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Free/bound water absorption in an epoxy adhesive

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Abstract

The classic Fickian approach for describing the kinetics of liquid diffusion/absorption in solids was supplemented some 25 years ago by the 2-phase model of Carter and Kibler, referred to by them (modestly) as 'Langmuir-type'. Their theory assumes the existence of 'mobile' and 'bound' diffusant molecules. In this contribution, we have studied water uptake by an epoxy resin, using gravimetry, and found a good, overall, empirical agreement with the Carter and Kibler description. The 'mobile' and 'bound' components have also been considered separately. In addition, deuterium NMR analysis has been employed to study the mobility of water absorbed. Analysis and decomposition of spectra permitted us to assign two signals to the fractions of 'mobile' and 'bound' water. We suggest that the 'mobile' phase corresponds to diffusing molecules, whereas the 'bound' phase corresponds to 'clusters'.

Keywords: Epoxy resin; ^{2}H NMR; Langmuir diffusion

1. Introduction

Epoxy resins are considered to be hardy polymers capable of withstanding deleterious conditions for considerable times. As such, they are much used as adhesives, matrices for composite materials, encapsulating agents, etc. However, extended exposure to water (or water vapour) can lead to damage, and much work has been devoted to better understanding of the mechanisms involved [1–10]. Initially, damage would seem to be reversible and the main consequence of exposure to water is plasticisation, leading in turn to reduction of elastic modulus, strength and lowering of the glass transition temperature, T_g. After adequate drying, this effect can be eliminated and a return to properties before humid ageing can be obtained (or almost, anyway) [6,9,11,12]. Further ageing leads to irreversible damage [1,3,13] and cracking can ensue.

Diffusion of water within the polymer and its kinetics are clearly intrinsically related to the degradation process. The classic Fickian treatment [14,15] has often been used to explain water uptake by epoxy resins [2,8,10,12] but this is not always adequate. In a classic paper by Carter and Kibler, dating back to 1978 [16], the so-called Langmuir-type (by virtue of its similarity to Langmuir adsorption) diffusion model was developed. When mass increase is represented as a function of the square root of ageing time, the initial linear portion of the curve, successfully described by the Fick (constant diffusion coefficient) treatment, transforms at later times to an essentially linear part of lower, but non-zero, gradient (thus precluding evaluation of a diffusion coefficient due to the lack of an asymptotic saturation value of water uptake). Carter and Kibler suggested a model involving bound water and mobile (free) water, with γ (respectively β) the probability per unit time (in s^{-1}) for free (respectively bound) molecules to become bound (respectively free). Considering $n(t)$ mobile H_2O molecules and $N(t)$ bound molecules per unit volume at time t, at equilibrium (suffix ∞) we have

$$\gamma n_\infty = \beta N_\infty \tag{1}$$

The model has been used with some success at times [16–18]. Several studies have been effected to clarify the existence, and form, of the bound and free water components in epoxies, as partially reviewed by Feng et al. [19], who themselves used infrared spectroscopy as their main experimental technique in an attempt to differentiate between the two 'types'. Various propositions have been made concerning this dual-sorption invoking, for example, voids within the polymer

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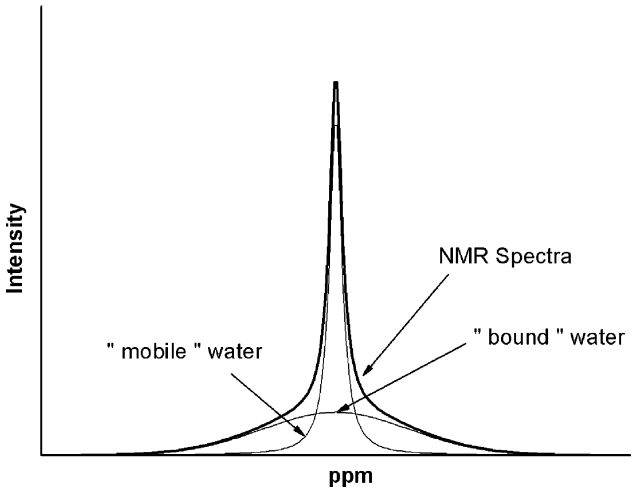

Fig. 1. Example of ^{2}H NMR peak decomposition. The overall NMR signal is usually considered to consist of the superposition of a broad, base peak of ‘bound’ water, and a (growing) thin, central peak of ‘mobile’ water.

[20], hydrogen bonding and heterogeneous morphology [21, 22]. However, the literature often shows simplistic or, at the other extreme, complex interpretations, sometimes with limited agreement between experimental data and models. Another problem is that ageing is often over relatively short periods and in humid atmospheres, rather than by immersion, leaving some doubt as to final equilibrium.

Carter and Kiblers’ model is based on a hypothesis: the existence of probabilities β and γ describing two ‘states’, or ‘types’, of absorbed water. Despite the literature referred to above, we ask the (still relevant) question: what do these probabilities represent in reality? A totally unambiguous answer still remains to be found, but the present study attempts to make a contribution. On the one hand, we have used classic gravimetric analysis to elucidate the absorption behaviour of an epoxy resin, and on the other hand, we have undertaken nuclear magnetic resonance (NMR) studies [23] on the polymer aged to various degrees. This latter technique of NMR is of considerable interest since the decomposition of signals obtained (peaks) can be associated with two water phases. Fig. 1 shows the usual method for decomposition of ^{2}H NMR spectra, assuming that, for present, the narrow peak is due to the ‘mobile’ (or ‘fast’-moving) phase, and the broad peak is due to the ‘bound’ (or ‘slow’-moving) phase of D_2O. The correlation of results allows us to attach a physical meaning to probability coefficients, β and γ.

By using an epoxy resin capable of relatively high water absorption, and effecting long-term immersion, good experimental evidence supporting Carter and Kiblers’ mathematical model has been obtained, accompanied by plausible explanations, supplied by NMR data, of the basic physical chemistry behind the two water types.

2. Experimental

The material used was a flexible, epoxy resin adhesive (type EC 2216 from 3 M), with an initial glass transition temperature, T_g, near ambient temperature (ca. 32 °C, as obtained by DSC). Curing conditions were 7 days at 23 °C in ambient, atmospheric conditions of humidity in a regulated oven. All samples were dried at 40 °C and 20% relative humidity (RH) in a drying oven over a period of 3 weeks before testing. Samples of $20\times15\times1$ mm^3 for gravimetric analysis and $5\times5\times1$ mm^3 for NMR analysis were cut from a sheet of bulk polymer. Those for gravimetric analysis were left in deionized water at 19, 35, 45, 60 and 90 °C (±1 °C). They were weighed, after different times, on a Mettler AT250 balance (precision ±0.05 mg), after careful drying with a soft, clean paper towel. Similarly, the NMR samples were immersed in D_2O 99.9% and weighed periodically. The interest of using deuterium is that it allows one to observe only the water and not the resin.

Most of the ^{2}H NMR experiments were undertaken on a Brucker 300 MHz apparatus, with the following parameters: 400 scans, the ^{2}H resonance frequency, ω_0, was 46 MHz, a spin-echo pulse sequence was used, the time interval between the two pulses was 16 μs, the time interval between the second pulse and signal acquisition was 12 μs, the 90° pulse duration was 3 μs, and the delay between two successive pulse sequences was 3 s. It was verified that dry resin gave a quasi-null flat continuous NMR spectrum. It is thus reasonable to suppose that NMR peaks correspond to epoxy–liquid interactions. Complementary experiments were carried out on a wide bore Brucker 400 MHz spectrometer using a pulse delay of 11 μs and a recycle delay of 3 s. In order to obtain a good signal to noise ratio, 1024 scans were necessary. The ratio of areas of ‘bound’ and ‘mobile’ water signals was obtained by spectral decomposition using the ‘dmfit’ programme [24].

Some mechanical properties were measured as a function of ageing time. In particular, using a Metravib Viscoanalyseur and an Instron tensile tester, the T_g and elastic moduli of the polymer were monitored.

3. Basis of Carter and Kibler model

Details of this model for diffusion can be found in [16], but we summarise the essentials needed in our development below.

Carter and Kibler assume that the diffusion of mobile molecules conforms to simple diffusion theory, modified by sources and sinks. For the one-dimensional case, the molecular number densities at position z and time t satisfy the coupled pair of equations

$$D\frac{\partial^2 n}{\partial z^2} = \frac{\partial n}{\partial t} + \frac{\partial N}{\partial t} \tag{2}$$

$$\frac{\partial N}{\partial t} = \gamma n - \beta N \tag{3}$$

where D is a (constant) coefficient of diffusion. We recall that n represents the number of mobile molecules (per unit volume) with a probability γ (s^{-1}) to become bound and N the number of bound molecules with a probability β (s^{-1}) to become mobile. In the experimental case, for a sample thickness $e=2\delta$, $z=0$ representing the central plane with surfaces at $z=\pm\delta$, exposed to a constant moisture environment on both sides at $t=0$, the boundary and initial conditions are

$$n(z,0)=0 \text{ and } N(z,0)=0 \text{ for } |z|<\delta$$

and

$$n(\delta,t)=n_\infty \text{ and } n(-\delta,t)=n_\infty \text{ for all } t$$

At a given thickness z and time t, the number of n-type molecules is [16]

$$\begin{aligned} n(z,t) = n_\infty \Bigg\{ 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)\left(r^+_{2n+1} - r^-_{2n+1}\right)} \\ \times \left[r^+_{2n+1} \mathrm{e}^{-r^-_{2n+1} t} - r^-_{2n+1} \mathrm{e}^{-r^+_{2n+1} t} \right] \cos\left(\frac{\pi(2n+1)z}{2\delta} \right) \Bigg\} \\ + n_\infty \frac{4}{\pi\beta} \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)\left(r^+_{2n+1} - r^-_{2n+1}\right)} \\ \times \left(r^+_{2n+1} r^-_{2n+1} \right) \left[\mathrm{e}^{-r^-_{2n+1} t} - \mathrm{e}^{-r^+_{2n+1} t} \right] \cos\left(\frac{\pi(2n+1)z}{2\delta} \right) \end{aligned} \tag{4}$$

where

$$\begin{aligned} r^{\pm}_{2n+1} = \frac{1}{2}\left(\kappa(2n+1)^2 + \gamma + \beta\right) \\ \pm \sqrt{\left(\kappa(2n+1)^2 + \gamma + \beta\right)^2 - 4\kappa\beta(2n+1)^2} \end{aligned} \tag{5}$$

and

$$\kappa = \frac{\pi^2 D}{(2\delta)^2} \tag{6}$$

In many applications of the Carter and Kibler theory to present water diffusion in polymers, it has been common to be contented with overall water uptake as a datum. In the following, we wish to consider separately the mobile and bound contributions, respectively $n(z,t)$ and $N(z,t)$. To do this, it is convenient to rearrange Eq. (3) and solve it by use of an integrating factor, $\mathrm{e}^{+\beta t}$, leading to

$$N(z,t) = \gamma \mathrm{e}^{-\beta t} \int n(z,t) \mathrm{e}^{\beta t} \mathrm{d}t \tag{7}$$

Let $\mathbf{N}$ be the total number of water molecules per unit area perpendicular to z in the polymer at saturation ($+\delta > z > -\delta$). The equilibrium is defined by

$$2\delta(n_\infty + N_\infty) = \mathbf{N} \tag{8}$$

Use of Eqs. (1) and (6) leads to

$$n_\infty = \frac{\beta}{\gamma+\beta} \frac{\mathbf{N}}{2\delta} \tag{9}$$

With judicious approximation, we obtain, for the case β and $\gamma \ll \kappa$

$$\frac{n(t)}{\mathbf{N}} = \frac{\beta}{\gamma+\beta} \left\{ 1 - \frac{8}{\pi^2} \mathrm{e}^{-\kappa t} \right\} \tag{10}$$

$$\frac{N(t)}{\mathbf{N}} = \frac{\gamma\beta}{\gamma+\beta} \mathrm{e}^{-\beta t} \left\{ \frac{1}{\beta}(\mathrm{e}^{\beta t} - 1) - \frac{8}{\pi^2 \kappa}(\mathrm{e}^{-\kappa t} - 1) \right\} \tag{11}$$

Useful approximations are given below, with $\mathbf{N}(t) = n(t) + N(t)$ the total amount of water molecules in polymer at time t.

For short exposure time

$$\frac{\mathbf{N}(t)}{\mathbf{N}} \cong \frac{4}{\pi^{3/2}} \left(\frac{\beta}{\beta+\gamma} \right) \sqrt{\kappa t} \tag{12}$$

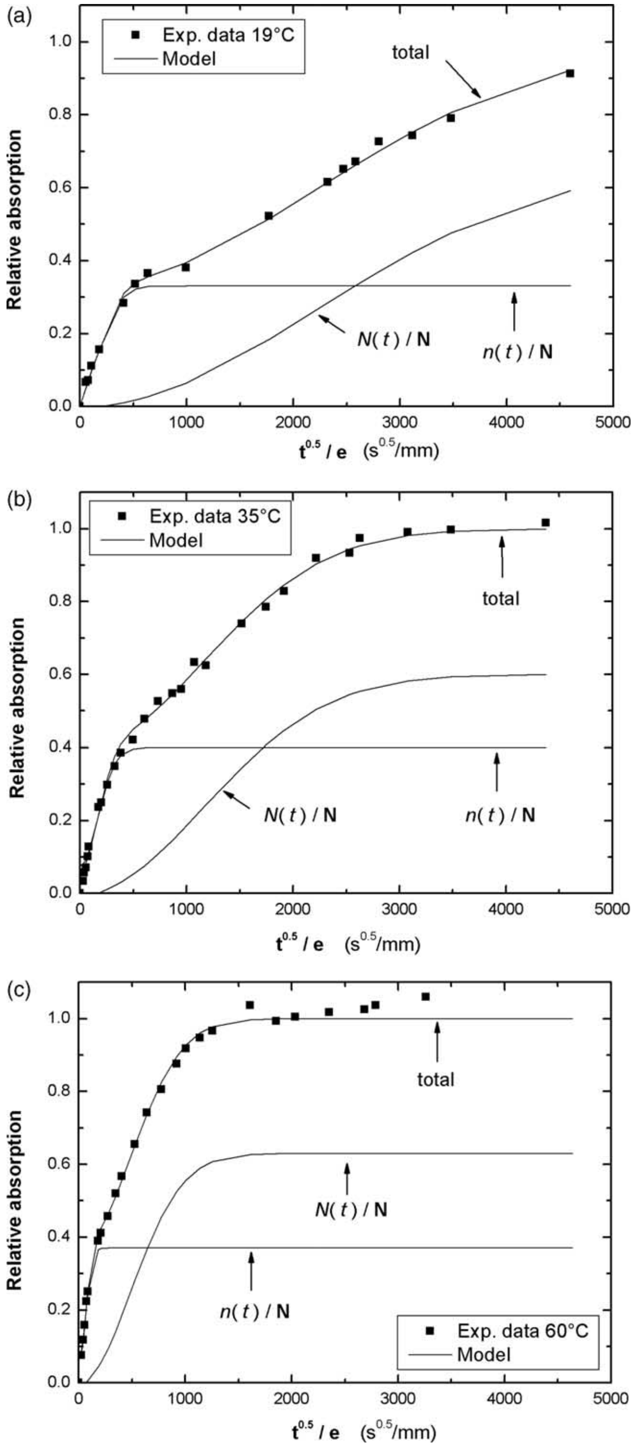

Fig. 2. Gravimetric data for water absorption in deionised water at (a) 19 °C, (b) 35 °C, (c) 60 °C. (■) experimental, (—) model.

Table 1
Parameters corresponding to best fit of Carter and Kibler model to gravimetric data

	19 °C	35 °C	45 °C	60 °C	90 °C
Weight inc. at saturation (%)	9.7 ± 0.1	10.2 ± 0.1	9.3 ± 0.1	9.6 ± 0.1	8.9 ± 0.1
Weight inc. at pseudo-eq. (%)	3.2 ± 0.1	4.0 ± 0.1	3.6 ± 0.1	3.6 ± 0.1	3.5 ± 0.1
D (m^2/s)	$1.3\pm0.1\times10^{-12}$	$1.8\pm0.1\times10^{-12}$	$4.0\pm0.1\times10^{-12}$	$1.2\times10^{-11}\pm0.1\times10^{-12}$	$1.03\times10^{-11}\pm0.1\times10^{-12}$
β (s^{-1})	$4.0\pm0.1\times10^{-8}$	$1.55\times10^{-7}\pm0.5\times10^{-8}$	$3.10\times10^{-7}\pm0.5\times10^{-8}$	$1.00\times10^{-6}\pm0.5\times10^{-7}$	$3.05\times10^{-6}\pm0.5\times10^{-7}$
γ (s^{-1})	$8.1\pm0.1\times10^{-8}$	$2.35\times10^{-7}\pm0.5\times10^{-8}$	$4.90\times10^{-7}\pm0.5\times10^{-8}$	$1.70\times10^{-6}\pm0.5\times10^{-7}$	$5.70\times10^{-6}\pm0.5\times10^{-7}$

For long exposure time

$$\frac{\mathbf{N}(t)}{\mathbf{N}} \cong \left(1-\frac{\gamma}{\beta+\gamma}\mathrm{e}^{-\beta t}\right) \tag{13}$$

The ratio $\mathbf{N}(t)/\mathbf{N}$ seems to be consistent with a pseudo-equilibrium moisture content which appears at medium times. The value of the pseudo-equilibrium is

$$\frac{\mathbf{N}(t_{\text{pseudo-eq.}})}{\mathbf{N}} = \frac{\beta}{\beta+\gamma} \tag{14}$$

4. Results

4.1. Gravimetric experiments

It is conventional and convenient to report absorption behaviour as a function of the square root of time (of exposure to water), t, since classic Fickian behaviour commences with a linear mass uptake on such a scale [14,15]. Since we are dealing with essentially one-dimensional diffusion in both the gravimetric and NMR experiments, we normalise to allow for sample thickness. Thus in Figs. 2, 4, 6 and 7, the abscissa is $t^{0.5}/e$, where e is the sample thickness.

In Fig. 2(a)–(c), we present as ordinate experimental gravimetric data as (water) mass uptake (at time t)/saturation mass uptake (black squares) and three curves: a line representing overall mass uptake ($\mathbf{N}(t)/\mathbf{N}$), and therefore corresponding to Eqs. (12) and (13) and matching the experimental points, a line showing the relative fraction of mobile water ($n(t)/\mathbf{N}$) (Eq. (10)), and a line showing bound water uptake ($N(t)/\mathbf{N}$) (Eq. (11)). The data shown correspond to temperatures of 19, 35, and 60 °C, but similar trends were shown at 45 and 90 °C, although not illustrated here for brevity.

The parameters used to fit ($\mathbf{N}(t)/\mathbf{N}$) with experimental measurements are shown in Table 1. These were deduced as follows. For short exposure time, κ (or D) was obtained from experimental measurements. At pseudo-equilibrium, the ratio $\gamma/(\gamma+\beta)$ was determined from Eq. (14). Then for long exposure times, Eq. (13) was fitted to experimental measurements with varying β. Finally, from Eq. (14), γ was deduced.

For the temperature range from 19 to 90 °C, the theoretical curves obtained from the model of Carter and Kibler are in good agreement with the experimental data, for all temperatures and absorption times studied. The maximum absorption at saturation seems to be similar, irrespective of temperature, in the range considered ($9.5\pm0.5\%$) (Table 1). D varies with temperature, and if we assume the classic Arrhenius dependence

$$D = D_0\exp\frac{-\Delta H}{RT} \tag{15}$$

where D_0 is a constant, ΔH is an activation energy for diffusion and R and T represent the ideal gas constant and absolute temperature, respectively, then we obtain a reasonable, if not perfect, correlation, as shown in Fig. 3(a), where $\ln D$ vs $1/T$ is shown.

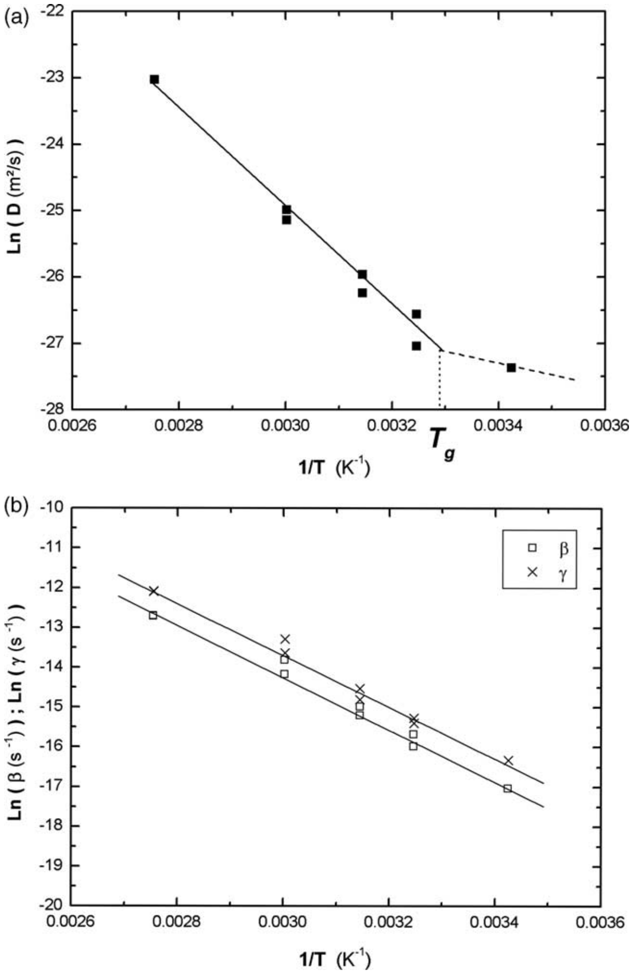

Fig. 3. Arrhenius representation of (a) D and (b) γ and β, on a logarithmic scale vs $1/T$.

Table 2
Activation energies E_a of the three diffusion process parameters D, β, γ

E_aD (kJ mol^{-1})	$E_a\beta$ (kJ mol^{-1})	$E_a\gamma$ (kJ mol^{-1})	Error (kJ mol^{-1})
56	55	55	±2

From the best fits of the Carter and Kibler theory to experimental data, we also obtain γ and β (Table 1), and these may also be postulated to follow an Arrhenius-type temperature dependence. As shown in Fig. 3(b), this is indeed the case. Activation energies for all three, D, γ and β, were found at ca. 55 kJ/mol (±2 kJ/mol) (Table 2), which is fairly typical for thermally-activated polymeric behaviour. At 60 °C, after a long time of exposure (2 years), the water uptake seems to recommence. It is possible to link this revival with the beginning of (at least) superficial physical degradation of the polymer. Indeed, the sample's colour changes from grey/green to brown and black, and the surface becomes rough and hard. This phenomenon occurs more rapidly for samples soaked in water at 90 °C (after 3 months).

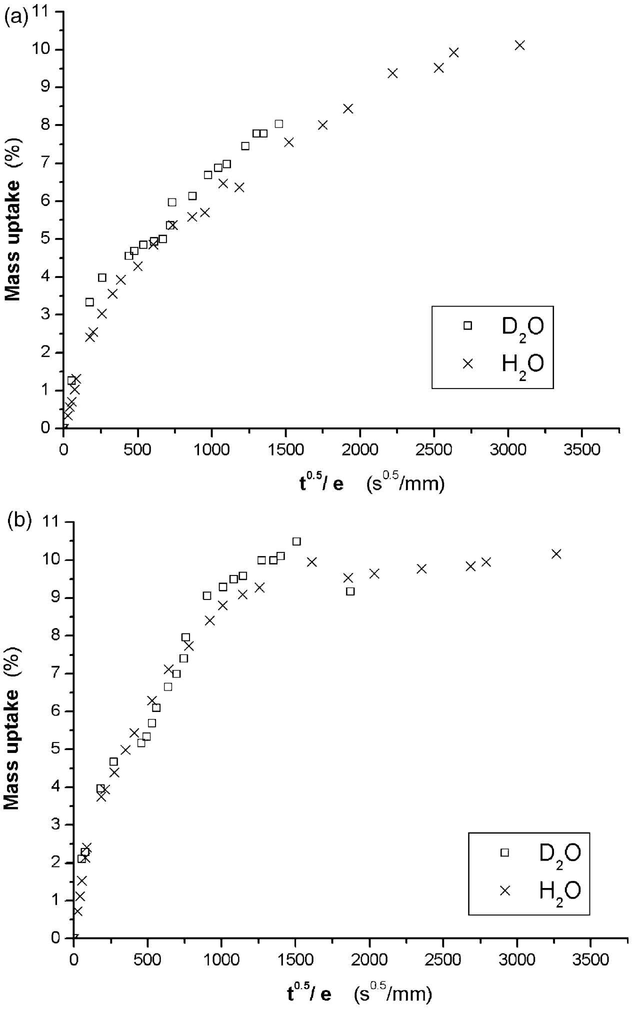

Fig. 4. Gravimetric measurements of water and deuterium uptake at (a) 35 °C and (b) 60 °C.

4.2. Solid-state ^2H NMR experiments

For two samples with the same geometry, the kinetics and values of mass uptake of D_2O or H_2O are quite comparable for a given absorption time at 35 °C and at 60 °C (Fig. 4). Therefore, we reasonably assume that the heavy water diffusion is the same as that of the light water in the polymer.

Fig. 5(a) shows ^2H NMR spectra, corresponding to absorbed water, for different exposure times at 35 °C, and Fig. 5(b) at 60 °C. At 35 °C, the deuterium signal increases with absorption time. It is true for the 2-day and the 3-week peaks at 60 °C but the intensity of the 2-month peak is lower than the 3-week peak. A shoulder in the 2-month peak appears to cause a global decrease of the maximum intensity. This observation is presently poorly understood. The area of the 2-day broad peak at 35 °C corresponds to the base area of the other peaks. From 2 days of water exposure, it is only the thin central peak, virtually co-centric with the initial broad peak, which grows. The base stays constant. On the basis of previous experience of NMR data [25], our results strongly suggests the presence of two types of water contained within the polymer: one saturating after 2 days, and a second increasing with time of exposure. The ratio of areas of 'bound' and 'mobile' phase peaks, converted into relative absorption are estimated with this simple law of proportionality

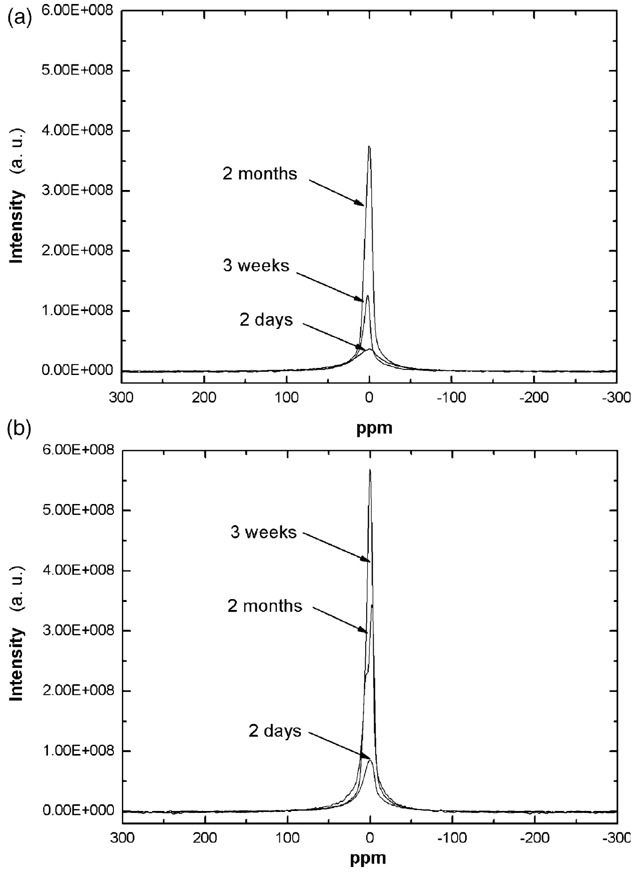

Fig. 5. ^2H NMR peaks after immersion in D_2O (a) at 35 °C and (b) at 60 °C.

$$\frac{\text{Bound (or mobile) water}}{\text{Total water}}(t) = \frac{\text{Bound (or mobile) water peak area}}{\text{Total peak area}}(t) \times \frac{\text{Relative absorption of } D_2O\ (t)}{\text{Relative absorption of } D_2O\ (t=\infty)} \qquad (16)$$

Following Fig. 1, we assume that the (2 days at 35 °C) peak area is the amount of ‘bound’ D_2O after 2 days, but also after 3 weeks and 2 months for immersion at 35 °C. In theory the saturation of ‘bound’ molecules occurs at shorter times for higher temperatures of immersion. Thus, we assume that the (2 days at 35 °C) peak area also corresponds to the amount of bound D_2O in 2 days, 3 weeks and 2 months peaks for immersion at 60 °C.

For (1 week at 35 °C) and (1 day at 60 °C and 1 week at 60 °C) tests, peak areas of bound and mobile D_2O are given by a decomposition programme.

Relative absorption of D_2O at time t is given in Fig. 4, and relative absorption of D_2O at infinite time is estimated from water absorption (about 10%).

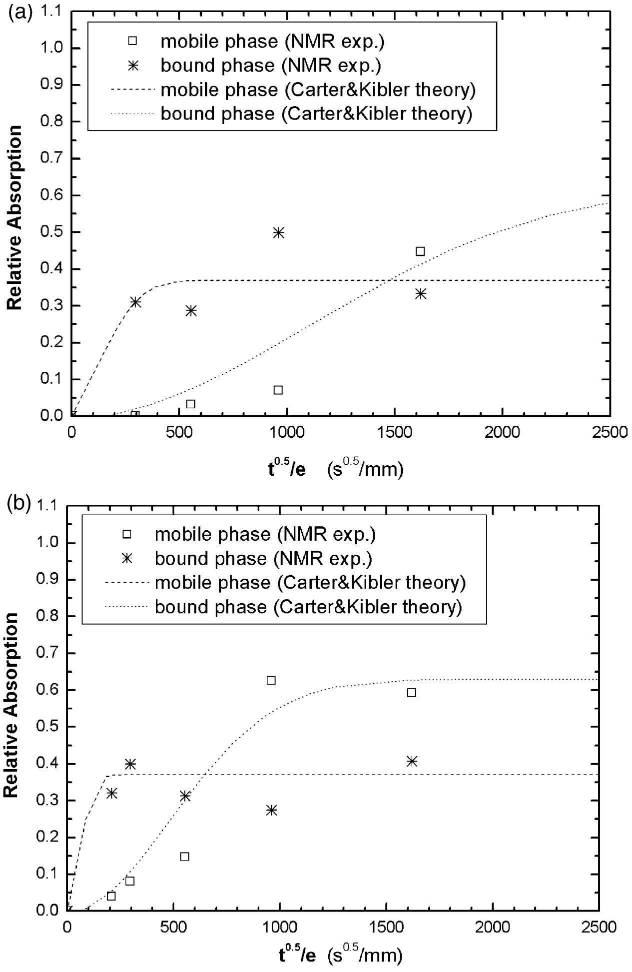

Fig. 6. Comparison of the model for water uptake of both types as obtained from gravimetric data, and those estimated from ^{2}H NMR experiments (a) at 35 °C and (b) at 60 °C.

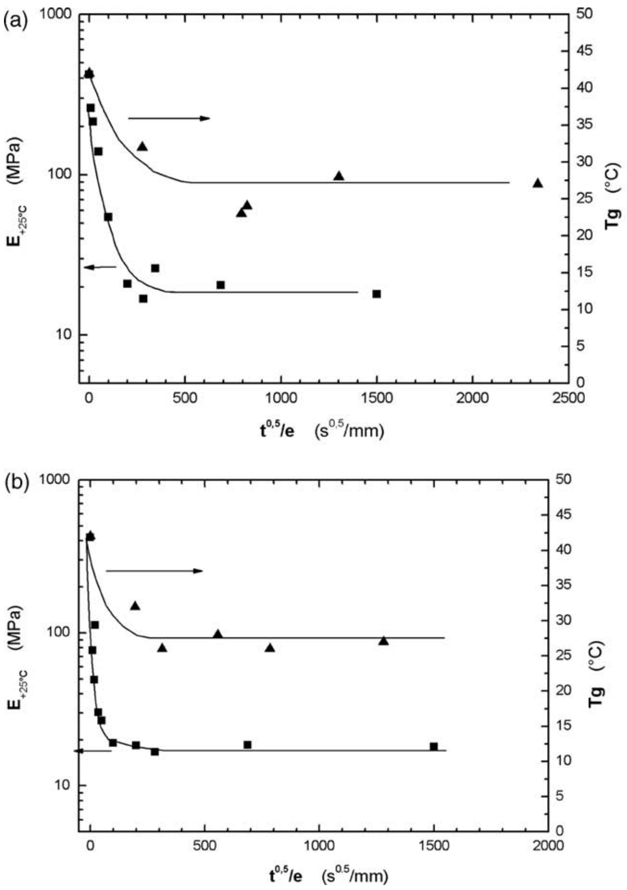

Fig. 7. Young’s modulus, E, and glass transition temperature, T_g, of the epoxy resin as a function of ageing time, t, at 35 °C and 60 °C.

The results are plotted in Fig. 6. The experimental data are compared to the gravimetric study reported above.

4.3. Mechanical behaviour

Fig. 7 summarises the decrease in both Young’s modulus and the T_g of the polymer as a function of ageing. The salient points to be retained here are the times at which these two properties have decreased approximately to their plateau values.

5. Discussion

As can be seen from Fig. 2, the model originally developed by Carter and Kibler [16] describes very well the kinetics of overall water uptake in this type of epoxy resin. The hypothesis made in this model, assuming that the temperature does not influence the equilibrium value seems correct (Table 1). Indeed, this value is an intrinsic parameter of the material. Carter and Kibler do not consider any temperature dependence of γ and β in their model. However, our results clearly suggest one for the present epoxy resin. The β and γ parameters are representative of motion of molecules, and therefore it is not unreasonable to expect them to be dependent on temperature, as is the global diffusion coefficient.

Table 3
Time to pseudo-equilibrium or equilibrium for different tests

	19 °C	35 °C	45 °C	60 °C	90 °C	Estimated error
Time to plateau of T_g ($s^{0.5}$/mm)	700	500	–	300	–	±100
Time to plateau of E ($s^{0.5}$/mm)	–	400	–	150	–	±100
Time to saturation of $n(t)/\mathbf{N}$ ($s^{0.5}$/mm)	500	400	250	150	<100	±50
Time to plateau of swelling ($s^{0.5}$/mm)	–	400	250	100	–	±50

Despite the very good agreement between our experimental results and the application of the Carter and Kibler theory, the central question is the following: what distinguishes the two ‘types’ of water postulated and corresponding to an intrinsic element in their theory? Despite various attempts to elucidate this problem, mentioned in the introduction, definitive understanding of the physico-chemical mechanism(s) is still lacking. (There may of course be more than one mechanism, depending on the conditions and/or on the polymer!).

There is a difference between the NMR and Carter and Kibler interpretations. ‘Free’, or ‘pure’, molecules in NMR lead to narrow peaks, which develop slowly in the present context, whereas more attached molecules lead to broader spectra, here reaching equilibrium quickly. This is, at first sight, the inverse of the Carter and Kibler interpretation of the same trends observed in absorption.

The simultaneous exploitation of gravimetric data and NMR analysis allows us to suggest a plausible explanation of this. Our central result is summarised in Fig. 6. Despite non-negligible dispersion, Fig. 6 shows a relatively good agreement between the ^{2}H NMR-measured kinetics of water diffusion and the initial (apparently) Fickian type diffusion estimated by gravimetry. We could suppose that this Fickian absorption corresponds to the diffusion of water having strong interactions with the polymer. These interactions may be secondary bonding, van der Waals interactions, or polar interactions with polar sites within the polymer. They may cause plasticisation, swelling, and lowering of the elastic modulus and T_g of the polymer, or some microvoids could appear. Certainly the evidence of physical measurements on the polymer suggests this, as shown in Figs. 6 and 7, and in Table 3. The plateaux of Young’s modulus, E, the glass transition temperature, T_g, and swelling behaviour correspond well with saturation of the Fickian style, mobile water.

The relatively good agreement between the ^{2}H NMR-measured kinetics of free (NMR interpretation), or bound (Carter and Kibler interpretation) water increase and the sigmoidal-type diffusion estimated by gravimetry and use of the Carter and Kibler theory indicates that weak-interaction water diffuses after the (apparently) Fickian diffusion reaches saturation, as if the ‘bound’ water (Carter and Kibler interpretation) only appears to an appreciable extent after all the bonding sites are filled, somewhat paradoxically. This ‘bound’ water (Carter and Kibler interpretation) may be ‘stored’ in microvoids or microporosity, thus producing clusters [26,27]. Only the external water molecules of clusters may interact with the polymer. Those molecules could even be free molecules which have diffused initially during immersion. The internal molecules of the clusters have weak interactions with the polymer since they are screened from it. Thus, as Fig. 5(b) shows, the thin spike of the NMR signal should correspond to an increase in the weakly interactive phase. This corresponds to an increasing degree of clustering (number and/or size). The rather paradoxical situation in this explanation, is that the ‘mobile’ diffusant in Carter and Kibler’s theory, is effectively our ‘bound’ phase, and vice versa. This can be accounted for physically by considering the initially penetrating water molecules to be ‘solo’ and thus highly mobile, whereas the later formed clusters are large and lugubrious, and thus effectively bound. We highlight the fact that ‘mobile’ and ‘bound’ refer to the kinetics and not directly to interactions with the polymer.

6. Conclusion

By using both ^{2}H NMR and gravimetric techniques, we have shown that water diffusion in an epoxy resin can be explained quantitatively by the Carter and Kibler theory. What is more, by using solid-state NMR, we have correlated different resonance signals with the two (postulated) ‘types’ of solvent assumed in the theory. We can summarise the process of diffusion of water in the present polymer in four steps

1. At the beginning of absorption, molecular water with strong interactions diffuses into the polymer. These are ‘solo’ molecules and thus quite ‘free’ or ‘mobile’.
2. After a given absorption time (depending on the temperature), the interaction sites for molecular water become saturated: absorption reaches a quasi-equilibrium.
3. Water absorption recommences, but water molecules can only stay in microvoids, and form clusters. These are large, inertial and thus, to all intents and purposes, bound.
4. Water absorption reaches a real equilibrium when all the microvoids are filled.

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References

[1] Gillham JK, Glandt CA, McPherson CA. In: Labana SS, editor. Chemistry and properties of crosslinked polymers. New York: Academic Press; 1977. p. 491–520.

[2] Brewis DM, Comyn J, Tegg JL. Polymer 1980;21:134–8.

[3] Morgan RJ, O'Neal JE, Fanter DL. J Mater Sci 1980;15:751–64.

[4] Peyser P, Bascom WD. J Mater Sci 1981;16:75–83.

[5] Johncock P, Tudgey GF. Br Polym J 1986;18:292–302.

[6] Adamson MJ. J Mater Sci 1980;15:1736–45.

[7] Sharon G, Dodiuk H, Kenig S. J Adhes 1989;30:87–104.

[8] De'Nève B, Shanahan MER. Polymer 1993;34:5099–105.

[9] De'Neve B, Shanahan MER. J Adhes 1995;49:165–76.

[10] Zanni-Deffarges MP, Shanahan MER. Int J Adhes Adhes 1995;15: 137–42.

[11] El-Sa'ad L, Darby MI, Yates B. J Mater Sci 1990;25:3577–82.

[12] Xiao GZ, Shanahan MER. Polymer 1998;39:3253–60.

[13] Xiao GZ, Shanahan MER. J Appl Polym Sci 1997;69:363–9.

[14] Crank J. Mathematics of diffusion. 1st ed. Oxford: Oxford University Press; 1956.

[15] Crank J. In: Crank J, Park GS, editors. Diffusion in polymers. London: Academic Press; 1968 [Chapter 5].

[16] Carter HG, Kibler KG. J Compos Mater 1978;12:118–31.

[17] Bonniau P, Bunsell AR. J Compos Mater 1981;15:272–93.

[18] Dewas JN. AMAC, JNC 3, Paris, 21–23 September 1982, pp89–96.

[19] Feng J, Berger KR, Douglas EP. J Mater Sci 2004;39:3413–23.

[20] Barrie JA, Sagoo PS, Johncock P. J Membr Sci 1984;18:197–210.

[21] Maggana C, Pissis P. J Polym Sci, Part B: Polym Phys 1999;37: 1165–82.

[22] Vanlandingham MR, Eduljee RF, Gillespie JW. J Appl Polym Sci 1999; 71:787–98.

[23] Klotz J, Brostow W, Hess M, Veeman WS. Polym Eng Sci 1996;36: 1129–33.

[24] Massiot D, Fayon F, Capron M, King I, Le Calvé S, Alonso B, et al. Magn Reson Chem 2002;40:70–6.

[25] Fuller RT, Fornes RE, Memory JD. J Appl Polym Sci 1979;23:1871–4.

[26] Aleman JV, Garcia-Fierro JL, Legross R, Lesbats JP. Transport properties of epoxyde prepolymers, Prague, Czech Republic. Berlin: W. De Gruyter; 1986 p. 61–71.

[27] Brewis DM, Comyn J, Tegg JL. Polymer 1980;21:134–8.