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Vibrational Spectroscopy Evidence for the Dual Nature of Water Sorbed into Epoxy Resins

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The physical interactions occurring between absorbed water molecules and the network of a tetrafunctional epoxy resin were studied by mid-infrared (MIR) and near-infrared (NIR) Fourier transform spectroscopy. The spectrum of the sorbed water molecules was isolated in both frequency ranges and the assignments of the various components of the spectrum were proposed accordingly. The results of the vibrational analysis reaffirm the existence of two populations of penetrant molecules, a mobile variety residing within microvoids and those strongly bound to the polymeric network through hydrogen bonding interactions. A comparative analysis of the NIR spectra makes it also possible to deduce the most likely structures of these adducts and their stoichiometry. Finally a method was identified for the quantitative estimation of the bound water responsible for the plasticization of the matrix.

Introduction

Epoxy resins are among the oldest, but still the most vigorously developed cross-linked glassy polymers for industrial uses. In particular, tetraglycidil-4,4′ diamino diphenylmethane (TGDDM) resins cross-linked through reactions with 4,4′-diamino-diphenylsulfone (DDS), is widely used in adhesives and as matrices for high performance fiber composites, owing to its excellent mechanical properties and high glass transition temperature.[1−3]

A major limitation of cross-linked epoxy resins is their tendency to absorb considerable amounts of moisture from humid environments, which has a detrimental effects on physical properties.[3−5] A typical TGDDM cured resin may absorb between 4.5 and 7.0 wt % of water at equilibrium, which may reduce the glass transition temperature (T_g) by 80−140 °C. Moreover sorption of water may cause irreversible damage to the material as a result of the formation of microcracks through repeated absorption/desorption cycles.[6−8] It has been shown that under severe aging conditions a TGDDM/DDS cross-linked resin may undergo also irreversible degradation at specific sites of the network.[22]

To explain some of the anomalies in the behavior of glassy network polymers containing an equilibrium amount of sorbant, several authors have proposed that the penetrant population is made up of two species, i.e., those forming a molecular solution and those confined into areas of abnormally large free volume, often referred to as *holes* or *microvoids*. There is, however, no direct evidence for the presence of of these microvoids and whether they are, indeed, formed as a result of the penetration of water into the network. In any case the duplicity of molecular species gives rise to different types of interactions with structural entities of the polymer network and, therefore, the overall amount of penetrant up-take is not a reliable predictor of possible effects on physical properties, such as the lowering of the T_g through plasticization.[9−11] In an early investigation by proton nuclear magnetic resonance (NMR), Fuller and al. claimed that water molecules absorbed in an amine-cured epoxy resin are less mobile than in pure liquid water but are more loose than water molecules bound to the hydroxyl groups in cellulose.[12,13] Other NMR studies have given some indications that the water absorbed in epoxy resins may be present as both bound and mobile water molecules.[14,15] A more recent investigation by Jelinski et al., however, using

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quadrupole-echo deuterium NMR spectroscopy does not support the hypothesis on the "dual" state of aggregation of water. According to these authors dissolved water molecules migrate through the bulk of the polymer network via "jumping" motions from one site to another, with a characteristic time of 7×10^{-10} s.[16,17]

On the other hand, several investigations based on dielectric measurements, are supportive of the theory of water molecules partly bound to polymer chains and partly clustered into microvoids. Grave et al. were able to calculate the relative amounts of bound and free water from the magnitude of the relaxations at 10^5 and 10^9 Hz, respectively. It is instructive to note that the relaxations at 10^9 Hz are in good agreement with the characteristic "jumping" time in NMR studies put forward by Jelinsky et al. for the water molecules to move from one site to another.[18−20]

FTIR spectroscopy studies in the 4000−400 cm^{-1} range have, hitherto, only revealed the occurrence of reversible hydrogen bonding interactions between the absorbed water and the polymer network.[21]

In the present study FTIR in the mid-infrared (4000−400 cm^{-1}) and in a near-infrared (8000−4000 cm^{-1}) has been used to obtain further elucidation of the type of interactions that take place between sorbed water molecules and the active groups of the TGDDM/DDS network.

The position and shape of the absorption peaks in these regions are expected to provide information on the chemical environment of sorbed molecules, while the intensity should be helpful in obtaining a quantitative assessment of the population of the different water species.

The results obtained are evaluated in relation to those derived from different spectroscopic and nonspectroscopic techniques

Experimental Section

Materials. The epoxy resin was a commercial grade of tetraglycidyl-4,4′ diamino diphenylmethane (TGDDM) supplied by Ciba Geigy (Basel, Switzerland), and the curing agent was 4,4′-diamino-diphenylsulfone (DDS) from Aldrich (Milwaukee, WI). A total of 30 g of DDS were dissolved in 100 g of TGDDM at 130 °C, degassed under vacuum, and poured in a stainless steel mold. The first step of the curing schedule was conducted at 140 °C for 16 h, followed by a post-curing step at 200 °C for 4 h.

Measurement Techniques. Transmission FTIR spectra were obtained in the mid-infrared range (MIR, 4000−400 cm^{-1}) and in a near-infrared range (8000−4000 cm^{-1}). A Perkin-Elmer System 2000 spectrometer was used, equipped with a Ge/KBr beam splitter and a deuterated triglycine sulfate detector. Measurements were made in the transmission mode using 30−300 scans for each measurement to enhance the signal-to-noise ratio. Isothermal desorption experiments were conducted in the apparatus described in detail in a previous publication.[23]

Sample Preparation and Conditioning. For FTIR measurements in the MIR range a sample ~50 μm thick was used to detect the whole spectrum and, in particular, the OH stretching region from 3800 to 3100 cm^{-1} (see Figure 1, parts A and B).

To avoid the problem of water absorption during handling for the dry (control) film, samples were conditioned at room temperature and at 80% relative humidity up to equilibrium sorption, corresponding to 4.6 wt % of absorbed water, as determined by thermogravimetric analysis (TGA). These were subsequently placed in the environmental chamber of the spectrometer and desorbed at 55 °C under a flux of nitrogen, while monitoring continuously the decrease in absorbance of the band centered at 3405 cm^{-1} and the shoulder at 1655 cm^{-1}, both of which being associated with the fundamental modes of vibration of water. The desorption process was considered complete when no further changes in absorbance were detectable in the above frequency range, which took about 7 min. To obtain the spectrum at room temperature for the dry material, the sample was cooled in the same environmental chamber under a continuous flow of nitrogen. For measurements in the NIR range the thickness of the samples was between 2.0 and 4.0 mm. A cured sheet was cut into pieces 3.0 mm long and 2.0 mm wide to be able to fit them in the sample holder of the measuring instrument, and were stored overnight in a vacuum oven at 100 °C to ensure that they were completely dry. The samples were weighed on a laboratory balance and placed in a deionized water bath, thermostatically controlled at 70 ± 0.1 °C. Periodically the samples were removed from the bath and transferred to the FT-NIR sample holder to record the spectra. The surface water of the samples was removed by blotting with a paper tissue. This procedure was continued until no further changes in weight were observed, normally after about 180 days.

Data Analysis. For the case of unresolved multicomponent bands the individual peaks were separated by using a curve resolving algorithm, based on the Levenberg−Marquardt method.[24] To reduce the number of adjustable parameters the baseline, the band shape and the number of components were fixed. The minimum number of components was analyzed by visual inspection to identify changes in slope of the experimental line-shape. The algorithm was then used to calculate the height, the full width at half-height (fwhh) and the position of the individual components by a nonlinear curve-fitting routine.

The peak function was a mixed Gauss-Lorentz line shape of the form:

$$f(x) = (1 - L)H \exp - \left[\left(\frac{x - x_0}{w} \right)^2 (4 \ln 2) \right] + L \frac{H}{4\left(\frac{x - x_0}{w} \right)^2 + 1} \tag{1}$$

where x_0 = peak position; H = peak height; w = fwhh; L = fraction of Lorentz character.

The spectrum of water sorbed into the epoxy resin was isolated by eliminating the interference from the polymeric substrate, using the subtraction spectroscopy technique,[25,26] i.e.

$$A_d = A_s - KA_r \tag{2}$$

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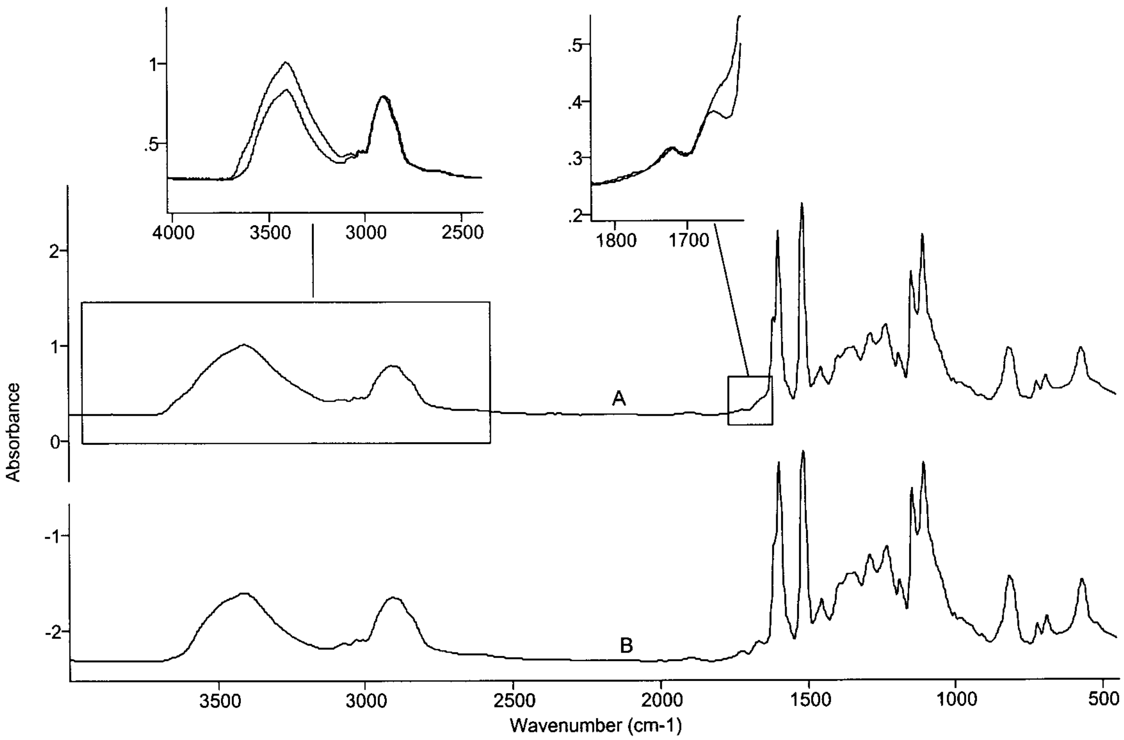

Figure 1. Transmission FT-MIR spectra in the range 4000−400 cm^{-1} of a fully cured TGDDM/DDS resin in the dry state (trace A) and after absorbing 4.5 wt % of water (trace B).The two spectra are reported in an absolute absorbance scale. Spectrum B is arbitrarily shifted along the ordinate axis to facilitate comparison. The insets highlight the intervals where differences between the two spectra are detected.

where: (i) A is the absorbance, (ii) the subscripts d, s, and r denote the difference, the sample, and the reference spectra, and (iii) K is an adjustable parameter used to compensate for thickness differences between the sample and the reference spectra and was chosen so as to reduce to the baseline an internal standard peak characteristic of the polymeric substrate.

Results and Discussion

Medium Infrared Range (4000−400 cm^{-1}). The transmission FTIR spectra in the MIR range of a fully cured TGDDM/DDS resin, both in the dry state and after absorbing 4.5 wt % of water, are reported in Figure 1, parts A and B. The two major differences that are noted in the spectra as a result of the absorption of water are (a) an increase in intensity of the broad unresolved ν_{OH} band at 3408 cm^{-1}, and (b) the appearance of a shoulder for the TGDDM aromatic ring mode at 1594 cm^{-1}.

The reduction in absorbance of the band at 3405 cm^{-1} occurring during drying is shown Figure 2 and is expressed quantitatively as a plot of the change in aborbance against the square root of desorption time in Figure 3. It is noted that because of the extremely small thickness of the sample the desorption behavior is Fickian, the small deviation near the origin being due to the time lag needed to equilibrate the temperature of the sample.

The fundamental stretching vibrations and the in-plane bending mode of water occur within the 3800−2800 cm^{-1} region and at around 1640 cm^{-1}. The discussion that follows will focus on the 3800−2800 cm^{-1} wavenumber interval, where the peaks are considerably more intense and can be suitably resolved (see later). In addition, more information about hydrogen bonding is expected from the analysis of the wavenumber region characteristic of the O−H stretching vibrations.

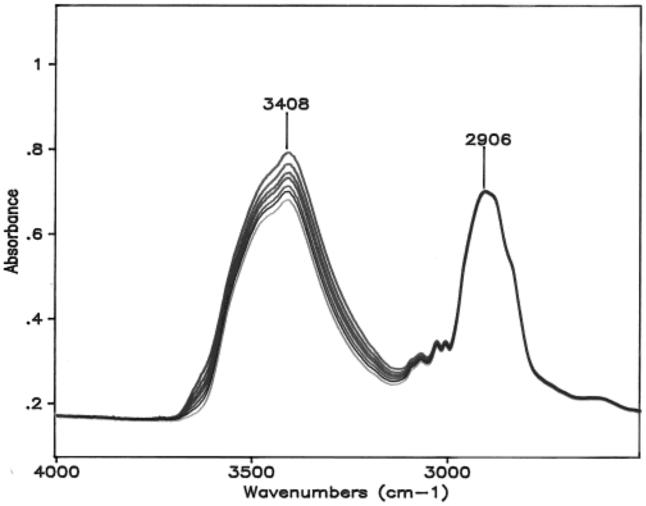

Figure 2. Transmission FT-MIR spectra for a TGDDM/DDS film sample at different desorption times, starting with an initial water content of 4.5 wt % (upper spectrum) until completely dry (lower spectrum).

A difficulty encountered in the analysis of these spectra arises from the fact that the spectrum of water in the 3800−3000 cm^{-1} region is superimposed on to a broad absorption band associated with the multiplicity of hydrogen bonding interactions of OH groups in the polymer network.

An attempt has been made in the present work to eliminate this interference through spectral subtraction analysis, taking as internal standard the complex epoxy

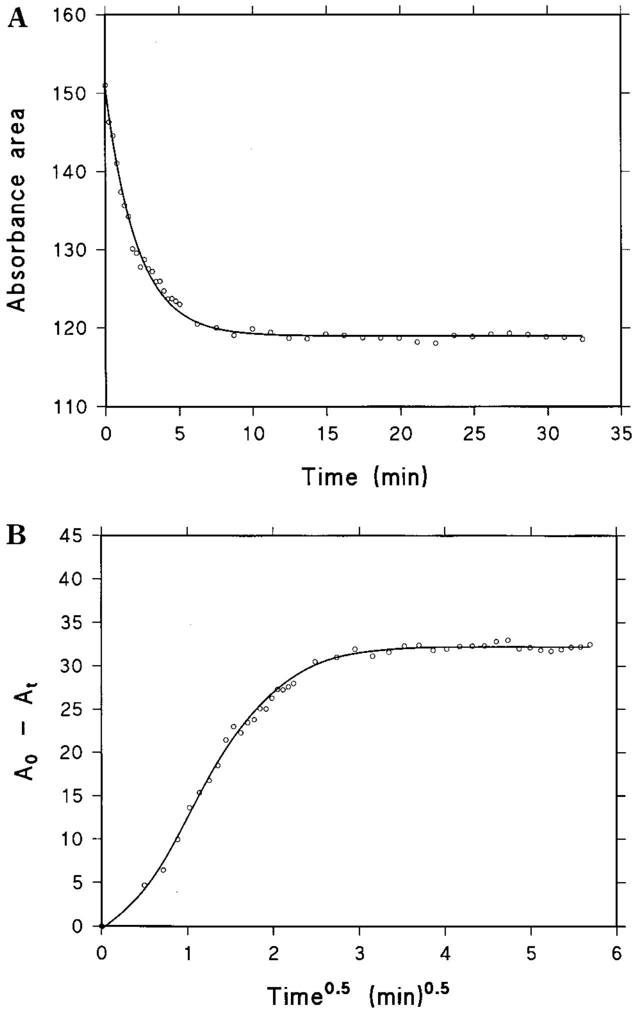

Figure 3. Integrated absorbance of the ν_{OH} band as a function of time for the desorption of water from the cured TGDDM/DDS epoxy resin at 55 °C.

multiplet centered at 2900 cm^{-1}.[25,26] The nature of these vibrations, consisting of nearly 100% stretching, makes the absorption in this region insensitive to the presence of water in the resin, as illustrated in Figure 2, and in the difference spectra shown in Figure 4. The latter shows that the ν_{CH} multiplet is completely eliminated and a sharp peak emerges at 3628 cm^{-1}, which is partly superimposed on a broader absorption at 3370 cm^{-1}. This result is highly reproducible and can, therefore, be taken as the representative spectrum of water dissolved into a cross-linked epoxy resin.

A close inspection of the broad band centered at 3370 cm^{-1} reveals a fine structure in the form of discontinuities in the line shape, which have been indicated by arrows on the spectrum in Figure 4A. The spectral profile was resolved into its individual components by using the curve-fitting algorithm described in the Experimental Section. The results predicted from this analysis are compared with the experimental line shape in Figure 4B. From this comparison it is deduced that the spectral profile can be accurately reproduced by using the number of visually identified components (four). The spectral parameters of the single peaks (position, fwhh and line shape) were also found to be highly reproducible for a series of samples containing different amounts of sorbed water.

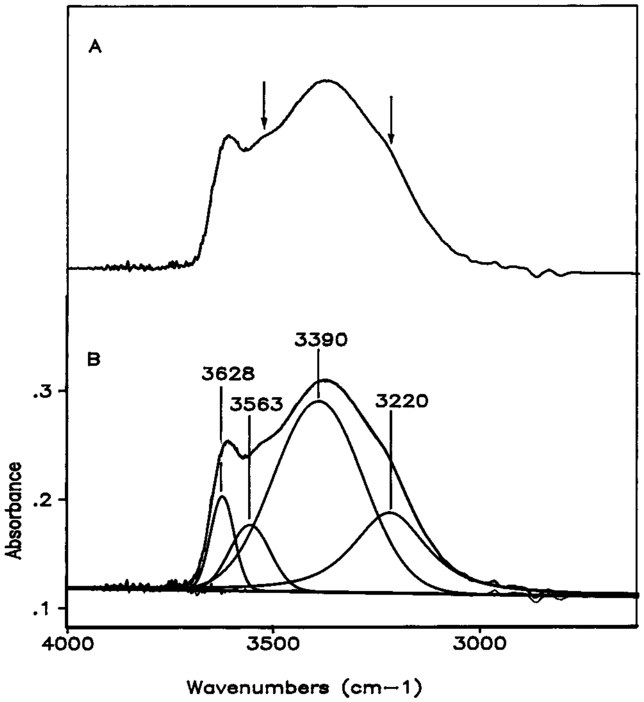

Figure 4. (A) Subtraction spectrum in the range 4000−2500 cm^{-1} corresponding to water absorbed in the epoxy resin and (B) curve-fitting analysis of the above profile showing, respectively, the four resolved components, the simulated profile, the experimental line shape, and the residual (experimental − best fit).

The results of the spectral subtraction analysis in the MIR range have important implications. For instance, the fact that it has been possible to isolate the water spectrum by difference spectroscopy indicates that the spectrum of the dry resin matches exactly the spectrum of the sample after water sorption, particularly in the O−H stretching region, irrespective of the amount of water present in the sample. Even minor differences in the peak positions and/or in the relative intensities of the individual components which are responsible for the ν_{OH} band of the epoxy resin, would give rise to clearly detectable derivative-type features in the difference spectrum. This implies that the network of hydrogen bonding interactions formed among the hydroxyl groups of the epoxy resin is not perturbed by the presence of sorbed water.

In any case, to make a more accurate interpretation of the difference spectrum in Figure 4, it is useful to consider some salient features of the infrared spectrum of water.[27,28] For the isolated molecule in the gas phase there are three distinct peaks in the OH stretching region, centered at 3151 cm^{-1} ($2\nu_2$), 3652 cm^{-1} (ν_1, symmetric stretching), and 3756 cm^{-1} (ν_3, asymmetric stretching). It is worth noting that the ν_3 peak is about 10 times more intense than the ν_1 peak.

In passing from vapor to liquid, the resulting hydrogen-bonding interactions causes a shift of the stretching vibrations to lower frequencies and of the bending vibrations to slightly higher frequencies. As a consequence, the spectrum for liquid water displays a broad

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and asymmetric absorption with a maximum at about 3450 cm^{-1}, which does not have any features of a fine structure.

For water in the liquid phase, two main types of structural models have been proposed, the continuum models and the mixture models. In the continuum models, the water molecules are assumed to be completely hydrogen bonded at room temperature and the length and the angle of these bonds are continually distributed over a relatively wide range.[29−32,37] The continuum aspect, in combination with the occurrence of three distinct vibrational modes in the ν_{OH} range, provides an explanation for the broadening of the OH stretching band in the spectrum of liquid water.

In the mixture models, the structure of water is described in terms of a relatively small number of discrete species.[31−35,37] A well-established model assumes the existence of three spectroscopically distinguishable species denoted S_0, S_1, and S_2, where the subscripts denote the number of hydrogen atoms of the H_2O molecule involved in hydrogen bonding. In this model hydrogen bonding through the electron lone pairs of the oxygen atom is not considered because, although such interactions may increase the width of the absorption bands of the three species, they do not provide sufficiently large energy gaps for their resolution.[36,37]

The absence of a fine structure in the ν_{OH} band of liquid water has initially been used by some authors[38] as an argument against the mixture model, but has later been shown to be unfounded.[39,40] Many of the disagreements about the two models can be attributed, however, to experimental artifacts and/or to the characteristic time scale of the technique used.

In light of this, the following interpretation of the difference spectrum for water absorbed in cross-linked TGDDM/DDS epoxy resin can be put forward:

The partially resolved peak at 3627 cm^{-1} is attributed to unassociated water, i.e., water which is not neither associated with itself nor with the polymer network, on account of the peak position being far above that of the principal absorption ($\Delta\nu$ = 270 cm^{-1}), and because of the relative sharpness (fwhh = 65 cm^{-1}) of the peak. This originates from the asymmetric stretching vibration (ν_3). The corresponding symmetric mode (ν_1), on the other hand, is likely to be obscured under the broad principal band at 3370 cm^{-1}, as it is about 10 times less intense and occurs at lower wavenumbers over the range 50−90 cm^{-1}, depending on the chemical environment.[41]

The three components at 3563, 3390, and 3220 cm^{-1}, which form the main absorption, are clearly due to hydrogen-bonded water in view of the well-known reduction of the force constant for the O−H bond. This produces a corresponding shift of the relative stretching vibrations toward lower wavenumbers. The reduction in force constant brought about by such interaction, is directly related to the frequency shift. On the basis of the harmonic oscillator model the reduction in force constant, Δf, can be represented by the equation:[27]

$$\Delta f = f_{nb} - f_b = \frac{\mu(\nu_{nb}^{\;2} - \nu_b^{\;2})}{4\pi^2} \qquad (3)$$

where $\mu = m_1m_2/(m_1 + m_2)$, corresponding to the reduced mass of the oscillator, ν is the oscillating frequency and f is the force constant. The subscripts b and nb denote, respectively, bonded and nonbonded oscillators. Thus, the lower the peak frequency the stronger the interaction. The presence of multiple components in the 3700−2800 cm^{-1} range, in this case, is due to the occurrence of various types of interactions. The MIR range is of limited value for the identification and quantitative assessment of these interactions. This is not only due to poor resolution, but also to the unavailability of reliable values for the molar absorptivity of the various adducts. Since these absorptivities are a sensitive function of frequency[42,43] (therefore highly dependent on the strength of the interaction), it is not possible to use the assumption of an average value for all the species. This is not the case for absorptivities in the NIR interval (see later discussion).

Near Infrared Range (8000−4000 cm^{-1}). For several reasons NIR spectroscopy has important advantages over MIR for studies of extensively hydrogen-bonded molecular structures.[44,45] For instance, since the absorptions in the NIR frequency range are multiples, or the sum of the MIR peaks, the frequency shifts resulting from hydrogen bonding follow accordingly. This improves the resolution in the ν_{OH} region and makes it possible to separate out the individual components which remain unresolved in the MIR spectrum. Furthermore, while in the fundamental region the absorptivities of hydrogen-bonded species are generally much larger than those of the nonbonded species, in the overtone and combination region these absorptivities are similar in magnitude.

Against these advantages, there are more uncertainties for assignment in the NIR interval than in MIR.

The transmission FT-NIR spectrum in the wavenumber range 8000−4000 cm^{-1} for a fully cured TGDDM/DDS resin in its dry state, and that of the same resin containing 6.0 wt % of absorbed water, are compared in Figure 5. A detailed discussion on the NIR spectrum of the TGDDM/DDS resin has been reported elsewhere.[23] In the present study attention is given to the peaks of the absorbed water appearing at 5216 cm^{-1} and in the region between 7200 and 6000 cm^{-1}. The characteristic water peak at 5216 cm^{-1} is assigned to a

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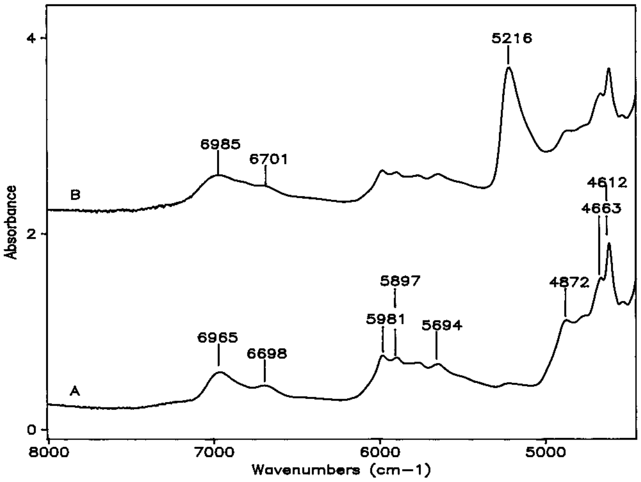

Figure 5. Transmission FT-NIR spectra in the range 8000−4500 cm^{-1} for a fully cured TGDDM/DDS resin: (A) dry state and (B) containing 6.0 wt % absorbed water.

combination of the ν_{as} (ν_3) and the deformation fundamentals (ν_2). This peak is free of any interference from other peaks in the resin spectrum, hence it is suitable for a quantitative estimation of the water content in the sample, as it has been previously demonstrated for both TGDDM/DDS systems[23] and for other polymer/water pairs.[46,47] Less information can be gathered, however, from the analysis of this absorption with respect to the molecular interactions of the sorbed molecules. As already noted, this is because hydrogen bonding has an opposite effect on stretching and bending vibrations, which makes it difficult to provide an accurate interpretation of the overall effect on the combination mode. The 5216 cm^{-1} peak, however, reveals the occurrence of a fine structure, which is indicative of the simultaneous presence of different molecular species of water in the sample, in agreement with the MIR results.

A broad absorption due to the combination of the two stretching fundamentals ν_1 and ν_3, is known to occur in liquid water at around 6900 cm^{-1}. In this wavenumber range is located the intense and complex ν_{OH} overtone band due to the hydroxyl groups of the epoxy resin, which obscures the water spectrum. In Figure 6 are reported the spectra in the 7800−5500 cm^{-1} range for a dry sample (Figure 6B) and for a sample containing 6.0 wt % sorbed water (Figure 6A).

The presence of water causes a general increase in absorbance, particularly at around 6800 and 6400 cm^{-1}.

A spectral subtraction analysis was carried out to eliminate the interference of the epoxy network and to isolate the spectrum of water. The complex multiplet with a maximum at 5981 cm^{-1} due to ν_{CH} overtones and combinations, was used as reference band to be brought to zero (baseline). The result of the analysis relative to the spectra in Figures 6A and 6B, is reported in Figure 6C (see later).

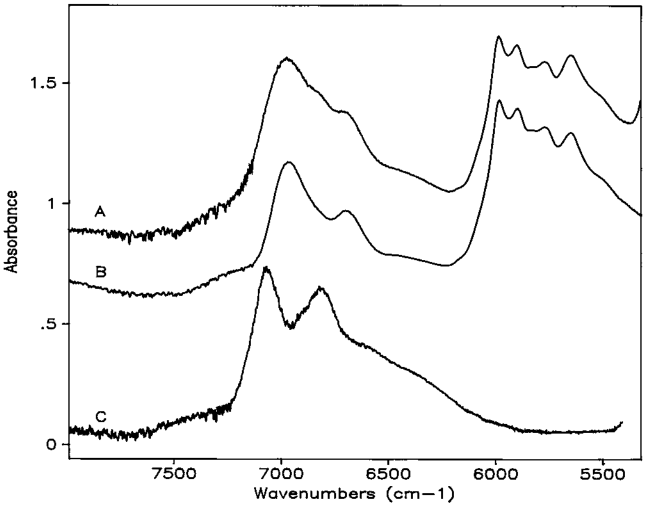

Figure 6. Transmission FT-NIR spectra in the range 8000−5500 cm^{-1} for the TGDDM/DDS cured resin (A) containing 6.0 wt % of absorbed water; (B) dry sample; (C) difference spectrum A − B. The absorbance scale refers to spectra A and B. To facilitate comparison, spectra A and B have been arbitrarily shifted along the ordinate axis, and the absorbance scale of spectrum C has been amplified by a factor of 4.

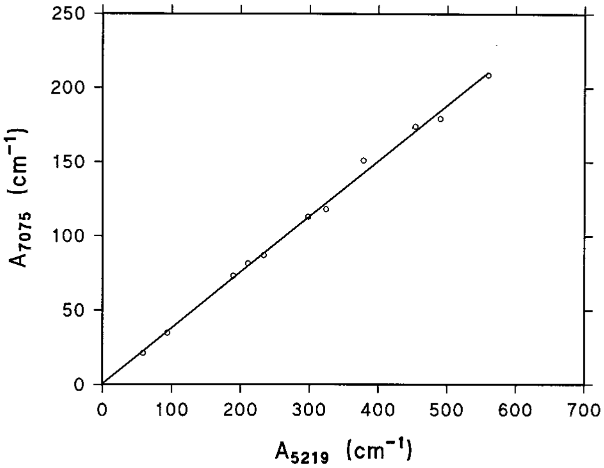

Figure 7. Reduced absorbance for the water absorption in the 7500−5800 cm^{-1} range as a function of the reduced absorbance of the water peak at 5216 cm^{-1}.

In Figure 7 is reported the integrated absorbance of the difference spectrum in the range 7550−5500 cm^{-1}, normalized for sample thickness (reduced absorbance) as a function of the reduced absorbance of the water peak at 5216 cm^{-1}. The fact that the plot produces a straight line passing through the origin, in accordance with the Beer−Lambert law, confirms the reliability of the spectral subtraction analysis and further supports, in agreement with solid-state NMR[16,17] and the MIR spectroscopy results discussed earlier, the conclusion that the absorbed water molecules do not perturb the hydrogen-bonding network formed by the hydroxyl groups of the epoxy network.

The NIR spectrum of water sorbed into the epoxy resin has three distinct components centered, respectively, at 7075, 6820, and 6535 cm^{-1}. For an interpretation of such a complex profile, it is useful to refer to the spectra obtained on model systems consisting of water/solvent mixtures.[37] In particular, one notes that the difference spectrum in Figure 6C is strikingly similar to that obtained for diluted solutions (up to 0.1 mol fraction) of water in acetone. In this case three main components are also observed (trace A of Figure 8), respectively at 7063, 6850, and 6535 cm^{-1}. The relative

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(46) Fukuda, M.; Miyagawa, M.; Kawai, H.; Yagi, N.; Kimura, O.; Ohta, T. *Polym. J.* **1987**, *19*, 785.

(47) Fukuda, M.; Kawai, H.; Yagi, N.; Kimura, O.; Ohta, T. *Polymer* **1990**, *31*, 295.

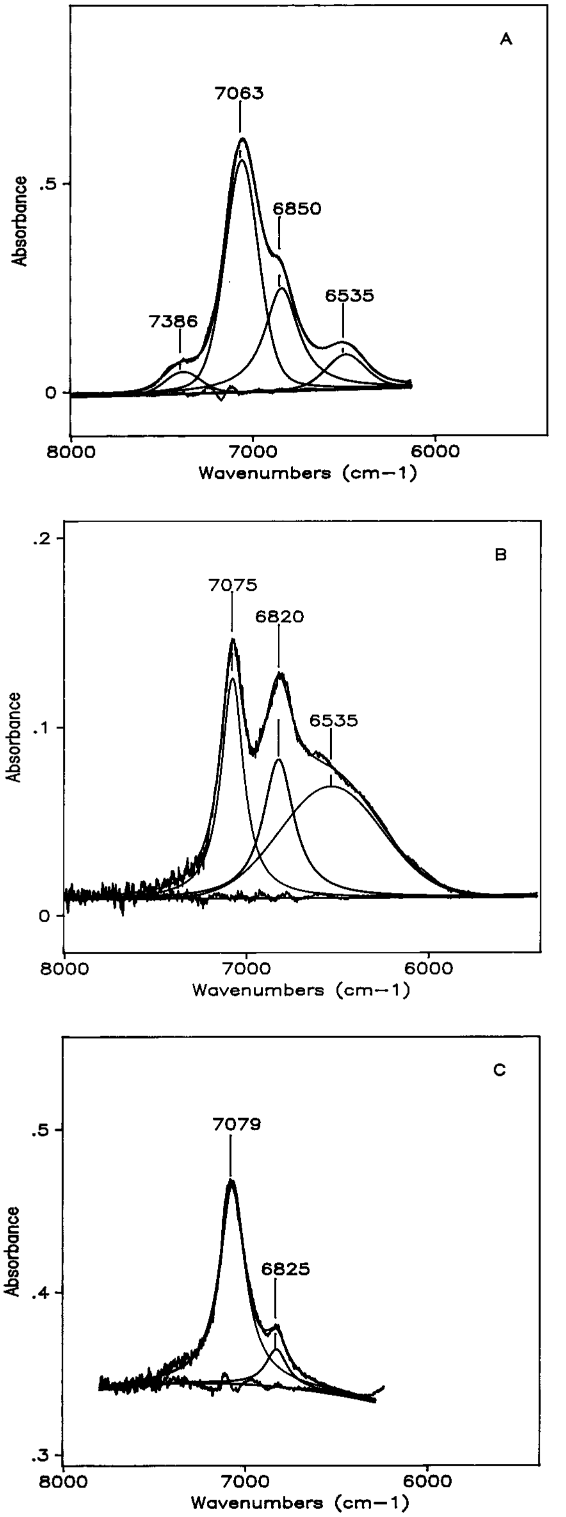


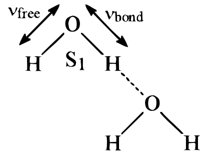
Figure 8. Curve-fitting analysis in the 8000−5500 cm^{-1} range, relative to the spectrum of water in different environments: (A) 5.0 wt % mixture of water in acetone; (B) water sorbed in a cross-linked TGDDM/DDS resin (6.0 wt %); (C) water sorbed in a cross-linked bismaleimide resin (2.5 wt %). The figures show the resolved components, the simulated profile, the experimental line shape, and the residual (experimental − best fit).

intensity of the component at 6535 cm^{-1} was found to increase, at the expenses of the one at higher frequency, with increasing water concentration and temperature. The same behavior was observed with dioxane/water mixtures.[37]

The three-component spectrum clearly demonstrates the existence of three distinct water species in solution. The above authors have assigned the peaks at 7063 cm^{-1}, at 6850 cm^{-1}, and at 6535 cm^{-1} to isolated water molecules of the type S_0, to singly hydrogen-bonded water molecules of the type S_1, and to doubly hydrogen-bonded water molecules of the type S_2. A fourth, low-intensity peak was detected at 7386 cm^{-1} and was tentatively attributed to a ($\nu_1 + \nu_3 + \nu_L$) combination, where ν_L is a librational mode.[37] This peak was, however, neglected in the analysis of the water equilibrium as a function of temperature and concentration.

By analogy with solution spectra, the component at 7075 cm^{-1} of the spectrum of sorbed water is assigned to a combination of ν_3 and ν_1 modes of non-hydrogen bonded water (S_0 molecules). The corresponding ν_3 fundamental has been isolated in the MIR difference spectrum at 3628 cm^{-1}.

The peak at 6820 cm^{-1} is due to the combination of ν_{free} with ν_{bonded} fundamentals in self-associated water molecules forming a single hydrogen bonding interaction (S_1 molecules):

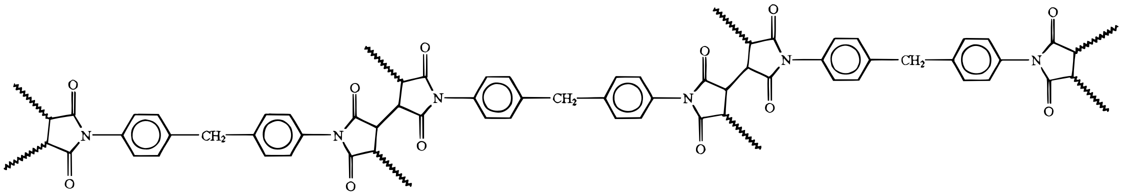


The ν_{bond} fundamental may tentatively be associated with the 3563 cm^{-1} component obtained by the curve resolving analysis of the MIR profile (see Figure 4B).

Finally, the broad component centered at 6535 cm^{-1} must be due to a ($\nu_3 + \nu_1$) combination of water molecules whose hydrogens are both involved in strong hydrogen-bonding interactions with proton-accepting groups (S_2 molecules). The breath of this band (three times larger than the 7075 cm^{-1} peak and four times larger than the peak at 6820 cm^{-1}) is related to the occurrence of several interactions (i.e., with different proton accepting groups) which produce a comparatively large distribution of hydrogen-bonding strengths. Instead, the S_0 and S_1 species have a well-defined stoichiometry and a correspondingly narrower force constant distribution. Thus, the two high-frequency peaks must correspond to water molecules characterized by a high molecular mobility since they do not interact with the polymeric network. It is reasonable to presume that these species are confined into excess free volume elements (microvoids) of an appropriate size not to have any effect on physical properties related to molecular relaxations. Furthermore, nonassociated water can be easily removed by heating at relatively low temperatures. Conversely, the water molecules bound onto specific sites along the polymer network, giving rise to the low-frequency band, are responsible for the plasticization of the epoxide network.

Further support for the above assignments is evident from a comparison with the spectrum of a model system, i.e., the spectrum in Figure 8C, for a cured thermosetting bismaleimide (BMI) resin containing 2.5 wt % of absorbed water. The BMI resin was *N*,*N*′-bismaleimide-4,4′-diphenyl methane system, cured, without the addition of extraneous hardeners, at 200 °C for 4 h and

Chart 1



post-cured at 290 °C for 2 h in a N_2 atmosphere. The resulting network, shown in Chart 1 is essentially hydrophobic, due to the negligible capabity of the imide carbonyls to act as proton accepors.[48] For this system, therefore, it can be expected that all the sorbed water is located into microvoids, not forming any hydrogen-bonding interaction with the polymeric network. This is confirmed by the observation that only two water peaks are observed in the spectrum of Figure 8C, corresponding to the S_0 and S_1 species. These peaks are equivalent, with respect to shape and position, to those assigned to the same species in the spectrum of water sorbed in the epoxy resin (compare the values of the spectral parameters reported in Table 1). It is worth noting that the BMI network has no interfering signals in the 8000−5800 cm^{-1} range and the spectrum of sorbed water is clearly distinguished.

A quantitative analysis of the spectral profile reported in Figure 6C has been performed using the curve-fitting algorithm described in the Experimental Section (see Figure 8B). This approach makes it possible to obtain a more precise evaluation of the relevant spectral parameters and to estimate their relative amount. The results of such an analysis, relative to a water/acetone mixture and to water sorbed in the cured epoxy and bismaleimide resins, are reported in Table 1.

For the identification of the proton-accepting groups of the epoxy network two considerations can be made:

(a) The interaction stoichiometry corresponds to two proton acceptors per molecule of water because the interacting water molecules are S_2 species.

(b) The interaction strength should be of the same order of magnitude as that for self-associated water molecules ($\Delta\nu = 540$ cm^{-1} for water absorbed into the epoxy resin, and 530 cm^{-1} for water/acetone mixtures). This should, therefore, involve proton acceptors with interaction strength comparable to that of oxygen in water molecules.

From the above considerations it is possible to elucidate the structures of the complexes formed by hydrogen-bonding associations in the epoxy network, as shown Chart 2.

Plots of both peak position and full width at half-height (fwhh) for the three components as a function of the water content in the sample, are shown in Figures 9 and 10. These reveal that the peak position of the three components is independent of the amount of water in the resin. A similar behavior is apparent with respect to the fwhh of the peaks at 7075 and 6820 cm^{-1}. Slight widening of the fwhh is observed for the low-frequency component at 6535 cm^{-1} with increasing water content. The plots in Figure 11 reveal that increasing the sorbed water in the resin results in a slight decrease in the relative absorbance area for the 7075 and 6820 cm^{-1} peaks and a corresponding increase for the band at 6535 cm^{-1}. These observations indicate that there is a slight increase of the penetrant molecules interacting with the polymeric network with increasing concentration of sorbed water. The difference between the absorbance areas of the peaks at 7075 and 6820 cm^{-1}, however, remains essentially constant, due to an equilibrium being reached between S_0 and S_1 water species within the microvoids.

An analysis of water/acetone and water/dioxane mixtures as a function of temperature, based on a curve resolving approach similar to that used in this study, has enabled previous authors to estimate the integrated absorption coefficients, *a*, for the S_0, S_1, and S_2 species,[37] which is defined as

$$a = 2.303\int_{\nu_1}^{\nu_2}\epsilon_\nu \, \mathrm{d}\nu \tag{4}$$

where ϵ_ν is the molar absorptivity at frequency ν, and the two limits ν_1 and ν_2 refer to the range of frequency over which the integration is performed. In terms of *a*, the absorbance area corrected for path length, *A*, is given by

$$A = aC \tag{5}$$

where *C* is the concentration of the absorbing species.

The values of *a* for the S_0, S_1, and S_2 species were found to be, respectively, $(4.1 \pm 0.1) \times 10^{-7}$, $(4.8 \pm 0.2) \times 10^{-7}$ and $(5.3 \pm 1.2) \times 10^{-7}$ for acetone solutions and $(4.1 \pm 0.1) \times 10^{-7}$, $(4.8 \pm 0.1) \times 10^{-7}$ and $(5.3 \pm 1.4) \times 10^{-7}$ for dioxane solutions. As these values for the two systems are very close, it can be inferred that the integrated absorption coefficients do not depend on the nature of the solvent used, particularly those relative to the S_0 and S_1 species.

Table 1. Results of the Curve-Fitting Analysis of the Spectrum of Water in Different Environments in the Wavenumber Range 8000−6300 cm^{-1}

		peak 1 (S_0)			peak 2 (S_1)			peak 3 (S_2)		
environment	concentration (wt %)	center (cm^{-1})	fwhh (cm^{-1})	area (relative)	center (cm^{-1})	fwhh (cm^{-1})	area (relative)	center (cm^{-1})	fwhh (cm^{-1})	area (relative)
acetone	5.0	7063	220	55.0	6850	220	29.3	6535	265	9.5
TGDDM/DDS	6.0	7076	160	29.5	6820	230	28.0	6535	665	43.5
BMI	2.5	7079	165	86.3	6825	185	13.7			

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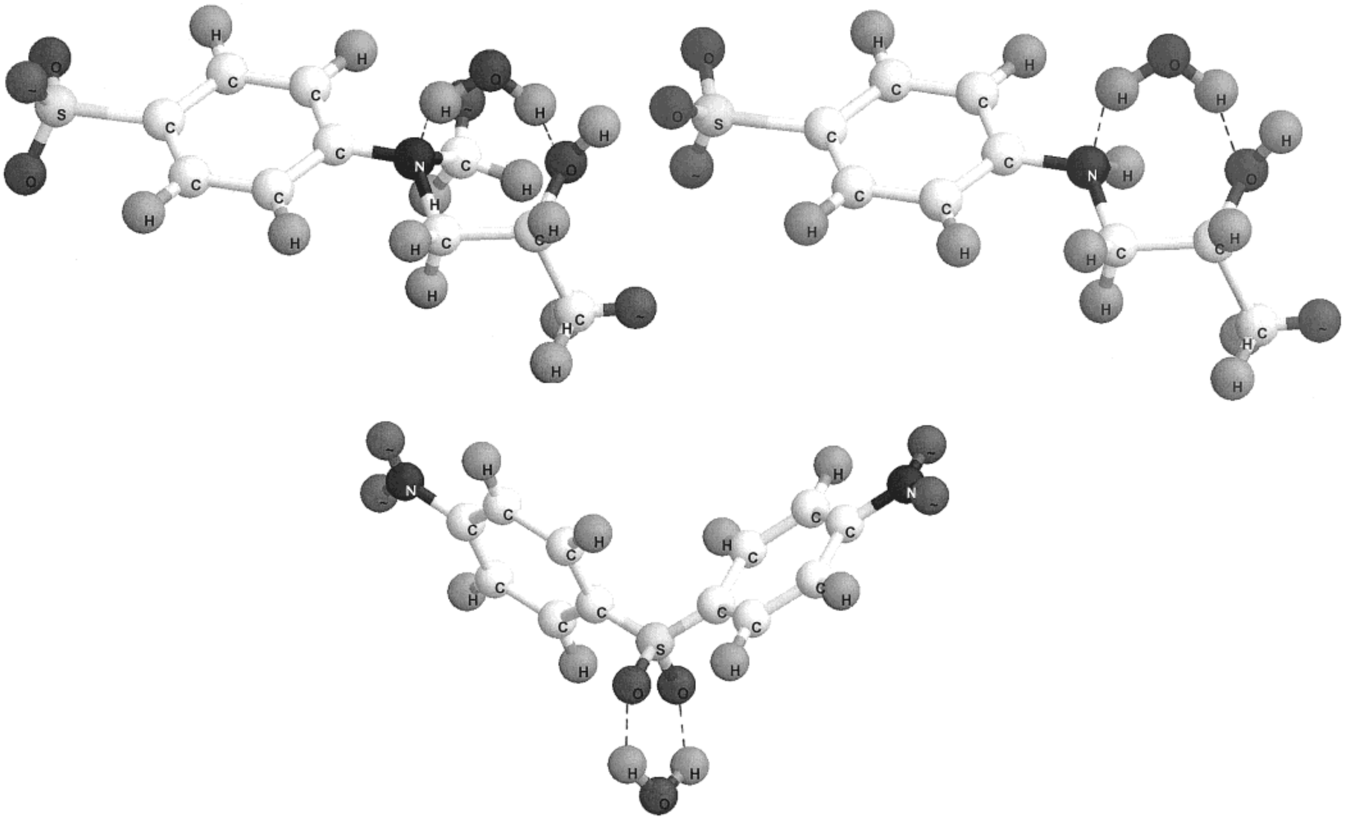
[48] Musto, P.; Karasz, F. E.; MacKnight, W. J. *Polymer* **1989**, *30*, 1012.

Chart 2. Structures of the Complexes Formed by Hydrogen-Bonding Associations in the Epoxy Network



Thus, by taking the above a_i values for the water/epoxy system and from the knowledge that

$$a_{S_0} \cong a_{S_1} \quad \text{and} \quad \frac{a_{S_0}}{a_{S_2}} = 0.81 \tag{6}$$

it is possible to estimate the relative concentration of each species, i.e.

$$\frac{C_{S_0}}{C_{\text{tot}}} = \frac{A_{7076}/a_{S_0}}{(A_{7076} + A_{6820})/a_{S_0} + A_{6536}/a_{S_2}} \tag{7}$$

from which

$$\frac{C_{S_0}}{C_{\text{tot}}} = \frac{A_{7076}}{(A_{7076} + A_{6820}) + \dfrac{a_{S_0}}{a_{S_2}} A_{6526}} \tag{8}$$

Similar relationships hold for the other two species.

By using the above equations, the relative amount of nonbonded [$(C_{S_0} + C_{S_1})/C_{\text{tot}}$] and bonded ($C_{S_2}/C_{\text{tot}}$) water were estimated and plotted against the total water content (see Figure 12). These data show that the relative amounts of free and bound water change linearly and in the opposite direction with increasing the total amount of sorbed water. The amount of bound water increases with increasing the total water content in the resin, but is always lower than the amount of free water.

It is noted, however, that the proportional changes with increasing the total water content are relatively small, i.e., ranging from approximately 70/30 (free/bound water) for water concentrations tending to zero-to-a ratio of 60/40 at the maximum water content of 6.0 wt %.

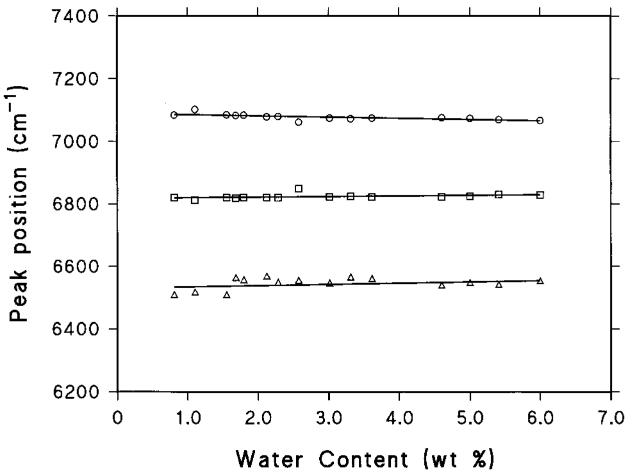


Figure 9. Peak position of the components at 7075, 6828, and 6535 cm^{-1} for the spectrum of absorbed water as a function of the total amount of water present.

These findings are in good agreement with the results of Grave et al. obtained from dielectric spectroscopy measurements using various molar ratios of amine hardener to epoxy resin.[20]

The issue of whether water molecules sorbed in a cross-linked epoxy resin are free or bound may have to be considered in terms of molecular dynamics.

In other words, one has to take into account the response time of the molecules relative to the duration of the excitation of the measurement. In relation to the above one can consider the conclusions from the work

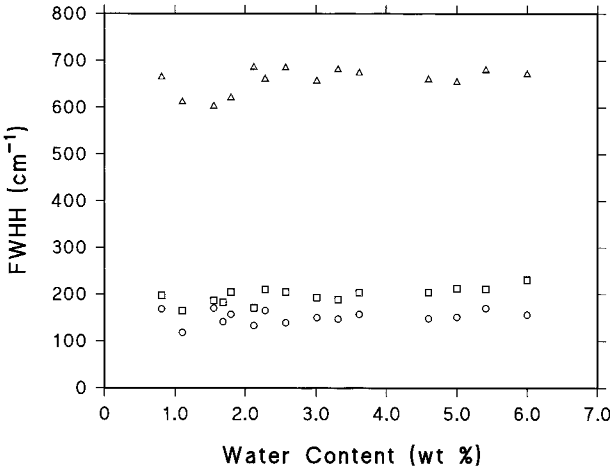


Figure 10. Full width at half height (fwhh) of the three components for the spectrum of absorbed water in the 8000–5500 cm^{-1} range as a function of the total amount of water present.

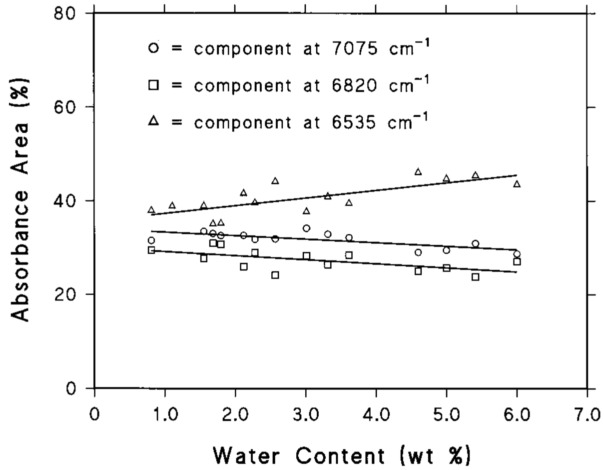


Figure 11. Relative absorbance area of the three components of the spectrum for absorbed water in the 8000–5500 cm^{-1} range as a function of the total amount of water present.

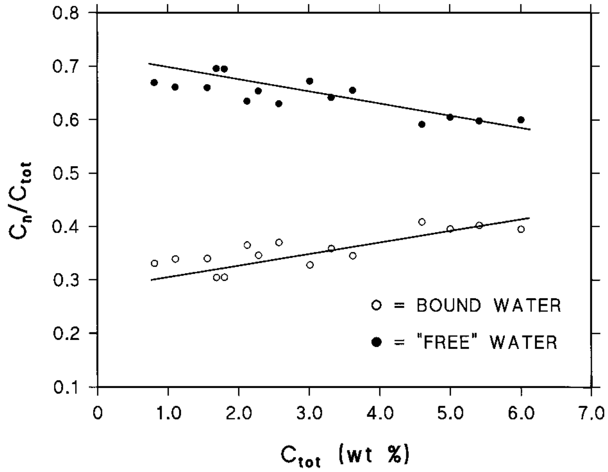


Figure 12. Plots of the relative concentration (C_n/C_{tot}) of bound (○) and nonbound (●) water, as a function of the total amount of absorbed water.

of Jelinski at al. based on quadrupole-echo NMR measurements.[16,17] This is to say that (a) the sorbed water molecules are restricted in their movements and have a site residence time of $\sim 7 \times 10^{-10}$ s, (b) there is no evidence fo free water, (c) there is no evidence of tightly bound water, and (d) it is unlikely that the water disrupts the hydrogen-bond network in the epoxy resin.

The results of the work of these authors indicate that water interacts with specific sites (or "traps") on the epoxy backbone, insomuch as the water molecules jump from site to site rather than diffusing continually as a gas through an inert medium. The jumping water molecules which are seen to be "very mobile" in NMR studies, are seen to be "static" in vibrational experiments because the time required for IR radiation to interact with the absorbing molecules is of the order of 10^{-14} to 10^{-12} s. In other words, the water molecules would respond to IR radiation within a time which is about 3 orders of magnitude higher than their natural "relaxation time". Thus, the "jumping" water molecules identified in NMR experiments may well correspond to the hydrogen-bonded S_2 species which produce the broad signal centered at 6535 cm^{-1} in the NIR spectrum.

The statement that no tightly bound water is observed by NMR, whereby for tightly bound water it is meant water species with relaxation times of 10^{-3} s or longer, is not in disagreement with the present results. In any case, both the above NMR studies and the present investigation provide strong evidence that sorbed water does not perturb significantly the hydrogen-bonding network within the epoxy matrix. The most significant difference that emerges from the two probing techniques is that quadrupole-echo NMR spectroscopy does not detect unassociated water into the system, while a very clear signal associated with this species is observed in the vibrational spectra, both MIR and NIR.

Concluding Remarks

The presence of signals arising from mobile water localized in microvoids, and not capable of interacting with the polymer network, has been clearly revealed in both the MIR and NIR spectra. A fraction of water molecules firmly bound to the network by hydrogen-bonding interactions has also been detected. The stoichiometry of the interaction has been determined and the most likely proton-accepting groups along the polymer network have been identified. By using the spectroscopic data for water in different solvents, it has also been possible to obtain quantitative estimates of the amount of bound water in the system. Since only bound water is expected to affect the longer relaxations associated with the glass transition of the cross-linked resin, the use of NIR spectroscopy makes it possible to determine the extent of plasticization due to absorbed water. This will have an enormous advantage over thermal techniques, which rely on measurements of the depression of the glass transition temperature insofar as a certain amount of water is expected to desorb from the sample during the course of the experiment. This is effect is particularly pronounced if the sample is in the form of thin film or powder and if the T_g of the resin system is particularly high, as in the present case. The results of this study are in close agreement with the data obtained by dielectric measurements with respect to the estimated amount of bound and free water. The discrepancy in the conclusions from this work, with regard to the nature of absorbed water in epoxy resins, relative to the findings from quadrupole-echo NMR experiments can be partly attributed to the different time scales of the two spectroscopic techniques.

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