Influence of Stoichiometric Ratio on Water Absorption in Epoxy Resins

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ABSTRACT: Dielectric, gravimetric, dynamic mechanical, and infrared measurements are reported on the effect of different stoichiometric ratios on the water absorption of diglycidyl ether of bisphenol A (DGEBA), MY720 (Ciba Geigy) cured with stoichiometric variations of triethylenetetramine (TETA), (BDH). Resin samples were prepared with stoichiometric ratios of epoxy:amine from 3 : 1 through 1 : 1 to 1 : 3. Analysis of the water absorption characteristics of these materials showed the existence of water in two different environments; molecules bound to specific sites in the matrix and clustered in microvoids as "free water." Diffusion coefficients and equilibrium water uptake were shown to markedly increase with an increase in the amine ratio. An anomaly observed in dielectric results is attributed to a high rate of diffusion in the high amine ratio materials. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 2369–2376, 1998

Key words: dielectric; gravimetric; mechanical; epoxy resin; water uptake

INTRODUCTION

Amine-cured epoxy resin systems frequently used in structural composite applications will contain after cure residual unreacted amine or epoxy functionality.[1,2] Complete reaction during cure is only achieved if the system is raised close to its ultimate glass transition (T_g), and for many practical reasons this may not always be achieved.[3] It is common for a resin formulation to be designed so that it contains small amounts of residual amine or epoxy functions. Changes of the composition from the ideal stoichiometric ratios produces materials with improved impact properties, although there may also be a loss of ultimate tensile properties. Our previous studies of water absorption on high performance epoxy resins systems have in-

vestigated the influence of change in the cure temperature[4] and chemical structure[5] on the gravimetric and dielectric profiles for water absorption. This study confirms the gravimetric studies of Johncock,[6] where it was found that the extent of absorption and rate of water uptake depended on the temperature used in the cure. Because water is a very polar molecule dielectric, measurements may be used to monitor the absorption process.[7] Changes in the dielectric loss and permittivity with time in the frequency range -10^{-3} to 10^{10} Hz, allows identification of the state of the water molecules in the system. Dielectric analysis revealed that the proportion of water molecules bound to chemical functions in the resin compared with those clustered in microcavities changed with cure temperature.[4] The amount of clustered water increased with increasing cure temperature, and is a facet of the nature of the nonuniformity of the crosslinked network generated during the cure process. The incomplete reaction may produce stresses due to the nonhomogeneous dis-

tribution of the topographical features generated during cure and can create "large cycles"[8-11] or "voids" in which water may cluster. Surprisingly, the introduction of halogens that have an important effect on the thermal degradation of epoxy resins does not increase the equilibrium water absorption, but decreases the equilibrium water absorption and influences the rate of water uptake.[5,12-17] Comparison between fluorinated and nonfluorinated analogues of the same system demonstrated the effects of plasticization of the matrix leading to collapse of the microvoids in which the clusters are found.

This artricle focuses on the effects of non stoichiometric ratios of the reaction mixtures on the water absorption process and explores the effects of topography, specific site binding, and glass transition temperature on the process. The system selected for study, diglycidyl ether of bisphenol A (DGEBA) with triethylenetetramine (TETA), has been studied previously at 1:1 stoichiometric ratio and is capable of forming glassy materials over a range of compositions.

EXPERIMENTAL

Materials

Diglycidylether of Bisphenol A (DGEBA), Araldite MY750 (Ciba Geigy Polymers), M_w 700, and triethylenetetramine (TETA), (BDH Chemicals Ltd.) were used as supplied without further purification. Six different stoichiometric ratios of epoxy and amine were used to produce resin and ranged from, 3 : 1 through 1 : 1 to 1 : 3. Both components were thoroughly degassed before being mixed at 343 K. Cure was carried out at 343 K, as the viscosity of the components was sufficiently low to ensure good mixing. Samples were initially cured for, respectively 12, 17, 22, 64, and 72 h to determine the optimum cure time at this temperature, which was found to be 17 h. Molds constructed from two glass plates separated by a uniform spacer were used for sample fabrication. The glass plates, $60 \times 60 \times 6$ mm, were notched on one edge so as to form a funnel for the resin in the final mold. The glass plates were cleaned with water, acetone, and then sprayed with PTFE Release Agent, Dr. Lubricant MS 122/123 spray, Miller Stephenson Chemical Company Inc., Connecticut. The plates were baked at 523 K for 2 h, then carefully wiped clean with lens tissue to remove excess powder, and polished. Spacers were made from glass filled polyester and allowed a controlled thickness of film to be generated between 0.03 and 1.2 mm. All films were stored in a dissector until they were used.

Infrared Measurements

Infrared spectra were recorded in the mid infrared (MIR) region using a Perkin-Elmer 125 Grating Spectrophotometer ($10,000-400$ cm^{-1}). Infrared spectra were obtained for pristine films and films aged by immersion in deionized water at 298 K for 14 days.

Gravimetric Measurements

Thin films, approximately 0.2-mm thick were immersed in deionized water at 298 K and weighed periodically using a Mettler M5 balance capable of measuring to ± 0.00001 g, and the film weight was typically 0.2 g. The samples were removed from the water and wiped to remove excess water. After 2 min the samples were weighed and reimmersed after 3 min total out of water.

Low-Frequency Dielectric Measurements 10^{-2} to 10^5 Hz.

Dielectric measurements, from 10^{-2} to 10^5 Hz were carried out on a sandwich construction[18] formed by silver coating two surfaces of a thin film. It has been previously found that a 50 nm-thick film of silver is completely permeable to water yet forms a sufficiently coherent conducting film to act as a good electrode. One of the surfaces was coated with a 50-nm film, and the other with a film thicker than 100 nm, and this latter acts as an impermeable active electrode. The active electrode was further covered with silicone sealant and made effectively impermeable to water ingress. After the first 18 h of measurement the change in dielectric response was slow enough to be measured down to 10^{-3} Hz.

High-Frequency Dielectric measurements 10^5 to 3×10^9 Hz

High-frequency measurements, 300 kHz to 3 GHz, were obtained using a Hewlett-Packard 8753A network analyzer and were performed on samples that formed the termination of a coaxial line, and had a diameter of 17 mm and were silvered onto both sides. Thermostating was achieved using a water condenser assembly sur-

Table I Relaxation Temperatures for Both Wet and Dry Samples of Different Stoichiometric Ratio

Ratio	Curing Time	Relaxation Onset Temperature (°C)	
		Dry Sample	Wet Sample
3 : 1	17 h/22 h	49/49	59/51
2 : 1	17 h/22 h	55/52	55/55
1.5 : 1	17 h/22 h	*/*	61/59
1 : 1	17 h/22 h	85/85	65/68
1 : 1	17 h/22 h	88/88	65, 90/67, 92
1 : 1	17 h/22 h	65/64	35, 71/30, 71

rounding the coaxial line, and maintained a temperature of 298 K. Measurements were performed in the reflection mode, and correction was made for the mismatches between the sample and the connectors.

Dynamic Mechanical Thermal Analysis

A Polymer Laboratories Dynamic Mechanical Thermal Analyzer MKIII was operated at a frequency 1 Hz, a strain of ×4, and a scanning rate of 3 K per minute using samples $20 \times 10 \times 0.5$ mm. The clamping torque in the single cantilever arrangement was $30 \, N$. Measurements were performed from 273 K to above the T_g. With the softer materials careful attention was given to problems of clamping of the sample.

RESULTS AND DISCUSSION

State of Cure

The NIR spectra were used to determine the extent of opening of the epoxy groups by monitoring the intensity of the 916 cm^{-1} ring absorption. Unfortunately, a strong band due to hardener TETA lies close to the 916 cm^{-1} band, and it was, therefore, not possible to make quantitative determination of the epoxy ring content. However, in the epoxy-rich materials significant levels of residual epoxy groups were observed, whereas in the amine-rich material this absorption is absent. The DMTA traces for the pristine materials were obtained and values of the T_g determined (Table I). Only relatively small changes in the value of T_g with cure time and composition were observed. Reproducibility of the DMTA traces indicated that

the procedures used were producing consistent samples.

Sorption of Water Studies

Gravimetric Measurements

Although the sorption processes of liquids and vapors in glassy polymers follow complex mechanisms, water diffusion in epoxy resin matrices has been frequently represented by a Fickian behavior,[19–21] and has the following features[22]: (a) the sorption curves are linear in the initial stages; (b) above the linear portion both absorption and desorption curves are concave to the abscissa. For absorption, the linear region extends to over 60% or more of the region studied; and (c) when a series of reduced absorption curves are plotted for films of different thickness the curves are superimposable. If a plane polymer sheet is exposed to a fluid, the change of the concentration (C) of a diffusing substance as a function of time (t) and position (x) is given by Fick's second law[21]:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \qquad (1)$$

where D is the diffusion coefficient. If the material has a uniform initial diffusant concentration (C_o) and the surface is kept at a constant concentration C_{max}, the solution of eq. (1) is[20]:

$$\frac{C - C_o}{C_{max} - C_o} = 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n + 1}$$
$$\times \exp[-D(2n + 1)^2 \pi^2 t/h^2] \cos \frac{(2n + 1)\pi x}{h} \qquad (2)$$

The concentration of a substance diffusing into the polymeric material (M) as a function of time is given by the integral of eq. (2) across the thickness (h):

$$\frac{M}{M_{max}} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n + 1)^2}$$
$$\times \exp[-D(2n + 1)^2 \pi^2 t/h^2] \qquad (3)$$

where M_{max} is the maximum quantity of the diffusing substance at infinite time. A simplified form of eq. (3) for values of M/M_{max} lower than 0.6[21] has the form:
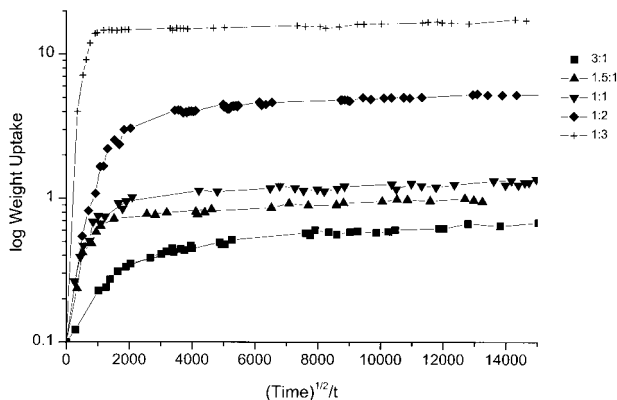
Figure 1 Weight uptake plots for different stoichiometric ratios.

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

For gravimetric analysis, eq. (4) is a valid representation of the time dependence of the water uptake.

Analysis of the water absorption data, which is presented in Figure 1, allows determination of the maximum weight gain M_∞ and the diffusion coefficient D (Table II). A log scale is used to present the data so as to enable all the data to be displayed in the same figure. The curves can be split into two regions: the initial absorption, which follows a pseudo-Fickian behavior and can be analyzed using eq (4). Subsequent absorption leads to a much slower rate of weight increase, and following Johncock,[17] the value of M_∞ was obtained by extrapolation of the second curve back to zero. The second region is a reflection of the changes that occur in the matrix as a result of the stress relaxation of the resin. An excess of epoxy groups does not significantly increase the equilibrium water absorption but does lead to a lower value of the rate of water absorption. In contrast the use of an excess of amine leads to higher water absorption and higher rates of water absorption. Previously, Carfagna,[23] using differential scanning calorimetry, has observed that if a large excess of hardener is used high levels of water uptake are observed, and has attributed this behavior to the formation of microcavities within the matrix and that the process is exothermic. The behavior reported here from gravimetric measurements are consistent with the observations reported here.

Dielectric Measurements

Measurements were performed over the frequency range 10^{-3} to 3×10^9 Hz over a period of 2 weeks. An initial rapid increase in the dielectric permittivity and loss for all of the samples is observed, after which the profile becomes almost constant. An example of this behavior is shown in Figure 2 for the 1 : 1 stoichiometric ratio sample. The dielectric relaxation can be classified into three regions: (1) nelow 10 Hz the observed loss is associated with a combination of processes associated with the heterogeneous nature of the epoxy and the tail of the glass transition process; (2) the peak at $\sim$ 10 kHz is associated with relaxation of the hydroxyl group. The increase in the value for this relaxation reflects the fact that water molecules are binding to this group; (3) the relaxation at $\sim 10^9$ Hz and above is associated with "free" water.[6] The relaxation of pure water at room temperature occurs at 2×10^{10} Hz. A relaxation at this frequency in a solid indicates clusters of water molecules have formed a mobile phase within microvoids. There is sufficient separation between the process at 10 kHz and that at 10^9 Hz for these relaxations to be ascribed to different types of mechanism.

Interpretation of the dielectric measurements requires an extension of the diffusion theory in which access is only allowed from one side. Under isothermal conditions the increase in the permittivity observed during water diffusion ($\varepsilon' - \varepsilon'_0$) is proportional to the number of water dipoles present in the system.[24,25] Therefore, a linear relationship between and the water concentration in the polymer is expected. It has, however, been pointed out previously[20,24,26] that there is a discrepancy observed between the observed increment and that predicted on the basis of the amount of water absorbed. The change in the dielectric increment as a result of diffusion can be modeled according to the following equation:

Table II   Maximum Weight Gain and Diffusion Coefficients from Dielectric Measurements at 10 Hz

Ratio	M_∞ (%)	D (cm^2 s^{-1})
3 : 1	0.5	1.20×10^{-8}
1.5 : 1	0.8	2.12×10^{-8}
1 : 1	1.1	3.11×10^{-8}
1 : 2	4.4	4.93×10^{-8}
1 : 3	14.2	$26.9 \ \times 10^{-8}$

$$D = -\frac{h^2}{t_{1/2}\pi^2} \ln\left[\frac{\pi}{8}\right] \quad (6)$$

Furthermore, eq. (6) can be written in the approximate form:

$$D = 0.0947h^2/t_{1/2} \quad (7)$$

It has been observed that measurements of the diffusion permittivity at different frequencies lead to different values of the apparent diffusion coefficient,[27] lower apparent values being observed at higher frequencies. It may be assumed that the variation of the dielectric permittivity measured at 10 Hz reflects the total relaxation spectrum of the water molecules in the matrix and, hence, is correlated with the total sorption process. Water molecules in the matrix are, in general, bound to the hydroxyl group generated during the ring opening process and, hence, contribute to the relaxation process located at about 10^5 Hz at room temperature. Measurements at about 10^6 Hz will reflect only water molecules that are loosely bound in the matrix and are designated "free" water. Analysis of the dielectric permittivity variation at these frequencies will be used to discuss the difference between "free" and "bound" water in the matrix. The permittivity of free water is 80.4 at 293 K, and apparent discrepancies between prediction and theory have been reported.[24-27] The water molecules may be assumed to be either clustered, in which case the dielectric increment should closely correlate with the value for water, or be bound to the matrix, in which case a lower value may be expected. Studies of the DGBA/TETA system indicate that the calculated diffusion coefficients are not significantly changing with changes in nonstoichiometry. The results are presented in Table III, and the normalized dielectric permittivity plots at 10 Hz in Fig-

(a)

(b)

Figure 2 (a) Dielectric permittivity, and (b) Dielectric Loss for the 1 : 1 stoichiometric ratio.

$$\frac{\varepsilon' - \varepsilon_0'}{\varepsilon_{max}' - \varepsilon_0'} = 1 - \frac{4}{\pi}\sum_{n=0}^{\infty}\frac{(-1)^n}{2n+1}$$
$$\times \exp[-D(2n+1)^2\pi^2 t/h^2] \quad (5)$$

where ε_{max}' is the maximum value of the dielectric permittivity achieved by the water diffusing into the polymer matrix. In this case, the diffusion coefficient (D) can be estimated by considering only the first term in eq. (5) (i.e., $n = 0$) and using the half-time $(t_{1/2})$ corresponding to $\varepsilon' - \varepsilon_0'/\varepsilon_{max}' - \varepsilon_0'$, with the condition that

$$\exp[-D\pi^2 t_{a/2}h^2]\pi 1.$$

Thus:

Table III   Relative Maximum Permittivity and Diffusion Coefficients from Dielectric Measurements at 10 Hz

Ratio	ε_{max}' (rel)	D (cm^2 s^{-1})
3 : 1	0.36	1.91×10^{-8}
2 : 1	0.37	0.83×10^{-8}
1.5 : 1	0.39	1.18×10^{-8}
1 : 1	0.53	1.43×10^{-8}
1 : 2	> 1.3	0.95×10^{-8}
1 : 3	> 100	—

ure 3. No results were obtained for the sample of ratio 1 : 3, as the electrodes became detached from the material. This ratio was repeated several times, but on each occasion the sample warped and the dielectric electrode continually failed. The warping of the sample was possibly due to a large amount of water taken up by the sample in a short space of time. Analysis of the dielectric permittivity variation showed the difference between the amount of "free" and "bound" water in the matrix, and the values of these can be seen in Table IV. The results show that as the hardener ratio is increased there is an increase in the amount of free water in the system. The water molecules will initially move through the matrix, and generation of "free" water can only occur once the water molecules find a microvoid. This, in part, explains the differences in the behavior reflected in the analysis at low- and high-frequency data.

Assuming a linear relationship between $\varepsilon' - \varepsilon'_0$, the low-frequency values for ε'_{max}, and the amount of water absorbed, we see that the amount of absorbed water for the excess epoxy ratios is nearly constant, and only increases significantly for excess hardener. A small increase in ε'_{max} between the first three ratios (Table III), are of the order of the precision in the measurement of the dielectric permittivity. The diffusion coefficients observed from dielectric measurements in the case of the high amine content materials exhibit lower values than those observed by gravimetric measurement. The amine has the possibility of influencing the ability of the deposited metal to form a coherent film, and the traces obtained are consistent with the formation of a partially blocking coherent film being formed in these cases. The effect that this
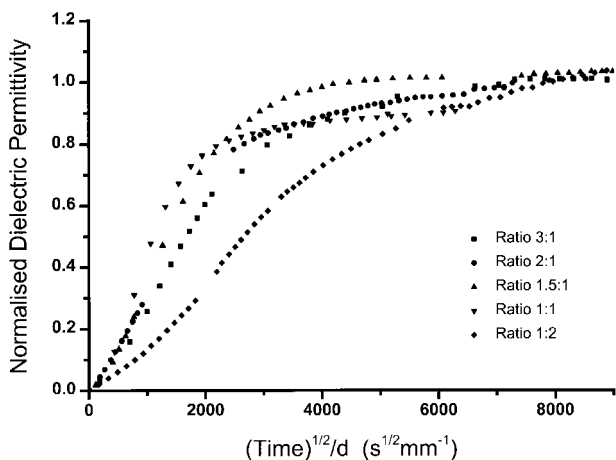
Table IV   Calculated Values of Bound and Free Water from Dielectric Measurements at 10 Hz and 10^6 Hz

Ratio	% Bound	% Free
3 : 1	70.3	29.7
2 : 1	66.7	33.3
1.5 : 1	47.0	53.0
1 : 1	46.0	54.0
1 : 2	18.1	81.9
1 : 3	10.0	90.0

will have is to slow the initial rate of water absorption leading to lower apparent diffusion coefficients than those observed from gravimetric measurement. Although we have to caution on the validity of the diffusion coefficients, the analysis of the distribution of water between bound and free states is unaffected by the electrode problem.

Dynamic Mechanical Analysis

DMTA measurements were performed for the initial dry samples and samples stored in deionized water for 21 days for each stoichiometric ratio of epoxy and for both 17 and 22 h cure times. As an example of the data, the traces obtained for the 1 : 1 stoichiometric ratio are shown (Fig. 4), and the values of the glass transition temperatures, T_g are presented in Table I. In general, increasing cure time leads to an increase in the value of T_g, and the apparent drop for 2 : 1 and 1 : 3 dry ratios is an indication of the reproducibility of the sample preparation method and, therefore, shows the limits of accuracy of the applied technique. The highest value of the T_g is observed for equimo-
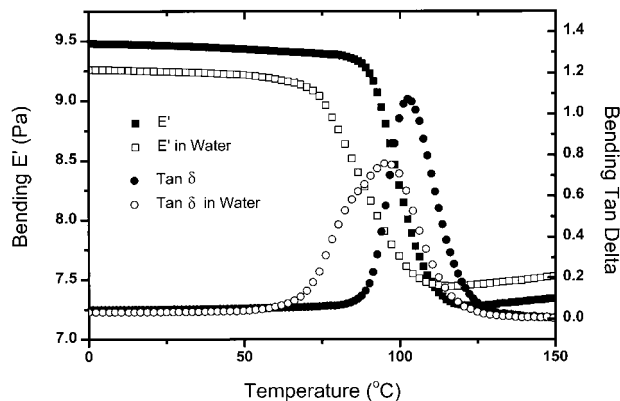

Figure 3   Normalized dielectric permittivity plots at 10 Hz for different stoichiometric ratios.

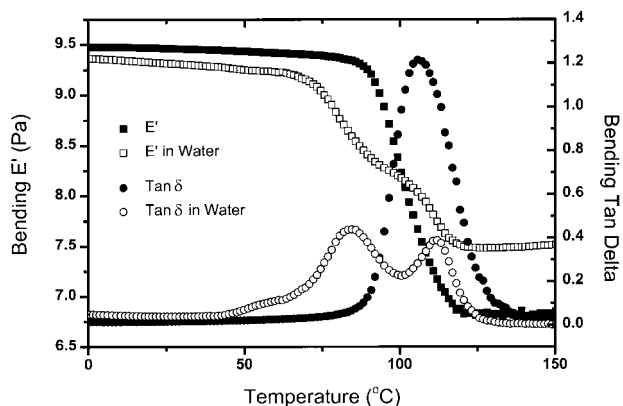**Figure 4**   Dry and wet DMTA traces for the 1 : 1 stoichiometric ratio.

Figure 5 Dry and wet DMTA traces for the 1 : 2 stoichiometric ratio.

lar ratio or the material with a slight excess of hardener (ratio 2 : 1), consistent with the ratio at which the highest crosslinking should develop and, hence, highest value of T_g. The 1 : 3 ratio material behaves like a low molecular mass thermoplastic, the T_g process extending into viscous flow behavior. For samples with an excess of epoxy, no significant change in T_g seems to occur as a consequence of water uptake, implying that gross plasticization does not occur in this system. It was, however, interesting that a shoulder on the low temperature side of the T_g peak was observed in the wet 1 : 1 ratio sample and becomes a separate process for higher hardener ratio (Fig. 5). This implies the existence of network inhomogenities that may also contain a higher concentration of hydroxyl groups and that water may be plasticizing particular regions of the material more effectively than others.

Ir Spectra of Films Exposed to Water

Spectra of the cured materials before and after water uptake were measured and are assigned in

Table VI   Wavenumbers and Relative Absorbance Values for the O—H/N—H Stretching Band with the Band at 3035 cm^{-1} as Standard ($A_{3035 \text{ cm}^{-1}} = 1$)

Ratio		Wavenumber (cm^{-1})	Rel. Absorbance
3 : 1	dry	3471	0.88
	wet	3446	1.06
2 : 1	dry	3446	0.99
	wet	3427	1.23
1.5 : 1	dry	3427	1.15
	wet	3415	1.18
1 : 1	dry	3415	1.40
	wet	3402	1.72
1 : 2	dry	3370	1.26
	wet	3382	1.92
1 : 3	dry	3351–3301	1.14
	wet	3369–3302	1.48

For comparison, calculations were taken for spectra of four different dry samples per ratio (not shown).

Table V. The main change observed on exposure to water is an increase in the absorption located around 3300–3400 cm^{-1} (Table VI), which are associated with the OH/NH absorption bands. The absorption was observed to generally increase, and no new specific bands were observed. This observation would be consistent with strong association of the water molecule with the pendant hydroxyl group. A small shift was observed to lower frequencies with increasing hardener concentration or moisture uptake, and the absorbance is also increased, being highest for ratio 1 : 1 and decreasing for the higher ratios. For the dry spectrum of the ratio 1 : 3, the band splits into two peaks, possibly indicative of resolution of OH and NH absorptions.

Table V   Assignments for the MIR Spectrum of Cured DGEBA/TETA, Both Wet and Dry

Band (Wavenumber in cm^{-1})	Assignment
3350–3471	v (O—H)hydrogen bound
	v (N—H)primary + secondary
3035	v (CH$_2$)epoxy ring
2965	v (C—H)aliphatic
1645 (shoulder) in wet samples	δ(HOH)
1608	v (C—C)aromatic
1506	v (C—C)aromatic
916	epoxy ring

Midinfrared Spectra

Liquid water shows two characteristic bands at 1635 cm^{-1} and, very broad, at around 3446 cm^{-1}. The former can be observed as a shoulder at around 1645 cm^{-1} in the spectra for the wet samples, most obviously for the amine content materials.

CONCLUSIONS

Increasing the amine ratio in an epoxy resin has the effect of increasing the rate of water absorption and increasing the equilibrium water uptake. Analysis of the dielectric results at low and high frequency over a range of stoichiometric ratios shows the extent to which the water molecules are bound to the resin or exist as free water. As the amount of amine is increased, the amount of free water increases, which could indicate more free volume in the system. Dynamic mechanical analysis showed the expected trend with the highest value of T_g occurring for the 1 : 2 stoichiometric ratio material, which would be expected to have the highest crosslink density. The occurrence of two relaxations in the high amine ratio DMTA traces implies the existence of different environments within the samples. The FTIR data showed that there were no significant effects with compositional change in the nature of water absorption in these materials.

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