Effect of thermal history on water sorption, elastic properties and the glass transition of epoxy resins

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The DGEBA/TETA (diglycidyl ether of bisphenol-A/triethylene tetramine) system was examined in postcuring conditions at 100°C for 3 and 6 days. Sorption kinetics and equilibria at different temperatures and mechanical tests have been performed on the two sets of samples. Thermal treatment of the epoxy resin containing sorbed water affects its subsequent water sorption characteristics, elastic modulus and glass transition temperature. Attention has also been given to the effects on solubility on thermal history in the presence of water. It was observed that the saturation values in such systems are determined once the higher temperature of the thermal cycle is defined. The differences in solubility of samples with different hygrothermal history are explained in terms of microcavities that can be formed by effect of crazing in the plasticized system exposed to high temperatures.

INTRODUCTION

Literature results on water sorption in epoxy resins$^{1-3}$ show that both the kinetics and the apparent equilibrium of the sorption phenomena can be strongly influenced by the history of temperature and humidity which the sample has undergone prior to the experiment. Previous studies^{1,4} on composite materials subjected to an arbitrary selected 'real-life' simulation cycle with high peak temperatures (thermal spikes) are very difficult, if not impossible, to interpret. In this work an attempt has been made to study the behaviour of the resin itself when subjected to various thermal histories in the presence of sorbed water.

Although true equilibrium cannot depend on past history, polymeric systems may exhibit apparent equilibrium on a time scale so slow as to make the true one inaccessible to experiment. These effects have been discussed in some detail$^{5-8}$.

In this work, we have performed a series of systematic experiments on water sorption in epoxy resins related primarily to the effects of postcure conditions on the properties of the resulting crosslinked resins. The essential features of a well-defined hygrothermal history on the apparent water sorption equilibrium are also considered. The results have been interpreted on the basis of a physical model for which independent, albeit indirect, experimental support has been obtained.

EXPERIMENTAL

Materials

Specimens were prepared from Epikote 828 (Shell Co.), using commercial triethylene-tetramine (TETA), (Montedison S.p.A.) as curing agent. Distilled water was used in sorption experiments.

Preparation of samples

The resin and crosslinking agent were hand-mixed at room temperature in a 100 to 14 ratio without further purification, and then vigorously mixed under vacuum for 15 min, without any appreciable loss of TETA. The mixture was then poured into PMMA moulds of 0.60 to 3.00 mm thickness, kept under vacuum for 1 h to degas the system completely and then kept in a dry atmosphere at 23°C for 24 h.

Curing was initiated at 80°C under vacuum for 24 h and finally the temperature was brought to 100°C for a curing stage of 3 days. A second batch of samples was prepared in an identical manner; however, the final curing period was increased to 6 days.

Samples were subsequently stored in a dessicator containing anhydrous $CaCl_2$ before determining the effects of hygrothermal history on the resin properties.

Mechanical procedures

Clash–Berg experiments; mechanical tests were performed by using a Clash–Berg torsional stiffness apparatus. Untreated specimens, 60 x 10 x 3.0 mm and otherwise identical samples, previously immersed and saturated in water at two temperatures (75° and 45°C), were subsequently tested over a broad range of temperatures while the specimen was completely submerged in paraffin oil. The angular deflection α, was measured after application of a torque, Mt, per 10 s. The values of the shear moduli were calculated according to the following equation:

$$G(10) = 917 \frac{M_t l}{u\alpha ab}$$

where a, b and l are, respectively, the width, thickness and length of the specimen and u is a tabulated parameter which depends upon the ratio a/b^9.

Stress–strain experiments; specimens, in dumb-bell shape, with thickness of 0.6 mm, a minimum width of 5 mm

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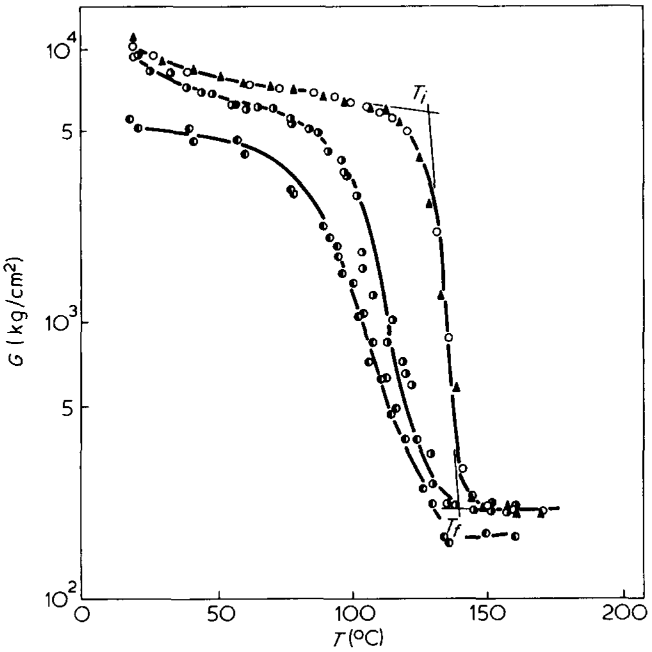

Figure 1 Torsional test results for dry samples: ▲, 6 days cured samples; ○, 3 days cured samples; ◑, saturated 75°C; ◐, saturated 45°C. $T_g = (T_i + T_f)/2$

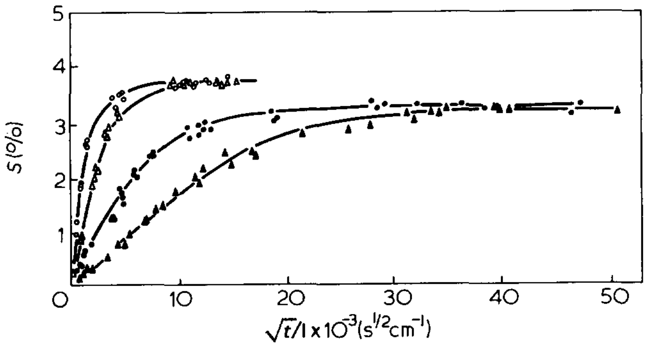

Figure 2 Sorption behaviour of 3 days cured samples as prepared. Solid triangles: 23°C. Solid circles: 45°C. Open triangles: 75°C. Open circles: 90°C

and distance between the grips of 5 cm, were loaded in tension by the Instron tester equipped with a temperature controlled chamber for dry tests and with a thermostatically controlled water bath for tests on saturated samples. Constant temperature level was of 75°C. Constant strain rate of about 0.1 min^{-1} was used.

Sorption kinetics and equilibria

Gravimetric liquid sorption experiments were performed by weighing 3.0 cm x 3.0 cm x ~0.05 cm samples repeatedly on a 'Galileo' analytical balance following repeated immersion in water maintained at constant temperature. The samples were removed from the water, blotted, placed in a weighing bottle, weighed, and then replaced in the constant temperature water bath. Water sorption values were indicated as S, percentage of weight gain from the dry weight, and plotted as a function of $t^{1/2}/l$, where l is the thickness of samples ranging from 0.4 to 0.6 mm, consistent with Fickian behaviour. Sorption equilibria were achieved over 2 to 8 weeks, depending on the temperature of the test.

RESULTS AND DISCUSSION

Effects of postcuring

Mechanical results in torsion experiments for the two batches of samples are reported in *Figure 1*. Mechanical tests do not reveal any significant difference between the samples postcured for 3 and 6 days. Water sorption data for samples postcured for 3 days are reported in *Figure 2*. The four curves refer to sorption into samples immersed in liquid water at four temperatures: 23°, 45°, 75° and 90°C. Some of the samples, first preswollen in water at 90°C for two weeks, were dried under vacuum at temperatures above the glass transition for 24 h, and then weighed again in the dry state. The weight after such a treatment was systematically below the original weight, by an amount of between 0.4 and 0.5%. This suggests that desorption of some low molecular weight component (which may be either the crosslinking agent or the monomer or both) may take place in the swollen state during the sorption test as observed in previous experiments by Faulkner *et al.*[10,11] for trapped solvent in glassy systems. If indeed that is so, the weight increase observed during sorption may be the difference between the water sorbed and the low molecular weight component desorbed so that the data in *Figure 2* may in fact be misleading.

Figures 3 and *4* report sorption data at 23° and 45°C respectively, for samples postcured for 3 days. The two curves in each Figure refer to the sample 'as-prepared' (lower curve), and to the sample after the preswelling–drying procedure. The difference between the final asymptotic values is indeed of the order of 0.5%, which supports the idea that desorp-

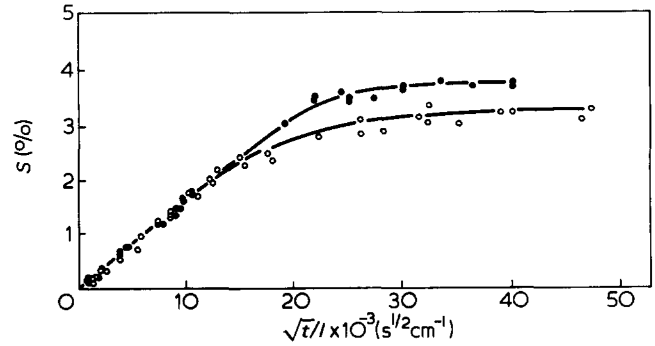

Figure 3 Sorption behaviour at 23°C for 3 days cured samples. Open circles, samples as prepared. Solid circles, samples previously swollen and dried

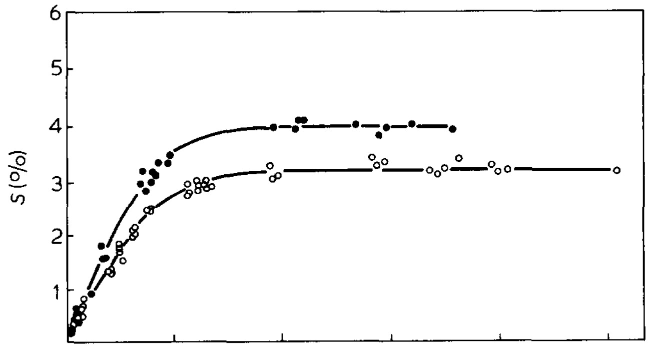

Figure 4 Sorption behaviour for 3 days samples at 45°C. Open circles as prepared. Solid circles, samples previously swollen and dried

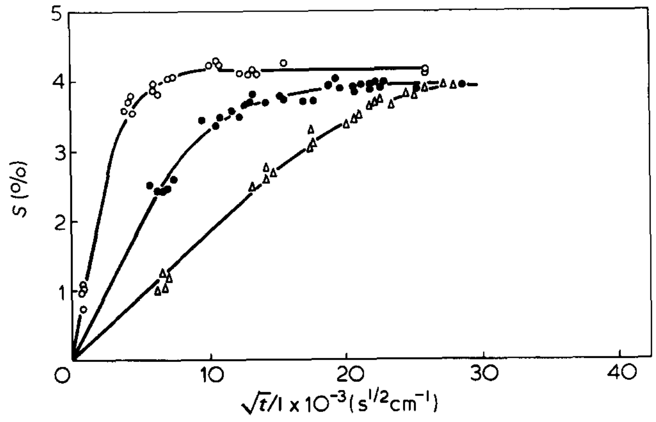

Figure 5 Sorption behaviour for 6 days cured samples. Open triangles, 23°C. Solid circles, 45°C. Open circles, 75°C

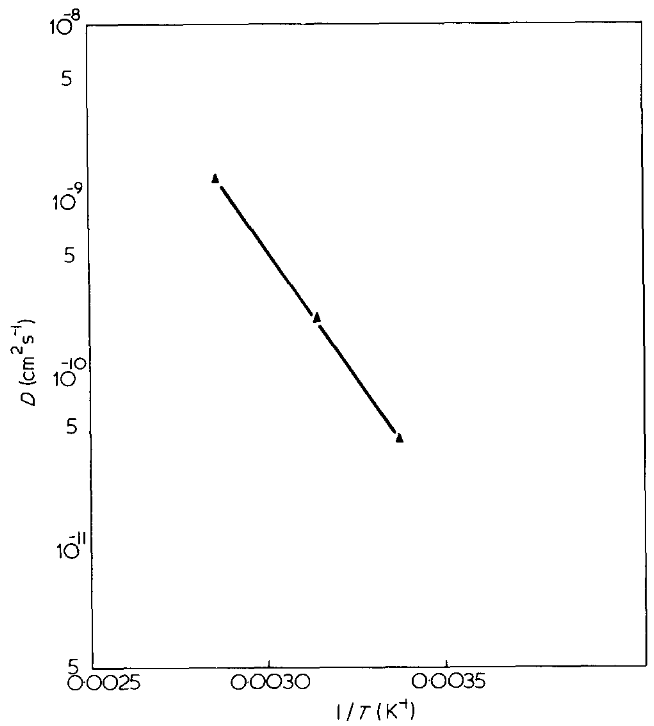

Figure 6 Arrhenius plot for apparent diffusivities extracted from *Figure 5*

tion of the low molecular weight component takes place at the same time as water sorption in 'as-prepared' samples. At 45°C (*Figure 4*) the two processes appear to be about equally as fast, since the two curves are separated both in the kinetics and the asymptotic regions; at 23°C (*Figure 3*) desorption appears to be slower than water sorption.

No such phenomena have been observed with the samples postcured for 6 days, which did not exhibit any measurable weight loss when exposed to the preswelling–drying cycle. The sorption behaviour of samples 'as-prepared', and of samples which had undergone the preswelling–drying cycle was identical. These results suggest that 6 days of postcure at 100°C are required to completely cure the epoxy. Good reproducibility was obtained for the sorption behaviour of such samples in several different tests. All the results discussed in the following refer to 6 days postcured samples.

Effects of hygrothermal history

Water sorption data in 6 day cured samples at 23°, 45°, and 75°C are reported in *Figure 5*. The final asymptotic value of the apparent solubility, S, is a weakly increasing function of temperature. The kinetic behaviour appears to be described adequately by ordinary diffusion, since a finite initial slope is exhibited by the sorption curves in the S vs. $(t^{1/2})/l$ diagrams. Moreover, data obtained on films with varying thickness superimpose on an S–$(t)^{1/2}/l$ diagram (though the range of thickness investigated is not very wide, 0.4 mm $< l <$ 0.7 mm) can extract an apparent diffusion coefficient from the initial slope by making use of the classical early time approximation:

$$\frac{S}{S_\infty} = \frac{4}{\pi^{1/2}}\left(\frac{Dt}{l^2}\right)^{1/2} \qquad (1)$$

where S_∞ is the asymptotic value of S and D is the apparent diffusion coefficient.

Figure 6 is an Arrhenius plot of diffusion coefficients obtained from the initial slopes of the curves in *Figure 5*. A straight line has been drawn through the three data points; the corresponding activation energy is 13.3 kcal/mol.

While the solubility values at 23° and 45°C are not significantly different, the value at 75°C is certainly higher than the other two. We would therefore expect that a sample brought to equilibrium at 75°C, would exhibit water desorption if brought to 23°C at a later stage.

When this experiment was performed, however, the opposite behaviour was observed as shown in *Figure 7*. The sample had apparently reached equilibrium at 75°C; when brought down to 23°C significant additional sorption of water occurred. The new value of the apparent solubility at 23°C is 4.86%, as compared with 3.92% observed in the virgin sample.

Figure 8 shows, on an expanded scale, the additional sorption at 23°C of a sample previously equilibrated at 75°C (open circles). When the same sample is brought back to 75°C, water desorption takes place and the final apparent solubility is the same as that of a virgin sample, i.e. 4.12%. If a sample is first equilibrated at 23°C, then at 75°C, and then again at 23°C, its behaviour (full circles) is the same as that of a sample just equilibrated once at 75°C. It appears that the only relevant parameter of the hygrothermal history of the sample is the highest temperature at which it has been equilibrated with water. A similar analysis has been made for 75°–45°–75°C and 45°–23°–45°C cycles.

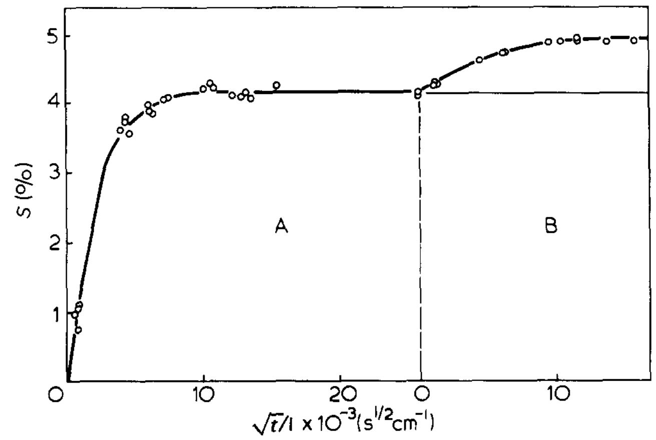

Figure 7 Sorption behaviour at 23°C (B) of a sample previously equilibrated at 75°C (A)

Tentative interpretation of results

The experimental results discussed so far clearly indicate the influence of a hygrothermal history on the apparent sorption equilibria. Such history-dependent apparent equilibria have been discussed in the literature[5–8], and it has been suggested, also in more general terms, that history-dependent thermodynamics may be approached from the viewpoint of internal, or hidden, state variables[12,13]. Such an approach has been explicitly considered for the modelling of diffusion behaviour in polymeric solids[14]. Specifically, we may assume that the state of the sample may be identified (in addition to the usual state variables such as temperature and pressure) by at least one additional state variable x.

For the phenomena considered here, a concrete physical interpretation for the internal state variable x may be suggested: x may be regarded as the volume percent of microcavities which may form in the sample under the combined action of temperature and humidity. This specific physical identification of x, however, is not crucial to the subsequent analysis, and although we will refer to volume percent microcavities in the following, we do not claim to have definite experimental proof that such microcavities do form, though physical support for this kind of interpretation of x is discussed below.

The apparent solubility in any given sample, S_∞, may be regarded as the sum of two terms, the first one, S_p, representing the equilibrium content of water in the compact resin, and the second, S_2, representing the amount of water which may be present in the microcavities:

$$S_\infty = S_p + S_2$$

S_2 is equal to $\rho \cdot x$, where ρ is the density of the water at that temperature and x the volume fraction of microcavities.

Assuming a standard state at 23°C in which $S_2 = 0$ and also that the rate of formation of microcavities at 75°C is sufficiently fast, so that while sorption proceeds to apparent equilibrium, the value of S_2 also reaches some equilibrium value S_2^{75}.

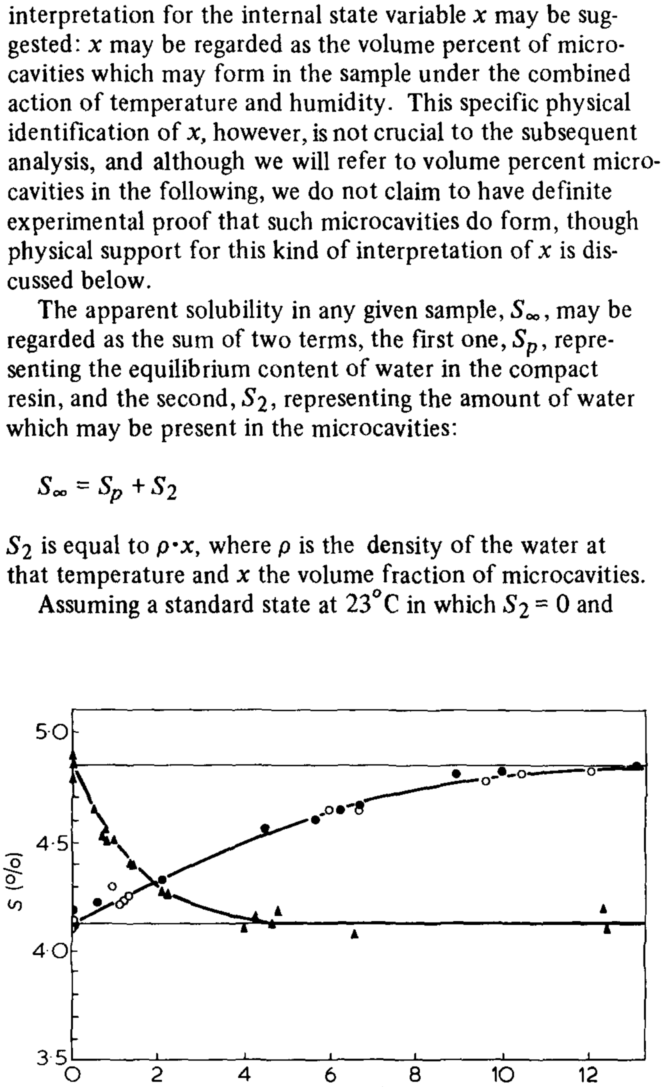

Figure 8 Sorption behaviour at 23° C of a sample previously equilibrated at 75° C (open circles). Desorption behaviour when same sample is brought back to 75° C (triangles). Sorption at 23° C with different temperature history, see text (solid circles)

A sample previously equilibrated at 75°C is characterized by a value $S_2 = S_2^{75}$, while a virgin sample is characterized by $S_2^{23} = 0$ (S_2^{75} can be then calculated as: $S_\infty^{75}(23) = 4.86\% = S_p(23) + S_2^{75}$, but $S_p(23)$ is obtained from $S_\infty^{23}(23) = S_p(23) = 3.92\%$, being $S_2^{23} = 0$ by definition then: $S_2^{75} = 4.86\% - 3.92\% = 0.96\%$). The temperature of measurement is given in brackets and the equilibrating temperature is given by a superscript.

A similar analysis on S at 23°C for virgin and first equilibrated at 45°C samples yields for S_2^{45}, the equilibrium microcavities vol% at 45°C, the value 0.23%. It may be observed that a definite decreasing trend is observed with increasing temperature for the calculated values of S_p reported in the sixth column of *Table 1*, while no such regular trend is observed for the entries in the second column. Assuming that the density of water is constant and unity we will have: $S_2 = x$.

An alternative interpretation can be suggested from previous literature[6–8] on relaxation phenomena occurring in the swollen state. Samples allowed to be saturated in water at high temperatures can show a more relaxed glassy state compared with that of samples saturated at low temperatures. In the more relaxed state water sorption can take place when the water environment is cooled to a lower temperature.

The tentative interpretation based on microvoid formation would need to be subjected to scrutiny. The following points are offered as support:

(1) the difference between the two values of $S_2^{75} = 0.94$ and $S_2^{45} = 0.23$ is 0.71%. This compares very favourably with the different apparent solubilities at 45°C observed in the 45°–75°–45°C cycle: $S_\infty^{75}(45) - S_\infty^{45}(45) = 4.60\% - 3.70\% = 0.70\%$.

(2) Clash–Berg mechanical tests have been performed on samples previously saturated with water, at temperatures of 75° and 45°C. The results are reported in *Figure 1*. We can notice that shear modulus drop above T_i (initial glass transition temperature as defined in *Figure 1*) takes place for dry samples within a small temperature range while the range becomes larger for saturated samples. This can be interpreted as favouring water desorption from the samples during testing times, at temperatures above the initial glass transition temperature.

Water desorption at temperatures below T_i can be assumed to be negligible in relation to the still glassy state of the system. This assumption seems to be confirmed by the fact that T_i for the dry system, as for those saturated at 75° and 45°C, are well separated in the temperature scale while T_f, the final glass transition temperatures, are quite coincident.

Glass transition temperatures for saturated samples, reported in *Table 2*, can be then calculated as $T_i + \Delta T/2$, where ΔT is the value $(T_f - T_i)$ extracted for dry samples.

Table 1 Effect of temperature and prior history on the apparent sorption equilibria

Temperature (°C)	S_∞ for virgin sample, (%)	S_∞ for sample first equilibrated at 75°C (%)	S_∞ for sample first equilibrated at 45°C (%)	Calculated volume void fractions (%)	Calculated Sp (%)
23	3.92	4.86	4.15	0	3.92
45	3.90	4.60	3.90	0.23	3.67
75	4.12	4.12	–	0.94	3.18

Table 2

Samples	T_g (°C)	S_p (%)
Dry	135	0.0
Saturated, 75°C	108	3.18
Satureated, 45°C	88	3.63

It may be observed that the samples saturated at 45°C show lower moduli and glass transition temperatures than those saturated at 75°C, in spite of the more plasticized state that can be expected because the value of S_∞ at 45°C (3.90%) is less than the value at 75°C (4.12%). Yet, if microcavities are formed, we would expect that only the water actually dissolved in the compact resin (the value of S_p) is responsible for the plasticizing action; and indeed the value of S_p ar 45°C (3.63%) is larger than the value at 75°C (3.18%).

(3) The largest value of x reported in *Table 1* is 0.94%; this value is not expected to change the mechanical properties significantly: the shear modulus would only decrease about 3% (15), well below experimental accuracy.

(4) Stress–strain mechanical tests on dry and previously equilibrated 75° and 45°C samples have also been performed. For saturated sample tests have been run in a water environment to avoid moisture desorption. At a temperature of 75°C (*Figure 9*) a brittle behaviour for dry and 75°C saturated samples and a ductile behaviour for 45°C saturated samples has been observed, in accordance with the shear moduli and glass transition temperatures calculated from *Figure 1*.

Water content changes in samples saturated at 45°C and exposed to a water environment at 75°C were calculated to be negligible in the short stress–strain time test.

(5) Stress-induced crazing in epoxy resins and in various glassy systems has been reported in the literature[3,16,17]; furthermore, the energy required for the craze formation is known to decrease with increasing temperature[17,18].

Therefore, the interpretation based on the formation of microcavities, favoured at higher temperatures, is in agreement with the available information.

A sample previously equilibrated at 75°C, dried and brought to temperatures above the glass transition temperature, exhibits the same sorption behaviour as virgin samples. It is indeed physically intuitive that any microcavities which may have formed would disappear through the annealing process.

CONCLUSIONS

The reproducible and well-defined influence of thermal history on water sorption in epoxy resins has been determined experimentally; tentative interpretations of the effect have been suggested.

Future work in the area can usefully be carried out in two directions. First, experiments would need to be performed where sorption from a vapour (rather than liquid) phase is monitored. Such experiments would allow a greater flexibility of operating conditions (fugacity and temperature of H_2O in the external phase could be controlled independently) and *in situ* continuous monitoring of the weight of the sample. Therefore, more precise and meaningful data could be obtained for the kinetic part of the sorption behaviour.

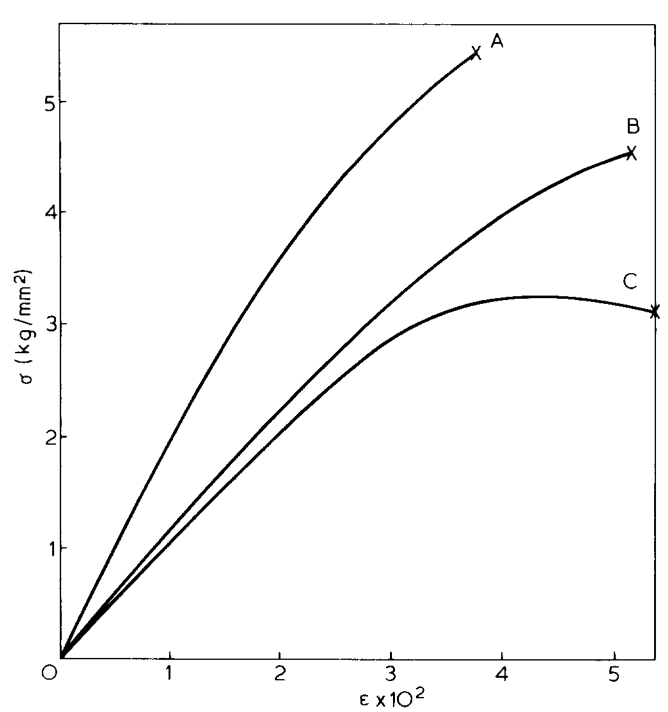

Figure 9 Stress–strain curves at T = 75°C for A, dry; saturated at B, 75° and C, 45°C in epoxy resins samples

The second line of investigation, to be developed after more extensive experimental evidence is available, is the mathematical modelling of the observed behaviour, possibly along the lines suggested by available thermodynamic and kinetic theories of systems with internal state variables.

In particular, since the structure induced by the hygrothermal effects discussed in this work is of a two-phase nature (microcavities and compact polymer), modelling of the kinetic behaviour could be based on concepts drawn from the dual sorption theory, which has recently been successfully applied to a variety of diffusion phenomena in structured materials[19,10]. Work along both directions is currently in progress.

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