

Aging in Water and in an Alkaline Medium of Unsaturated Polyester and Epoxy Resins: Experimental Study and Modeling

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ABSTRACT: The change in stiffness with temperature in the presence of different media has been discussed for a long time because the ability to predict this behavior becomes fundamental to the design of new materials and their applications. That is why, in this work, the application of a mathematical model, which is able to predict the elastic properties of two polymers, is presented. The study takes into account the relationship between the viscoelastic and absorption properties of these materials in alkaline solution ($\text{Ca}(\text{OH})_2$, pH 12.5) and in distilled water (H_2O , pH 7) as the immersion media. Diffusion coefficient values were higher when the resins were immersed in water than in the alkaline solution. In addition, the effect of the alkaline medium was higher for the unsaturated polyester resin (UPR). The highest decrease in modulus at the glassy state of the polymer network was observed for the UPR immersed in the alkaline medium. The greatest reduction of the T_g value due to network plasticizing was found for the epoxy resin (ER) in the alkaline medium. Therefore, the ER exhibited a more stable behavior after aging at moderate temperature than the UPR. © 2016 Wiley Periodicals, Inc. *Adv Polym Technol* 2018, 37, 21684; View this article online at wileyonlinelibrary.com. DOI 10.1002/adv.21684

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Introduction

There is an increasing use of fiber-reinforced plastics (FRPs) as an alternative to traditional materials such as wood, metals, and ceramics due to their outstanding properties (high rigidity, high dimensional stability, good electrical properties, and corrosion resistance).¹ In recent years, different polymers (epoxy, phenolic, polyester, and vinyl ester resins) have been chosen for matrices of FRP in many industrial applications such as automotive, aerospace, and civil engineering.^{1–4} However, the acceptance of polymer composites in civil engineering applications is still limited as a result of the degradation of the polymeric

resin in the presence of water or alkaline media. When FRPs are to be used as replacement of steel bars for reinforcing Portland cement, the selection of the polymeric matrix becomes essential as the cement in contact with the resin produces a high alkaline medium. Therefore, not only the study of the effect of water on thermosetting resins but also that of alkaline conditions seem to be essential for using FRP in civil applications. Among the different thermosetting resins, polyester and epoxy have been extensively applied in these applications mainly because of their versatility.¹

Figure 1 is a simplified scheme of the molecules and reactions of polyester resins. Diols other than propylene glycol are used such as various diacids or anhydrides, as well as styrene replacements, which allow tuning of the polyester resin properties. When a catalyst (usually methyl ethyl ketone hydroperoxide) is added, a free radical polymerization reaction takes place forming a network of polyester molecules cross-linked by styrene units. In addition, styrene molecules sometimes react directly with

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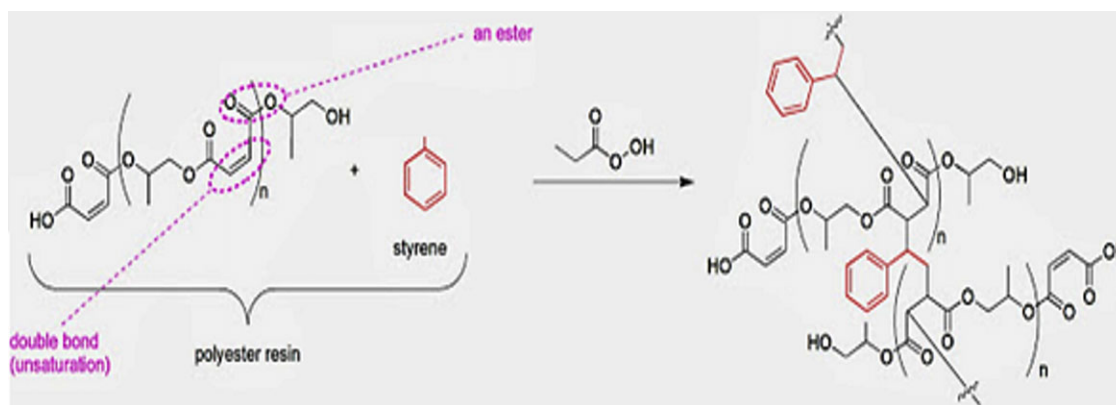


FIGURE 1. Simplified scheme of the molecules and reactions of polyester resins.

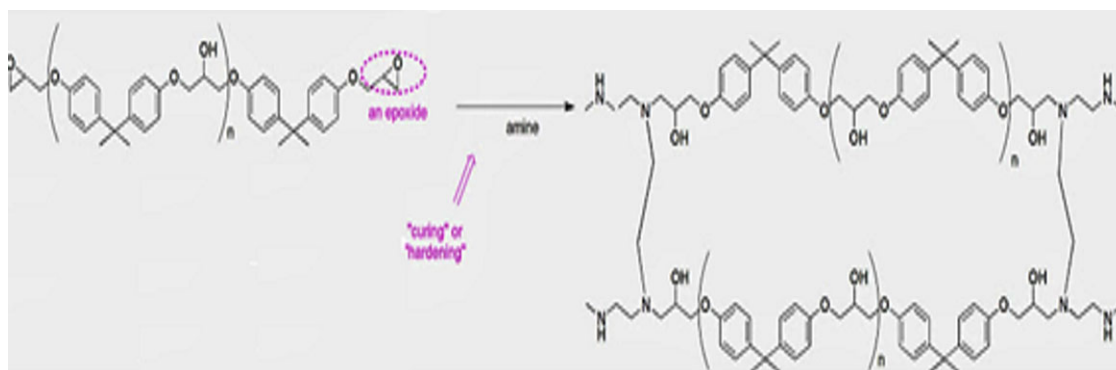


FIGURE 2. Simplified scheme of the molecules and reactions of epoxy resins.

other styrene molecules and polyester molecules react with other polyester molecules with different reaction constants,⁵ where the unsaturated in the polymer chain means they contain carbon-carbon multiple bonds (in this case double bonds) that are necessary for the polymerization/cross-linking reaction and finally form unsaturated polyester resins (UPRs).

On the other side, an epoxy resin (ER) network can be the result of the reaction between the hydrogen of the amine and the oxirane group of the ER. For this, primary amino groups react first, followed by the reaction of secondary amino groups formed after the reaction of the primary amino groups as well as secondary amino radicals, which are embedded in the structure of the molecule. The corresponding rate of reaction of primary amino groups is greater than that of the secondary amino groups because of the higher reactivity of the primary amines with respect to the secondary ones (having two hydrogen susceptible assets to be transferred to the oxirane group to become the hydroxyl group). Figure 2 shows a simplified scheme of the reactions of the ER and amine to form a network, where the cross-linking points are formed by the amine compound.⁶

Several intrinsic factors influence the viscoelastic properties of thermosetting resins and their solvent absorption behavior: free volume,^{7,8} polymer network density,⁹ and the hydrophilic groups of the polymer network,^{10–16} as well as cross-linking density and chemical composition.¹⁷ These intrinsic factors strongly affect solvent sorption behavior in terms of diffusion coefficients, equilibrium value or capacity, and solubility.

Degradation of thermosetting resins during water absorption can induce physical and chemical processes. First, the water is

attracted to areas of air entrainment or voids. Thus, these areas can collect water over time. Even microscopic cracks and voids allow the easy penetration of water into the resin via capillary action and diffusion. After an initial period of seeking out and filling of cracks and voids, water begins to swell the resin,¹⁸ resulting in an increase in the free volume and a decrease in the glass transition temperature, as well as the water with double hydrogen bonds can act as a physical cross-linking agent.¹⁹

Over the past decades, significant efforts have been made to study the aging of UPRs. Zhijun et al.²⁰ have investigated this phenomenon by immersing the resin in water and UV for different time intervals. Hydrolytic and oxidative reactions produced by hydroxyl and carbonyl groups during the aging process, wettability of UPR from changes in the chemical structure, and swelling of the polymer have been studied. Belán et al.²¹ have also analyzed four unsaturated polyester networks with chain ends modified by isocyanate or dicyclopentadiene. The UPRs were immersed in distilled water at 100°C or exposed in humid atmosphere at 70 and 50°C. These authors indicated that water absorption was dependent on the ester nature and the reactivity toward water, as well as on the ester concentration. They pointed out that the replacement of acids by non-catalytic and nonreactive species could have a stabilizing effect. Bifunctional molecules could even have suppressed chain ends, thus having a double effect: acidic suppression and a decrease in the yield of small molecules per chain scission. A comparison of the sample spectra in their initial state and during aging showed a decrease in the absorption band at 1295 cm⁻¹ representative of the CO group of the aliphatic ester. The reference band

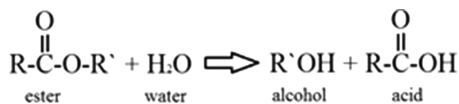


FIGURE 3. Scheme of the reaction of ester and water.

chosen, located at 700 cm^{-1} , was representative of the styrene benzene rings ($-\text{CH}$ aromatic ring) and did not change during aging, as styrene could not be hydrolyzed. When miscibility is high, esterification starts to compete with hydrolysis (Fig. 3). The kinetic constant for the hydrolysis seems to increase rapidly with T above T_g .

On the other hand, Coniglio et al.²² have studied the cyclic water absorption–desorption of ERs. They showed that the hydrothermal aging can lead to matrix cracking after an immersion time at temperatures ranging from 20 to 85°C (absorption tests) and drying in a furnace between 60 and 85°C (desorption tests). They explained the effect of water absorption into cracks and the expansion of the resin with temperature, resulting in the squeezing of water out and the reduction of void spaces. Moisture and temperature together can induce irreversible damage in the polymeric network in the form of microvoids. These microvoids contribute to the moisture absorption properties of ERs.^{23–27}

Prolonged hydrothermal aging above a threshold temperature leads to irreversible damage of the resin such as oxidation,²⁸ microcavity growth,²⁹ and polymer network relaxation,^{30,31} and, as a consequence, strongly affects the mechanical properties.

To understand the phenomenon of water absorption in polymers, it is important to know that the absorbed water is composed of free water and bound water. The free water is formed by water molecules that are able to move independently through gaps and cracks, whereas the bound water is composed of those water molecules that are limited to the polar groups of the polymer.

To analyze the effect of solvent absorption, different experiments have been performed by several authors in which samples are immersed in a liquid or solution and the variation of mass uptake as a function of time is measured. From these experiments, the absorption and effective diffusion coefficients can be estimated. Fick's law describes the diffusion in matter or energy into a medium in which initially there is no (chemical or thermal) equilibrium. Fick's law tells that the diffusive flux through a surface (J , $\text{mol}/\text{cm}^2 \cdot \text{s}$) is directly proportional to the concentration gradient (∇C). The coefficient of proportionality is called diffusion coefficient (D , cm^2/s). An extensive description and comparison among several models have been published by Masaro and Zhu.³² In addition, Liang et al.³³ have studied the water diffusion into an ER. They found that the driving force for the diffusion resulted in energy released by the hydrogen bonds, whereas the transportation rate was essentially related to the local chain mobility as well as to the dissociation of water molecules from the epoxy network.

The aim of the present work was to study the viscoelastic behavior of UPR and ER, when they were exposed to distilled water (H_2O) at pH 7 and to an alkaline solution of ($\text{Ca}(\text{OH})_2$) at pH 12.50 (simulated pore concrete solution). The alkaline solution simulated the case when these polymers are used as matrices of FRP employed instead of steel bars as reinforcement of concrete. A temperature of 50°C was chosen to accelerate the

degradation behavior of the resins without high evaporation that could produce mechanical damage of the samples. To the authors' knowledge at the time of writing, few published papers showed the effect of aging in water and in an alkaline solution on the viscoelastic properties of UPR and ER.

Materials and Methods

A commercial UPR (type orthophthalic), catalyzed with 1 wt% of methyl ethyl ketone (supplied by Resinplast Tigre S.R.L, Buenos Aires, Argentina), and a commercial ER (diglycidyl ether of bisphenol A with $n = 0.14$), catalyzed with tetraethylene amine (70%, Huntsman Chemical imported by Distraltec S.A., Buenos Aires, Argentina), were chosen for this study.

Samples of UPR and ER were prepared in glass plates of $10\text{ cm} \times 10\text{ cm}$. To avoid problems with the stripping of the piece, both the base and the lid were placed on Teflon adhesive paper. Samples were cut off in plates ($6 \times 6 \times 0.25\text{ cm}$) according to ASTM D570 standard recommendations. The following temperature ramp was used to cure the resins: 40°C for 2 h, 60°C for 2 h, 80°C for 8 h, 120°C for 1 h, 160°C for 1 h, and 180°C for 1 h.

Absorption tests were carried out in accordance with ASTM D570 standard. Samples were dried for 1 h at 50°C to reach a constant initial mass. Then, some samples were immersed in distilled water and other samples in a saturated calcium hydroxide solution (referred to as alkaline solution in the following text). A thermostatic bath at 50°C was used for absorption tests to accelerate the process of absorption and to keep the temperature constant. To record the absorption, samples were removed from the containers and cleaned with a soft dry paper before weight measurement. After this, samples were immersed again in water or in the alkaline solution. Samples weight was measured at different times: 30 min, 1 h, 24 h, and 48 h. The measurement was continued until saturation was reached. Percentage of absorption was calculated as follows:

$$\% \text{ Absorption} = Q_t = \frac{M_t - M_0}{M_0} \times 100 \quad (1)$$

where M_0 is the initial sample weight at time $t = 0$ and M_t is the sample weight after absorption at time t .

A Fourier transform infrared (FTIR) spectroscope (IRAffinity-1 FTIR; Shimadzu, Japan) was used to characterize ER and UPR (KBr pellets). Each spectrum was collected between 4400 and 450 cm^{-1} with 40 scans at a spectral resolution of 4 cm^{-1} .

Viscoelastic properties of the resins were determined by using a dynamic mechanical analyzer (DMA 8000; Perkin Elmer, USA). Tests were performed on rectangular bars ($30\text{ mm} \times 8\text{ mm} \times 2.5\text{ mm}$) in the simple beam configuration with a span length of 12.55 mm . Temperature was scanned from ambient temperature to 180°C with a ramp rate of $2^\circ\text{C}/\text{min}$. Oscillation amplitude was set at 0.05 mm at a constant frequency of 1 Hz. Reported results are the average of three replicates.

Samples surface was analyzed using a Zeiss Supra 40 Field emission scanning electron microscope operated at 5 kV and different magnifications (500, 2000, and $7000\times$). Samples were

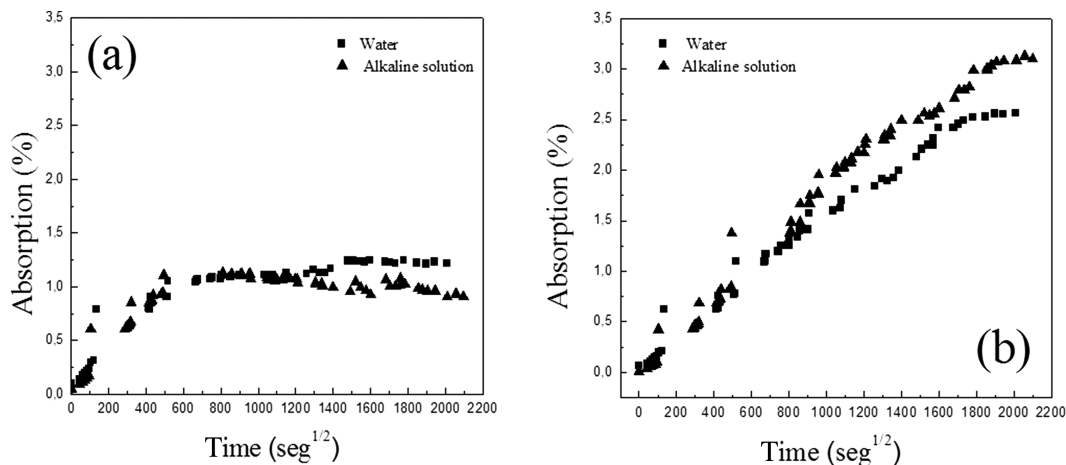


FIGURE 4. Percentage of absorption in water and in the alkaline solution versus time ($\text{seg}^{1/2}$) at 50°C . (a) Unsaturated polyester resin. (b) Epoxy resin.

TABLE I
Absorption Results for Unsaturated Polyester and Epoxy Resins Immersed in Water and in the Alkaline Solution at 50°C

Sample	Medium	Q_t (%)	Time ($\text{seg}^{1/2}$)
UPR	Water	1.2	2015.1
UPR	Alkaline solution	0.9	2179.9
ER	Water	2.6	2015.1
ER	Alkaline solution	3.1	2179.9

polished with emery paper of different sizes between 320 and 1000 to obtain a surface suitable for viewing the content of voids.

Results and Discussion

Figure 4 shows the rate of absorption of the samples immersed in water and in the alkaline solution and equilibrium values of absorption are listed in Table I for the different samples.

It was observed that the absorption behavior of UPR in both media (water and alkaline solution) was significantly different than that of ER, which exhibited much higher percentage of absorption values. This can be due to the higher amount of polar groups (secondary OH^- groups), which were present in the ER at the initial state. Polymerization of epoxy with the hydrogen of the amine produces a secondary OH^- and this makes the epoxy networks more hydrophilic.^{34,35} In addition, after 200 h of immersion in the alkaline solution, the weight of UPR decreased with time. In the case of polyester films, Gu et al.³⁶ have also found that the mass loss increased with increasing exposure time in an alkaline solution. They attributed this phenomenon to the hydrolysis of ester groups and the subsequent leaching of low molecular mass and water soluble fragments of the polyester into the alkaline medium.^{37–40} The leaching can be due to molecules with very low molecular weight such as styrene dimers or due to the hydrolytic reactions that produce higher quantities of OH^-

groups and acid end-chains groups. Therefore, in the UPR investigated here, there is a superimposed effect of the hydrolytic reaction and the water diffusion mechanism. This behavior was not observed in the epoxy system.

Absorption data are useful for estimating the diffusion coefficient of the fluid within the polymers and, thus, to determine the rate of absorption. The diffusion is calculated assuming a one-dimensional diffusion flow, and that the material is homogeneous and inert to the fluid. To calculate the diffusion coefficient, the second Fick's law equation is employed in Eq. (2).

$$J = D \times \nabla C \quad (2)$$

where J is the diffusive flux, D is the diffusion coefficient, and ∇C is the concentration gradient.

According to the literature, there are two main mechanisms of absorption in materials that are associated with a diffusion coefficient. The first corresponds to a diffusion of solvent molecules between the polymer chains and the second is the transport of solvent molecules by bubbles in the matrix, which are formed during mixing,⁴¹ or air included and cracks created into the polymer during the absorption process.

These two mechanisms can be distinguished theoretically by the shape of the absorption curve as a function of time, represented by Eq. (3)^{2,3,8} and normally used for describing the Fickian and non-Fickian behavior. To understand the mechanism of absorption, diffusion can be fitted with the empirical Eq. (4) derived from the equation of transport phenomena.⁸

$$Q = \frac{Q_t}{Q_\infty} = k t^n \quad (3)$$

$$\log Q = \log k + n \log t \quad (4)$$

where Q is absorption and Q_t and Q_∞ are the weight gain at the time " t " and at infinity, respectively, k is a constant that depends on the structural characteristics of the polymer and its interaction with the solvent, and n determines the mode of transport or diffusion within the polymer.

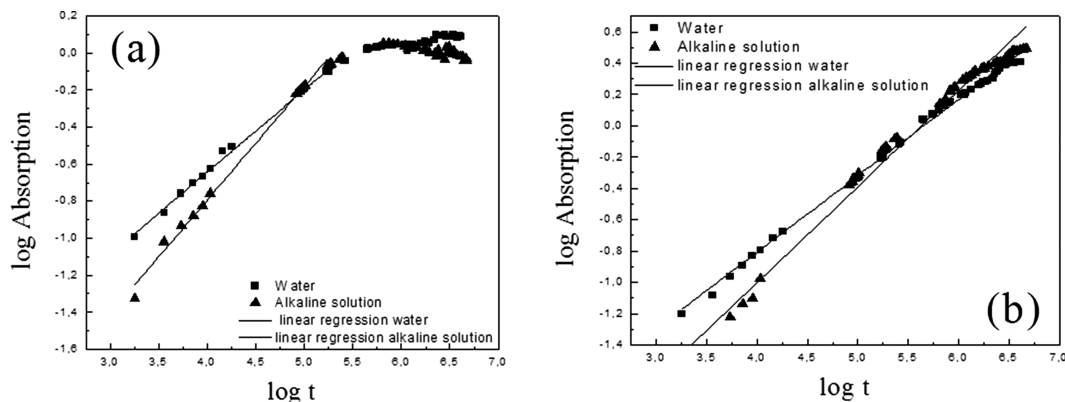


FIGURE 5. Log absorption as a function of $\log t$ (s) in water and in the alkaline solution at 50°C: (a) Unsaturated polyester resin. (b) Epoxy resin.

TABLE II
 k and n Coefficients for Unsaturated Polyester and Epoxy Resins Immersed in Water and in the Alkaline Solution at 50°C

Sample	Medium	k (1/s ^{n})	n
UPR	Water	2.4	0.44
UPR	Alkaline solution	3.2	0.61
ER	Water	2.7	0.48
ER	Alkaline solution	3.4	0.61

For the diffusion mechanisms operating within the resin, the coefficients (n , k) are obtained from the slope and the intercept of the plot of $\log Q$ as a function of $\log t$, respectively. Figure 5 shows the fit of experimental data for the investigated resins immersed in water and in the alkaline solution at 50°C.

The transport mechanisms in polymers can be described by the following cases where the value of the coefficient n gives an idea of the diffusion behavior within the resins. Table II presents the values of k and n for each sample.

Case 1 or Fickian diffusion: For values of $n = 0.5$, the diffusion rate is much lower than the mobility of the polymer segments. The balance within the polymer is rapidly achieved and maintained regardless of the time.^{1,2,4}

Case 2: In this case, transport is characterized by a non-Fickian behavior, where the diffusion is faster than the relaxation rate of the polymer. If n is less than 0.5, then transport is termed as “pseudo-Fickian.”

Case 3: Intermediate behavior between cases 1 and 2. If n is between $0.5 \geq n \geq 1$, then the behavior is called anomalous transport, where rate of diffusion and relaxation are comparable.^{4,7}

For the UPR and ER investigated here, n values for the diffusion of water were 0.44 and 0.48 respectively, so water transport in these resins obeys a pseudo-Fickian behavior.

For both resins immersed in the alkaline solution, the same value of n was found (0.61), suggesting an anomalous diffusion behavior.⁴² Anomalous diffusion can be attributed to two phenomena: the chemical interaction between the diffusing solution and the polymer, and the relaxation of the polymer structure.⁴³ Another possibility is that the fluid penetrates into the interior of the resin causing damage and cracking.³⁰

TABLE III
Effective Diffusion Coefficient Values for the Unsaturated Polyester and Epoxy Resins Immersed in Water and in the Alkaline Solution at 50°C

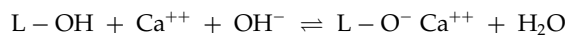
Sample	Medium	D_{eff} (mm ² /s)
UPR	Water	4.36E-09
UPR	Alkaline solution	4.02E-11
ER	Water	1.95E-08
ER	Alkaline solution	4.77E-10

The most important parameter that can be obtained from Fick's law is the diffusion coefficient D , which represents the ability of solvent molecules to penetrate inside the compound. In our case, we used an effective diffusion coefficient (D_{eff}), which represents a process not involving pure diffusion, but which takes into account other effects, such as the existence of voids, and the fact that the fluid is inert to the material. The effective diffusion coefficient can be calculated from Eq. (5).^{44,45}

$$D_{\text{eff}} = \frac{\pi \times M^2 \times a^2}{16 \times t} \quad (5)$$

where $M = M_t / M_\infty$, M_∞ is the weight of the sample when saturation is reached and M_t is the weight of the sample at time t . D_{eff} is the effective diffusion coefficient, t is the time, and a is the sample thickness.

Table III shows the effective diffusion coefficient values for each resin in water and in the alkaline media at 50°C. It was observed that the effective diffusion coefficient values were higher for samples immersed in water probably because the ions of Ca^{++} of the alkaline solution prevented its entry into the polymer. The following reaction can occur within a polymer having hydroxyl groups.



Where L is the polymer, Ca^{++} is the calcium ion, and OH is the hydroxyl group.

Similar equilibrium absorption (Q_t) and diffusion coefficient values were obtained by Mei³⁵ for UPR and ER immersed in

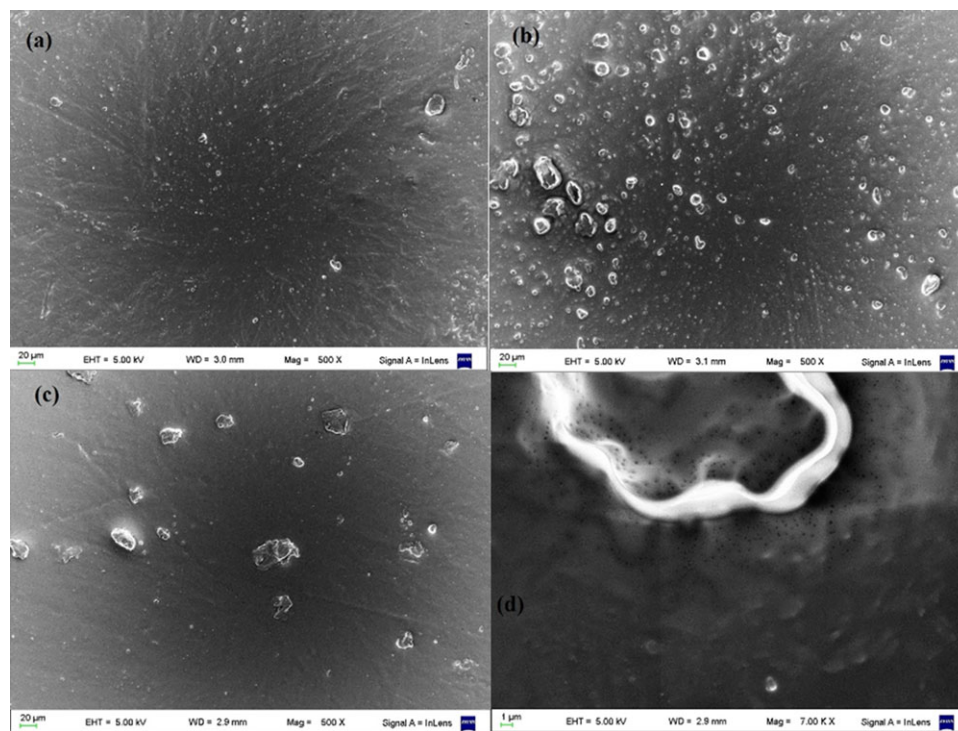


FIGURE 6. SEM micrographs showing unsaturated polyester samples: (a) Before immersion, (b) after immersion in water, (c) after immersion in the alkaline solution, and (d) closer view of a sample after immersion in the alkaline solution.

distilled water at 50°C for 2500 h. He obtained Q_t values of 1.8 and 3% and diffusion coefficient values of 3.7×10^{-9} and 2.4×10^{-8} mm²/s for UPR and ERs, respectively.

Effect of the Exposure to Water and Alkali Solution on the Polymer Microstructure

To investigate the effect of hydrolysis on the morphology of UPR and ER, samples were examined by a scanning electron microscope (SEM; Carl Zeiss Microscopy GmbH, Germany) before and after immersion in water and in the alkaline solution.

Figures 6 and 7 are SEM micrographs of the surface of UPR and ER samples, respectively. A nonuniform distribution of bubbles can be observed for both types of samples immersed in water. This observation can be analyzed from a chemical point of view. In general, solvent uptake is the first step of the degradation process, which is influenced by bulk polarity, microstructure, cross-linking density, and heterogeneity of the sample. Previous studies of organic coatings by SEM showed that water did not diffuse into a sample uniformly along the boundaries of the polymer structural units, and then penetrated itself into the polymer structure.⁴⁶ Osmotic pressure also plays a role in the intrusion of water in bulk polymers and their subsequent chemical and mechanical failure.³⁰ After entering the resin, water attacks the “hydrophilic” regions by hydrolysis, swelling, or dissolution. These hydrophilic regions are presumably regions

that contain low molecular mass/low cross-linked materials. They take up a large amount of water, have a low resistance to ion transport, and are susceptible to water attack.⁴⁷

Bubbles were also observed on the exposed surface of samples immersed in the alkaline solution (Figs. 6 and 7). For the ER, no significant differences were found between the morphology of the samples immersed in water and those exposed to the alkaline medium. In the case of the UPR, a significantly different morphology was observed. A few larger and more irregular bubbles containing pits were found in this resin after immersion in the alkaline medium (Fig. 6d). The occurrence and the development of these pits are believed to be due to the higher degradation of UPR in that medium. These topographic changes are consistent with the mass loss data presented in Fig. 1 and might have some correlation with the microvoids reported by Abeyasinghe et al.³⁸ for degraded polyester samples. These authors found that the pits were caused by solvent contact, which increased with immersion in some specific solvents.

FTIR Analysis

To investigate the spectral changes during aging of epoxy samples (Fig. 8), the aromatic peak at 830 cm⁻¹ was taken as the reference peak since aromatic groups were expected to be unreactive with water and stable at the temperature under study.⁴⁸ During exposure, an incremental increase in the broad absorbance around 3423 cm⁻¹ was observed. This band is

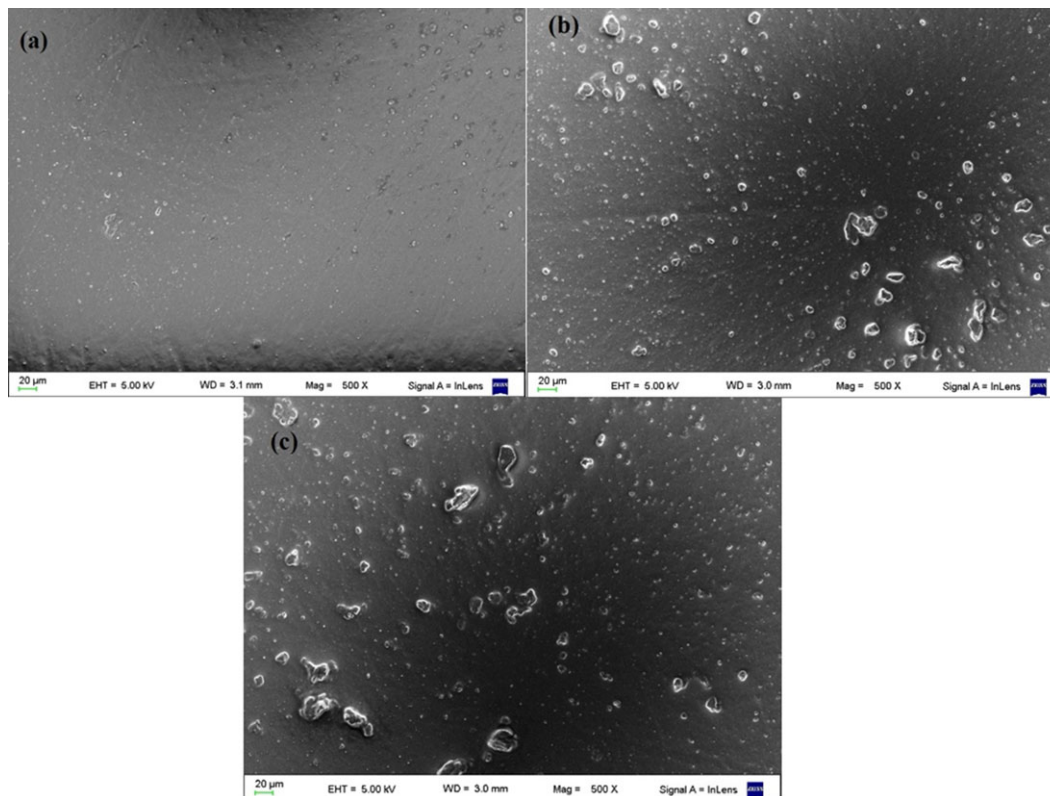


FIGURE 7. SEM micrographs showing epoxy samples: (a) Before immersion, (b) after immersion in water, and (c) after immersion in the alkaline solution.

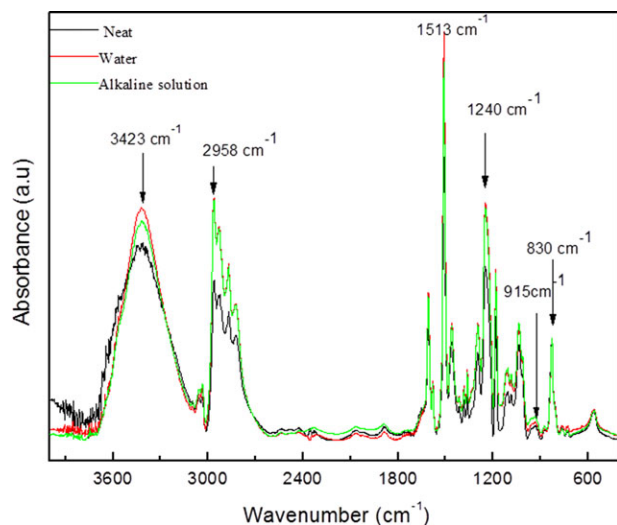


FIGURE 8. FTIR for the epoxy resin immersed in water and in the alkaline solution.

attributed to the OH^- stretching of hydroxyl groups, which increases due to the hydrolysis reaction. The ether bonds are the most sensitive bonds to hydrolysis in the epoxy network, leading to the formation of phenol groups and increasing the amount of OH^- groups.

For the unsaturated polyester sample, the band located at 700 cm^{-1} was taken as the reference band. This is representative of the styrene benzene rings ($-\text{CH}$ aromatic ring) and does not change during aging, as styrene cannot be hydrolyzed.²¹ During exposure, an incremental increase in the broad absorbance around 3416 cm^{-1} was observed. This band is attributed to the OH^- stretching of hydroxyl groups that appears as the hydrolysis reaction proceeds. The peak centered at 1727 cm^{-1} is attributed to $\text{C}=\text{O}$ stretching of the ester groups and the multiple strong absorption bands in the $1250\text{--}1000\text{ cm}^{-1}$ region are assigned to $\text{C}-\text{O}$ stretching vibrations. The bands peaking at 1600 , 1580 , 1492 , and 1453 cm^{-1} are due to $\text{C}-\text{H}$ in-plane bending of the benzene ring. It was observed that the ester linkage at 1727 cm^{-1} increased in water and in the alkaline solution (Fig. 9). For the alkaline solution, there was no apparent increase in the intensity of the carboxylate ions. For water, in contrast, there was an increase in the intensity of the carboxylate ions indicating the high carboxylic group content as a consequence of the hydrolysis. Also, the band of 3517 cm^{-1} corresponding to the OH^- groups of the alcohols increased with the hydrolysis in water and in the alkaline solution. The peak at 1268 cm^{-1} corresponding to $\text{C}-\text{O}$ stretch also showed an increase in peak height due to the hydrolysis. The highest increase in OH^- and carboxylic groups was observed in water for each peaks analyzed. The complex formed between the OH^- end chain in unsaturated polyester network and Ca^{++} ions could produce the less availability of water to react with the ester groups of the polymer.

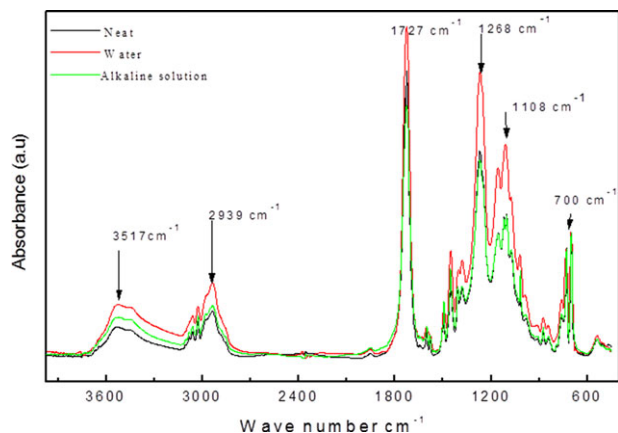


FIGURE 9. FTIR for the unsaturated polyester resin immersed in water and in the alkaline solution.

Dynamic Mechanical Analysis

Thermal and mechanical behaviors of UPR and ER exposed to the two media described above were also analyzed. Immersion in different media produces swelling and plasticization of the matrix, which lead to a loss of mechanical and thermal properties.^{1,7}

Figure 10 presents the storage modulus and $\tan \delta$ values as a function of temperature for the different samples after immersion in water and in the alkaline solution at 50°C and Table IV shows glass transition temperature values, determined from the maximum of the $\tan \delta$ peak. It was observed that glass transition and storage modulus values decreased as a result of the hydrolysis. Storage modulus value for the UPR was found to be more affected by hydrolysis than that of the epoxy, because of the OH^- bridges between the polar groups of the polyester and water, and chain scission. In addition, the ER T_g value was the most affected property in this process, because of the existence of secondary OH^- groups in this network. This is also the main reason of the degradation of ERs. The water acts as bridge between the OH^- groups in some part of the epoxy network, but also acts as lubricant and produces higher mobility of these chains. Two peaks can be seen in Fig. 10b, indicating bimodal chain lengths. However, these OH^- bridges are the reason for the more stable storage modulus of the ER. The height of $\tan \delta$ decreased for both resins after immersion in the two media. However, the epoxy network exhibited a higher drop of $\tan \delta$, indicating a harder network after immersion due to their chain bridges with water.

The decay of the storage modulus with temperature was found to be more pronounced for the UPR. Gu et al.³⁶ have studied the degradation of polyester and reported that the base-catalyzed hydrolysis of this resin was a heterogeneous process and produced voids that increased in number and size with exposure time. The alkaline solution acted as a catalyst of the hydrolytic reactions, and this was the reason why the glassy modulus for unsaturated polyester in the alkaline solution decreased more than under water medium. The hydrolytic reaction

produced acid ends in the polymer; hence, the pH could change during the absorption under alkaline medium.

In addition, the width of the $\tan \delta$ peak was higher for the UPR than the ER, indicating that the polyester network is formed by a wide chains length distribution. Partini and Pantani demonstrated that the degradation rate increased with increasing polydispersity in the resin.⁴⁹ For the polyester, they also suggested that the controlling mechanism was the chemical hydrolytic reaction rather than water diffusion.

Modeling of Viscoelastic Properties

To understand the viscoelastic behavior of thermosetting polymers, the mechanical response is driven by the movement of the smallest chain segments (only a few monomers long). The number and strength of the links involved in the process of relaxation can be associated with a Weibull parameter m_i and with the relaxation of a given point.⁵⁰

$$E(t) = E_1 \exp\left(-\left(\frac{\tau}{\tau_1}\right)^{m_1}\right) \quad (6)$$

Using the time-temperature relationship proposed by Aklonis and MacKnight⁵¹ for instantaneous response and introducing a conversion constant (7):

$$E(t) = E_1 \exp\left(-\left(\frac{T}{T_1}\right)^{m_1}\right) \quad (7)$$

where T_1 is the characteristic temperature of the region and E_1 is a reference value of the modulus for the region. For each relaxation, new Weibull parameters m_i appear. These parameters are related to the bond failures and to the strength of the intermolecular bonds that is required for a relaxation to occur. Finally, as we have different mechanisms, it is possible to sum different relaxations in a single Eq. (8).

$$E = \sum_{i=1}^N E_i \times \exp\left(-\left(\frac{T}{T_i}\right)^{m_i}\right) \quad (8)$$

The general equation can be represented with different coefficients. The coefficients (E_i and T_i) can be obtained by different means, experimental or analytical. For the case of a material that does not undergo any change before reaching the rubbery state, its behavior is described by Eq. (9), for a material with two changes by Eq. (10), and for the case in which the material undergoes three changes, Eq. (11) can be applied.⁵²

$$E = E_3 \times \exp\left(-\left(\frac{T}{T_3}\right)^{m_3}\right) \quad (9)$$

$$E = (E_2 - E_3) \times \exp\left(-\left(\frac{T}{T_2}\right)^{m_2}\right) + E_3 \times \exp\left(-\left(\frac{T}{T_3}\right)^{m_3}\right) \quad (10)$$

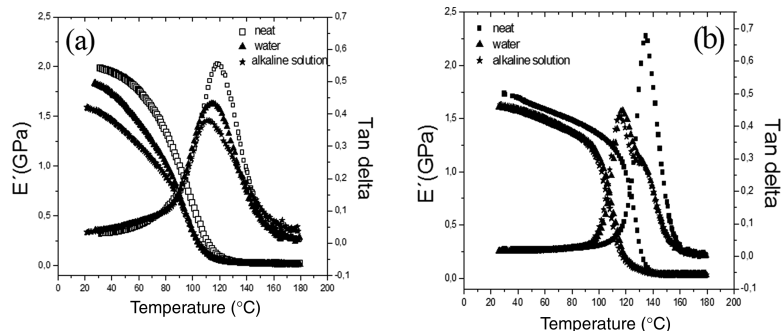


FIGURE 10. Storage modulus and $\tan \delta$ values as a function of temperature after immersion in water and in the alkaline solution at 50°C. (a) Unsaturated polyester and (b) epoxy resins.

TABLE IV Values of Modulus E' at 50°C, T_g , Percentage Decrease in Modulus, and E' at 180°C for the Unsaturated Polyester and Epoxy Resins

Sample	Medium	m_1	m_2	Modulus E' Glassy (GPa) at 50°C	Percentage Decrease in Modulus	T_g (°C)	Percentage Decrease in T_g	Modulus E' Rubbery (MPa) at 180°C
UPR	Neat	1.56	6.22	1.86	–	119	–	19.3
UPR	Water	2.78	10.85	1.60	14.3	114	4.2	15.9
UPR	Alkaline solution	2.42	10.88	1.34	16.1	111	6.7	11.0
ER	Neat	2.50	20.98	1.63	–	134	–	25.5
ER	Water	2.08	16.71	1.52	6.4	117	12.7	34.9
ER	Alkaline solution	2.28	15.86	1.55	5.1	115	19.0	30.7

$$E = (E_1 - E_2) \times \exp\left(-\left(\frac{T}{T_1}\right)^{m_1}\right) + (E_2 - E_3) \times \exp\left(-\left(\frac{T}{T_2}\right)^{m_2}\right) + E_3 \times \exp\left(-\left(\frac{T}{T_3}\right)^{m_3}\right) \quad (11)$$

To describe the transition, it is necessary to consider several elements. As a result, a model with two elements that allows to describe our experimental curve regions can be proposed. For each element, we define a Weibull parameter m_i showing the behavior of the material in each region, as indicated in Eq. (12).

$$E = (E_1 - E_2) \times \exp\left(-\left(\frac{T}{T_1}\right)^{m_1}\right) + E_2 \times \exp\left(-\left(\frac{T}{T_2}\right)^{m_2}\right) \quad (12)$$

The reference temperature and modulus can be independently measured or calculated. The reference temperature corresponds to the inflection point of the transition rather than temperature (T_i), and the reference modulus (E_i), on the other hand, is taken as the average value for each region (Fig. 11).

E_i represents the instantaneous storage modulus at the beginning of each region. E_1 is the instantaneous storage modulus at the beginning of the glassy transition and E_2 is the instantaneous storage modulus at the beginning of the rubbery region.

Changes in the modulus in different regions (E_i) are the most important mechanisms of the relaxation processes. These values

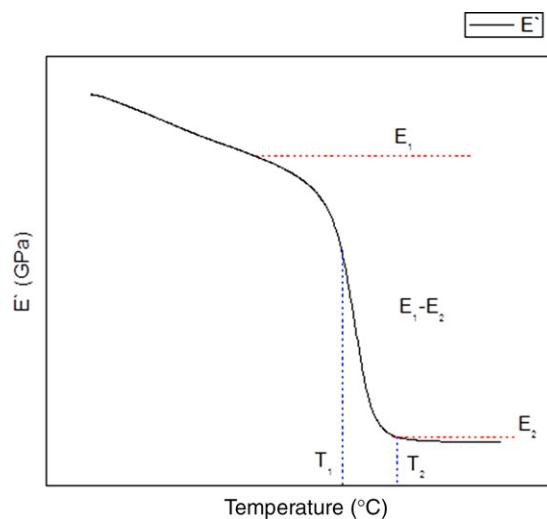


FIGURE 11. Reference values for model calculations.

depend on the chemistry of the polymer (stiffness of the material, molecular weight, crystallinity, and the degree of cross-linking). From the glassy state to the region of rubber, the primary links of the molecules remain intact. However, the secondary bonds (hydrogen, dipole, and Van der Waals) will be altered by the molecular movements during temperature increase in the relaxation process. When reaching the rubbery state, there are no longer secondary bonds, and thus, the degradation of the material begins.

The Weibull parameters (m_i) (Table IV) are continuous probability distributions corresponding to the behavior of the

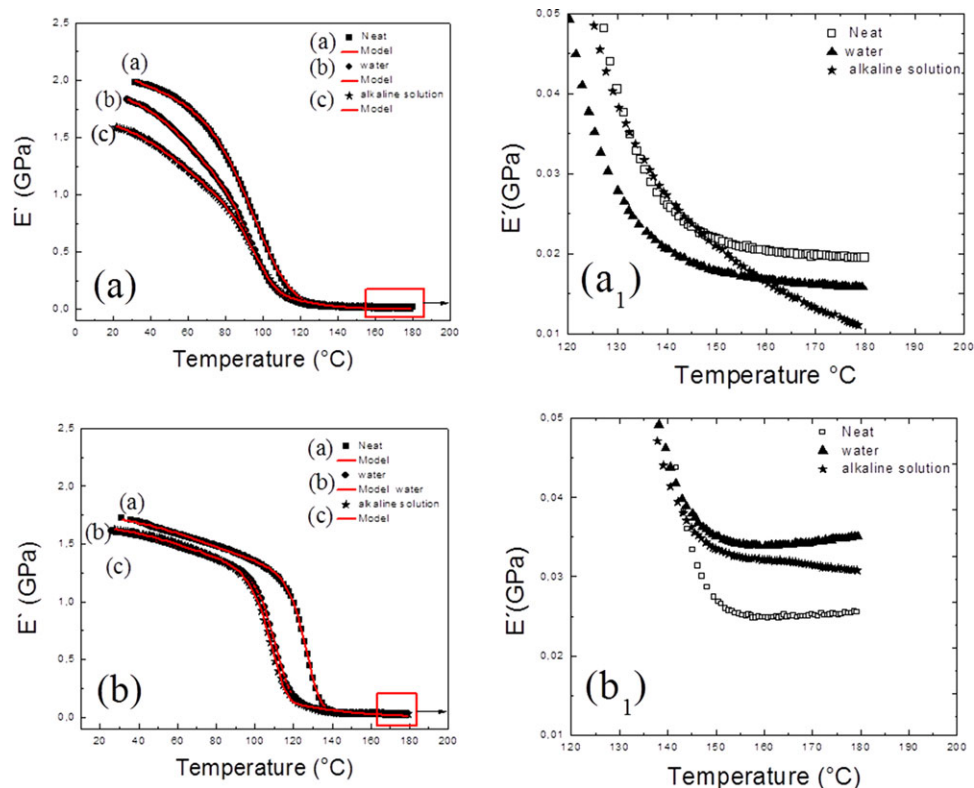


FIGURE 12. Modeling of storage modulus at the rubbery state after immersion in water and in the alkaline solution at 50°C. (a) Unsaturated polyester resin and (b) epoxy resin. (a₁) Closer view of the unsaturated polyester resin in the rubbery state. (b₁) Closer view of the epoxy resin in the rubbery state.

breaking of bonds in the material. However, these parameters will depend on the degree of molecular motion (cross-linking, molecular weight, and crystallinity). If the movement of the molecular chains is severely restricted in precise locations (for cross-linking, etc.), we expect m_i will be very low (approaching a Boltzmann distribution). However, if mobility becomes more significant, the value of m_i will increase.⁴⁸

Above T_g , the mobility of the polymer chains increases and the system reaches the "rubbery" state. The storage modulus at the rubbery state ($T = T_g + 50 \text{ K}$) can be related to the rubbery model and is directly proportional to the cross-linking density. Figure 12 shows the different behaviors obtained for the unsaturated polyester and the epoxy network in the rubbery state and Table IV lists E'_{rubber} and Weibull parameters values obtained. The values of m_1 and m_2 represent the behavior of the polymer in the glassy and rubbery states, respectively. For the UPR, immersion in water and the alkaline solution led to a decrease in the rubbery modulus (E'_{rubber}) and an increase in the m_2 parameter and, consequently, to a decrease in the cross-linking density and an increase in the molecular weight between the cross-linking points, indicating the presence of chain scission. For the ER, the immersion in both media produced an increase in the rubbery modulus (E'_{rubber}) and a decrease in the m_2 parameter as a result of chain bridges between the OH^- from the water and the secondary OH^- of the epoxy network.⁴³

Conclusions

- It was observed that diffusion coefficient values were higher in both resins (UPR and ER) when immersed in water than in the alkaline solution. However, the effect of the alkaline solution was found to be more pronounced on the UPR. These results were also confirmed from SEM observations of exposed surfaces.
- After 200 h at 50°C, the absorbed mass decreased for the UPR due to the loss of low molecular weight compounds (i.e., non-reacted styrene and short length chains formed during the hydrolytic reactions).
- For a resin to be used in civil applications, the decrease in the T_g value due to degradation is not a critical factor if the polymer is maintained in the glassy state and the modulus decay is not significant. The greatest decrease in glassy modulus was found for the UPR immersed in the alkaline medium, whereas the highest decrease in the T_g value was observed for the ER in the same medium. Therefore, the most stable behavior was exhibited by the ER after immersion in water at a moderate temperature.
- It was also found that the value of n in the transport equation for the diffusion of water in unsaturated polyester and epoxy was 0.44 and 0.48, respectively, which indicated pseudo-Fickian behavior. On the other hand, in the case of the

specimens immersed in the alkaline solution, the value of n was 0.61 that represented an anomalous transport within these resins.

In addition, the values of m_2 for the unsaturated polyester in both media increased and the rubbery storage modulus (E'_{rubber}) decreased, indicating a decrease in the cross-linking density and an increase in the molecular weight between the cross-linking points, and consequently the presence of chain scission. For the ER, on the other hand, the rubbery modulus (E'_{rubber}) increased and the m_2 parameter decreased, confirming the existence of chain bridges between the OH^- from the water and the secondary OH^- of the epoxy network.

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