Interaction of epoxy resins with water: the depression of glass transition temperature

T. S. Ellis and F. E. Karasz

Department of Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts 01003, USA
(Received 5 May 1983; revised 22 July 1983)

The depression of T_g in a number of epoxy–water systems has been investigated calorimetrically. Except where an unbalanced reaction stoichiometry was used, experimental results are in good agreement with theoretical predictions based on equations developed for the composition dependent T_g in polymer diluent-systems. Thermal analysis also demonstrates a complex thermal behaviour on rescanning of samples, attributed to diluent diffusing out of the sample. The importance of this behaviour in the context of solvent-induced physical ageing of epoxy resin composites is discussed.

INTRODUCTION

The plasticization and interaction of structural network epoxy resins and their fibre reinforced composites continues to be of both fundamental and technical interest[1–4]. The susceptibility of these materials to substantial changes in properties on exposure to humid environments is manifested in particular by a seemingly large depression in the measured glass transition temperature T_g[1,3], typically 20°C/wt% of water. Because of the polar nature of the epoxy–water system and the results of several spectroscopic studies[5–7] indicating some form of molecular association, the most widely accepted explanation has been that this large depression in T_g is the result of specific interactions. It has been suggested that in systems where such interactions are present, then a greater than normal change in T_g could be expected[8]. It is the contention of this and earlier studies that these effects of water are not the result of specific interactions, but are consistent with predictions based upon theoretical expressions developed to describe the compositional dependence of T_g in miscible blends[9,10].

The free volume approach to the compositon dependent T_g[11] has been applied to epoxy–water systems, sometimes with contradictory results[1,3,4]. These disparities are probably due in part to the value chosen for the T_g of water, as has been noted by other workers[12]. Recent work by Moy[13] has shown that the plasticization of epoxy resins by water could be qualitatively accounted for by applying a limiting condition to the classical thermodynamic treatment of the composition-dependent T_g. The shortcomings in this approach were considered recently and improved upon to explain successfully on a quantitative basis the plasticization of network styrene polymers[14]. The details of these improvements have been discussed elsewhere[15] and only the central result is shown here:

$$T_{g_{12}} = \frac{x_1 \Delta C_{p_1}{}^{act} T_{g_1} + x_2 \Delta C_{p_2} T_{g_2}}{x_1 \Delta C_{p_1}{}^{act} + x_2 \Delta C_{p_2}} \quad (1)$$

where 1 and 2 refer to polymer and diluent, respectively, x refers to weight or mole fraction and $\Delta C_{p_1}{}^{act}$ is the incremental change in specific heat at T_{g_1} of the units capable of activation[14].

Here, the complex thermal behaviour induced during thermal analysis[16], which is attributable to diluent diffusing out of polymer at high temperature, is also considered. This in turn leads to a solvent-induced physical ageing, manifested by a pre-T_g enthalpy relaxation, which although has been observed in other polymer–diluent systems[17], has not previously been reported in the epoxy–water system.

To verify the concepts described previously the validity of this treatment has been tested on a wide variety of epoxy resins ranging from a linear polymer to a relatively highly cross-linked network. The funadamental variables are the topology and chemistry of the system. Variation of physical structure by choice of starting materials will ultimately influence the thermal properties, and variation of reaction stoichiometry will influence not only the structure, but also the chemistry of the resultant system. The thermal properties of the diluent remain constant.

It is important to consider the measured or extrapolated accuracy of the parameters which will be used in equation (1). The glass transition temperature of water (T_{g_2}) has now been determined by a number of experiments[8,18] to be approximately 134 K. Several experiments[19,20] involving the measurement of the compositional dependence of T_g in aqueous systems have also indicated this to be a realistic value. It is straightforward to show that equation (1) is relatively insensitive in terms of the predicted depression to small errors in T_{g_2} or T_{g_1}. In this and a previous study[14], large (20–35 mg) and, therefore, thick (1–2 mm) samples were used to simplify the task of measurement of thermal properties in materials with a low ΔC_p and to minimize the effects of plasticizer loss to the surrounding space in the sample pan during thermal analysis. The use of thick samples in a d.s.c. scan in turn leads to errors in interpretation of

the correct T_g^{21}. However, for comparative purposes, and because all measurements of T_g were made using thick samples, the errors caused by this can be neglected.

The value of ΔC_{p_2} (1.94 J g^{-1} K^{-1} or 34.9 J mol^{-1} K^{-1})[18,22] is low compared to that for common organic solvents (cf. ethylbenzene; 80.8 J mol^{-1} K^{-1}), and the larger the value of ΔC_{p_2}, then the greater the expected depression of T_g at low plasticizer concentrations. This is evident from equation (2), which has been obtained from equation (1) by taking the derivative with respect to x_2. Thus, as shown later, relatively large depressions in T_g caused by water are in good agreement with theoretical predictions despite this relatively low value of ΔC_{p_2}.

$$\frac{dT_{g_{12}}}{dx_2}\bigg|_{x_2 \to 0} = -\frac{\Delta C_{p_2}}{\Delta C_{p_1}{}^{act}}(T_{g_1} - T_{g_2}) \qquad (2)$$

EXPERIMENTAL

A series of epoxy resins were prepared from Epon 825 (predominantly the diglycidyl ether of bisphenol A, DGBA) and MY 720 (predominantly tetraglycidyl-4,4'-diaminodiphenylmethane, TGDDA) supplied by Shell and Ciba-Geigy respectively. The curing agents used were aniline (A), and m-phenylenediamine (MPD).

DGBA

TGDDM
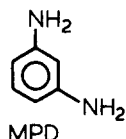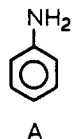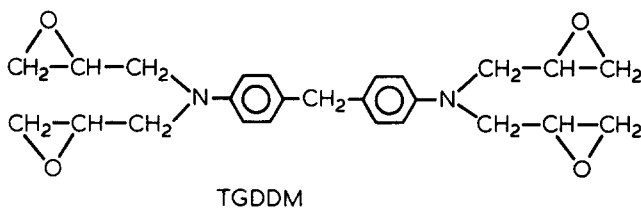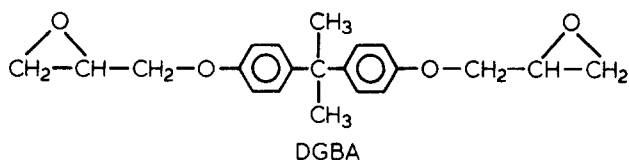
After complete mixing of the components, the resins were cured in an oven using cycles which varied according to the final T_g. Essentially this involved mild temperatures ($\approx 60°C$) up to gelation or vitrification and then stepwise increments ($\approx 50°C$) in temperature to a point above the T_g of the fully cured system. The resins were then vigorously dried under vacuum in the presence of a desiccant at a temperature above T_g, and then stored over a drying agent. The determination of thermal properties (T_g and ΔC_p) and experimental procedures used to add diluent to the resins are identical to those described elsewhere[14]. Details concerning cure stoichiometry, chemical composition, and thermal properties of the resins are shown in Table 1.

It was important that the prepared resins were both completely dry and fully cured. This was achieved by heating above $T_{g\infty}$ under vacuum in the presence of phosphorous pentoxide for an extended period of time. D.s.c. was used to establish that $T_{g\infty}$, representative of complete reaction, had been attained and was also used to show that plasticized samples when redried have the same thermal properties as the dried resin before imbibition.

RESULTS AND DISCUSSION

In these experiments both the onset and mid-point T_g were determined, not to compare their accuracy in the predictive treatment, but to test for the presence, if any, of plasticizer gradients in the samples. This may be relevant particularly where samples are simply allowed to imbibe water by immersing at ambient conditions, where especially in thick samples a diluent concentration gradient may be expected across the sample leading to a greater depression in the onset T_g than in the mid-point T_g. In these studies diluent was introduced into the epoxy at high temperatures with substantial equilibration times and thus the possibility of concentration gradients were small. However, in a few cases the depressed T_g was also measured in samples placed in water at ambient conditions for approximately 5–7 days. No significant variation in the depressed onset or mid-point T_g could be detected, suggesting that concentration gradients across the samples are not a problem with samples 1–2 mm thick, as used in this study.

The experimentally determined value of ΔC_{p_1}, is also used as the value of $\Delta C_{p_1}{}^{act}$. The relation between ΔC_{p_1} measured experimentally and $\Delta C_{p_1}{}^{act}$ is much more difficult to define in epoxies than it is in network styrene polymers[15]. Because of their differing mode of formation, very highly cross-linked networks are not produced in the epoxy systems used here as was the case for the network styrene systems[14]. Therefore, the proportion of units incapable of activation at T_g is considerably less, and it has been assumed that all units undergo the appropriate co-operative molecular motions at T_g. In the case of EX3, EX5 and EX6, which are either linear or very lightly cross-linked, $\Delta C_{p_1}{}^{act}$ can be regarded as being equivalent to the experimentally-determined value.

Table 1 Properties of the polymers

Sample code	Chemical composition	Reaction stoichiometry	Onset T_g (K)	Mid-point T_g (K)	ΔC_p (J g^{-1} K^{-1})
Ex 1	TGDDM/A	1 : 1	409.4	423.3	0.34
Ex 3	DGBA/A	1 : 1	338.9	346.3	0.53
Ex 4	DGBA/MPD	1 : 1	424.2	432.0	0.35
Ex 5	DGBA/MPD	1 : 0.5	321.2	337.8	0.47
Ex 6	DGBA/MPD	0.5 : 1	371.7	379.1	0.47

The depression of T_g in the stoichiometric compositions (*Figures 1–3*) shows very close agreement between theory and the experimentally-determined depression of T_g. The sample EX3 is essentially a linear polymer of low molecular weight and consequently has a low T_g and relatively high ΔC_p so that only an 8°–9°C/wt% reduction in T_g is observed. Conversely, EX1 and EX4 are substantially cross-linked, have a high T_g and lower ΔC_p, thus a 13°–15°C/wt% reduction is observed. This suggests that in very highly cross-linked systems with a high T_g (>200°C) and consequently a small ΔC_p, a depression of 25°C/wt% water content may easily be seen. This is large when compared to the plasticization of polystyrene by ethylbenzene (4°–5°C/wt%). Attempts to synthesize a more highly cross-linked system with a higher T_g and a lower ΔC_p, using TGDDM and MPD were unsuccessful owing to thermal degradation in either the curing stage or during thermal characterization. In noting the good agreement between theory and experiment, it is also noteworthy that the values of ΔC_{p_2} and T_{g_2} for water cannot be regarded as unusual and as mentioned previously ΔC_{p_2} is in fact relatively small. The seemingly large effect on T_g in epoxies, and for that matter other polymers, caused by water is largely attributable to the low molar mass of the plasticizer.

The investigation of the non-stoichiometric composition resins EX5 and EX6 was prompted in part by a previous study[23] which appeared to suggest anomalous plasticization by water in a similar epoxy system. The stoichiometrically cured resin exhibited an approximate 15°C/wt% reduction in T_g, as may be expected. However, the amine-rich and epoxide-rich formulations showed
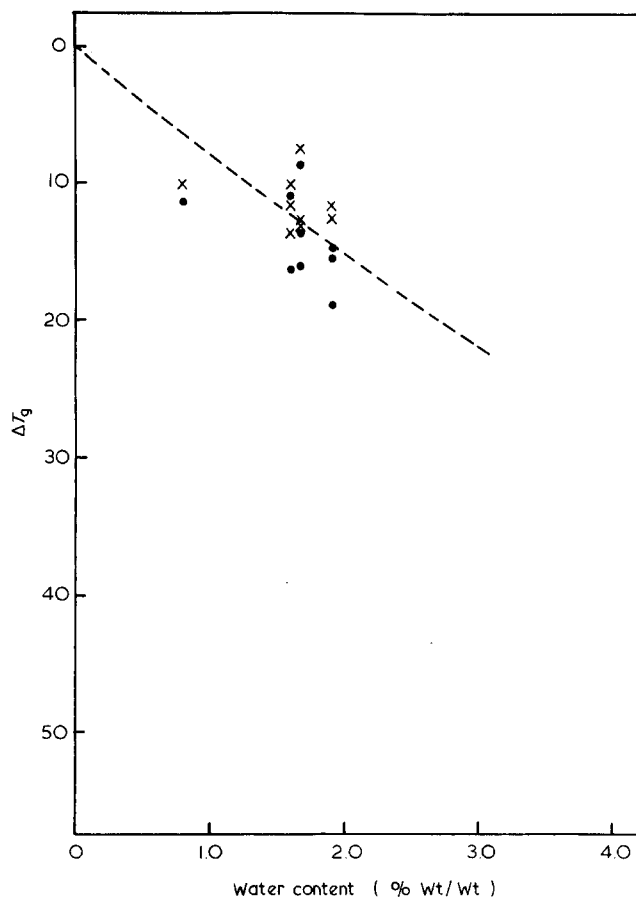

Figure 2 The depression of T_g in EX3. ●, Onset T_{g_1}; x, midpoint T_g; — — —, theoretical depression
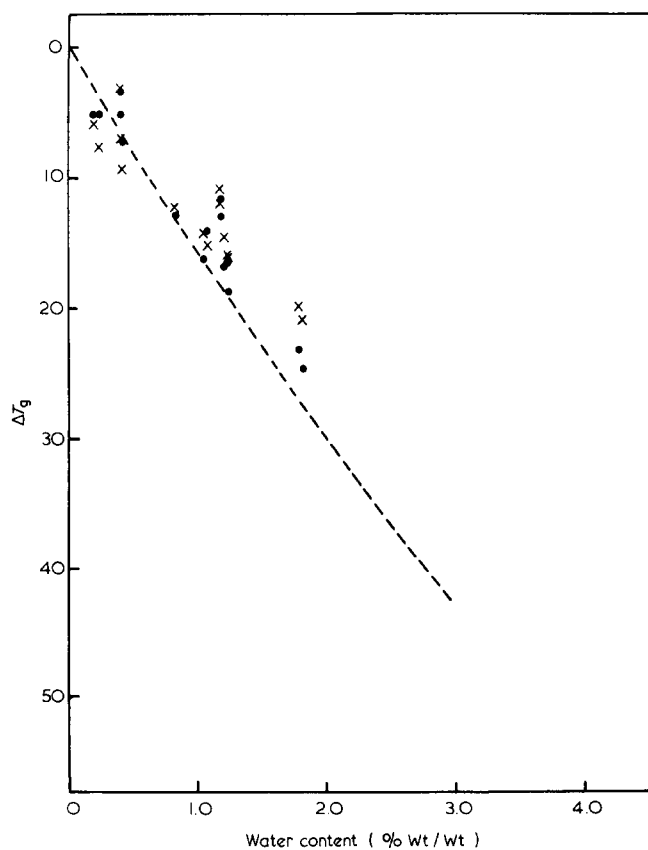

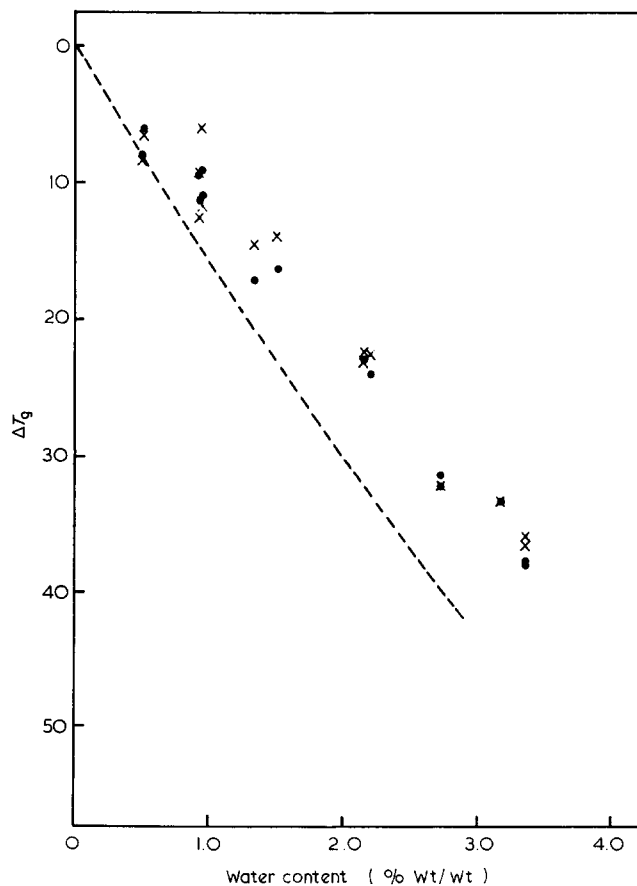**Figure 1** The depression of T_g in EX1. ●, Onset T_{g_1}; x, midpoint T_g; — — —, theoretical depression

Figure 3 The depression of T_g in EX4. ●, Onset T_{g_1}; x, midpoint T_g; — — —, theoretical depression

only an approximate 4°C/wt% reduction. Although a different curing agent is used in this study the origin of such large observed deviations from theory when ΔC_{p_1} of all the formulations were reported as being virtually identical, was of particular interest.

Plasticization of EX5, the epoxide-rich formulation, shows considerable scatter and deviation from the predicted curve, as shown in *Figure 4*. On drying the plasticized samples, however, the observed T_g had been elevated by 10°–20°C above its original value indicative of a chemical change during the water imbibition cycle which was carried out at 90°C. The reaction of water with the excess epoxide moieties is well known to proceed by addition forming a glycol unit. This change in structure would, it is believed, account for the variation in the observed T_g of the sample. Significantly, a second sample allowed to imbibe water at ambient conditions exhibited a depressed T_g close to that predicted.

Plasticization of the amine-rich formulation EX6 shows a depressed T_g greater than that predicted by theory, as shown in *Figure 5*. Drying and determination of T_g shows a small and insignificant change from the original value. The results (see *Figure 5*) indicate an excess depression of the order 8°C which appears to be independent of the water content. In this case a water–amine reaction cannot account for this; and the greater than predicted depression of T_g in this system is as yet not accounted for and is contrary to that found in ref. 23. The stoichiometric compositions may also have unreacted chemical moieties similar to those found in abundance in EX5 and EX6 but in sufficiently small
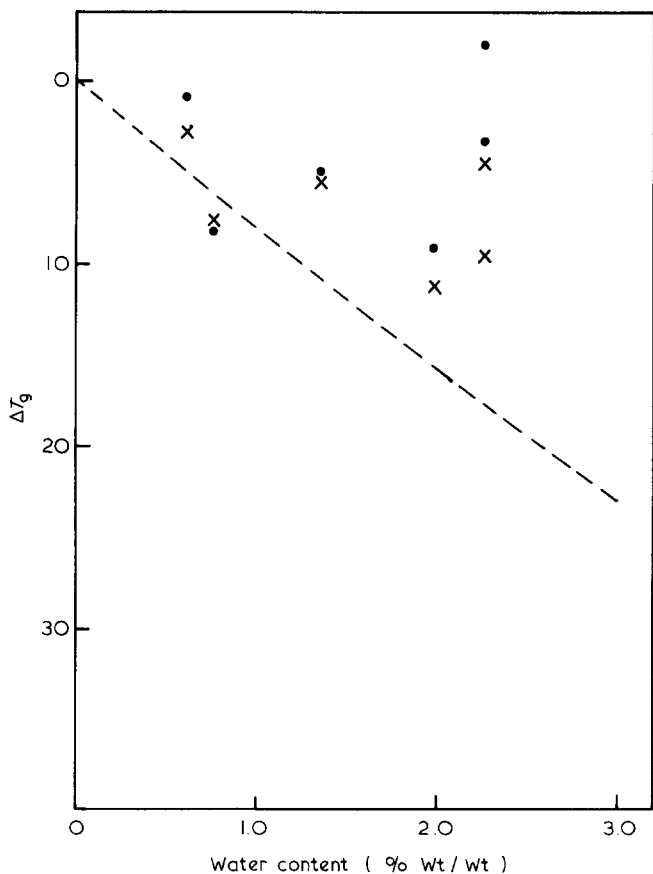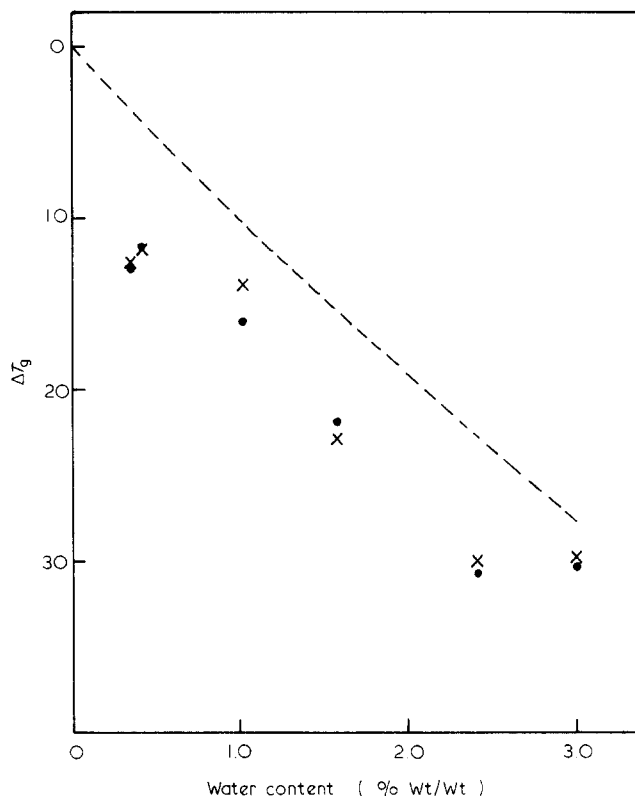

Figure 5 The depression of T_g in EX6. ●, Onset T_{g_1}; x, mid-point T_g; ———, theoretical depression

amounts so as to not significantly affect the depression of T_g when water is added. Clearly, care must be exercised when making conclusions from systems where the diluent may chemically react with or have a degradative effect on the material.

With respect to diluent diffusing out of the sample during thermal analysis, it had previously been assumed that in relatively thick samples (1–2 mm) contained in sealed sample containers that the time scale of a d.s.c. scan was sufficiently short such that only an insignificant quantity of plasticizer could diffuse out of the sample. It now appears now that this is not the case, particularly in samples with a high T_g (>120°C) as in the case of EX1 and EX4. This results in a rather complex thermal behaviour on rescanning of the samples as shown in *Figure 6*.

On the first scan of the freshly prepared sample no free water can be seen, as noted by the absence of an ice melting endotherm. On quench cooling from above T_g and rescanning, a significant ice melting endotherm is now observed. The magnitude of this endotherm is dependent upon the cooling rate such that at rates of 2.5 or 5°C min^{-1}, it has virtually disappeared. However, on quench cooling, again from above T_g, the same effects are observed. If the sample pan cover is removed during measurement all the events disappear and subsequent scans result in an elevated T_g on each scan, clearly indicating plasticizer evaporation. This implies that the endotherms observed are due solely to the presence of free water produced by the diluent diffusing out of the sample during thermal analysis. Experiments have also shown that the ice endotherm appears only when samples have been heated previously up to at least the respective glass transition temperature. Such a result is not unexpected as diffusion processes would increase

Figure 4 The depression of T_g in EX5. ●, Onset T_{g_1}; x, mid-point T_g; ———, theoretical depression

significantly at T_g. Cooling studies have also shown that the free water freezes at approximately 273 K indicating macroscopic regions of water and not small domains which freeze at much lower temperatures as has been observed in other polymer–water systems[24]. The other events which are observed are a slight exotherm prior to a pre-T_g enthalpy relaxation (C and E in *Figure 6*). It is believed that these events are related and can be accounted for as follows.

On fast cooling from above T_g the free water which had diffused out of the sample, but remains within the sample container, freezes and on reheating appears as an endotherm. On further heating some or all of this is re-absorbed giving rise to a small exotherm. This in turn causes a volume change analagous to that produced by sub-T_g annealing[25] which results in a pre-T_g relaxation. Absorption of water by epoxies is known to be a strongly exothermic process[26] and solvent-induced enthalpy relaxations prior to T_g have been observed in other polymer–diluent systems[17]. It is noteworthy that all these effects referred to here are produced during the very short time scale of a d.s.c. scan (20 K min^{-1} heating rate). On slow cooling a significant portion of the water which had diffused out is probably re-absorbed at a sufficiently high temperature that a pre-T_g relaxation is not observed on subsequent reheating. Attempts to duplicate this behaviour in the d.s.c. by adding a small quantity of water to a dry sample in a sealed pan resulted only in the observation of the ice endotherm and none of the other events. This would appear to suggest that the free water is somehow distributed in minute cracks or fissures through the sample which allows a high surface area of contact, for the re-
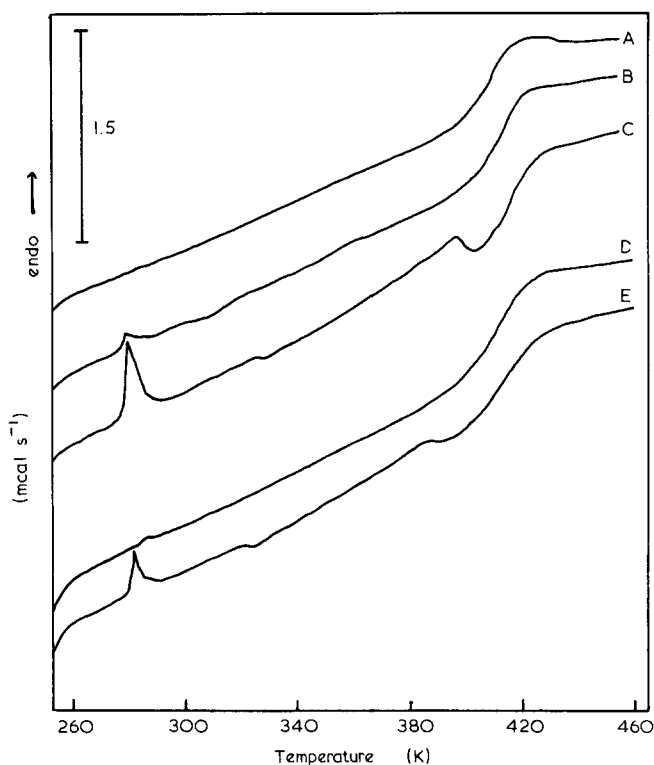
absorption process to occur in the short time scale of a d.s.c. scan.

These observations, although an apparent artefact of experimentation are important for several reasons. Firstly, solvent-induced enthalpy relaxations do not appear to have been reported previously in epoxy–water systems. These events have been observed in sub-T_g annealing studies and have been associated with physical ageing leading to embrittlement[25]. If such an effect can also be rapidly induced by water in structural network epoxies and their composites then it has an important bearing on the mechanical performance of these materials in certain applications. The type of thermal cycles used in the d.s.c. described here are very similar to the so called 'thermal spike' used by some workers[1] to examine the performance of such materials exposed to moisture in aerospace applications. While these materials usually have a higher T_g when dry, once exposed to moisture, a greatly depressed T_g may bring them into the range of the upper limit of the 'thermal spike' allowing the processes described here to occur. This may be particularly true in fibre-reinforced composites where microvoids at the fibre–resin interface may allow moisture to collect and thus duplicate the events observed in a sealed d.s.c. sample pan.

CONCLUSIONS

These studies on epoxy resins with a relatively low T_g have shown that the plasticizing power of water is in complete accord with theoretical predictions and as such does not place water in a special category away from other plasticizers. Current useage of epoxy resins includes materials with a very high T_g ($\simeq 250°C$) and, therefore, a low incremental change in heat capacity at T_g. Clearly, a small amount of water will have a marked plasticizing action in these systems. Such an effect is to be expected in the context of this discussion and is in part simply a reflection of the low molar mass of water. A water content of 1–2 wt% represents a relatively large concentration of plasticizer when expressed as a mole fraction.

These experiments have also indicated that water can quickly diffuse out of epoxy resins at elevated temperatures ($>100°C$) with two important consequences. The first being that any studies on epoxy–water systems with a high T_g may be problematic simply due to the inability to maintain a stable, known plasticizer content at the transition temperature. This would be particularly true at low heating rates where purge gas is allowed to sweep away volatiles allowing further diffusion of plasticizer out of the sample to occur. Such a situation can occur, for example, in a dynamic mechanical determination of T_g. A second and perhaps more important consequence of this phenomenon, although up to now observed only during a d.s.c. analysis, is that of solvent-induced physical ageing. Clearly, this aspect requires further experimental work to verify its practical significance in a real environment.

Figure 6 D.s.c. thermograms of EX4 containing 2.16 wt% water and EX1 containing 1.24 wt% water. A, EX4 first scan; B, EX4 second scan after cooling at 5K min^{-1}; C, EX4 third scan after quench cooling; D, EX1 after cooling at 5K min^{-1}; E, EX1 after quench cooling

REFERENCES

1 Browning, C. E. *Polym. Eng. Sci.* 1978, **18**, 16
2 Illinger, J. L. and Schneider, N. S. in 'Water in Polymers' (Ed. S. P. Rowland), Am. Chem. Soc. Symp. Ser., 1979, 127
3 McKague, E. L., Reynold, J. D. and Halkais, J. E. *J. Appl. Polym. Sci.* 1978, **22**, 1643
4 Morgan, R. J. and O'Neal, J. E. *Polym.-Plast. Tech. Eng.* 1978, **10**, 49
5 Moy, P. and Karasz, F. E. *Polym. Eng. Sci.* 1980, **20**, 315
6 Banks, L. and Ellis, B. *Polym. Bull.* 1979, **1**, 377
7 Antoon, M. K., Koenig, J. L. and Serafini, T. *J. Polym. Sci., Polym. Phys. Edn.* 1981, **19**, 1567
8 Angell, C. A., Sare, J. M. and Sare, E. J. *J. Phys. Chem.* 1978, **82**, 2529
9 Couchman, P. R. and Karasz, F. E. *Macromolecules* 1978, **11**, 117
10 Couchman, P. R. *Macromolecules* 1978, **11**, 1156
11 Kelly, F. N. and Bueche, F. *J. Polym. Sci.* 1961, **50**, 549
12 Peyser, P. and Bascom, W. D. *J. Mater. Sci.* 1981, **16**, 75
13 Moy, P. *Ph.D. Thesis*, University of Massachusetts, 1980
14 Ellis, T. S., Karasz, F. E. and ten Brinke, G. *J. Appl. Polym. Sci.* 1983, **28**, 23

15 ten Brinke, G., Karasz, F. E. and Ellis, T. S. *Macromolecules* 1983, **16**, 244
16 Ellis, T. S. and Karasz, F. E. 'Organic Coatings and Plastics Preprints' Am. Chem. Soc. Meeting, Seattle, 1983, p 721
17 Berens, A. R. and Hodge, I. M. *Macromoledules* 1982, **15**, 756
18 Sugisaki, M., Suga, H. and Seki, S. *Bull. Chem. Soc. Jpn.* 1968, **41**, 2591
19 Tan, Y. Y. and Challa, G. *Polymer* 1976, **17**, 739
20 Yannas, J. B. and Tobolsky, A. V. *J. Macromol. Chem.* 1966, **1**, 723
21 Donoghue, E., Ellis, T. S. and Karasz, F. E. 'Analytical Calorimetry' Vol. 5. To be published by Plenum Press, 1983
22 Johari, G. P. *Philos. Mag.* 1977, **35**, 1077
23 Carfagna, C., Apicella, A. and Nicholais, J. *J. Appl. Polym. Sci.* 1982, **27**, 105
24 Bair, H. E., Johnson, G. E. and Merriweather, R. *J. Appl. Phys.* 1978, **49**, 4976; and Johnson, G. E., Bair, H. E., Matsuoka, S., Anderson, E. W. and Scott, J. E. 'Water in Polymers' (Ed. S. P. Rowland) Am. Chem. Soc. Symp. Ser. 1980, **127**, 451
25 Ophir, Z. H., Emerson, J. A. and Wilkes, G. L. *J. Appl. Phys.* 1978, **49**, 5032
26 Crank, J. and Park, G. S. (Eds.) 'Diffusion in Polymers' Academic Press, 1968, London