evaluate the structure of the network after degradation the glass transition temperature of samples lyophilized, extracted and dried were studied. Assuming that water and low molecular weight degradation products were removed, the glass transition temperature can be related to the network crosslinking degree. Figure 10 shows the glass transition temperature versus its mass increasing of samples named C in Figure 2; similar behavior is observed in samples aged at different temperatures. Three stages can be clearly identified. In the first one the network present only one Tg; up to about 1.5% mass increase, Tg decreases less than 5%. Around 1.5 % a second stage initiates,
this is characterized by the appearance of a second transition at lower temperature. The presence of a second Tg allows to infer that the material contains two phases with different crosslinking density. The second phase could be related to domains where the hydrolysis rate is higher than it is in the bulk. Two main reasons could explain the presence of those domains. Firstly, it is well known [17,29] that acids catalyze hydrolysis; secondly the crosslinking density reduction increases chain mobility. Both effects could produce highly degraded areas (domains) where Tg drops up to 70 °C. During the second stage both Tgs decrease gradually. Between 2.5 – 3.0 % mass uptake the higher Tg disappear. The third stage is characterized again by a single Tg; however in this case it can be correlated with a homogeneous behavior of a completely degraded network where the glass transition is below 60°C. Calorimetry thermograms of samples at different degradation stage are shown in the supplementary material file

Conclusions

Four steps have been identified during the in-water degradation of the epoxy-anhydride system. The first one is mainly characterized by a diffusion behavior. Water uptake reaches a pseudo equilibrium up to approximately 1.5 % mass increase. This part mostly occurs during a short period
considering possible service life of commercial products. Network plasticization due to water uptake seems to be the main cause of the slight decrease observed in Tg during this period. Water uptake can be evaluated by FTIR considering the 5250 cm$^{-1}$ peak area. Although hydrolysis should exist, there are no visible signals that it affects the network structure.

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

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

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

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References


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.