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Fluorescence labels to monitor water absorption in epoxy resins

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Abstract

Water uptake phenomena was studied in a group of commercial epoxy based thermosets using gravimetric and fluorimetric analysis. The different epoxy formulations were labeled with two dansyl derivatives differing in the spacer length between the chain and the fluorophore moiety. The fluorimetric method consisted of monitoring the changes in the first moment of the dansyl emission band as a function of water immersion time. Using the fluorescence, it was possible to obtain the parameters that govern the water diffusion process and there was a good concordance with gravimetric results. Furthermore, the fluorescence response of the dansyl moieties was used to study the effect of the molecular structure of the polymers in the water absorption process.

Keywords: Water absorption; Epoxy resins; Fluorescence

1. Introduction

The epoxy resins are very important thermosetting polymers commonly used as structural adhesives, coatings and matrices for composite materials. These resins have good thermal, electrical and mechanical properties but their main drawback is its sensitivity to water either in the liquid or in the vapor state. Small amounts of water can penetrate into the bulk of the polymer causing a loss of the mechanical properties [1–4] due to: (a) plasticization, reducing the T_g of the resin typically by 10–20 °C for every 1% of absorbed water, (b) appearance of stresses due to differential swelling or even, (c) chemical degradation, specially in anhydride cured systems. In fiber reinforced composites, the fiber/matrix interface region uses to fail when water access through it. Therefore, it is important to control the parameters that govern the water absorption mechanism. In addition, it is necessary to understand the underlying molecular details of the moisture-transport process studying the combined effects of the presence of nanopores, the specific epoxy–water interactions and the molecular motion to provide a molecular description of the moisture-transport mechanism in amine-cured epoxy systems [5].

Usually, the water uptake in epoxy systems has been monitored:

(a) measuring the gain of mass at constant temperature as a function of time (gravimetric methods) [6–9].
(b) Using the near and mid infrared spectroscopy. When near IR is used, the increase of the band at 5210 cm^{-1} is followed as a function of time. This band is assigned to a combination of the ν_{as} and δ fundamental vibrations which occur, respectively, at 3755 and at 1595 cm^{-1} in the vapor phase spectrum of water [10, 11]. In the case of using the mid IR, the broad band ranging from 3800 to 2800 cm^{-1} is analyzed to study the variations in the different O–H stretching vibrations associated to water molecules [12].
(c) Using dielectric techniques, which measure the change in the permitivity of the media. Under isothermal conditions, the increase in the permitivity observed during water diffusion, ε', is proportional to the number of the water dipoles present in the system. Therefore, a linear relationship between ε' and the water concentration in the polymer is expected [13].

Nevertheless, any of these methods can be used as a non-destructive method to 'in situ' monitor the water absorption in the epoxy resins when they are in service. In addition, these methods allow measuring the whole water content

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and, therefore, they are not useful when it is required the determination of the water absorption in specific sites such as interfaces.

It is well documented that the fluorescence response from some molecules inserted in polymeric materials can be used to study the characteristics of specific sites (polarity, mobility) [14].

Water uptake in epoxy networks has been monitored using extrinsic [15] and intrinsic [16] fluorophores, measuring the changes in the fluorescence intensities through the quenching or deactivation of the excited state obtaining nearly linear correlations with water content. Nevertheless, the intensity of fluorescence is a fluorescence parameter that, although can be used to sense the presence of water, it depends on a number of instrumental and material factors such as sample thickness, the intensity of the excitation source, the excitation geometry, etc. Therefore, fluorescence intensity does not seem to be a good parameter to control the water content of materials in service.

There are some fluorescent molecules whose excited state dipole moment is quite higher than the dipole moment in the ground state. When excited, those molecules are able to establish an effective dielectric coupling with the dipoles of the surrounding chemical groups in the system. When the dielectric coupling occurs, a stabilization of the excited state appears and the more effective coupling the more stabilization. This characteristic behavior is manifested as a shift towards lower energy in the fluorescence emission spectrum of the fluorophore [17] (longer wavelengths). Among other factors, the magnitude of the dielectric coupling depends also on the number of interacting dipoles at least until the solvation shell of the fluorophore is completed; therefore it is possible to measure the changes in dipole concentration (for example, water dipoles) by monitoring spectral shifts. Using a bifurcated optical guide, it is possible to excite the sample and to record its fluorescence, non-destructively, in situ and even when the material is in service. Furthermore, since the energy of the emission band is only dependent on the fluorophore and its immediate surroundings, it can be used, after a previous calibration, as a method to determine water content in epoxy systems.

Other important factor determining the efficiency of the dielectric coupling is the fluorophore mobility, which in turn depends on the system microviscosity. It is well known that both the fluorescence intensity and emission energy of solvatochromic probes and labels strongly depend on the local viscosity. This effect has been used by the authors to monitor polymerization reactions [18–22]. In the case of labels, the spacer length between the fluorophore moiety and the polymer chain should determine its mobility. But the problem is quite complex since the hydrophobicity of the spacer as well as the plasticization effect of the incoming water should be taken into account.

Dansyl derivatives are well known fluorophores with: (a) a dipole moment in the excited state higher than in the ground state [23]; (b) a high fluorescence quantum yield; (c) emission in the visible region and (d) a Stokes shift large enough to avoid autoabsorption effects. In fact, all these properties are in the origin of the common use of dansyl derivatives for polar sites characterization in polymeric systems [24,29].

In this work, 5-dimethylaminonaphthalene-1-[*N*-(2-aminoethylenesulfonamide)] (DNS-2) and 5-dimethylaminonaphthalene-1-[*N*-(2-aminopentylenesulfonamide)] (DNS-5) are inserted as labels in different commercial epoxy resins and their florescence response is used to monitor the amount of absorbed water. These two molecules differ in the methylenic spacer length between the fluorophore moiety and the amine reactive group involved in the labeling to the epoxy component. As in bichromophoric systems, where an intramolecular photophysical property (excimer formation or energy transfer) is measured as a function spacer length an odd-even effect [25,26] should be expected. Five methylenic units in the DNS-5 chromophore may provide higher mobility than for DNS-2 to couple more efficiently to the water dipoles and this effect will be studied also in this work.

2. Experimental

2.1. Materials and curing procedure

A group of six two-component epoxy resins supplied by GAIRESA (Lugo, Spain) was used. Commercially they are type coded as Bepox 1268, Bepox 626, Bepox 1073, Lab 1389, Lab 1411 and Triepox L,M, respectively. In Table 1 the chemical description of each epoxy resin is presented joined with the final T_g in the cured state.

The Bepox named resins have a very similar structure, being the first component the reaction product between epoxidized polyols and diglycidylether of bisphenol A (DGEBA). The DGEBA proportion increases in this order: Bepox 1268 < Bepox 626 < Bepox 1073. The first component of the formulations Lab 1389 and Lab 1411 consists only of DGEBA. Finally, the first component of Triepox is a mixture of DGEBA (10% w/w) and trimethylpropane based epoxy resin. On the other hand, for all the epoxide formulations, except for the Lab 1411, a diamine was used as the second component. The Lab 1411 formulation has as the second component an acid anhydride.

The resin mixtures were prepared by dissolving the second in the first component (stoichiometric proportions specified by the supplier) at room temperature with magnetic bar stirring. The mixtures were degassed under vacuum at room temperature, immediately injected in a homemade mould and subjected to the following cure schedule: 24 h at 22 °C and post-cured at 60 °C for 24 h; Lab 1411 was cured at 102 °C for 9 h.

5-Dimethylaminonaphthalene-1-[*N*-(2-aminoethylenesulfonamide)] (DNS-2) was synthesized according to the

Table 1
Glass transition temperatures and chemical composition of several commercial epoxy formulations from Gairesa

Supplier code	T_g	First component	Second component
Bepox 1268	30	Product of reaction between bisphenol A epoxy resin and long chain epoxyded polyol (0% of DGBA)	Modified cycloaliphatic polyamine
Bepox 626	54	Product of reaction between bisphenol A epoxy resin and long chain epoxyded polyol (10% of DGBA)	*m*-xylene diamine adduct
Bepox 1073	76	Product of reaction between bisphenol A epoxy resin and long chain epoxyded polyol (20% of DGBA)	Cycloaliphatic diamine plus modified rubber (ATBN)
Lab 1389	61	Diglycidylether of bisphenol A (100% of DGBA)	Mixture of benzyl alcohol and *meta*-xylene diamine
Lab 1411	109	Diglycidylether of bisphenol A (100% of DGBA)	Acid anhydride derivative
Triepox L,M	58	Epoxy resin based on trimethylol propane (10% of DGBA)	Unmodified cycloaliphatic diamine

method reported in Refs. [18–21]. 5-Dimethylamino-naphthalene-1-[*N*-(2-aminopentylenesulfonamide)] (DNS-5) was supplied by Molecular Probes Inc. Both fluorophores were inserted as labels in the first component of the epoxy resins. A chemical reaction between epoxy groups in the first component of the epoxide formulation and the amine group of the fluorescence molecule was achieved by using the method described elsewhere [22]. The final concentration of fluorophore was about 10^{-3} mol/kg.

The specimens prepared for water uptake experiments have a thickness of 0.56 ± 0.01 mm, dimensions 50 mm × 10 mm and a surface of 10 cm^2 approximately.

2.2. Gravimetric measurements

The samples were immersed in deionized water at 50 °C using a thermostatic bath. In those conditions, the samples were periodically weighted using an analytical balance with a precision of 0.1 mg. The specimens were removed from the water, carefully wiped (avoiding the electrostatic charge to be created) to remove excess of water, weighted and re-immersed. For each sample, two specimens were measured.

2.3. Fluorescence measurements

An Edinburgh spectrofluorimeter with Xe lamp of 150 W with double excitation and emission monochromators was used. Fluorescence measurements were done in the transmission mode to get information from the whole of the sample at 45° with respect to excitation beam. Corrected emission spectra were scanned from 375 to 600 nm using an excitation wavelength of 360 nm with 1 nm for all the slits.

3. Results and discussion

3.1. Gravimetric measurements

To study the absorption of water, the mass gain of water, ΔM_{rel}, is represented as a function of the root square of time (Fig. 1). ΔM_{rel} is defined as

$$\Delta M_{\text{rel}} = \frac{M_t - M_0}{M_0} \times 100 \qquad (1)$$

where M_t and M_0 are the masses of the specimens at water immersion times t and $t = 0$, respectively. The equilibrium water content, ΔM_{eq}, is ΔM_{rel} when $t = \infty$.

In separate experiments it was observed that there was no appreciable difference between water uptake results of labeled resins (either with DNS-2 or DNS-5) and non-labeled resins. This result evidences that the labeling of the epoxy formulations with the DNS fluorophores at a concentration of 10^{-3} mol/kg does not seem to affect the water absorption process in the systems studied, at least within experimental error. The curves of Fig. 1 show the typical sigmoid behavior with an initial nearly linear region, which shows the diffusional control of the process, and a second one that corresponds to the swelling control [8]. There are two exceptions: Lab 1411 and Bepox 1389. Lab 1411 experiences a considerable loss of mass. The main difference with the other epoxy systems is that an anhydride hardener was used in this case. This result is in accordance with those obtained by Bonniau [6] that also used an

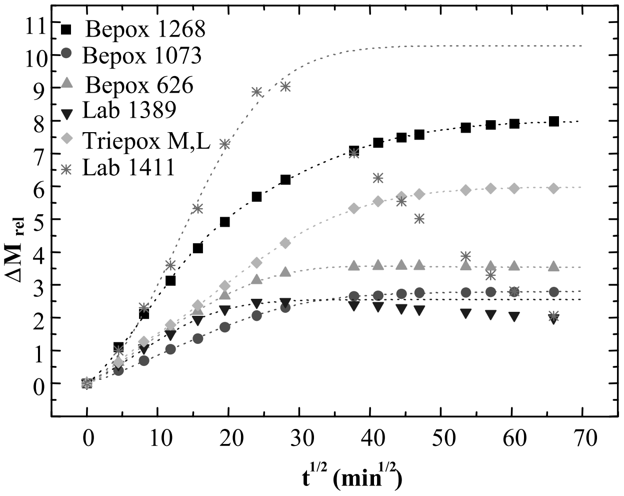

Fig. 1. Water gain (ΔM_{rel}) as a function of square root of time for different commercial epoxy systems.

anhydride as a hardener; this irreversible damage was explained in terms of microcracks formation or erosion of the surface. In the case of Bepox 1389, it can be observed a slight decreasing trend at long immersion times. It should be noted that this resin contains benzyl alcohol in its formulation, as catalyst for the addition process that can migrate outwards through the water medium.

Experimental data are usually fitted to the classical single free phase diffusion model based on Fick's law [6,27,28]. The mathematical expression used for data fitting is presented in Eq. (2):

$$\frac{\Delta M_{\mathrm{rel}}}{\Delta M_{\mathrm{eq}}} = 1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)}\exp\left(-\frac{Dt}{h^2}\pi^2(2n+1)^2\right) \quad (2)$$

where ΔM_{eq} is the water gain at saturation, that usually is let as an adjustable parameter, D the diffusion coefficient and h is the thickness. Data from Fig. 1 were fitted to this function and D and ΔM_{eq} were obtained from the fitting. As it will be shown, good fits could be obtained for all samples except for Bepox 1389, Lab 1411 and Bepox 1268 system. For the later system better fits were obtained when the Langmuir two phase model [27,28] was used. This model considers a free diffusion phase and a second phase, where water is combined with the matrix and does not involve diffusion [6]. The mathematical expression derived from this model is given in Eq. (3) and has been used to fit experimental data of system Bepox 1268

$$\frac{\Delta M_{\mathrm{rel}}}{\Delta M_{\mathrm{eq}}} = 1 - \frac{\beta}{\alpha+\beta}\exp(-\alpha t) - \frac{\alpha}{\alpha+\beta}\frac{8}{\pi^2}\sum_{n=0}^{\infty} \times \frac{1}{(2n+1)}\exp\left(-\frac{Dt}{h^2}\pi^2(2n+1)^2\right) \quad (3)$$

α is the probability of a water molecule to pass from the combined state to the free phase and β the probability of a molecule of water to pass from the free phase to the combined phase [6]; the other symbols have the meaning defined above. Eqs. (2) and (3) consider that sample thickness is constant during the absorption process. In the studied systems, this is obviously not the case but, if it assumed that all the absorbed solvent swells isotropically the resins and taking into account the low values for the maximum water content, then the maximum thickness increase can be estimated as to be in the order of the error associated to the determination of the thickness.

The use of the two-phase model is justified on the basis of some reported experimental evidences stating that (a) the resin may not be fully cured and some water molecules open the excess epoxide rings [30], (b) when water enters into the epoxy resin, some molecules may interact with the functional groups that are present [8]; for instance, Cotugno et al. [12] proposed, from the analysis of the mid infrared spectra, the existence of both kinds of water: H-bonding and non-bonding water. It should be noted that when $\beta = 0$, Eq. (3) transforms into Eq. (2).

Table 2
Diffusion coefficient, equilibrium water content and fitting parameters of the two phase model, for commercial epoxy resins

Resin	$\beta/\alpha+\beta$	$D \times 10^8$ (cm^2/s)	ΔM_{eq}
Bepox 1268	0.4 ± 0.12	2.0 ± 0.4	7.6 ± 0.2
Bepox 626	0	1.6 ± 0.2	3.5 ± 0.1
Bepox 1073	0	1.2 ± 0.3	2.8 ± 0.1
Lab 1389[a]	–	~2	~2.4
Lab 1411[a]	–	~1.8	~12
Triepox M,L	0	0.8 ± 0.03	6.0 ± 0.05

[a] Approximated values obtained from the initial slope.

Table 2 gives averaged values (over four samples) for the equilibrium water content, ΔM_{eq}, and the diffusion coefficient, D, calculated using Eq. (2) for the resins Bepox 626, Bepox 1073 and Triepox. Values for the samples Lab 1411 and Lab 1389 were obtained by the initial slope method. Values for sample Bepox 1268 were calculated using Eq. (3), which provides, in addition, $\beta/\alpha + \beta$. Attempts to fit the other systems with Eq. (3) gave systematically $\alpha/\alpha + \beta = 1$. This result suggests that for Bepox 1268 there is a high amount of combined water in accordance with the high polarity of the first component and its low glass transition temperature (Table 1). In fact, water up-take process takes place for this system at a temperature (50 °C) that is higher than the initial T_{g} of the cured polymer. There is a large amount of free volume enhancing the ability of water to access the interaction sites [5]. Furthermore, for this epoxy formulation the equilibrium water content is the highest one.

For the Bepox series it can be observed also that the equilibrium water content decreases as the amount of DGEBA increases in the formulation, which may be consequence of the higher T_{g} attained for these systems (Table 1).

3.2. Fluorescence measurements

For all the samples, the fluorescence emission spectra were scanned as a function of immersion time in water and a red shift was obtained in all cases. An example of such variation is presented in Fig. 2 for the system Triepox labeled with DNS-2.

According to the photophysical behavior of the dansyl moiety (solvatochromic effect) [18–22] the variations of the emission band energy were studied as a function of water content. Normally, the changes of the wavelength or wavenumber at the maximum of the emission band are studied. Nevertheless, when small shifts are obtained, the spectra may not have enough resolution as to detect variations with a reasonable dispersion of the data [31]. In order to solve this problem, it is proposed to use a method developed by the authors [31], which is based in the use of the emission wavenumber average or, in other words, the first moment, $\langle \nu \rangle$, of the emission band in the wavenumber scale, which is

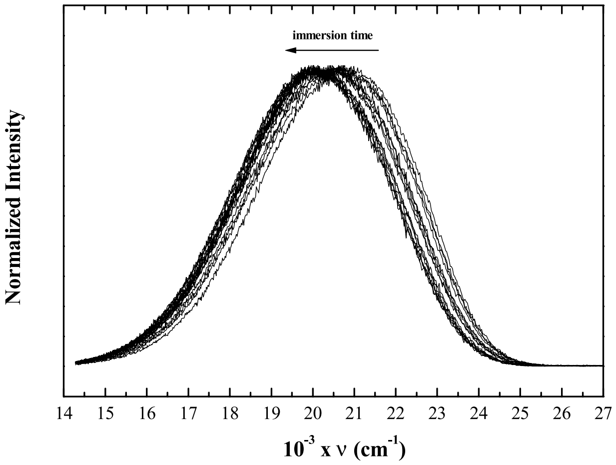

Fig. 2. Variation of the emission spectra of the system Triepox labeled with DNS-2 as a function of immersion time in water at 50 °C.

defined in Eq. (4):

$$\langle \nu \rangle = \frac{\sum_i \nu_i I(\nu_i)}{\sum_i I(\nu_i)} \tag{4}$$

where $I(\nu_i)$ is the intensity at wavenumber ν_i. A more convenient way of using this parameter for the purposes of this work consists of the use of the relative variation of $\langle \nu \rangle$, as stated in Eq. (5)

$$\Delta\langle \nu \rangle_{\text{rel}} = \frac{\langle \nu \rangle_0 - \langle \nu \rangle_t}{\langle \nu \rangle_0} \times 100 \tag{5}$$

where subscripts t and 0 mean, time $t = t$ and $t = 0$, respectively. In Fig. 3 it is plotted the variation of $\Delta\langle \nu \rangle_{\text{rel}}$ as a function of the root square of time. For both probes, DNS-2 and DNS-5, it can be observed the same behavior for all the epoxy systems. There is an initial linear increase of the first moment variation that levels off at certain time. Apparently, these plots are very similar to the gravimetric plots (Fig. 1).

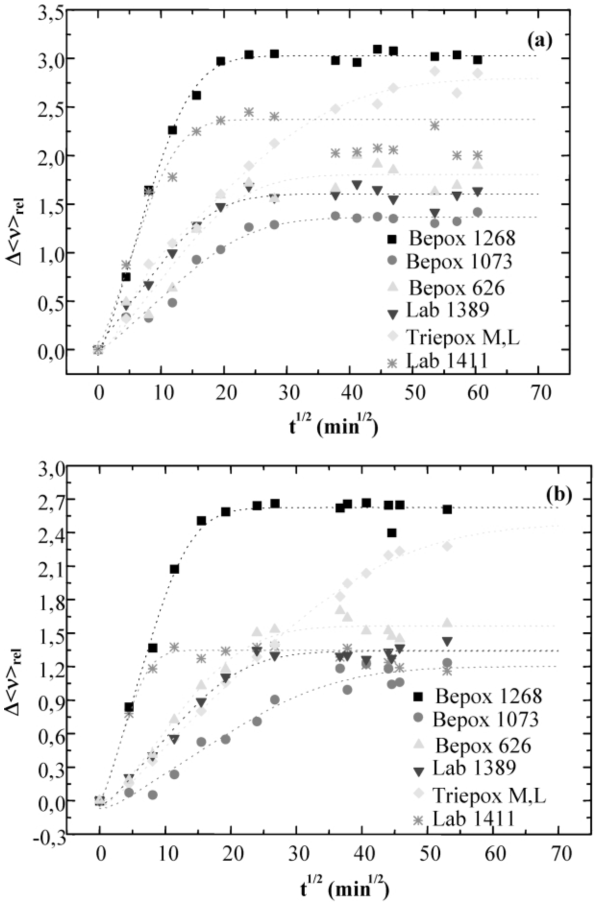

Fig. 3. Variation of the emission wavenumber average, $\Delta\langle \nu \rangle_{\text{rel}}$, as a function of the root square of immersion time (a) DNS-2; (b) DNS-5.

In order to compare the fluorescence results for all the studied epoxy systems, Fig. 4 shows a bar diagram of the magnitude of the total spectral shift variation from dried conditions to water saturation. It is observed for label DNS-2 that in dry conditions (the right side of each bar) the value of the first moment follows this order: Bepox 1073 < Bepox 626 < Bepox 1268 < Triepox M,L < Lab 1389 < Lab 1411 being almost identical for the probe with the longer spacer (DNS-5). Taking into account the photophysics of the dansyl moiety, this result suggests the order in the relaxed character of its excited state, which should be a function of the local polarity and/or flexibility of the label-environment system in those resins. For the Bepox formulations, the basic unit consists of a polyol with an increasing content of DGEBA which rises the T_g of the cured specimens (Table 1). In accordance with their T_g values (Table 1), the changes in the rigidity of the system seems to be the main contribution to the value of $\langle \nu \rangle$. The three other studied formulations differ in their chemical composition and there is not a clear correlation between T_g value and energy of the excited state of dansyl.

For all the resins, when DNS-5 is used as label instead of DNS-2, the fluorescence emission is more shifted to the red

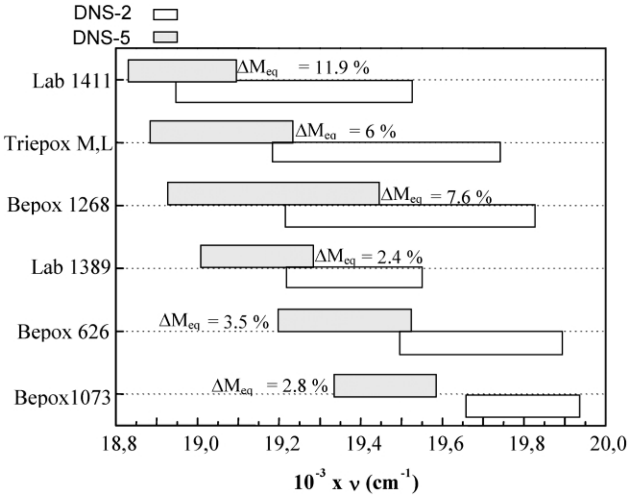

Fig. 4. Bar diagram of the magnitude of the total spectral shift variation from dried conditions to water saturation for the fluorescence labels used: DNS-2, DNS-5.

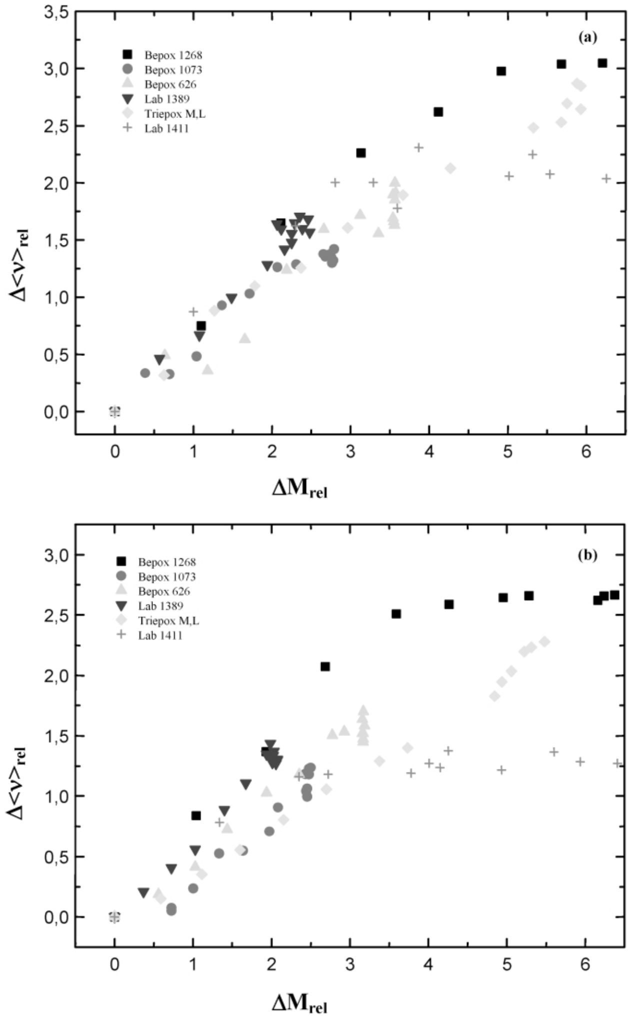

Fig. 5. Variation of the emission wavenumber average, $\Delta\langle\nu\rangle_{rel}$, as a function of the mass gain (a) DNS-2; (b) DNS-5.

(lower wavenumbers). Since DNS-5 has five single bonds between the chromophore and the polymer chain, it must present more conformational flexibility. Its excited state must couple more easily with its surroundings and becomes more stabilized.

As can be observed in Fig. 4, where ΔM_{eq} is indicated for each label-resin system, the total spectral shift variation is related with the amount of adsorbed water. The total spectral shift variation increases, as the equilibrium water content is higher. This correlation is more clear for the Bepox series, where there is a smooth variation in chemical composition. Nevertheless, the correlation between water content and spectral shift can be more clearly studied in Fig. 5, where the variation of $\Delta\langle\nu\rangle_{rel}$ is represented as a function of the mass gain. It is observed that there is an approximately linear correlation for all the systems except for Lab 1411, which degrades, and for Bepox 1268. For the later, there appears to be a leveling off in the fluorescence signal before ending the water uptake process, which is detected to appear at 6% of water gain for the DNS-2 label and at 3.5% for the DNS-5 label.

Table 3
Diffusion coefficients obtained from fluorescent data, D_f, and first moment of the emission at saturation $\Delta\langle\nu\rangle_{eq}$

Resin	$D_f \times 10^8$ (cm^2/s)		$\Delta\langle\nu\rangle_{eq}$	
	DNS-2	DNS-5	DNS-2	DNS-5
Bepox 1268	4.2 ± 0.8	4.7 ± 0.9	3.2 ± 0.6	2.6 ± 0.5
Bepox 626	1.3 ± 0.3	1.7 ± 0.3	1.9 ± 0.4	1.7 ± 0.3
Bepox 1073	1.5 ± 0.3	0.9 ± 0.2	1.4 ± 0.3	1.3 ± 0.3
Lab 1389	2.2 ± 0.3	1.9 ± 0.3	1.7 ± 0.3	1.5 ± 0.3
Lab 1411	3.3 ± 0.5	11.4 ± 0.2	2.4 ± 0.4	1.4 ± 0.2
Triepox M,L	0.9 ± 0.1	0.5 ± 0.1	2.9 ± 0.3	2.6 ± 0.3

It is interesting to observe that the probe with the longer spacer (DNS-5) is less sensitive to water content than probe DNS-2. The flexibility introduced by the length of the spacer seems to be compensated by the hydrophobic nature of the methylenic chain.

The linear correlation between water gain and spectral shift suggests that the variation in the $\Delta\langle\nu\rangle_{rel}$ as a function of immersion time must be described by the same diffusion equation as the one governing the mass gain (Eq. (2)) but changing the variable ΔM_{rel} by $\Delta\langle\nu\rangle_{rel}$, at least in the first steps of the diffusion process. Fitting parameters are presented in Table 3, from which it has been omitted the constant value of $\beta/\alpha + \beta = 0$. Except for the Bepox 1268 and Lab 1411 samples, values of the diffusion coefficient obtained by fluorescence and gravimetry are in good agreement confirming the previous assumption.

As mentioned above, the difference found for Lab 1411 can be understood taking into account the loss of mass associated to some kind of surface erosion. The difference found for Bepox 1268 need some additional explanation.

It has been reported [32] that the variation of the dielectric permitivity measured at 10 Hz reflects the total relaxation spectrum of the water molecules in the matrix and hence is correlated with the total sorption process measured gravimetrically. Dielectric measurements in the range 10^6–10^9 Hz will reflect only water molecules which are able to move more easily in the matrix [32], this water was designated as free water.

The stabilization of the excited state in a fluorophore can only occur if the dielectric relaxation time of the surrounding molecules is shorter than the fluorescence lifetime of the fluorophore [17]. It is reported that the dansyl fluorophore has a fluorescence lifetime of about 12 ns in different environments [33]. Therefore, only free water molecules with relaxation time in the order of 10^{-8} s can relax as fast enough as to produce an effective dielectric coupling between them and the excited state of the dansyl group. The peculiar behavior of Bepox 1268 system can be understood in the frame of these ideas. Recalling Table 2, only for this resin it was obtained a value of $\beta/\alpha + \beta$ of 0.4, that is to say, a high amount of combined water. Therefore, for this system it should be expected an important fraction of water molecules with low mobility in this frequency range and, as a consequence, Dansyl could only detect the presence of the complementary fraction. This argument would be in agreement with the measured value of $D_f > D_g$.

It is thought [12] that if sorbed water in epoxy matrices do establish different types of interactions with the matrix, a range of different effects on physical properties are expected to be associated to each of them. Due to this, efforts are being carried out in our lab to correlate fluorescence results with mechanical properties in order to confirm that fluorescence monitoring can be a good method to prevent failures in epoxy systems under humidity conditions.

4. Conclusions

The water absorption process has been investigated in a broad selection of epoxy resins with different compositions using gravimetry and a fluorescence technique. A modified diffusion equation has been used to calculate diffusion coefficients and to characterize the fraction of combined water. Combined water has been detected for the Bepox 1268 formulation, which contains a high proportion of hydrogen bonding sites.

Two different labels based in the same fluorescent moiety but differing in the length of the spacer, DNS-2 and DNS-5, were used as reporters of the water uptake process. A recently reported method for treating fluorescence data was used successfully being possible to obtain the parameters for the diffusion process with good concordance with those obtained gravimetrically, except in those cases with high concentration of polar groups. Taking into account the time scale of the fluorescence method used in this work, it is thought that it only can detect water with free character. Therefore, higher the polar groups in the epoxy system higher the concentration of combined water and poorer agreement between fluorescence and gravimetric results. However, monitoring of fluorescence response from fluorophores showed a potential tool to be used for detecting absorbed water in epoxy based materials when they are in service.

Acknowledgements

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