# Influence of Water Absorption on the Mechanical Properties of a DGEBA (n = 0)/1, 2 DCH Epoxy System

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Received 13 October 1998; accepted 27 February 1999

**ABSTRACT:** The diffusive, calorimetric, and mechanical behavior of a system composed of a diglycidyl ether of bisphenol-A (DGEBA, n = 0) and 1, 2 diamine cyclohexane (1, 2 DCH) were investigated during water sorption at different temperatures (23, 47, 58, 77, and 100°C). Experimental results showed that the water absorption at these temperatures fitted well to Fick's law. The water moisture content at the equilibrium temperature and the water moisture content at the equilibrium-curing conditions dependences have been checked. The activation energy for diffusion was calculated obtaining a value 26.01 kJ/mol. Dynamic mechanical analysis of several samples immersed in water at 100°C during different periods of time showed no significant changes in the glass transition temperature, and a decrease in the storage modulus at 2% of water content was observed. Storage modulus remained essentially constant above that water content. Values of glass transition temperature were corroborated by differential scanning calorimetric measurements. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 353–358, 1999

Key words: water absorption; diffusion; DMA; DSC; gravimetry

# **INTRODUCTION**

Because of the highly polar nature of the specific functional group of epoxy resin, water can exist as bound water, characterized by strong interactions with the matrix, and as free water present in capillaries and microvoids within the polymer. The presence of water in a polymer (e.g., epoxy resin) can lead to marked changes in the resin chemical and physical state. Morgan et al.,<sup>1</sup> Pryde et al.,<sup>2</sup> and Apicella et al.<sup>3</sup> have reported that absorbed water in an epoxy can lower  $T_g$  (by as much as 20°C) and elastic modulus E'. In fact, sorption water may act as a plasticizer and crazing agent for epoxies. Knowledge of the mechanisms that drive moisture sorption, as well as of

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Journal of Applied Polymer Science, Vol. 74, 353-358 (1999)

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the influence of sample dimensions, temperature, and relative humidity, becomes crucial when long-term properties of the material are needed.

For this study, we chose a system consisting of an epoxy resin, diglycidyl ether of bisphenol A (BADGE, n = 0) and 1, 2 diamine cyclohexane (DCH) as the curing agent. This system was chosen because of its high reactivity in a wide range of temperatures. In two previous articles,<sup>4,5</sup> the kinetics of cure and TTT diagram of this epoxy system were studied by DSC.

In this paper, we studied the water sorption by this system. The objective of this investigation was twofold: first, a dynamic mechanical analysis, from which the effect of water sorption on parameters as E' and  $T_g$  can be seen, and second, a study of the water diffusion process.

Although the sorption processes of liquids and vapor in glassy polymers follow complex mechanisms, water diffusion in epoxy resin matrices has frequently been represented by Fickian behavior. If a polymer is exposed to a fluid, the change in concentration C of a diffusing substance as a function of time t and position x is given by Fick's second law:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \tag{1}$$

where D is the diffusion coefficient.

# **EXPERIMENTAL**

#### **Materials**

BADGE (n = 0) was the epoxy resin used (Resin 332, Sigma Chemical Co, St. Louis, MO), and 1, 2 diamine cyclohexane (DCH, Fluka) was the curing agent. The epoxide equivalent weight of the resin was 173.6, as determined by wet analysis,<sup>6,7</sup> and that of the diamine was taken as 28.5.

### **Sample Preparation**

The epoxy resin and the curing agent were carefully and homogeneously mixed, at stoichiometric ratio, before being introduced into a cylindrical frame. Curing reaction was programmed according to a TTT diagram previously described for this material.<sup>5</sup> It consists of two stages: a first step, at 23°C over 24 h and a second one in a stove, at 77°C, over 16 h (postcure). After curing, the samples were removed from the frame. For diffusion experiments, samples were prepared in the form of discs of about 0.3-mm thickness that were introduced in flasks containing water, and were kept there for different periods of times, at different temperatures (23, 47, 58, 77, and 100°C), before being studied. Samples of 15 to 20-mm length were used to study dynamic mechanical properties at 100°C. For calorimetric analysis (DSC), samples were 20 to 25 mg in weight and 6-mm in diameter.

### Dynamic Mechanical Analyzer

Dynamic mechanical properties were measured by a Perkin–Elmer DMA7 operated in the threepoint bending horizontal measuring system. The DMA was calibrated using indium as a standard. The experiments were carried out in a temperature range from 30 to 250°C. Experimental conditions were: dynamic force (700 mN), static force (750 mN), number of points to be determined in the chosen temperature range (500), heating rate (10°C/min). Before starting every experiment, the equipment was stabilized at 30°C. All the experiments were carried out at a fixed 1-Hz frequency.

#### **Differential Scanning Calorimeter**

A Perkin–Elmer DSC7 unit, under control of a 1020 system controller, was used for calorimetric measurements. The experiments were carried out in a temperature range from 5 to 250°C at a heating rate 10°C/min. Because of the low range temperature necessary for the performance of measurements, a cooling device (Intercooler II supplied by Perkin–Elmer) was adapted to DSC-7 equipment. Because of the wide temperature range used in this study, the calorimeter was calibrated using two standars (indium and bidistilled water obtained by the milipore method).

## **RESULTS AND DISCUSSION**

#### Water Diffusion Study, Thermogravimetric Analysis

Water diffusion in epoxy resin matrices has frequently been represented by a Fickian behavior (Fick's second law), whose mathematical expresion is represented by Eq. (1). The total amount of substance diffusing in the polymeric material  $M_t$ as a function of time is given by the integral of the solution of eq. (1) across the thickness h.

$$\frac{M_t}{M_{\text{max}}} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \\ \times \exp\left[-D(2n+1)^2 \frac{\pi^2 t}{h^2}\right]$$
(2)

where  $M_{\rm max}$  is the maximum quantity of the diffusing substance at infinite time.

The curve can be divided in two parts:

If  $Dt/h^2 > 0.05$ , eq. (2) can be rewritten as the following expression:

$$\frac{M_t}{M_{\text{max}}} = 1 - \frac{8}{\pi^2} \exp\left[-\left(\frac{Dt}{h^2}\right)\pi^2\right]$$
(3)

If Dt/h  $^2$   $\ll$  0.05 (or  $M_{\it t}/M_{\rm max}$  < 0.6), eq. (2) can be simplified and written as:

$$\frac{M_t}{M_{\rm max}} = \frac{4}{h\sqrt{\pi}} \sqrt{Dt} \tag{4}$$

The diffusion coefficient can be calculated from the slope of the linear region of the diffusion curve, that is obtained fitting experimental values of water uptake  $M_t$  (%) versus  $t^{1/2}$ .

The  $M_t$  (%) values were obtained from the water uptake of three samples after exposure to identical conditions. The relative weight increase in each one was calculated as:

$$\Delta m_{t_i} = \frac{m_{t_i} - m_{0_i}}{m_{0_i}} \, 100 \tag{5}$$

and the average weight increase as:

$$M_t(\%) = \frac{\sum_{i=1}^3 \Delta m_{t_i}}{3}$$
(6)

To present results, it was considered that  $M_t$  (%) is affected by an error equal to the double of the standard deviation value  $2\sigma(M_t)$ .

Diffusion behavior of BADGE n = 0/1, 2 DCH at different water temperatures is shown in Figure 1, where experimental measurements of  $M_t$ (t) against  $t^{1/2}$  are shown. As can be seen, the behavior is similar to that predicted by Fick's law. The features of Fickian diffusion have been described by Fujita<sup>8</sup>: (1) sorption curves are linear in the initial stages; (2) above the linear portions, sorption curves are concave to the abscissa axis; and (3) reduced sorption curves, plotted for films of different thickness, are superimposables. Our experimental results reasonably fulfilled these criteria.

The experimental curves were plotted up to the beginning of the equilibrium plateau (three experimental points with similar values within the



**Figure 1** Diffusion behavior of BADGE (n = 0)/1, 2 DCH at different water temperatures.

Table I Equilibrium Water Uptake at DifferentTemperatures

<i>T</i> (°C)	$M_{ m sat}\left(\% ight)$	$2\sigma(M_{\rm sat})$
23	0.952	0.019
47	1.478	0.072
58	2.057	0.030
77	2.656	0.057
100	2.847	0.028

limits of experimental error). Fitting of experimental data results in curves shown in Figure 1. The arrows on every curve indicate the last experimental point taken for each temperature. From these points, a fitting to Fick's equation was made at each temperature. Except for one (23°C, R = 0.987), correlations were better than 0.99, thus indicating a Fickian behavior. Shape of the curves suggest that the arrow indicated points correspond to the beginning of the quasiequilibrium stages.

In the first steps, the diffusion behavior is strongly influenced by temperature; as conditioning temperature is increased, the diffusion process speeds up. The equilibrium water uptake and its errors are listed in Table I. It can be seen that at low temperatures, the saturation value is around 1%. Moy et al.<sup>9</sup> and Jelinski et al.<sup>10</sup> have predicted that water is essentially bound water below this value. The increase of excess water uptake caused by microvoiding has been found to be progressively more relevant as the temperature is increased. This observation is in line with the low energies for craze formation required at high temperatures.

As Loos et al.<sup>11</sup> and Moy et al.<sup>9</sup> have shown, we checked that diffusion behavior is extremely sensitive to curing conditions. We studied the difussion process at 47°C in samples that were cured simultaneously and at 23°C in samples corresponding to different curing series. Although for the test performed with samples cured at 47°C, the diffusion curves are superimposable, the study of samples cured at 23°C shows that the diffusion rate is greatly influenced by the curing conditions. These behaviors are shown in Figures 2 and 3.

From the linear fits in the first step of the  $M_t$  (%) versus  $t^{1/2}$  curves (Fig. 4), the diffusion coefficients were calculated by means of the following expression:



Figure 2 Water diffusion at 23°C for two different series of curing.



where m is the slope of these fittings.

The diffusion coefficients at the different water temperatures are summarized in Table II. As can be seen, the diffusion coefficients rise as the water temperature increases. An increase of the conditionating temperature significantly reduces the time required to reach the equilibrium moisture content. Barral et al.,<sup>12</sup> Moy et al.,<sup>9</sup> and Loos et al.<sup>11</sup> checked the same behavior for similar systems.

From data shown in Table II, and assuming a Fickian behavior of water diffusing into the system, an Arrhenius-like equation can be used to



Figure 3 Water diffusion at 47°C for two similar series of curing.



**Figure 4** Linear regions of the water diffusion curves at the different temperatures.

calculate the diffusion activation energy. This equation is

$$D = D_0 e^{-(E_a/RT)} \tag{8}$$

where  $D_0$  is a pre-exponential factor,  $E_a$  is the activation energy, R is the gas constant, and T is the absolute temperature.

Taking logarithms in Eq. (8)

$$\ln D = \ln D_0 - \frac{E_a}{R} \frac{1}{T}$$
(9)

A linear fitting of  $\ln D$  against 1000/T (Fig. 5) gives a slope  $E_a/R$ , from which activation energy can be determined. The activation energy obtained was 26.01 ± 1.66 kJ/mol. Apicella et al.<sup>3</sup> and P. Nogueira<sup>13</sup> obtained values of 41.8 kJ/mol and 25.8 kJ/mol for similar systems.

#### **Calorimetric and Dynamic Analysis**

To study the effect of water taken up by the BADGE n = 0/1, 2 DCH system, several samples

Table 1	II	Diffusion	Coefficients	at	Different
Water	Ten	operature	s		

<i>T</i> (°C)	$D \over (10^{-12} \text{ m}^2/\text{s})$	$S(D) \ (10^{-12} \text{ m}^2/\text{s})$
23 47 58 77	$1.18 \\ 2.46 \\ 3.86 \\ 7.23$	0.40 0.66 1.19 2.25
100	10.72	3.38



**Figure 5** Water diffusion coefficient versus the reciprocal temperature.

were immersed in water at 100°C during different periods of time. In our system, the equilibrium value was around 3%. To prevent water desorption from the samples during dynamic tests, they were coated with silicon vacuum grease.<sup>13</sup>

The behavior of the storage modulus versus the increase of sorbed water is shown in Figure 6. It can be observed that E' decreases as the water uptake increases because of the plasticizing effect produced by water.<sup>12,14</sup>

A plot of  $T_g$  values versus water uptakes is shown in Figure 7. As can be seen,  $T_g$  values stay almost independent of the percentage of equilibrium moisture absorption. Our results were corroborated by means of a calorimetric analysis, and a similar behavior was observed. The  $T_g$  values corresponding to the different uptake water contents, measured by DSC, are summarized in Table III. From these values, a difference of 10°C between the DSC and DMA measurements is ob-



Figure 6 Storage modulus versus water uptake.



**Figure 7** Glass transition temperature versus water uptake.

served. This difference was previously predicted by Lee and Peppas,<sup>14</sup> Fraga et al.,<sup>15</sup> and Oleinik et al.<sup>16</sup> As is known, the glass transition temperature measured by dilatometry or DSC is 5–25°C lower than that measured by DMA.

It should be pointed out, as a result of the plasticizating effect originated by the water uptake, that the storage modulus decreases; however, this effect can be considered as negligible, because the glass transition temperature is not affected below the saturation level.<sup>14,17</sup>

# CONCLUSIONS

- 1. The water absorption by the epoxy system BADGE (n = 0)/1, 2 DCH was studied by means of a gravimetric analysis. The water uptaked temperature and water uptaked curing conditions dependences were checked.
- 2. The diffusion coefficients at different temperatures were determined. These coefficients increase as temperature rises, so the time required to reach the saturation level

Fable III	$T_g$ Values to the Different Uptake	ļ
Water Co	ntents, Obtained by DSC	

$T_g$ (°C)	$M_t$ (%)
164.7	0
165.4	1.67
166.2	1.92
164.7	2.50
157.41	SAT

decreases as temperature is increasing. The diffusion activation energy was calculated to be 26.01 kJ/mol.

- 3. A dynamic mechanical analysis on several samples that had been inmersed in water over different periods of time was performed. It was observed that the  $T_g$  values stay almost independent of the percentage of water absorption. The E' values showed a decrease at low percentages, but from a certain value of water absorption, the storage modulus remains esentially constant.
- 4. To corroborate our DMA results, DSC analysis were performed on similar systems. By this method, a small decrease of the glass transition temperature was observed only when saturation level was reached.

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