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Structure-properties relationships for densely cross-linked epoxide–amine systems based on epoxide or amine mixtures

Part 2 *Water absorption and diffusion*

V. BELLENGER, J. VERDU
ENSAM, 151 Bd de l'Hôpital, 75640 Paris, CEDEX 13, France

E. MOREL
IRCHA, BP 1, Vert le Petit, France

The solubility and diffusivity of water at 100° C, 95% relative humidity were studied for 14 stoichiometric epoxide–amine networks based on epoxide or amine mixtures. Neither the packing density nor the glass transition temperature nor the crosslink density seemed to play a significant role. The water absorption is essentially linked to the concentration of polar structures, but also decreases with the extent of intramolecular hydrogen bonding. This can be accurately predicted using a simple additive relationship. The diffusivity decreases with the hydrophilicity and packing density, but in a complex way probably involving the nature of hydrogen bonds between the water and the substrate.

1. Introduction

The amine crosslinked epoxies are relatively hydrophilic materials able to absorb 1 to 6% by weight of water in the most frequently used industrial formulations. The affect of water absorption on the short and long term thermomechanical behaviour has been widely studied for obvious practical reasons [1].

From a theoretical point of view, two approaches to these problems can be more or less clearly distinguished.

(a) The "volumic" approaches neglect, often implicitly, the existence of specific interactions between water and hydrophilic sites of the network. It has been, for instance, proposed that the water equilibrium concentration is mainly governed by the available free volume [2–4], or that water molecules occupy essentially the microvoids, internodular areas and other morphological defects [1, 5–7] which can offer preferential ways for their diffusion. The free volume theory was also used to predict the plasticization effects [8].

(b) The "interaction" approaches, often based on spectrometric observations [9, 10], state that water molecules are neither distributed randomly in the network nor concentrated in its morphological defects, but rather linked by strong hydrogen bonds to some hydrophilic loci, mainly hydroxyls [11] or amines [12]. The contribution of both types of groups could be interdependent [13].

It is interesting to note that in the "volumic" approach, the behaviour of the water–epoxy system is mainly controlled by the physical state of the polymer whereas in the "interaction" approach, the chemical structure plays a dominant role. For some authors, both approaches could be valid, each one for a restricted sample family [14] or both simultaneously [4]. The aim of this work is to study the relationships between the water solubility and diffusivity and the structure for 14 stoichiometric epoxide–amine networks. Among these, six samples were based on epoxide mixtures, three were diphasic (part I of this article) and three were based on diamine–monoamine mixtures.

2. Experimental procedure

2.1. Materials

Series A: mixture of diglycidyl ether of bisphenol A (DGEBA) and triglycidyl p-aminophenol (TGAP) crosslinked by a stoichiometric amount of diamino diphenyl methane (DDM) Series B: mixture of DGEBA and TGAP crosslinked by a stoichiometric amount of the tetraethyl derivative of DDM (DDMe). Series C: TGAP crosslinked by a DDM-aniline mixture, were described in the preceding part of this article. Their composition and some of their important characteristics are recalled in Table I. The method for the calculation of the packing density $\varrho^* = V_w/V$ where V_w is the Van der Waals volume and V the molar volume was previously described [15] and will be recalled in the next part of this article. Parallelipipedic bars (40 × 10 × 3 mm), cut from moulded blocks were studied in all cases.

2.2. Exposure

The samples were exposed at 100° C, 95% relative humidity in a climatic chamber and periodically weighted with an analytical balance giving a relative precision of 10^{-4}. The heat deflection temperature

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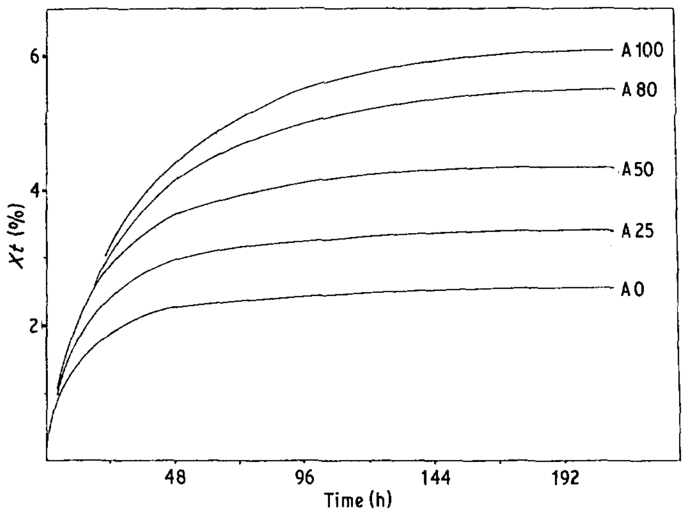


Figure 1 Sorption curves of systems A.

which is closely related, for these systems, to the glass transition temperature (T_g) was measured before and after 48 h of exposure.

3. Results

All the samples were exposed during 192 h. The absorption curves are shown in Figs 1–3, for the sample families A, B and C respectively. In all cases, the weight gain between 168 and 192 h was less than 2% of its total value. It can be, therefore, considered that all the samples were practically equilibrated after 192 h. In series A and B, the water equilibrium concentration w_m increases regularly with the concentration of polar groups, mainly amines and hydroxyls. DDM_e systems (series B) are always less hydrophilic than their DDM homologues (series A), which confirms all the previous observations [4, 13]. In series C, w_m decreases with the aniline weight fraction, which was also observed in DGEBA–metaphenylene diamine–aniline systems [5].

The Fickian diffusivities were determined using the following relationship

$$D = \phi \frac{\pi}{16}\left(\frac{w_1}{w_m}\right)^2 e^2 \quad (\mathrm{cm^2\,h^{-1}}) \qquad (1)$$

where D is the diffusivity, e the sample thickness and w_1 the water concentration after 1 h exposure, interpolated from the curves $w = f(t^{1/2})$, which are linear in the first stage of sorption. ϕ is a shape factor determined from the Shen and Springer relationship [16]. $\phi = 0.53$ for the samples under study. All the quantitative data on w_m, D and the glass transition temperature decrease after 48 h exposure are reported in Table II.

4. Discussion

4.1. Water equilibrium concentration

It is often assumed that the higher the crosslink density, the higher is the free volume fraction. This theory which will be discussed in the next part of this article, lead Johncock and Tudgey [4] to interpret the positive correlation found between the water equilibrium concentration and the glass transition temperature in terms of free volume occupancy by water molecules.

The data of Table I are not very consistent with the above theory, at least in the series A and B where the packing density increases with the crosslink density (and the glass transition temperature). In the Fig. 4, w_m is plotted against ϱ^*. An unexpected

TABLE I Composition and characteristics of the samples studied

Code	DGEBA (%)(†)	TGAP (%)[†]	DDM (%)[‡]	Aniline (%)[‡]	DDMe (%)[‡]	T_g (K)[§]	ϱ^* ([¶])	n[‖] ($\mathrm{M\,kg^{-1}}$)	[OH][‖] ($\mathrm{M\,kg^{-1}}$)
A0	100	0	100	0	0	443	0.668	2.28	4.56
A25	75	25	100	0	0	466	0.670	3.30	5.26
A50	50	50	100	0	0	472	0.680	4.23	5.91
A80	20	80	100	0	0	486	0.687	5.25	6.62
100	0	100	100	0	0	499	0.695	5.88	7.05
C25	0	100	75	25	0	470	0.690	4.98	7.09
C50	0	100	50	50	0	440	0.695	4.10	7.13
C75	0	100	25	75	0	408	0.694	3.24	7.19
C100	0	100	0	100	0	391	0.691	2.40	7.20
B0	100	0	0	0	100	417	0.667	2.02	4.04
B25	75	25	0	0	100	439	0.665	2.86	4.57
B50	50	50	0	0	100	456	0.670	3.63	5.07
B75	25	75	0	0	100	465	0.677	4.30	5.50
B100	0	100	0	0	100	471	0.678	4.91	3.89

[†] Wt % in the epoxide mixture.
[‡] Wt % in the amine mixture.
[§] HDT.
[¶] Extrapolated value at 100° C using the ϱ^* value at 20° C and the expansivity coefficient.
[‖] Theoretical values.

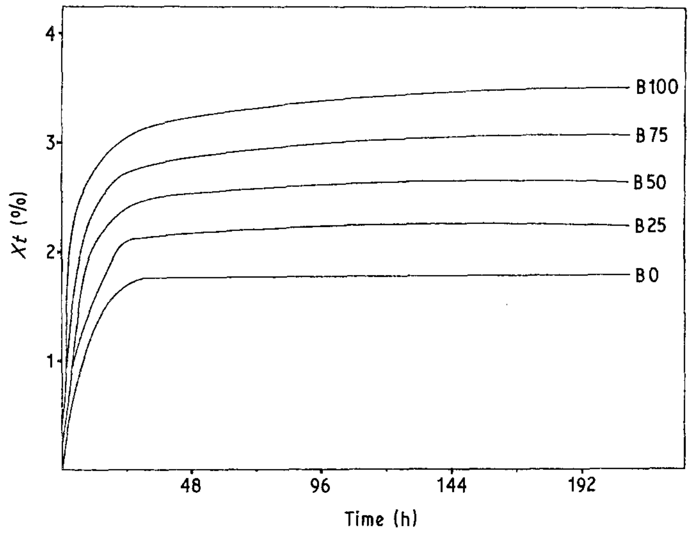


Figure 2 Sorption curves of systems B.

positive correlation appears clearly. In other words, the water equilibrium concentration increases when the fraction of the theoretically penetrable volume decreases. This result can be considered as an argument against the "volumic" theories of absorption.

The correlation observed in Fig. 4 is not fortuitous, it can be easily verified that the most hydrophilic linear polymers, for instance, polyamides and polyvinylalcohols are among the most densely packed. This can be explained by the fact that the packing density increases with the intensity of cohesive forces which in turn increases with the concentration of highly polar groups able to establish strong interactions with water molecules.

With regard to "interaction" theories, whose predictive value was established for linear polymers [17], it was recently proposed [13] that for amine–epoxy networks

$$w_m = \frac{1800\beta}{M}(xH_a + yH_e) \qquad (2)$$

where β is a parameter linked to the exposure conditions ($\beta = 1.20$ in the case under study). M is the molar mass of the "monomer unit" of the network which contains x amine and y epoxide structural units whose molar contributions to water absorption are respectively H_a and H_e expressed in water moles per structural unit mole. The previously found molar contributions H were 0.79 (DDM), 0.32 (DDMe), 0.15 (DGEBA) and, 0.53 (TGAP). The system of Equation (2) applied to aniline systems (series C) and leads to H (aniline) $\simeq 0.29$ (average value). With these data, w_m was calculated for each system and the results are listed in Table II. The average error for the prediction is less than 7% for example, within the experimental scatter. It can be, however, remarked that w_m is systematically underestimated for DDMe systems (series B), which was also the case for the DGEBA-DDM$_e$ system precedingly studied [13]. All the results would be therefore significantly improved using H (DDMe) = 0.40, all the other contributions being unchanged. It was earlier found that the contribution of the amine moiety, which includes the hydroxyl groups [13], decreases with the amine nucleophilicity, which was explained by the existence of intrasegmental (OH . . . N) bonds

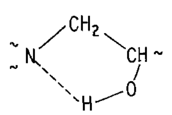
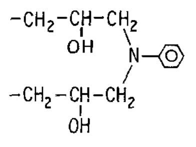


TABLE II Experimental and calculated equilibrium concentrations of water, diffusivity value and T decrease after 48 h exposure

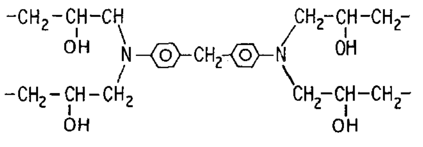
Code	W_m exp (%)	W_m calc (%)	D ($10^9\,cm^2\,sec^{-1}$)	ΔT_g (K)
A0	2.54	2.68	64	36
A25	3.40	3.42	55	58
A50	4.36	4.32	47	68
A80	5.50	5.17	35	76
A100	6.09	6.33	30	79
C25	5.47	5.52	27	69
C50	4.98	5.35	28	53
C75	4.92	5.19	33	66
C100	5.29	5.01	47	40
B0	1.81	1.53†	149	13
B25	2.26	2.12†	126	31
B50	2.68	2.64†	121	45
B75	3.08	3.10†	95	53
B100	3.52	3.52†	82	53

†Calculated with H (DDMe) 0.40.

The higher the electron density on nitrogen, the higher the concentration of intrasegmental hydrogen bonded hydroxyls which cannot be involved in water bonding. This is confirmed here with the aniline systems (series C). IR spectrophotometric measurements showed that the molar fraction of the (OH . . . N) species increases with the aniline fraction in DGEBA–DDM–aniline systems [17]. Thus, it is not surprising to find H_a (DDM) > $2H_a$ (aniline), whereas an equality would be expected in the case of equal nitrogen basicities



Aniline structural unit



DDM structural unit

The predictive value of the "interaction" approach

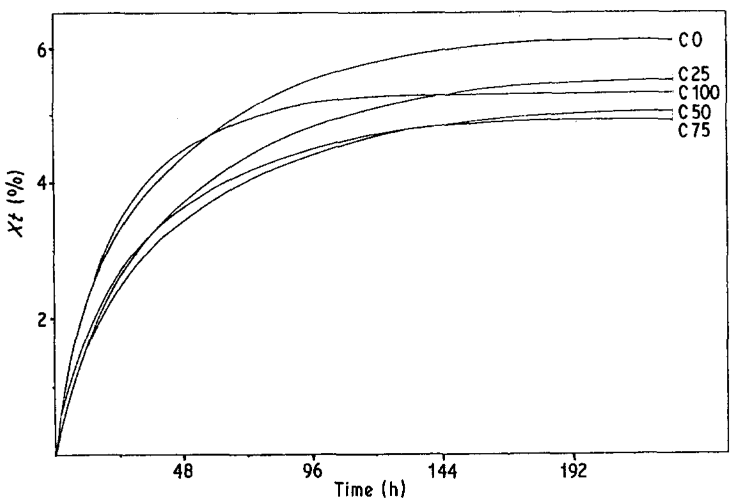


Figure 3 Sorption curves of systems C.

based on the additivity of group molar contributions and the physical meaning of these latter seem to be confirmed (Fig. 5). Many authors observed w_m variations for a given system, during cyclic sorption–desorption tests [4, 18] or variable temperature tests [6, 19]. They concluded generally that a volumic component of the water sorption linked to the network expansion during the swelling or to the volume relaxation [19], was put in evidence in that manner. It may be noted however, that these processes occur necessarily with conformational changes which, in turn, induce a shift of the equilibrium between the various hydrogen bonded associates [17]. Thus, although a more extensive investigation would be needed to give a precise interpretation of these phenomena, they do not constitute, *a priori*, a rigorous proof in favour of the "volumic" theories.

4.2. Diffusivity

The diffusivity values D are listed in the Table II which calls for the following comments.

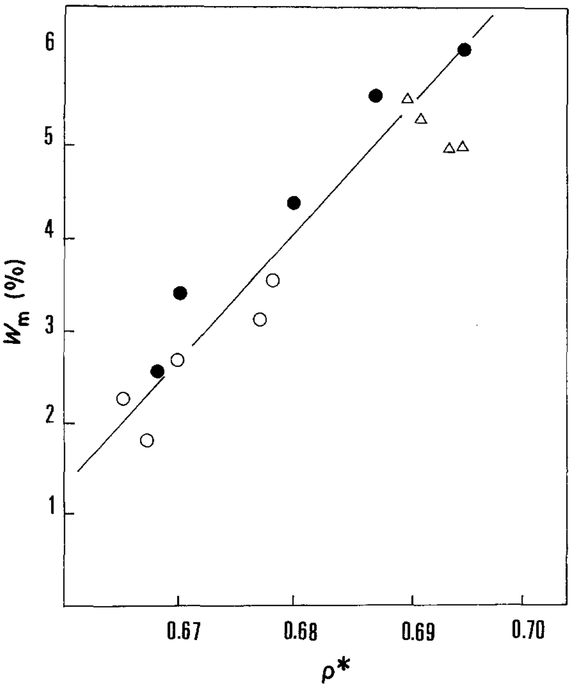


Figure 4 Water equilibrium concentration plotted against the compacity.

(a) The results obtained with the samples of high aniline content: C75 and C100 cannot be compared to the others because these samples become rubbery as a consequence of water absorption ($T_{g_{wet}} \leqslant 100°\,C$ – Table II), whereas all the other samples under study stay in the glassy state. Indeed, a noticeable increase of water mobility is to be expected when a sample goes beyond its glass transition point during the sorption test. From the results obtained on samples C 25 and C 50, it can be observed that (i) the diffusivity in the glassy state is lower for series C than for the series A and B; (ii) In series C, the diffusivity is almost constant or decreases slightly with the aniline concentration.

(b) According to the preceding observation, the effect of the crosslink density or the glass transition temperature on diffusivity is practically insignificant. Thus, other structural parameters would be involved in the dependence of D with the composition in the series A and B. Globally, the diffusivity seems to be a decreasing function of the packing density ϱ^* (series B > series A > series C). However, D is higher in the TGAP–DDMe system (B 100) than in the samples A

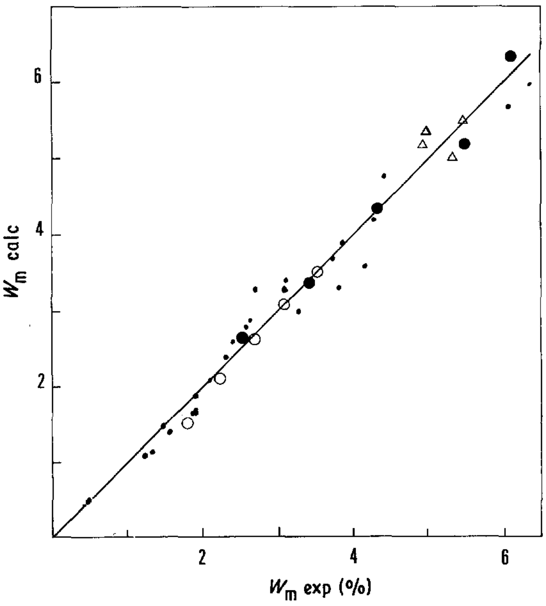


Figure 5 Correlation between the experimental and calculated values of the water equilibrium concentration. Remark: (·) data from [13].

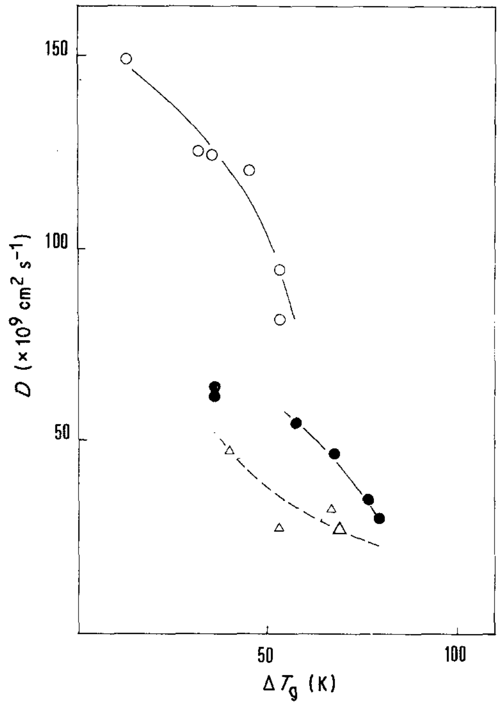


Figure 6 Diffusivity plotted against the glass transition temperature decrease.

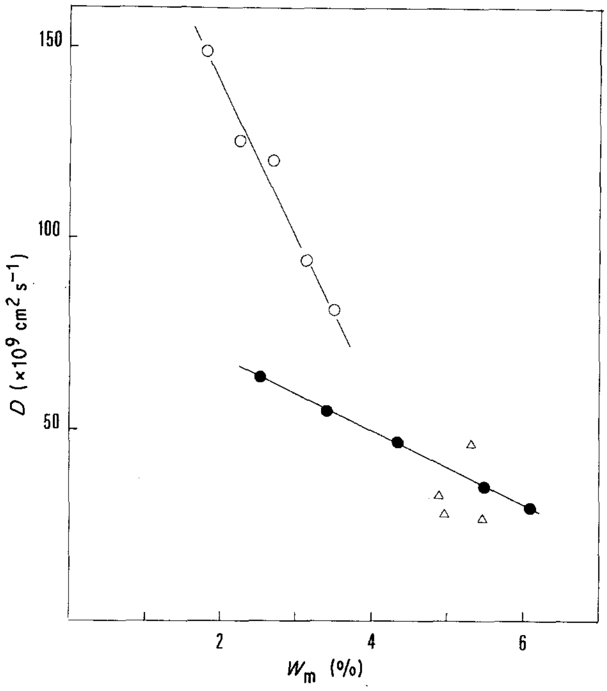


Figure 7 Diffusivity plotted against the water equilibrium concentration.

of comparable packing density (A25 and A50). Furthermore D is lower for the rubbery C 100 sample than for the glassy samples of comparable crosslink density – for instance A0 and B25 – despite its obviously higher free volume content. These results seem to indicate that parameters other than volumetric ones control the diffusion rate as already reported for linear polymers [20].

(c) Indeed, morphological heterogeneities could be involved in the water transport [21] and would not be taken into account in ϱ^* values. However it can be observed that D varies almost linearly with the sample composition in series A despite the fact that the intermediate systems A25, A50 and A80 were diphasic whereas the corresponding "homopolymers" A0 and A100 were monophasic (see part I of this article). This result seems to be inconsistent with the hypothesis that the diffusivity is controlled by the sample morphology. It could be suggested that the diffusion occurs essentially in "defects" – for instance internodular zones – which could be present in both phases of the "copolymers" as well as in the "homopolymers", but in this case, the regular variations of D with the sample composition in series A and B would be coincidental, which seems unlikely.

(d) Strong plasticizing effects occur in the great majority of cases, as shown by the T_g depression values: $\Delta T_g > 30$ K except for DGEBA–DDMe (ΔT_g(B0) = 13 K). Surprisingly, the diffusivity appears as a decreasing function of ΔT_g (Fig. 6). This result can be considered as a supplementary argument against free volume theories of the water diffusion in epoxies since these theories can be applied to the prediction of T_g in many cases where $\Delta T_g / w_m$ ranges between 10 and 20 K per weight per cent [8] as for the majority of the samples under study.

(e) All the above observations lead to the conclusion that the rate of water transport in epoxide–amine networks is probably governed essentially by the polymer–water interactions. It is noteworthy that, globally, the diffusivity decreases with the hydrophilicity (Fig. 7), which could be consistent with the hypothesis that water molecules are fixed to the polar sites by hydrogen bonding. Indeed, the strength of hydrogen bonds would influence this process, which could explain, for instance, the fact that for a given water solubility, the diffusivity is higher in series B than in series A.

(f) In series C, the fact that the diffusivity decreases slightly with the aniline concentration for the samples in the glassy state, could be attributed to the partial suppression of beta motions by the aniline moiety (see the next section). As a matter of fact, it can be considered that local motion plays an important role in water diffusion in glassy polymers [20].

5. Conclusion

The water sorption characteristics of epoxide–amine networks under study are essentially governed by water–polymer interactions. The water equilibrium concentrations can be predicted using a simple additive law in which the molar contributions of the amino–alcohol groups predominate largely but vary with the amine structure, depending essentially on the extent of intramolecular hydrogen bonding. The diffusivities seem to be independent on the morphology and the free volume (or packing density), they decrease in each sample family with the hydrophilicity, but other factors such as hydrogen bond strength and segmental mobility are probably involved in the transport phenomenon.

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