



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.

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1. 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 nonlinearly 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

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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.

2. Materials and experimental methods

2.1. 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 $55 \times 12 \times 1 \text{ mm}^3$ were cut from the obtained sheets.

2.2. Water absorption tests

Rectangular samples previously dried in a vacuum oven at 80 °C for 48 hr, 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

$$\text{Mass change (\%)} = \frac{m_t - m_i}{m_i} \times 100 \quad (1)$$

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 of 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.

2.3. 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.

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

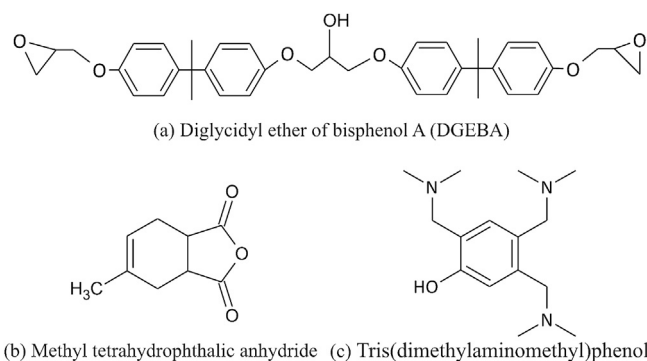


Fig. 1. Chemical structure of the reactants.

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