

Swelling of DGEBA/DDA epoxy resin during hygrothermal ageing

G. Z. Xiao and M. E. R. Shanahan*

Centre National de la Recherche Scientifique, Ecole Nationale Supérieure des Mines de Paris, Centre des Matériaux, B. P. 87, 91003 Evry Cedex, France
 (Accepted 25 July 1997)

Understanding the swelling behaviour of polymers during hygrothermal ageing is potentially important for both composite materials and structural adhesives, since swelling may significantly influence the mechanical behaviour due to the increase of residual stresses at interfaces. In this article, the swelling of a DGEBA/DDA epoxy resin has been investigated. It has been found that the swelling of the polymer lags behind the behaviour predicted from the ideal mixing law. More importantly, our results show that swelling induced by hygrothermal ageing is not fully reversible, particularly at higher temperatures. Based on the assumption that water diffusion is governed by a classic diffusion controlled process and a swelling controlled process, a model is proposed to describe water uptake and swelling kinetics during hygrothermal ageing. The results show that the model is in good agreement with the experimental values. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: diffusion; epoxy resin; hygrothermal ageing)

INTRODUCTION

Diffusion of water into epoxy-based adhesives and epoxy-based composites has been well documented in the literature. Various models have been proposed to describe the kinetics of water diffusion^{1–6}. More favoured treatments include those based on Fick's law^{1,2}, and the Langmuir two-phase model^{3,4}. However, there is no universal model to cover all types of water diffusion. In most cases, each model is found to be only relevant to a particular material under a particular set of conditions. This is believed to be due to the complexity of the molecular interactions between water and the resin, as well as the consequence of those interactions.

Swelling is a specific response accompanying moisture diffusion in epoxy resins or composites based on them. It is very important in both composites and adhesive joints because it can significantly influence mechanical behaviour through the build-up of residual stresses at and near interfaces.

Swelling phenomena have been observed by various researchers^{7–11}. It has been found generally that the volume of the resin-containing water is less than that of the volume of the water absorbed plus the volume of dry resin^{7–10}. In addition, different relationships between the swelling and the moisture content have been noted. Wright⁸ and Gazit¹¹ found a linear relationship between the amount of water absorbed and overall volume, or length, change above relatively very low concentrations of water. Adamson⁷ found that swelling is concentration and temperature dependent, while MacKague *et al.*⁹ concluded that the relation between the length change and the moisture content can be best described by a power law. Their results also suggested that swelling is only concentration dependent.

Although the diffusion kinetics of water in epoxy resins has been well documented, the swelling kinetics during the hygrothermal ageing period have been scarcely reported.

Also rarely studied is the reversibility of water uptake and swelling of polymers, which is believed to be an important issue, since irreversible swelling could permanently damage the material.

The present paper presents experimental findings regarding isothermal water uptake and swelling behaviour of a DGEBA/DDA epoxy resin below its glass transition temperature (T_g). Also presented are the results of volume changes during the desorption process, which can be used to clarify whether the swelling is reversible. Finally, we suggest a tentative model to explain the swelling behaviour.

EXPERIMENTAL

A model epoxy resin based on diglycidyl ether of bisphenol A (DGEBA) and dicyandiamide (DDA) without fillers was studied. The material was supplied by CECA S. A. France. This resin was cured by maintaining the polymer at a temperature of 140°C for 1 h after heating from ambient temperature at a rate of 3°C/min. Both DSC and DMTA studies confirmed that the resin was fully cured under these conditions by leading to a maximum possible value of T_g . Moreover, FTIR analysis confirmed that there was no residual curing agent or epoxide groups in the cured resin. After curing, the polymer was cut into plates with dimensions of approx. 18.5 mm × 5.6 mm × 1.5 mm.

Specimen weight was determined using a METTLER AT250 analytical balance which was accurate to ± 0.05 mg. Weight change was found negligible during the measurement, even after prolonged exposure to water.

Specimen volume was calculated from length, thickness, and width measurements made with micrometers accurate to ± 0.001 mm. For each specimen, thickness and width were calculated as the average of five measurements, one near each end, and three at approximately equidistant positions along the length. Length was determined from the average of six measurements by turning around the sample.

* To whom correspondence should be addressed

Dimensional changes were measured at least 2 min after removal from water or from the drying oven.

Before ageing, the specimens were dried in a desiccator at 40°C and weighed periodically until the weight change was less than 0.08% per week. The weight and volume of dry resin were recorded as initial values for the resin. Specimens were then placed in distilled water at 20, 40, 50, 70 and 90°C.

At different time intervals, samples were taken out, surface-dried, weighed, volume change estimated and then returned to their water. For each of the temperatures 50, 70 and 90°C, the average of three replicates was treated. After the water absorption had approached equilibrium, specimens were removed from their water and dried until a good estimation of the final equilibrium weight after desorption could be obtained. The weight and volume changes during these desorption processes were also followed.

RESULTS AND DISCUSSION

Isothermal water absorption and swelling

Figure 1 shows experimental results for water uptake of DGEBA/DDA epoxy resin after immersion at 20, 40, 50, 70 and 90°C. Also shown are lines corresponding to predictions of our model, which will be discussed later. Although not shown for clarity, the average standard deviation corresponds to a value of 8×10^{-4} on the $\Delta W/W_0$ scale. From Figure 1, several noteworthy points are apparent.

Firstly, the absorption curve can be treated as linear with the square root of time from the beginning to a few per cent weight gain or higher. This linearity suggests that absorption is predominantly diffusion controlled in this region^{2,12}.

Secondly, increasing temperature increases the initial water diffusion rate and the final weight gain. Increasing diffusion rate with temperature is in agreement with classic diffusion theories¹⁻⁴.

Thirdly, when the temperature is below 70°C, the absorption rate appears to decrease (on a $t^{1/2}$ scale) when the water uptake approaches ca. 5%; final moisture content is approached asymptotically. These observations suggest

that the final absorption stages are delicate to observe. Adamson⁷ commented that this phenomenon may reflect the difficulty with which water enters the highly cross-linked micro-gel particles or micelles within the resin, while the two-phase model suggests that it is due to the reversible trapping of water by certain functional groups in the resin³.

Finally, in the case of absorption at 90°C, the resin starts to lose weight after attaining a maximum value, even though the observed absorption was not accompanied by any visible damage to the material except colour change. In previous work¹³, we concluded that water could cut the intercross-linked chains during ageing, and that the scissioning products can leach out of the resin. This finding probably explains the results obtained at 90°C shown in Figure 1.

Figure 2 presents temperature effects on the swelling of the DGEBA/DDA epoxy resin during hygrothermal ageing (experimental results and theoretical curves). We shall discuss theoretical aspects later. For all the temperatures, swelling takes place very quickly during the initial ageing period, then slows down and approaches an equilibrium, even though this may take a much longer time. Temperature significantly affects the swelling process, particularly the initial swelling rate (as shown in Figure 2). Another point worth noting in Figure 2, is that the difference between behaviour at 90 and 70°C is much more significant than that between other equivalent temperature intervals.

Irreversible water uptake and swelling

To study the reversibility of water uptake and swelling during hygrothermal ageing, specimens aged at 50, 70 and 90°C were removed from water after their weight increase approached the asymptotic final value. They were then dried at their initial ageing temperature and subsequently further dried at 70 and 90°C (depending on the specimen). Weight and volume changes during the drying period were monitored. The results are shown in Figures 3 and 4.

As can be seen from these two graphs, both water uptake and swelling induced during the ageing period were only partially reversible. After drying to (asymptotic) equilibrium values, a net mass increase was observed,

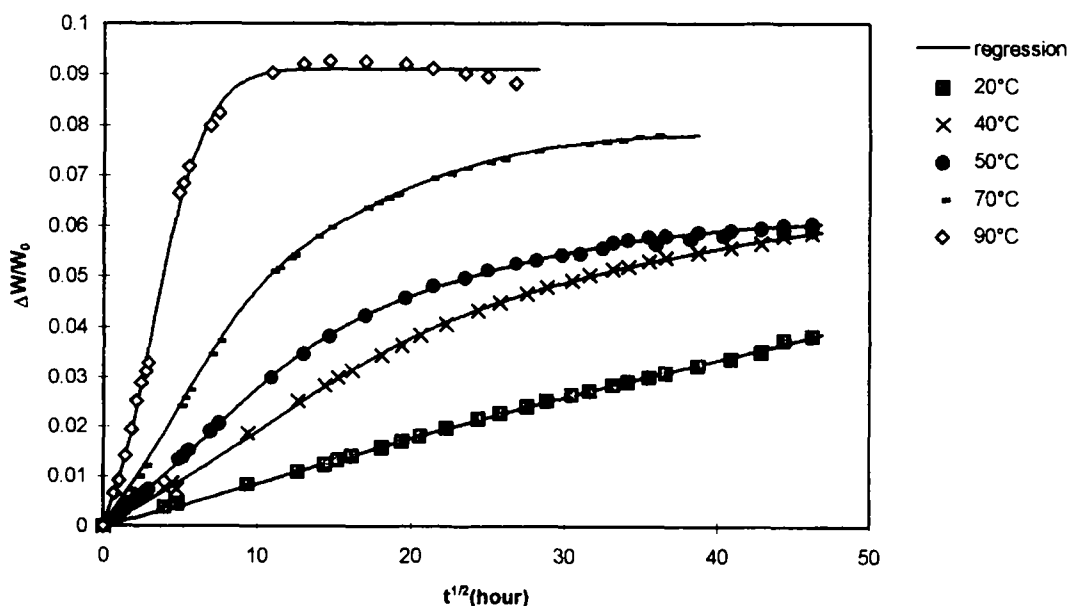


Figure 1 Isothermal water uptake of DGEBA/DDA epoxy resin with non-linear regression curves corresponding to equations (11)–(13)

compared with the unaged polymer, suggesting the presence of some chemically attached water. In addition, some degree of volume increase was also noted after long-term drying, with the irreversible swelling increasing with the ageing temperature. These results, particularly the dilation, suggest irreversible degradation after ageing.

An interesting phenomenon in *Figure 3* can be seen, namely, the water absorbed by the resin at lower temperatures is desorbed with difficulty at the same lower temperatures. To desorb all reversibly absorbed water, a higher temperature is needed, suggesting that some func-

tional groups in the resin can form very strong interactions with water.

Relations between water uptake and swelling

We have compared actual and expected volume increases due to water absorption at the five temperatures studied. *Figure 5* gives a typical example; that at 70°C. In *Figure 5*, we present the experimentally found fractional polymer volume increase $\Delta V/V_0$, (V_0 is initial dry volume), as a function of the (hypothetical) equivalent value $\Delta V_m/V_0$, calculated from mass increase and the assumption of

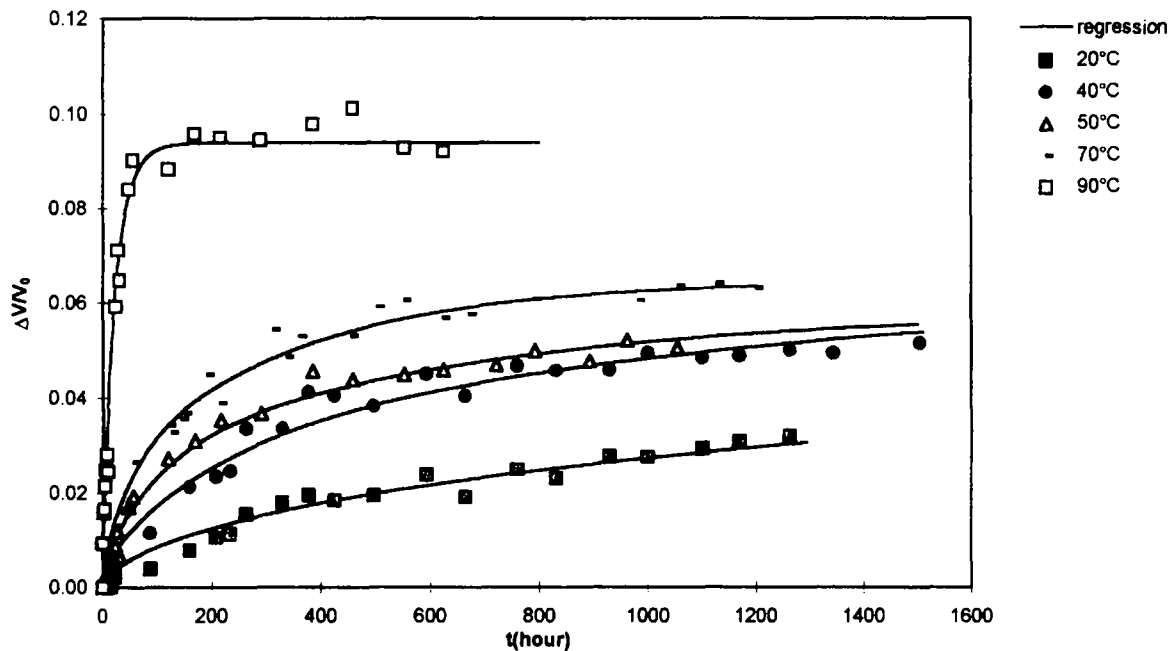


Figure 2 Volume change of DGEBA/DDA epoxy resin during hygrothermal ageing with non-linear regression curves corresponding to equations (11) and (12)

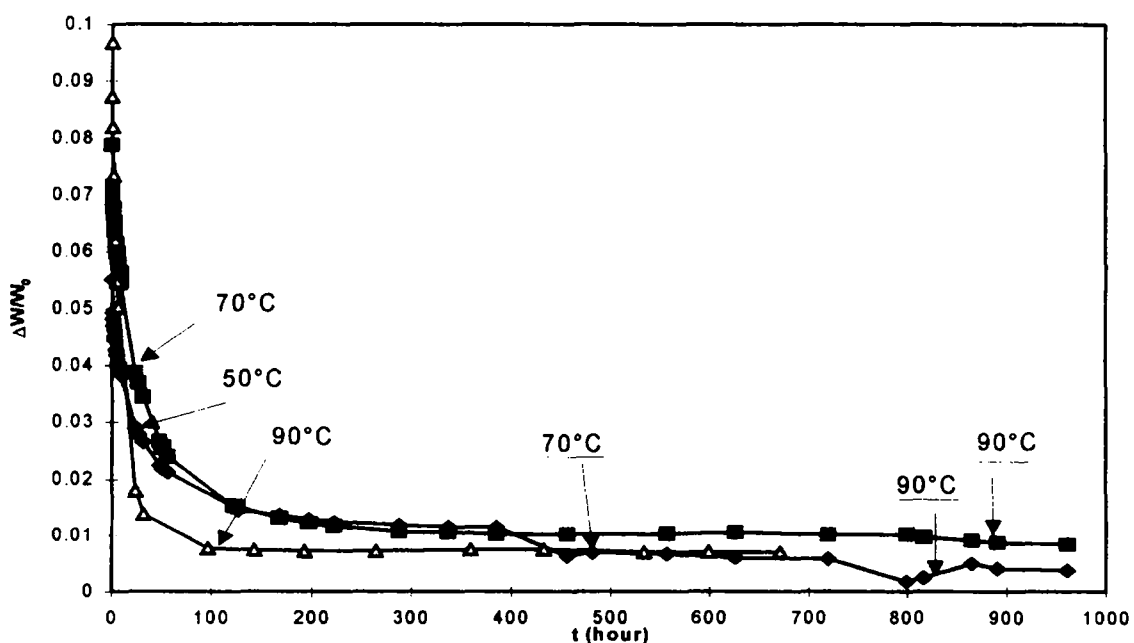


Figure 3 Weight change of the aged specimens during the drying process: underlined temperature and corresponding arrows indicate changes in drying temperature

absorbed water retaining its intrinsic density ($\Delta V_m = \Delta W / \rho_w$, where ρ_w is the density of water). Also shown in this figure is the line corresponding to the prediction of our model.

As can be seen, the observed swelling is not in agreement with the ideal mixing law, i.e. the volume increase of the polymer during the ageing period is not equal to the volume of the water absorbed. These results are in agreement with those reported in the literature⁷⁻¹⁰. The exception to the type of behaviour demonstrated by Figure 5 is that corresponding to ageing at 90°C and shown in Figure 6 (to be discussed later).

Additionally, a line of slope 1 is also shown in Figure 5, which represents the swelling that would be expected if the volumes of the dry resin and the absorbed water were additive. The results of Figure 5 can be roughly divided into

two regions. In region I, from essentially zero moisture content up to a certain value, swelling of the resin is less than the volume of water absorbed. In region II, corresponding to higher water uptake, additional swelling of the resin is approximately equal to the volume of absorbed water. Results for ageing at 90°C, however, show a somewhat different trend, as indicated in Figure 6. Initially, calculated and measured swelling values are the same, within experimental limits. After a value of $\Delta V_m / V_0$ of ca. 0.01, the behaviour deviates, much as for the other temperatures. First, the measured swelling rate drops below the value predicted from the law of mixtures and then, from ca. 0.06 upwards, the rates again become similar. This unexplained initial behaviour may well be related to T_g , as discussed below.

It has been theoretically postulated and experimentally

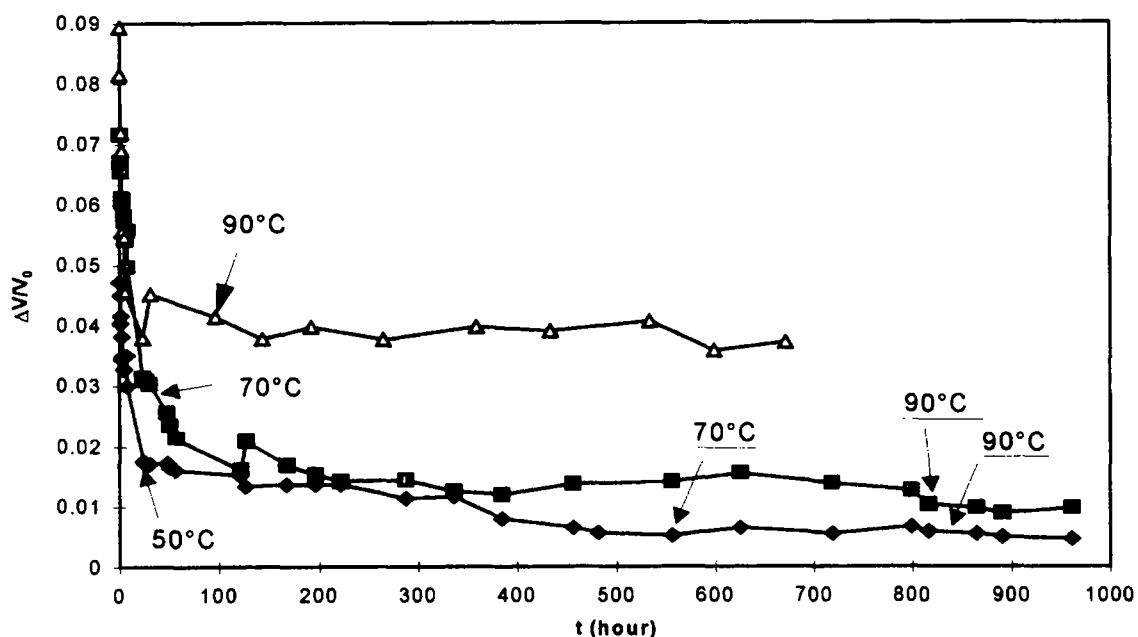


Figure 4 Volume change of the aged specimens during the drying process: underlined temperature and corresponding arrows indicate changes in drying temperature

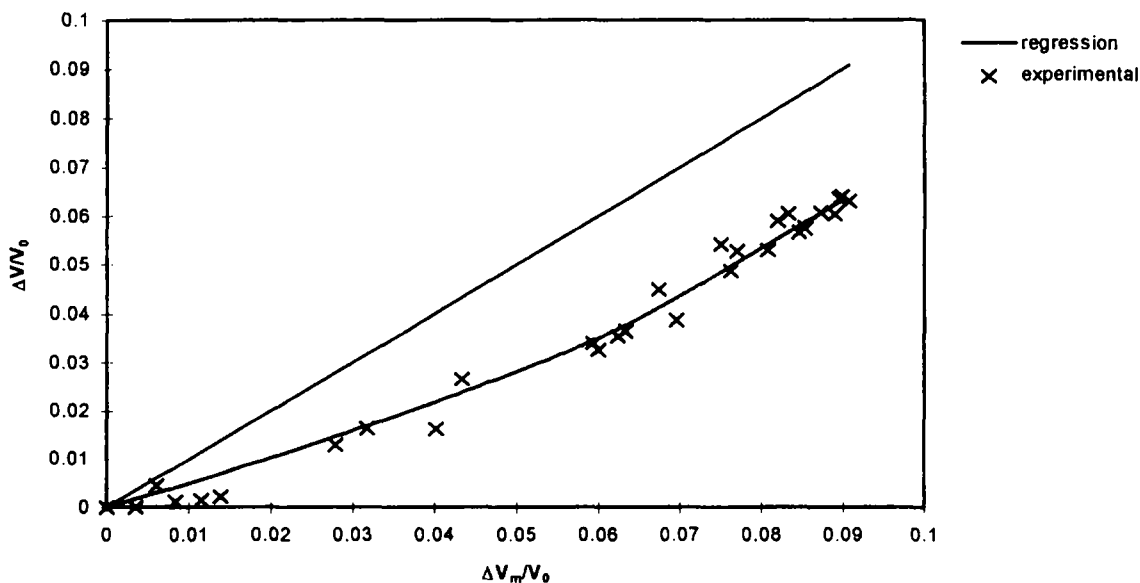


Figure 5 Experimental volume increase, $\Delta V / V_0$, versus hypothetical volume change, $\Delta V_m / V_0$, based on assumption of absorbed water retaining its intrinsic density. Results for ageing at 70°C with non-linear regression curve corresponding to equations (11) and (12)

confirmed that when water enters epoxy resin, some molecules will interact with the resin, since many functional groups are present^{3,7,13-15}. As the epoxy network is held together by hydrogen bonds and other secondary valence forces between adjacent polymer chains, these interactions will break interchain bonds by forming hydrogen bonds or other strong bonds with the functional groups in the resin. Such an effect could also partially be caused by chain scission^{13,15}. This water is termed bound water. Rupture of interchain bonds permits the polymer network to expand through relaxation of the stresses produced by osmotic pressure. The process is entropy driven¹⁶. Therefore, bound water induces swelling during hygrothermal ageing.

In addition to bound water, there is some free volume in the polymer (including voids). Obviously, water can occupy these free volumes. This water is termed free water. It is believed that the free water does not induce swelling⁷, therefore, any volume change of the polymer will not be in agreement with the ideal mixing law.

We have also compared actual and expected volume changes during desorption for the specimens aged at 50, 70 and 90°C. Figure 7 gives a typical example (specimen aged at 70°C). As can be seen, the real volume change also deviates from the value predicted by the ideal mixing law before the specimen is fully dried. However, as full drying is approached, the extra volume of the specimen is roughly equal to the volume of the retained water. This is true at 50 and 70°C. As previously mentioned, strange behaviour occurs at 90°C: the corresponding data at this temperature are given in Figure 8, which shows a much larger retained swelling than the volume of the water retained.

The significantly different swelling behaviour observed between the specimens aged in 90°C water and the specimens aged in other hygrothermal ageing conditions might suggest that after a certain period of ageing, the glass transition temperature of the material was lowered to below 90°C, but higher than 70°C. This hypothesis has been confirmed elsewhere by our DMTA test.

Modelling of isothermal water diffusion and swelling kinetics

The results discussed above show: (a) water uptake is initially diffusion controlled; (b) the final water uptake

proceeds very slowly; and (c) the swelling of the polymer at later stages approximately equals the volume of water absorbed. We therefore postulate that two simultaneous processes occur during hygrothermal ageing, namely a diffusion controlled process and a swelling controlled process. The former will be considered to be virtually instantaneous (compared with diffusion). Some water molecules will undoubtedly fill available free volume whilst others will become rapidly bound, leading to secondary (and possibly some primary) bond failure and polymeric network dilation. We assume that the ratio of the two 'types' of water remains approximately constant. The latter process, in our simplified model, corresponds to time-dependent behaviour. Some water will take a non-negligible time to lead to network bond failure and/or the corresponding polymer relaxation will be time dependent. (We shall not draw any distinction between these two possibilities.)

As a consequence, during the diffusion controlled process the swelling of the resin can be assumed to be directly proportional to the water uptake:

$$\Delta V_d = A \Delta W_d \quad (1)$$

where A is a constant, ΔW_d is the water uptake during the diffusion controlled process, and ΔV_d is the corresponding volume increase.

The swelling controlled process will include the attachment of water to some functional groups in the polymer which occurs relatively slowly, and the viscoelastic relaxation of the polymer, which may accommodate the further influx of water. To a first approximation the volume increase and the weight gain during this process can be approximated on a one-to-one basis to give:

$$\Delta W_s = \rho_w \Delta V_s \quad (2)$$

where ΔV_s is the volume increase during the swelling controlled process, ΔW_s is the corresponding water uptake, and ρ_w is the density of water.

Existence of this swelling controlled process may explain the results in the second stage of swelling, in which the rate of swelling equates approximately with the rate of water absorption (Figure 5).

The total water uptake and volume increase during

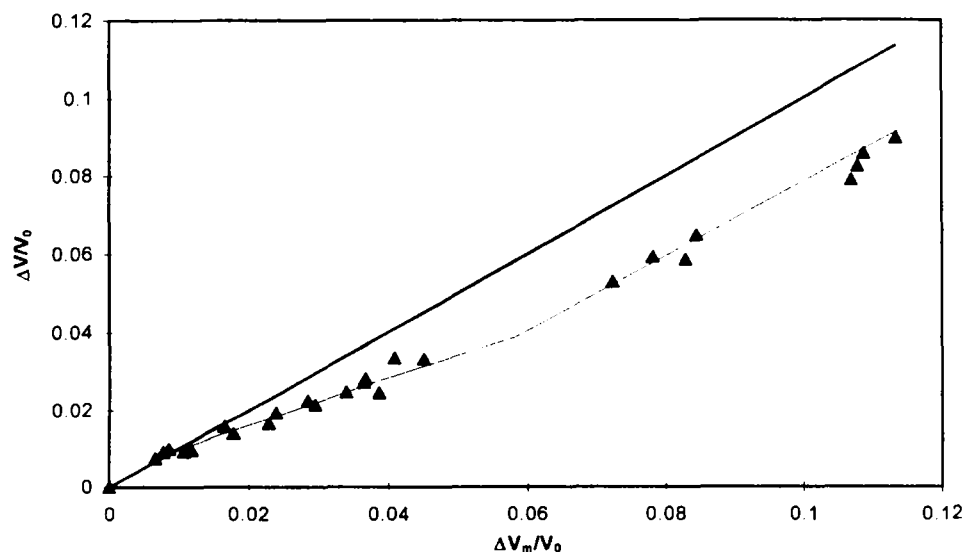


Figure 6 As for Figure 5, but ageing at 90°C

hydrothermal ageing can, therefore, be treated as the summation of their respective values during the diffusion controlled and the swelling controlled process.

$$\Delta W = \Delta W_d + \Delta W_s \quad (3)$$

$$\Delta V = \Delta V_d + \Delta V_s \quad (4)$$

where ΔW and ΔV are respectively the weight uptake and volume increase during the ageing period.

According to Crank¹, the diffusion controlled process can

be described by Fick's second law. Hence, we have:

$$\Delta W_d = \frac{4\Delta W_{d\infty}}{h} \sqrt{\frac{Dt}{\pi}}; t \leq \frac{0.05h^2}{D} \quad (5)$$

$$\Delta W_d = \Delta W_{d\infty} \left[1 - \frac{8}{\pi^2} \exp\left(-\frac{D\pi^2 t}{h^2}\right) \right]; t > \frac{0.05h^2}{D} \quad (6)$$

where D is the diffusion coefficient, h is the thickness of the specimen, and $\Delta W_{d\infty}$ is the maximum weight gain through the diffusion controlled process.

Combining equations (1), (5) and (6), we obtain the

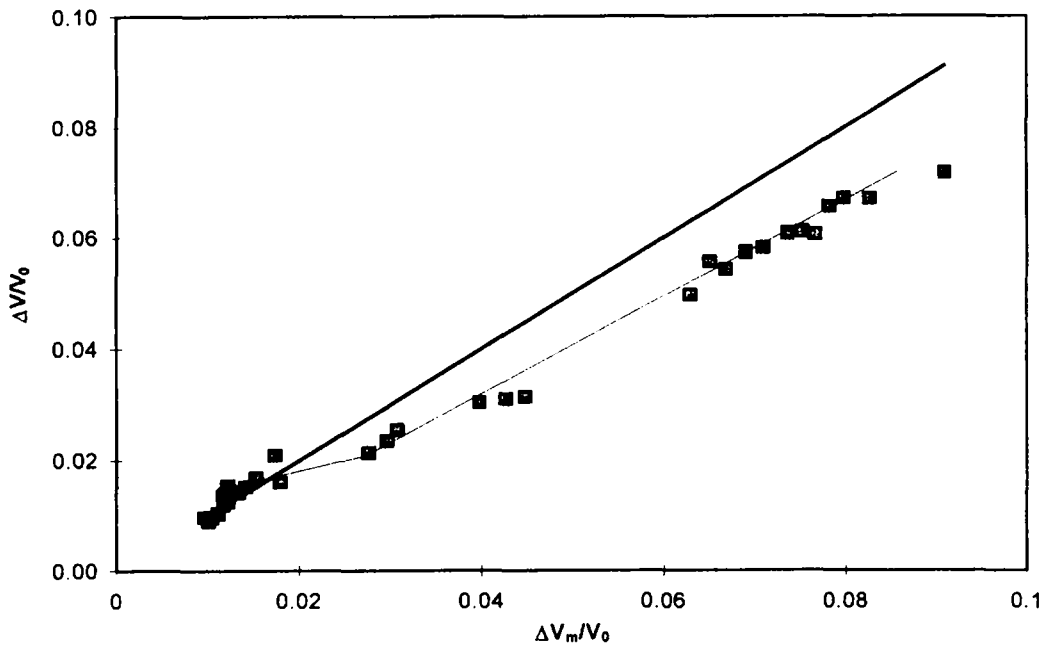


Figure 7 Real volume change during the desorption process versus the volume change predicted by the ideal mixing law (specimen aged in 70°C water)

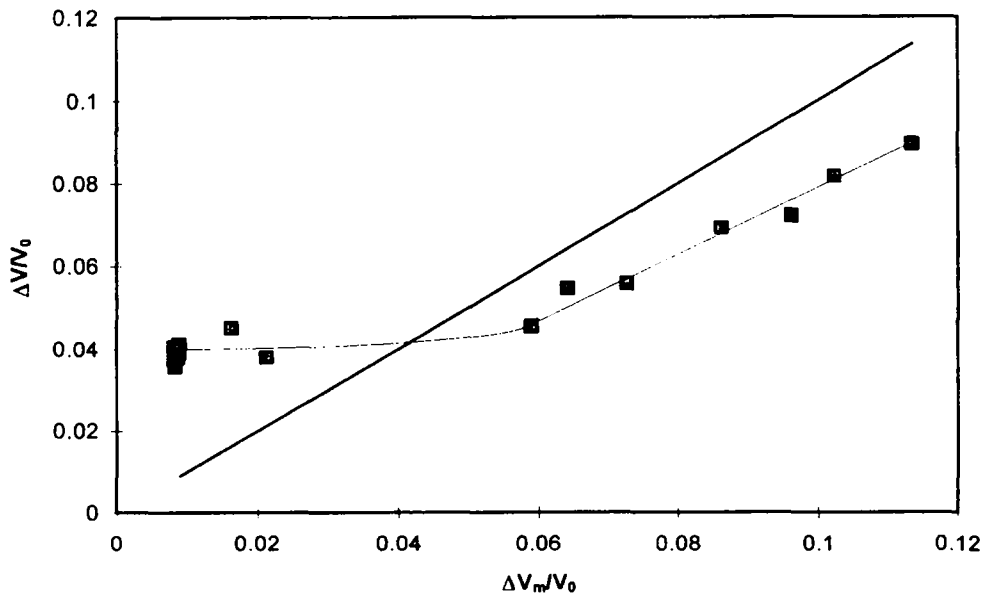


Figure 8 As for Figure 7, but ageing at 90°C

volume change due to the diffusion controlled process as:

$$\Delta V_d = \frac{4\Delta V_{d\infty}}{h} \sqrt{\frac{Dt}{\pi}}; t \leq \frac{0.05h^2}{D} \quad (7)$$

$$\Delta V_d = \Delta V_{d\infty} \left[1 - \frac{8}{\pi^2} \exp\left(-\frac{D\pi^2 t}{h^2}\right) \right]; t > \frac{0.05h^2}{D} \quad (8)$$

where $\Delta V_{d\infty}$ is the maximum volume increase through the diffusion controlled process.

For the swelling controlled process, to simplify the mathematical work, we assume to first approximation that the volume increase is directly proportional to the remaining swelling capacity, i.e. first-order kinetics:

$$\frac{d(\Delta V_s)}{dt} = k(\Delta V_{s\infty} - \Delta V_s) \quad (9)$$

where $\Delta V_{s\infty}$ is the maximum volume gain attainable through the swelling controlled process, and k is a rate constant.

With the initial conditions of $\Delta V_s = 0$ at $t = 0$, equation (9) is readily solved to give:

$$\Delta V_s = \Delta V_{s\infty} [1 - \exp(-kt)] \quad (10)$$

By combining equation (1), equation (4), equation (7), equation (8) and equation (10), we obtain the swelling kinetics during the ageing period as:

$$\Delta V = \frac{4\Delta V_{d\infty}}{h} \sqrt{\frac{Dt}{\pi}} + \Delta V_{s\infty} [1 - \exp(-kt)]; t \leq \frac{0.05h^2}{D} \quad (11)$$

$$\Delta V = \Delta V_{d\infty} \left[1 - \frac{8}{\pi^2} \exp\left(-\frac{D\pi^2 t}{h^2}\right) \right] + \Delta V_{s\infty} [1 - \exp(-kt)]; t > \frac{0.05h^2}{D} \quad (12)$$

The total water uptake of the polymer is then given by:

$$\Delta W = \Delta W_d + \Delta W_s = \Delta V_d/A + \rho_w \Delta V_s \quad (13)$$

Equations (11)–(13) have been applied to experimental data using regression analysis, and as can be seen in *Figures 1, 2, and 5*, agreement is satisfactory. The simple assumption that the swelling controlled process is governed by first-order kinetics seems amply justified.

However, as usual, results at 90°C differ! The corresponding regression lines of *Figures 1 and 2* are therefore only approximate. Indeed, in *Figure 1*, experimental results show a peak in weight gain followed by slight weight loss. This is probably due to the onset of primary bond chain scission and leaching, as described elsewhere^{13,18}.

Table 1 gives values of the parameters in equations (11)–(13) obtained from the non-linear regression analysis. The diffusion coefficient obtained from this analysis is between $2.15 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$ (20°C) and $5.11 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ (90°C), which is quite reasonable and similar to values given in the literature^{3,15,17}. Values of $\ln D$ are plotted against reciprocal temperature $1/T$ in order to apply the Arrhenius relationship:

$$D = D_0 \exp\left(-\frac{\Delta H}{RT}\right) \quad (14)$$

where D_0 is a constant (equal to the extrapolated value of D for $1/T = 0$), ΔH is the activation energy for diffusion, R is the universal gas constant and T is the absolute temperature of diffusion (*Figure 9*).

Using a regression analysis we obtain $\Delta H = 70.4 \text{ kJ mol}^{-1}$. This value is similar to that reported in Ref. 15.

$\Delta V_{d\infty}$ is the maximum volume increase corresponding to

Table 1 Simulation results for the data shown in *Figures 1 and 2*

Parameters	20°C	40°C	50°C	70°C	90°C
$10^{-8} D$ ($\text{cm}^2 \text{ s}^{-1}$)	0.0215	0.0986	0.792	1.58	5.11
$\Delta V_{d\infty}$ (%)	5.4	3.6	2.3	2.1	2.3
$\Delta V_{s\infty}$ (%)	0.4	1.2	2.7	3.5	5.7
$10^{-3} k$ (h^{-1})	3.31	8.02	1.55	2.95	3.81
A ($\text{cm}^{-3} \text{ g}^{-1}$)	0.831	0.747	0.677	0.474	0.677

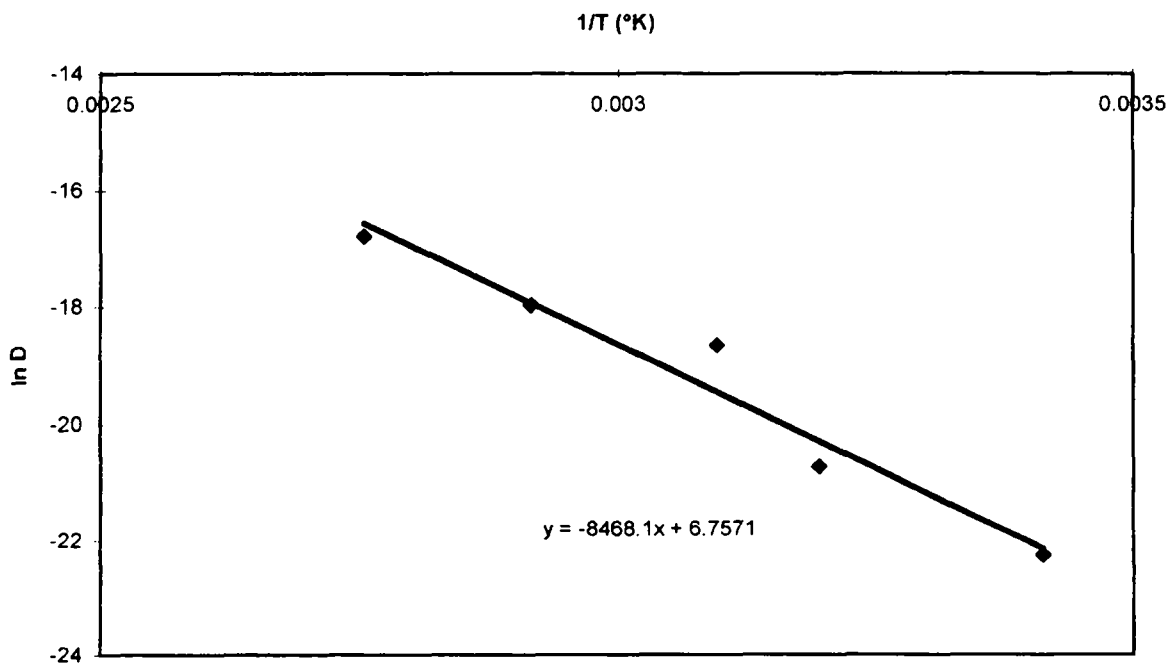


Figure 9 Relationship between diffusion coefficient and reciprocal temperature

the diffusion controlled process. Table 1 shows this parameter to decrease with increasing temperature (with the exception of the unusual behaviour reported above for 90°C). A priori this tendency is difficult to explain. At the present time, we may only speculate. On increasing temperature, it is reasonable to assume that the free volume and, to some extent, any microvoids present in the polymer, will expand. This could possibly account for a higher proportion of absorbed water, leaving less water available to combine with the polymeric structure leading to the (hypothesised) rapid relaxation. A similar argument may be applied to the decrease of A (which is the ratio between the volume increase (ΔV_{dx}) and the corresponding water uptake (ΔW_{dx}) through the diffusion controlled process) with increasing temperature.

By contrast, ΔV_{sx} , the maximum volume increase corresponding to the slow swelling controlled process, increases with temperature. This result may possibly be expected since temperature increase, in the long term, should increase the probability of a water molecule being bound by a functional group in the resin; moreover, due to the thermal agitation effect, at higher temperatures, more water should have the possibility to interact with the functional groups in the polymer as time goes by.

k is a rate constant describing the swelling controlled process. We do not intend to comment on its values obtained owing to the exceedingly complicated nature of the swelling process.

CONCLUSIONS

Swelling of a model epoxy resin (DGEBA/DDA) during hygrothermal ageing has been investigated. The results show that the rate of swelling of the polymer is less than that attributable to the mass of water absorbed initially, but that the rates equalise (approximately) later. It has also found that the swelling process is not fully reversible. When the aged specimens are dried asymptotically, their volumes are larger than their corresponding volumes before ageing. The retained swelling is similar to the volume of the retained water when the ageing temperature is lower than 70°C, and much larger than the volume of the retained water if the

specimen is aged in water at 90°C (and presumably above). The results suggest that hygrothermal ageing irreversibly changes the molecular structure of the resin studied.

By assuming that water diffusion is governed by a classic diffusion controlled process and a swelling controlled process, a model has been proposed to describe the water uptake and swelling kinetics during hygrothermal ageing. The results show that the model is in good agreement with the experimental data.

ACKNOWLEDGEMENTS

The authors thank the French Ministry of Foreign Affairs and Electricité de France, Centre des Renardières, for financial support and CECA S. A., France for supplying the model resin.

REFERENCES

1. Crank, J., *The Mathematics of Diffusion*, 2nd edn. Oxford University Press, London, 1975.
2. Shen, C. H. and Springer, G. S., *J. Comp. Mater.*, 1976, **10**, 2.
3. Carter, H. G. and Kibler, K. G., *J. Comp. Mater.*, 1978, **12**, 118.
4. Gustin, M. E. and Yatomi, C., *J. Comp. Mater.*, 1979, **13**, 126.
5. DeWilde, W. P. and Shopov, P. J., *Comp. Struct.*, 1994, **27**, 243.
6. Xiao, G. Z. and Shanahan, M. E. R., *J. Polym. Sci., Phys. Ed.*, 1997, **35**, 2659.
7. Adamson, M. J. J., *Mater. Sci.*, 1980, **15**, 1736.
8. Wright, W. W., Adamson, M. J., *J. Mater. Sci. Composites*, 1981, **12**, 201.
9. MacKague, E. L., Reynolds, J. D. Jr and Halkias, J. E., *J. Appl. Polym. Sci.*, 1978, **22**, 1643.
10. El-Sa'ad, L., Darby, M. I. and Yates, B., *J. Mater. Sci.*, 1989, **24**, 1653.
11. Gazit, S., *J. Appl. Polym. Sci.*, 1978, **22**, 3547.
12. Crank, J. and Park, G. S., *Diffusion in Polymers*. Academic Press, London, 1968.
13. Xiao, G. Z., Delamar, M. and Shanahan, M. E. R., *J. Appl. Polym. Sci.*, 1997, **65**, 449.
14. Luoma, G. A. and Rowland, R. D., *J. Appl. Polym. Sci.*, 1986, **32**, 5777.
15. De'Nève, B. and Shanahan, M. E. R., *Polymer*, 1993, **34**, 5099.
16. Schott, H., *J. Macromol. Sci.-Phys.*, 1992, **B31**, 1.
17. Johncock, P. and Tudgey, G. F., *British Polym. J.*, 1986, **18**, 292.
18. De'Nève, B. and Shanahan, M. E. R., *J. Adhesion*, 1995, **49**, 165.