resentation over the entire domain of molecular weights (curve C). The value of a in the MHS relation is 0.73 and we obtain $D = 2.76 \times 10^{-4}$ (equation 3) and $C = 16.6 \times 10^{-12}$ (equation 4). Equation (1) gives a linear representation up to $\alpha_\eta^3 \sim 3.2$, (curve B), while the SFB equation has an upper limit $\alpha_\eta^3 \sim 2.4$ (curve A).

The extrapolation of curve C gives a value of K_Θ equal to 6.5×10^{-2} cm^3 g^{-1}. This value is lower than the value obtained in the solvent mixture nitromethane/propanol[10] (curve D). This difference can be explained on the basis of the thermodynamic properties of the binary solvent mixtures[11]. The value of K_Θ obtained for pure nitromethane approaches that obtained by Cowie and Toporowski[12].

Poly(ethyl methacrylate)/toluene

For this system we used only polymer samples of high molecular weight[13] and application of the SFB equation (*Figure 5*) gives an ambiguous extrapolation ($K_\Theta = 10.69 \times 10^{-2}$)[13]. The application of equation (2) not only gives a linear representation between $[\eta]$ and M but extrapolation to $M = 0$ also gives a correct K_Θ value ($K_\Theta = 5.5 \times 10^{-2}$, *Figure 5*). A similar K_Θ value is obtained for the same polymer in a Θ solvent[13] or using the Flory–Fox plot[14] when the polymer is dissolved in a good solvent[13].

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Interaction of water with some epoxide adhesives

D. M. Brewis, J. Comyn, R. J. A. Shalash and J. L. Tegg
School of Chemistry, Leicester Polytechnic, P. O. Box 143, Leicester LE1 9BH, UK

(Received 9 July 1979; revised 24 September)

The effect of water on the epoxides is generally an undesirable one: adhesive joints suffer a decrease in strength, sealants transmit water to components such as microprocessors which they are meant to protect, and matrix resins may suffer loss of stiffness by plasticization.

Several factors may be involved in these unwanted processes. These may include: the rate of diffusion of water and the solubility of water in the epoxide; modification of mechanical properties by water ingress, which in some cases may involve the material passing from the glassy to leathery state; and the effect of water on interfaces, be they fibre–matrix, adhesive–adherend, or sealant–substrate.

We have attempted to examine some of these factors, namely solubility, diffusion coefficient, and depression of glass transition temperature for a series of epoxides. Six commonly used epoxides were chosen for this work, and from the start it was intended to choose later one of these for a more detailed study which would include the use of the chosen adhesive in durability trials on bonded metal joints. This work has been completed[1] and will be published later. The simple experimental method was based on following mass uptake of water by weighing on a laboratory balance.

EXPERIMENTAL

A commercial liquid resin consisting largely of the diglycidyl ether of bisphenol A, having an epoxide molar mass in the range 182–194 was used. It was employed with the six hardeners which are recorded with their formulations and conditions of cure in *Table 1*, the information being taken from the sources quoted and so typical of the current use of these materials. With the exception of TETA which is hygrocopic and which was distilled at reduced pressure from over calcium hydride, all materials were used as supplied.

Adhesive films were prepared by a modified version of a method described by Perera and Heertjes[8] for the preparation of paint films. Tin foil (0.13 mm thick) was rollered to a smooth finish on a wet glass plate using a rubber roller. Adhesive was spread onto the tin foil using a thin layer chromatography spreader. After cure, the tin foil was removed by peeling. The tin foil (from Hopkin and Williams Ltd.) was used as supplied. It seems very likely that its successful use for this purpose depended on it being covered with a layer of rolling oil. To assist spreading, the adhesive was applied whilst hot onto a surface which had been preheated in an overn.

Cured films were cut into samples approximately 20 mm x 20 mm, and the thickness of each sample was measured in at least 5 places with a micrometer. Typically the samples were (350 ± 17) μm thick.

The sorption of liquid water was investigated. Film samples were placed in individual 50 g screw-capped jars containing distilled water. Some jars were kept in a water bath maintained at 25 ± 0.5°C and others in an oven at either 45 ± 0.8°C or 70 ± 1°C. Films were removed periodically, dried with filter paper, weighed, and then returned. The sorption process was followed in this manner until equilibrium was reached, which was usually after 2 to 4 months.

0032–3861/80/030357–04$02.00

Table 1 Details of epoxide formulation and cure

Hardener		Amount of hardener/100 g diepoxide	Mixing temperature (°C)	Substrate temperature (°C)	Curing conditions	Reference
di-(1-aminopropyl-3-ethoxy ether)	DAPEE	32.5	80	60	3h at 80°C	2
triethylene tetramine	TETA	11.0	40	40	3h at 60°C	3
1,3-diaminobenzene	DAB	13.0	80	80	2h at 80°C then 2h at 150°C	4
4,4'-diaminodiphenyl methane	DDM	27.0	100	80	2h at 80°C	5
tris(dimethylaminomethyl)phenol	DMP	60.0	80	50	16h at 50°C	6
borontrifluoride monoethylamine	BF_3 MEA	4.0	100	80	1h at 130°C then 2h at 180°C	7

All experiments were done in duplicate and duplicate runs showed very good agreement.

Some samples were exposed to water at 100°C in a Soxhlet apparatus. These films were transported to and from the balance in ice-cold water.

Heat distortion temperatures were measured on both dry and wet epoxides using a Perkin–Elmer thermomechanical analyser in the penetrometer mode. A 10 g weight was loaded on the probe, and the scan rate was 10°C $\min^{-1}$. The instrument incorporated a second derivative computer, and the peak in the recorder trace generated by this device was taken as the heat distortion temperature.

RESULTS

Masses from sorption experiments were plotted in the form of fractional uptake (M_t/M_∞) against $t^{1/2}/l$, where t is the time and l is film thickness. All plots showed the sorption process to be Fickian; i.e. the plots were linear up to $M_t/M_\infty = 0.6$.

Diffusion coefficients D were evaluated from the linear section by using the following relationship[9]:

$$\frac{M_t}{M_\infty} = \frac{4}{l}\left(\frac{Dt}{\pi}\right)^{1/2}$$

Most plots showed a plateau associated with the initial equilibrium uptake, but exceptions to this were seen in the following cases:

(a) with BF_3MEA hardener at 45°C and 70°C, M_t increased to a maximum and then decreased monotonously. Here for the purpose of evaluating D, M_∞ was evaluated by extrapolating the falling part of the plot to zero time. Sorption with this hardener at 100°C was not attempted;

(b) at 100°C with DDM hardener, a second slow uptake step was evident (see *Figure 1*), but this eventually led to equilibrium;

(c) with TETA hardener at 100°C, no mass uptake equilibrium occurred, but after an initial linear rise, the sorption plot continued to rise at a slower rate.

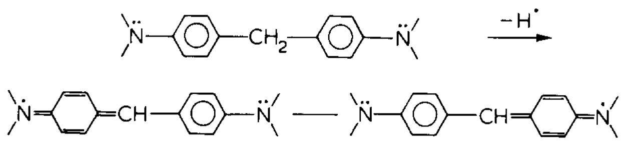
Diffusion coefficients are collected in *Table 2*, the estimated uncertainty in these values being ±20%. Equilibrium uptake results also appear in *Table 2*; the estimated error in values of M_∞ is ±7%. Heat distortion temperatures for the adhesives, both dry and after they had been immersed in water at room temperature for long enough to reach equilibrium, and also after a 10 month immersion, are shown in *Table 3*.

DISCUSSION

The technique described is simple to perform and gives reproducible mass uptake results.

Water diffusion appears to be Fickian for all the epoxide adhesives over the temperature range studied. This is in agreement with findings of several other workers who have investigated water uptake by epoxides 8, 10, 11, 12. It would seem from our findings as well as those of others that, even when uptake commences at temperatures a good way below the glass transition temperature, uptake is of the form associated with leathery rather than glassy polymers.

With the exception of the DDM system, the values of D at 25°C for the various adhesives are not significantly different, the average value of D being $1.7 \times 10^{-13} m^2 s^{-1}$. This value lies within the typical range of D for water diffusion in polymers[13]. The value of DDM is smaller by a factor of about 20. One possible explanation for this anomaly lies in the fact that DDM is the only hardener which may exist in a conjugated form which permits no freedom for rotation. To attain this state it would be necessary for the DDM unit to lose a H$^\cdot$ radical, but this might be achieved at the curing temperature possibly by the intervention of oxygen:



The effect of this would be to stiffen and immobilize the network, and so hinder the passage of a diffusing molecule. The stiffness of this network is possibly also reflected by its relatively high heat distortion temperature of 119°C. It is not reflected however in an exceptionally high value of E_D.

Activation energies for four epoxides are in the region of 70 kJ mol^{-1}, but BF_3MEA has a negative value. Values in the 70 kJ mol^{-1} region seem common for the diffusion of water in epoxides and have been reported by others[12,14]. It seems clear from the weight losses observed with the BF_3MEA system that hydrolysis occurs, and that this contributes to an apparent negative value of E_D.

Solubilities of water in the adhesives are all similar, and none of the systems shows a strong dependence of solubility on temperature; i.e. heats of solubility have values fairly close to zero. This could well arise from the clustering of water within the epoxide, so that the interaction which occurs between water and epoxide is limited to the surfaces of the clusters. Clustering has been observed for water in many polymers[15,16].

Heat distortion temperatures of the dry adhesives are in moderately good agreement with values reported in the

Table 2 Results of liquid sorption experiments

Hardener	Diffusion coefficient, D ($10^{-13}m^2s^{-1}$) 25°C	45°C	70°C	100°C	Activation energy for diffusion (E_D (kJ mol^{-1}))	Equilibrium water uptake (M_∞ (g 100 g^{-1} adhesive)) 25°C	45°C	70°C	100°C	Heat of solution ΔH_s(kJ mol^{-1})
DAPEE	1.3	4.6	36	500	68	5.0	4.7	4.2	4.9	–2.8
TETA	1.6	3.2	4.5	170	74	3.8	3.4	3.2	(3.89)*	–2.6
DAB	1.9	9.7	13	49	38	2.3	3.1	3.2	1.9	–†
DDM	0.099	0.06	2.1	20	63	4.1	1.6	1.4	(4.04)*	–†
DMP	2.0	3.6	21	380	63	4.4	4.0	4.0	3.89	–1.1
BF$_3$MEA	1.6	1.3	0.76	–	–15	2.3	(2.4)	(2.9)		+4.1

* Values in brackets are for cases which were not truly at equilibrium

† The absence of an entry in the last column indicates that the plot of log M_∞ against 1/T was non-linear

Table 3 Heat distortion temperatures of wet and dry adhesives

Hardener	T_d (°C) Dry	After equilibriation	After 10 months in water	Depression of T_d ΔTd (experimental (K))	ΔTd (Fox equation (K))
DAPEE	67	37	49	30	23
TETA	99	86	111	13	23
DAB	161	143	157	18	22
DDM	119	110	130	9	27
DMP	68	51	54	17	21
BF$_3$MEA	173	155		18	22

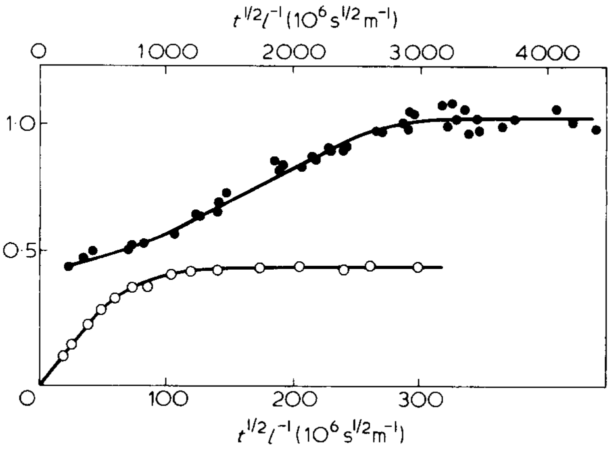


Figure 1 Sorption plot for epoxide with DDM hardener at 100°C. Upper abscissa, ●, long times; lower abscissa, ○, short times

literature[17,18,19]. All show a lowering of T_d upon equilibrium with water, due to the plasticizing effect of the latter, but leaving samples in water for 10 months always caused an increase in T_d, sometimes to a value greater than that in the dry. This may be explained by the formation of additional crosslinks between unreacted groups in the water plasticized adhesive. Additional crosslinking of epoxides in the wet state has been observed by Browning using near-i.r. spectroscopy[12].

Heat distortion temperatures of epoxides have been shown to be similar in value to their glass transition temperature T_g[20], which, in the case of polymer plasticizer mixtures, can be treated by the Fox[21] equation:

$$\frac{1}{T_g} = \frac{w_1}{T_{g_1}} + \frac{w_2}{T_{g_2}}$$

where w_1 and w_2 are weight fractions of polymer and plasticizer and T_{g_1} and T_{g_2} are their corresponding glass transition temperatures. Experimentally the glass transition temperature of water has been reported in the –134 to –138°C range[22,23,24,25] using differential thermal analysis and other techniques. Using a value of T_{g_2} = –137°C it has been possible to calculate T_g depression using the Fox equation; these are compared with actual depressions in *Table 5*. Agreement between the two values is probably within experimantal error in the cases of DAPEE, DAB, DMP and BF$_3$MEA, and the interpretation of this result would be that water is molecularly dispersed in these epoxides rather than being isolated in clusters to any significant extent. The values for DDM are distinctly different, and here the difference indicates the possibility of cluster formation.

CONCLUSIONS

(1) Immersion of epoxide films in liquid water, with periodic removal for weighing is a reliable method of studying water uptake by these materials.
(2) The epoxides studied all exhibited Fickian diffusion, and in most cases a water uptake equilibrium was attained.
(3) Heat distortion temperatures of epoxides are initially depressed on immersion in water, but prolonged immersion leads to an increase in this parameter.

ACKNOWLEDGEMENTS

The authors wish to express their thanks to the following for the assistance they have given to this work: Mr. E. W. Garnish, Mr. J. H. Golding and Mr. R. J. Martin of Ciba–Geigy (U.K.) Ltd., Dr. B. M. Parker of the Royal Aircraft Establishment and Mr. A. Hardy of Bostik Ltd.

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Molecular model for mobilities of copolymer liquids

A. A. Miller
1070 Hickory Road, Schenectady, NY 12309, USA

(Received 31 August 1979)

Introduction

Earlier papers[1,2] have presented a molecular interpretation of the Vogel equation for polymer liquid mobility:

$$-\ln \mu \sim B/(T - T_0) \tag{1}$$

where B, T_0 are constants which are independent of temperature but increase with pressure[3]. On the basis of a rotational isomeric model it was shown that:

$$U = mRT_0 \tag{2}$$

and

$$E_0 = RB \tag{3}$$

in which U is the energy difference between the rotational states and E_0 is related to the rotational barrier(s) between these states. For the simplest 3-state rotational model (a *trans* state, t, and two equivalent *gauche* states, g^+ and g^-) with independent bond rotations[1], $m = 4.2$ in equation (2). A 3-state model in which transitions between *gauche* states of opposite sign are excluded (the 'pentane interference') gives $m = 4.0$ or 4.4, depending upon which of two rotational partition functions is chosen[2]. The conformational entropy calculated for linear polyethylene (PE) with $m = 4.4$, together with a new calculation of the volume entropy, gave excellent agreement with the experimental entropy of fusion[2].

A procedure for extrapolating U and E_0 from the real polymer liquid to the 'isolated' chain and the relation of E_0 to the barriers against rotation in the 'forward' ($t \to g^+, g^-$) and 'reverse' ($g^+, g^- \to t$) directions have also been reported[4].

Combining equations (1)–(3) leads to

$$-\ln \mu \sim E_0/(RT - U/m) \tag{4}$$

The glass transition is considered to be an isomobility state[3,5] with a constant value of the Vogel term for a given polymer:

$$B/(T_g - T_0) = D \tag{5}$$

or

$$T_g = T_0 + B/D \tag{5a}$$

where also $D = 2.303C_1^g$ in the WLF context, its value ranging between 30 and 40 ($1/D = 0.033$–0.025) for different vinyl-type polymers[6,20].

By substituting equations (2) and (3) in equation (5a) we obtain for the glass-transition temperature:

$$T_g = (U + mE_0/D)/mR \tag{6}$$

For a binary copolymer liquid, if both U and E_0 were simply additive in mol fractions, n_a and n_b, of the components and m remained constant over the composition range, then from equations (2) and (3):

$$T_0 = n_a T_{0a} + n_b T_{0b} \tag{7}$$

and

$$B = n_a B_a + n_b B_b \tag{8}$$

By equation (5a) this would also require that T_g of the copolymer be simply additive i.e. T_g would be linear in n_a or n_b.

Usually, however, T_g against mol fraction is nonlinear, showing either a positive or a negative deviation and in some cases even a maximum or a minimum[7,8]. This suggests that equations (7) and (8) cannot apply simultaneously, i.e. either T_0 or B can be linear in n but not both. A choice can be made only on the basis of experimental measurements of the Vogel (or WLF) constants as a function of composition. Only a very few such measurements have been reported in the literature, in contrast to the abundance of data on T_g versus composition for copolymers.

0032–3861/80/030360–04$02.00