

# Hygrothermal Aging of Rubber Modified and Mineral Filled Dicyandiamide Cured Diglycidyl Ether of Bisphenol A Epoxy Resin. I. Diffusion Behavior

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**ABSTRACT:** The effect of hydration–dehydration cycling on the properties of a rubber modified, mineral filled epoxy resin is reported. This resin was based on diglycidyl ether of bisphenol A and cured with dicyandiamide. The material was aged in deionized water and a 5% (w/w) NaCl solution at 65°C. Gravimetric measurements, transmission electron microscopy, and diffusive reflectance IR Fourier transform spectroscopy were used to monitor the water sorption and physical and chemical changes occurring in the material. Two-stage absorption was observed with deionized water, and the quasiequilibrium-state water content was independent of the hygrothermal history. The equilibrium weight after dehydration depended on the hygrothermal history due to the presence of irreversibly absorbed water and leaching of material. The first stage of the absorption was found to be Fickian and was interpreted as being related to the process of saturation of the epoxy matrix. The driving force for the second stage was the osmotic pressure, and it was not observed when the material was aged in NaCl solution. The water caused irreversible damage to the resin through microcavity formation, and part of the water was molecularly dispersed in the epoxy matrix and part resided in microcavities. Absorption–desorption cycling resulted in an increased rate of absorption during subsequent rehydration. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 3468–3476, 2001

**Key words:** epoxy resin; two-stage water absorption; microcavity formation; osmotic mechanism; hydration–dehydration cycling

## INTRODUCTION

Epoxy resins are widely used as structural adhesives and as the matrix in composite structures in the formulation of anticorrosive, chemically resistant coatings. The effects of environmental aging, especially at high temperatures and high humidity, on the physical properties of the resin are associated with moisture-induced chemical modification, plasticization, and/or micromechanical

damage. Although plasticization is usually considered a reversible phenomenon, the effects of microcavitation are not.

Apicella and coworkers<sup>1–8</sup> found that the amount of water absorbed by a resin depends on its previous history of exposure to water. Equilibrium weight gains were described as being progressively affected by microcavity formation. The additional weight gain observed when the samples were repeatedly exposed to cyclic changes in humidity and temperature was attributed to moisture entrapped in the microcavities. Filled epoxy resins are more sensitive to microcavitation than unfilled polymers,<sup>6</sup> suggesting that the wa-

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ter may be creating voids at the matrix-filler interface. The subsequent growth of the cavities may occur by degradation of the resin matrix, extraction of soluble components of the resin, or osmosis.

Long-term exposure to water can lead to loss of weight by leaching of the by-products of synthesis, unreacted material, or products of degradation. Degradation may take place by hydrolysis, oxidation, and dehydration reactions at specific locations on the polymer chain.<sup>9</sup> Castaing and Lemoine<sup>10</sup> observed that, when epoxy resins are left in water for an extended period and the immersion media is evaporated, a small residue remains of unclear origin and with an IR spectrum that resembles that of the resin.

If voids in the epoxy resin contain an electrolyte, then the osmotic pressure may be the driving force for their growth into microcracks or microcrazes. For osmosis to occur the resin should behave as a semipermeable membrane (permeable to the water but not to the electrolyte), and cracking would probably be controlled by the rate of water diffusion through the bulk of the resin.

The effect of hydration-dehydration cycling on the absorption behavior of a rubber modified, mineral filled diglycidyl ether of bisphenol A/dicyandiamide (DGEBA/DICY) epoxy adhesive was the object of our study. This system was selected for investigation because it represents the type of formulation that is widely used as a tough structural adhesive. The study attempted to gain insight into the complexity of moisture absorption into such systems. Samples of the epoxy resin were exposed to deionized water and a salt solution at elevated temperature. The water ingress was monitored using gravimetric measurements. In order to link the anomalous diffusion behavior to the variation in the chemical and physical changes of the material, diffusive reflectance IR Fourier transform spectroscopy (DRIFTS) and transmission electron microscopy (TEM) were employed. Subsequent articles will present the dynamic mechanical thermal analysis (DMTA) and dielectric spectroscopy investigation of the hygrothermal aging of this material.

## EXPERIMENTAL

### Materials and Sample Preparation

The material used was a DGEBA-based epoxy resin that was toughened with carboxyl-terminated butadiene-acrylonitrile rubber, filled with

fumed silica and calcium silicate, and cured with DICY. The total filler content, determined from combustion, was  $17.67 \pm 0.05$  wt %. The material was molded in the form of 105-mm diameter, 2.6  $\pm 0.2$  mm thickness disks and cured for 30 min at 170°C and a pressure of 5.75 MPa. The initial heating rate was 5°C/min and a pressure of 1.15 MPa/min was applied to the mold after the cure temperature had reached 170°C. All of the generated disks were dried in an oven at 50°C for 1 month, and then a 40  $\times$  40 mm sample was cut from each disk. These samples were used for the gravimetric and dielectric measurements. The remaining material was cut into 30  $\times$  10 mm samples, which were subjected to DMTA. Each set of data was obtained using samples cut from a single disk.

### Exposure Procedure

Prior to aging, the thickness and weight of each of the samples were determined. The thickness was estimated by averaging several micrometer measurements taken across the sample. The samples were aged by being immersed in deionized water or a 5% (w/w) solution of NaCl in sealed jars maintained at a constant temperature of 65  $\pm$  1°C in an electronically controlled oven. The water solution was replaced weekly, and tests showed that the pH of the water and solution remained at about 6.0. Gravimetric measurements were performed on a regular basis during the aging study. The samples were removed from the container, dried superficially, and cooled to ambient temperature prior to the measurements.

The samples were removed from the deionized water and salt solution at selected times and placed in an oven with silica gel at 65°C to allow desorption of water. After reaching an equilibrium weight, selected samples were rehydrated and then redried.

The hygrothermal history of the samples is given in Table I. Samples A, B, and C were aged in deionized water. Samples D, E, and F were aged in 5% (w/w) NaCl solution.

### Gravimetric Measurements

The weight of the samples was determined using a Mettler AJ100 electronic balance with an accuracy of  $\pm 0.1$  mg. The times required for the weighing of the samples were considered sufficiently short for water evaporation or absorption not to be significant. As revealed later, there was no noticeable scatter in the weight data curves,

**Table I Aging History of Samples Exposed to Deionized Water (A-C) or Aged in 5% (w/w) NaCl Solution (D-F)**

Sample	Sorption Cycle I		Sorption Cycle II	
	Hydration Time (h)	Dehydration Time (h)	Hydration Time (h)	Dehydration Time (h)
A	74	280	4000	400
B	163	420	5100	445
C	7250	430	—	—
D	74	280	7050	330
E	152	280	6850	330
F	7700	330	—	—

confirming the high accuracy of the measurements. Further, repetition of the experiment with another batch of the polymer gave good agreement with the previous results. The percentage of water content was defined as the weight of water absorbed at a certain moment in time per unit weight of dry polymer, which is multiplied by 100:

$$\text{water content} = \frac{W_t - W_{\text{initial}}}{W_{\text{initial}}} \cdot 100 \quad (1)$$

where  $W_t$  is the weight of the sample at a certain moment of time and  $W_{\text{initial}}$  is the initial weight of the sample.

### TEM Analyses

The TEM observations were carried out on ultra-thin cross-sectioned samples. The samples were prepared by sectioning the epoxy films using an Ultracut (Reichert-Jung) ultramicrotome supplied with a diamond knife. The samples with thicknesses of less than 1000 Å were mounted on a copper grid for subsequent TEM analyses, which were carried out using a Jeol 2000FX transmission electron microscope operating over a range of accelerating voltages from 200 to 80 kV.

### DRIFTS Measurements

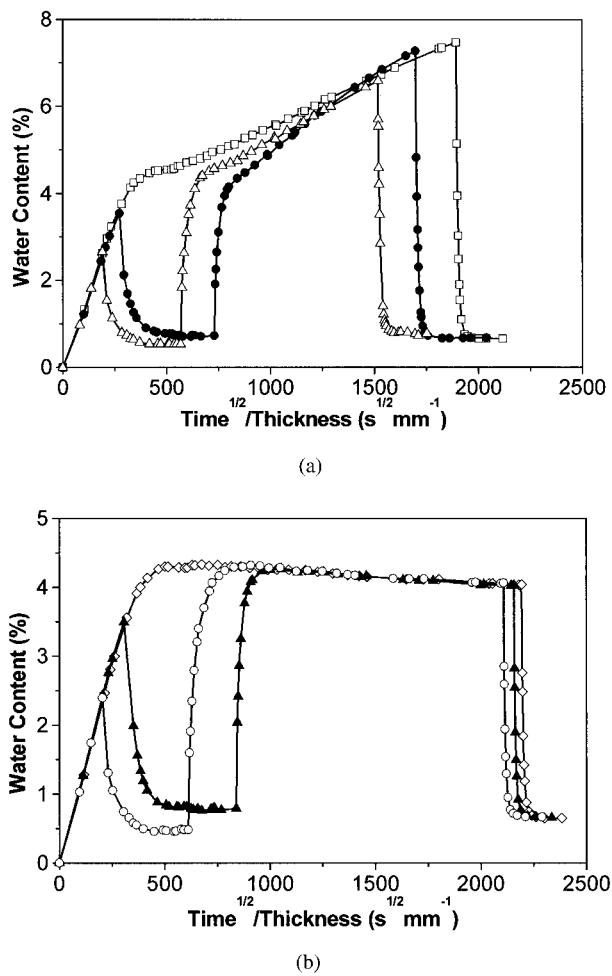
The DRIFT spectra were recorded from 4000 to 400 cm<sup>-1</sup> at a resolution of 4 cm<sup>-1</sup> using a Nicolet Protegè 460 spectrometer. The powder samples were prepared using a Si-Crab™ Sampling Kit in conjunction with a COLLECTOR™ diffuse reflectance accessory (Spectra-Tech). The polymer surface was scrubbed with an abrasive pad to generate a powder for the DRIFT measurement.

## RESULTS AND DISCUSSION

### Gravimetric Measurements

The results from the gravimetric measurements are shown in Figure 1. The three curves in Figure 1(a) refer to the samples immersed in deionized water at 65°C. Sample A was immersed in water for 74 h, resulting in a 2.7% water content. The sample was then removed from the water bath and placed in an oven at 65°C to allow dehydration. The equilibrium weight after dehydration was 0.54% above the original weight. The sample was then rehydrated until the water content reached 6.6%, and after final dehydration the equilibrium weight of the sample was 0.78% higher than the initial one. Sample B underwent a similar aging cycle. The initial short-term immersion in water led to 3.2% water content and after the subsequent dehydration, 0.73% water content remained in the sample. The second exposure to deionized water resulted in a 7.3% water content and the equilibrium weight after dehydration was 0.68% higher than the original weight of the sample. Sample C was continuously exposed to deionized water and took up water to a 7.5% water content; it was then dried to an equilibrium weight that was 0.67% higher than the initial one.

Figure 1(b) represents the results obtained from the salt solution tests. Sample D was immersed in a 5% (w/w) NaCl solution for 74 h, and the weight of the water absorbed was 2.3% of the weight of the dry resin; after dehydration there was 0.48% residual water content. The sample was then exposed to the salt solution to allow rehydration; after 7050 h it was placed in an oven and dried to a constant weight. Sample E was initially exposed to the salt solution for 152 h,



**Figure 1** The percentage of water content versus the ratio of the square root of time to the thickness of the sample for aging at 65°C in (a) deionized water and (b) a 5% (w/w) water solution of NaCl. The data are presented for ( $\triangle$ ) sample A, ( $\bullet$ ) sample B, ( $\square$ ) sample C, ( $\circ$ ) sample D, ( $\blacktriangle$ ) sample E, and ( $\diamond$ ) sample F. The estimated error bars are smaller than the symbols in the figure.

resulting in a 3.2% water content, and then dried to an equilibrium weight that was 0.79% higher than the initial one. The sample was then subjected to a second hydration–dehydration cycle. Sample F was continuously exposed to the salt solution for 7700 h and then dried. All three of the samples exhibited a maximum 4.3% increase in weight during exposure to the salt solution and the subsequent weight loss of 0.3%. The equilibrium weight after the final dehydration was 0.67% higher than the initial weight for all three samples.

The shapes of the curves in Figure 1(a) clearly indicate two-stage water absorption. The first stage was a Fickian type and took place up to

4.5% water content; above this value the water content linearly increased with the square root of time. The water content at the inflection point of the absorption curves was independent of the hygrothermal history. Two-stage absorption is one of the most general sorption features of glassy polymers.<sup>11</sup> It is generally accepted that the penetrant diffuses rapidly into the polymer, which is accompanied by reversible elastic swelling of the matrix. The stress that is developed is then slowly relieved by a molecular relaxation process such that the chemical potential of the sorbed water is decreased, leading to further sorption.<sup>12</sup>

In the exposure to the 5% (w/w) NaCl solution at 65°C there was no second stage of absorption [Fig. 1(b)]. The water content increased with the square root of time in a Fickian manner and after reaching a maximum at approximately 4.3%, there was a loss of weight due to leaching of material from the sample. There was evidence that leaching of material took place when the sample was exposed to deionized water also, but the high level of water absorbed during the second stage of absorption did not allow the small changes in weight due to leaching to be detected.

The experimental results presented so far indicate that the first stage of the water absorption was related to the process of saturation of the epoxy matrix and the second stage was possibly osmotic pressure driven. Hydrophilic impurities are often retained in polymers during synthesis. Because of their good compatibility with water, they may form an electrolyte solution. The ratio of the internal pressure of the solution to that of the external pressure<sup>13</sup> showed that the osmotic pressure became a driving force for water absorption. In this case, the water caused irreversible damage to the material in the form of microcavities, and part of the water was dispersed within the material and part resided in the microcavities.

A certain amount of water invariably remained within all of the samples after dehydration at 65°C. It was observed in previous lower temperature studies of the hygrothermal aging of this material that the longer the exposure, the greater the amount of residual water; this effect was attributed to water absorbed by the more hydrophilic rubber phase of the system.<sup>14</sup> Zhou and Lucas<sup>15</sup> worked on DGEBA with *m*-phenylene diamine, tetra glycidyl diaminodiphenyl methane with diaminodiphenyl sulfone, and Fiberite 934; they also observed a residual weight after dehydration at temperatures lower than the glass-transition temperature that increased with both the exposure temperature and time. They as-

signed it to water molecules forming multiple hydrogen bonds with the resin network, which possess a high activation energy and are correspondingly harder to remove. However, in this case the equilibrium residual weight after dehydration following short-term exposure to both deionized water and a salt solution increased with the time of exposure. The long-term exposure to moisture led to a decrease in the equilibrium weight after dehydration that was due to leaching of material from the samples. It was difficult to define the origin of the leaching products, which is discussed later in this article. The equal residual weights after dehydration of samples C and F was an indication that the water was reversibly absorbed by the material during the second stage of absorption. Annealing of the samples at a temperature in excess of the glass-transition temperature and under a vacuum led to a decrease in the weight to a value that was approximately 0.05% lower than the original. During the exposure to the salt solution, sample F lost approximately 0.3% of the weight of the dry resin, which led to the conclusion that water was irreversibly absorbed by the material at approximately 0.25% water content.

Figure 2 represents the normalized water uptake as a function of the ratio of the square root of time to the thickness of the samples. The water uptake is defined as

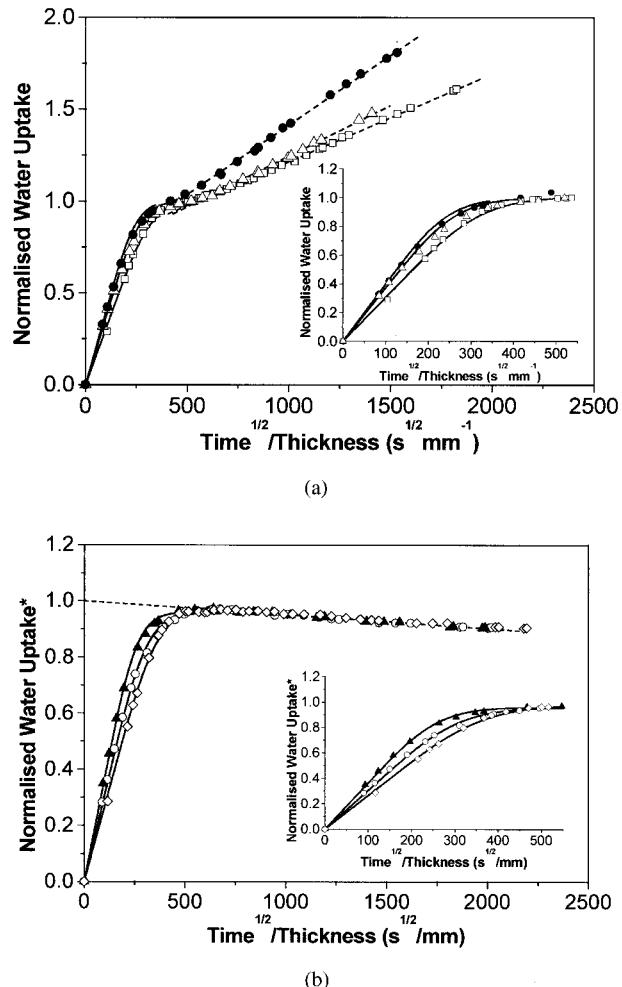
$$\text{water uptake} = \frac{W_{t'} - W_{t'=0}}{W_{t=0}} \quad (2)$$

where  $W_{t'}$  is the weight of the sample at a certain moment of time from the start of the exposure process and  $W_{t=0}$  is the weight of the sample at the start of the exposure. In the exposure to deionized water the normalized water uptake is defined as

$$\text{normalized water uptake} = \frac{[\text{water uptake}]_{t'}}{[\text{water uptake}]_{\text{inflexion}}} \quad (3)$$

where  $[\text{water uptake}]_{t'}$  is the water uptake at a certain moment of time  $t'$  and  $[\text{water uptake}]_{\text{inflexion}}$  is the water uptake at the inflection point of the plot of the water uptake versus the ratio of the square root of time to the thickness of the sample. For the aging in the salt solution the normalized water uptake is defined as

$$\text{normalized water uptake} = \frac{[\text{water uptake}]_{t'}}{[\text{water uptake}]_{\text{intercept}}} \quad (4)$$



**Figure 2** The normalized water uptake versus the ratio of the square root of time to the thickness of the sample for aging in (a) deionized water and (b) a 5% (w/w) water solution of NaCl. The data are presented for ( $\triangle$ ) sample A, ( $\bullet$ ) sample B, ( $\square$ ) sample C, ( $\circ$ ) sample D, ( $\blacktriangle$ ) sample E, and ( $\diamond$ ) sample F. The data for samples A, B, D, and E were collected during the second exposure to a deionized water and salt solution. (—) The best fit with a Fickian model to (a) the data obtained for samples A, B, and C up to the inflection point of the absorption curve and (b) the data obtained for samples D, E, and F before maximum water content was reached.

where  $[\text{water uptake}]_{\text{intercept}}$  is the intercept of the line fitted through the data obtained after the maximum in the plot of the water uptake versus the ratio of the square root of time to the thickness of the sample.

The solid lines in Figure 2 represent the best fit with the Fickian model for the data obtained for samples A-C up to the inflection point of the absorption curve [Fig. 2(a)] and the data for samples D-F obtained before reaching the maximum in

**Table II** Diffusion Coefficients Obtained for Water Absorption–Desorption at 65°C

Sample	Absorption ( $\times 10^{-8}$ $\text{cm}^2 \text{s}^{-1}$ )	Desorption ( $\times 10^{-8}$ $\text{cm}^2 \text{s}^{-1}$ )
A (II)	2.7	2.6
B (II)	3.1	2.2
C	1.8	2.3
D (II)	2.0	3.2
E (II)	2.8	3.2
F	1.5	3.2
DGEBA/DICY with Ciba-Geigy XB3131 fillers <sup>a</sup>		
40°C	0.26	
55°C	0.70	
70°C	3.6	

The (II) symbol indicates the data obtained from the second absorption cycles. The results are compared to values for the diffusion coefficient obtained for material based on the same resin but containing different fillers at three different temperatures of exposure to water.

<sup>a</sup> Data from De'Nève and Shanahan.<sup>25</sup>

weight gain [Fig. 2(b)]. The dashed lines represent the least squares line obtained for the data during the second stage of absorption [Fig. 2(a)]. The weight loss due to leaching during the first stage of absorption was considered negligible.

One can see that previous short-term exposure to deionized water resulted in an increased rate of both stages of absorption. Table II gives the values for the diffusion coefficient calculated from the initial stage of the absorption curves.

Figure 3 represents the desorption curves obtained for the final dehydration of the samples aged in deionized water [Fig. 3(a)] and in salt solution [Fig. 3(b)]. The calculated diffusion coefficients are presented in Table II, and there was no apparent dependence of the values on the hygrothermal history.

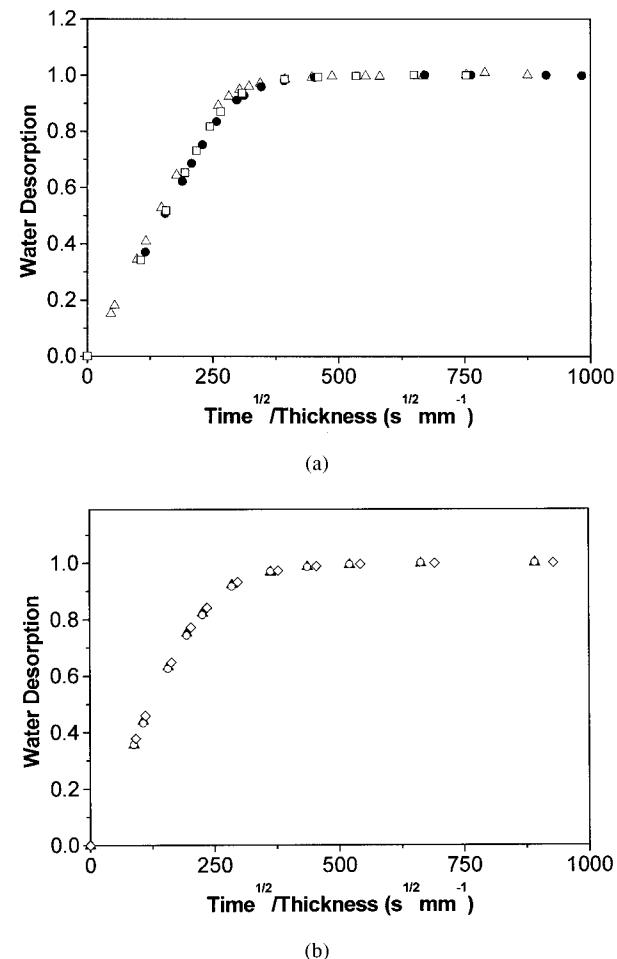
#### TEM Analysis

The TEM images taken of ultrathin cross sections of the unaged material [Fig. 4(a,b)] and the material aged for approximately 6000 h in deionized water at 65°C [Fig. 4(c–e)] are presented in Figure 4. The finely dispersed nanometer-sized particles are fumed silica, which is often added to resins to improve their rheological properties. The micron-size particles are calcium silicate. Microcavities (100-nm diameter) were formed after aging in deionized water. There were no apparent changes in the material when it was aged in a salt

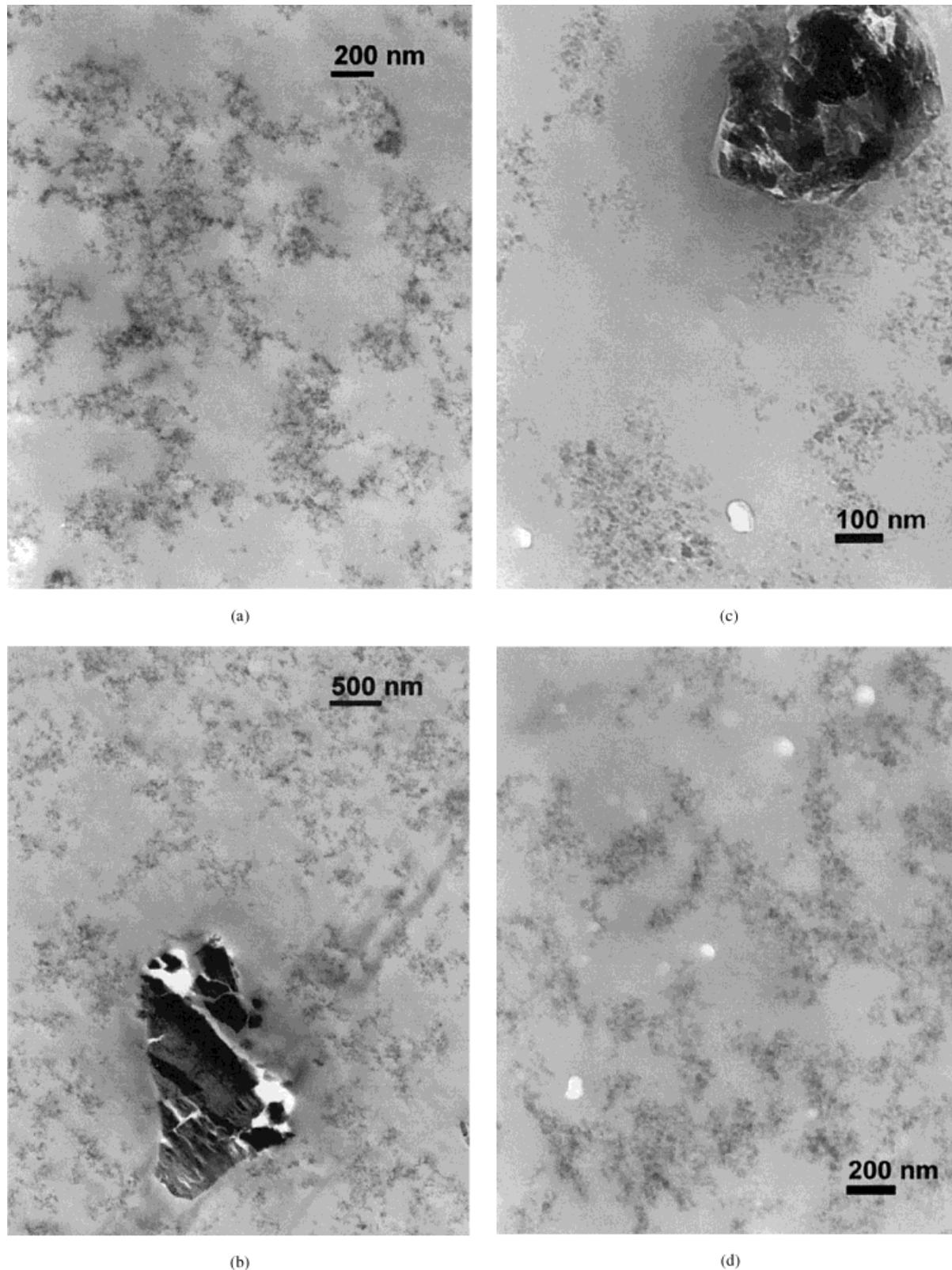
solution. These results confirmed the hypothesis that the water taken up during the second stage of absorption resides in microcavities.

#### DRIFTS Analysis

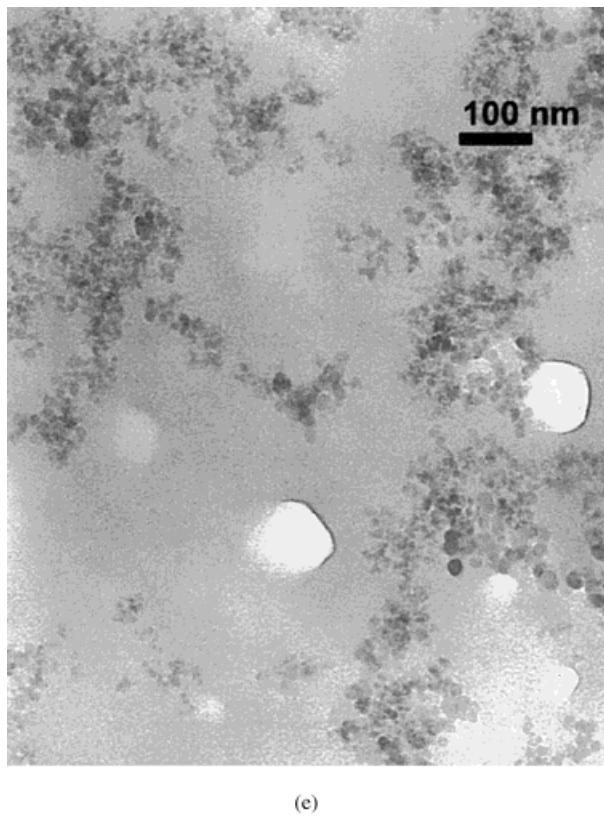
The IR spectra were obtained for the unchanged resin and the resin aged for approximately 6000 h at 65°C in deionized water and a 5% (w/w) NaCl solution. Figure 5(a) shows the FTIR spectrum of the adhesive before aging and corresponds to the sum of the spectra of epoxy, DICY, and fillers (spectrum i); the FTIR spectrum of the resin after aging in deionized water at 65°C (spectrum ii); and the subtraction of the normalized spectra,



**Figure 3** The water desorption at 65°C versus the ratio of the square root of time to the thickness of the sample after immersion in (a) deionized water and (b) a 5% (w/w) NaCl solution. The data are presented for ( $\triangle$ ) sample A, ( $\bullet$ ) sample B, ( $\square$ ) sample C, ( $\circ$ ) sample D, ( $\blacktriangle$ ) sample E, and ( $\diamond$ ) sample F. The data for samples A, B, D, and E were obtained from the final dehydration of the samples.

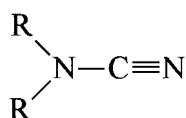


**Figure 4** Transmission electron microscopy images of a cross section of the material (a,b) before undergoing hygrothermal aging and (c–e) after approximately 6000-h exposure to deionized water at 65°C.

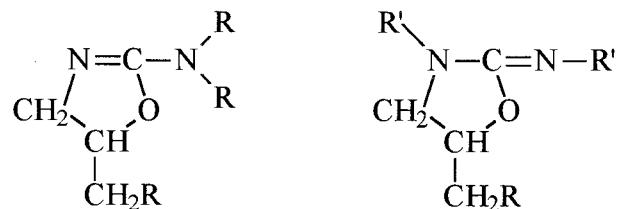


**Figure 4** (Continued from the previous page)

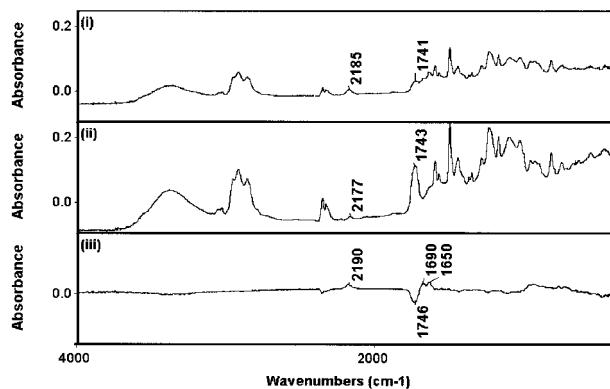
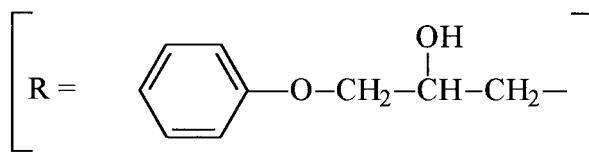
(spectrum i) – (spectrum ii) = (spectrum iii). The area of the peak at  $1509\text{ cm}^{-1}$  that corresponded to the aromatic ring of DGEBA and remained unchanged during the aging process was used as a normalizing factor. Before aging, the band at  $2185\text{ cm}^{-1}$  was an indication of an excess of DICY hardener. After aging there was a decrease in the absorbance at  $2190$ ,  $1690$ , and  $1650\text{ cm}^{-1}$ . All of these bands were associated with the DICY, and the changes indicated removal of unreacted hardener from the system. The main change in the spectra was an increase in the absorbance at  $1746\text{ cm}^{-1}$ . Several authors<sup>16–24</sup> observed the emergence of a peak near  $1740\text{ cm}^{-1}$  during cure of DGEBA with DICY. The exact position and origin of this peak were uncertain, and there was disagreement between the authors. Sprouse et al.<sup>18</sup> considered thermal oxidation of the sample as the cause of this increase. According to Zahir,<sup>21</sup> the reaction of epoxide with DICY led mainly to products with two different structural units, namely, a dialcyldicyanamide,



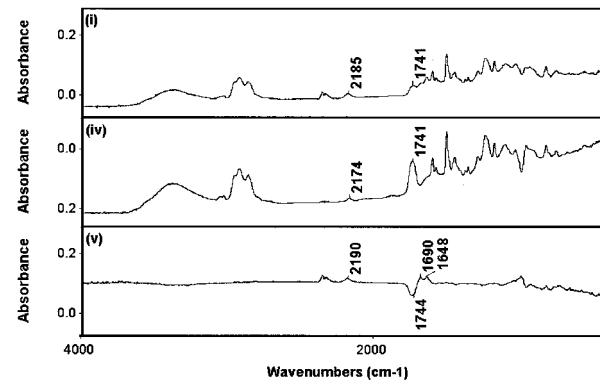
and an organic base derivative of 2-amino-2-oxazoline (or its tautomer 2-amino-oxazolidine),



where



(a)



(b)

**Figure 5** FTIR spectra of the resin before the aging process (spectrum i), after approximately 6000 h in deionized water at  $65^\circ\text{C}$  (spectrum ii), subtraction of spectrum ii from spectrum i (spectrum iii), after approximately 6000 h in the 5% (w/w) NaCl solution at  $65^\circ\text{C}$  (spectrum iv), and subtraction of spectrum iv from spectrum i (spectrum v).

He suggested that carbonyl and urethane ester groups may be formed in the resin via intramolecular and/or intermolecular rearrangement reactions of the above products. DeNève and Shanahan<sup>25</sup> observed an increase in the absorbance at  $1740\text{ cm}^{-1}$  after aging of DGEBA/DICY in water at  $70^\circ\text{C}$ . They suggested addition of water across the imino double bond, followed by ring opening and formation of a carboxylic group, which was analogous with the base-catalyzed addition of an alcoholic OH group proposed by Zahir.<sup>21</sup> Xiao et al.<sup>26</sup> studied the degradation of a model epoxy resin (DGEBA/DICY) with X-ray photoelectron spectroscopy (XPS) and FTIR and proposed a tentative degradation mechanism. They observed an increase in the band at  $1736\text{ cm}^{-1}$  for the leached products in comparison with the unaged resin and, because the XPS results did not suggest that there were  $-\text{COOH}$  groups present, they assigned it to a carbonyl group.

Figure 5(b) shows the FTIR spectrum of the adhesive before aging (spectrum i), the FTIR spectrum of the resin after aging in the 5% (w/w) NaCl solution at  $65^\circ\text{C}$  (spectrum iv), and the subtraction of the normalized spectra, (spectrum i) – (spectrum iv) = (spectrum v). The changes observed were analogous to those for the aging in deionized water.

## CONCLUSIONS

The combined effects of elevated temperature and moisture on the DGEBA/DICY resin were studied using deionized water and a salt solution.

The exposure to deionized water led to a two-stage absorption. The first stage of the absorption was a Fickian type and was attributed to the process of saturation of the epoxy matrix. The driving force for the second stage of the absorption was the osmotic pressure, and it was not observed when the material was immersed in the 5% (w/w) NaCl solution.

The hydration–dehydration cycling led to an increase in the diffusion coefficient of the first stage of the rehydration process and increased the rate of the second stage because of progressive cavity formation.

The hygrothermal aging led to chemical modification of the resin and removal of excessive hardener from the samples.

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