Effects of humidity on an epoxy adhesive

B. De Nève and M.E.R. Shanahan

(Ecole Nationale Supérieure des Mines de Paris, France)

The ageing effects on a structural epoxy adhesive due to exposure to relatively high temperature and high humidity have been studied. Both the modifications to the bulk properties of the polymer and the reduction in adhesive strength have been considered. Concerning the mechanical properties of the bulk adhesive, various techniques have been exploited but, in particular, viscoelasticimetric measurements have shown how the complex modulus alters with water uptake and the glass transition temperature decreases. Adhesive properties have been investigated using a torsional shear test. Preliminary results suggest that this technique is well suited to the investigation of ageing effects.

Key words: adhesives; environmental ageing; bulk properties; joint strength; epoxy

Structural adhesives are now widely used in various sectors, particularly in the aerospace and automotive industries. Various advantages are offered by this means of joining compared with the more conventional methods such as bolting or riveting. Lightness and reduction of stress concentrations are two major factors but other considerations such as sealing to fluid flow and streamlining are also significant. Nevertheless, during its service lifetime, a structural adhesive joint often has to withstand deleterious — and, in particular, humid — environments over long periods. Although high temperature alone may lead to the degradation of a structural joint, there is much evidence in the literature to show that the synergic effects of humidity together with temperature are particularly pernicious[1-3]. The mechanism(s) by which strength reduction occurs are not entirely understood although the immediate causes of failure can usually be attributed to the breakdown of interfacial bonds (either of a primary or a secondary nature) and/or a decrease in mechanical (cohesive) strength of the polymeric material constituting the adhesive itself. There is some evidence that a marked reduction in strength is accompanied by absorption of a critical concentration of water in the joint[4].

The present work describes preliminary investigations of the effects of high humidity and relatively high temperature on both bulk adhesive and bonded joints, using various experimental techniques. Materials chosen for this study are an epoxy resin with zinc-coated steel plate as the principal substrate. Viscoelasticimetric tests have been employed as a means for following variations of the bulk adhesive characteristics during ageing. The structural resistance of adhesive joints has been assessed using a torsional shear test developed with an aim of reducing to a minimum unwanted stress contributions due to tensile and cleavage effects.

Experimental

Materials and preparation

The adhesive chosen for this study was a structural epoxy adhesive comprising a diglycidyl ether of bisphenol A (DGEBA) with dicyandiamide as the cross-linking agent (Permabond ESP 470). A preliminary investigation was carried out using a differential scanning calorimeter (DSC manufactured by Setaram) to determine the curing cycle of the adhesive resulting in the highest glass transition temperature, T_g (readily attainable). Samples of epoxy weighing ~30 mg in standard aluminium DSC vessels, were run initially at a heating rate of 10°C min^{-1} for a primary scan and the T_g values were obtained from a secondary scan at the same heating rate. As a result, the curing cycle adopted consisted of heating at 10°C min^{-1} to 160°C with the temperature being maintained at this value for 30 min.

Bulk samples of the epoxy resin were obtained by moulding into sheets of dimensions $130 \times 115 \times 5\ \text{mm}^3$.

0143-7496/92/030191-06

After curing, individual test-pieces were cut and machined from these sheets for the viscoelasticimetric experiments described below. Before testing, samples were dried at 60°C for 15 days.

Two types of adherend were employed to constitute the adhesive joints. The principal substrate was zinc-coated (10 μm) steel plate of thickness 0.7 mm. It is the interface between this material and the adhesive which is of primary interest. The secondary, or supporting, substrate was a hollowed cylinder in aluminium of specification AU4G. This material was chosen as a means of applying stresses to the adhesive layer since it is well known that adhesion between epoxy resins and aluminium is good provided the latter undergoes a suitable surface treatment.

Pre-bonding preparation of the steel plate was limited to ultrasonic cleaning using trichloroethylene for a period of 10 min. The cylindrical aluminium adherend was treated using a well established recipe[5, 6] in which the procedure is as follows. Initial cleaning is effected in trichloroethylene vapour for 20 min. The aluminium is then etched in a sulpho-chromic acid bath (consisting of 100 parts of water, 30 parts of concentrated sulphuric acid (1 N) and 6 parts of $Na_2Cr_2O_7 \cdot 2H_2O$) at a temperature in the range 66 to 71°C for 15 min. The treatment is completed by rinsing in distilled water and drying at 60°C.

Test procedures

Various experimental techniques have been employed with the aim of following the evolution of both adhesive bulk properties and bonded joint characteristics during ageing effected at a temperature of 70°C and 100% relative humidity (RH).

Bulk adhesive

After having established the curing conditions leading to the highest value of T_g, as described above, the dynamic mechanical properties of the adhesive were investigated. As is well known, the mechanical behaviour of polymers is generally modified by water absorption. A Viscoanalyseur manufactured by Metravib was used to measure the complex mechanical response of the epoxy resin as a function of ageing time. Polymer samples of dimensions $10 \times 4 \times 4$ mm^3 were tested in the compression–compression mode. In this type of experiment a sinusoidally varying compressive strain is applied to the smaller faces of the test-piece, already maintained under slight compression.

The complex mechanical behaviour was measured:

- at a fixed frequency of 5 Hz whilst increasing the temperature from −130°C to 180°C at a rate of 2°C min^{-1}; and
- at frequencies varying between 5 Hz and 600 Hz in the temperature range of 20°C to 180°C, again using a heating rate of 2°C min^{-1}.

These experiments were complemented by gravimetric vapour sorption measurements on bulk adhesive sheets of dimensions $130 \times 115 \times 4$ mm^3.

Bonded joints

Structural joints are often subjected to various combinations of stress distribution but a well designed assembly has to resist primarily in shear. It has been known for many years that simple shear, as encountered with the single lap configuration, induces a cleavage component and tensile stresses[7]. Joint failure usually initiates due to tearing stresses near the ends of the overlap[8]. The torsional shear test presents the advantage of subjecting the adhesive joint essentially to shear stresses. Gillespie and Rideal first developed the napkin ring test in which two hollow cylinders are bonded together[9]. Other studies have since been performed using this geometry[10–15]. A modification of the napkin ring test has been used to study the adhesion and cohesion of coatings on steel[16, 17]. The essential difference is that one of the cylindrical members is replaced by a plate or sheet adherend. This geometry has been adopted in the present work in which a hollowed-out cylinder of aluminium (of internal radius, r_i, and external radius, r_e, respectively equal to 5 and 10 mm) is bonded onto the zinc-coated steel adherend. Torsional testing equipment was designed and built specifically for studying this type of joint. The joint is shear loaded by rotating the cylinder whilst the steel plate remains fixed. In the present work, the angular displacement rate was kept constant. Deformation of the plate/cylinder system is monitored using an extensometer consisting of a lever arm attached to the cylinder and contacting a displacement transducer (LVDT). Simple geometrical considerations allow the linear displacement to be converted to a measurement of shear strain. The applied couple, M, is measured using a strain gauge bridge mounted on the load-transmitting axis of the apparatus. Equating the external couple to the internal moments within the annular adhesive layer, we have:

$$M = \int_{r_i}^{r_e} \int_0^{2\pi} \tau(r, \phi)\, r^2 \, \mathrm{d}r \, \mathrm{d}\phi$$

$$= 2\pi \int_{r_i}^{r_e} \tau(r)\, r^2 \, \mathrm{d}r \qquad (1)$$

where r and ϕ are polar coordinates. Defining e as the glueline thickness and θ as the angle of rotation (see Fig. 1), the shear strain, γ, is given by:

$$\gamma(r) = \frac{r\theta}{e} = \frac{\tau(r)}{G} \qquad (2)$$

where G is the shear modulus of the adhesive. Equations (1) and (2) lead to:

$$G = \frac{2eM}{\pi\theta(r_e^4 - r_i^4)} \qquad (3)$$

It should, however, be pointed out that this equation assumes that the rotation measured, θ, is entirely due to adhesive strain. A correction is required to allow for strain contributions from the plate and (part of) the cylinder. Equation (3) thus leads to an apparent value of G. By conducting a series of experiments on joints of different thicknesses, it was possible to assess the stiffness of the metallic parts of the system at

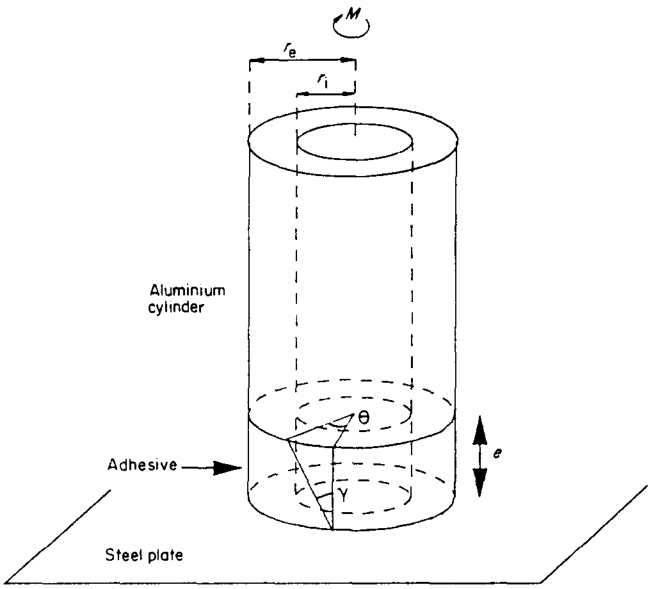

Fig. 1 Schematic diagram of strain in cylindrical test-piece due to applied couple

5.9×10^{-5} rad N^{-1} m^{-1} and thus calculate the true shear modulus of the adhesive.

Results and discussion

Bulk properties

Results of the viscoelasticimetric study conducted on the bulk adhesive at a constant frequency of 5 Hz are shown in Fig. 2. The dynamic glass transition, defined by the temperature, T_g, at which the principal maximum in the loss tangent, tan δ, occurs, is at 126°C. Other transitions of a secondary nature exist at temperatures T_β and T_γ of −40°C and −100°C. Young's modulus for the polymer, obtained as the absolute value of the complex modulus, is of the order of 4000 MPa at 30°C (in the glassy state) and about 45 MPa at 150°C (in the rubbery state). The glass transition extends over about 60°C. Ageing at 70°C and 100% RH leads to a shift of the loss tangent maximum to lower temperatures (see Fig. 3). Similar results have been reported in the literature[18, 19]. After 360 h of ageing, the loss tangent maximum broadens and at 430 h a split in the peak occurs. Experiments have been conducted up to 1260 h of ageing; results are summarized in Table 1. After 1000 h the principal loss peak is twice its original width.

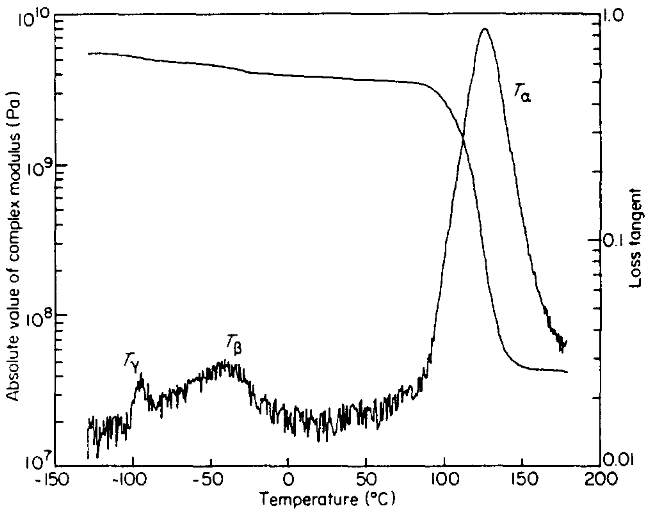

Fig. 2 Complex modulus data for unaged epoxy at a frequency of 5 Hz

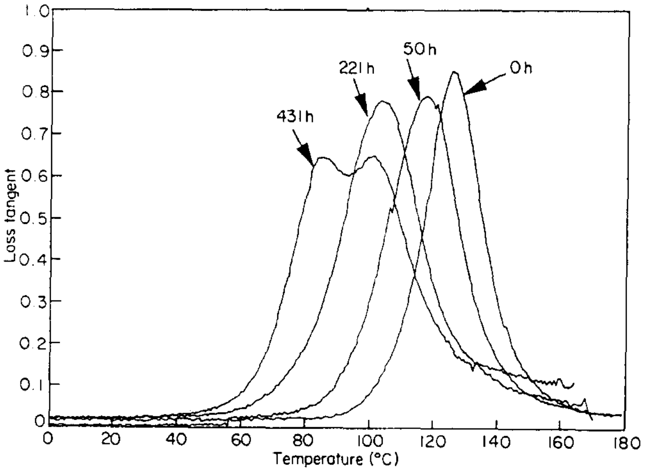

Fig. 3 Comparative loss tangent data for epoxy aged for various times

The frequency scanning experiments give results

Table 1. Comparative values of various parameters with time of ageing. The two values for tan δ_{max} and T_g indicate the presence of a double peak

Ageing time (h)	E_{20} (MPa)	tan δ_{max}	T_g (°C)	T_i (°C)	ΔT (°C)
0	4000	0.853	125.6	78	60
50	4100	0.793	117.3	75	65
73	4100	0.755	113.9	70	70
221	4000	0.780	103.3	50	80
365	4000	0.748	98.8	45	85
431	3900	0.646/0.649	85.1/101.5	45	—
503	3900	0.658/0.689	82.5/98.9	45	—
763	—	0.657/0.746	78.2/95.5	40	100
1261	3800	0.583/—	76.9/—	30	—

E_{20}	storage modulus at 20°C
tan δ_{max}	loss tangent maximum
T_g	glass transition temperature (corresponding to tan δ_{max})
T_i	temperature at onset of marked modulus decrease
ΔT	temperature range corresponding to marked modulus decrease

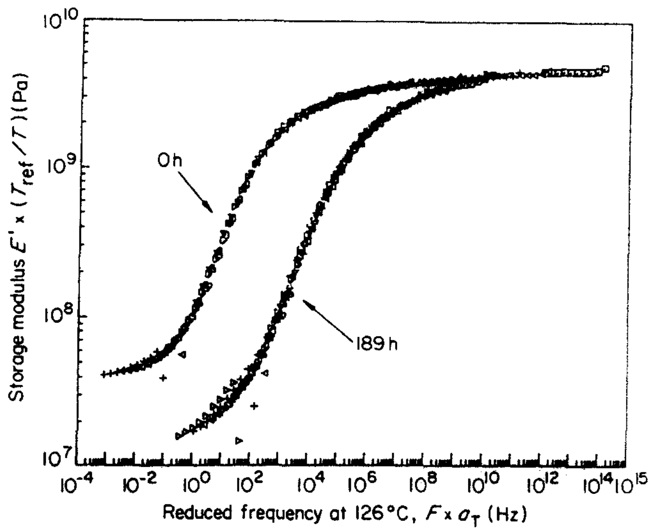

Fig. 4 Master curves for adhesive storage modulus, unaged and after 189 h ageing

which may be treated using the time-temperature superposition principle of Williams, Landel and Ferry[20]. WLF master curves have been plotted both for the freshly cured adhesive and that aged for 189 h. These curves, shown in Fig. 4, were constructed using horizontal shifts of the storage modulus corresponding to a reference temperature, T_{ref}, of 126°C. The shift factor, a_T, is expressed by the well-known equation:

$$\log a_T = \frac{-C_1(T - T_{ref})}{C_2 + T - T_{ref}} \qquad (4)$$

in which C_1 and C_2 are constants depending on the polymer in question. Using T_g for the unaged material as T_{ref}, the values for C_1 and C_2 obtained were respectively 19.4 and 130.2 for the freshly cured polymer and 48.1 and 439.4 for that aged over a period of 189 h.

The gravimetric experiments conducted to study water uptake led to the results summarized in Fig. 5. M_t represents water absorption by weight at time t and M_∞ the equivalent asymptotic value corresponding to apparent equilibrium (second stage). As can be seen, the behaviour can be essentially split into three stages. The initial stage of water uptake is a smoothly increasing function of the square root of time, $t^{1/2}$, until the second stage corresponding to apparent equilibrium is attained. This behaviour is termed Fickian and has previously been reported for epoxy resins[18, 21, 22]. The equilibrium value of water uptake corresponds to 2.2% by weight. Exploiting the linear section of the initial uptake stage, the diffusion coefficient, D, may be calculated from:

$$\frac{d(M_t/M_\infty)}{d(t^{1/2})} = \frac{4}{l}\left(\frac{D}{\pi}\right)^{1/2} \qquad (5)$$

where l is the adhesive sheet thickness. Edge effects are neglected. The value of D obtained was $11.9 \times 10^{-9}\,cm^2\,s^{-1}$ at 70°C and 100% RH, in reasonable agreement with that of $18.1 \times 10^{-9}\,cm^2\,s^{-1}$ at 60°C and 100% RH reported elsewhere[23].

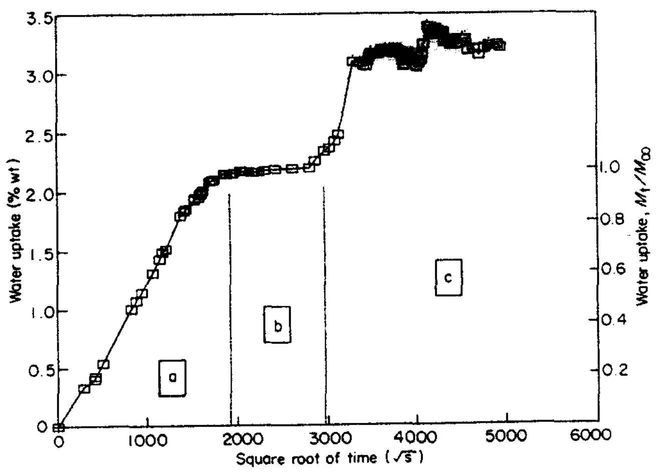

Fig. 5 Water uptake, M_t/M_∞, vs. $t^{1/2}$ for bulk adhesive: (a) Fickian increase; (b) 'equilibrium' zone; and (c) tertiary behaviour

The third stage of the absorption curve shows an increase in uptake attaining a second, apparently equilibrium, value of 3.2% by weight after 2000 h of ageing. This phenomenon has not, to the authors' knowledge, previously been reported in the literature.

These results effectively show that hydrothermal ageing of the bulk epoxy adhesive leads to marked changes in the mechanical properties of the material, due presumably to plasticization effects to a large extent.

Joint properties

Fig. 6 shows typical nominal stress/strain curves for torsional adhesive joints of various thicknesses. The apparent shear modulus clearly increases with joint thickness. This effect, described above, is due to the fact that the angle of rotation measured takes into account strain in the steel plate and part of the aluminium cylinder as well as that in the adhesive layer. As the glueline thickness is increased, the proportion of θ accounted for by the polymer grows and thus the recorded behaviour tends towards that of the adhesive alone. The apparent modulus thus increases. Correcting for these extraneous effects leads to a value of the true adhesive shear modulus of 2430 ± 50 MPa (before ageing).

Tensile tests were performed on standard dumb-bell

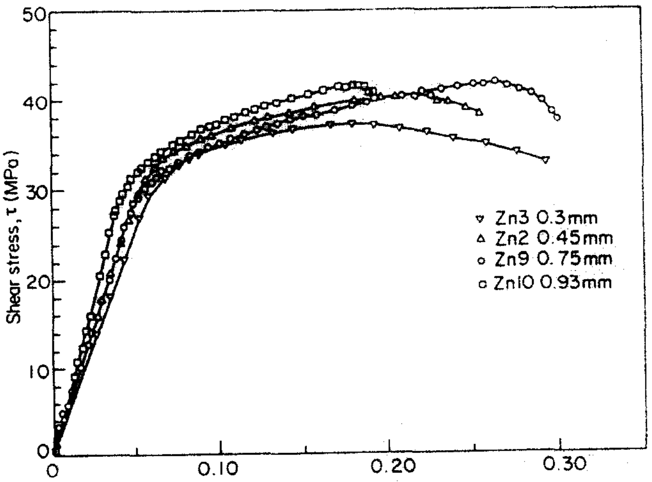

Fig. 6 Nominal stress/strain curves for torsional joints of various thicknesses

shaped samples of the polymer (moulded and machined as described above). These led to values of Young's modulus, E, of 6550 ± 620 MPa and Poisson's ratio, ν, of 0.36 ± 0.01. Although the discrepancy between the values of E obtained by viscoelasticimetry and tensile tests remains unexplained, good agreement between the latter and that obtained from torsional joints was found. Using the values of E and ν above and the relationship:

$$G = \frac{E}{2(1 + \nu)} \qquad (6)$$

the shear modulus of the adhesive, G, was found to be 2410 ± 230 MPa using results from the tensile tests.

Both yield stress, τ_y, and failure stress, τ_f, were found to be independent of joint thickness, mean values being respectively 29 ± 1 MPa and 36 ± 6 MPa. This is somewhat in contradiction to observations reported in the literature where τ_f tends to decrease with increasing glueline thickness[10, 11].

Failure surfaces were found to depend on adhesive thickness. For values of e less than about 0.3 mm, failure is generally cohesive. Above this value, a mixed adhesive and cohesive type of failure occurs. This is apparent in Fig. 7 which shows in (a) a typical cohesive failure and in (b) a mixed-mode failure. On the right hand side of Fig. 7(b), the grooves correspond to the impression of the machined cylinder. Nevertheless, it must be pointed out that it has not yet been ascertained whether this apparently adhesive failure is truly adhesive or whether a thin layer of polymer remains attached to the metal.

Ageing tests were conducted on joints of thickness 0.6 mm for up to 475 h. Adhesive shear modulus apparently decreases with ageing time as shown in Fig. 8. Both τ_f and failure strain, $\tan \gamma_f$, also evolve with exposure at 70°C to 100% RH. Both decrease with ageing time although there is no apparent change in $\tan \gamma_f$ before 200 h. After ageing, a circular white line concentric with the cylinder axis appears in fractured joints which apparently corresponds to water penetration within the glueline. Depth of penetration increases (see Fig. 9) with time of ageing until the line of separation becomes indistinct (after about 200 h). A plot of penetration distance versus the square root of time, $t^{1/2}$, is reasonably linear (see Fig. 10) thus leading

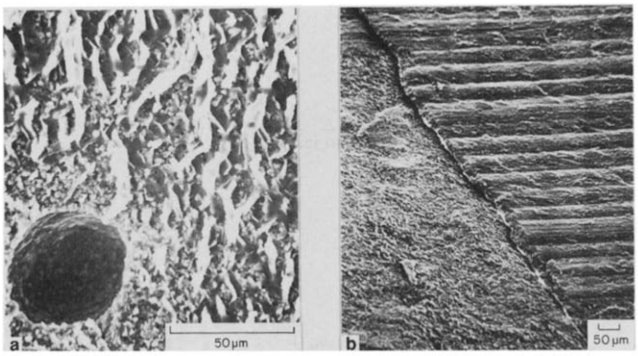

Fig. 7 Typical failure surfaces: (a) joint thickness of 0.3 mm giving cohesive failure; and (b) joint thickness of 0.7 mm giving mixed failure (cohesive on left and (apparent) adhesive on right)

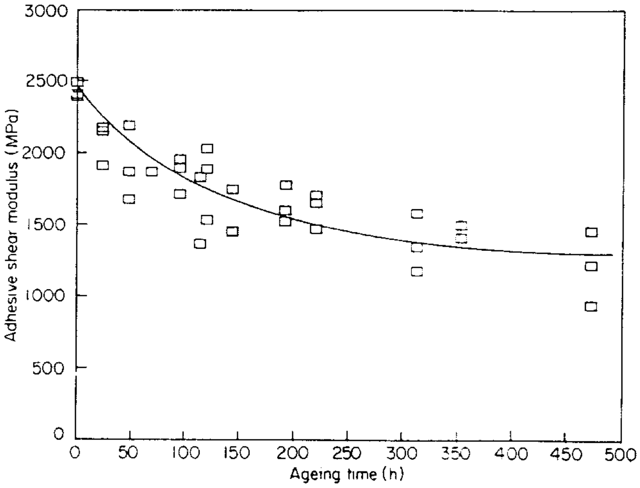

Fig. 8 Adhesive shear modulus (torsional test) vs. time of ageing

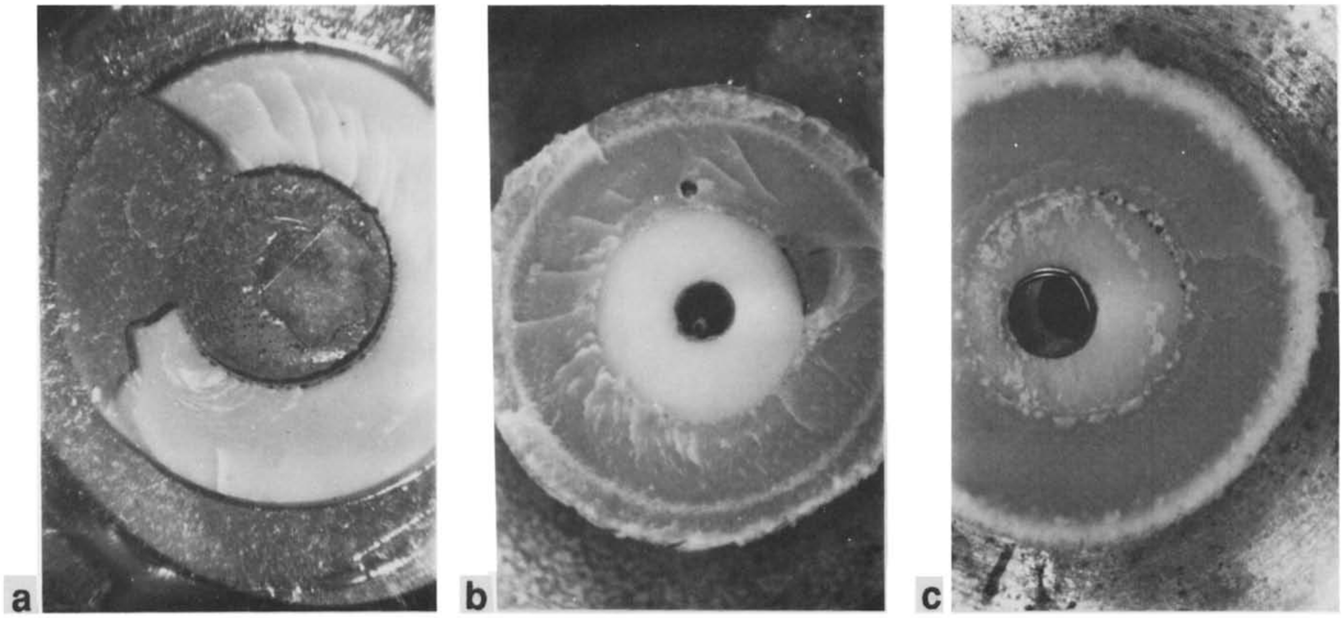

Fig. 9 Failure surfaces after various times of ageing, t: (a) Al/adhesive interface, t = 0 h; (b) steel plate/adhesive interface, t = 114 h; and (c) steel plate/adhesive interface, t = 472 h

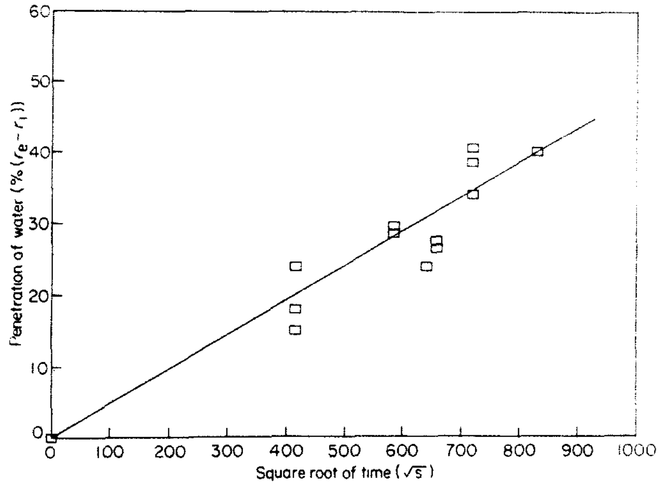

Fig. 10 Apparent penetration depth of water within annular glueline vs. square root of time, $t^{1/2}$

to the supposition that water ingress is Fickian.

Concerning the steel plate/epoxy interfacial zone, it was noticed that less adhesive remained on the substrate after failure following exposure to humid conditions. This effect is presumably due to local physical and/or chemical modifications caused by the presence of water and leading to interfacial weakening. Taking this into account together with the fact that no marked reduction in adhesive modulus was observed by viscoelasticimetry, suggests that the observed reduction in shear modulus in torsional tests is an artefact caused essentially by a reduction in the effective outer radius of the glueline annulus after water ingress.

Conclusion

The work described here represents initial results of a study of humid ageing of an epoxy structural adhesive both as a bulk material and in bonded joints. Gravimetric and viscoelasticimetric results indicate that water uptake is significant at 70°C and 100% relative humidity and that absorption behaviour is essentially Fickian. The glass transition temperature, T_g, and the elastic modulus corresponding to the rubbery state both decrease with water uptake. These phenomena are very probably related to plasticization of the polymer.

A torsional shear test has been developed and preliminary results suggest that this technique is well adapted to studies of the evolution of mechanical properties of bonded joint characteristics after ageing. The inherent joint geometry allows homogeneous water ingress. Joint failure after ageing appears to be intimately related to plasticization of the polymer by water and to weakening of the steel substrate/adhesive interfacial zone.

Acknowledgements

This work was made possible by financial aid from both Régie Renault and Peugeot SA and by the supply of adhesive by Permabond. The authors thank Y. Auriac for his technical assistance in developing the torsional apparatus.

References

1 **Gledhill, R.A. and Kinloch, A.J.** *J Adhesion* **6** (1974) pp 315-330
2 **Andrews, E.H. and Stevenson, A.** *J Adhesion* **11** (1980) pp 17-40
3 **Fay, P.A. and Maddison, A.** *Int J Adhesion and Adhesives* **10** (1990) pp 179-186
4 **Brewis, D.M., Comyn, J., Raval, A.K. and Kinloch, A.J.** *Int J Adhesion and Adhesives* **10** (1990) pp 247-253
5 **Adams, R.D. and Wake, W.C.** *'Structural Adhesive Joints in Engineering'* (Elsevier Applied Science Publishers, London, UK, 1986) pp 223-227
6 **Mahoney, L.C.** in *'Handbook of Adhesives', 3rd edn* edited by I. Skeist (Van Nostrand Reinhold, New York, NY, USA, 1990) pp 74-93
7 **Goland, M. and Reissner, E.** *J Appl Mech* **2** (1944) pp A17-A27
8 Reference 5, op. cit., pp 115-134
9 **Gillespie, T. and Rideal, E.** *J Colloid Sci* **11** (1956) pp 732-747
10 **Bryant, R.W. and Dukes, W.A.** *Brit J Appl Phys* **16** (1965) pp 101-108
11 **Foulkes, H., Shields, J. and Wake, W.C.** *J Adhesion* **2** (1970) 254-269
12 **Lin, C.J. and Bell, J.P.** *J Appl Polym Sci* **16** (1972) pp 1721-1733
13 **Peretz, D.** *J Adhesion* **9** (1978) pp 115-122
14 **Stringer, L.G.** *J Adhesion* **18** (1985) pp 185-196
15 **Schmit, E.** *Double Liaison* **407** (1989) pp 29-36
16 **Haïdara, H.** *PhD Thesis* (Université de Haute Alsace, France, 1985)
17 **Shanahan, M.E.R., Haïdara, H. and Schultz, J.** in *'Mechanical Behaviour of Adhesive Joints'* edited by G. Verchery and A.H. Cardon (Pluralis, Paris, France, 1987) pp 105-116
18 **Robert, A.** *PhD Thesis* (Institut National Polytechnique de Toulouse, France, 1987)
19 **Mazich, K.A., Holubka, J.W. and Kiligoar Jr, P.C.** *Ind Eng Chem Prod Res Dev* **25** (1986) pp 273-276
20 **Williams, M.L., Landel, R.F. and Ferry, J.D.** *J Amer Chem Soc* **77** (1955) pp 3701-3707
21 **Gledhill, R.A., Kinloch, A.J. and Shaw, S.J.** *J Adhesion* **11** (1980) pp 3-15
22 **Brewis, D.M., Comyn, J., Shalash, R.J.A. and Tegg, J.L.** *Polymer* **21** (1980) pp 357-360
23 **Kinloch, A.J.** *J Adhesion* **10** (1979) pp 193-219

Authors

The authors are with the Centre National de la Recherche Scientifique, Ecole Nationale Supérieure des Mines de Paris, Centre des Matériaux P.M. Fourt, B.P. 87, 91003 Evry Cedex, France. Correspondence should be addressed to Dr Shanahan.