

Hygrothermal Aging of Rubber-Modified and Mineral-Filled Dicyandiamide-Cured DGEBA Epoxy Resin. II. Dynamic Mechanical Thermal Analysis

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Received 16 November 2000; accepted 24 February 2001

ABSTRACT: The effects of hydration–dehydration cycling on the dynamic mechanical response of a rubber modified, mineral-filled epoxy resin based on the diglycidyl ether of bisphenol A cured with dicyandiamide are reported. Samples of the resin were aged in both deionized water and 5% w/w NaCl solution at 65 °C. A dynamic mechanical thermal analyzer was used to detect the changes in the mechanical spectrum of the material induced by moisture ingress. Water absorbed at weight fractions up to 4.3% caused plasticization of the polymer matrix, and the measured decrease in the glass transition temperature could be interpreted in terms of the polymer network–diluent theory. Water absorbed at levels >4.3% weight fraction resides in microcavities formed as result of the aging process and did not further affect the dynamic mechanical response of the resin. The dynamic mechanical properties of the material were independent of the previous history of exposure to humidity. In the presence of NaCl, the microcavity growth was prevented and the amount of water absorbed did not exceed 4.1% weight fraction. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 3477–3485, 2001

Key words: epoxy resins; hydration–dehydration cycling; dynamic mechanical thermal analysis; plasticization; microcavity formation

INTRODUCTION

The interaction of structural network epoxy resins and their composites with water is of both fundamental and technical interest. The susceptibility of these materials to substantial changes in properties on exposure to humid environments is manifested by a large depression of the glass transition temperature,^{1–10} typically 8–20 °C per percent w/w of absorbed water.

Some spectroscopic and calorimetric data have been interpreted to indicate a highly specific ‘binding’ between the water molecules and the

polar groups of the epoxy resin,^{4,9,11} suggesting that the water disrupts the hydrogen-bonding network.^{9,12} However, other works suggest that the water acts simply as a plasticizer^{5,13} and that the plasticization of epoxy resins by water could be explained in terms of the composition dependence of the glass-transition temperature (T_g) of miscible polymer–diluent mixtures.⁵

The free-volume approach to the composition-dependent T_g was introduced by Kelly and Beuche.¹⁴ They assumed that the diluent media diffusing in polymers do not enter the pre-existing free volume, but rather reside in the free volume created by the diffused media. According to this model, the depression in T_g is simply a function of the diffusing media content in the material and is independent of exposure temper-

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Journal of Applied Polymer Science, Vol. 82, 3477–3485 (2001)
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ature and time. This model has been applied to epoxy–water systems with limited success.^{1,3,6}

Karasz and co-workers^{5,15} have shown that the effect of small amounts of absorbed water can be explained quantitatively by applying a limiting condition to the Couchman¹⁶ classical thermodynamic treatment of the composition-dependent T_g in compatible polymer mixtures.

Other studies have revealed that the T_g variation for epoxy resins differs significantly from the T_g values calculated with the polymer–diluent model.^{9,17–19} DeIasi¹⁷ studied a number of neat epoxy resins and composites and found that the water behaves as a plasticizer of the epoxy resins, lowering the T_g as predicated by Kelly and Beuche,¹⁴ with the exception of one epoxy resin that exhibited anomalously high T_g values at high moisture concentration (~ 9 – 10% w/w). The poor agreement was explained by the presence of an inorganic flow control agent with high affinity for water due to its polar nature and high surface-to-volume ratio. It is suggested that either a substantial portion of total absorbed water is absorbed on the surface of the filler or formation of water clusters at the surface of the filler or phase interfaces takes place. These clusters would be highly organized and the T_g of the material would not be affected. Mijovic and Wenstein¹⁹ found that sorbed water induced depression of the T_g in graphite–epoxy composite was strongly dependent on the temperature used during the water absorption process. Zhou and Lucas^{9,17} have also reported effects of the hygrothermal history on the T_g variation.

This study is concerned with the effect of hydration–dehydration cycling on the dynamic mechanical properties of a complex epoxy resin system. The influence of an elevated exposure temperature and the effect of salt presence are also examined. In a previous paper,²⁰ the diffusion behavior of the resin was discussed. Anomalous two-stage absorption was observed when the resin was exposed to deionized water. It was found that water causes irreversible damage to the resin in the form of microcavities and it was hypothesized that the first stage of the absorption is related to the process of saturation of the epoxy matrix by moisture and the second stage is due to water diffusing into the microcavities. Microcavity formation and a second stage of absorption were not observed when the resin was immersed in 5% w/w NaCl solution, suggesting that the microcavities grow via an osmotic mechanism.

EXPERIMENTAL

The material used was the same as that described in the previous paper;²⁰ that is, a DGEBA-based epoxy resin, toughened with carboxyl-terminated butadiene acrylonitrile rubber, filled with fumed silica and calcium silicate, and cured with dicyandiamide. The material was molded in the form of 105-mm diameter, 2.6 ± 0.2 -mm thick disks. All of the produced disks were dried in an oven at 50 °C for a month and then cut into samples with dimensions of 30×10 mm. Each set of data was generated using the samples cut from one disk only, although the results obtained from different disks were compared.

The samples were aged by being exposed to deionized water or 5% w/w NaCl solution in sealed jars maintained at a constant temperature of 65 ± 1 °C in an electronically controlled oven. At selected times, the whole sets of samples were removed from the deionized water/salt solution and placed in an oven with silica gel at 65 °C to allow desorption of water to occur. After reaching equilibrium weight, some of the sets were rehydrated and then dried again. Six sets of samples were generated and they were assigned as A, B, C, D, E, and F. The first three sets were aged in deionized water and the remainder in 5% w/w NaCl solution. The sets of samples underwent the same aging regime as the samples assigned with identical code and described in Part I²⁰ (see Table I). Samples A, B, and C were aged using deionized water. Samples D, E, and F were aged in 5% w/w NaCl solution.

On a regular basis, samples from each set were subjected to dynamic mechanical thermal analysis. Prior to testing, the conditioned samples were wiped with absorbent paper to remove excess water and weighed to determine their moisture content. A Polymer Laboratories dynamic mechanical thermal analyzer (DMTA) was used to measure the variation in the dynamic mechanical properties. A single cantilever mode was used to produce bending deformation in the sample. The specimens were clamped into the clamping frame using a torque-driver to tighten the clamp bar nuts to a torque of 25 cN m. A free (unclamped) specimen length of 12 mm, a frequency of 1 Hz, and a peak displacement of 64 μ m were selected. The temperature was scanned from 20 to 160 °C and ramped up at a rate of 3 °C/min. The T_g was taken as the temperature at which the loss factor $\tan \delta$ reached a maximum. Alternatively, the T_g may be defined as the softening point indicated by

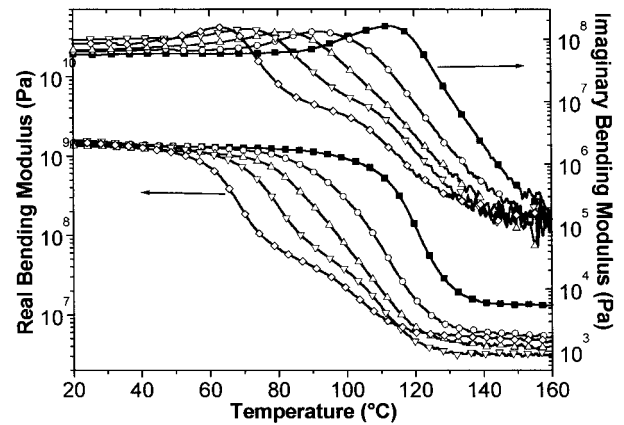
Table I Aging History of Samples A, B, and C Exposed to Deionized Water and Samples D, E, and F Aged in 5% (w/w) NaCl Solution

Sample	I Sorption Cycle		II Sorption Cycle	
	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	—	—

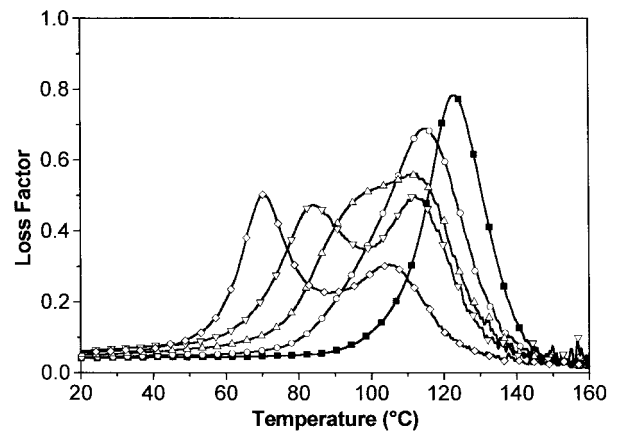
the first dip in the modulus, which occurs 10–15° lower than the peak in $\tan \delta$.

RESULTS AND DISCUSSION

Figure 1(a) represents the variation of real and imaginary bending moduli of samples from set C with time of exposure to deionized water. Samples C were continuously exposed to deionized water at 65 °C for 7250 h, resulting in a 7.5% water content, which was defined as weight of water absorbed per weight of dry polymer. A two-stage absorption was observed. A Fickian-type stage took place during the first 600 h of exposure and was attributed to the process of moisture saturation of the epoxy matrix. The second stage gave a linear increase of the water content with the square root of exposure time and was hypothesized as being due to water diffusing into microcavities. The samples were then dehydrated for 430 h, reaching a constant weight 0.67% higher than the original weight of the samples. The real bending modulus or storage modulus of the unaged material drops from 1.50×10^9 Pa in the glassy state to 1.15×10^7 Pa in the rubbery state. The absorption of water by the material does not affect the storage modulus in the glassy state, which is not surprising because the storage modulus in the glassy state is a complex function of the overall resin density and is not directly related to the cross-link density or the moisture content.²¹ However, the storage modulus in the rubbery state is decreased by the water absorption from 1.15×10^7 to 5×10^6 Pa. It is seen that the temperature at which the storage modulus begins to decrease rapidly, the softening point, is reduced on absorbing moisture. The shift of the



(a)



(b)

Figure 1 (a) Real (left axis) and imaginary (right axis) bending moduli and (b) loss factor of samples C versus temperature at different stages of aging in deionized water at 65 °C. Key: (■) the DMTA spectrum before the start of the experiment; (○, △, ▽, ◇) the spectra after aging in deionized water at 65 °C for 13.5, 38, 116, and 7250 h, respectively.

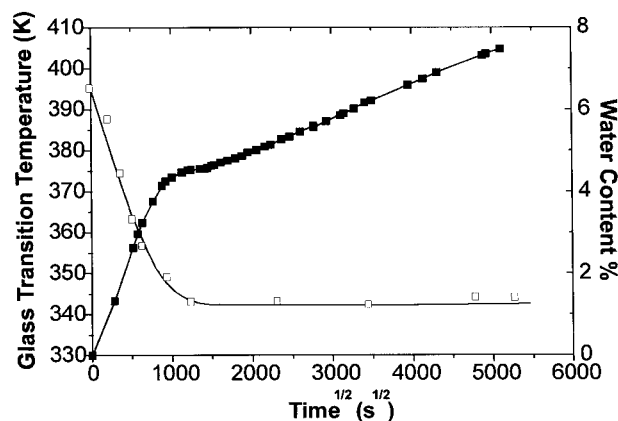


Figure 2 Changes in (\square) the glass transition temperature, $T_g^{(1)}$, and (\blacksquare) the percentage water content of samples C with square root of time of exposure to deionized water at 65 °C.

peak in the imaginary or loss bending modulus toward lower temperatures is a result of the plasticization of the polymer matrix. Figure 1(b) shows the changes in the loss factor curves for samples C. A primary loss factor peak was observed in the unaged, dry material that, on absorption of moisture, first moved to lower temperature and then split into two peaks. The temperature of the primary, lower temperature peak was reduced on absorption; however, the secondary, upper temperature peak became better defined with time of exposure and its position proved to be less sensitive to changes in the water content. The secondary loss factor peak could be a result of drying of the samples due to the increasing temperature in the DMTA chamber. Another possible explanation is that when the samples are removed from the water bath prior to analysis and cooled very fast (minutes), instabilities are created that give rise to regions of alternately dense and dilute phases.²²

The change in the T_g with the square root of time is shown in Figure 2. The T_g that was taken as the position of the primary peak in the loss factor, $T_g^{(1)}$, was decreased from 124 to 70 °C. The fast decrease in $T_g^{(1)}$ during the first 600 h of exposure to deionized water is followed by a plateau region. The comparison with the data for the water content shows that water absorbed during the second stage of absorption does not lead to changes in T_g . It should be noted that not only the T_g but also the overall dynamic mechanical spectrum of the material remained unchanged after the first 600 h, when a value of 4.5% water content was reached.

The changes in the traces of the real and imaginary bending moduli and the loss factor of samples C during dehydration at 65 °C are shown in Figure 3. It is seen that the effects of the absorbed water on the dynamic mechanical properties of the resin are partially recoverable. During the first 45.5 h of the dehydration, although the water content dropped from 7.5 to 3.4%, there is no shift of the primary loss factor peak toward higher temperatures; thus, there is no increase in the T_g of the material. In comparison, during absorption, 3.5% water content led to decrease in the T_g of ~ 40 °C. As the dehydration proceeds, the T_g increases but does not regain its original value. The T_g of the sample dried to a constant weight is 13

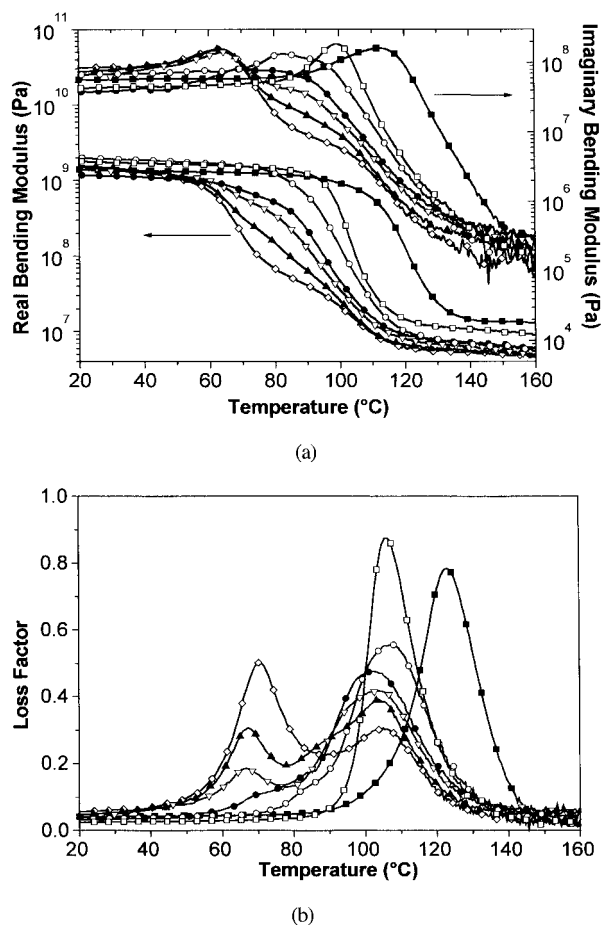
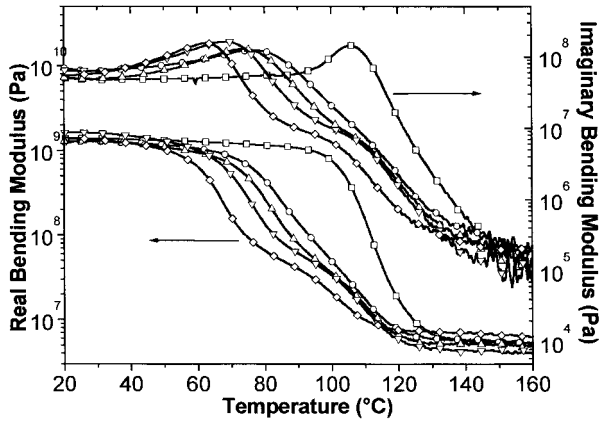
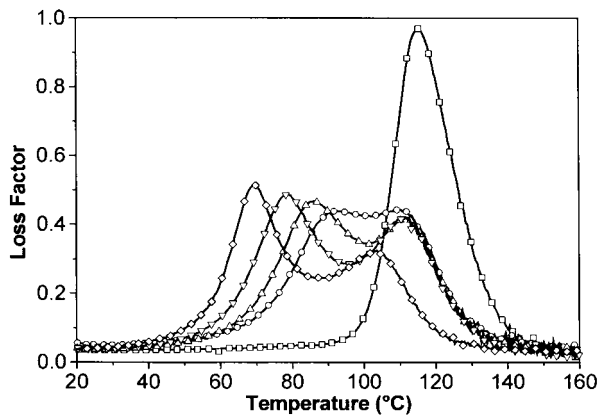


Figure 3 (a) Real (left axis) and imaginary (right axis) bending moduli and (b) loss factor of samples C versus temperature at different stages of dehydration at 65 °C. Key: (\diamond) the DMTA spectrum of the material after 7250 h exposure to deionized water at 65 °C; (\blacktriangle , ∇ , \bullet , \circ , \square) the DMTA spectra of the samples after 5, 45.5, 88, 118, and 430 h drying at 65 °C, respectively; (\blacksquare) the spectrum of the unaged, dry material.



(a)



(b)

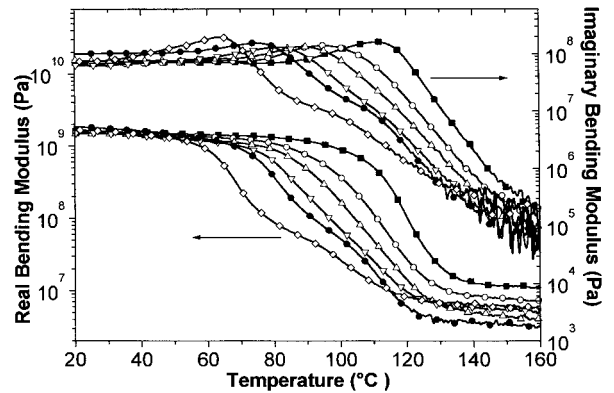
Figure 4 (a) Real (left axis) and imaginary (right axis) bending moduli and (b) loss factor of samples A versus temperature at different times during the second exposure of samples A to deionized water at 65 °C. Key: (□) the DMTA spectrum after the first absorption-desorption cycle; (○, △, ▽, ◇) DMTA spectra after aging in deionized water at 65 °C for 42, 66.5, 117, and 4000 h, respectively.

°C lower than that of the dry, unaged material. The suppressed T_g can be attributed to retained moisture.

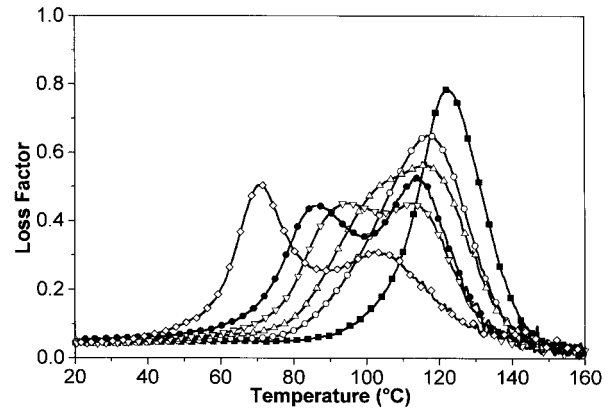
The changes in the traces for the storage and loss moduli and the loss factor of samples A during their rehydration are shown in Figure 4. Samples A were exposed to deionized water at 65 °C for 74 h, resulting in 2.7% water content. The samples were then dried in an oven at 65 °C for 280 h, and a residual amount of 0.54% water content remained. The samples were then returned to the water bath to allow rehydration for 4000 h, and they reached a 6.6% water content. It can be seen from Figure 4 that the DMTA spec-

trum of the material changes in a very similar manner to that of the material that has not been aged previously. The changes induced by moisture ingress on the DMTA spectrum of the material were completed during the first 450 h of exposure, when a value of 4.5% water content was reached.

The changes in the DMTA spectrum of samples F during their exposure to 5% w/w NaCl solution are illustrated in Figure 5. Samples F were immersed in the salt solution for 7700 h. After ~600 h, the samples gained 4.3% water and for the remaining time they lost about 0.3% of their weight due to leaching of material (Figure 6). The spectrum of samples F changes in a mode identical to that of the spectrum of samples C, although there is a significant difference in the water ab-



(a)



(b)

Figure 5 (a) Real (left axis) and imaginary (right axis) bending moduli and (b) loss factor of samples F versus temperature at different stages of aging in 5% w/w NaCl solution at 65 °C. Key: (■) the DMTA spectrum of the unaged, dry material; (○, △, ▽, ●, ◇) the spectra after 16, 49, 73.5, 113, and 7700 h exposure, respectively.

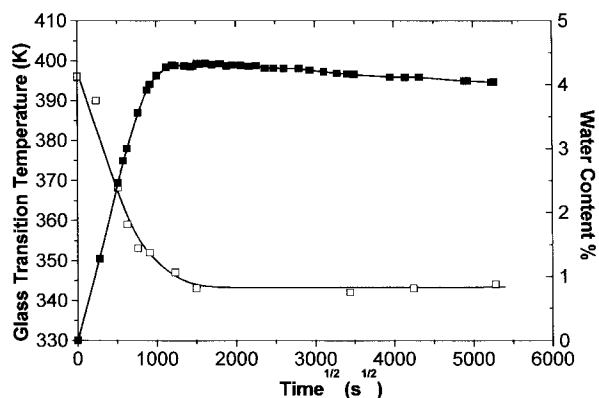


Figure 6 Changes in (\square) the glass transition temperature, $T_g^{(1)}$, and (\blacksquare) the percentage water content of samples F with square root of time of exposure to 5% w/w water at 65 °C.

sorption behavior. The spectrum of the material changes only during the first 600 h of aging. The change in the T_g with the time is given in Figure 6.

However, the changes in the DMTA spectrum of samples F during their dehydration (Figure 7) are not quite the same as those in the case of samples C. There is no initial stage of dehydration when the removal of a significant amount of water is not accompanied by an increase in the T_g . The storage modulus increases and the peak in the loss modulus shifts toward higher temperatures but both do not regain their original values. The T_g of the material after 330 h drying to a constant weight, which was 0.68% higher than the original weight, was 13 °C lower than the T_g of the unaged material. Taking into account the 0.3% weight loss, it could be estimated that water at $\sim 1\%$ water content remained in the sample after dehydration. It should be noted that both the residual weight and the final T_g of samples F do not differ from those of samples C.

The changes in the DMTA spectrum of samples D during the rehydration process following the previous hydration–dehydration cycle are shown in Figure 8. Samples D were exposed to 5% w/w NaCl solution for 74 h and took up water at 2.3% of the weight of the dry material; the residual amount of water after the subsequent drying in an oven at 65 °C for 280 h was 0.48% of the weight of the dry resin. During the rehydration for 7050 h, the samples reached a maximum gain in the water of 4.3% of their original weight after ~ 550 h, and for the remaining time of exposure they lost $\sim 0.3\%$ of their weight. One can see that the dynamic mechanical properties undergo sim-

ilar changes to that of the material that has not been aged previously. The changes in the DMTA spectrum were completed after the first 550 h of exposure.

The comparison between the DMTA spectra of all sets of samples at different stages of aging in deionized water/salt solution is illustrated by Figure 9(a). The spectra of samples A, B, D, and E were obtained during the second exposure of the samples to deionized water/salt solution. For samples A, B, and C the data presented were collected at different water contents of 4.5, 5.7, and 7.5%, respectively. The water content for samples D, E, and F is 4.3%. The results indicate that the dynamic mechanical properties of the

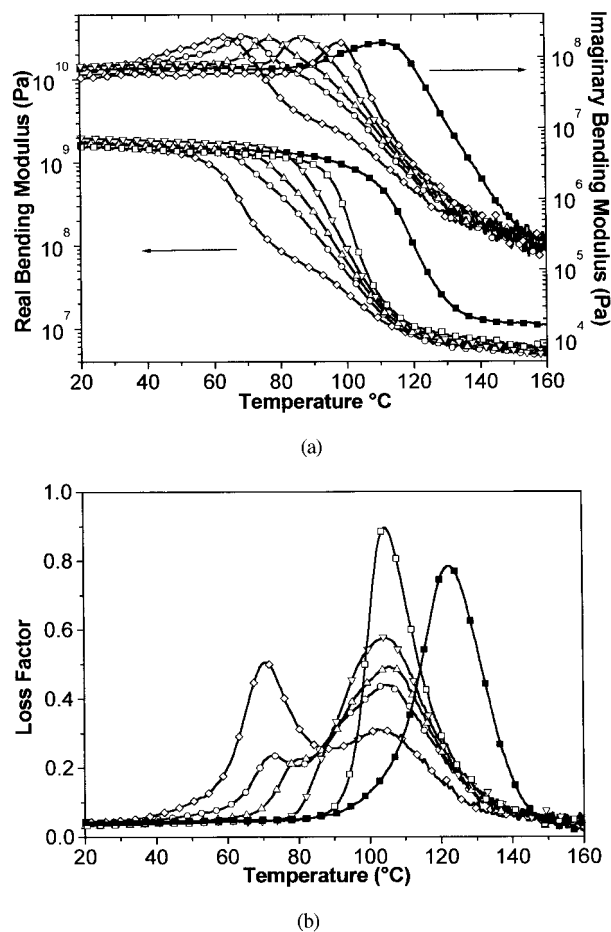
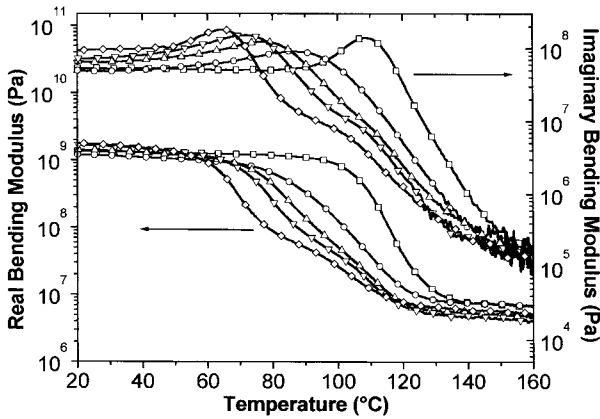
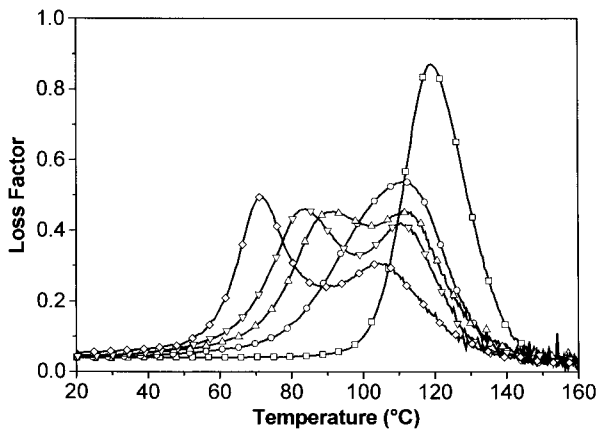


Figure 7 (a) Real (left axis) and imaginary (right axis) bending moduli and (b) loss factor of samples F versus temperature at different stages of dehydration at 65 °C. Key: (\diamond) the DMTA spectrum of the material after 7700 h exposure to 5% w/w NaCl solution at 65 °C; (\circ , \triangle , ∇ , \square) spectra of the samples after 13, 35, 69, and 330 h drying, respectively, at 65 °C; (\blacksquare) the spectrum of the unaged, dry material.



(a)



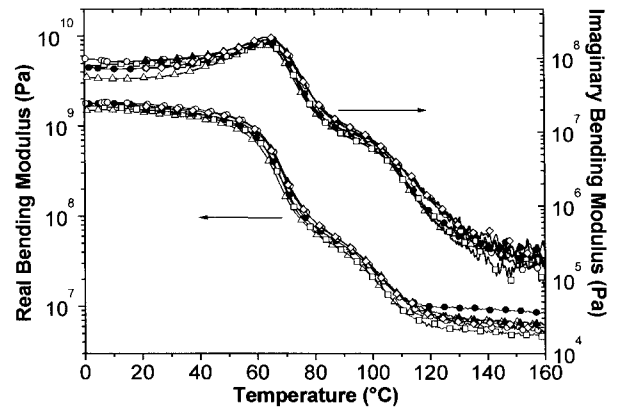
(b)

Figure 8 (a) Real (left axis) and imaginary (right axis) bending moduli and (b) loss factor of samples D versus temperature at different stages of the rehydration in 5% w/w NaCl solution at 65 °C. Key: (\square) the DMTA spectrum of material after the first hydration–dehydration cycle; (\circ , \triangle , ∇ , \diamond) the spectra after 26, 64.5, 116, and 7050 h exposure, respectively.

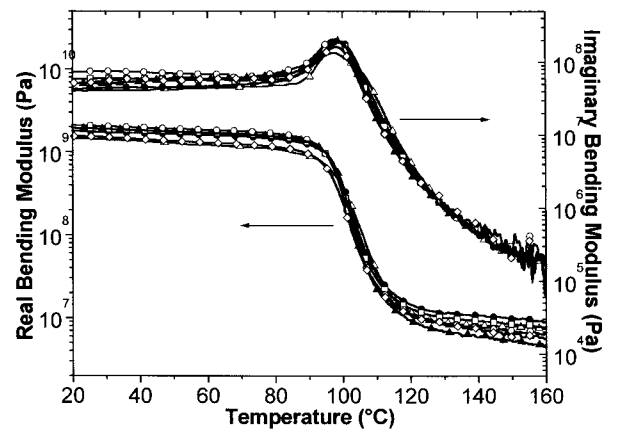
material are independent of the previous history of exposure to humidity and, for samples aged in deionized water, moisture absorbed at levels $>4.5\%$ does not further modify the DMTA spectrum. This result is consistent with the hypothesis that the water causes damage of the material in the form of microcavities and the water absorbed during the second stage of absorption remains in these microcavities. According to Karasz,²³ condensed water entrapped in cracks and microvoids would not be expected to contribute to a reduction in the mechanical properties, which explains why water absorbed at levels $>4.5\%$ does not further affect the DMTA spectrum of the material. The comparison between

the spectra obtained after the final dehydration, when all samples contain approximately the same amount of water ($\sim 1\%$ of the weight of the dry resin) is illustrated in Figure 9(b). All the traces coincide, confirming once again that there are no history-dependent effects on the DMTA properties.

The T_g dependence on the water weight fraction is shown in Figure 10. The T_g sharply decreases with the water weight fraction up to 4.3%. Water absorbed at weight fractions $>4.3\%$ does not further suppress T_g ⁽¹⁾. Ten Brinke et al.²⁴ extended the Couchman–Karasz polymer–diluent model to networks introducing the following parameter:



(a)



(b)

Figure 9 Real (left axis) and imaginary (right axis) bending moduli versus temperature (a) at different stages of aging at 65 °C in deionized water and 5% w/w NaCl solution and (b) after the final dehydration of the samples at 65 °C. Key: (\triangle , \bullet , \square , \circ , \blacktriangle , \diamond) the data for samples A, B, C, D, E, and F, respectively. The data for samples A, B, D, and E were obtained from the second hydration–dehydration cycle.

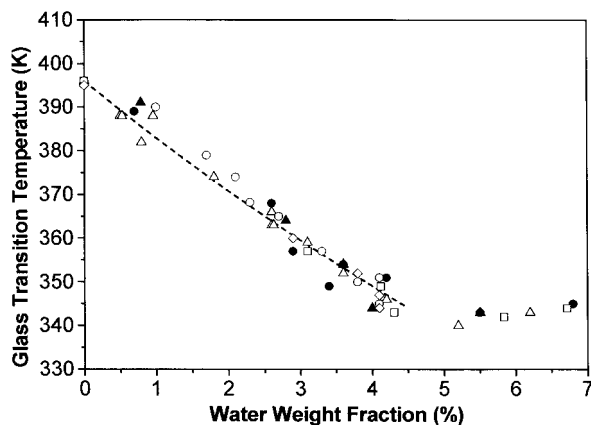


Figure 10 Glass transition temperature versus the water weight fraction. Key: (Δ , \bullet , \square , \circ , \blacktriangle , \diamond) the data for samples A, B, C, D, E, and F, respectively. For samples A, B, D, and E, the results obtained during both experimental cycles are presented.

$$T_{g12} = \frac{x_1 \Delta C_{p1}^{\text{act}} T_{g1} + x_2 \Delta C_{p2} T_{g2}}{x_1 \Delta C_{p1}^{\text{act}} + x_2 \Delta C_{p2}} \quad (1)$$

where '1' and '2' refer to polymer and diluent, respectively, x refers to weight or mole fraction, ΔC_{p2} is the specific heat of the diluent, and $\Delta C_{p1}^{\text{act}}$ is the incremental change in specific heat at T_{g1} of the units capable of thermal activation. The T_g of the water, T_{g2} , has been determined to be $\sim(134 \text{ K})$;^{25,26} the value of the specific heat for water is $(1.94 \text{ Jg}^{-1}\text{K}^{-1})$,^{26,27} and a reasonable approximation²² of ΔC can be obtained from

$$\Delta C_{p1}^{\text{act}}(X)T_{g1}(X) = \Delta C_{p1}(X=0)T_{g1}(X=0) \quad (2)$$

where X refers to the degree of cross-linking, such that $X = 0$ represents the monomer. The T_g of the DGEBA monomer is $-22 \text{ }^\circ\text{C}$,²⁸ with a heat capacity discontinuity, ΔC_p of $(\sim 0.60 \text{ Jg}^{-1}\text{K}^{-1})$.²⁹ The value of $\Delta C_{p1}^{\text{act}}$, calculated from eq. 2, is $0.38 \text{ Jg}^{-1}\text{K}^{-1}$. The dashed line in Figure 10 represents the theoretical predictions for the T_g of the plasticized epoxy resin, T_{g12} , using eq. 1. The polymer network-diluent model gives a good prediction of the T_g depression for values of the water weight fraction up to 4.3%. Above that value, the T_g is independent of the water weight fraction. As discussed earlier, water absorbed at levels $>4.5\%$ of the weight of the dry sample (4.3% weight fraction) is water that resides in microcavities and does not lead to T_g depression.

Derivatization of eq. 1 gives

$$\left. \frac{dT_{g12}}{dx_2} \right|_{x_2 \rightarrow 0} = - \frac{\Delta C_{p2}}{\Delta C_{p1}^{\text{act}}} (T_{g1} - T_{g2}) \quad (3)$$

The value calculated for the initial slope of the composition dependence of the T_g is $\sim 13 \text{ }^\circ\text{C}$ per percent water weight fraction.

CONCLUSIONS

The effects of hydration-dehydration cycling on the dynamic mechanical response of DGEBA-DICY epoxy resin were studied. No effect of the hygrothermal history on the dynamic mechanical thermal properties was apparent and they are a function only of the water content. The absorption of water up to 4.3% weight fraction leads to plasticization of the material in accordance with the theoretical predictions of the polymer network-diluent model. Water absorbed at levels $>4.3\%$ weight fraction remains in microcavities, formed during the aging process, and does not further modify the DMTA spectrum of the resin. The presence of NaCl at 5% w/w in the aging solution prevents microcavity growth and thus does not allow water absorption at levels $>4.1\%$ weight fraction, but does not affect the DMTA spectrum of the material. After dehydration, the T_g does not recover its original value because of a residual amount of water effectively trapped within the material.

Further confirmation of the nature of the water distribution in the material can be obtained from a dielectric analysis of the water absorption process, which will be the subject of a subsequent publication.

We thank Alcan International Ltd. (Banbury) for helpful discussion and for their support of KII in the form of a studentship for the period of this study.

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