

Structure–water absorption relationships for amine-cured epoxy resins

E. Morel

IRCHA, 91710 Vert le Petit, France

and V. Bellenger and J. Verdu

ENSAM, 151 Boulevard de l'Hopital, 75640 Paris Cedex 13, France

(Received 16 January 1985; revised 13 May 1985)

The equilibrium water absorption has been measured for 23 epoxide–amine networks of various structure including di, tri, and tetra functional epoxides, and diamines, which were mainly of the dianiline type (more or less sterically hindered in some cases). The comparative study of these systems shows clearly that the main hydrophilic loci are in the vicinity of tertiary amines, and that these latter groups play a concerted role with hydroxyl groups in the β position, in water bonding. Additive relationships between structure and equilibrium water absorption derived from these observations are proposed.

(Keywords: epoxy resin; amine hardener; water absorption; equilibrium concentration; hydrophilic loci; predictive relationships)

INTRODUCTION

It is well known that water absorption is an important factor in the durability of epoxy based composites which undergo plasticization and swelling stresses¹. N.m.r.^{2,3}, i.r.⁴ or dielectric measurements⁵ have shown that the sorbed water molecules are mainly hydrogen bonded to the polymer. A large amount of work based on spectroscopy or on the comparison of water absorption of samples differing in their structure has been made in order to identify the main hydrophilic loci of the network. With 'tetraglycidyl methylene dianiline (TGMDA)–diaminodiphenyl sulphone (DDS)' samples subjected to different curing conditions, Danieley *et al.*⁶ found that the water uptake increases with the extent of cure, and concluded that hydroxyl groups play a predominant role since they originate from epoxide–amine reactions. However, it should be noted that epoxide–epoxide and epoxide–alcohol side reactions are also important in these systems for which the higher degree of cure is obtained with a relatively low hardener concentration¹; so that it is somewhat difficult to speculate on the hydroxyl build-up in the final stage of cure. On the other hand, tertiary amines are formed at the same time as hydroxyl groups and their contribution to hydrophilicity cannot be excluded. Carfagna *et al.*⁷ found that, for 'diglycidyl ether of bisphenol A (DGEBA)–triethylene tetramine systems', the water solubility increases with the tertiary amine concentration.

It is also interesting to note the very high hydrophilicity of systems based on nitrogen containing epoxides such as derivatives of hydantion⁸. Finally, amine polarity and/or polymer morphology could also influence the water absorption⁹.

In linear polymers, it has been shown that the equilibrium water absorption (in given exposure conditions) is an additive property^{10,11}

$$H = \frac{W_m M}{1800} = \sum n_i H_i \quad (1)$$

where H is the number of water molecules in a monomer unit

W_m is the equilibrium water absorption in weight percent

M is the molecular weight of the monomer unit

H_i is the molar contribution of the group i

n_i is the number of groups i in the monomer unit.

H_i can vary between almost zero for hydrocarbon structures to 2 moles of water per mole of group for groups able to establish strong hydrogen bonds such as hydroxyls, amines, acids or amides, and takes intermediate values ($H_i=0.1-0.3$) for groups of medium polarity such as ethers, ketones or esters.

The aim of our work is to apply the same approach to a wide series of epoxide–amine networks, in order to establish structure–property relationships.

EXPERIMENTAL

Materials

We studied three diepoxides derived from bisphenol, a triepoxide and a tetraepoxide of which the structures, designating codes and epoxide index are given in Table 1. Aliphatic and aromatic amines were used as hardeners. Their structures are also given in Table 1.

Samples

Two kinds of samples were used: cast films of 20–100 μm thickness and plates of 3 mm thickness. Films were cast on a clean mercury surface from a solution of the two components in tetrahydrofuran.

A two step thermal treatment was carried out: the first step allows the solvent evaporation and the formation of a film of epoxy–amine mixture possibly pre-crosslinked; the second one, the achievement of the crosslinking reaction. The temperature and times cycles for each sample were determined in order to get the highest possible T_g value (the maximum value obtained whichever cure tempera-

Table 1 Compounds under study, structure and code

DIEPOXIDES			
Sample number	X	\overline{DP}	Epoxy Index mol/kg
1 to 7	C(CH ₃) ₂	0.11	5.4
9 and 10	C(CH ₃) ₂	0.14	5.3
13	C(CH ₃) ₂	0.38	4.5
11, 20, 24	-CH ₂ -	0.0	6.4
TGMDA			
Epoxy Index mol/kg 8			
TGAP			
Epoxy Index mol/kg 10.8			
DIANILINES			
	Code	R	Z
	DDM	H	-CH ₂ -
	DDM _m	CH ₃	-CH ₂ -
	DDM _e	C ₂ H ₅	-CH ₂ -
	DDM _i	iC ₃ H ₇	-CO ₂ -
	DDS	H	-SO ₂ -
	DDE	H	-O-
OTHER AMINES			
PDA			
IPD			

ture is chosen for systems having epoxide and amine concentrations in stoichiometric ratio) and are summarized in Table 2.

For other samples hardener was incorporated in the resin at 90°C. These samples were moulded and a final curing at 180°C was carried out for 3 h. Amine and epoxide concentrations were fixed at the stoichiometric ratio (Table 3).

Measurement of the equilibrium water absorption W_m

Two sets of experiments were carried out:

- A** Films were exposed at 20°C to air with 100% relative humidity, and periodically weighed with a Perkin-Elmer AD2Z microbalance. Before exposure, they were conditioned at 50°C for 24 h. The equilibrium was reached after less than one day; then, the weight remained stable over a period of weeks. For each system, six to ten samples were studied.
- B** Plates were exposed in a climatic chamber at 100°C, 95% relative humidity and periodically weighed. The equilibrium weight gain, which is obtained after

approximately 150–200 h, is reported for only one sample per system.

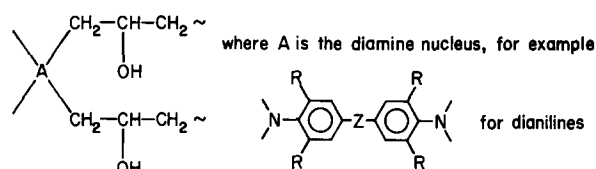
Infra-red spectrometry

Three films of respectively DGEBA-DDM, DGEBA-DDE and DGEBA-DDS systems were analysed on a Perkin-Elmer 580 spectrophotometer. The peak area and maximum absorbance were measured from a tangent baseline.

DETERMINATION OF THE MOLAR WATER ABSORPTION

The number of absorbed water moles per mole of 'monomer unit' (H) is calculated from experimental W_m values by the relation (1).

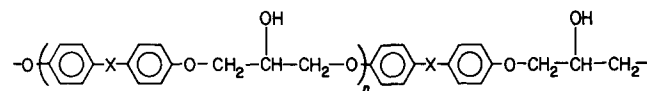
In all structural units under consideration, D will represent the following structure:



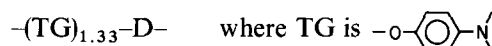
The reasons for this choice will appear in the discussion of results.

In this case, the structural units (reflecting the epoxide/amine stoichiometry) are:

- (a) For systems based on diepoxides: -E-D-E- where E is



- (b) For systems based on TGAP (whose epoxide index is very near to its theoretical value):



- (c) For systems based on TGMDA (whose epoxide index is 84% of its theoretical value):

$$T-(D)_x \quad \text{where } x = \frac{m M_e}{100 M_d}$$

m being the weight fraction of hardener in percent of epoxide weight, M_e and M_d are the molar weights of respectively pure TGMDA and hardener.

The structural unit (of molar weight $M_e + xM_d$) contains therefore x moles of D units. The remaining part will be called T. Indeed, a T unit contains at least x moles of

Table 2 Temperature cycle expressed in minutes for the sample cure

	105°C	120°C	140°C	180°C	180°C under vacuum	230°C
DGEBA-IPD		120				
DGEBA-PDA	60		120			
DGEBA-DDM	60				75	
DGEBA-DDM _m		60	120			
DGEBA-DDM _e		60	120			
DGEBA-DDM _i		60	120			
DGEBA-DDS	60			60	75	
DGEBA-DDE	60		60		90	
TGAP-DDM	120					75
TGMDA-DDM	120					75
TGMDA-DDE	120					60

Table 3 Description of systems, exposure conditions, experimental and calculated values of W_m , number of water moles per structural unit (H), per nitrogen atom (H_N), electron density on the nitrogen atom for the corresponding amine (see ref. 14 for this latter parameter)

Sample	\overline{DP}	m (%)	Exp. conditions	W_m exp (%)	W_m exp. (%)	H	H_N	Q_N
DGEBA-DDM	0.11	27	A	2.1 ± 0.2	2.1	1.10	0.395	1.859
DGEBA-DDM _m	0.11	35	A	1.9 ± 0.1	1.7	1.05	0.372	
DGEBA-DDM _e	0.11	42	A	1.25 ± 0.1	1.1	0.73	0.212	
DGEBA-DDM _i	0.11	50	A	0.50 ± 0.1	0.5	0.31	0.00	
DGEBA-DDS	0.11	34	A	2.6 ± 0.1	2.8	1.43	0.476	1.653
DGEBA-DDE	0.11	27	A	1.9 ± 0.2	1.9	0.99	0.343	1.882
DGEBA-IPD	0.11	23	A	1.5 ± 0.3	1.5	0.74	0.211	
DGEBA-PDA	0	16	A	3.1 (ref. 9)	3.3			
DGEBA-DDM	2.3	10	A	1.58	1.4			
DGEBA-DDM	6.0	5	A	1.34	1.15			
DGEBA-DDM	0.14	27	B	2.45	2.6			
DGEBA-DDS	0.14	34	B	2.70	3.3			
DGEBA-DDS	0.38	28	B	3.3	3.0			
DGEBF-DDM	0	31	B	2.63	2.9			
DGEBF-DDS	0	40	B	3.74	3.7			
TGMDA-DDM	–	39	B	4.34	4.2			
TGMDA-DDM _m	–	50	B	3.16	3.4			
TGMDA-DDM _e	–	60	B	2.33	2.4			
TGMDA-DDE	–	40	B	3.84	3.9			
TGMDA-PDA	–	21	B	6.32	6.0			
TGAP-DDM	–	50	B	6.08	5.7			
TGAP-DDM	–	50	A	4.40	4.8			
TGMDA-DDM	–	39	A	4.19	3.6			
TGMDA-DDE	–	40	A	3.81	3.3			

TGMDA nuclei (one mole if the TGMDA impurities are only oligomers), and a noticeable weight fraction of aliphatic segments containing ether and hydroxyl groups whose composition cannot be precisely defined and which can vary from grade to grade¹² and from batch to batch. In our set of samples, based on the same batch of TGMDA, T can be considered invariant.

RESULTS AND DISCUSSION

Influence of the hardener structure

Seven samples of experiment A were based on the same diepoxide (DGEBA \overline{DP} = 0.11). It is clear, from the results of Table 3, that the diamine structure plays an essential role in water solubility since the molar water absorption H varies from 0.31 to 1.43 moles per network structural unit. These variations are non-specific to the chosen epoxide as shown by the correlation occurring between the W_m values of DGEBA systems measured at 20°C, 100% relative humidity and those of TGMDA systems (with the same hardeners), measured at 100°C, 95% relative humidity (Figure 1).

Assuming that H is an additive function of the molar contributions of groups in the 'monomer unit', and neglecting the contributions of hydrocarbon groups, we can write the following system of equations:

$$\text{DDM: } 4.22H_{\text{OH}} + 4.44H_{\text{O}} + 2H_{\text{N}} = 1.097 \quad (2)$$

$$\text{DDM}_m: 4.22H_{\text{OH}} + 4.44H_{\text{O}} + 2H_{\text{N}} = 1.051 \quad (3)$$

$$\text{DDM}_e: 4.22H_{\text{OH}} + 4.44H_{\text{O}} + 2H_{\text{N}} = 0.731 \quad (4)$$

$$\text{DDM}_i: 4.22H_{\text{OH}} + 4.44H_{\text{O}} + 2H_{\text{N}} = 0.308 \quad (5)$$

$$\text{DDE: } 4.22H_{\text{OH}} + 4.44H_{\text{O}} + 2H_{\text{N}} = 0.994 \quad (6)$$

$$\text{DDS: } 4.22H_{\text{OH}} + 4.44H_{\text{O}} + H_{\text{SO}_2} + 2H_{\text{N}} = 1.430 \quad (7)$$

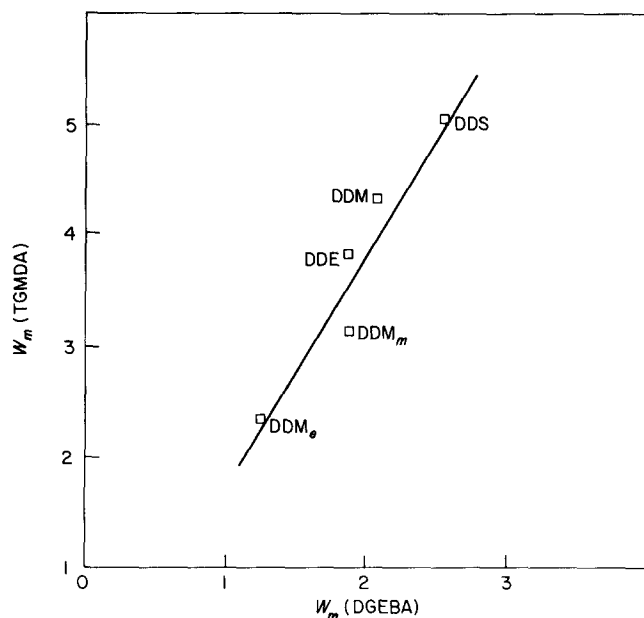


Figure 1 Correlation between W_m for TGMDA and DGEBA systems crosslinked by the same diamines

$$\text{IPD: } 4.22H_{\text{OH}} + 4.44H_{\text{O}} + 2H_{\text{N}} = 0.740 \quad (8)$$

It is obvious (see for instance equations (2) to (5)) that this system does not admit a single solution; we must consider that at least one term, presumably H_N , depends on hardener structure. Two interesting remarks can be made:

(i) Whatever the structure, H_{OH} is always smaller than 0.35, i.e. at least six times lower than in linear polymers.

(ii) The *o*-alkyl substitutions on diamine nuclei decrease the water solubility (see data on DDM_m, DDM_e, DDM_i in Table 2). This is not due only to the 'diluting' effect of hydrophobic alkyl groups since H is expressed in moles of water per mole of structural unit. The increase of this effect

with the group bulkiness, suggests that the steric hindrance on nitrogen inhibits the water bonding, and a comparison of quantitative data on DDM and DDM_i shows that tertiary amines are the main hydrophilic loci in these networks. The same effect of amine shielding by bulky alkyl groups can be observed in the case of hydantoin based epoxies⁸.

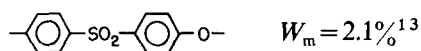
The existence of additive laws such as equation (1), implies that the molar group contributions H_i are not interdependent. In this case, we could solve the system of equations (2) to (8) on the basis of the following assumptions:

(a) hydroxyl and ether groups have, in all systems, the same structural environment, so that H_{OH} and H_O are independent of the diamine structure, which influences only H_N .

(b) in the case of DDM_i, the steric hindrance is complete so that $H_N(\text{DDM}_i) = 0$.

(c) $H_O \ll 4.22H_{OH} + 4.44H_{\Omega}$

(d) H_{SO_2} can be estimated from experimental data on linear polysulphone polymers. For a polyether-sulphone:



Taking $H_{\Omega} = 0.1^{11}$, we obtain $H_{SO_2} = 0.171$.

The solution is now possible and leads to the H_N values listed in Table 2. For oxygen containing structures, we obtain:

$$H_{OH} + 1.05H_{\Omega} = 0.073 \quad (9)$$

Two somewhat unexpected results are obtained:

(i) H_{Ω} is very low (note that if $H_N(\text{DDM}_i) \geq 0$,

$$H_{OH} + 1.05H_{\Omega} \leq 0.073.$$

(ii) In non-hindered amines, H_N decreases with the amine reactivity in crosslinking, i.e. with the amine polarity. The electron densities of nitrogen, Q_N for DDM, DDE and DDS are listed in Table 3. This propensity is confirmed with IPD¹⁴, which is more reactive in crosslinking than dianilines. Indeed, the opposite behaviour, i.e. H_N increasing with Q_N , would be normally expected.

These two results do not agree with the assumption of independence of group contributions H_N and H_{OH} ; the following hypothesis seems more reasonable:

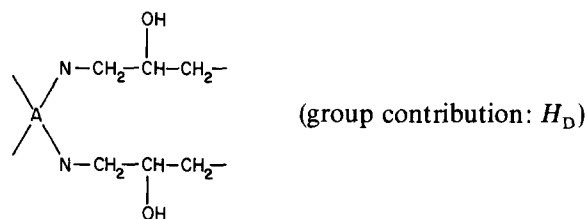
- (a) the hydroxyl and tertiary amine groups play a concerted role in water bonding to the network, so that their group contributions cannot be dissociated,
- (b) the formation of a water-amine hydrogen bond is directly or indirectly competitive with a hydroxyl-amine internal hydrogen bond whose strength increases with the amine nucleophilicity. The indirect effect would occur if the water placement needs a site of a peculiar steric configuration which, in turn, depends on the amine-hydroxyl interaction.

A comparative approach to the strength of polymer internal hydrogen bonds can be done on the basis of measurements of the shape of the i.r. hydroxyl (hydrogen bonded) band near to 3400 cm^{-1} . It is well known that this band is as wide as the hydrogen bond is strong¹⁵. We have compared three systems differing only by the dianiline bridge, respectively methylene (DDM), ether (DDE) and sulphone (DDS). For each system, three films of different thickness have been studied. The peak area S_{OH} versus maximum absorbance A_{OH} is shown in Figure

2. The bandwidth increases effectively in the order $\text{DDS} < \text{DDM} < \text{DDE}$, i.e. in the order of amine polarities. Although this result cannot be considered as a rigorous proof, it provides support for our hypothesis.

If, despite the above results, we keep the hypothesis of additivity of group contributions H_i , larger elemental structures involving both hydroxyl and tertiary amine must be taken into account.

In the case of a direct competition between water-amine and hydroxyl-amine hydrogen bonds, since only one hydroxyl can be linked to the lone pair of electrons on the nitrogen, we can consider the following elemental structure where D is the following unit:



Equations (2) to (8) can be rewritten as follows:

$$2.22H_{OH} + 4.44H_{\Omega} + H_D = H \quad (10)$$

or, generalizing:

$$(2 + 2\overline{DP})(H_{OH} + 2H_{\Omega}) + H_D = H \quad (11)$$

Assuming that $H_D(\text{DDM}_i) = 0$ (steric hindrance), the system of equations (11) applied to the data of Table 2 leads to H_D values twice as high as the preceding H_N values (Table 2) and to:

$$H_{OH} + 2H_{\Omega} = 0.14$$

This value remains considerably lower than in linear polymers; that can be explained, as for amines, by an internal 'hydroxyl-ether' hydrogen bond competitive with the 'hydroxyl-water' hydrogen bond.

Since in non-hindered amine systems, the group contributions of hydroxyls and ethers are smaller than the group contributions of H_D , it can be observed that equation (11) would be consistent with a decrease in water absorption with the \overline{DP} of the diepoxide DGEBA, which is experimentally verified (see below).

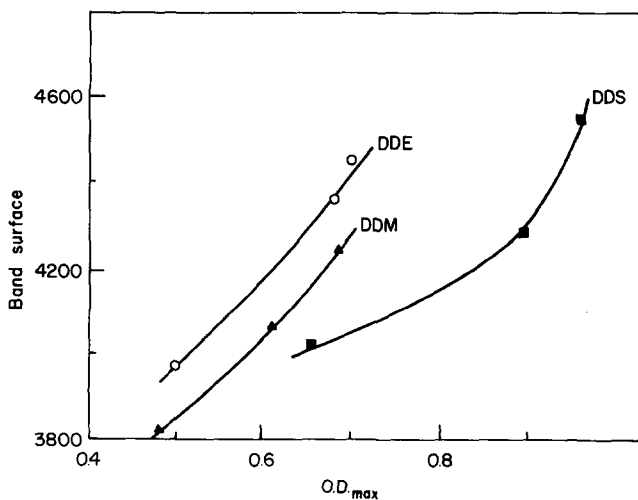
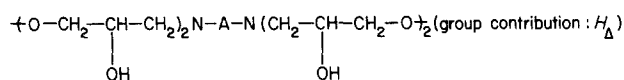


Figure 2 Area of the hydroxyl i.r. peak versus its maximum absorbance for three systems based on DGEBA ($\overline{DP} = 0.11$). The code of the corresponding diamine is indicated on the Figure

Supposing the influence of the amine structure is explained in terms of steric configurations around amine, it seems more convenient to consider the following structural unit:



(A: diamine nucleus as previously defined)

In this case, the system of equations (2) to (8) becomes:

$$2\overline{DP} (H_{\text{OH}} + 2H_{\text{O}}) + H_{\Delta} = H \quad (12)$$

If $H_{\Delta}(\text{DDM}_i) = 0$, the H_{Δ} are equal to the preceding H_{D} values but:

$$H_{\text{OH}} + 2H_{\text{O}} = 1.4$$

In this case, the contribution of a 'chain' glyceryl group would be higher than the contribution of a 'crosslink' β hydroxyl amine, and W_m would increase with the \overline{DP} of diepoxide, which is not experimentally verified.

It seems therefore that, if the additivity rule is respected, the better structure– W_m relationship would be represented by equation (11), which expresses the direct competition between hydroxyl–amine and amine–water hydrogen bonds.

Influence of epoxide-structure

(a) *Systems based on DGEBA oligomers and DDM.* We studied under conditions A two systems: DGEBA₂–DDM ($\overline{DP} \approx 2.3$) and DGEBA₆–DDM ($\overline{DP} \approx 6.0$). The results are listed in Table 3. It can be seen that W_m decreases with the \overline{DP} of DGEBA. Using equation (11) and $H_{\text{D}} = 0.79$ for DDM, for DGEBA₂–DDM we obtain $W_m = 1.41\%$ compared to an experimental value of 1.58%, and for DGEBA₆–DDM: $W_m = 1.15\%$ compared to an experimental value of 1.34%. Thus, the predictive value of equation (11) is confirmed.

(b) *Systems based on TGAP or TGMDA.* The experimental results obtained with conditions A and B are given in Table 3. In all cases, they are consistent with a predominance of tertiary amines as hydrophilic loci. For instance, in Figure 1 it can be observed that W_m values of corresponding DGEBA and TGMDA systems differ essentially by a constant which can be attributed to the two tertiary amine groups of the TGMDA structural unit.

Prediction of W_m from the network composition

On the basis of the above results, simple additive relationships linking W_m to the network composition can be proposed. Their generalized form could be:

$$W_m = \frac{1800\beta}{M} (xH_{(\text{epoxide})} + yH_{(\text{amine})})$$

where M is the molecular weight of the structural unit taken for the calculation, x and y are stoichiometric parameters. $H_{(\text{epoxide})}$ does not depend on $H_{(\text{amine})}$ and vice versa.

β is a factor depending on experimental conditions (sample preparation, weight measurement, relative hygrometry, and temperature). Since it has been shown that W_m is almost temperature independent¹⁶, only small variations of β must be expected in our exposure conditions (relative humidity $\approx 100\%$). We took arbitrarily $\beta = 1$ for conditions A.

Table 4 Parameters used for the prediction of W_m

Parameter	Value	Parameter	Value
β (100°C, 95% RH)	1.20	$H_{\text{D}}(\text{DDM})$	0.79
H_{E}	0.15	$H_{\text{D}}(\text{DDM}_m)$	0.59
H_{T}	0.50	$H_{\text{D}}(\text{DDM}_e)$	0.32
H_{TG}	0.53	$H_{\text{D}}(\text{DDM}_i)$	0.00
$H_{\text{D}}(\text{IPD})$	0.33	$H_{\text{D}}(\text{DDS})$	1.20
$H_{\text{D}}(\text{PDA})$	1.13	$H_{\text{D}}(\text{DDE})$	0.68

Our set of samples includes only one system with *m*-phenylene diamine (TGMDA–PDA). To determine unambiguously $H_{\text{D}}(\text{PDA})$, we used a previously published result on DGEBA–PDA⁹: $W_m = 3.1\%$ in conditions near to conditions A.

Thus, the three following relationships can be proposed:

For systems based on difunctional epoxides:

$$W_m = \frac{1800\beta}{2M_e + M_d} ((2 + 2\overline{DP})H_{\text{E}} + H_{\text{D}}) \quad (13)$$

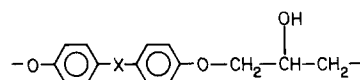
For systems based on TGAP:

$$W_m = \frac{1800\beta}{M_d + 1.333M_e} (1.333H_{\text{TG}} + H_{\text{D}}) \quad (14)$$

For systems based on TGMDA:

$$W_m = \frac{1800\beta}{M_c \left(1 + \frac{m}{100}\right)} \left(H_{\text{T}} + \frac{m}{100} \frac{M_e}{M_d} H_{\text{D}}\right) \quad (15)$$

where M_e is, in all cases, the molar weight of the epoxide under study: $M_e = 340 + 284\overline{DP}$ for DGEBA; $M_e = 277$ for TGAP and $M_e = 422$ for TGMDA. H_{E} refers to the structural unit:



all other parameters being previously defined.

Applying the above relationships to the experimental results of Table 2, we obtain a system of 25 equations whose unknown quantities are: β_B , H_{E} , H_{T} , H_{TG} and H_{D} for each hardener under study. This system admits effectively a satisfactory solution for the values listed in Table 4. It can be observed that the β_B value is reasonably near to unity, which confirms the physical validity of the results.

The mean deviation between calculated and measured W_m values is almost 7%, e.g. within experimental scatter.

REFERENCES

- Morgan, R. S. and O'Neal, J. E. *Polym. Plast. Techn. Eng.* 1978, **10**(1), 120
- Moy, P. and Karasz, F. E. *Polym. Eng. Sci.* 1980, **20**, 4, 315
- Fuller, R. T., Fornes, R. E. and Memory, S. D. *J. Appl. Polym. Sci.* 1979, **23**, 1871
- Fuller, R. T., Sherrow, S., Fornes, R. E. and Memory, J. D. *J. Appl. Polym. Sci.* 1979, **24**, 1383
- Maxwell, I. D. and Pethrick, R. A. *J. Appl. Polym. Sci.* 1983, **28**, 2363
- Danieley, N. D. and Long, R. E. *J. Polym. Sci., Polym. Chem. Edn.* 1981, **19**, 2443

Structure–water absorption relations in epoxy resins: E. Morel et al.

- 7 Carfagna, C., Apicella, A. and Nicolais, L. *J. Appl. Polym. Sci.* 1982, **27**, 105
- 8 Catsiff, E. H., Couleman, R. E., Diprima, J. F., Gordon, D. A. and Seltzer, R. in 'Epoxy Resins Chemistry', *Adv. Chem. Ser.* 1979, **114**, 115
- 9 Diamant, Y., Marom, G. and Brouman, L. J. *J. Appl. Polym. Sci.* 1981, **26**, 3015
- 10 Barrie, J. A. in 'Diffusion in Polymers', Ch. 8 (Eds. J. Crank and G. S. Park), Academic Press, London, 1968
- 11 Van Krevelen, D. W. 'Properties of Polymers', Elsevier, Amsterdam, pp. 420–425, 1976
- 12 King, J. J., Castonguay, R. N. and Zizzi, J. P. 27th National SAMPE Symposium May 4–6, 1982
- 13 ICI Technical note on polyethersulphone
- 14 Eichler, V. J. and Mleziva, J. *Angew. Makromol. Chem.* 1971, **19**, 31
- 15 Pimentel, G. C. and McClellan, A. L. 'Hydrogen Bonding', Reinhold, New York, 1960
- 16 See for instance Loos, A. C. and Springer, G. S. *J. Compos. Mater.* 1979, **13**, 131 and also the results of this work