

This article was downloaded by:

On: 22 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



The Journal of Adhesion

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713453635>

Physical and Chemical Effects in An Epoxy Resin Exposed to Water Vapour

B. De Neve^a; M. E. R. Shanahan^a

^a Centre National de la Recherche Scientifique, Ecole Nationale Supérieure des Mines de Paris, EVRY Cedex, France

To cite this Article De Neve, B. and Shanahan, M. E. R.(1995) 'Physical and Chemical Effects in An Epoxy Resin Exposed to Water Vapour', *The Journal of Adhesion*, 49: 3, 165 – 176

To link to this Article: DOI: 10.1080/00218469508014353

URL: <http://dx.doi.org/10.1080/00218469508014353>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Physical and Chemical Effects in An Epoxy Resin Exposed to Water Vapour*

B. DE NEVE and M. E. R. SHANAHAN**

*Centre National de la Recherche Scientifique, Ecole Nationale Supérieure des Mines de Paris,
Centre des Matériaux P. M. Fourt, B.P. 87, 91003 EVRY Cédex, France*

(Received December 29, 1993; in final form February 11, 1994)

A commercial epoxy adhesive based on DGEBA cured with dicyandiamide (DDA) and containing fillers has been aged in water vapour (*ca.* 100% RH) at various elevated temperatures. Viscoelastic characterisation was effected after ageing for various times up to saturation and after subsequent drying. Young's modulus in the glassy state is reduced after water sorption but returns virtually to its original value after drying, suggesting physical weakening due to plasticisation whereas, in the rubbery state, the observed diminution is only slightly restored on drying. An analysis based on the theory of rubber elasticity leads to the conclusion that chemical degradation is occurring by hydrolysis and chain scission. Gravimetric measurements effected on the polymer exposed to vapour for a fixed time and then dried to (virtual) equilibrium show an increase in weight followed by a decrease and finally a weight loss as exposure time is increased. A theory is proposed to explain the phenomena by initial chemical combination of water followed by leaching of severed chain segments. Calculations of average inter-crosslink molecular weight using both viscoelastic and gravimetric data are in good agreement. It is concluded that long-term exposure of the epoxy adhesive to water leads to both reversible (physical) and irreversible (chemical) degradation of the material.

KEY WORDS: ageing; degradation; epoxy resin; gravimetry; hydrolysis; plasticisation; viscoelastometry; water vapour.

INTRODUCTION

Structural adhesives are becoming widely used as a means of mechanical assembly. Many advantages are offered by this type of joining, such as the reduction of stress concentrations, the possibility to join thin and/or dissimilar materials, rendering the joint fluid tight, etc., but certain problems are still to be overcome. Amongst these, long-term resistance to aggressive conditions is probably the most important. The most common aggressive environment is water, especially at elevated temperatures. In many cases, reduction in mechanical integrity is brought about by phenomena occurring at the interface, or interphase, between the substrate and the polymeric adhesive.^{1–3} It is often considered that premature failure is a result of chemical and/or physical

*Presented at Adhesion '93, the Fifth International Conference of the Adhesives Section of the Polymer Industry Division of The Institute of Materials, held at The University of York, York, UK, September 6–8, 1993.

**To whom correspondence should be addressed.

modification of the structure and subsequent weakening near the adhesive/substrate boundary due to diffused water, separation taking place either at the interface itself or in a weak interphase (weak boundary layer⁴) near, but not at, the interface. However, changes may occur to the bulk properties of the macromolecular adhesive itself following water ingress, thus leading to reduction in bond strength. Weakening of the polymer by more or less reversible plasticisation has previously been reported.⁵ Over relatively short periods of exposure to high degrees of humidity, purely physical plasticisation of the polymer, resulting in softening and reduction of the glass transition temperature, may occur, but after drying initial properties are essentially restored. Nevertheless, under conditions of prolonged exposure irreversible damage can potentially occur. In the present study, we consider physico-chemical and irreversible phenomena related to hydrolysis taking place during the humid ageing of a bulk structural adhesive. By submitting samples to humid ageing/drying cycles, it is shown that both reversible and irreversible modifications to the adhesive may occur at high relative humidity and elevated temperature. Although a commercial adhesive is considered here, the techniques and theory described should be applicable to other polymeric materials.

EXPERIMENTAL

The epoxy adhesive material studied (Ciba-Geigy XB 3131) is based on diglycidyl ether of bisphenol A (DGEBA), crosslinked with dicyandiamide (DDA), and contains fillers. Crosslinking was effected by maintaining the polymer at 150°C for 1 hour after heating from ambient temperature at a rate of 8°C/minute. Gravimetric analysis of absorption and desorption of moisture was performed both on sheets of polymer of dimensions 90 × 70 × 2 mm and on smaller samples, of dimensions 12 × 6 × 4 mm. The latter sample size was adopted also for obtaining viscoelasticity data on the polymer in different states of ageing, the apparatus used being a Metravib Viscanalyseur. Tests were conducted in compression-compression mode at a frequency of 5 Hz with the temperature increasing from -130°C to 180°C at a heating rate of 2°C/minute.

Ageing of adhesive samples was effected by exposing them to a vapour environment of *ca.* 100% relative humidity (RH) at 40, 55 and 70°C whilst desorption was carried out at the same temperatures in drying ovens. For the gravimetric work discussed here, samples of cured adhesive were exposed to high humidity and elevated temperatures for various periods ranging from less than 10 hours up to over 15,000 hours (about 2 years). After humid ageing, the samples were surface dried (blotted) and weighed. Drying was continued, at the same temperature as that used for ageing, and the samples periodically weighed until a good estimation of the final equilibrium weight after desorption could be obtained from the asymptotic nature of the desorption process. Typically, a drying period of six months was adequate for such an estimation to be assured, although, for shorter periods of humid ageing, rapid attainment of equilibrium was observed. In the following, time *t* will refer to the length of the period of humid ageing, that required for drying being unimportant, except to estimate final weight after desorption of physically-attached water.

RESULTS

A description of the diffusion behaviour of water into the present epoxy adhesive appears elsewhere in more detail⁶, but a summary of findings pertinent to the following analysis of degradation phenomena will be given here. Absorption appears to be essentially Fickian although close inspection does reveal finer behaviour to be sigmoidal⁷. Results obtained at the three temperatures of 40, 55 and 70°C allowed the activation energy for the water diffusion process to be estimated at *ca.* 80 kJ mole⁻¹, a value somewhat higher than those typically found in the literature (of the order of 40–60 kJ mole⁻¹).

Samples of adhesive were aged for various periods up to 2500 hours at the three temperatures and spectra of both the loss modulus, $\tan \delta (= E''/E')$, and the absolute value of the complex Young's modulus, $E (= (E'^2 + E''^2)^{1/2})$ where E' and E'' represent, respectively, the storage and loss moduli, were obtained as a function of temperature, T . Variations in the $\tan \delta$ behaviour due to water ingress are treated in Reference 6, but what is of direct relevance here is the evolution of E . Figure 1 shows examples of Young's modulus*, E , as a function of temperature for various periods of humid ageing at 70°C and demonstrates that the reductions due to prolonged exposure are relatively

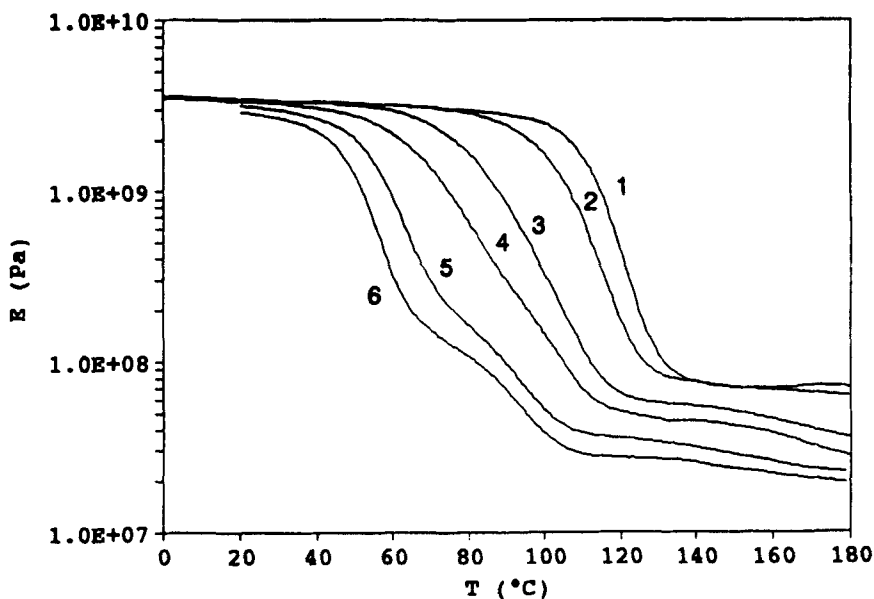


FIGURE 1 Examples of Young's modulus of the epoxy adhesive, E , vs. temperature, T , for different times of humid ageing. Ageing times: 1–0 hr, 2–9 hr, 3–48 hr, 4–71 hr, 5–168 hr, 6–1195 hr.

*In fact the values obtained here for E in the glassy state have been shown to be somewhat underestimated, due to effects of machine stiffness, but this is of no direct consequence in the present context, since relative values before and after ageing (and drying) are being considered.

more marked in the rubbery state (modulus E_R), above *ca.* 130°C, than in the glassy state (modulus E_G), below about 50°C (depending on the state of ageing). Presumably at least part of this softening is due to plasticisation effects and so moduli were also measured after ageing followed by drying for six months. Figure 2 shows the glassy modulus, E_G , at 30°C as a function of humid ageing time at 40°C and also the results after ageing followed by drying. In Figure 3 we present equivalent results but for the rubbery modulus, E_R , at 150°C and corresponding to ageing and ageing/drying at 55°C. Similar results were obtained for the other test temperatures. It may be noted that reductions in E_G due to water ingress are essentially recovered after drying, whereas modifications in E_R are practically irreversible. A summary of the data obtained concerning changes to glassy and rubbery moduli after humid ageing to saturation and subsequent drying is given in Table I. These data suggest strongly that both reversible and irreversible damage is occurring to the polymer after sufficiently long exposure to water. As far as E_G is concerned, the main effect would seem to be plasticisation and presumably in this vitreous state, once physically attached water becomes eliminated, the essentially rigid bulk returns almost to its original state, molecular mobility being significantly reduced. However, the drop in E_R is clearly only slightly related to plasticisation phenomena since the recovery observed after desorption of physically-attached water is relatively small. This irreversible drop in the value of E_R is taken to be evidence of chemical modification to the polymer network after sufficient exposure.

In Figure 4 are presented results corresponding to the gravimetric experiments of exposure to humid ageing for a period, t , followed by drying to equilibrium. Residual weight increase, or decrease, ΔW , as a percentage of initial weight, W , is shown as a function of exposure time, t , for the three ageing temperatures of 40, 55 and 70°C. It can

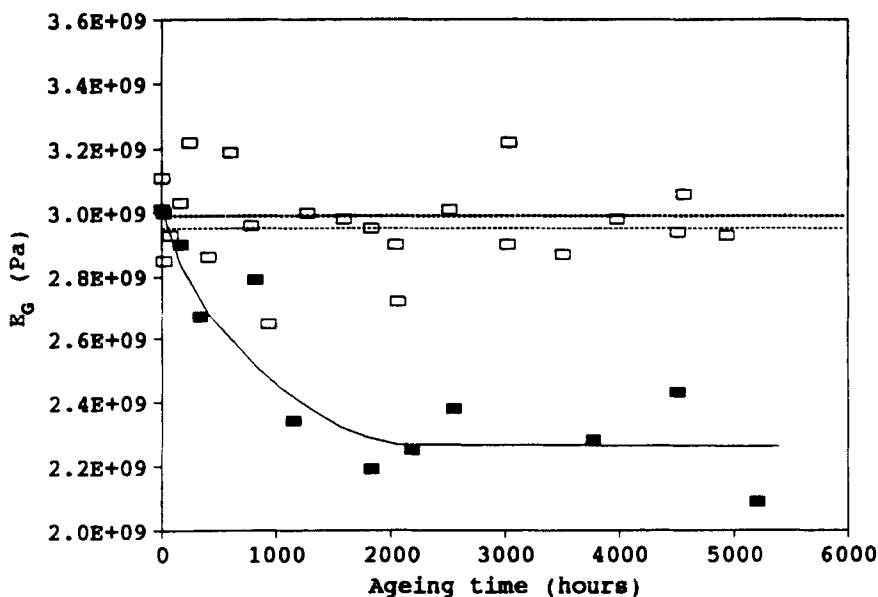


FIGURE 2 Evolution of glassy modulus, E_G , at 30°C after ageing (■ —) and ageing/drying (□ ···) at 40°C.

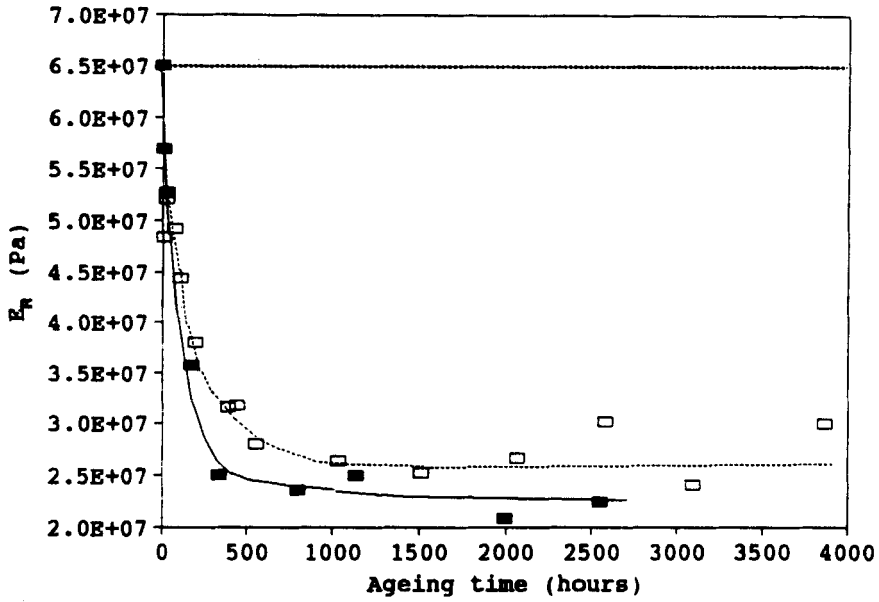


FIGURE 3 Evolution of rubbery modulus, E_R , at 150°C after ageing (■—) and ageing/drying (□···) at 55°C.

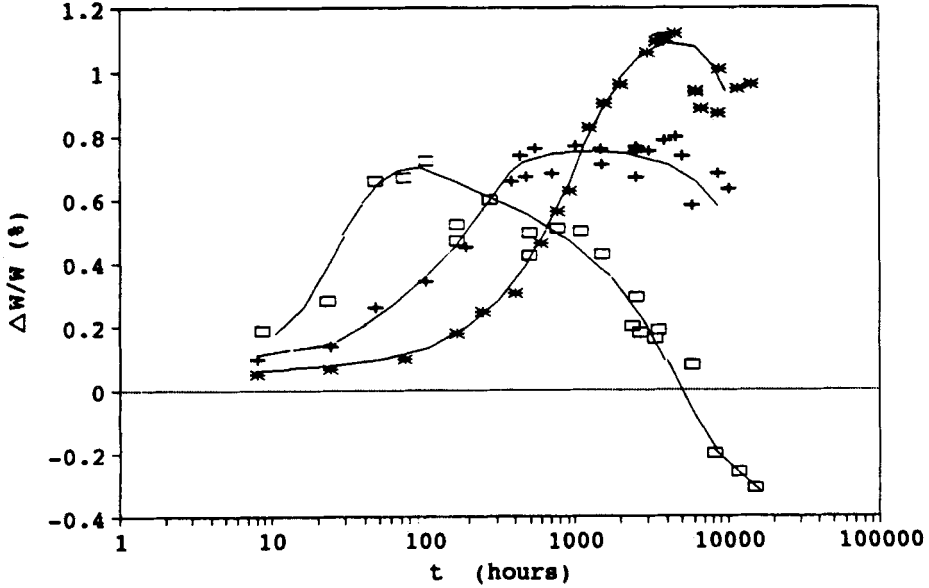


FIGURE 4 Percentage weight change, $\Delta W/W$, vs. humid ageing time, t , after humid ageing and drying. □: 70°C, +: 55°C, *: 40°C.

TABLE I
 Values of the glassy modulus, E_G , at 30°C, and the rubbery modulus, E_R , at 150°C, obtained by viscoelastometry before humid ageing, after ageing to saturation and after ageing and drying, for test temperatures of 40, 55 and 70°C

	Ageing temperature, (°C)	Initial state	After ageing	After ageing and drying
E_G (GPa)	40	3.0 ± 0.2	2.3 ± 0.1	3.0 ± 0.1
	55	3.0 ± 0.2	2.5 ± 0.1	3.1 ± 0.2
	70	3.0 ± 0.2	2.3 ± 0.1	2.9 ± 0.3
E_R (MPa)	40	65 ± 4	22.9 ± 2.8	26.6 ± 1.9
	55	65 ± 4	23.4 ± 1.8	27.7 ± 2.8
	70	65 ± 4	20.2 ± 3.4	25.8 ± 1.4

clearly be seen at all three temperatures that there is an initial tendency for the polymer weight to increase followed by a reduction in gained weight which leads eventually to a weight loss after *ca* 6000 hours (9 months) in the case of ageing at the highest temperature of 70°C. As may be expected, the kinetics of the process is slower at the lower temperatures and, within the time scale of the experiments, although the trend can be seen to be the same, an adequate description of behaviour after the maximum in weight gain is not accessible. This overall behaviour, particularly the weight loss, strongly suggests that chemical modification to the polymer is occurring on long-term exposure to a humid atmosphere, an observation which qualitatively corroborates the modifications to viscoelastic behaviour presented above. In the following, we effect two semi-quantitative analyses of results corresponding to those obtained by viscoelastometry and by gravimetry in order to explain the observed phenomena and relate these to degradation.

INTERPRETATION AND DISCUSSION

Viscoelastometric Data

The reduction in Young's modulus, E_R , of the epoxy adhesive in its rubbery condition, after ageing to saturation (and drying) is a clear indication of chemical degradation occurring in the bulk material. We shall model this behaviour using, as a basis, the theory of rubber elasticity.

The shear modulus of a (pure) rubbery matrix, G_M , is related to the average intercrosslink molecular weight, M_c , by the equation:⁸

$$G_M(T) = \frac{\rho RT}{M_c}, \quad (1)$$

where ρ is the polymer density, R and T the gas constant and (absolute) temperature, respectively. Although a rubber is Hookian in shear, strictly speaking it never is Hookian in tension or compression. Nevertheless, for very small strains the deviation is

minimal and using the fact that Poisson's ratio for a rubber is *ca.* 1/2, we may write:

$$E_M(T) \approx \frac{3\rho RT}{M_c}, \quad (2)$$

where E_M is the equivalent rubbery Young's modulus.

Although the epoxy adhesive studied at 150°C is in the rubbery state, it is known that the matrix material contains *ca.* 40% fillers by weight. We assume that the resulting "composite" material may be modelled by a simple (series) law of mixtures. In this case, the effective value of the adhesive modulus in the rubbery state may be estimated as:

$$E_R \approx \frac{E_M E_F}{V_f^{1/3} E_M + (1 - V_f^{1/3}) E_F}, \quad (3)$$

where E_F is the average filler Young's modulus and V_f is the volume fraction of fillers. The fillers are mainly of a mineral origin and so $E_F \gg E_R$. Using this fact together with equation (2), equation (3) may readily be shown to be equivalent to:

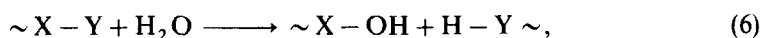
$$M_c \approx \frac{3\rho RT}{E_R(1 - V_f^{1/3})}. \quad (4)$$

The term $V_f^{1/3}$ may be estimated from the surface fraction of fillers, S_f , using the expression:

$$V_f^{1/3} \approx \left(\frac{4}{3}\right)^{1/3} \frac{S_f^{1/2}}{\pi^{1/6}} \approx 0.9 S_f^{1/2}. \quad (5)$$

Using a value of S_f of *ca.* 0.16, as obtained by image analysis, and a value of density, ρ , of 1.5 gm cm⁻³ (these both correspond to values at 20°C but temperature dependence will be slight) and the values of E_R given in Table I, we may estimate the average inter-crosslink molecular weight, M_c , of the adhesive both in its initial and aged/dried states from equation (4). With a value of 65 MPa for E_R for the polymer in its unaged condition, we obtain an average inter-crosslink molecular weight of *ca.* 380 gm. mole⁻¹. After ageing, the calculated value of M_c increases to the range of *ca.* 900 to 1000 gm. mole⁻¹, depending on the ageing temperature. Although the calculation is simplified, and certain criticisms may be levelled at it (use of simple law of mixtures, doubtful applicability of equation (2) at high degrees of crosslinking), it does show that the effective value of M_c is considerably increased after prolonged exposure to water. It is worth noting that M_c for the aged polymer is indeed an *effective* value, since it is highly unlikely that water will "undo" crosslinks. The value reflects chain scission due to hydrolysis. Several mechanisms for hydrolysis have been suggested⁹⁻¹¹, depending on the type of epoxy and curing agent.

Although the exact nature of the degradation is unknown in the present case, presumably hydrolysis will lead to chain scission following the scheme:



where X and Y represent chemical groups in the epoxy main chain. Also of interest is the value obtained for M_c before ageing. The exact composition of the adhesive is unknown to us, but the basic material is DGEBA for which the molar mass is typically

300–400 gm mole⁻¹ (depending on the type). This is of the same order as M_c , suggesting that the initial degree of crosslinking of the polymer is high in the state obtaining using the curing conditions described above.

Gravimetric Data

Having proposed chain scission due to hydrolysis as a cause for degradation of the adhesive after long-term exposure to water, let us now consider gravimetric data and suggest a mechanism by which an ageing/drying cycle may initially lead to weight increase of the polymer, followed by a drop and finally a weight loss (albeit observed only at 70°C, but presumably also true at lower temperatures for sufficiently long exposure times). Only chemically attached water is considered. The behaviour is attributed to two, related, mechanisms. It is assumed that hydrolysis follows the scheme shown by expression (6). Initially, when a water molecule causes chain scission between two crosslinks it will combine chemically to the polymer leading to an overall weight increase. This will be the predominant process for relatively small amounts of water diffused into the polymer. However, for larger quantities, the probability of an inter-crosslink polymeric chain being cut by hydrolysis in two places will increase. When this occurs, the central polymeric segment will become detached from the network and be free to diffuse out of the bulk material by leaching. When this phenomenon starts to predominate, sample weight will decrease. We, therefore, have competition between weight gain due to chemically-attached water and weight loss by leaching of severed segments.

From a mathematical standpoint, we consider the polymer sample, of mass W , to consist essentially of “one molecule” due to crosslinking (this is not absolutely necessary but facilitates the following description). If n water molecules, each of mass a , react with the polymer in accordance with the scheme of expression (6), we may define a scission frequency, $\lambda = n/W$, corresponding to the formation of a number of chain segments of average mass \bar{l} equal to W/n . Taking a critical segment mass as l_c , the probability of obtaining a segment of mass $l < l_c$ is given by:

$$P\{l < l_c\} = P = 1 - e^{-\lambda l_c} \quad (7)$$

and the number of these segments is equal to nP . In the following, l_c corresponds to the maximum mass of a segment capable of diffusing out of the polymer network and, thus, leach out. This value should be close to the average inter-crosslink molecular weight, M_c . Provided that $l_c \ll \lambda^{-1}$, the average weight of a segment satisfying equation (7) will be near to $l_c/2$. Since the water molecule having caused chain scission is assumed to combine chemically with the polymer, we may estimate the mass of segments capable of leaving the network, w_+ :

$$w_+ \approx n \left(a + \frac{l_c}{2} \right) (1 - e^{-\lambda l_c}) \quad (8)$$

Now, the number of water molecules, n , having diffused into the polymer is a function of exposure time, t , and as a consequence, so is w_+ . Nevertheless, after time t , a certain mass, w_- , of segments will have already diffused out of the polymer. Ignoring possible

complications due to concentration gradients, we adopt first order kinetics to describe the leaching process:

$$\frac{dw_-}{dt} = k(w_+ - w_-), \quad (9)$$

with k being a rate constant. Since we can reasonably assume that $l_c \ll \lambda^{-1}$, combination of equations (8) and (9) leads to:

$$\frac{dw_-}{dt} + kw_- \approx kn\lambda l_c \left(a + \frac{l_c}{2} \right). \quad (10)$$

As previously stated, water diffusion is approximately Fickian and so we may consider two regimes. (a) During the first stage, absorption is an approximately linear function of $t^{1/2}$ and thus we assume $n \approx bt^{1/2}$ up to saturation at $t = t_s$. (b) After $t = t_s$, no further absorption occurs and thus $n \approx bt_s^{1/2} = \text{constant}$. Introducing $n \approx bt^{1/2}$ into equation (10) and using the initial condition that $w_- = 0$ at $t = 0$, we obtain, after integration:

$$w_- \approx \frac{b^2 l_c}{kW} \left(a + \frac{l_c}{2} \right) (kt + e^{-kt} - 1). \quad (11)$$

Realising that the net weight change to the polymer, ΔW , is given by $(na - w_-)$, we may write:

$$\Delta W \approx b \left\{ at^{1/2} + \frac{bl_c}{kW} \left(a + \frac{l_c}{2} \right) (1 - kt - e^{-kt}) \right\}; \quad t < t_s. \quad (12)$$

After saturation, $n \approx bt_s^{1/2}$ and equation (10) may be solved directly by quadrature using the boundary condition of continuity of ΔW at $t = t_s$. This leads to:

$$\Delta W \approx b \left\{ at_s^{1/2} + \frac{bl_c}{kW} \left(a + \frac{l_c}{2} \right) [(e^{kt_s} - 1)e^{-kt} - kt_s] \right\}; \quad t > t_s. \quad (13)$$

Equations (12) and (13) have been applied to the results for ageing at 70°C given in Figure 4 (those corresponding to the temperatures of 40 and 55°C not extending sufficiently into the weight loss region for statistical analysis to be really worthwhile). In Figure 5 are presented the experimental values of $\Delta W/W$ vs. t at 70°C. For the smaller size adhesive blocks (12 × 6 × 4 mm), corresponding to most of the experimental data, the majority of values represent the mean of three separate samples. Although not shown, for clarity, the average standard deviation corresponds to a value of 0.08% on the $\Delta W/W$ scale. The values obtained with the larger samples correspond mainly, but not uniquely, to higher values of t . These correspond to only one sample per time t for practical reasons related to the size of the ageing ovens. Nevertheless, we may infer from the acceptable value of the standard deviation quoted above and the general trend of weight change with time t that the absorption/desorption cycles lead to a satisfactory level of reproducibility.

In the above equations, three unknowns are present: b , k and l_c . In principle, b may be obtained from the initial gradient of the $\Delta W/W$ vs. t relationship, but in practice this

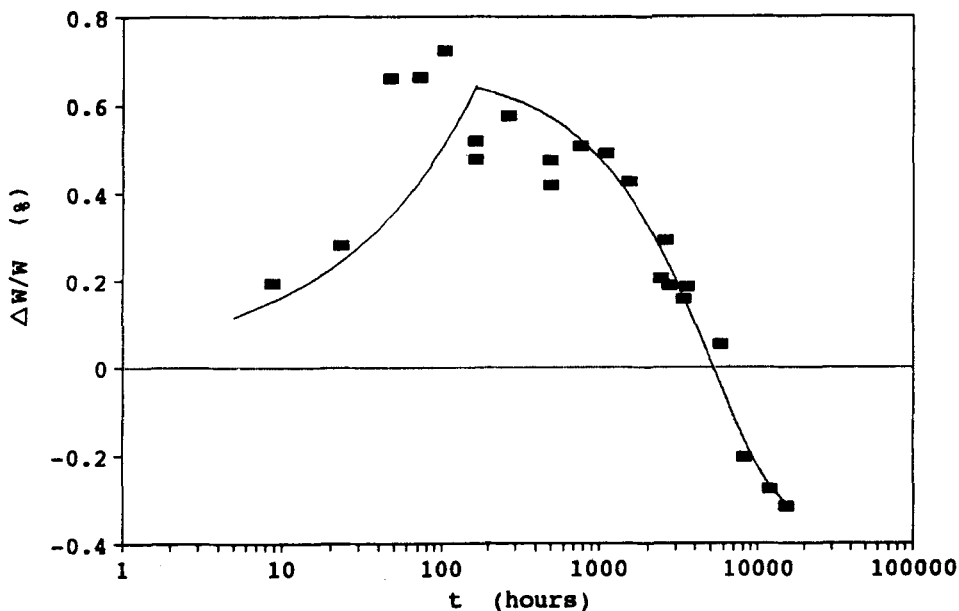


FIGURE 5 Percentage weight change, $\Delta W/W$, vs. humid ageing time, t , after humid ageing and drying at 70°C , with non-linear regression curves corresponding to equations (12) and (13).

is not really feasible with the experimental results available. Nevertheless, we have estimated t_s at *ca.* 170 hours from gravimetric results (without drying).

Also shown in Figure 5 is the curve corresponding to equations (12) and (13) obtained by a non-linear regression analysis with three degrees of freedom and imposing t_s at 170 hours. It may be noted that although the agreement is satisfactory, there is a discontinuity of gradient at *ca.* 170 hours. This is a direct consequence of simplifying the absorption phenomenon into two regimes, *viz.* $n \approx b t^{1/2}$ for $t < t_s$ and $n \approx b t_s^{1/2} = \text{constant}$ for $t > t_s$. In fact, the square root dependence on t really only applies to Fickian diffusion up to *ca.* 0.6 of the saturation absorption, although results obtained with the present adhesive suggest that it is valid for a larger range.⁶ Nevertheless, there is necessarily continuity of the first-derivative of weight increase *vs.* $t^{1/2}$ and this is not allowed for in the model proposed here since it would complicate the development enormously.

The three degrees of freedom involved in the non-linear regression analysis amount to determination of b , k and l_c . Of these, b is of little fundamental interest. The second, k , is a rate constant and the value obtained is *ca.* $6 \times 10^{-8} \text{ s}^{-1}$. This may be taken to be a parameter characterising the self-diffusion of the uncrosslinked polymer. However, caution is required since clearly the leaching process will be exceedingly complicated and no allowance has been made for variable segment mass, concentration gradients and maybe other complicating factors. The parameter of most interest is l_c , which corresponds approximately to the largest leachable segment. A value of *ca.* 370 gm.mole^{-1} has been calculated. It seems reasonable to suppose that l_c must be roughly equivalent to M_c . An inter-crosslink chain may be severed in two places and

then diffuse out of the network. The maximum size will be of the order of M_c . For anything much larger than M_c to become separated, typically three or more scissions will be necessary and the probability of this is vastly inferior. Certainly the agreement between *ca.* 370 gm.mole⁻¹ for l_c derived from this degradation model and the value of *ca.* 380 gm.mole⁻¹ obtained for M_c from viscoelastometry data in the previous section is most satisfactory. Unfortunately, the type of regression analysis used does not readily afford an estimate of the potential error involved in calculating l_c . However, in order to consider the influence of the saturation time, non-linear regression analysis with four degrees of freedom was applied, in which t_s was also treated as a variable. In this case, the value of t_s was determined to be 54 hours and the corresponding l_c was found to be *ca.* 410 gm.mole⁻¹. Although this estimate for saturation time is too low, it can be seen that the effect on l_c is not enormous. Clearly the statistical weight of the values of $\Delta W/W$ at higher values of t is sufficiently important for the exact time of transition from the first to the second domain (equation (12) to equation (13)) to be relatively unimportant. In fact, there is no reason, in principle, that the start of weight loss in the absorption/desorption cycle should necessarily occur at, or after, saturation as determined by a classic absorption experiment without subsequent drying. Nevertheless, it should not be overlooked that the time scale in Figure 5 (and 4) is logarithmic and any imprecision in determining the transition time will be relatively minor (a few days) compared with the overall time scale treated (approaching 2 years).

The model presented here has been developed along fairly simplified lines and applied to a commercial epoxy adhesive, which is a rather complex formulation. Nevertheless, the agreement between viscoelastometry analysis and gravimetric results is quite acceptable and indicates that an epoxy adhesive may suffer severe chemical degradation by hydrolysis after sufficient exposure to water, as well as physical softening due to plasticisation.

CONCLUSIONS

A commercial epoxy resin has been exposed in its bulk form to conditions of high humidity at elevated temperatures. Mechanical properties have been evaluated using viscoelastometry whilst absorption and desorption have been investigated by simple gravimetry. Considering behaviour after saturation in water vapour, it has been found that both Young's modulus in the glassy state, E_G , and that in the rubbery stage, E_R , are considerably reduced compared with values obtained for the unaged material. After drying, allowing physically-attached water to be eliminated, E_G returns essentially to its initial value, suggesting that softening is due essentially to the physical effects of plasticisation. However, E_R is only partially restored after drying, from which we infer that chemical degradation is occurring due to the presence of water. Analysis based on the theory of rubber elasticity suggests that the initial average inter-crosslink molecular weight, M_c , is of the order of 380 gm.mole⁻¹ but that after saturation, the effective value is increased to something like 1000 gm.mole⁻¹. Clearly water is unlikely to "undo" crosslinks but hydrolysis causing chain scission is believed to be responsible for this effective reduction in network density.

Gravimetric experiments have been effected in which the polymer is exposed to humidity for a pre-determined time, t , and then dried such that equilibrium weight may be estimated after physically absorbed water has been eliminated.

It is found that equilibrium weight after the absorption/desorption cycle initially increases and then decreases as a function of t until, at least at sufficiently high temperature, a net weight loss is experienced. This has been attributed to chain scission, the initial weight increase being due to chemically combined water and the subsequent weight loss resulting from leaching of severed chain segments. A theoretical model has been developed explaining the phenomena semi-quantitatively and leading to an estimate of the average initial intercrosslink molecular weight of *ca.* 370 gm.mole⁻¹, in good agreement with viscoelastometry findings. Although the model could be refined and the polymer is a rather complex material not lending itself readily to modelling, it is suggested that this analysis could pave the way for obtaining a potential method for assessing the microscopic structure of a polymer from simple gravimetric experiments.

Finally, it is concluded from this work that an epoxy adhesive may suffer not only physical (reversible) weakening due to water ingress caused by plasticisation but also chemical (irreversible) degradation brought about by hydrolysis.

Acknowledgements

The authors thank the Régie Renault and Peugeot S.A. for financial support and Y. Auriac for his experimental assistance with the gravimetric measurements.

References

1. L. H. Sharpe, *J. Adhesion*, **4**, 51 (1972).
2. R. A. Gledhill and A. J. Kinloch, *J. Adhesion*, **6**, 315 (1974).
3. M. P. Zanni-Deffarges and M. E. R. Shanahan, *J. Adhesion* (in press).
4. J. J. Bikerman, *The Science of Adhesive Joints*, 2nd edition (Academic Press, New York, 1968), Chap. 6.
5. C. Li, R. A. Dickie and K. N. Morman, *Polym. Eng. Sci.*, **30**, 249 (1990).
6. B. De'Nève and M. E. R. Shanahan, *Polymer* **34**, 5099 (1993).
7. J. Crank, *J. Polym. Sci.*, **11**, 151 (1953).
8. L. R. G. Treloar, *The Physics of Rubber Elasticity* (Clarendon Press, Oxford, 1949), p. 187.
9. R. L. Levy, *Technical Report AFML-TR-77-41*, April 1977.
10. M. K. Antoon and J. L. Koenig, *J. Polym. Sci., Polym. Phys.*, **19**, 197 (1981).
11. B. C. Ennis, P. J. Pearce and C. E. M. Morris, *J. Appl. Polym. Sci.*, **37**, 15 (1989).