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Water absorption by uncrosslinked polymers, networks and IPNs having medium to high polarity

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Abstract

The water absorption characteristics of five epoxy networks, one vinylester network and two interpenetrated networks resulting from the blending of the vinylester with two of the epoxy resins, have been studied in the 50–100 °C temperature range. In all of the cases, the water solubility follows the Arrhenius law. The pre-exponential factor S_0 and the heat of dissolution H_s have been determined and compared with previously reported values for other networks and linear polymers. These results show that water absorption increases with the polymer polarity and is higher for interpenetrating polymer networks than for the individual network components but it is less dependent on the large-scale network structure The correlation between the logarithm of S_0 and H_s indicates the existence of a compensation phenomenon, with a compensation temperature of $T_c = 376$ K. This phenomenon may be explained by the fact that the number of hydrophilic sites is determined not only by the number of polar groups, but is also influenced by the spatial distribution of the polar groups and their ability to form H-bonds with water molecules. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The mechanisms of water absorption by polymers and the corresponding structure–property relationships have received considerable attention in the literature, due to the technical importance of these phenomena in general and in particular in the case of environmental ageing of polymers and of high performance composites. Certain authors believe that the polymer hydrophilicity is directly linked to the free volume fraction [1,2], while others [3–5] consider that it is linked to the presence of polar groups capable of forming hydrogen bonds with water molecules. The latter view is partially justified, at least as an approximation, by the fact that the equilibrium water concentration behaves as a molar additive function [6,7] as found in restricted polymer families, for instance, amine crosslinked epoxies [8,9]. This theory, however, does not bear a detailed investigation: for instance, the molar increments (e.g. the number of water molecules absorbed per functional group) are not integers and they vary with the group concentration [10]. Alternative analyses of water absorption derived from the concept of unidimensional [11] or tridimensional [12] solubility parameters have not provided better prediction of the properties of a given system [13]. A recent theory proposed by two of us [10] could constitute a possible way of explaining this matter: water is always doubly or triply bonded through the lone pair and through the H atoms, so that a hydrophilic site is constituted of at least two polar groups. The number of hydrophilic sites (which determines the hydrophilicity) is thus linked to the probability of finding pairs of polar groups separated by the optimum distance to establish bonds with the same water molecule. This probability is not a linear function of the concentration of polar sites and so the water absorption will not be linear with the polar group concentration.

Until recently, it was generally considered that the most fundamental parameter defining water absorption was the equilibrium mass fraction of water (w_∞) absorbed by the polymer in a water-saturated atmosphere. One reason for the common choice of the water equilibrium concentration as the representative quantity of the water–polymer

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interaction may be that w_∞ is, in polymers of medium to high polarity, almost temperature independent, which suggests that it can be directly correlated to the structure. In fact, this behaviour results from a coincidental cancellation of effects—as is shown below, the most fundamental quantity is the solubility S of water in the polymer, defined by Henry's law

$$C = Sp \tag{1}$$

where C is the equilibrium water concentration and p is the water vapour pressure at the experimental absorption temperature. When experiments are made in saturated atmosphere at various temperatures (T), p varies with T

$$p = p_0 \exp\left(-\frac{H_w}{RT}\right) \tag{2}$$

with $\ln p_0 = 25.35$ and the enthalpy of water vaporisation, $H_w = 42\ \mathrm{kJ\ mol^{-1}}$ [14]. S also obeys an Arrhenius law [10,14,15]

$$S = S_0 \exp\left(-\frac{H_s}{RT}\right) \tag{3}$$

where H_s is the heat of dissolution. Thus the equilibrium water concentration has a temperature dependency:

$$C = S_0 p_0 \exp\left(\frac{-H_w - H_s}{RT}\right) \tag{4}$$

The fact that C is almost independent of T results from the fact that $H_s \sim -H_w = -42\ \mathrm{kJ\ mol^{-1}}$ and so the exponential term in Eq. (4) is close to unity. The large negative value of H_s means that water dissolution in a polymer of medium to high polarity is highly exothermic, which, incidentally, disqualifies the theories which suggest that water occupies only the free volume [1,2], since such a process is expected to have a zero activation energy. If one agrees with the idea that solubility is a more representative property, then two quantities (the pre-exponential factor S_0 and the heat of dissolution H_s) have to be considered which complicates the analysis of structure–property relationships.

Our aim in this study is to determine the values of S_0 and H_s of epoxy–vinylester interpenetrated networks in the glassy state and to compare them with previously reported data [10,14,15] on various epoxy networks and amorphous linear polymers in order to establish the trends of structure–property relationships. The data from these systems will allow us to:

- confirm the previously observed trends of structure–property relationships, especially the fact that the heat of dissolution is an increasing function of the polymer polarity.
- establish any substantial difference between linear and tridimensional polymers.
- determine if network polymer blends obey the rule of mixtures for H_s and S_0.

2. Experimental

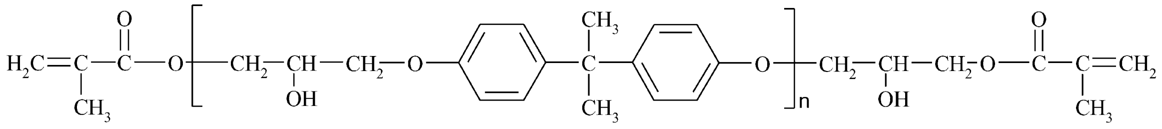
2.1. Materials

Epoxy networks based on triglycidylaminophenol (TGAP), respectively, cured by diaminodiphenyl methane (DDM) to form a network, by aniline (ANI) to form a linear polymer or by a 50/50 mixture (ANI + DDM) were chosen for their very high polarity resulting from their high hydroxyl content (~7 mol kg^{-1}). Plaques of 4 mm thickness were cast using the stoichiometric amine–epoxide mixture with a cure schedule of (70 °C for 12 h followed by a postcure at 180 °C for 2 h). It was confirmed by IR and DSC that these networks are almost fully cured. Some characteristics of these samples are summarised in Table 1. The water absorption characteristics of these systems were compared with that obtained previously [10] for the epoxy networks prepared from the diglycidylether of bisphenol-A (DGEBA) and diethyldiaminotoluene (ETHA).

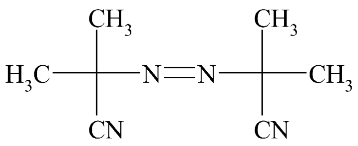
A second series of epoxy networks were also studied—these were based on DGEBA crosslinked by either 2 wt% methylimidazole (MeI) or stoichiometric amounts of AN or DDM and cured at 70 °C for 12 h and postcured at 180 °C for 2 h. For comparison, a model vinylester resin was also chosen for study due to the similarity of its backbone structure to the DGEBA-based epoxies. This VER was formed from a 70 wt% solution of the diglycidyl ether of bisphenol-A dimethacrylate (commonly known as bisGMA) in 30 wt% styrene and was cured with 1 wt% AIBN at 50 °C for 12 h and at 70 °C for 3 h followed by a postcure at 180 °C for 2 h.

Table 1
Values of density, ρ, and glass transition, T_g (determined from the tan δ maximum in the DMTA spectrum at 1 Hz), for the systems under study

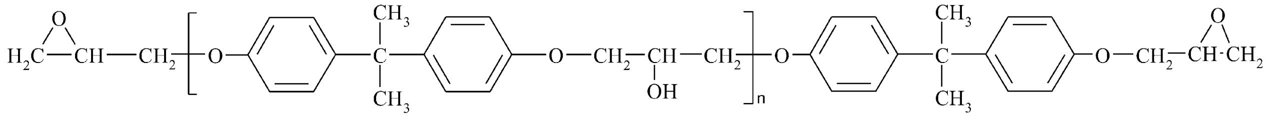
	ρ (kg m^{-3})	T_g (°C)
DGEBA–MeI	1.18	164
DGEBA–MeI + VER	1.18	150
VER	1.17	120
DGEBA–ANI	1.18	90
DGEBA–ANI + VER	1.18	110
VER	1.17	120
DGEBA–DDM	1.19	160
VER	1.17	120



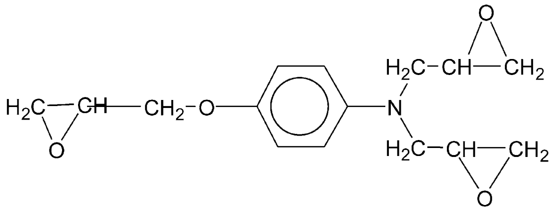
bisGMA



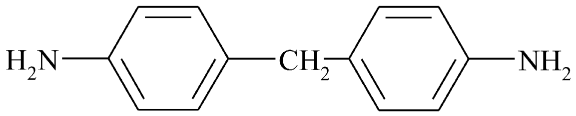
AIBN



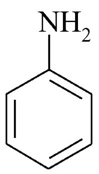
DGEBA



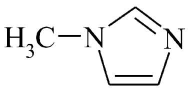
TGAP



DDM



Aniline



The MeI, ANI and DDM and epoxy resin components were also blended in the liquid state with an equal mass fraction of the VER to form a series of interpenetrating polymer networks (IPNs). Further details of the preparation and curing characteristics of these samples have been previously published [16,17].

These results were compared with the water absorption behaviours of the linear polymers: polyetherimide (PEI), polysulfone (PSU) and poly(methylmethacrylate) (PMMA)—these results are part of a PhD Thesis [18] and some of this has been published [14].

2.2. Water absorption experiments

The samples were exposed in a water-saturated atmosphere at various temperatures ranging from 50 to 100 °C and

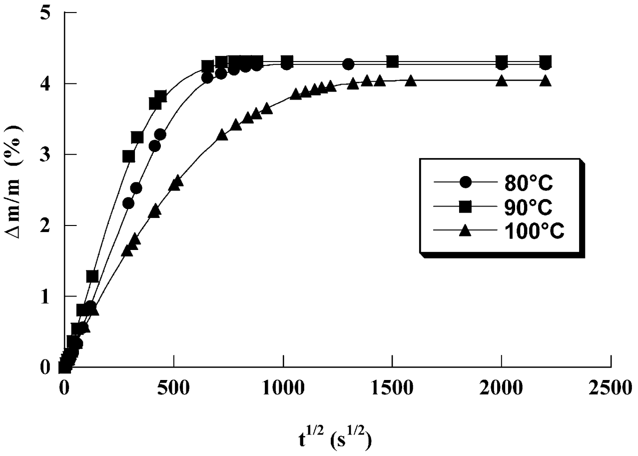


Fig. 1. Sorption curves of water in TGAP–AN–DDM at different temperatures.

were periodically removed, surface dried and quickly weighed in order to determine the weight gain. In the current paper, the discussion will focus on the asymptotic (equilibrium) weight gain values w_∞, from which one can determine the equilibrium water concentration C

$$C = \frac{10\rho w_\infty}{18} \quad (5)$$

where w_∞ is expressed in percent, ρ is the density in kg m^{-3} so that C is in mol m^{-3}.

Then one can determine the solubility S

$$S = C/p \quad (6)$$

where S is in mol m^{-3} Pa^{-1} and p is calculated from Ref. [14]. H_s and ln S_0 were then graphically determined from the Arrhenius plot of S versus reciprocal temperature.

Table 2
Values of equilibrium water concentration, w_∞, at various temperatures for the systems under study, and for some previously studied systems

System	Temperature (°C)				
	50	70	80	90	100
IPNs					
DGEBA–MeI	1.7	1.9	–	1.93	–
DGEBA–MeI + VER	2.34	2.65	–	2.66	–
VER	0.92	1.39	–	1.86	–
DGEBA–ANI	1.5	1.7	–	1.88	–
DGEBA–ANI + VER	1.93	2.3	–	2.5	–
VER	0.92	1.39	–	1.86	–
DGEBA–DDM	1.97	1.98	2.35	–	–
VER	0.92	1.39	–	1.86	–
Amine blends					
TGAP–DDM	–	–	4.22	3.99	3.84
TGAP–ANI + DDM?			4.3	4.33	4.31
TGAP–ANI	–	–	4.4	3.8	4.35
DGEBA–DDM	1.97	1.98	2.35	–	–
DGEBA–ANI	1.5	1.7	–	1.88	–
Other polymers					
PEI	1.40	1.44	1.47	1.49	1.50
PSU	0.56	0.59	–	–	0.82
PMMA	1.26	1.31	1.74	1.94	1.97
DGEBA–ETHA	1.98	1.92	–	–	1.75

Table 3
Values of heat of dissolution, H_s, and pre-exponential factor, S_0, for the systems under study

	H_s (kJ mol^{-1})	ln S_0 (mol m^{-3} Pa^{-1})
IPNs		
DGEBA–MeI	−39	−16.93
DGEBA–MeI + VER	−39	−16.58
VER	−25.1	−12.36
DGEBA–ANI	−36.9	−16.26
DGEBA–ANI + VER	−36.6	−15.87
VER	−25.1	−12.36
DGEBA–DDM	−38.1	−16.46
VER	−25.1	−12.36
Amine blends		
DGEBA–DDM	−38.1	−16.46
DGEBA–AN	−36.9	−16.257
TGAP–DDM	−47.2	−18.828
TGAP–ANI + DDM?	−43	−18.806
TGAP–ANI	−41.3	−16.968

3. Results

Examples of sorption curves are shown in Fig. 1. The values of asymptotic (equilibrium) mass gain w_∞ are given in Table 2 for the new systems. The values of the heat of dissolution H_s and pre-exponential factor ln S_0 are given in Table 3 for the new systems and Table 4 for previously published [7,11,12] or unpublished [18] systems.

From this data, one can distinguish, as a first approximation, three polymer families with distinct behaviours:

Family A. VER and PMMA, polymers characterised by a relatively low hydrophilicity related to their structure (as measured by w_∞) but which increases noticeably with temperature.

Family B. Polymers of intermediate hydrophilicity and where the hydrophilicity depends only slightly on temperature.

Family C. The polymers, DGEBA–ETHA and TGAP–DDM/ANI, which display the highest hydrophilicity, but for which the equilibrium water concentration is a decreasing function of temperature.

Table 4
Values of heat of dissolution, H_s, and pre-exponential factor, S_0, for some previously studied systems

	H_s (kJ mol^{-1})	ln S_0 (mol m^{-3} Pa^{-1})	Reference
PEI	−42.0	−18.07	[15]
PSU	−37.0	−17.11	[15]
PMMA	−33.3	−15.08	[15]
DGEBA–ETHA	−44.4	−18.78	[7]

For both IPN blends under study, DGEBA–MeI/VER and DGEBA–ANI/VER, the hydrophilicity (as measured by w_∞) is significantly higher than for each of the parent network components. In both systems, this difference results essentially from the fact that addition of VER to an epoxy network increases the pre-exponential factor but does not reduce significantly the activation energy which remains close to the value characteristic of the epoxy network. This is surprising because the structure of the cured bisGMA component of the VER contains the backbone of the reacted DGEBA unit including two hydroxyl groups.

4. Discussion

The fact that water dissolution into the polymers is a highly exothermic process ($|H_s| > 25\ \mathrm{kJ\ mol^{-1}}$ for all the systems under study) is clearly confirmed here and agrees, at least semi-quantitatively, with the empirical relationships established by Michaels and Bixler [19] which correlate the solvent solubility with its Lennard–Jones temperature. The practical consequences of this result are as follows.

(i) The water absorption process is a true dissolution, not a free volume occupancy as previously hypothesised [1,2]. As a matter of fact, this free volume process is expected to have a zero activation energy because, in this case, the dissolution process would be athermic [10,14,15,18].

(ii) The differing trends shown in the temperature dependence of the equilibrium concentration is now easy to understand from Eq. (4). The three above-defined sample families would correspond to distinct ranges for the values of H_s, for instance:

Family A: $|H_s| \leq H_w - \Delta H$ (weak water–polymer interaction)
Family B: $H_w - \Delta H \leq |H_s| \leq H_w$ (intermediate water–polymer interaction)
Family C: $|H_s| \geq H_w$ (strong water–polymer interaction)

where H_w is 42 kJ mol^{-1} and ΔH is the enthalpy of water concentration, in the cases under study ΔH equal approximately to 8 ± 1 kJ mol^{-1}.

From the available information on the cohesive properties of these systems [4] showing that, generally, the cohesive energy density is in the order: TGAP systems > DGEBA systems > VER, it is tempting to correlate H_s to the cohesive energy density. However, it is easy to show that the dispersive component of the latter does not contribute to hydrophilicity, for instance, polystyrene and poly(2-6 dimethyl phenyl ether), in which cohesion is essentially due to dispersion (London) forces, are almost hydrophobic. Thus, only dipolar and hydrogen bonding interactions are responsible for hydrophilicity, but it is not clear how one can determine their relative influence—a large study of polymers in a structurally related series would be probably necessary to answer this question.

From the data in Tables 3 and 4, two complementary remarks can be made about the structure–property relationships.

(a) The effect of crosslink density per se can be investigated for both the DGEBA and TGAP-based epoxides by comparing TGAP–DDM with TGAP–ANI or by comparing DGEBA–DDM with DGEBA–ANI. These systems differ only by the presence of the methylene bridge of DDM which produces a crosslink, a difference which is expected, in principle to have a very small influence on water absorption properties since it does not necessarily disturb the spacing between the water-binding sites. Table 3 shows that there are apparently no systematic differences between linear and tridimensional polymers.

(b) The VER is much less hydrophilic than the epoxy resins, despite the similarity in the structure—the reacted bisGMA molecule contains the same fragment of DGEBA as is found in the amine-cured DGEBA resins, including the two hydroxyl groups. Thus, it appears that the presence of the styrene bridge between the reacted methacrylate units of the bisGMA changes the spacing between polar sites or sterically restricts the binding of the water molecules.

(c) For both IPNs under study DGEBA–MeI/VER and DGEBA–ANI/VER, the solubility parameters of the IPN are closer to those of the epoxy network than to that of the vinylester resin. The fact that the hydrophilicity is increased in the IPN results from the fact that the pre-exponential factor is more affected than the activation energy.

Fig. 2 shows that S_0 and H_s are related, this indicates the existence of a compensation phenomenon for networks as has been found for linear polymers [18] and having the form

$$\ln(S_0) = a + bH_s \tag{7}$$

where $a = -4.32$ and $b = 0.32 \times 10^{-3}$ mol kJ^{-1}. Thus, if this is substituted into Eq. (3), the Arrhenius dependence of

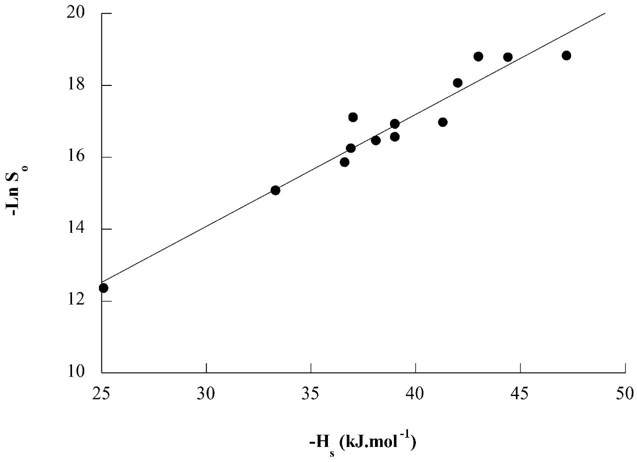


Fig. 2. Compensation curve of solubility relating S_0 to H_s.

S can be rewritten as

$$\ln S = a + \frac{H_s}{R}\left(\frac{1}{T_c} - \frac{1}{T}\right) \tag{8}$$

where $T_c = 1/Rb = 375.6$ K. Compensation phenomena can be artefacts linked to the non-Arrhenius character of the property under study; however, they can also correspond to a physical reality when enthalpy and entropy vary proportionally to the same quantity [20]. Thus, if S is analysed in terms of transition state theory, one can write

$$S = A\exp\left(-\frac{\Delta G_s}{RT}\right) \tag{9}$$

with

$$\Delta G_s = H_s - T\Delta S_s \tag{10}$$

where ΔG_s is the change of free energy (at constant pressure) linked to dissolution, and ΔS_s is the corresponding entropy change. Thus Eq. (10) can be expanded to:

$$S = A\exp\left(\frac{\Delta S_s}{R}\right)\exp\left(-\frac{H_s}{RT}\right) \tag{11}$$

If Eqs. (8) and (12) equated, it can be deduced that

$$A = \exp a = 0.0133 \tag{12}$$

and

$$\Delta S_s/R = bH_s \tag{13}$$

so that:

$$\Delta S_s = H_s/T_c \tag{14}$$

In other words, Eq. (14) indicates that the free energy ΔG_s is zero at the compensation temperature, T_c.

This raises the question as to why the entropy and enthalpy of dissolution should be so closely correlated. A possible explanation could be derived from the theory cited in the introduction according to which a hydrophilic site is constituted of at least two polar groups. Hydrophilicity would thus be linked to the probability to find polar groups sufficiently close to establish bond with the same water molecule. This probability is, indeed, expected to increase with the overall polar groups concentration which presumably governs matrix properties (polarity, solubility parameters, etc.) playing also an important rule in hydrophilicity. It is thus not very surprising to find, in these conditions, a correlation between dissolution entropy (linked to the probability to have a favourable configuration for water bonding) and enthalpy (apparently related to average matrix properties).

5. Conclusion

The water solubility characteristics have been studied, in 50–100 °C temperature interval, for a series of polymers including various epoxy networks, a vinylester resin and two epoxy–vinylester blends. The pre-exponential factor S_0 and the heat of dissolution H_s have been determined and found to be intercorrelated through a compensation law: $\ln(S_0) = a + bH_s$. The following structure–property relationships can be derived from the present results and those previously reported. There is apparently no influence of the large-scale (crosslinking) structure on water absorption characteristics: linear polymers have similar behaviour as do thermosets. The effect of temperature on equilibrium water concentration is well explained by the value of H_s relative to H_w: w_∞ increases with T if $|H_s| < 42$ kJ mol^{-1} and decreases with T if $|H_s| > 42$ kJ mol^{-1}. The fact that, for medium polarity polymers, H_s is close to -42 kJ mol^{-1} explains the apparently low influence of temperature on hydrophilicity. The high absolute value of H_s indicates that water absorption results from a true (exothermic) dissolution. However, the precise role of dipolar and hydrogen bonding interactions has not been elucidated. IPNs are more hydrophilic than the component networks which can be explained if blending affects essentially the pre-exponential factor, and if the enthalpy of dissolution H_s remains close to the value of the most hydrophilic component. The compensation phenomenon has been tentatively explained by the existence of a correlation between the entropy and the enthalpy of dissolution, due to the fact that the number of hydrophilic sites are determined by the spatial distribution of polar groups.

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