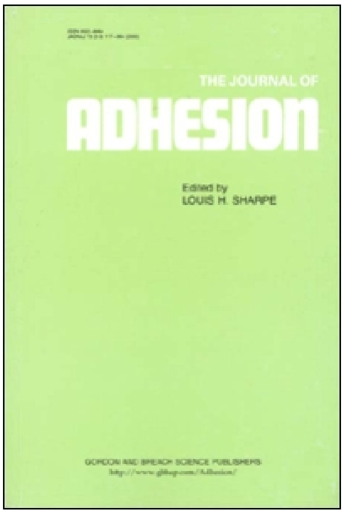

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

A Model for Predicting Joint Durability

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To cite this Article Gledhill, R. A. , Kinloch, A. J. and Shaw, S. J.(1980) 'A Model for Predicting Joint Durability', The Journal of Adhesion, 11: 1, 3 — 15
To link to this Article: DOI: 10.1080/00218468008078901
URL: http://dx.doi.org/10.1080/00218468008078901

J. Adhesion, 1980, Vol. 11, pp. 3–15
0021-8464/80/1101-0003$04.50/0

Printed in Great Britain

A Model for Predicting Joint Durability

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(*Received November 6, 1979; in final form November 28, 1979*)

A model has been developed to describe the mechanics of environmental failure of adhesive joints. This model has led to the combination of thermodynamic and water diffusion data with a continuum fracture mechanics approach which has enabled quantitative predictions to be undertaken for the durability of tensile butt joints, consisting of mild steel substrates bonded with a simple epoxide adhesive, exposed to aqueous environments. The agreement between the predictions of the model and experimental measurements is good.

INTRODUCTION

A major problem which has retarded the use of adhesives in structural bonding has been the adverse effect moisture may have upon the strength of the adhesively bonded component. Recent developments[-6] in the pretreatment of metallic substrates prior to adhesive bonding have improved this situation and led to considerable increases in the durability of structural joints. However, little progress has been made in establishing techniques for quantitatively predicting the service-life of a bonded component and the present paper addresses this aspect of the problem.

MECHANICS OF ENVIRONMENTAL FAILURE

In a recent review by one of the authors[7] the various parameters involved in the environmental failure of structural adhesive joints were considered and a qualitative model proposed for the overall mechanics of the process.

The first stage was suggested to be the accumulation of a critical concentration of water in the interfacial regions. The rate of attaining this critical concentration appears, in many instances, to be governed by the rate of water diffusion through the adhesive and this is obviously accelerated by temperature and, possibly, by stress. Indeed, with some simple adhesive/substrate combinations the kinetics of the environmental failure mechanism are governed by the rate of water diffusion.

The second stage involves a loss in the integrity of the interfacial regions. The precise mechanism responsible for this depends upon the particular adhesive/substrate combination being studied but two common mechanisms are:

i) The rupture of interfacial bonds. This may simply involve the rupture of interfacial secondary bonds due to the displacement of adhesive on the metal oxide by the ingressing water or involve a more complex reaction sequence, e.g. the hydrolysis of interfacial covalent bonds.

ii) Subtle changes occurring in the oxide structure, e.g. hydration, which causes a mechanical weakening of the oxide layer.

The rate of loss of strength of the interfacial regions may be faster if a tensile or shear stress is present, albeit an externally applied stress or internal stresses induced by adhesive shrinkage incurred during cure, or by adhesive swelling due to water uptake. However, while the presence of a tensile or shear stress as a necessary requirement for environmental attack to occur has yet to be conclusively established, a primary or secondary bond will obviously be more susceptible to attack if stressed.

The third stage concerns the ultimate failure of the adhesive joint. For the joint to fracture or lose an appreciable amount of its original strength upon subsequent testing it is not usually necessary for the weakening of the interfacial regions to have proceeded completely through the joint. From basic continuum fracture mechanics[8] considerations only a relatively small crack is required to have developed before a substantially decreased failure time, under a constant-load test, or a diminished joint strength is observed. Indeed, with many joint geometries subjected to an imposed load and moisture, catastrophic failure will occur when the ingressing environmental debond region, which is growing by the mechanisms outlined above, for example, attains a critical length; this is analogous to a critical Griffith crack size in homogeneous materials.

The present paper attempts to employ this model quantitatively to predict the durability of tensile butt joints which consist of mild steel substrates bonded with a simple epoxide adhesive. This adhesive system was selected because the mechanisms and kinetics of environmental attack have been previously reported and the kinetics are governed by the rate of water diffusion. This latter feature considerably eases the problems of quantification.

EXPERIMENTAL

Materials

The epoxide resin adhesive employed was a diglycidyl ether of bisphenol A mixed with 9.4 mass per cent of a *tert* amine curing agent, tri-2-ethyl hexanoate of 2,4,6-tris(dimethylamino-methyl) phenol. To effect cure of the adhesive it was held at 23°C for 96 h, followed by 1¼ h at 100°C and finally 2½ h at 180°C and then allowed to cool slowly.

Water absorption studies

Cast sheets of the adhesive were prepared of constant thicknesses between about 0.7 and 1.3 mm and cut into squares of approximately 3 × 3 cm. These samples were then dried and weighed and immersed in water baths at 20°, 40°, 60° and 90°C and in an environmentally controlled laboratory maintained at 20°C and 55% R.H. Four replicates were employed at each condition. At various intervals a sample was removed, dried of surface water with blotting paper, weighed on an analytical balance and returned to the bath.

Fracture studies

Cast sheets of the epoxide adhesive were prepared of thickness 57.8 ± 0.8 mm. These sheets were then machined and drilled to form the compact-tension specimen shown in Figure 1. A sharp crack was formed at the base of the slot by carefully tapping a razor blade into the base which caused a natural crack to grow for a short distance ahead of the razor blade. The specimen was then mounted in an Instron tensile testing machine and loaded at 20°C and a constant displacement rate of 2×10^{-5} m/s until crack growth was observed.

Joint durability studies

These studies have been described in detail previously.[9] Essentially the substrate was mild steel to specification BS 970, EN3B, and was in the form of blocks, 25.4 mm^3. The surface to be bonded was first subjected to a liquid and vapour degreasing bath of trichloroethylene, then grit blasted with 180–220 mesh alumina, then degreased again and finally allowed to dry in air in a desiccator. Adhesive was spread on the treated faces and two blocks were pressed lightly together to form a coaxial butt joint. Small lengths of copper wire, previously inserted in the adhesive near the centre of the joint, were employed to control the glue line thickness to 0.5 mm (this technique has been shown not to significantly affect the joint strength[10,11]). To effect cure of the adhesive the joint was subjected to the same time/temperature schedule as described previously.

The joints were then exposed to various environments, namely 20°C, 55% R.H. and immersion in distilled water at 20°, 40°, 60° and 90°C. At intervals joints were removed from the above environments, kept at 20°C, 55% R.H. for about half an hour, and then fractured in tension at 20°C and a constant displacement rate of 2×10^{-5} m/s.

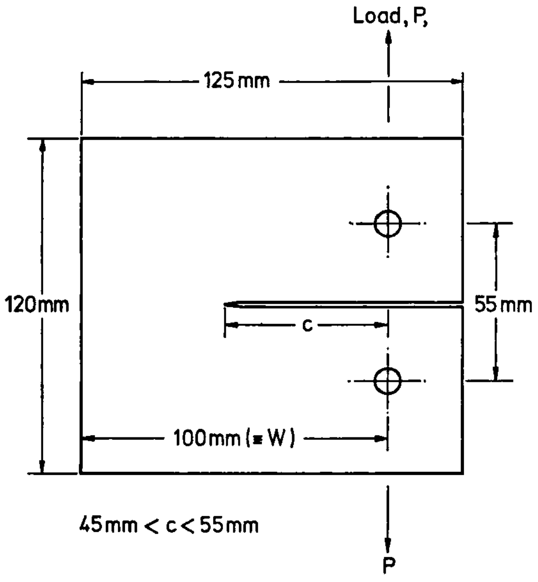

FIGURE 1 Compact tension specimen used for crack growth studies.

RESULTS

Determination of diffusion coefficient and solubility

To determine the diffusion coefficient and solubility of water in the bulk epoxide adhesive under the different conditions studied the ratio of the weight of water absorbed at time, t, to the initial dry weight of the polymer, i.e. M_t/M_0, was plotted against $t^{\frac{1}{2}}/h$, where h is the thickness of the sample. In Figure 2, M_t/M_0 versus $t^{\frac{1}{2}}/h$ relations are plotted for the epoxide adhesive. The uptake curves are linear at first and smoothly lead to equilibrium values of M_t/M_0 being attained. This type of diffusion is termed Fickian and has been previously reported for water diffusing through glassy, cross-linked, epoxide polymers.[12-14] Fickian behaviour was observed at 20°, 40° and 90°C but at 90°C, which is above the glass transition temperature of the epoxide,[9] i.e. 85°C, a deflection in the uptake curve was observed indicating non-Fickian diffusion. However, even at 90°C the first part of the curve was linear and eventually a steady, equilibrium value of M_t/M_0 was achieved.

The value of the diffusion coefficient, D, may be deduced from these plots from the relation[15]:

$$D = \frac{0.04919}{(t/h^2)_{\frac{1}{2}}} \tag{1}$$

where $(t/h^2)_{\frac{1}{2}}$ is the half-time of the sorption process. Values of D so calculated are shown in Table I together with the equilibrium water concentration, C_∞.

The value of D at 20°C is, within experimental error, independent of the water vapour pressure and this observation is in accord with previous work[12]

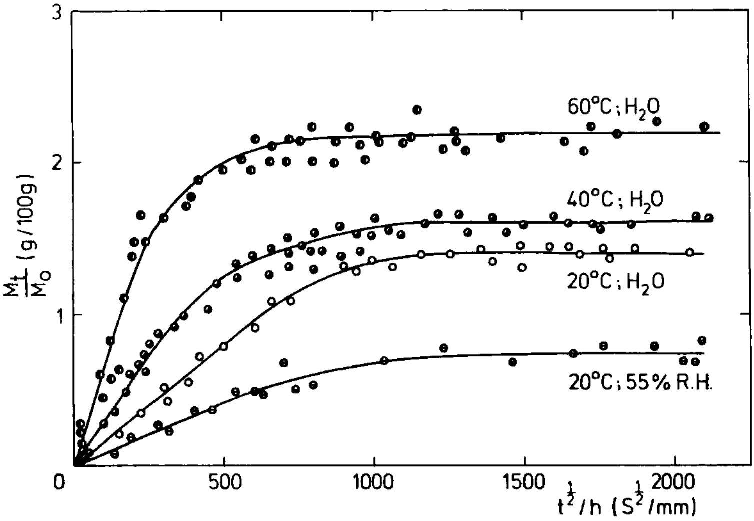

FIGURE 2 Water uptake, M_t/M_0, plotted against (time)$^{\frac{1}{2}}$/thickness for the bulk adhesive.

TABLE I

Diffusion coefficient and solubility for water in the bulk adhesive

Environment	$D \times 10^9$ (cm^2/s)	C_∞ (g/100 g)
20°C; 55% R.H.	2.54	0.75
20°C; H_2O	2.43	1.40
40°C; H_2O	6.50	1.60
60°C; H_2O	18.1	2.20
90°C; H_2O	60.7	6.90

on similar epoxide materials. However, as the temperature increases both the value of D and C_∞ increases. The diffusion coefficient is shown as a function of temperature in the form of Arrhenius plot in Figure 3 and several interesting points emerge. Firstly, for the three lowest temperatures a linear correlation exists which yields an activation energy of 37 kJ/mol. Secondly, at 90°C the rate of diffusion is greater than would be expected from an activation energy of 37 kJ/mol and this arises from the glass transition temperature, *Tg*, of the adhesive being 85°C and at temperatures above this segmental motions of the polymer chains greatly increase. This permits diffusing species to penetrate more rapidly than would be predicted from experiments conducted below the Tg.

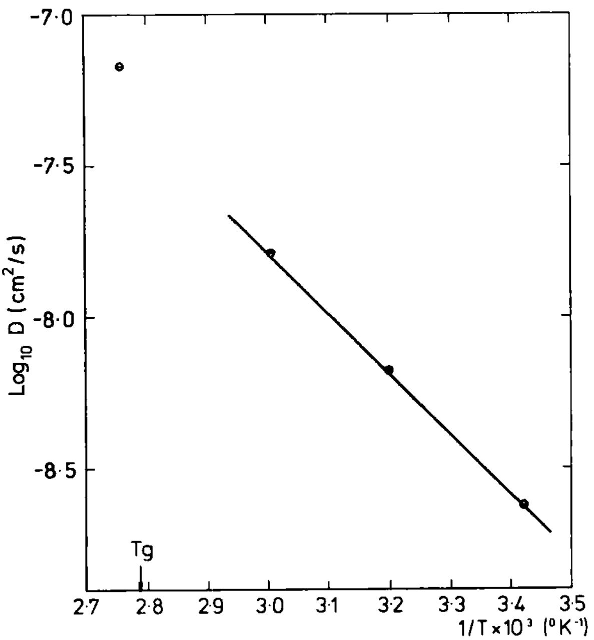

FIGURE 3 Logarithm of diffusion coefficient versus reciprocal water temperature.

Fracture studies

Values of the plane-strain stress-intensity factor, K_{Ic}, for the bulk adhesive were obtained by using the compact-tension geometry shown in Figure 1. The load-displacement relation recorded upon loading the specimen was linear elastic and when crack propagation occurred unstable, rapid crack growth was observed. The value of K_{Ic} was calculated from[8]:

$$K_{Ic} = Q_1 P_c \sqrt{c}/HW \tag{2}$$

P_c = load at crack propagation
c = crack length
H = thickness of specimen
W = width of specimen as defined in Figure 1
Q_1 = geometry factor
$= [29.6 - 185.5\,(c/W) + 655.7\,(c/W)^2 - 1017.0\,(c/W)^3 + 638.9\,(c/W)^4]$

The value of K_{Ic} so deduced was 0.96 ± 0.04 MN $m^{-3/2}$, in good agreement with values for crack propagation in joints employing this epoxide adhesive where cohesive fracture in the adhesive occurred.[16,17]

Joint durability

The data for the change in the fracture stress of the tensile butt joints as a function of the time the joints were exposed to the various environments, prior to testing at 20°C, are added to the theoretical curves (*vide infra*) given in Figure 6. The joints exposed to the control environment of 20°C and 55% R.H. suffered no significant change in joint strength. However, for the joints immersed in water the measured strengths decreased with increased rapidity the higher the temperature.

DISCUSSION

Mechanism and kinetics of environmental failure

As discussed earlier it is well documented that the interfacial regions of structural adhesive joints are those most susceptible to environmental attack by water. Indeed for the relatively simple mild steel-epoxide joints examined in the present investigation previous work,[18] employing surface-specific analytical techniques such as Auger and X-ray photoelectron spectroscopy, has identified the precise site of attack. This was found to be exactly at the interface between the metallic oxide and epoxide adhesive. However, in those inner regions of the joint where environmental attack had not yet penetrated then fracture was cohesive in the adhesive layer; the extent of such cohesive failure obviously decreased as the length of time spent by the joint immersed in water, prior to testing, increased.

Further, it has been shown[9] that for the epoxide-metal oxide interface the thermodynamic work of adhesion, W_A, is 290 mJ/m^2 and, being positive, the interface is stable in dry environments. However, when there is an adsorbed layer of water at the interface, the thermodynamic work of adhesion becomes W_{AL}, and has a negative value, namely -255 mJ/m^2. This change from a positive to negative work of adhesion provides a driving force for the displacement of adhesive on the metal oxide surface by water. It is therefore to be expected that if a joint is subjected to a humid environment there will be a progressive encroachment into the joint of debonded interface. This will have the effect of progressively reducing the joint strength and changing the locus of failure from cohesive within the adhesive to interfacial between adhesive and substrate. This is exactly what is observed.

An energy of activation of 32 kJ/mol was determined for this mechanism with the rate of environmental attack being greater at temperatures above the epoxide's *Tg* than that predicted from experiments conducted at temperatures below *Tg*. Comparing these features to those observed for the diffusion of water through the bulk adhesive clearly confirms the earlier conclusion[9] that the kinetics of this mechanism are governed by water diffusion. This highlights the intriguing observation that when the joints were kept at 20°C and 55% R.H. prior to testing then they did not appear to suffer from attack by moisture even when so conditioned for long times. There was no significant decrease in joint strength and the locus of joint failure remained unchanged, being always by cohesive fracture in the adhesive. Nevertheless, the adhesive did, of course, absorb water up to an equilibrium value, C_∞, as may be seen from Table I. This clearly reveals that there must be a critical level of water concentration, C_c, in the adhesive layer in the joint below which environmental attack is precluded. Other workers[13,19] have also observed a critical value of R.H. but, not surprisingly, the value of this parameter appears to depend upon the joint system, i.e. adhesive, substrate, substrate surface pretreatment, etc.

Water concentration profiles

The above comments lead to a consideration of the water concentration in the adhesive layer in the joint as a function of time and location. If it is assumed that the diffusion of water into the adhesive layer is Fickian, as it is in the bulk adhesive, then this information may be readily calculated. Support for this assumption comes from recent work[20] which has employed tritiated water and so enabled the water concentration in the joint to be directly measured; good agreement with calculations based upon Fickian diffusion has been obtained.

Thus, the concentration, C_t^1, of water at time, t, in the adhesive layer resulting from one-dimensional diffusion may be calculated[21] from:

$$\frac{C_t^1}{C_\infty} = 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)} \exp\{-D(2n+1)^2\pi^2\, t/4l^2\} \cos\{(2n+1)\pi\, x/2l\} \quad (3)$$

where $2l$ is the depth of the layer, x the depth from the layer's boundary given $0 \geqslant x \geqslant l$ and assuming the initial concentration of water in the layer is zero. For the present requirement of an adhesive layer of square cross-section involving two-dimensional diffusion (no water may penetrate through the metallic substrates) then the concentration, C_t, of water is now given by[21,22]:

$$C_t/C_\infty = 1-(1-C_t^1/C_\infty)^2 \tag{4}$$

A computer program was written to solve Eqs. (3) and (4) and n was allowed to take the values 0, 1, 2, 3, 4 . . . etc. until the difference between successive terms was less than 10^{-5}.

Plots of C_t against depth into adhesive layer as a function of time are shown in Figures 4 and 5 for immersion in water at 20°C and 60°C respectively. Similar graphs were obtained for all the environments employed. The computer program was written so that the concentration profile plot near the edge of the joint could be expanded to enable more accurate measurements to be made from these graphs, as discussed below.

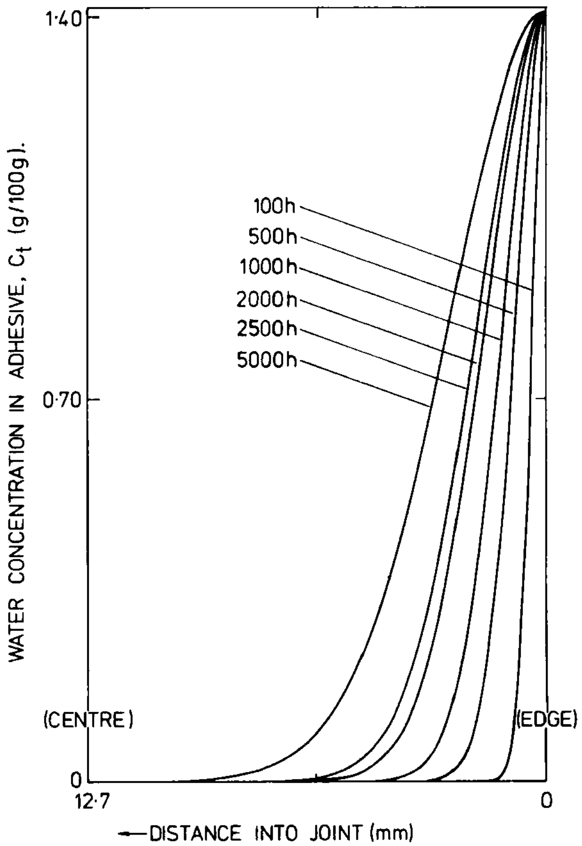

FIGURE 4 Water concentration, C_t, in adhesive layer as a function of penetration depth for butt joints immersed in water at 20°C.

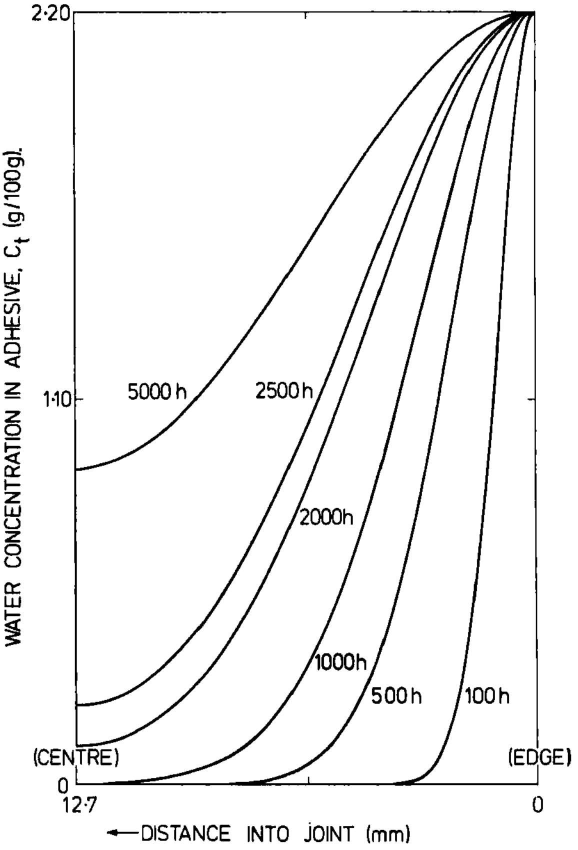

FIGURE 5 Water concentration, C_t, in adhesive layer as a function of penetration depth for butt joints immersed in water at 60°C.

Prediction of joint durability

The fracture stress, σ_f, of a structure may be related to the stress-intensity factor, K_{Ic}, via[8]:

$$K_{Ic} = Q\sigma_f\sqrt{\pi a} \tag{5}$$

where Q is a geometry factor and a the crack length. Thus, rearranging yields:

$$\sigma f = K_{Ic}/(Q\sqrt{\pi a}) \tag{6}$$

To use this relation to predict the absolute value of the fracture stress after various environmental exposure times requires a knowledge of the values of K_{Ic}, Q and a.

Now if the hypothesis of a critical water concentration, C_c, for the debonding mechanism to operate is valid then at the point where the concentration, C_t, in the adhesive exceeds C_c there will exist a relatively sharp boundary between the outer weakened regions of the joint and the inner regions, as yet unaffected by environmental attack. The extent of interfacial debonding, or incipient interfacial debonding, that has occurred during environmental exposure is equivalent to the environmental crack length, a, and may be calculated from the water concentration profiles, e.g. Figures 4 and 5, if the value of C_c is known. Upon subsequent testing of this environmentally aged joint this crack propagates through the inner unaffected regions of the joint and this implies that a value of K_{Ic} of about the same value as for the bulk adhesive is appropriate to this stage, i.e. $K_{Ic} = 0.96\ \mathrm{MN\ m^{-3/2}}$.

The value of the geometry factor, Q, is usually ascertained from published tables and frequently $Q \rightarrow 1$. The exact solution for an edge, interfacial crack in a butt joint could not be found in the literature and the nearest available solutions were for a central crack at the interface in a butt joint[23] and for an edge, circumferential crack in a solid bar.[24] In both cases the value of Q was close to unity and was not highly dependent upon the crack length, a; in the former case $Q = 1.05$ for $a/l \leqslant 0.6$ and in the latter case $Q = 1.1$ to 1.25 for this ratio. A value of $Q = 1.1$ was used in Eq. (6).

Therefore it only remains to determine the value of the critical concentration, C_c, of water in the adhesive for the interfacial debonding mechanism to operate and so enable the environmental crack length, a, to be deduced from the concentration profiles. Unfortunately the value of C_c is not known but Eq. (5) was used to calculate a value of crack length, a, for the joints exposed to water immersion for 2500 h at 40°C. This condition was selected since it was in the middle of the immersion temperatures employed. The concentration profile of water in the adhesive layer at 40°C and after 2500 h was then consulted to deduce the water concentration, i.e. C_c, needed to yield this value of a. The value of C_c so found was 1.35 g/100 g. The value of C_c was now fixed at this value and the concentration profiles employed to deduce values of a as a function of temperature and time of exposure to environment.

Values of the joint's fracture stress, σ_f, were now deduced from Eq. (6) as a function of the temperature and time of environmental exposure prior to testing. These theoretically predicted values are shown in Figure 6 as the solid curves and may be compared to the experimentally determined strength values, shown as individual points. The agreement is generally very good and there are several interesting features. Firstly, C_c was ascertained, as described above, to be 1.35 g/100 g thus, since at 20°C and 55% R.H. the water concentration in the adhesive never attains this value, i.e. $C_c > C_\infty$ (20°C, 55% R.H.), environmental attack under this exposure condition is predicted not to occur; exactly as experimentally observed. Secondly, the intrinsic crack length of the joint, prior to environmental exposure, deduced from Eq. (6), is 0.17 mm and until the environmental debond length is greater than this value no decrease in joint strength is predicted. This may be seen in the predicted relation for the joints immersed in water at 20°C. Thirdly, after immersion in water at 90°C for periods longer than about 750 hours the environmental crack length is excessively large and this prevents an accurate determination of the geometry factor, *Q*. Predictions over longer time periods have not therefore been attempted.

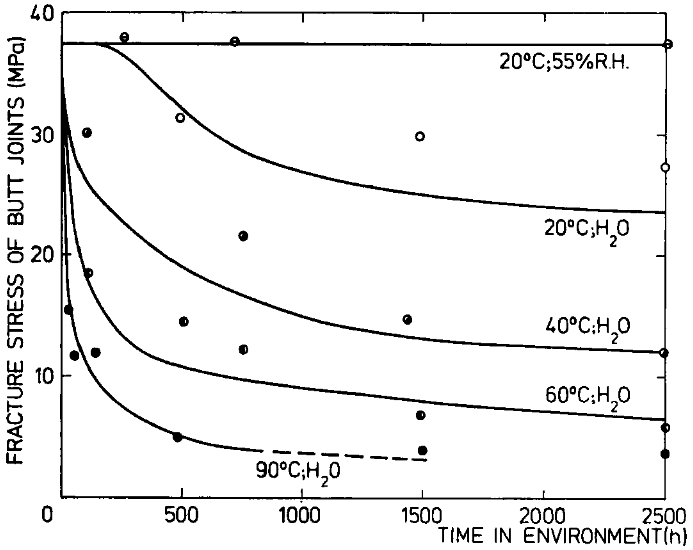

FIGURE 6 Butt joint fracture stress, σ_f, versus time in environment. Points are experimental measurements and solid curves theoretical predictions.

CONCLUSIONS

A model has been developed to describe the mechanics of environmental failure of adhesive joints. For an epoxide-mild steel interface, where the kinetics of such failure are governed by the rate of diffusion through the adhesive, this model has led to quantitative predictions of the fracture stress of these joints after they had been exposed to a wide range of environmental exposure conditions. The information required for this analysis included the diffusion coefficient and solubility of water in the adhesive and the short-term mechanical properties of the adhesive. The value of one parameter, namely C_c, had to be ascertained implicitly for one condition but thereafter was taken to be a constant. The agreement between the predictions and experimental measurements was good.

Acknowledgements

The authors would like to acknowledge the experimental assistance of Mrs. M. Corthine and Mr. M. Bergh for his considerable help with the computer programs. Also to thank Dr. J. Comyn (Leicester Polytechnic) and Dr. T. Lewis (PERME) for helpful comments and discussions.

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