Epoxy−Amine Reticulates Observed by Infrared Spectrometry. I: Hydration Process and Interaction Configurations of Embedded H₂O Molecules

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This article is the first one of a series devoted to the study of hydration processes in epoxy resins using infrared (FTIR) spectrometry, with a view to eventually determining the role of ambient H₂O molecules in the degradation of these resins, particularly when they are exposed to irradiation. The starting experiment consists of recording spectra of thin films of these resins which allows us to propose a preliminary assignment of the bands of interest. The second experiment consists of heating these resins. As the main effect of a temperature elevation is to break hydrogen bonds, the analysis of the corresponding spectra enables us to more precisely assign bands which will be of importance in the hydration process. The third experiment consists of hydrating these resins in a humid atmosphere. The pressure of the water vapor of this atmosphere is directly measured in the IR spectra where the corresponding, extremely narrow bands are easily isolated. The analysis of the spectra obtained, after subtraction of these bands due to water vapor, allows us to determine the interaction configurations of H₂O molecules which are embedded in the resins, that is, the various ways they establish or accept hydrogen bonds to or from hydrophilic groups.

Introduction

Epoxy resins are widespread materials, found in numerous industrial fields, which exhibit interesting mechanical and chemical properties. These properties may however be modified by the environment which often acts as a degrading agent. Of particular importance is the effect of ambient humidity. Despite the fact that some epoxy resins, and among them amine-cured resins, are known to be chemically insensitive to water, micro crazes and micro cracks can be found inside them due to H₂O molecules. It is also known that absorption of water leads to plasticization by lowering their glass transition temperature T_g,[1−3] and may more generally be a cause of aging.[4−6]

Contrary to common belief, H₂O molecules are not easy to observe when present in polymers. This is because, when using basic techniques to study polymeric materials at molecular level (such as diffraction of X-rays, scattering of neutrons or light), one encounters difficulties to localize such small and versatile molecules which can rapidly change their interactions with neighboring molecules. On the other hand infrared (IR) spectroscopy, certainly the most sensitive and precise technique to study hydrogen bonds,[7−9] has recently proved to be a very

powerful technique to determine the interaction configurations that these H₂O molecules establish with neighboring molecules,[10,11] provided one is able to avoid saturation of bands due to these H₂O molecules.[12] The appearance of such catastrophic saturations is the reason why H₂O molecules have long been paradoxically considered as a poison in IR spectroscopy.

In this paper we describe the hydration process of two epoxy resins as determined by IR spectrometry. We more specifically describe three experiments which are aimed at assigning spectral bands of these resins and determining the mechanism of their hydration at the molecular level. The two epoxy resins which we consider in this paper are of a general use in the nuclear industry. They are, for instance, used in the conditioning of some nuclear waste. This is why we have considered the effects of both humidity and irradiation in the degradation of these resins. In a subsequent article we observe, by IR spectrometry, the effects of irradiation, study the hydration process of irradiated samples, and compare it to that described in the present article. In a third part of this work we will use IR spectrometry to determine how humidity of the atmosphere surrounding the sample during irradiation influences degradation of these resins.

Materials and Methods

The two kinds of resins we have studied were obtained by reticulation of diglycidyl ether of bisphenol A (LY 556 from Ciba-Geigy) either with aromatic diamine HT 972 (we shall label this resin DGEBA-DDM in the following) or with

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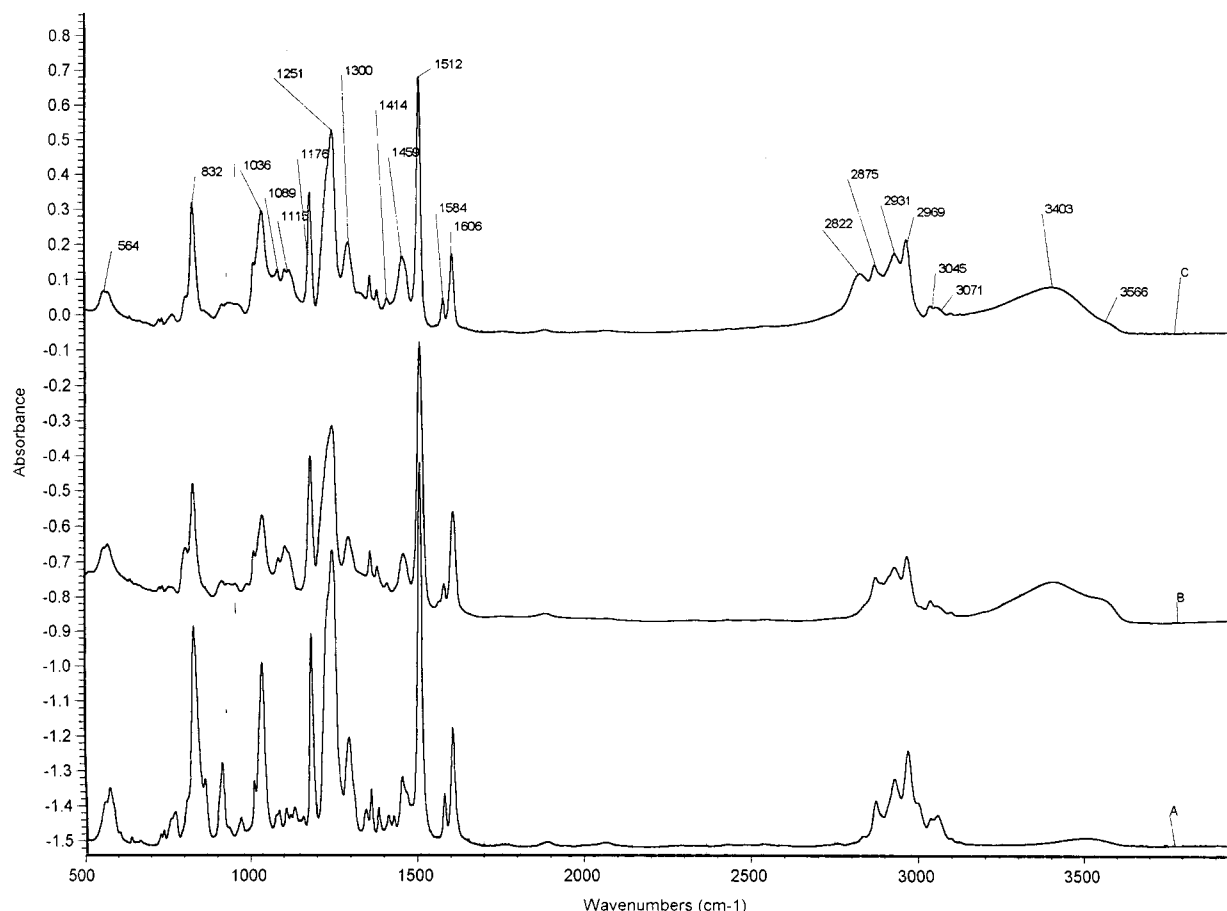
Figure 1. IR spectra of DGEBA prepolymer (A), of DGEBA-DDM (B), and DGEBA-TETA (C) cured resins. The two latter spectra have been multiplied by $10/e$ so as to correspond to spectra of 10 μm thick samples (e is the thickness of the sample in μm).

triethylene tetramine HY 956 (labeled DGEBA-TETA). The condensation index n, as given by Ciba-Geigy, has a value of 0.11. For DGEBA-DDM a mixture of 10 g of DGEBA for 2.7 g of aromatic diamine was prepared. The curing session consisted of heating the mixture at 120 °C for 2 h, followed by a session at 160 °C for 2 h. For DGEBA-TETA, a mixture of 10 g of DGEBA for 2 g of triethylene tetramine was prepared and was heated at 80 °C for 1 h, and then at 140 °C for 1 h.

Sample films displaying thicknesses falling between 10 and 20 μm, which are optimal for absorption spectra in the infrared region, were prepared by compressing the mixture of epoxy and amine components between two Teflon lamellae between which it was left reacting for several hours. Circular disks of a diameter somewhat less than 1 cm were cut out of these films. They were positioned in a special closed cell designed in the laboratory.[11] Inside this cell, which was equipped with KBr windows, temperature and humidity could be precisely controlled. The thicknesses of films could be measured, often at the end of experiments, by cutting three small pieces out of them, positioning these small pieces between two optical windows, and recording on the IR spectrometer the interference patterns due to multiple reflections of an IR beam on the inner surfaces of these two windows.

FTIR spectra were recorded on a Nicolet-Magna 760 Fourier transform spectrometer equipped with a low noise detector (HgCdTe) cooled at 77 K. The displacement of the moving mirror of the interferometer was 0.5 cm, corresponding to a resolution of 2 cm^{-1}. A spectrum was the Fourier transform of 128 co-added interferograms.

Assignments of IR Bands. To assign the numerous IR bands of epoxy resins, we have to perform two preliminary experi-

ments. The first one consists of recording the IR spectra of dried samples at room temperature. A comparison between these spectra and the spectrum of the DGEBA prepolymer (before addition of amine to epoxy) conveys useful information on the main spectral bands. Such a comparison has already been described for O−H stretching bands in former studies.[13] In a second experiment we vary the temperature of the resins. As the bonds which are most sensitive to temperature variations around room temperature are hydrogen bonds, these experiments give information on the hydrogen bonds which exist in these species and will be of importance when studying the hydration process.

Spectra of Dried Samples. In Figure 1 we have represented the absorption spectra of both DGEBA-DDM and DGEBA-TETA cured resins, together with the spectrum of the initial (prior to reticulation) diglycidylether of bisphenol A. In both spectra of resins we can distinguish three groups of bands. At wavenumbers higher than 3100 cm^{-1} we find bands which are due to O−H stretching vibrations. The broad bands which culminate around 3400 cm^{-1} are the O−H stretch in hydrogen-bonded O−H$\cdots$ groups[8,9,13,14] (they will be labeled $\nu_{O-H\cdots}$ in the following) while the narrower humps around 3565 cm^{-1} are the O−H stretch (ν_{O-H}) in non hydrogen-bonded or weakly hydrogen-bonded O−H groups. These are quite well-established assignments.[15,16] We already see that the proportion of non-bonded O−H groups is greater in DGEBA-DDM than in DGEBA-TETA. We also note that the proportion of such non hydrogen-bonded groups is important, because the hump at 3565 cm^{-1} clearly appears despite the fact that ν_{O-H} bands of free O−H groups are intrinsically much weaker, by an order of magnitude or more, than $\nu_{O-H\cdots}$ bands of O−H$\cdots$ groups.[17]

TABLE 1: Assignments of Main Bands of Figure 1[a]

wavenumber/cm^{-1}		
DGEBA-DDM (B)	DGEBA-TETA (C)	assignments
3550	3560	ν_{O-H} (alcohol)
3410	3414	$\nu_{O-H\cdots}$ (alcohol)
3034	3037	ν_{C-H} phenyl ring
2970	2963	
2930	2928	ν_{C-H} alkyl groups
2875	2866	
	2820	ν_{C-H} in CH_2 of aliphatic amines
1610	1612	
1585	1584	$\nu_{C=C}$ phenyl ring
1510	1515	
1465	1456	δ_{CH_2} scissors
1415	1415	δ_{OH} (alcohol)
1386	1386	δ_{CH_2} sym
1366	1363	
1303	1303	δ_{CH_2} wagg
1248	1255	$\nu_{C(\phi)-OC(alkyl)}$ ether
1185	1184	δ_{CH} of $\phi-O + \nu_{C(\phi)-OC(alkyl)}$
1110	1115	$\nu_{C-OH\cdots}$ (alcohol)
1090	1090	ν_{C-OH} (alcohol)
1042	1042	$\nu_{C(\phi)O-C(alkyl)}$ ether
828	833	γ_{OH} alcohol (out-of-plane)
		γ_{CH} phenyl ring
		$\delta_{C-O-\phi}$ ether
800	800	δ_{CH_2} rock

[a] Numbers are wavenumbers of maxima of bands.

The second and well-identified group of bands is that one which falls in the region 2750−3050 cm^{-1}. These bands are due to C−H stretch[15,16] (ν_{C-H}). From a comparison of these bands in both spectra of resins we can assign all the subbands of this group (Table 1). Thus the band around 2820 cm^{-1} exists only in spectrum C and can consequently be safely assigned to ν_{C-H} found in aliphatic amine groups.

The third group consists of the set of more compact bands which appear below 1650 cm^{-1}. We assign the most important components of this group in Table 1, following usual assignments[15,16] and after a comparison of the three spectra of Figure 1. The small bands around 1415 cm^{-1} in spectra B and C are assigned to bending δ_{O-H} bands in alcoholic groups, as a result of deuteration in heavy water (spectra not displayed). Let us note that the band at 1610 cm^{-1} might have been assigned to the bending band δ of H_2O molecules (vibration of H−O−H angle). We finally excluded this possibility because the shapes and intensities of this band are the same in the three spectra of Figure 1, whereas the shapes and even more the intensities of the whole O−H stretch bands ($\nu_{O-H\cdots} + \nu_{O-H}$ in the region 3200−3700 cm^{-1}) display marked variations (these O−H stretch bands almost completely disappear in Figure 1A, whereas the band at 1610 cm^{-1} keeps an intensity comparable to that in Figure 1 B,C). This implies that these O−H stretch bands are not those of hypothetical H_2O molecules, which remain almost invisible in all three spectra, but those of alcohols. The absence of visible features due to H_2O molecules is consistent with the absence of the characteristic and intense libration band of H_2O which we will see (Figure 4) to clearly appear around 670 cm^{-1}. As a consequence the band at 1610 cm^{-1} is assigned to $\nu_{C=C}$.

We have assigned the intense band around 1250 cm^{-1} to ν_{C-O-C} modes which appear in aromatic ethers. We have labeled it $\nu_{C(\phi)-OC(alkyl)}$ in Table 1. The other ν_{C-O-C} band, labeled $\nu_{C(\phi)O-C(alkyl)}$, appears around 1040 cm^{-1}. We might have assigned this band as a C−OH stretch in secondary alcohols (ν_{C-OH}). The presence of a similar band of comparable intensity and same position in the spectrum of DGEBA prepolymer (A), where alcoholic groups are much less numerous, is a strong argument

against this latter assignment. The ν_{C-OH} band appears then as being that band around 1100 cm^{-1} which is weak in the spectrum of the prepolymer (A). For the same reason the band at 915 cm^{-1} which appears only in spectrum A is assigned to C−O vibrations in epoxide groups.

A question mark regarding the assignment to the ν_{C-N} mode remains unanswered: these modes appear in the same region as C−O stretch modes. The intense band at 1255 cm^{-1}, which we have assigned as ν_{C-O-C} seems to have at least two components. The smallest one might be ν_{C-N}. This is the only argument we have for this assignment, and it remains questionable.

Effect of Temperature. In Figure 2 we display the effect of temperature on the aromatic DGEBA-DDM system. Corresponding spectra for the DGEBA-TETA system are very similar to those displayed in Figure 2. As they convey no extra information we do not display them. The difference spectrum C in Figure 2 is only composed of differential-type bands, displaying a minimum and a maximum at close wavenumbers. This proves that no evaporation of H_2O molecules occurs upon such a temperature raising, as evaporation would appear in this spectrum in the form of the three full (not differential-type) bands of H_2O which we shall encounter in Figure 4. This is a further argument which supports our former conclusion that no bands due to H_2O are visible in Figure 1. The presence in Figure 2C of the positive $\nu_{O-H\cdots}$ intense band around 3365 cm^{-1} and negative ν_{O-H} band around 3590 cm^{-1}, which is, as already mentioned, intrinsically less intense, shows that at 122 °C hydrogen bonds are broken. As we have seen that the number of H_2O molecules is very small in the dried samples, these hydrogen bonds are established by COH groups of alcohols. The change of $\nu_{C-OH\cdots}$ bands into ν_{C-OH} bands upon rupture of the hydrogen bond established by alcohols may be located as the weak features displaying a maximum at 1127 cm^{-1} and a minimum at 1085 cm^{-1}. The apparent weaknesses of these features is certainly due to the relatively important width of these C−OH stretching bands (Figure 1) and also to the relatively small number of alcoholic groups which break their hydrogen bonds when passing from ambient temperature to 120 °C (unbroken hydrogen bonds are still present in spectrum B, 122 °C). We attribute the differential-type bands with maxima at 1255, 1187, and 1040 cm^{-1} (corresponding minima at 1285, 1180, and 1010 cm^{-1}) to a slight modification of the force constants governing the vibrations of the C−O−C ether group, due to rupture of the hydrogen bond. It implies that hydrogen bonds are established by alcohols on oxygens of ether groups. The relatively intense difference bands which appear around 1610 and 1505 cm^{-1} correspond to $\nu_{C=C}$ (C=C stretch) in phenyl groups (Table 1). Their presence suggests that these phenyl groups may act as acceptors of hydrogen bonds, a possibility already postulated by P. Perret.[14] However, other mechanisms, such as changes in chain conformation, may accompany these local ruptures of hydrogen bonds and be at the origin of this differential band. We summarize all these assignments in Figure 3.

We may estimate the proportion of hydrogen-bonded C−O−H··· alcoholic groups to non hydrogen-bonded C−O−H groups at room temperature: in order to suppress the ν_{O-H} band at 3590 cm^{-1} in Figure 2A we must add spectrum 2C multiplied by a factor falling between 2 and 3 (the precision is not good, because, upon heating, the shape of this ν_{O-H} band somewhat varies). To make the same operation for the $\nu_{O-H\cdots}$ band at 3365 cm^{-1}, we must subtract spectrum C multiplied by a factor close to unity from spectrum A. As in spectrum C one hydrogen-
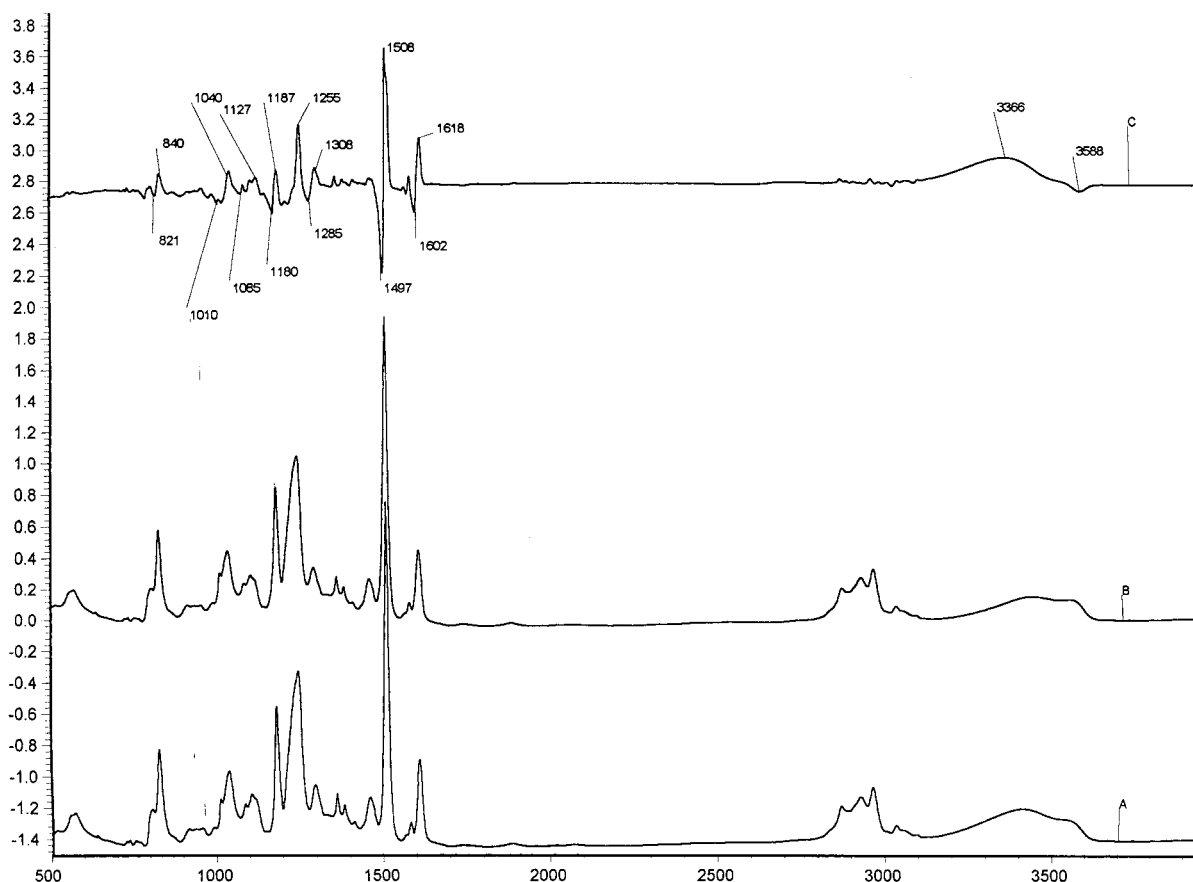
Figure 2. Spectra of DGEBA-DDM at 26 °C (A) and 122 °C (B). Spectrum C is equal to A − B multiplied by 2.5.
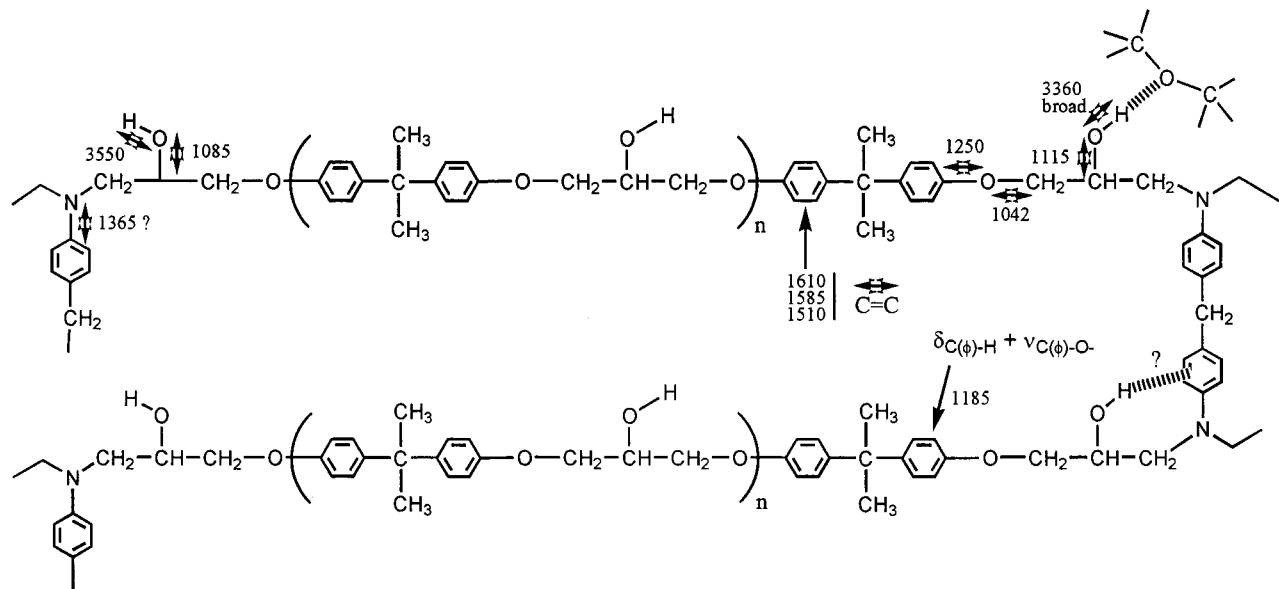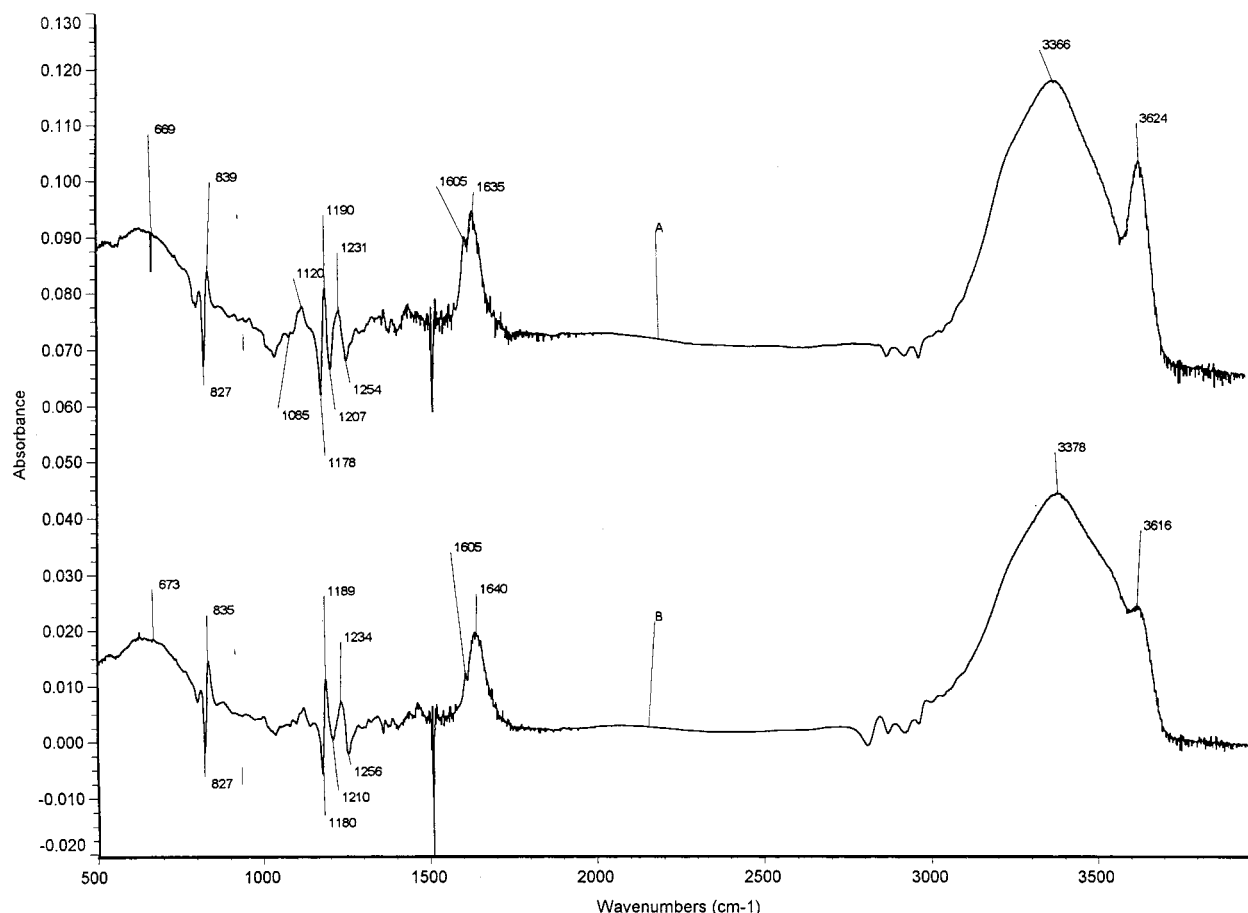

Figure 3. Structure of the DGEBA-DDM network showing wavenumbers of the most significant IR bands. Stretching modes are represented with double-headed arrows (↔), in-plane bending modes are represented with curved double-headed arrows, and out-of-plane bending modes with ⊕. The structure of DGEBA-TETA is obtained by replacing aromatic >N−Φ−CH₂−Φ−N< reticulating groups by aliphatic >N−(CH₂)ₘ−N< sequences.

bonded O−H··· group is transformed into one free O−H group, we deduce that at 25 °C (spectrum A) we have between 2 and 3 C−O−H groups for one C−O−H··· group. At 122 °C some 40% of these C−O−H··· groups are transformed into C−O−H groups. In the case of the DGEBA-TETA system we find 2 C−O−H groups for one C−O−H··· group at 25 °C.

Hydration. In these experiments we immerse the sample in water vapor by blowing inside the cell air having some predefined humidity after having passed through a liquid water reservoir. The water vapor pressure surrounding the sample is directly measured in the IR spectrum of the sample by subtracting a standard spectrum of the cell containing H₂O vapor with a known pressure, multiplied by a coefficient which is adjusted in such a way that there remain no bands of these easily identified H₂O vapor molecules. After a modification of the humidity of the atmosphere we may have to wait for a sufficient

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Figure 4. Hydration spectra of DGEBA-DDM(A) and DGEBA-TETA(B) films 10 μm thick in a humid atmosphere at 25 °C characterized by a water-vapor pressure $p = 2350$ Pa, corresponding to a relative hygrometry $p/p_0 = 0.7$. Spectrum A corresponds to equilibrium with this atmosphere, while in spectrum B the number of H_2O molecules is 85% that at equilibrium. In both spectra the characteristic lines due to water vapor are subtracted but are still visible as difference narrow bands in the region 1400−1800 cm^{-1} and above 3600 cm^{-1}.

time for the spectrum of the sample to be stabilized, an indication that the sample has reached its equilibrium with the surrounding atmosphere. This time is typically of 2−3 h, in agreement with values found for diffusion coefficients of H_2O molecules in these species[18] which show that H_2O molecules are uniformly spread inside 20 μm thick films in a time somewhat less than 2 h. The fact that such a spectrum does not display any further evolution when waiting for several days indicates that water has really penetrated inside the bulk of the resin and does not stay only on its surface. Another argument that comes in support of this assertion is that when we replace water vapor by heavy-water vapor we have, within some hours, all O−H groups exchanged into O−D groups, leaving no C−O−H groups inside the resin.

In Figure 4 we display "hydration" spectra of DGEBA-DDM and DGEBA-TETA epoxy resin films. Each spectrum is equal to the spectrum of the sample immersed in a humid atmosphere, with bands due to water-vapor subtracted as indicated above, minus the spectrum of the initially dry sample. Both difference spectra are then multiplied by a coefficient equal to $10/e$, where e is the thickness of the film in micrometers, so as to correspond to hydration of films 10 μm thick. The hydration process of these resins is unique and fully described by spectra of Figure 4. All hydration spectra have the same shape and differ only by a scaling factor. This factor depends on the vapor pressure of the surrounding atmosphere and also depends on whether equilibrium with this atmosphere has been reached or not. This characterizes the quantity of water or, more exactly, the number of H_2O molecules which are embedded inside the sample.

Both spectra of Figure 4 consist of full bands due to H_2O and of differential-type bands due to modifications of bands of polymers induced by addition (or evaporation) of H_2O molecules. The full bands due to H_2O molecules are consequently easily identified. These are in spectrum B the broad band at 3378 cm^{-1} with shoulder at 3616 cm^{-1} (O−H stretch), the band at 1640 cm^{-1} with satellite at 1605 cm^{-1} (H_2O bend δ), and the broad band which culminates around 670 cm^{-1} (libration, that is hindered rotation of the whole H_2O molecule). They furthermore much resemble the bands found in liquid water.[19,20]

The broad and intense $\nu_{O-H}...$ band which culminates at 3366 cm^{-1} in A (3378 cm^{-1} in B) may be due either to H_2O molecules or to alcoholic groups which establish hydrogen bonds, or to both of them. The shoulder at 3624 cm^{-1} in A (3616 cm^{-1} in B) is the ν_{O-H} band due to O−H groups of H_2O molecules which do not establish hydrogen bonds (the corresponding ν_{O-H} band in alcohols appears at lower wavenumbers, 3565 cm^{-1} in Figure 1C). We see that the relative number of such free OH groups of H_2O is greater in DGEBA-DDM (Figure 4A) than in DGEBA-TETA (B) by a factor 1.6 (in the subtraction spectrum A − 1.6 B this band completely vanishes).

The bending band δ of H_2O, which is known to be much less sensitive to hydrogen bonds than O−H stretch bands,[12,19] is composed of a shoulder at 1605 cm^{-1} which we assign to H_2O molecules establishing no hydrogen bonds (in water vapor, this band is found[21] at 1595 cm^{-1}) and a band at 1635 cm^{-1} in A which we assign to bending vibrations in H_2O molecules establishing two hydrogen bonds (in liquid water,[19] this band

falls in a close vicinity of this value). We apparently have no intermediate case of H_2O molecules having one free O—H group and one O—H group which establishes an hydrogen bond and for which we expect an intermediate value for the maximum of the δ band.[22] Such an intermediate interaction configuration for H_2O molecules has been postulated as a result of gravimetric studies.[23] It may be present in spectrum B where the band at 1640 cm^{-1} is broader than that at 1635 cm^{-1} in A. It remains nevertheless small in number.

The integrated intensity of this δ band in A is the same as that found in the spectrum of a film of liquid water 0.18 μm thick[19,20] (0.15 μm for spectrum B). Assuming that the integrated intensity of this δ band scarcely depends on whether the H_2O molecule establishes or not hydrogen bonds,[12,19] we deduce that the number of H_2O molecules in the film corresponding to spectrum A is of the same order as the number of molecules in a film of water 0.18 μm thick, that is 6 10^{17}molecules/cm^2. This assumption will be shown in a forthcoming article to give results comparable to gravimetric methods in the case of water in polysaccharides or proteins, which might not be the case for ice.[24] The measured density of DGEBA-DDM epoxy is 1.22 (1.19 for DGEBA-TETA). We deduce that in Figure 4A the number of H_2O molecules is 0.18 molecules per alcoholic (C—O—H and C—O—H$\cdots$) group (0.15 for spectrum B), taking n (Figure 3) equal to 0.11 as given by the manufacturer. As we have seen in *Effect of Temperature* that in DGEBA-DDM the proportion of hydrogen-bonded C—O—H$\cdots$ groups to free C—O—H groups falls between 2 and 3, we deduce that only some of the free C—O—H groups in equilibrium with the ambient atmosphere establish a hydrogen bond with a H_2O molecule embedded in the resin.

The relatively weak hydration bands of the polymer (differential-type bands) with maxima at 1231, 1190, and 839 cm^{-1} correspond to modifications of the ν_{C-O-C} ether band. This indicates that H_2O molecules which are embedded in the polymer establish hydrogen bonds on these C—O—C groups. We may also distinguish a weakly marked maximum at 1120 cm^{-1} with minimum at 1085 cm^{-1}. We attribute these features to changes of the ν_{C-OH} band upon formation, during hydration, of C—O—H$\cdots$OH$_2$ hydrogen bonds. As this band is the same as that in Figure 2 multiplied by a factor of 0.2 we deduce, taking into account that at 25 °C we have approximately one hydrogen-bonded C—O—H$\cdots$ group for two free C—O—H group (See *Effect of Temperature*), that for the formation of one hydrogen bond of the form C—O—H$\cdots$OH$_2$ we have three H_2O molecules. As we have already seen that we have 0.18 H_2O molecule per alcoholic group, we see that a small proportion only (∼6%) of alcoholic groups bind to H_2O molecules. When they do bind a doublet of H_2O molecules is produced, as drawn in Figure 5A. With this interaction configuration alone we would have one COH group bound to two H_2O molecules. We have then to add the other configuration drawn in Figure 5B to respect the ratio of one COH site for 3 H_2O molecules. Figure 5 thus represents the main configurations we can deduce from our estimate. They do not exclude the presence of other configurations which are, however, smaller in number. In the case of DGEBA-TETA resins we have not precise enough measurements of the temperature effect to make the corresponding estimate. In view of the similarity of the spectra, we do not expect, however, a very different situation, except that the number of free O—H groups belonging to H_2O molecules is relatively small, a consequence of the relative weakness of the ν_{O-H} band in Figure 4B. This suggests that configuration B (Figure 5) may be predominant.
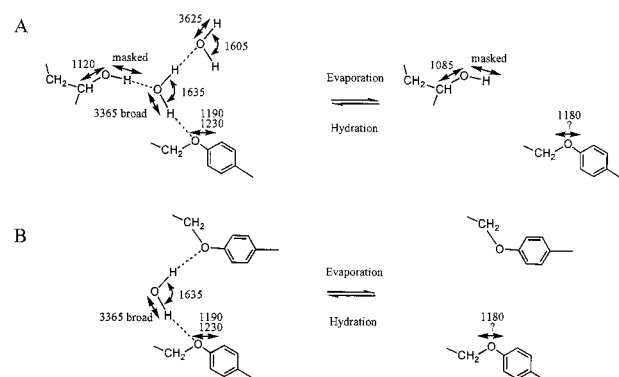
Figure 5. The two main interaction configurations (A and B) of H_2O molecules embedded in DGEBA-DDM films, as deduced from the analysis of the evaporation/hydration mechanism. Wavenumbers of IR bands are indicated as in Figure 3.

Conclusion

The analysis of FTIR spectra of two types of amine-cured epoxy resins, DGEBA-DDM and DGEBA-TETA, allowed us to follow their hydration processes and to determine the main interaction configurations that embedded H_2O molecules adopt in these resins. We display them in Figure 5. In both these resins H_2O molecules either establish two hydrogen bonds with their O—H groups or do not establish any hydrogen bond with their O—H groups. The relative numbers of these two kinds of molecules are of the order of 1 H_2O molecule establishing no hydrogen bond for 2 or 3 molecules establishing two hydrogen bonds. Intermediate cases of H_2O molecules establishing one hydrogen bond with one of their O—H groups and leaving their other O—H group with no hydrogen bond are not detected in the spectra. One of the hydrogen bonds formed by H_2O molecules establishing two hydrogen bonds with their own O—H groups is on the O atom of ether groups. The other hydrogen bond may be either on the O atom of another ether group (Figure 5B), a configuration which is certainly limited by steric conditions, or on another H_2O molecule (Figure 5A) which belongs to the category of H_2O molecules establishing no hydrogen bond with their O—H group. This configuration requires less severe steric conditions for the molecules establishing two hydrogen bonds and allows them to be held by an hydrogen bond established by the C—O—H group of an alcohol. The total number of H_2O molecules embedded in DGEBA-DDM resins, in equilibrium in an atmosphere of a relative humidity of 70% at 25 °C, is of the order of 20% of the total number of alcohol groups. It shows that the number of alcoholic sites on which H_2O molecules are fixed is small, of the order of 6% of the total number of these sites and suggests that steric hindrances play an important role for enabling H_2O molecules to be held by a C—O—H group.

In this article we have not described the kinetics of hydration. We shall do it in a forthcoming article which will be devoted to the effects on these resins of irradiation by electrons or γ rays. We shall then see that irradiation does have an effect on the kinetics of hydration. The results presented in the present article will also be useful when we shall examine, in a third article, the effect(s) of humidity of the surrounding atmosphere during irradiation, which is the problem to be considered for a safer control of nuclear waste.

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