Water Absorption Mechanism and Some Anomalous Effects on the Mechanical and Viscoelastic Behavior of an Epoxy System

G. C. Papanicolaou,[1] Th.V. Kosmidou,[1] A. S. Vatalis,[2] C. G. Delides[2]

[1]*Composite Materials Group, Dept. of Mechanical and Aeronautical Engineering, University of Patras, Patras 265 00, Greece*
[2]*Laboratories of Physics and Material Technology, Technological Education Institute of West Macedonia, 50 100 Kila, Kozani, Greece*

ABSTRACT: During the past decades there has been a great accumulation of important data on the diffusion of water molecules in polymeric solids and its effect on the mechanical and viscoelastic behavior of polymers. It has become apparent that in many cases diffusion in polymers as well as its effect exhibits features that cannot be expected from classical theories and that such departures are related to the molecular structure characteristics of polymers. In the present investigation, the mechanical and viscoelastic behavior of an epoxy resin system is studied as a function of absorbed water, temperature, and time of immersion. Water sorption was achieved by immersing the material in distilled water at constant temperature of 60°C and 80°C for 2, 5, 8, 13, 32, 74, 128, 266, 512, 1024, and 1536 h. Subsequently the specimens were tested in static and dynamic three-point bending tests to study their mechanical and viscoelastic behavior. The variation of T_g, tan δ, bending modulus, and strength was measured as a function of exposure time and respective percentage of water uptake for both temperatures. Some anomalies in their behavior due to water absorption were observed, and a model for the description of the experimentally observed mechanical behavior due to hygrothermal aging is proposed. The results show that the model predictions are in good agreement with experimental findings. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 1328–1339, 2006

Key words: epoxy resin; mechanical degradation; water diffusion

INTRODUCTION

Diffusion of water into epoxy resins and/or epoxy-matrix composites has been extensively studied, and relevant results can be found in literature.[1–7] Water diffusion can be described by Fick's law, although discrepancies from the Fickian behavior are very common. This is mainly due to the complexity of the molecular interaction mechanism between water and resin. These interactions result in structural modifications of the resin and this, in turn, results in variations of the thermal and mechanical behavior of the polymer. Thus, studying the effect of water absorption on polymeric material behavior is of significant interest, especially when designing structures working in aggressive environments. However, studying the environmental effects in such structures is not an easy task. It includes the effect not only of the amount of the absorbed moisture/water, the effect of water temperature, and the time of immersion, but also the effect of the interaction of all these parameters. Apart from pure scientific interest in understanding the net physical phenomenon, the practical goal of this kind of research is to minimize the probability of failure of structures.

Among the various types of polymers, thermosets are very important due to their wide use in the aerospace, automotive, civil, and electronics industries. However, one of the main disadvantages of these materials is their tendency to absorb water when exposed to humid environments. In addition, since moisture diffusion is a thermally activated process, the complex temperature effect on water diffusion is of major practical importance.

The present work concerns the effect of water absorption on the static and dynamic behavior of a DGEBA-DETA system. Three-point bending tests were conducted to investigate the effects of absorbed water on the mechanical properties of the material.

Dynamic mechanical thermal analysis (DMTA) was performed to study the effect of absorbed water on the viscoelastic behavior of the epoxy system. Dynamic mechanical experiments are extensively used to assess

the structure-property dependent nature of polymeric materials. Coevaluation of dynamic mechanical and sorption data for a polymer can serve as a tool to relate hygrothermal exposure to structure and property determinants. Many studies have been made on water absorption in polymers, and the way this affects mechanical and other properties, including the T_g and/or the dynamic moduli.[7–10]

Though in most of the published literature an increase in the peak of tan δ and a shift to lower temperatures of the glass transition region with an increase of the water content is observed, in the present investigation a decrease in the peak of tan δ and an increase in T_g values with water content was observed. The observed anomalous behavior is explained on the basis of recent research findings where analogous behavior was observed by others.[6,7,11] In addition, a theoretical model for the description of the experimentally observed residual mechanical properties after water absorption has been developed. Theoretical predictions are in good agreement with respective experimental values.

THE RESIDUAL PROPERTY MODEL (RPM)

A model for the description of the mechanical degradation of polymers due to water absorption

The RPM is a model developed by the CMG group, University of Patras, and it is used for the description of the residual behavior of materials after damage. As has already been proved, the model gives accurate predictions of the residual materials properties variations irrespective of the cause of damage and of the type of material considered at the time.[12] In the case of damage due to water absorption, the RPM model predicts well only for water conditioning temperatures below T_g and it will be applied in the sequence for the prediction of the bending modulus, the bending strength, and the strength at fracture variation during water uptake and for two different water conditioning temperatures.

The basic assumption of the model is that the mechanical degradation of a material, due to water absorption, follows an exponential decay law of the form:

$$\frac{P_r}{P_0} = 1 - e^{-u} \qquad (1)$$

where P_r is the current value of the mechanical property considered at any time of the absorption process, P_0 is the value of the same property for the dry specimen, and u is a function of the amount of water absorbed by the material at that time.

In the case considered in the present work, where three-point bending tests were performed in speci-

mens after water absorption, P may express one of the following properties: E (i.e., bending modulus), σ_{frac} ture (i.e., stress at fracture), or σ_{max} (i.e., bending strength).

The type of differential equation, having as a solution eq. (1), is of the form:

$$A = y + \frac{1}{A}\frac{dy}{dx},$$

where A is constant.

Thus, according to the model, the degradation of a property due to water absorption will be described by the following differential equation:

$$s = y + \frac{1}{s}\frac{dy}{dx} \qquad (2)$$

where

$$y = \frac{P_r}{P_0}$$

and

$$x = \frac{\Delta m}{m_{dry}} = M$$

where M is the water absorption percentage, that is, the cause of the observed degradation, and m is the mass.

In addition, for $M = M(\infty)$ (= water uptake at the saturation level), $dy/dx = 0$, and $s = \frac{P_\infty}{P_0}$, the ratio of the residual property value at the saturation level to the value of the same property for the dry material.

Solving eq. (2), the following solution is obtained:

$$\frac{P_r}{P_0} = 1 - (1 - s)\cdot[1 - \exp(-sx)]$$
$$= s + (1 - s)\cdot\exp(-sM) \quad (3)$$

The boundary conditions are fulfilled, since

$$M \to \infty \Rightarrow \frac{P_r}{P_0} \to s$$

and for

$$M \to 0 \Rightarrow \frac{P_r}{P_0} \to 1$$

To apply this model, three tests are needed. Namely, 2 three-point bending tests to determine P_∞ and P_0, and one additional test to measure the time
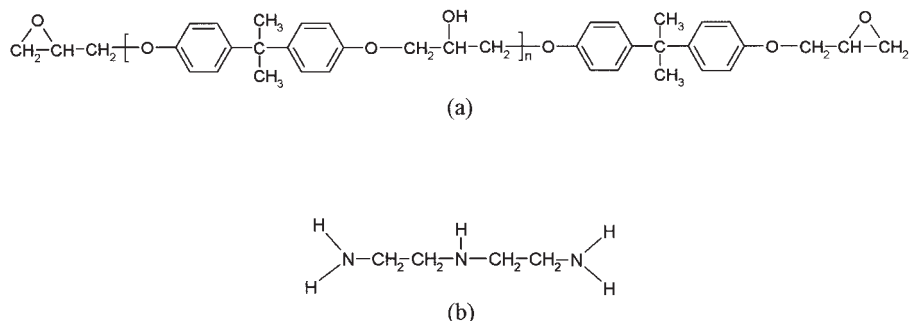
Figure 1   Chemical structures of (A) DGEBA and (B) DETA.

variation of the water uptake in the material. Once the time variation of the water uptake, M (t), is known, then the residual property variation versus time of immersion is obtained.

EXPERIMENTAL

Materials

The materials used were derived from a system based on diglycidyl ether of bisphenol A resin (DGEBA, Epikote 828, Shell Co.) as prepolymer, with an epoxy equivalent of 185–192, a molecular weight between 370 and 384, and a viscosity of 15,000 cP at 25°C. As curing agent, diethylenetriamine (DETA) was employed, that is, a highly reactive amine capable of curing diglycidyl ethers at room temperature. The chemical structure of these resin systems is shown in Figure 1. All components of the system were commercial products and were used without purification.

Sample preparation

Specimens were manufactured as follows: The prepolymer was heated up to 40°C, to decrease viscosity. Proper amounts of the curing agent were then added, and the mixture after being stirred thoroughly was put in a vacuum chamber for degassing. A digital balance (Adams equipment) having a resolution of 0.01mg was used. Subsequently, it was put in a metallic mold of suitable capacity. The mold type and the specimens' dimensions for each test are shown in Figures 2 and 3. The pot life, that is, the gelation time, was of the order of 15 min at 25°C. Then, the following curing process was applied: The temperature was raised at 5°C/h from ambient to 100°C, maintained constant for approximately 24 h, and then decreased at 1°C/h back to ambient. The molding was removed 24 h later and subjected to a thermal postcuring processing, aiming not only at complete curing but also at producing stress-free specimens. Two types of samples were manufactured, one with 8 phr in DETA (8g DETA per 100 g DGEBA) and another one with 10 phr.

RESULTS AND DISCUSSION

Material characterization

The thus manufactured materials were then characterized by means of tensile, three-point bending, Dynamic Mechanical Thermal Analysis (DMTA), and Differential Scanning Calorimetry (DSC) experiments. Results were then used as a reference for the description of the water conditioned materials.
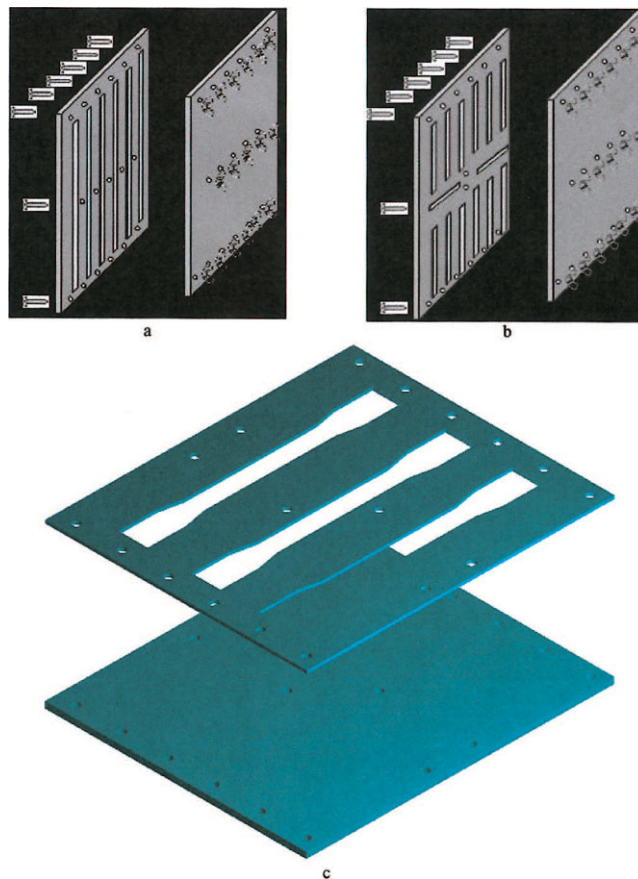

Figure 2   Molds geometry for (A) three-point bending, (B) DMA, and (C) tensile tests.
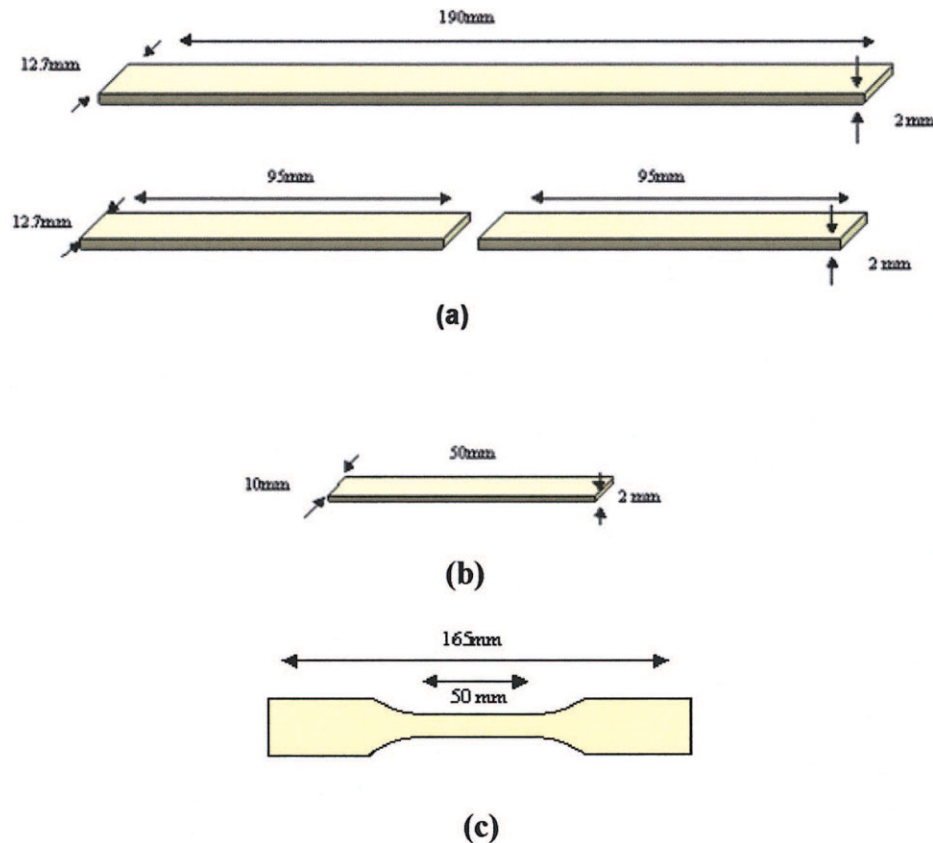
Figure 3 Specimens geometry for (A) three-point bending, (B) DMA, and (C) tensile tests.

Tensile characterization

Tensile tests were performed to obtain the tensile modulus and the fracture stress of the dry materials. Three dry specimens with 8phr amine and three additional with 10 phr amine were tested, to estimate the average mechanical behavior.

Tensile measurements were carried out with a conventional Instron type tester (INSTRON 4301), at room temperature. Specimens with a gauge length of 115 mm were tested at a constant strain rate of 5mm/min. Since experimental curves from the three specimens almost coincide, curves shown in Figures 4(a, b) represent the average tensile behavior of the materials tested. The repeatability of results confirms the good manufacturing conditions of the specimens as well as the appropriate selection of the curing processing conditions.

As expected, according to the results shown in Figure 4, the tensile strength of the specimens with higher amounts in amine hardener is higher than the respective one for the specimens with 8phr in amine. More precisely, it was found that for the 10 phr specimens, the tensile strength was σ_{max} = 53.30 MPa, while the respective value for the 8phr specimens was σ_{max} = 45.08 MPa. This kind of behavior was expected since the higher the percentage in the hardener, the more complete curing is achieved. On the contrary, the tensile modulus was not found so sensitive to hardener concentration variations. The results showed almost the same E-value for both cases, with a small increase for the 10 phr specimens for which E = 2230 MPa, when compared to the 8phr specimens for which the tensile modulus value was E = 2200 MPa.

DSC characterization

DSC tests were performed to estimate the transition region and the respective T_g- values for the materials investigated. Specimens of about 4mm in diameter and 1mm thick were tested in a differential thermal analyzer combined with a DSC analyzer. For each particular material, the test piece was loaded at ambient temperature and subsequently the temperature was increased at constant heating rate. To investigate the effect of the heating rate on the measured transitions, three separate heating rates, namely, 20°, 30°, and 40°C/min, were applied. All experiments were performed in dry specimens. As expected, the higher the heating rate, the higher the T_g-value obtained.[13] As shown in Table I, T_g values for 20°, 30°, and 40°C/min were found to be 123°C, 126°C, and 131°C, respectively, for the 8phr specimens. Respective values for the 10phr specimens were 128°C, 131°C, and 137°C.
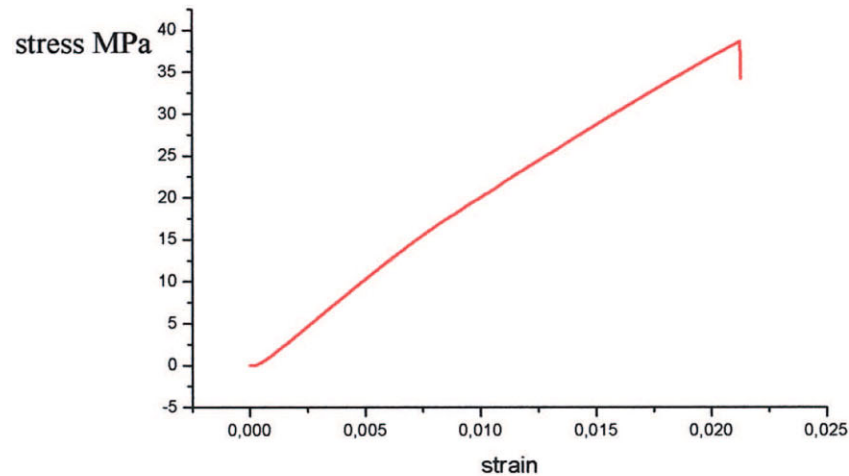
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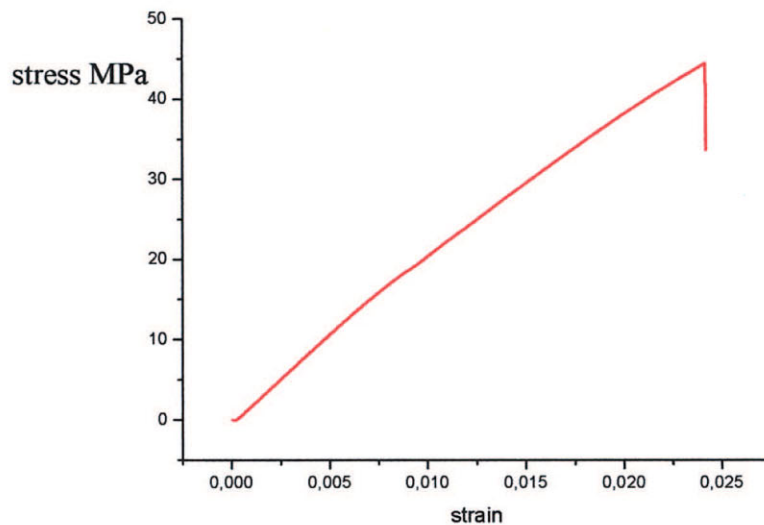
b

Figure 4   Average stress-strain curve from tensile testing of DGEBA with (A) 8 phr amine and (B) 10 phr amine.

Water absorption behavior

For the percent weight change, due to water absorption, specimens in the form of thin plates, with the dimensions shown in Figure 3(a), were used, to have a one-dimensional mode of diffusion. Before placing the test specimens into the water bath, they dried in an oven of 50°C until their weight loss was stabilized. The dried specimens were then placed in a high vacuum for 24h to create full-dried specimens, and their weights were mea- sured with an analytical balance. Then, the specimens were immersed in a distilled-water bath at constant tem- perature of 60 and 80°C, controlled to ± 0.5°C. The specimens, conditioned in water, were then removed at 2, 5, 8, 13, 32, 74, 128, 266, 512, 1024, and 1536 h, wiped, air dried for 5 min, and then weighed. The thus condi- tioned specimens were then mechanically tested, to in- vestigate the effect of water absorption on their static and dynamic behavior.

TABLE I
Transition Region and T_g Values as Measured from DSC Tests

DETA (phr)	Heating rate °C/min	Transition region °C	T_g value °C
8	20	109–135	123
8	30	114–138	126
8	40	116–159	131
10	20	115–141	128
10	30	120–141	131
10	40	122–165	137

The percent of water uptake, M(t), of the materials tested, or percent mass-gain, may be defined as the difference in masses of the wet (m_{wet}) and dry (m_{dry}) materials, normalized to m_{dry}, according to the following equation:

$$M(t)\% = \frac{m_{wet} - m_{dry}}{m_{dry}} \times 100 \qquad (4)$$

The water sorption profiles of the two hygrothermal-exposed epoxy systems for the two different water temperatures are shown in Figure 5. At the initial stage (first 100 h), water gain is linearly proportional to $t^{1/2}$. After exposure for 1000 h, specimens reached full saturation for both hygrothermal conditions. It can be observed that for a given material, the saturation water content ($M(\infty)$) is approximately the same irrespective of the immersion temperature. This kind of behavior indicates that water diffusion in the materials considered is Fickian in nature.[6]

Then, the diffusivity, D, of the material in a direction normal to the lateral faces was determined from the initial slope of the percentage M(t) versus $t^{1/2}$ curve:

$$D = \pi \left(\frac{h}{4M(\infty)} \right)^2 \left(\frac{M_2 - M_1}{\sqrt{t_2} - \sqrt{t_1}} \right)^2 \qquad (5)$$

where h is the thickness of the specimen, t is the exposure time, and $M(\infty)$ is the maximum water gain (saturation). Moreover, M_i (i = 1,2) is the water gain at exposure time t_i. Results are reported in Table II.

It is well known that in nonstoichiometric samples, there is an excess of unreacted epoxy. This means that in the sample there are regions of high crosslink density and regions with less density. These two phases of the material show quite different properties. Thus, the rate of diffusion into the lower density phase is much higher than that of the higher density phase, because the moisture diffusion into this region is severely hindered.[14] From the results shown in Table II, it is obvious that the diffusivity value is higher for the 8phr amine specimens compared to the respective one for the 10phr amine specimens, and the same difference is observed for the maximum water content absorbed by the specimens. Thus, the decrease in $M(\infty)$ with increasing amine content correlates with a decrease in the amount of low-density material.

There-Point bending tests

Three-point bending tests were performed to both dry and wet specimens. Three tests were conducted per each water absorption level and for both water conditioning temperatures. The specimens, conditioned in water, were then removed at 2, 5, 8, 13, 32, 74, 128, 266, 512, 1024, and 1536 h, wiped, air dried for 5 min, and then weighed. The thus conditioned specimens were then mechanically tested.

All tests were carried out on an INSTRON 1026 universal screw driven testing machine at a cross-head
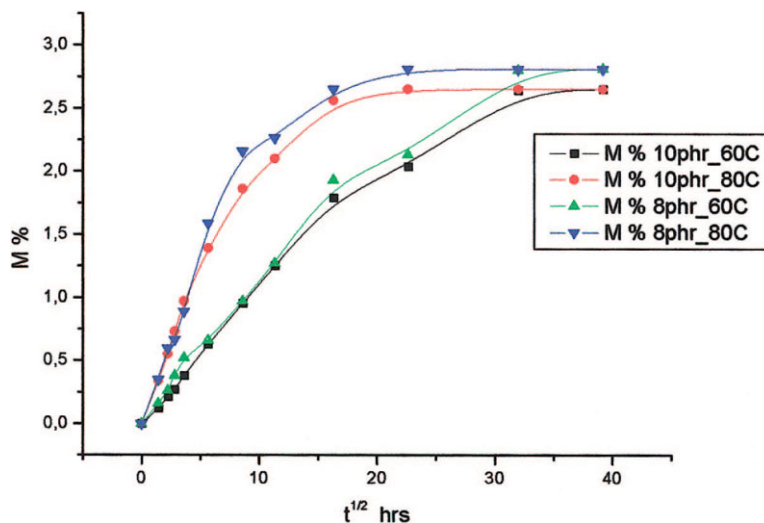
Figure 5 Absorbed water versus time of immersion for samples with 8 and 10 phr amine.

TABLE II
Diffusivity and Saturation Level for Each Specimen

DETA (phr)	Temperature (°C)	Diffusivity D (mm^2s^{-1})	Moisture M(∞) %
8	60	0.62×10^{-2}	2.81
8	80	1.22×10^{-2}	2.81
10	60	0.30×10^{-2}	2.65
10	80	0.92×10^{-2}	2.65

speed of 5mm/min. A special jig was designed and manufactured to perform the bending tests in extension mode. A schematic representation of the bending system used is shown in Figure 6. The gauge length was in all cases 63.5 mm, which resulted in a span to thickness ratio of approximately 32 : 1. All dimensions for the specimens used in the three-point bending tests are shown in Figure 3(a).

The three-point bending stress-strain curves provide valuable information about the elastic modulus, the strength, and the fracture stress versus immersion time, that is, water content and water conditioning temperature. The curves are shown in Figures 7 to 9.

The material degradation starts even at immersion time of only 2 h. The rate of degradation is faster at the beginning, and it subsequently becomes slower. The total degradation observed was of the order of 20% for the specimens conditioned at 80°C water and about 5% for the specimens conditioned at 60°C water environment.

Nogueira and coworkers,[7] in their epoxy resin system, observed a relative increase on the order of 2%, both in the tensile modulus and in the rubbery plateau E', with water uptake. The observed increase was attributed to a reactivation of curing reactions with the water temperature. Due to the reactivation of curing reactions, the polymer network initially becomes denser, so that the material shows an improved mechanical behavior, while as time passes the water plasticizing effect becomes stronger, leading to a subsequent lowering in the mechanical properties.

The degradation takes place because of the hydrogen bonding that is formed between the water molecules and the polar groups of the polymer chain, which disrupts the initial network. Also, crazes are developed within the material due to the hygrothermal stresses causing swelling.[7,9,15–17] Swelling is used to describe volumetric changes due to moisture content alone, independent of thermal expansion. Because the water molecule is polar, it is capable of forming hydrogen bonds with hydroxyl groups, thereby disrupting interchain hydrogen bonding with the net effect of increasing the intersegmental hydrogen bond length. Thermodynamic arguments have shown that liquid molecules can combine with polymer molecules in the glassy state and actually become part of the glassy structure, establishing an equilibrium between the liquid and glassy mixed phase.[15]

On the other hand, it is necessary to note that the network structure of crosslinked epoxy resins is not homogeneous, as generally assumed, but is really a mixture of highly crosslinked microgel particles (or micelles) embedded in a less highly crosslinked matrix. Because of their higher density, the micelles are not as easily penetrated by water as is the surrounding matrix. Although they are comparatively more dense, the micelles do contain a portion of the total polymer free volume. This two phase network structure has been observed by optical microscopic techniques.[15]

Moreover, internal stresses may be set up when a penetrant diffuses into a polymer film. It is to be expected that the inner, unswollen (or less swelling), part of the film will exert a compression force on the outer, swelling, part, causing swelling to be mainly along the direction of diffusion. On the other hand, the swollen region exerts, on the unattacked region, a force that tends to increase the area of the film. The distribution of these compression and expansion forces in the film will change as diffusion proceeds, since the thickness of the unattacked region decreases. It is not unreasonable to assume that the value of the diffusion coefficient is affected by an internal stress exerted at the point considered.

Due to the above reasons, both an increase and/or a decrease in the mechanical properties of the wet specimens can be expected.
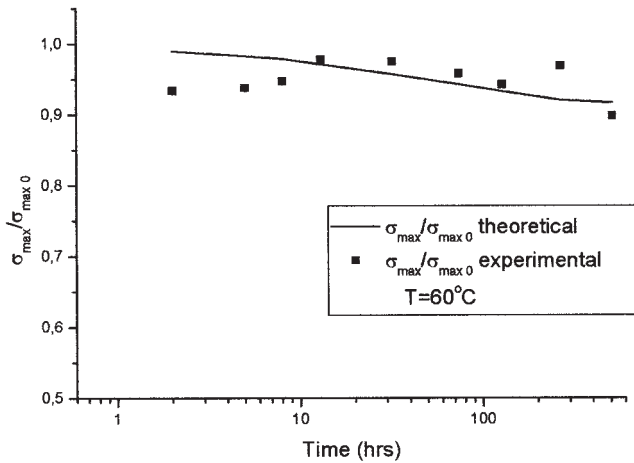
Application of the RPM model to the experimental results

In the sequence, the RPM model was applied and a comparison between experimental results and predictions derived by the model are presented.
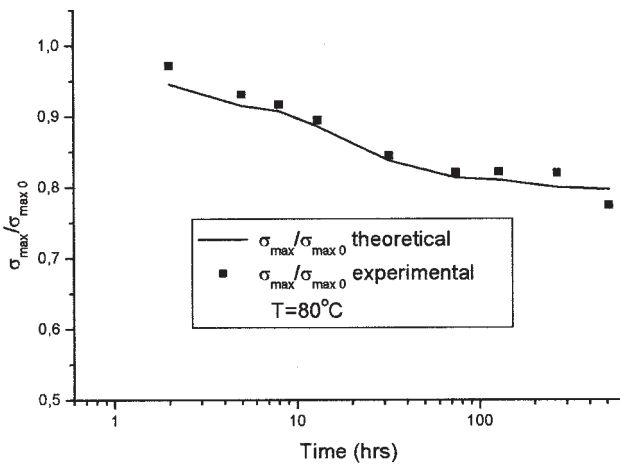
As one can observe, the three-point bending test results shown in Figures 7–9 are in very good agree-
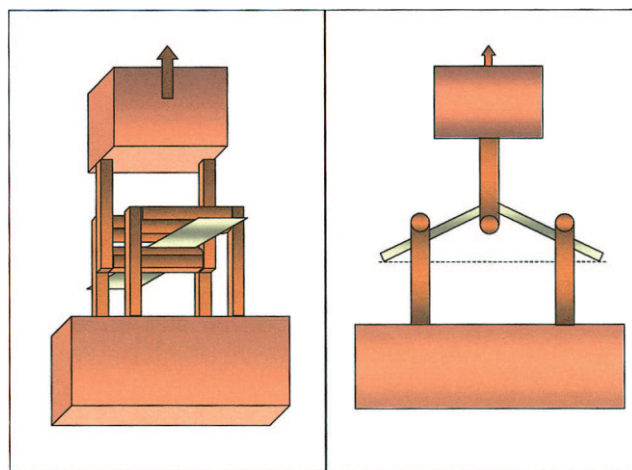
Figure 6   Clamps for three-point bending tests.

(a)

(b)

Figure 7 Experimental results and predicted values for the variation of the fracture stress with immersion time, for water temperature (A) 60°C and (B) 80°C.

ment with predictions as derived by the RPM application.

From these diagrams it is obvious that the model can easily and effectively be used to describe the mechanical behavior of a polymeric material, after water absorption at both temperatures.

Dynamic mechanical thermal analysis tests

Mechanical Spectroscopy is the scientific method to estimate the ability of materials to store or dissipate energy during their deformation. A material stores energy, when it becomes strained, and it yields it back with a rate, which is typical for the specific material. Most materials show a divergence from the ideal elastic behavior, so that they lose some of the deformation energy, in the form of heat. The properties measured

by means of the DMTA technique are the resonant frequency and the dissipation of energy. Mikols and coworkers[8] suggested that some threshold value for hygrothermal-induced changes can be evaluated using sorption-desorption experiments and that such information can be cross-correlated with dynamic mechanical data.

Extensive work has been performed focusing on water absorption mechanisms in epoxy resins.[1–7,18,19] Apicella and colleagues[20] proposed that there may be three ways for epoxy resins to absorb water: (1) formation of polymer-diluent solution, (2) adsorption at hydrophilic sites, and (3) adsorption on the surface of free volume elements. Adamson[15] postulates that the transport of moisture below T_g is a three stage process. First, water occupies the free volume in the form of
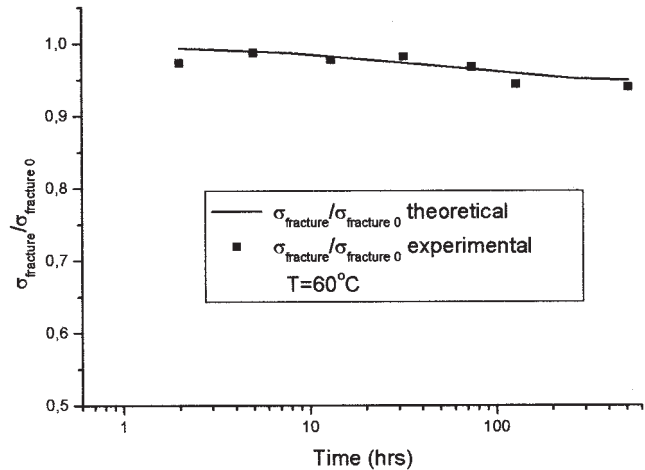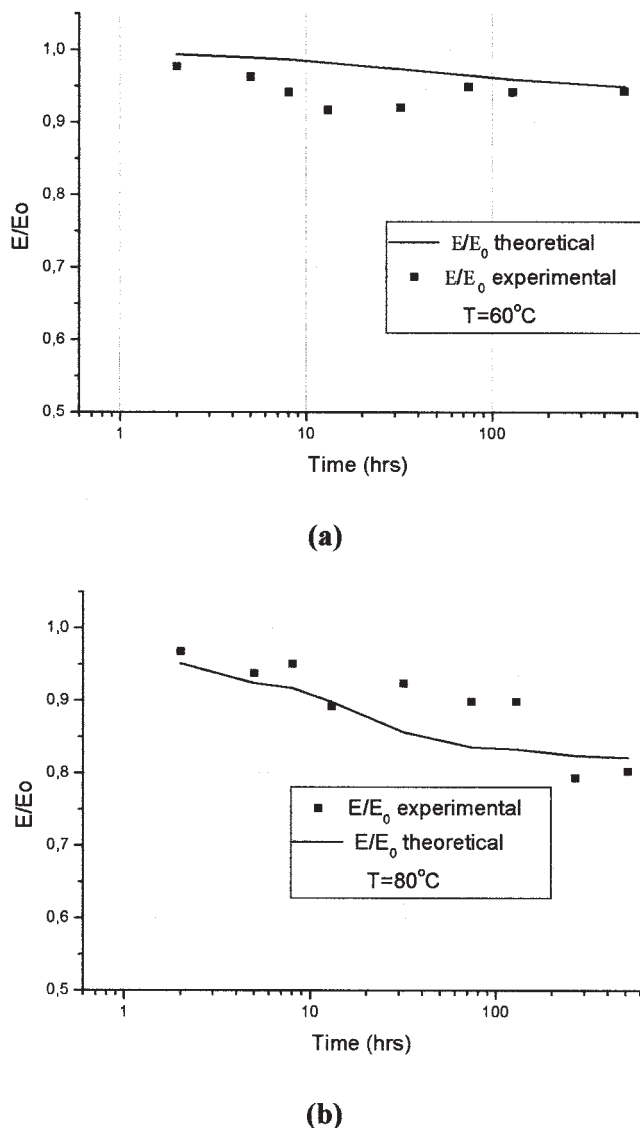

(a)
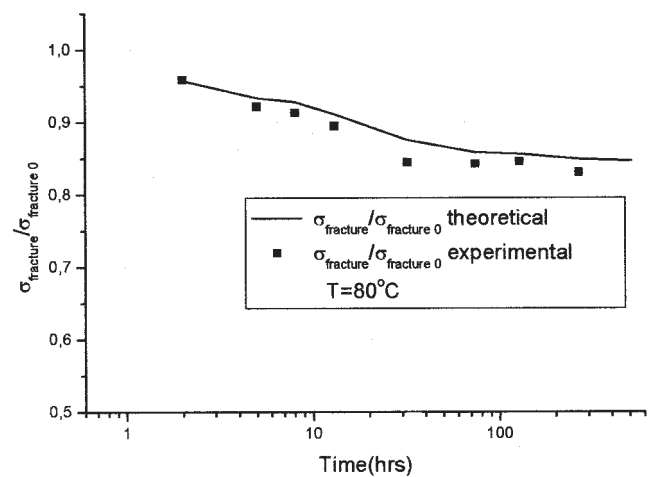
(b)

Figure 8 Experimental and predicted values for the variation of strength with immersion time, for water temperature (A) 60°C and (B) 80°C.

(a)

(b)

Figure 9 Experimental results and predicted values for the variation of elastic modulus with immersion time, for water temperature (A) 60°C and (B) 80°C.

voids. Water then becomes bound to network sites, causing swelling. Finally, it enters the densely crosslinked regions. Carter and Kibler[21] suggested that the spatial distribution of unbound water molecules becomes essentially uniform across the dimensions of thin specimens long before the specimen is saturated with bound water molecules. Li and colleagues[9] proposed that the non-Fickian diffusion behavior observed in BMI is due to the hydrogen bonding between water and the matrix. It takes a long time for equilibrium to be established between bound and unbound water. At the initial stage of absorption, more water that occupies free volume becomes unbound. At the same time, less water can form hydrogen bonds with the polymer to become bound. At a later stage of absorption, the majority of absorbed

water is bound, but unbound water can still diffuse into unoccupied free volume. The network structure determined by different curing schedules has an effect on the diffusion behavior of BMI. The less cured system is easier to plasticize by absorbed moisture and relaxes more easily.

Bao and coworkers[10] studied moisture diffusion in a high T_g BMI resin. It was found that the weight gain of the neat resin deviates significantly from Fick's law in that the uptake continues to slowly increase over an extended time scale (nearly a year). A two-stage diffusion model has been developed to fit the experimental data. According to the model, as the polymer responds to the swelling stress created by sorbed moisture, the network structure becomes more open and more accessible to additional water, which in turn decreases T_g. As the cycle goes on, the weight gain continues to increase with time, causing the observed deviation from Fickian behavior. On the other hand, when water is desorbed, the plasticizer (i.e., water) is removed and T_g increases. Because the relaxation process is suppressed, the network topology cannot relax to the original dry state. In other words, the absorption process is a self-accelerating process, while desorption is a self-retarding process. Therefore, the network structure change during water absorption is irreversible. However, although the relaxation process is irreversible upon desorption, annealing at elevated temperature after desorption may accelerate relaxation and reverse the moisture induced structural change.

Nogueira and colleagues[7] studied the characteristics of sorption and diffusion of water in an amine-cured epoxy system as a function both of the polymer microstructure and the temperature. The same authors studied the effect of water sorption on both the mechanical and viscoelastic behavior of the epoxy system considered. A decrease in the peak of tan δ and a shift to lower temperatures of the glass transition region with an increase of the water content was observed. The observed behavior was attributed to the combined effect of the free volume and the epoxy-water interactions.

In the present investigation, DMTA tests were executed in both wet and dry specimens, using a Polymer Labs Model PL-MK II DMTA device. More precisely, three tests were conducted in dry samples, and three tests per each water temperature and percentage water uptake were executed (i.e., totally 70 samples were used). Each test was performed at constant frequency of 5 Hz and a heating rate of 5°C/min. The temperature was raised from ambient to 180°C, and the aim was to measure the variation of the T_g, the dynamic modulus (E'), and the loss factor (tan δ), with the percentage of water uptake in the specimens. Results were provided in the form of tan δ, E', or E″ versus temperature curves, as shown in Figure 10. T_g was
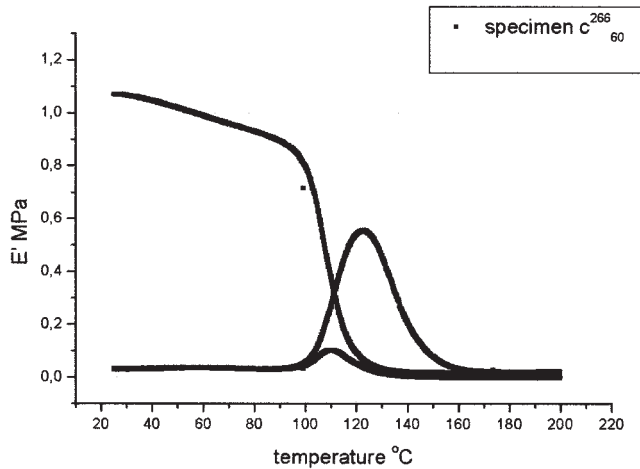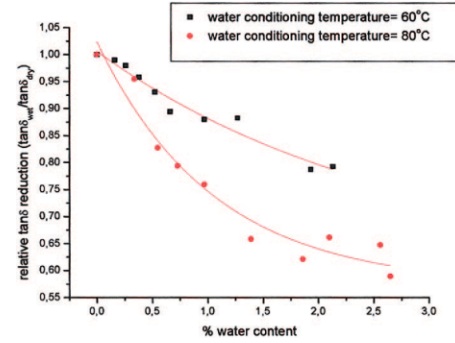
**Figure 10**   Results from DMA tests.

Figure 12   Tan δ versus time of immersion in water of 60°C and 80°C.

estimated from the temperature where the tan δ curve shows the peak. Though in most of the published literature[3,7,9,17,22] an increase in the peak of tan δ and a shift to lower temperatures of the glass transition region with an increase of the water content is observed, in the present investigation, as shown in Figures 11 to 14, the DMTA results were not as expected. In our case, a decrease in the peak of tan δ and an
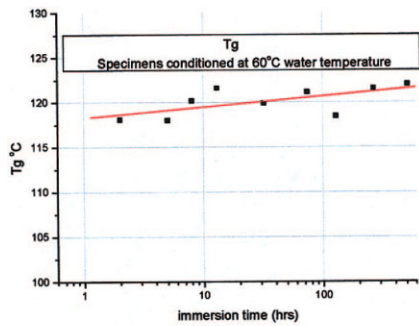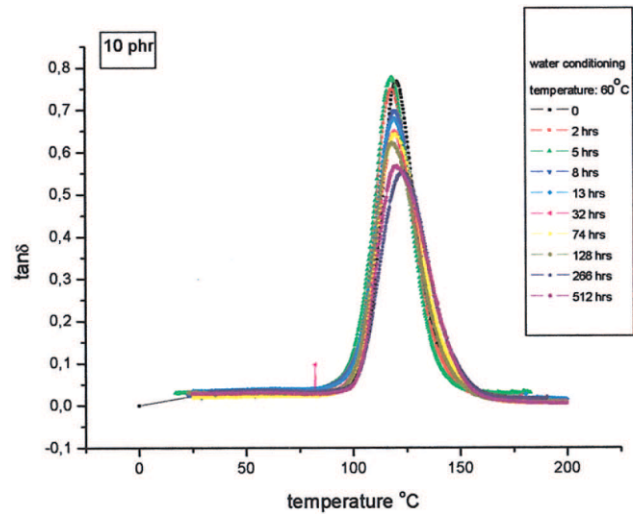

(a)
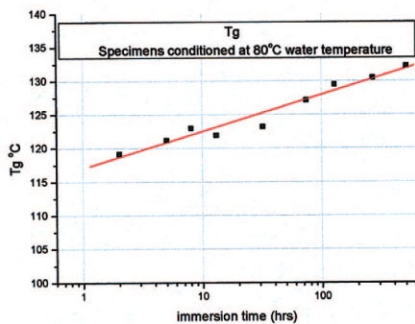
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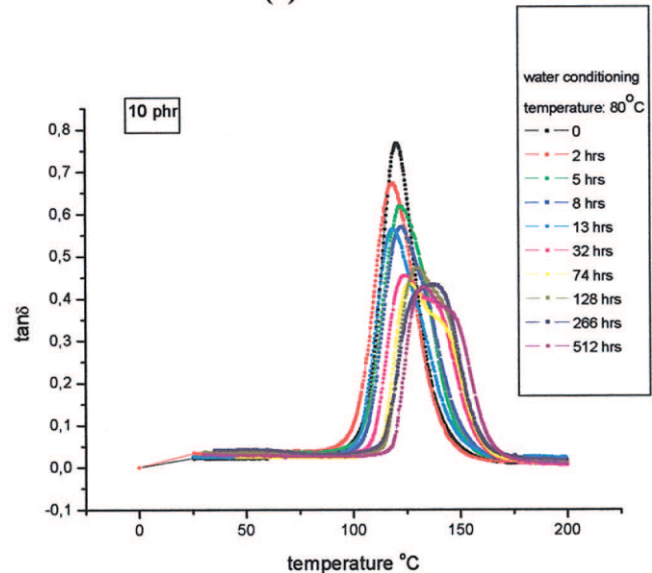
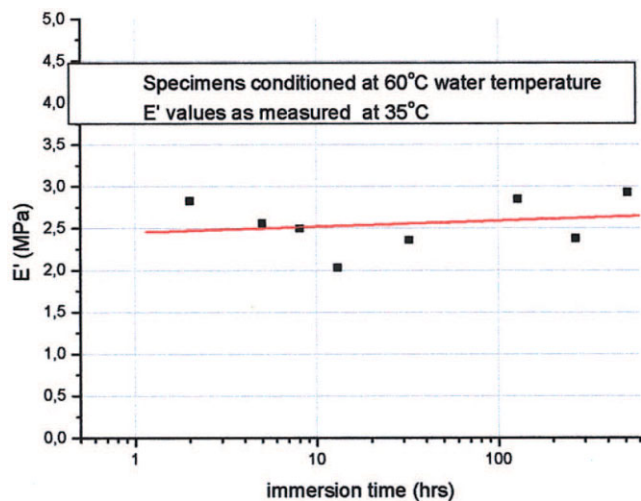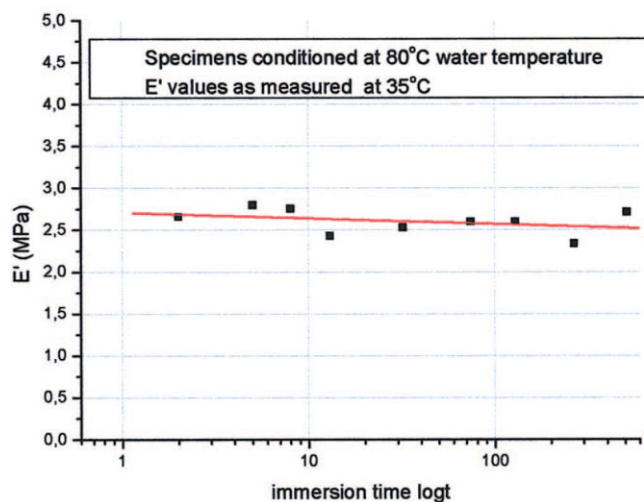**Figure 11** T_g versus time of immersion in water of (A) 60°C and (B) 80°C.

(a)

(b)

Figure 13   Tan δ versus temperature, during the DMA tests, of specimens conditioned in water of (A) 60°C and (B) 80°C.

Figure 14 E' versus time of immersion in water of (A) 60°C and (B) 80°C.

increase in T_g values with water content was observed, while E' values remained almost unaffected by the water absorption.

Figure 11 shows the T_g variation with time of immersion. In these diagrams a small increase in T_g values for specimens conditioned at 60°C and a larger increase, of about 30°C, for those conditioned at 80°C is obvious. This kind of behavior can only be explained on the basis of respective recent findings reported by Zhou and Lucas.[6,11]

More precisely, the nature of sorbed water and the related hygrothermal effects in epoxy resins were studied by Zhou and Lucas.[6] According to their findings, water molecules bind with epoxy resins through hydrogen bonding. Two types of bound water were

found in epoxy resins. The binding types are classified as Type I or Type II bonding, depending on differences in the bond complex and activation energy. The activation energy of Type I and Type II bound water is ~ 10 and ~ 15 kcal/mol, respectively. Type I bonding corresponds to a water molecule that forms a single hydrogen bond with the epoxy network. This water molecule possesses a lower activation energy and is easier to remove from the resin. Type II bonding is a result of a water molecule forming multiple hydrogen bonds with the resin network. This water molecule, therefore, possesses a higher activation energy and is correspondingly harder to remove. Type I bound water is the dominant form of the total amount of sorbed water. The amount of Type II bound water depends strongly on the exposure temperature and time. Higher immersion temperature and longer exposure time result in a greater amount of Type II bound water.

Next, Zhou and Lucas,[11] in a second publication, investigated glass transition temperature (T_g) variation of three different epoxy systems under hygrothermal environment exposure. The investigations revealed the following results: (1) the change of T_g does not depend solely on the water content absorbed in epoxy resins; (2) T_g depends on the hygrothermal history of the materials; (3) for a given epoxy system, higher values of T_g resulted for longer immersion time and higher exposure temperature; and (4) the water/resin interaction characteristics (Type I and Type II bound water) have quite different influence on T_g variation. Type I bound water disrupts the initial interchain Van der Waals force and hydrogen bonds, resulting in increased chain segment mobility acting as a plasticizer and decreasing T_g. In contrast, Type II bound water contributes, comparatively, to an increase in T_g in water saturated epoxy resin by forming a secondary crosslink network. Experimentally determined T_g values represent the combined effect of the two mechanisms. The popular polymer-diluent model used to predict T_g is insufficient when dual-sorption mechanisms are operative under hygrothermal conditions.

Thus, the observed behavior, in Figures 11, 12, and 13, agrees well with the secondary network assumption. Finally, Figure 14 shows the E' variation with time of immersion. It can be seen that there is a small effect of hygrothermal exposure on the storage modulus values.

CONCLUSIONS

In the present investigation, the mechanical and viscoelastic behavior of an epoxy resin system is studied as a function of absorbed water, temperature, and time of immersion. The variation of T_g, tan δ, bending modulus, and strength was measured as a function of

exposure time and respective percentage of water uptake for two different water temperatures. An increase in the Tg values and a respective decrease in tan δ with immersion time were observed. These variations could only be explained on the basis of the secondary network theory developed by Zhou and Lucas. The respective variation for the storage modulus was small. On the contrary, the variation of the static mechanical properties of the epoxy system with water absorption percentage and/or time of immersion was, as expected, that of a degraded material. A model for the description of the experimentally observed three-point bending behavior with time of immersion was developed, and its application showed that the model predictions are in good agreement with experimental findings.

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