Dielectric relaxation due to absorbed water in various thermosets

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The dielectric relaxation due to absorbed water has been studied with a number of epoxies and other thermosets. In all cases, the absorbed water relaxation strength, as measured by both the dielectric-constant increase and the increase in area under the ε'' *versus* $1/T$ curve, seems to be attributable to the relaxation of water dipoles and not to Maxwell–Wagner–Silars effects. The activation energies obtained are in the 11–16 kcal mol^{-1} range. The relaxation strengths observed show that the water molecules manifest roughly 70–100% of their free-state polarizability. In general, the dielectric constant increase per 1 wt% of water absorbed is given to a good approximation by $4.0[\varepsilon(\text{dry})+2]^2\rho f/T$ where f is the fractional polarizability of water in the polymer to its free-state value, found to be 0.7 to 1.0 for most thermosets, and ρ and T are the density and temperature.

(Keywords: dielectric properties; effects of water; dielectric constant; loss factors)

INTRODUCTION

The nature of water absorbed into polymers has been studied in detail using nuclear magnetic resonance (n.m.r.)[1-3] and differential scanning calorimetry (d.s.c.)[4-8]. Some of the results for hydrophilic polymers indicate that a certain amount of 'bound water' is associated with the polymer[1,5,6] and for that reason does not crystallize even at temperatures well below the freezing point of water. A recent study of water in saponified starch–acrylonitrile copolymer[5] showed that the partial molar heat capacity of water at 12°C increased from values close to those of ice to values typical of liquid water with increasing water content. This indicated that the initial water absorbed was bound and, due to decreased mobility, showed a smaller heat capacity in addition to not being freezable. Additional water was found to freeze and also to have a higher heat capacity. Work with water in collagen[8], however, showed all water absorbed to have a gradually decreasing partial molar heat capacity in going from 30°C to -90°C, with values in excess of free water values observed at the higher temperatures and ice-like smaller values observed as -90°C was approached. The absence of a phase transition seemed to demonstrate that there was only one phase and that it consisted of chains of hydrogen-bonded molecules of appreciable mobility at higher temperaures and little mobility at lower temperatures. Furthermore, the authors stated, in agreement with others[7], that the lack of crystallization of absorbed water at low temperature did not necessitate strong bonding to the polymer. With conflicting models of water–polymer interactions, dielectric data offer an additional perspective of the behaviour of absorbed water as a reflection of both the morphology and any orientational constraints that exist. A study of water absorbed in polycarbonate[4], for example, reported that a Maxwell–Wagner–Silars dielectric relaxation could be attributed to 'clustered' water while a dipolar dielectric loss was associated with the proportionally greater amount of non-crystallizable water.

The effect of water on the dielectric constants and loss characteristics of polymers has been discussed in terms of both the conductivity of water occlusions[9-11] and the dipolar nature of water[4,12,13]. The applicability of either perspective depends on whether the water exists as droplets or as individual molecules. If a Maxwell–Wagner–Silars[10] (MWS) model is adopted to explain the effect of interfacial polarization on the dielectric properties, the results are strongly dependent upon the average aspect ratio of the occlusion. In addition, the location of the loss peaks varies by orders of magnitude depending upon the observed conductivity of the water in the polymer, though usually falling in the 10^5–10^6 Hz region corresponding to a water conductivity of 5×10^{-6} to 5×10^{-5} (ohm cm)$^{-1}$. Assignment of loss peaks or dielectric constant increases to interfacial polarization or dipolar origin must be cautious as the effects can be similar in behaviour. In terms of *weight percentage* of water, m, absorbed, the effect of interfacial polarization (for the dilute case of spherical droplets) according to Silars or Hanai[10] can be shown to give a static dielectric constant as a function of m, $\varepsilon'(m)$, according to:

$$\varepsilon'(m)=\varepsilon'(\text{dry})+0.03\varepsilon'(\text{dry})\rho m \tag{1}$$

where ε(dry) is the polymer's dry dielectric constant and ρ is the polymer density.

Considering instead the dipolar nature of molecular

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water, the static dielectric constant is given, for $m \leq 3\%$, by:

$$\varepsilon'(m) \simeq \varepsilon'(\text{dry}) + 4.0[\varepsilon'(\text{dry}) + 2]^2(\rho/T)m \qquad (2)$$

This can be derived from either the Onsager equation or the Clausius–Mossotti equation, where the resulting expression is relatively insensitive to the modelling for the internal field for small amounts of water. The water relaxation strength per 1% of water absorbed, $[\varepsilon'(m) - \varepsilon'(\text{dry})]/m$, is higher for equation (2) than equation (1) by about a factor of 3–4. Since the constant in equation (2) is derived from the polarizability of free, unassociated water molecules, $\mu^2/3kT$, where μ is the electric dipole moment of water, any reduction in the slope of $\varepsilon(m)$ with respect to m should be a measure of the reduction of the polarizability of water molecules from the free, unassociated value. Such an analysis has been carried out in the case of polyimide films with water exhibiting most of its free-state polarizability[13]. Other studies[4,12] have examined the relaxation strength due to water by the temperature dependence of the relaxation strength, $\varepsilon_R - \varepsilon_U$, according to:

$$\varepsilon_R - \varepsilon_U = \frac{2E_{\text{act}}}{\pi R}\int_0^\infty [\varepsilon''(\text{wet}) - \varepsilon''(\text{dry})]\,\mathrm{d}(1/T) \qquad (3)$$

Here ε_R and ε_U are the relaxed and unrelaxed dielectric constants located on the low- and high-frequency sides of the relaxation, respectively, E_{act} is the activation energy, and $\varepsilon_R - \varepsilon_U$ here is the relaxation strength at the temperature of maximum loss and the activation energy can be taken as an average over any distribution of relaxation times present[14]. Any difference between $\varepsilon_R - \varepsilon_U$ obtained from the loss data and that calculated by the Onsager expression for $\varepsilon_R - \varepsilon_U$ would represent reduced polarizability of water in the polymer compared to its unassociated value. The results show that water exhibited about half of its unassociated polarizability in most cases.

The following study examines dielectric constant and loss data for a number of thermosets containing varying amounts of water. Changes in the dielectric properties with water content, frequency and temperature are used to lend understanding to the water relaxation process in thermoset polymers in terms of relaxation strength, effective water polarizability, activation energy and relaxation-time distribution.

EXPERIMENTAL

Dielectric measurements were made using a Hewlett-Packard 4192A impedance analyser interfaced to a series 200 computer and also a GenRad 1620A capacitance bridge. Owing to typical sample capacitances of 30–80 pF, the 4192A was usually only adequate for the frequency range of 10^4–10^7 Hz, while the 1620A could be used in the 10^2–10^4 Hz region. Room-temperature measurements were performed with an LD3 (Gilian) guarded cell. Measurements at varying temperatures were performed with silver-painted surfaces and contacting electrodes in an insulated cell operating in the −196 to 250°C range. Edge capacitance was subtracted out using the appropriate equations[15], and residual impedance and stray admittance was accounted for. Absolute accuracy in the dielectric constant was consistently ~1%. Absolute accuracy in dissipation factor is $\sim 10^{-4}$ in the 10^2–10^4 Hz region and $\sim 10^{-3}$ in the 10^4–10^7 Hz region. Temperature scans with wet samples were normally conducted at 1°C min^{-1} and usually limited to below 70°C as it was found that under these conditions little change in water content of the $\frac{1}{8}$ inch (3 mm) thick samples occurred.

Three epoxy systems were studied in detail. Two were difunctional epoxies based upon the diglycidyl ether of bisphenol A (see *Figure 1a*). One utilized DER* 383 epoxy resin (epoxide equivalent weight of ~181) with a diaminocyclohexane curing agent (105% stoichiometry), and the other was made from DER 331 epoxy resin (epoxide equivalent weight of ~186) with a hexahydrophthalic anhydride curing agent. The other epoxy studied was Quatrex* 5010. Quatrex 5010 is a one-component, high-performance laminating resin/hardener system ($T_g = 185$°C). The resin is based on tris(hydroxyphenyl)methane (*Figure 1b*). Oligomers as shown in *Figure 1c* are typical of the composition. The curing agent is based on a brominated aromatic polyhydric crosslinking agent. Also studied was a thermoset based on a bisphenol A dicyanate monomer (*Figure 1d*) which self-cures through trimerization to form a triazine ring network structure.

Equilibrium water contents were obtained by either direct water immersion at varying temperatures (25–100°C) or exposure to given temperature and humidity conditions (Blue M FRH-251). It was found that the dielectric constant corresponding to a given weight percentage of absorbed water, for a given sample, did not depend on the manner of water absorption with the materials studied. With many samples, the dielectric constant was monitored as a function of weight percentage of water through many cycles of saturation and drying with no apparent hysteresis. Water content was monitored by sample weights with differences of

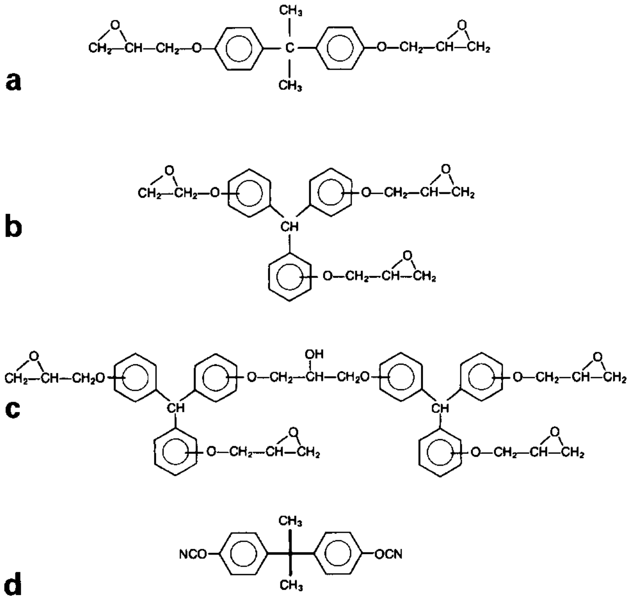

Figure 1 Chemical structures for (a) diglycidyl ether of bisphenol A, (b) tris(hydroxyphenyl)methane, (c) typical oligomers of tris(hydroxyphenyl)methane, and (d) bisphenol A dicyanate

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10 ppm detectable. Dry sample weights were determined by heating the sample at 100°C under vacuum for 2–4 days. The time dependence of the water pick-up is shown in *Figures 2–4* for three epoxies for conditions of 35°C/90% r.h. and 85°C/85% r.h. Data for samples with and without silver electrodes are shown with virtually no difference. The water pick-up is plotted *versus* $t^{1/2}$, where t is time, to show the Fickian behaviour. The diffusion coefficients for the 85/85 condition are obtained from the slope of the curves and lie in the range of (8–9)$\times 10^{-8}$ cm^2 s^{-1}.

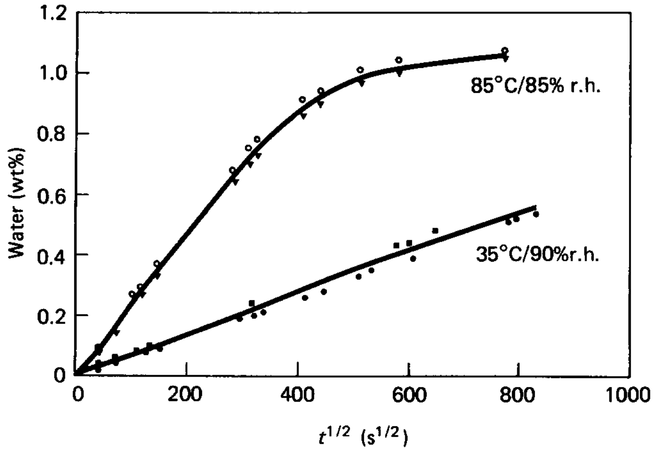

Figure 2 Water pick-up as a function of $t^{1/2}$ for Quatrex 5010 resin for electroded (▼, ●) and non-electroded samples (○, ■)

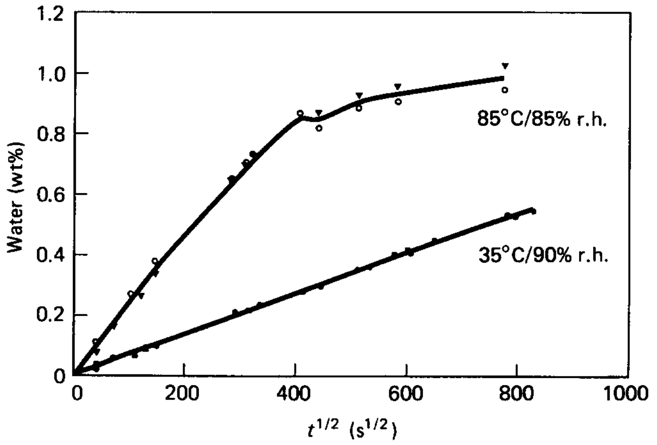

Figure 3 Water pick-up as a function of $t^{1/2}$ for DER 331 resin (cured with hexahydrophthalic anhydride) for electroded (▼, ●) and non-electroded samples (○, ■)

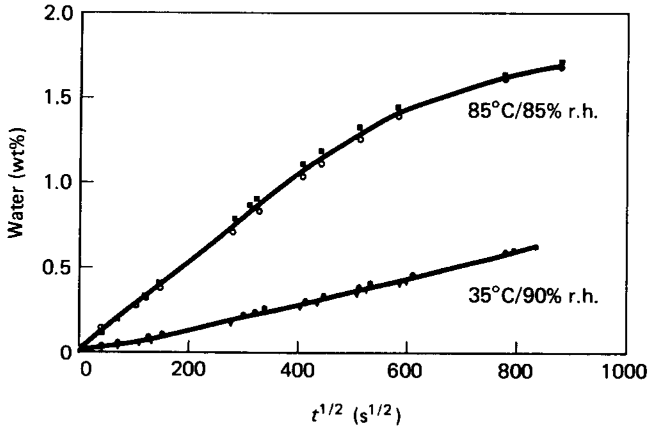

Figure 4 Water pick-up as a function of $t^{1/2}$ for DER 383 resin (cured with cycloaliphatic amine) for electroded (■, ●) and non-electroded samples (○, ▼)

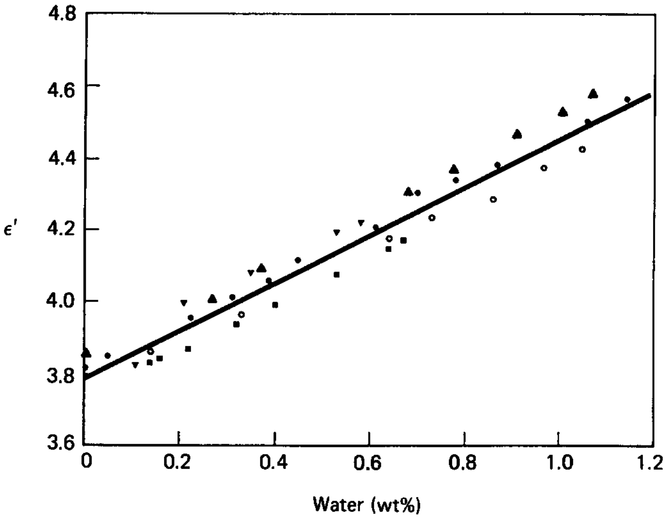

Figure 5 10 kHz dielectric constant as a function of water content for Quatrex 5010 resin: ●, boiled water (electroded); ■, 35°C/90% r.h. (electroded); ▼, 35°C/90% r.h. (non-electroded); ○, 85°C/85% r.h. (electroded); ▲, 85°C/85% r.h. (non-electroded)

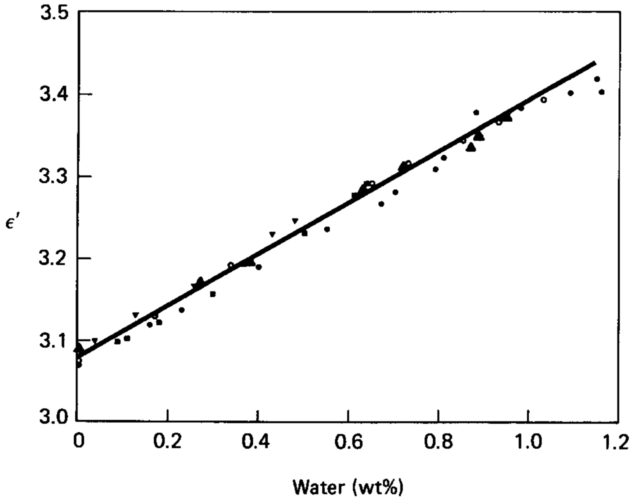

Figure 6 10 kHz dielectric constant as a function of water content for DER 331 resin (cured with hexahydrophthalic anhydride): symbols as for *Figure 5*

RESULTS AND DISCUSSION

Dielectric data as a function of water content, frequency and temperature were collected for the three epoxy systems studied in detail. The dielectric constant at 10 kHz as a function of water content is shown in *Figures 5–7* for all three epoxies. The effect of water pick-up for each epoxy is recorded as it occurs through (1) water immersion (at varying temperatures); (2) exposure to 90% relative humitidy at 35°C; and (3) exposure to 85% relative humidity at 85°C. Both electroded and non-electroded samples were used in the latter two cases, making five sets of data for each epoxy. It is seen that in the case of Quatrex 5010 and DER 383, there is some slight scatter (0.1) in the dry dielectric constant amongst the various data sets, but that the slopes are essentially the same with the linear correlation coefficient being $r = 0.99$ for any one data set. The discrepancy in dry dielectric constant amongst the data sets for a given epoxy is $\pm 1\%$ and is for the most part due to some residual moisture in some of the samples. A least-squares line is drawn in each figure based on all of the data sets for each epoxy with the value of the slope and dry dielectric constant recorded in *Table 1*.

Apparent activation energies for the water relaxation were obtained by examining the loss peaks due to water in the −150 to 50°C range. the loss peaks here are the values of ε''(wet)−ε''(dry) as a function of frequency. A typical spectrum is shown in *Figure 8*. Arrhenius plots for the water loss peak frequencies of the three systems are shown in *Figure 9*. These plots each use data for two weight percentages of water and show no noticeable change in slope with changing water content. This is important since if the loss peaks were in part due to plasticization of the polymer by water, it would be expected that the activation energy would be strongly influenced by the amount of plasticizer. It is noted also that excellent linearity is obtained for each epoxy with a number of data points utilized. The activation energies obtained are between 11 and 16 kcal mol^{-1}. Suzuki *et al.*[12] obtained values of around 10 kcal mol^{-1} for water in thermoplastics in the majority of cases. The values for the activation energy, E_{act}, and τ_0, related to the entropy of activation, are given in *Table 2*, where:

$$\tau = \tau_0 \exp(E_{act}/kT) \quad (4)$$

In all three cases, the room-temperature relaxation corresponds to a peak at ~10^5 Hz which fortuitously corresponds to the region where an MWS peak would be found. The 10 kHz relaxation peaks are all compared in *Figure 10* where T_{max}, the temperature of the loss maximum, falls in the 248–269 K range for all three systems. These loss spectra are again ε''(wet)−ε''(dry), but plotted *versus* $1/T$ instead of frequency and represent the resultant of separate temperature scans of wet and dry samples. The individual temperature scans of ε'' without normalization to the dry sample are shown in *Figures 11–13*, where two levels of water content and the dry condition are shown for each epoxy.

The effect of water on the dielectric constant can be considered from the standpoint of the Clausius–Mossotti equation as was done by Denton *et al.*[13] for a polyimide. The dielectric constant as a function of temperature, T, and frequency, ν, is given by:

$$\frac{\sum_i N_i \alpha_i(\nu,T)}{3\varepsilon_0} = \frac{\varepsilon(\nu,T)-1}{\varepsilon(\nu,T)+2} \quad (5)$$

where N_i and $\alpha_i(\nu,T)$ are the number densities and polarizabilities of the ith polarizable constituent and

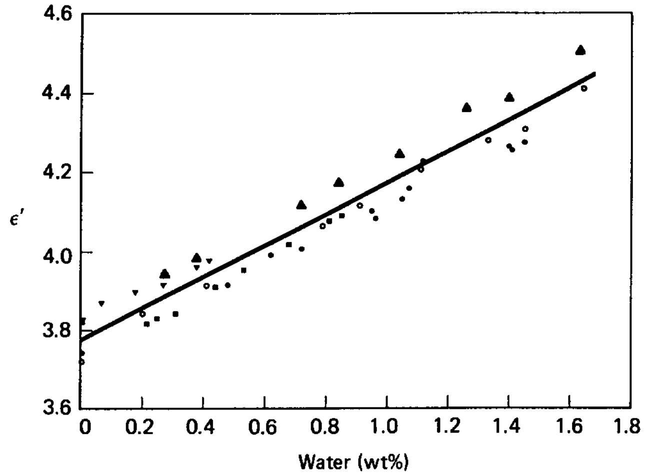

Figure 7 10 kHz dielectric constant as a function of water content for DER 383 resin (cured with cycloaliphatic amine): symbols as for *Figure 5*

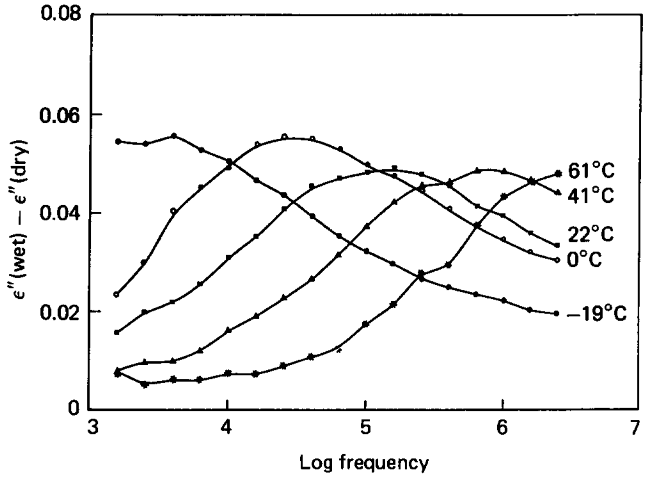

Figure 8 Loss factor due to water as a function of frequency and temperature for DER 383 resin (cured with cycloaliphatic amine) containing 1.2% water

Table 1 Slope, fractional water polarizability, relaxation strengths and activation energies for three epoxy systems

Resin	ε'(dry)	Slope[a]	f value[b]	f value[c]	$\Delta\varepsilon'/m$[d]	$\Delta\varepsilon'/m$[e]	T_{max}[f] (K)	E_{act}[g] (kcal mol^{-1})	τ_0 (s)
Quatrex 5010	3.78	0.68	1.0	0.7[h] 0.8[i]	0.52[h] 0.62[i]	0.80	251	16	4.8×10^{-19}
DER 383	3.78	0.39	0.7	0.5[j] 0.5[k]	0.31[j] 0.30[k]	0.42	268	15	4.8×10^{-19}
DER 331	3.08	0.31	0.8	0.4[l] 0.5[m]	0.19[l] 0.23[m]	0.37	248	11	1.3×10^{-15}

[a] Slope of dielectric constant with respect to weight percentage of water at 10 kHz and 298°C
[b] Fractional polarizability observed for water compared to calculated free values from slopes of dielectric constant
[c] Fractional polarizability observed for water compared to calculated free value from loss data
[d] Relaxation strength per 1 wt% of water calculated from water loss spectra area, $\int[\varepsilon''(\text{wet})-\varepsilon''(\text{dry})]\,d(1/T)$
[e] Relaxation strength per 1 wt% of water at T_{max} obtained from dielectric-constant slope multiplied by $298/T_{max}$
[f] Temperature of maximum water loss at 10 kHz
[g] Activation energy for relaxation time, $\tau=\tau_0\exp(E_{act}/kT)$
[h] 1.1% water
[i] 0.72% water
[j] 0.88% water
[k] 1.16% water
[l] 0.77% water
[m] 1.02% water

$\alpha_i(\nu,T)$ is a result of electronic and/or dipolar contributions. Using the limiting high-frequency ($\varepsilon' = \varepsilon_U$, $\alpha_{\text{dipole}} = 0$) and low-frequency ($\varepsilon' = \varepsilon_R$, $\alpha_{\text{dipole}} = \mu^2/3kT$) conditions, a relaxation strength, $\varepsilon_R - \varepsilon_U$, for any dipole-containing material is obtained that differs from the Onsager value by the fraction $2(\varepsilon_R - 1)(\varepsilon_R - \varepsilon_U)/3(\varepsilon_U + 2)\varepsilon_B$. For large dipole relaxation, as in epoxies, this fraction can be of the order of 15% due to the simplified treatment of the internal field; however, for smaller relaxations, as in the addition of small percentages of water, the difference decreases. The effect of water is derived to be:

$$\varepsilon'(\text{wet}) - \varepsilon'(\text{dry}) = \frac{\varepsilon'(\text{wet}) + 2}{\varepsilon'(\text{dry}) + 2}\left(\frac{\varepsilon'(\text{dry}) + 2}{3}\right)^2\left(\frac{\mu^2 N}{3kT}\right)f \qquad (6)$$

where μ is the dipole moment of water $(1.84 \times 10^{-18}\ \text{esu cm})$[14], N is the number density of water molecules, and f represents any fractional change of the observed water polarizability from its free, unassociated value. For weight percentages of water less than ~3%, we have:

$$\varepsilon'(m) - \varepsilon'(\text{dry}) = 4.0[\varepsilon'(\text{dry}) + 2]^2 fpm/T \qquad (7)$$

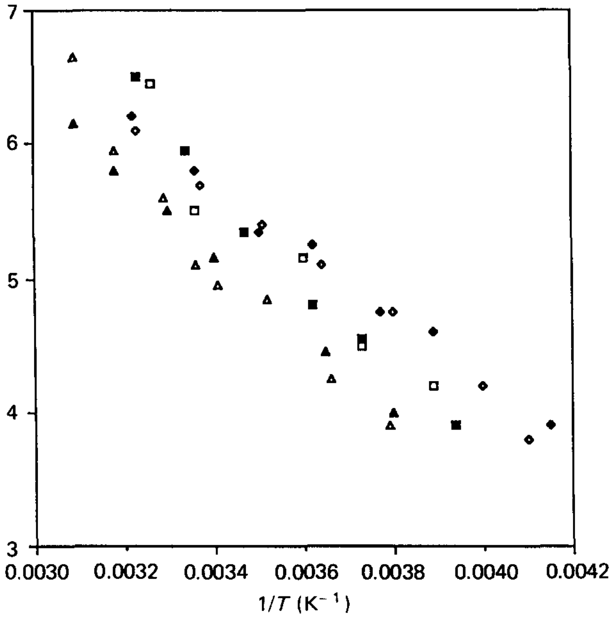

Figure 9 The frequency location of maximum loss for the water relaxation in the three epoxies studied where two weight percentages of water are given for each epoxy. The frequencies shown correspond to the maximum ε″(wet) − ε′(dry) value: □, Quatrex, 1.1%; ■, Quatrex, 0.7%; ◆, DER 331, 1.0%; ◇, DER 331, 0.8%; ▲, DER 383, 1.2%; △, DER 383, 0.7%

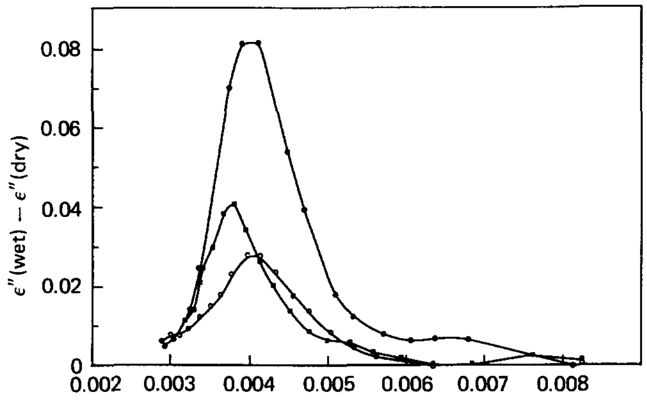

Figure 10 Water relaxations in three epoxy systems where the loss factor due to water at 10 kHz is plotted as a function of 1/*T*: ●, Quatrex, 1.10 wt% water; ■, DER 383, 0.88% water; ○, DER 331, 0.77% water

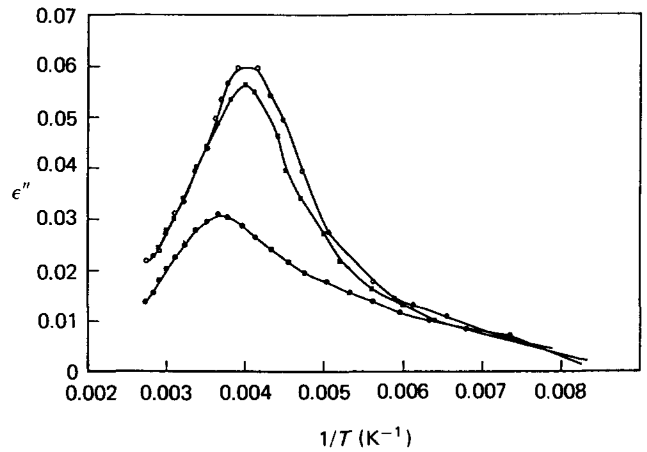

Figure 11 Loss factor at 10 kHz as a function of 1/*T* for DER 331 resin (cured with hexahydrophthalic anhydride): ●, dry; ■, 0.77% water; ○, 1.02% water

Table 2 Dry dielectric constants, slopes with respect to water pick-up and fractional polarizability observed for water for various polymers

Resin[a]	ε′(dry)	Slope[b]	*f* value[c]
DER 331 (hexahydrophthalic anhydride)	3.13[d]	0.22	0.6
DER 383 (cycloaliphatic diamine)	3.85[d]	0.42	0.8
Quatrex 5010	3.81[d]	0.67	1.0
Bisphenol A dicyanate thermoset	3.04[d]	0.24	0.7
Assorted triazine based thermosets	2.84[d]	0.26	0.7
	2.79[d]	0.30	0.9
	2.87[d]	0.26	0.7
	2.79[d]	0.27	0.8
Bisphenol A polyketone ether	2.97[e]	0.33	0.9
Tetramethylbisphenol A polyketone ether	2.85[e]	0.36	1.0
Amide based thermoset	3.75[d]	0.19	0.4
Diglycidylphenylbisphenol A epoxy (aminosulphone)	3.71[d]	0.34	0.7
Hydrocarbon based thermoset	2.60[d]	0.30	1.0
Bisphenol A based epoxy (polysulphide)	4.68[d]	0.51	0.8
Bisphenol A based thermoset	2.78[d]	0.34	1.0

[a] Curing agents in parentheses
[b] Slope of dielectric constant with respect to weight percentage of water
[c] Fractional polarizability exhibited by water
[d] 10 kHz
[e] 1 kHz

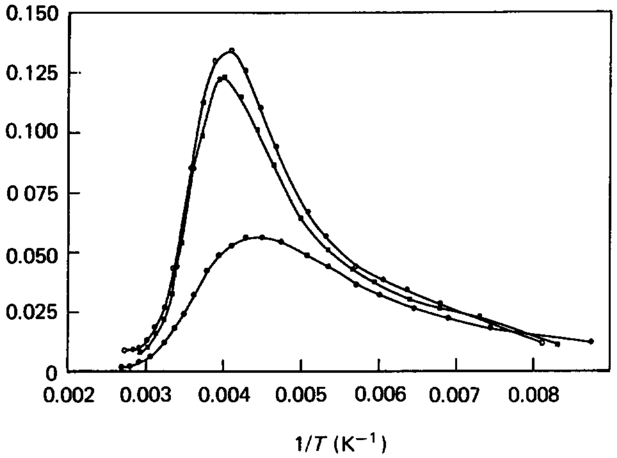

Figure 12 Loss factor at 10 kHz as a function of $1/T$ for Quatrex 5010 resin: ●, dry; ■, 0.72% water; ○, 1.10% water

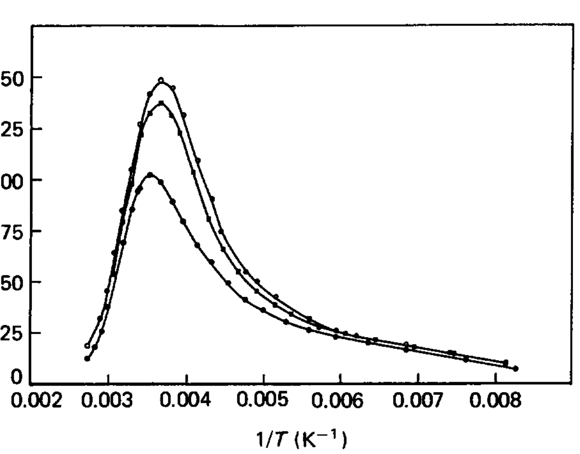

Figure 13 Loss factor at 10 kHz as a function of $1/T$ for DER 383 resin (cured with cycloaliphatic amine): ●, dry; ■, 0.88% water; ○, 1.16% water

where m is the weight percentage of water and ρ is the density of the polymer. It follows that $4[\varepsilon(\text{dry})+2]^2 f\rho/T$ is the water relaxation strength per 1 wt% of water, $\Delta\varepsilon'/m$, with $\varepsilon'(m)$ and $\varepsilon'(\text{dry})$ being equated to the relaxed and unrelaxed dielectric constants with regard to the water relaxation. The values of $\Delta\varepsilon'/m$ are recorded in *Table 1* where they are obtained from the room-temperature slope of the dielectric constant with respect to water content. Also given are the f values obtained, which indicate almost full participation of the water dipoles in the relaxation process.

The relaxation strength per 1 wt% of water can also be obtained through use of equation (3) and the loss data. The relaxation strength, $\varepsilon_R - \varepsilon_U$, entirely due to water is, however, the relaxation strength at T_{max}. Since relaxation strength is proportional to $1/T$, these values can be compared to room-temperature $\Delta\varepsilon/m$ values if the latter are multiplied by the factor $298/T_{\text{max}}$. Examination of both sets of values in *Table 1* shows reasonable agreement considering the $\Delta\varepsilon/m$ values obtained from the loss data are probably only accurate to ~15%. The fractional water polarizabilities (f values) obtained from the loss data are also shown in *Table 1* and are in all three cases lower than those obtained from the dielectric-constant slopes.

The broad nature of the water relaxation is evident from *Figure 8*. Choosing a Cole–Davidson distribution[15] for the complex permittivity, ε^*, we have:

$$\varepsilon^* = \varepsilon_U + \frac{\varepsilon_R - \varepsilon_U}{(1+i\omega\tau)^\gamma} \tag{8}$$

where γ is a measure of the spread of the distribution of relaxation times centred about τ. The maximum value of the loss factor is then given by

$$\varepsilon''_{\text{max}} = (\varepsilon_R - \varepsilon_U)(\cos\phi)^\gamma \sin\phi\gamma \tag{9}$$

$$\phi = \frac{\pi}{2}\,\frac{1}{\gamma+1} \tag{10}$$

Values for γ of 0.1–0.2 fit the data for the three epoxies studied, which compares with $\gamma = 1$ for a pure Debye relaxation. The use of a Cole–Davidson distribution follows from the skewed nature of the Cole–Cole plots[16]. *Figure 14* clearly indicates this where room-temperature Cole–Cole plots are shown for two weight percentages of water in Quatrex 5010. These Cole–Cole plots represent the pure effect of the water as the dielectric constants and loss factors shown represent the difference from the dry data. Also shown is that the same value of γ of 0.1 adequately fits both sets of data, indicating that differing amounts of water do not strongly affect the distribution of relaxation times in this case. Though these data only include frequencies up to a few megahertz, the curve must approach the origin at very high frequencies in both cases.

The use of non-static dielectric constants in analysis of the linear behaviour of water on the dielectric constant can be justified if, at the frequency and temperature studied, the loss factor is sufficiently below the maximum value. This is illustrated in *Figure 15* for Quatrex 5010, where room-temperature Cole–Cole plots are shown for varying water content. For the three frequencies indicated, spacings between the curves are about equal; however, it is the horizontal component that is being compared with equation (7). It is seen then for this sample that 1 kHz and 10 kHz yield the same slope as the static dielectric constant with respect to water content while 100 kHz data would yield a smaller slope.

Figure 16 shows 10 kHz dielectric-constant data for a variety of triazine-based thermosets as a function of water

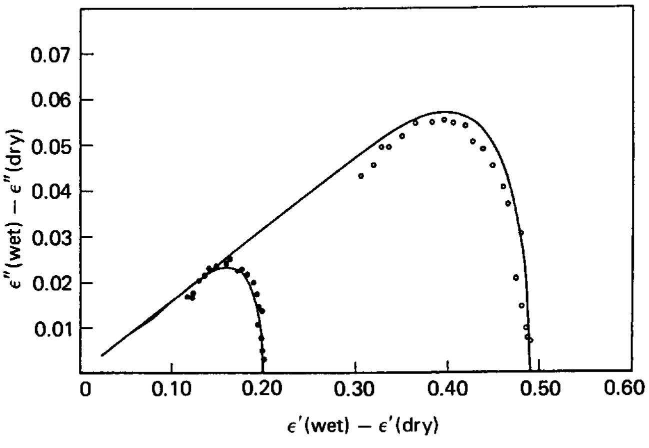

Figure 14 Cole–Cole plot of the loss-factor increase and dielectric-constant increase due to water in Quatrex 5010. Two water contents are shown: ○, 0.70% wt%; ●, 0.45 wt%. The full curve indicates calculated Cole–Davidson curves ($\gamma = 0.1$). Note that the vertical and horizontal axes are not on the same scale

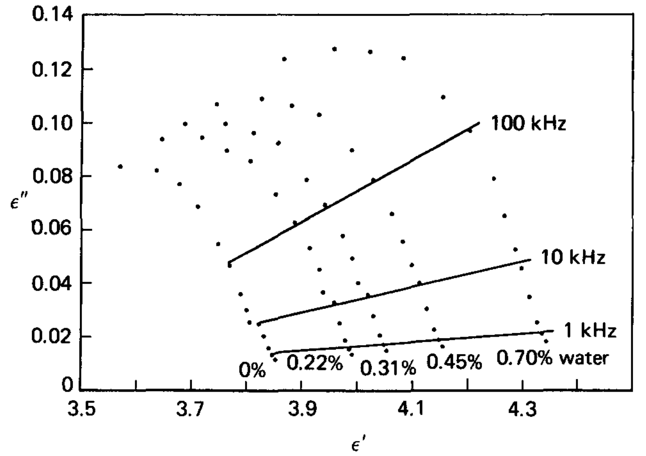

Figure 15 Cole–Cole plot for various water contents (shown below the dots) in Quatrex 5010 resin. Note that the vertical and horizontal axes are not on the same scale

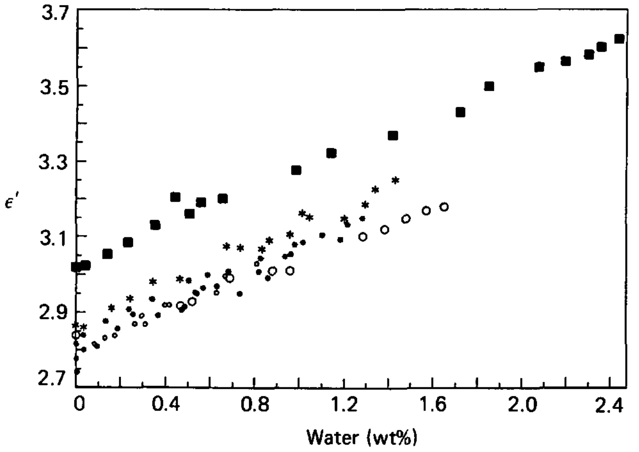

Figure 16 10 kHz dielectric constant for a variety of cyanate resins that cure to form triazine network structures. Upper data (■) are for bisphenol A dicyanate resin

content. Good linearity is observed in all cases. It is notable that the slopes are very similar in all cases. *Table 2* summarizes these data in terms of dry dielectric constant slope and the f value defined earlier. In all cases, the f value is between 0.7 and 0.9. Because of the larger water absorptions of the bisphenol A dicyanate resin, it is examined in more detail with respect to the water relaxation. *Figure 17* shows room-temperature Cole–Cole plots of the dielectric-constant and loss-factor increases. Notable is that the Cole–Cole plots approach the origin together with the high-frequency data.

CONCLUSIONS

Assignment of the observed relaxations to orientation of water molecules seems definite. The potential difficulty in distinguishing between an MWS relaxation and water dipolar relaxation has been discussed[17]; however, in the present case, examination of *Figure 9* shows no dramatic change in activation energy or frequency of maximum loss in the region of the melting point of water. The location of an MWS relaxation is proportional to the conductivity of the occlusion, which changes by orders of magnitude upon melting and also demonstrates a large change in activation energy[18,19]. Even if the freezing point of water occlusions was depressed, as has been seen in polycarbonate systems[4], the $1/T$ dependence of the loss peaks is a factor of 5 greater than liquid water conductivity. Also, the magnitude of the relaxation strength seems to agree far too well with expectation for dipolar relaxation to be coincidence. The possibility that the enhanced dielectric relaxation with water pick-up is due to plasticization of epoxy dipolar relaxation is also ruled out. The location of the loss peaks seems to be invariant to large changes in water pick-up. Note also that while, at 10 kHz, two of the epoxies have dry dipolar relaxation peaks ($T = 289$ K and $T = 270$ K) above the average water relaxation peak ($T \simeq 255$ K) and one below ($T = 238$ K), upon the addition of water the resultant relaxations all shift towards 255 K as expected. With plasticization, all would shift down in temperature.

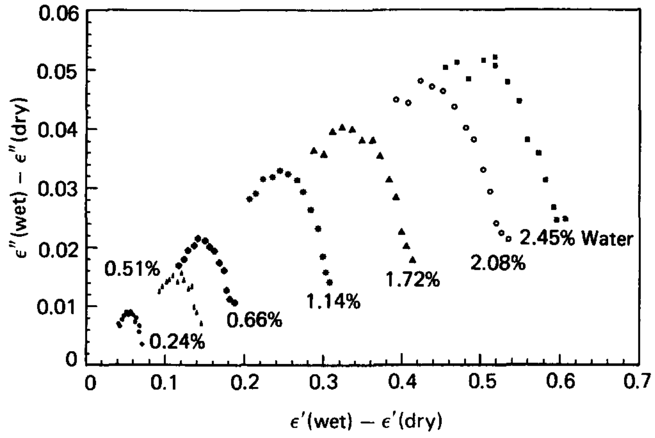

Figure 17 Cole–Cole plot for the loss-factor increase and dielectric-constant increase due to water in the bisphenol A dicyanate resin. The water contents are shown below the symbols. Note that the vertical and horizontal axes are not on the same scale

It appears then that the dielectric relaxation process due to water observed in all cases can be explained in terms of the dipolar relaxation of isolated water molecules. Equation (7) satisfactorily describes increases in the dielectric constant with water uptake where f, representing the fraction of unassociated water polarizability observed by water in the polymer, takes on values of 0.7 to 1.0 in almost all cases studied. It is interesting, however, that the relaxation strengths per 1 wt% of water derived from the loss spectra are somewhat smaller than those derived from the dielectric-constant data. The f values therefore derived from the loss data are smaller; however, the accuracy in obtaining the dielectric-constant slopes is far better than the corresponding accuracy in obtaining the area under the $\varepsilon''(\text{wet}) - \varepsilon''(\text{dry})$ *versus* $1/T$ curve; thus the higher f values are considered more reliable. The interpretation of the f values seems to be that, for the most part, water molecules are unassociated enough that their dielectric contribution is close to the Onsager predicted value, The activation energies for relaxation of the water molecules are 11–16 kcal mol^{-1} for the epoxies studied and were found to be ~10 kcal mol^{-1} in thermoplastics studied by Suzuki *et al.*[12] This is much higher than the ~5 kcal mol^{-1} for liquid water and is quite close to values observed for ice[19] where presumably three hydrogen bonds must be broken for orientation to occur.

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