

Effect of Water Sorption on the Structure and Mechanical Properties of an Epoxy Resin System

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ABSTRACT: The characteristics of sorption and diffusion of water in an amine-cured epoxy system based on tetraglycidyl diaminodiphenylmethane and a novolac glycidyl ether resin were studied as a function both of the polymer microstructure, known from previous works, and the temperature. Water-sorption experiments and dynamic mechanical analysis (DMA) were performed. Tensile stress-strain and Rockwell hardness tests were conducted to investigate the effects of absorbed water on the mechanical properties of the material. Competing effects of the sorption of water in the free volume and of strong interactions between water molecules and polar groups of the network were used to explain the diffusional behavior observed, which followed Fick's second law. DMA analysis seemed to be sensitive to the water effects and the viscoelastic behavior was related both to the water-sorption processes and to the microstructure of the system. An important impact of water uptake on the tensile properties at break was also appreciated. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 71–80, 2001

Key words: DMA analysis; epoxy microstructure; Fickian diffusion; mechanical properties; water sorption

INTRODUCTION

In this article, the effect of the structure on water-diffusion processes as well as the effect that absorbed water can have on the dynamomechanical and mechanical properties of an epoxy-rich formulation were studied. Epoxy resins are widely used as matrices for structural composite materials, adhesives, and organic coatings due to their good mechanical properties. However, it is well known that these properties are strongly affected by water sorption, which usually causes plasticization and diminishes the mechanical strength,

so the transport of water in epoxy systems is of great importance and is still under investigation.¹

Water transport is related to the availability of molecular-sized holes in the polymer structure and the polymer–water affinity. The availability of holes depends on the polymer structure, morphology, and crosslink density. The polymer–water affinity is related to the presence of hydrogen-bonding sites along the polymer chains, which create attractive forces between the polymer and the water molecules.

The nature of epoxy–water molecule interactions has been investigated by using various techniques.^{2,3} Apicella et al.^{4,5} proposed three different modes for the water sorption of epoxy systems: (a) bulk dissolution of water in the polymer network; (b) moisture sorption onto the surface of holes that define the excess free volume of the glassy structure; and (c) hydrogen bonding between hydrophilic groups of the polymer and wa-

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ter. Moy and Karasz,⁶ Mikols et al.,⁷ and Pethrick et al.⁸ reported that, in epoxy compounds, water exists in two distinct forms: free water that fills the microcavities of the network and bound water in strong interactions with polar segments.

The resin used in this study was a mixture of the epoxy prepolymer tetraglycidyl-4,4'-diaminodiphenylmethane and a novolac glycidyl ether resin, both cured with an aromatic amine hardener, 4,4'-diaminodiphenylsulfone. The cure kinetics and the construction of the TTT diagram of this system were studied previously by DSC.^{9,10} In a recent article,¹¹ the structure and the mechanical properties of this system were discussed as a function of the degree of cure. Three different curing paths were applied, by varying the temperatures and curing times, respectively: (cure 1) 120°C for 120 min followed by 170°C for 150 min; (cure 2) 180°C for 120 min; and (cure 3) 160°C for 120 min followed by 220°C for 120 min. The material reached increasing conversions ranging about 0.70–0.92 from cure 1 to cure 3. Etherification reactions became important in the highest-temperature treatment, and they influenced the properties of the system, mainly in cure 3.

Diffusion in Glassy Polymers

Alfrey et al.¹² introduced the following classification of the diffusion processes in glassy polymers: Case I or Fickian diffusion, Case II, and non-Fickian or anomalous diffusion, the rates of diffusion being much smaller, much faster, or more comparable than is the rate of the relaxation processes, respectively. Using eq. (1) valid for expressing the initial shape of the sorption curves,¹³ these different cases were identified:

$$\frac{M_t}{M_s} = kt^\alpha \quad (1)$$

where M_t represents the mass of water sorbed at time t , M_s refers to the mass sorbed by the polymer at equilibrium, and k and α are system parameters. For Fickian diffusion, $\alpha = 1/2$; for Case II diffusion, $\alpha \geq 1$; and for non-Fickian systems, $\alpha \in (1/2, 1)$. Fickian diffusion can be described by one parameter: the constant coefficient of diffusivity, D .

In a previous article,¹⁴ water sorption for the material with a curing schedule of 2 h at 177°C, followed by 2 h at 220°C, was reported. Dynamic mechanical analysis (DMA) analysis, showing

both α and β relaxations, revealed a shoulder in $\tan \delta$ curves for high water contents.

We have made new measurements with a slightly less severe curing schedule, cure 3, and extended the study to another curing path, with the aim to investigate the relations between the structure of the system and the water effects, including the dynamic mechanical behavior and tensile and hardness mechanical properties. First, isothermal sorption experiments for the different cures were made at several temperatures, and sorption parameters were determined from the curves. Next, the viscoelastic behavior of the material with increasing water contents was analyzed and is reported for cures 2 and 3, due to the significant variations in the $\tan \delta$ observed. Also, tensile stress–strain and Rockwell hardness measurements were made. Finally, some conclusions are pointed out.

EXPERIMENTAL

Materials

The system used throughout this work is a cured epoxy consisting of MY 720 and EPN 1138 epoxies, both manufactured by Ciba–Geigy (Basilea, Switzerland). The curing agent was DDS, manufactured by Fluka Chemie (Milwaukee, WI). The MY 720 is based on the prepolymer tetraglycidyl-4,4'-diaminodiphenylmethane (TGDDM). The EPN 1138 is a multifunctional novolac glycidyl ether resin, and DDS is an aromatic amine hardener, 4,4'-diaminodiphenylsulfone.

All the components of the TGDDM/EPN/DDS epoxy system were commercial products and were used as received without purification. The masses per epoxy equivalent for TGDDM and EPN were determined in our laboratory by hydrochlorination. The values obtained, respectively, were 130 and 180 g eq⁻¹. The hardener has a molecular weight of 248.31 and purity > 96% according to the supplier. An epoxy-rich formulation, with an amine/epoxide ratio of 0.64, was chosen because of the significance of this kind of mixture in the manufacture of high-performance composites.

Sample Preparation

The composition of the mixture was 43.3 wt % of TGDDM, 35.7 wt % of EPN, and 21.0 wt % of DDS. The thermosetting material was prepared by mixing the components at 120°C with contin-

uous mechanical stirring, until a homogeneous liquid was obtained, and then poured into a rectangular stainless-steel mold of 250×350 mm, which was preheated at the same temperature and placed into a forced-air convection oven, where the curing schedules were finally applied. In this way, we attained sheets of the material about 4 mm thick. These sheets were properly mechanized to obtain the samples for the different tests.

Water-sorption samples were square shapes of an average thickness of 0.6 mm. All samples were dried in a vacuum oven at 50°C . Initial dry weights and dimensions were measured and recorded. Afterward, the specimens were placed in deionized water at 20, 40, 70, or 100°C , using a constant temperature bath. Periodically, they were removed, dipped in water at room temperature to suppress water desorption, dried with filter paper, immediately weighed, and then returned to the water bath. The procedure was repeated until the samples reached a saturation level.

A digital balance AD4 of Perkin–Elmer having a resolution of 0.01 mg was used for all weight measurements. The dimensions were measured using digital callipers that were accurate to ± 0.01 mm.

The dynamic mechanical properties of cured samples measuring roughly $19 \times 4 \times 4$ mm were measured by a Perkin–Elmer DMA 7 analyzer operated in a three-point bending–loading configuration, with a loading frequency of 1 Hz and a temperature ramping rate of $5^\circ\text{C}/\text{min}$ over the range -100 to 300°C , obtained with a liquid nitrogen cooling accessory CCA-7 from Perkin–Elmer. For investigations of the influence of water sorption on the dynamic mechanical properties, dry samples and also samples immersed in water at 25 and 100°C , so as to afford various water contents, were used.

Tensile stress–strain properties were characterized using samples (M-II Type) according to general specifications of ASTM D638M and ISO 527, with an Instron universal testing machine 5566 operating at a crosshead speed of 1 mm/min. Ten specimens for each water content were measured, and the data reported are averages of the mechanical parameter results. Finally, Rockwell hardness measurements were made in samples with different water contents using an Instron Wolpert hardness-testing machine DIA-TESTOR 722 following ASTM D785.

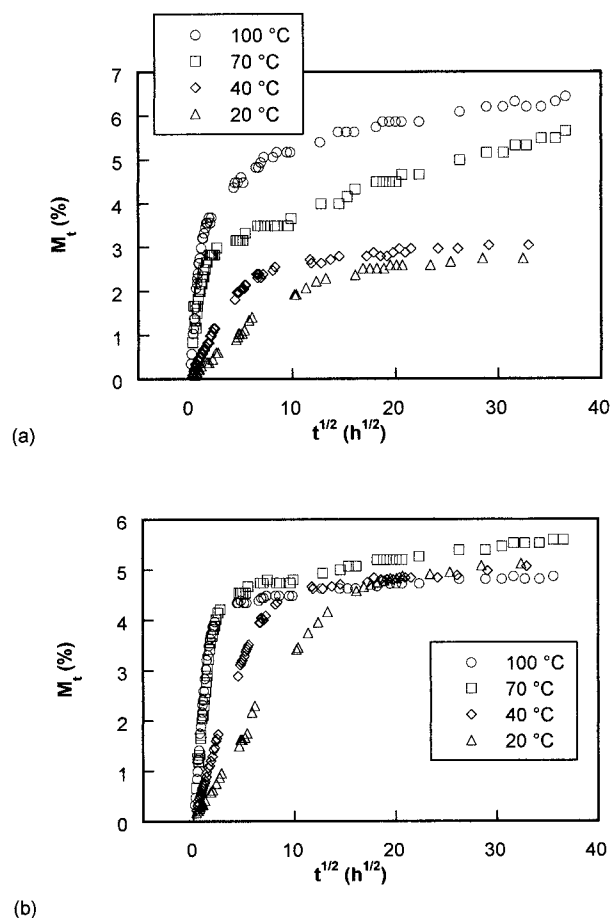


Figure 1 Sorption curves at various temperatures ($^\circ\text{C}$): (a) cure 1; (b) cure 3.

RESULTS AND DISCUSSION

Water-diffusion Studies

To correlate the structure of the epoxy network with its water-transport properties, experiments of water sorption in both cure 1 and cure 3 materials were made at 20, 40, 70, and 100°C . Cures 1 and 3 structures were expected to be quite different in comparison with the intermediate cure 2. Moreover, cure 2 sorption parameters at 100°C were calculated to form a contrast with those of cures 1 and 3, due to the dynamic mechanical response of cure 2 and the superior mechanical properties observed in the whole experimental work.

Figure 1(a,b) shows sorption curves at each temperature for cures 1 and 3, respectively. M_t is the percentage of weight gain due to water sorption and was plotted versus the square root of the time of exposure. Each curve was fitted applying

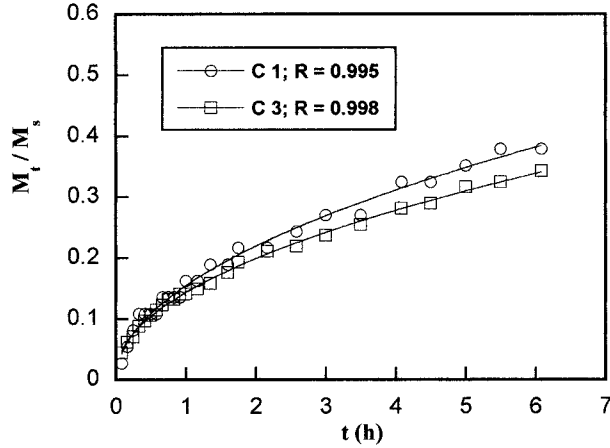


Figure 2 Fitted curves to eq. (1) for both cures of sorption experiments at 40°C.

eq. (1) to investigate the diffusion behavior observed. Good fits for $\alpha = 1/2$ were obtained, with correlations better than 0.99. Figure 2 shows the fit to eq. (1) for both cures in the initial stage of the sorption curves at 40°C.

Therefore, the system showed Fickian behavior, and the Fick's second law with a constant diffusion coefficient or diffusivity, D , was applied to obtain the parameters of diffusion. For one-dimensional diffusion through an infinite plate of thickness L , Fick's second law reduces to

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad (2)$$

where c is the water concentration; t , the time; and D , the diffusivity through the thickness of the material. Simplified solutions of eq. (2) by Crank¹³ showed that for the initial stage of the sorption process, that is, $Dt/L^2 \ll 0.05$ or $M_t/M_s < 0.6$, the following relation can be applied:

$$\frac{M_t}{M_s} = \frac{4}{\sqrt{\pi L}} \sqrt{Dt} \quad (3)$$

where M_s is the equilibrium water-saturation level for a particular sorption temperature. The plots of eq. (3) should be linear up to $M_t = 0.6 M_s$ with less than 2% deviation for true Fickian diffusion.¹⁵ The diffusivity values were calculated from the initial slope of these plots for all sorption curves.

Further, the diffusion coefficient exhibited a dependence on temperature that follows an Arrhenius relationship, given by

$$D = D_0 \exp\left(\frac{-E}{RT}\right) \quad (4)$$

where D_0 is the constant preexponential coefficient; R , the gas constant; T , the absolute temperature; and E , the activation energy for diffusion. A linear fitting of $\ln D$ versus the reciprocal of absolute temperature $1/T$ was used to determine the activation energy for each cure.

Table I lists the values of the diffusion parameters D , M_s , and P for each cure and temperature. P is the permeability, calculated¹⁶ as the product of D and M_s . The activation energies are given for each cure and agree with the range of the values reported by Loos and Springer¹⁷ for most polymers and their composites.

The following facts must be outlined from the data obtained: The diffusivity D and the permeability P of the system increased with temperature for both cures. These parameters are directly related to the rate of water diffusion in the network structure. At low temperatures, the differences between cures did not appear to be significant, but at high temperatures, the rate of diffusion in cure 3 was significantly increased.

Also, the saturation levels M_s were increased with temperature for cure 1, while in cure 3, this parameter did not show significant changes with temperature. The M_s values were higher in cure 3 at low temperatures, and only when the temperature was increased did cure 1 samples reach comparable or slightly superior levels.

Table I Parameters of Water Diffusion

T (°C)	Cure 1 $E = 28.3$ kJ/mol			Cure 3 $E = 47.7$ kJ/mol		
	M_s (%)	D ($\times 10^{-12}$ m ² /s)	P ($\times 10^{-14}$ m ² /s)	M_s (%)	D ($\times 10^{-12}$ m ² /s)	P ($\times 10^{-14}$ m ² /s)
20	2.74	0.15	0.41	5.12	0.12	0.61
40	3.05	0.43	1.31	5.06	0.46	2.33
70	5.32	0.57	3.03	5.52	1.39	7.67
100	6.21	2.32	14.41	4.82	9.25	44.58

The water-transport rate in epoxy resins is expected to increase with temperature, as was observed in this system. The activation energy is needed for transport processes since the water molecules have to overcome the energy barriers set up by the interaction potential from intramolecular forces. The higher value of the activation energy in cure 3 is related to the different network structures caused by the cures.

In previous work,¹¹ the existence of a heterogeneous structure in cure 1 was revealed, with a phase of unreacted and/or partially reacted material together with a minor phase of highly crosslinked material. Cure 3 revealed a more homogeneous network of a highly crosslinked phase. The conversion in cure 1 was about 0.70 and the glass transition temperature, T_g , was 172°C; both the conversion and T_g were near their maximum experimental values for this system in cure 3, being 0.92 and 251°C, respectively. Thus, the superior activation energy for cure 3 is attributed to the higher crosslink density of the network, which diminished the availability of molecular-sized holes in the polymer structure.

Therefore, changes in the epoxy microstructure as a result of the different curing treatments impacted the water diffusion in this material. The different behavior for the material with cures 1 and 3 cannot be explained just with free-volume considerations, which predict a higher water uptake in the materials with less crosslink density, independently of the temperature.¹⁸ In fact, water uptake was higher in cure 3 at low temperatures compared to cure 1.

The diffusional behavior observed might be explained by a combination of two factors: one of them, the unoccupied molecular volume of the epoxy resin. The second one, the polymer–water affinity due to the hydrophilic centers of the network. The increment in the crosslink density will produce lower water-absorption levels. Also, regions of high density might severely hinder water diffusion, due, at least in part, to the inaccessibility of hydrogen-bonding sites.^{6,19,20}

Temperature will affect the mobility in the low-density regions more than in the highly crosslinked regions. Thus, increasing temperature would have a larger effect on water diffusion in samples with higher contents of low-density material. The progressive increments of water-uptake levels with temperature in cure 1, the material with the lower crosslink density, seem to be related to this fact.

To explain the behavior observed in cure 3, it is necessary to take into account the epoxy–water

affinity of this epoxy-rich formulation. The previous work about cure kinetics⁹ showed that for the material being vitrified the epoxide–amine reaction was virtually complete, regardless of temperature, but the epoxide–hydroxyl reaction was only partially complete and dependent on the curing temperature.

The high curing temperature in cure 3 promoted etherification reactions, providing an additional source for the consumption of epoxide groups and thus modifying the distribution of various functional groups inside the epoxy network, that is, the presence of unreacted amine groups, with a highly polar nature. Apicella et al.⁴ reported increasing water sorption in epoxy–amine systems with higher unreacted secondary amine group content.

Therefore, the strong water affinity of this system because of the polar hydroxyl (—OH) groups created by the epoxy–amine reactions might be intensified by unreacted amine groups and hydroxyl–ether units as a consequence of etherification reactions. The superior water-uptake levels in cure 3 at low temperatures would be related to its highly polar structure.

The formation of the bond between —OH groups and water requires breaking of the intramolecular hydrogen bonds between the polar groups of the resin, but this hydrophilic procedure can take place only at low temperatures, when the hydrogen-bond formation is thermodynamically preferable.²¹ Thus, at 70 and 100°C, the epoxy–water molecule interactions will be reduced, but the effect of temperature on the molecular mobility will speed up the diffusion processes, that is, the water transport in the free volume of the network.

Effects of Absorbed Water on Viscoelastic Behavior

The hydrogen bonds between the water molecules and the polar hydroxyl groups of the network will disrupt the interchain hydrogen bonding. The molecular structure is thus altered, the results of which are often observed as dimensional changes and reductions in T_g values.⁶

Results on the cure 2 material showed a high conversion and a T_g of 211°C, but the curing temperature of 180°C was not high enough for the etherification reactions to become significant. Water-sorption experiments at 100°C were made, and values of 4.87% and 5.01×10^{-12} m²/s were obtained for M_g and D , respectively. The similar water-saturation level and a lower diffusivity

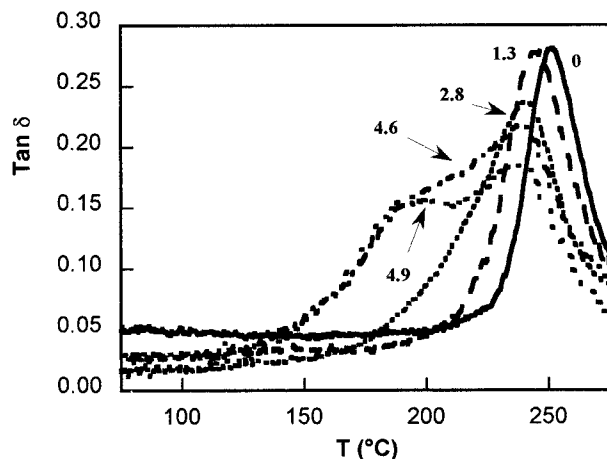


Figure 3 DMA curves for cure 3 with various water contents: 0, 1.3, 2.8, 4.6, and 4.9 wt %.

than those of cure 3 suggested a diminishing effect of the water–epoxy interactions and an increased effect of the transport in the free volume, so as to produce a similar water-uptake level. For this reason, this material was selected to compare the influence of the two factors proposed on the water-sorption processes.

Samples of cures 2 and 3 were immersed in water at 100°C, and dynamic mechanical tests were made for various water contents. Figure 3 shows $\tan \delta$ curves for cure 3 with 0, 1.3, 2.8, 4.6, and 4.9 wt % water. Figure 4 shows the $\tan \delta$ curves for cure 2 with 0, 1.7, 2.9, and 3.8 wt % water.

Table II lists the dynamic mechanical parameters related to the glass transition region: The glass transition temperature, T_g , was obtained from the $\tan \delta$ peaks, the height of the damping peak, h_{ω} , and the rubber plateau storage modulus, E'_r , taken at a T_g of +40°C. In Figures 3 and 4, a decrease in the peak of $\tan \delta$ and a shift to lower temperatures of the glass transition region with an increase of the water contents can be observed. This behavior is often referred to as a plasticizing effect of water on the polymer.²²

Nevertheless, the broadening of secondary $\tan \delta$ peaks in the glass transition region followed a different trend in each cure. For cure 3 (Fig. 3), the height of the secondary peaks, about 200°C, was less than the height of the main peaks at the higher temperatures. But for cure 2 (Fig. 4), the behavior was just the opposite, with the height of the lower-temperature peaks larger than that of the high-temperature peaks.

This behavior is better observed if the $\tan \delta$ signal for each water content is shifted under the

area of the $\tan \delta$ peak of the dry material, making the higher-temperature peaks coincide with the temperature of the reference peak of the dry material. This procedure was performed in Figure 5(a,b) for cures 3 and 2, respectively.

These figures revealed that while the $\tan \delta$ height was diminished in the region of the glass transition temperature of the dry material a net increment of $\tan \delta$ values in the temperatures below the T_g of the dry material had existed. This effect cannot be explained only in terms of water as a plasticizing agent. The increase in $\tan \delta$ values was observed by some authors in epoxy–amine systems with the sorption of water or other polar solvents.^{7,23}

An explanation based on the two factors previously discussed, that is, the free volume and the epoxy–water interactions, could explain the behavior observed. The rupture of the interchain hydrogen bonding by water molecules would produce an increment of the chain mobility during the glass transition region and a reduction in the effective crosslink density of the material. An increment of $\tan \delta$ height values and a reduction of the rubbery plateau moduli, E'_r , should be expected. Thus, the stronger the water–polymer interactions, the greater the increments of $\tan \delta$ and the reductions in E'_r values.

We developed a method to compare the differential area enclosed between $\tan \delta$ curves with a given water content and the curves of the reference dry material. Figure 6(a,b) shows the results for cures 3 and 2, respectively. With a similar water content, the effect of water interactions on the dynamic mechanical response is stronger for cure 3, with a higher differential area. Another

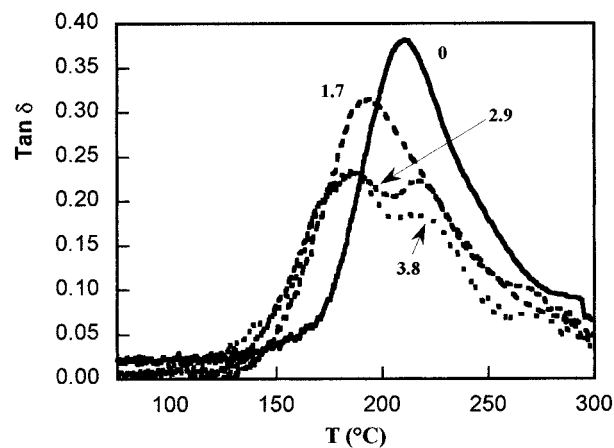


Figure 4 DMA curves for cure 2 with various water contents: 0, 1.7, 2.9, and 3.8 wt %.

Table II Effect of Water Sorption on the Dynamic Mechanical Properties

Cure 3				Cure 2			
M_t (%)	T_g (°C)	h_α	E'_r ($\times 10^7$ Pa)	M_t (%)	T_g (°C)	h_α	E'_r ($\times 10^7$ Pa)
0	251	0.286	7.28	0	211	0.405	3.47
1.3	245	0.285	5.08	1.7	193	0.325	3.89
2.8	240	0.241	3.17	2.9	185	0.237	2.88
4.6	238	0.224	4.12	3.8	185	0.236	2.88
4.9	237	0.187	3.92	4.3	177	0.237	3.06

factor to take into account is the important decrease in E'_r values for cure 3 (see Table II), which leads to the same conclusion.

The ordinary water sorption in the free volume of the network would hinder the chain mobility and an overall reduction in $\tan \delta$ values should be expected. Thus, the more important this sorption mechanism, the greater is the reduction in $\tan \delta$

values. This reduction should be more significant in cure 2.

The $\tan \delta$ height for a 4.9% water content reached 65% of the dry material maximum peak for cure 3. In cure 2, the height was only 43% with a similar water uptake, as a result of the lesser crosslink density of cure 2. In this cure, the water sorption in the free volume of the

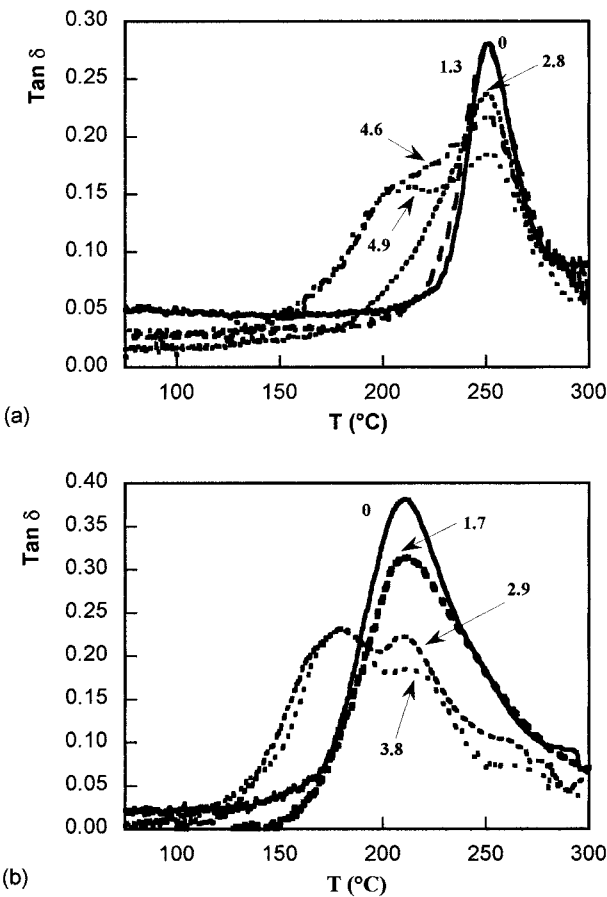


Figure 5 DMA curves shifted along the temperature axis: (a) cure 3; (b) cure 2.

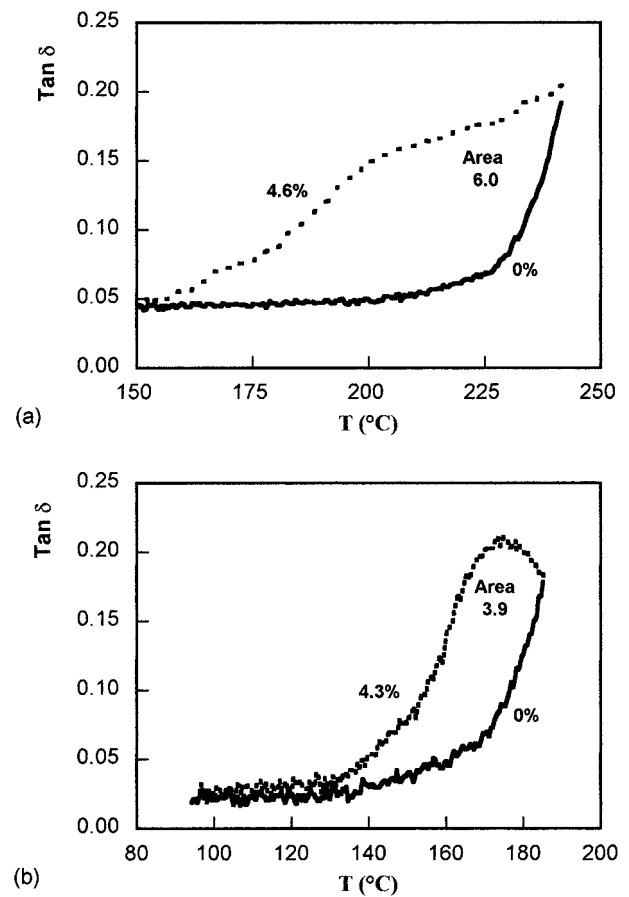


Figure 6 Differential area enclosed between $\tan \delta$ curves: (a) cure 3; (b) cure 2.

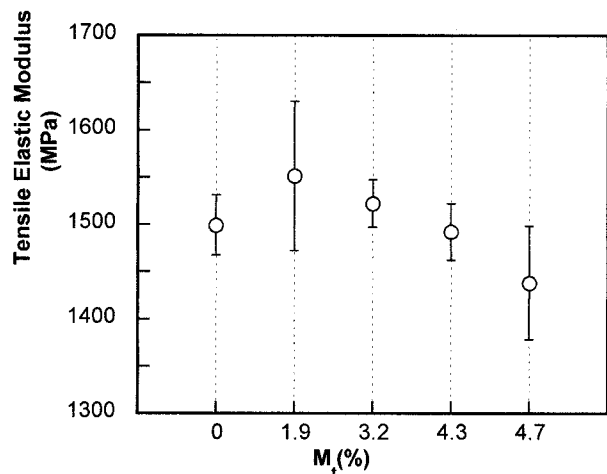


Figure 7 Tensile elastic modulus (MPa) with the water content; cure 2.

network was more significant, the water–polymer interactions were not so strong, and the combined effect originated a similar water-saturation level as in cure 3.

Effect of Absorbed Water on the Mechanical Properties

Tensile stress–strain tests for samples with increasing water contents were made to determine properties such as tensile stress at break (σ_B), percent elongation at break (ϵ_B), tensile elastic modulus (E), and tensile toughness, calculated as the area under the stress–strain curves and representing the energy absorption to break.

The measurements were made on cure 2 material, because of its superior mechanical behavior.¹¹ No yield points were observed on the stress–strain curves, so the tensile strength was the same as σ_B .

In addition to the tensile properties, Rockwell hardness was also evaluated. Results were obtained using the Rockwell E scale. Rockwell numbers are directly related to the indentation hardness of the material, with the higher the reading the harder the material.

The average results of the mechanical properties are plotted with their standard deviations against water uptake, M_t (%), shown in Figures 7–11. An overall reduction in the mechanical properties is seen, increasing the fragility of the material with the water content. The plasticizing effect of water can be related to the slight decrease in the hardness numbers and in the elastic moduli.

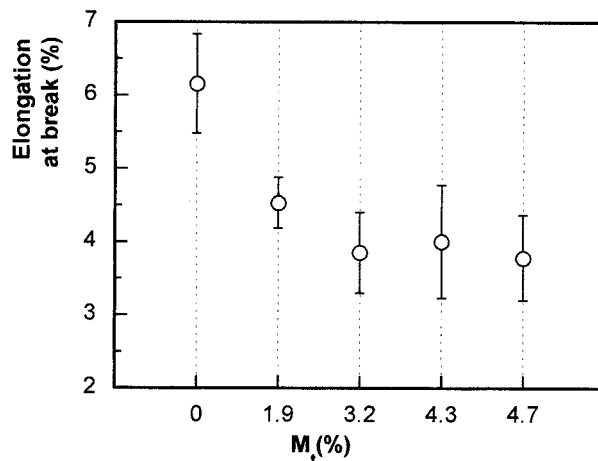


Figure 8 Elongation at break (%) with the water content; cure 2.

Nevertheless, relative increases, both in the tensile modulus (see Fig. 7) and in the rubbery plateau modulus E'_r (see Table II), were observed with water uptake of about 1.9%, in cure 2. This fact could be explained in terms of a reactivation of curing reactions with the water temperature, 100°C, for times of 24 h.

The larger variations occurred in the properties at break. For the highest water content, that is, 4.7%, the toughness was 40% of the dry material, and the stress at break and tensile strength were about 65% of their initial values. Plasticization and reductions in the mechanical strength were reported by other authors.^{24,25}

A significant decrease in the properties was produced during the initial stages of the diffusion

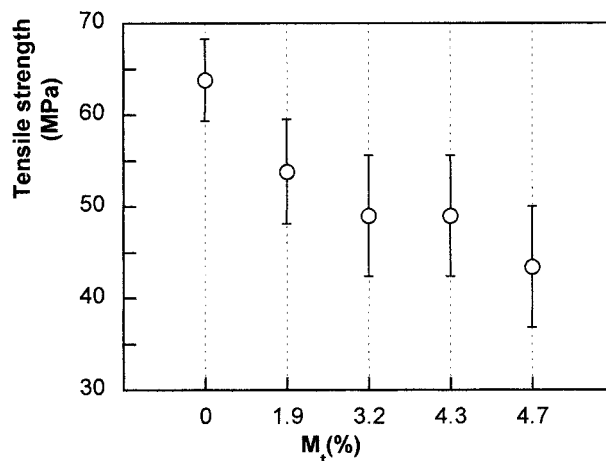


Figure 9 Tensile strength (MPa) with the water content; cure 2.

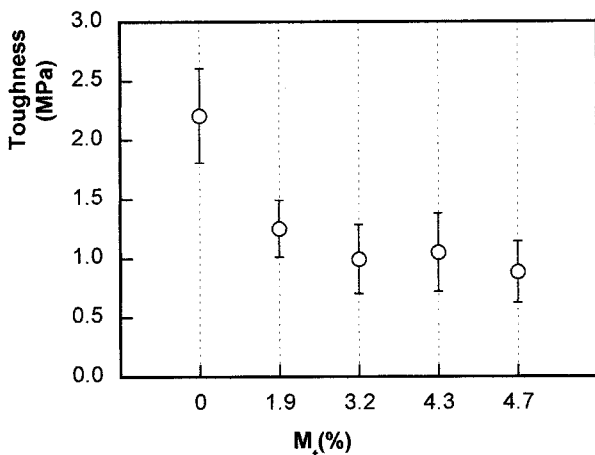


Figure 10 Tensile toughness (MPa) with the water content; cure 2.

process up to a water uptake of about 3%. For higher water contents, the properties seemed to stabilize. This initial decrease in properties suggests that the interactions between water and the polymer would be a fast and strong phenomenon, which reached an apparent stability at the early stages of diffusion. After the absorption of water molecules at the primary hydration sites, the strong hydrophilic character of the network was lost and a relative stabilization was produced.

CONCLUSIONS

Water-sorption experiments at various temperatures and DMA were undertaken to investigate

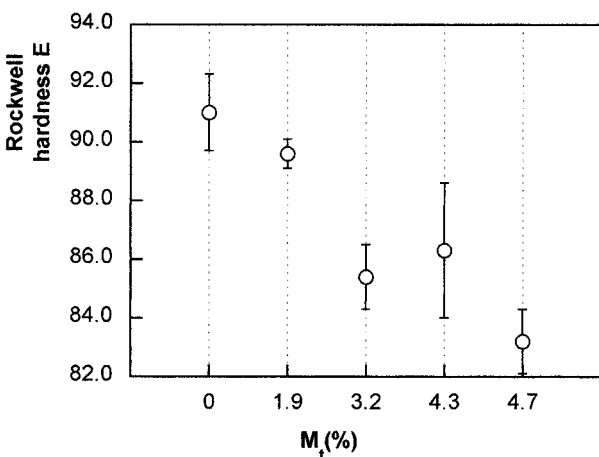


Figure 11 Rockwell hardness E number with the water content; cure 2.

Table III Cure Processes and Hydrophilicity

Cure Process	Conversion α	Hydrophilicity P ($\times 10^{-14}$ m ² /s)
Cure 1	0.65–0.70	14
Cure 2	0.79–0.82	24
Cure 3	0.92–0.95	44

the characteristics of the sorption and diffusion of water in the network structures arising from different curing schedules of a TGDDM/EPN/DDS epoxy system. The experimental results of diffusion showed an overall diffusion process following Fickian behavior, and the parameters for Fickian diffusion were determined. Also, the effect of the water absorbed on the tensile properties and the indentation hardness of the material was evaluated.

Changes in the epoxy microstructure, as a result of the different curing treatments, impacted the water diffusion in the material. Table III summarizes the cure processes, the range of conversion values¹¹ (where the variation due to the different experimental techniques employed, DSC and DMA, was considered), and the hydrophilicity at 100°C, estimated as the permeability parameter P , which includes both the water-saturation level and the rate of diffusion.

The highly crosslinked cure 3 material showed large water-uptake saturation levels at low temperatures, due to the strong hydrophilic character of the network arising from the etherification reactions during the curing processes at high temperatures. Also, higher activation energy for diffusion was required, as a consequence of the higher crosslink density of the material.

Temperature was an important factor that increased the rate of diffusion, that is, D and P values. The diffusivity followed an Arrhenius behavior. Also, the progressive increment of the water uptake M_s level in the lower crosslink density material, cure 1, was related to the increasing temperature that significantly influenced the molecular mobility. The values of M_s on cure 3 did not show the same trend, because of restrictions to the mobility of a higher crosslinked network.

Thus, to prevent high water-uptake levels at room temperatures in a TGDDM/EPN/DDS system, the factors that contributed to the hydrophilic character of the network should be avoided, for example, the existence of unreacted amine groups or the etherification reactions arising from

curing at high temperatures. It would be better for higher crosslinking to achieve a balance of curing times and temperatures.

DMA was a sensitive tool to observe the effects of water on the material structure, as well as to determine the variations in the viscoelastic properties. Increasing values of the $\tan \delta$ height at temperatures below the T_g of the dry samples were related to the changes in the effective crosslink density of the system caused by the polar water-polymer interactions. The reductions in the effective crosslink density increased the distribution of molecular weights participating in the glass relaxation and caused the observed broadening of the $\tan \delta$ peaks in the glass transition region to lower temperatures, that is, longer relaxation times.

The overall reductions in $\tan \delta$ values with increase in the water content and the shift of T_g to lower temperatures is often attributed to the plasticizing effect of water, but it should be pointed out that it could be related to the ordinary sorption of water in the free volume of the network, that is, unbound water. DMA results showed a higher decrease of $\tan \delta$ peaks and a larger shifting in T_g values for the cure 2 material, with a lower crosslink density, that is, a higher availability of molecular-sized holes.

The mechanical properties were also affected by the water uptake. A general reduction in the tensile properties at break was observed. The major changes occurred in the earlier stages of diffusion, up to water contents of 3%. A possible saturation of the stronger hydrophilic groups with a reduction of the water-polymer interactions could take into account this relative stabilization for higher water contents. The small losses in the tensile elastic moduli E and in the indentation hardness could be caused by the plasticizing effect of water.

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