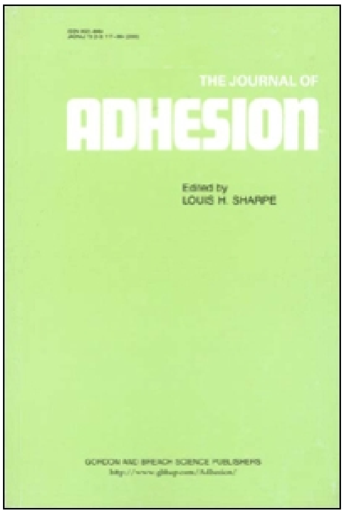

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Bulk and Interphase Effects in Aged Structural Joints

M. P. Zanni-deffarges[a]; M. E. R. Shanahan[a]
[a] Centre National de la Recherche Scientifique, Ecole Nationale Supérieure des Mines de Paris, Centre des Matériaux P.M. Fourt, EVRY Cédex, France

To cite this Article Zanni-deffarges, M. P. and Shanahan, M. E. R.(1994) 'Bulk and Interphase Effects in Aged Structural Joints', The Journal of Adhesion, 45: 1, 245 — 257

To link to this Article: DOI: 10.1080/00218469408026641

URL: http://dx.doi.org/10.1080/00218469408026641

J. Adhesion, 1994, Vol. 45, pp. 245–257
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

Bulk and Interphase Effects in Aged Structural Joints*

M. P. ZANNI-DEFFARGES 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 October 20, 1992; in final form March 10, 1993)

Although structural adhesives are becoming widespread in numerous applications, one important limitation at present is the long term behaviour of bonded assemblies under conditions of high humidity, especially at elevated temperatures. This study presents a comparison between bulk properties of a structural epoxy resin and its behaviour in a torsional joint consisting of a hollowed-out cylinder bonded to a plate—both substrates being in stainless steel. Exposure to *ca.* 100% relative humidity at 70°C leads to modification of the bulk properties of the polymer, notably reduction of its elastic modulus. Although this may explain some differences in behaviour of the torsional joint, premature failure is attributed to weaknesses in the interphase zone.

Auger Electron Spectroscopy (AES) has been employed to investigate both unbonded steel surfaces and fracture zones. Although prolonged exposure to water leads to a more extensive degree of (apparently) adhesive failure at the interface polymer/metal, AES has shown the presence of non-negligible quantities of carbon, attributed to residual polymer. Failure would seem to occur, at least partly, in a weak interphase of the polymer, near, but not at, the interface.

Various possible causes are evoked. For dry failure, residual polymer may be due to the topography of the metal surface and/or local modification of the adhesive during cure. In the case of aged joints, in addition there are potential effects due to swelling and differential stresses, secondary bond failure and molecular chain scission within the polymer, all provoked by the presence of water.

KEY WORDS Auger Electron Spectroscopy (AES); epoxy resin; humid ageing; interphase; steel; structural adhesive; torsional test.

INTRODUCTION

The use of structural adhesives, particularly in the automotive and aerospace industries, is becoming widespread due to the many advantages offered by this method of assembly. These advantages include, for example, reduction in stress concentrations, necessarily engendered after drilling holes in preparation for bolting or riveting, protection against corrosion, flexibility of conception, and the possibility of joining thin and/or dissimilar materials. However, certain disadvantages related to

---

*Presented at the International Symposium on "The Interphase" at the Sixteenth Annual Meeting of The Adhesion Society, Inc., Williamsburg, Virginia, U.S.A., February 21–26, 1993.

**Corresponding author.

the use of structural adhesives do exist. Apart from a relative lack of mechanical resistance shown by polymers at high temperatures (creep, relaxation), probably the most important problem remaining to be solved is that of the reduction of strength of bonded joints brought about by continued exposure to aggressive environments. An adhesive bond may present very high resistance to applied loads initially after formation and indeed over long periods in a neutral environment, but the presence of liquids, especially water, often leads to considerable weakening. The combination of high humidity and elevated temperatures is particularly deleterious. Various processes may contribute to this effect. The bulk properties of the adhesive may be altered by the uptake of water. (This may also apply to the substrates in certain cases, but is unlikely for present purposes where steel adherends are to be considered.) Changing thermodynamic conditions at the interface between the adhesive and the substrate due to the presence of water may lead to reduced mutual affinity and even spontaneous separation.[1] The existence of an interphase, or zone of variable structure separating the bulk substrate from the bulk adhesive, was suggested some years ago,[2] and if this interphase is weakened by the presence of water, a certain similarity with the theory of weak boundary layers[3] may be evoked. As pointed out by Kinloch, there is ample evidence that no single mechanism can explain all the different cases reported.[4] Details of the adhesive system and environment are all important.

With this in mind, we have undertaken a study of the behaviour of an epoxy resin, both as used in an adhesive joint with stainless steel adherends and as a bulk material, when subjected to conditions of accelerated ageing. Much work has been done on aluminium and titanium but, apparently, relatively little on stainless steel.

Several experimental techniques have been employed. A torsional test consisting of a variation on the long established "napkin ring" geometry[5,6] was used to assess changes in mechanical behaviour of bonded joints after exposure to humidity, whilst gravimetric analysis and viscoelastometry have been employed to investigate the kinetics of water sorption in the bulk resin and corresponding modifications to physical properties.

Apart from direct visual and microscopic examination of the fracture surfaces obtained from torsional joints, more sensitive methods of analysis are beneficial in an attempt to understand the effects of hygrothermal ageing on failure mode. We have therefore employed Auger Electron Spectroscopy (AES) to investigate the influence of the environment on the locus of failure. This technique has given promising preliminary results which indicate its potential for investigation of the interphase region.

EXPERIMENTAL

Materials

The modified epoxy resin used in this study is a material based on diglycidylether of bisphenol A (DGEBA), and tetraglycidyl methylene dianiline (TGMDA) with dicyandiamide (DICY) as the crosslinking agent. In the present work, the crosslinked adhesive was obtained after heating at 3°C/min up to 130°C and maintaining the material at this temperature for 90 minutes. Bulk samples of epoxy resin were prepared both for gravimetric studies and for viscoelastometry.

Stainless steel substrates were used. The steel chosen contains 0.05% C, 16% Cr, 4% Ni and 4% Cu. Surface treatment was restricted to an industrial procedure consisting of degreasing with trichloroethylene, acetone and alkaline solution and sandblasting with corundum (160 μm).

Bonded joints consisted of a steel plate of 3 mm thickness to which was bonded a hollowed-out cylinder of external radius and internal radius, respectively, of 10 and 5 mm. In order to minimise potential perturbations to the stress field in the adhesive layer caused by spew fillets,[7,8] these latter were essentially eliminated before crosslinking by the use of tight-fitting PTFE seals around and inside the cylinder. Curing conditions were the same as for the bulk adhesive.

Methods

Adhesive bulk characteristics were evaluated using a Metravib viscoanalyser. Samples were tested in tension-compression mode at a frequency of 5 Hz and at a rate of temperature rise of 2°C/min. This technique was used to estimate both the complex modulus and the glass transition temperature, T_g, of the adhesive and modifications due to ageing.

Gravimetric analysis was employed to investigate the kinetics of diffusion of water into the polymer.[9]

Adhesive joints were tested to failure on an apparatus developed in our laboratories and capable of applying a rotational couple about the axis of the bonded cylinder. This geometry has the advantage of simplifying the stress distribution and the mathematics of diffusion. Gillespie and Rideal,[5] originally employed a "napkin ring" geometry. In the present adaptation of this geometry, the steel plate is maintained stationary whilst an axial rotational displacement is applied to the cylinder at an essentially constant rate of 2×10^{-5} rad. s^{-1} (corresponding to a maximum strain rate in shear, $\dot{\gamma}$, of 2×10^{-4} s^{-1} for a joint of glueline thickness of 1 mm). Rotational displacement is followed by means of an extensometer consisting of a lever arm and LVDT assembly. The applied couple is monitored (indirectly) using a strain-gauge bridge fixed to the (thinned) load axis of the machine. After suitable corrections have been made allowing for extraneous deformation in the metallic parts of the bonded joint measured by the extensometer,[10] this experimental arrangement is capable of giving results leading to evaluation of the shear modulus, G, of the adhesive layer. Previous work has shown good agreement between the value of shear modulus of the unaged adhesive found by this method and that obtained from static tensile tests.[10]

Both adhesive joints and bulk polymer samples were aged for various periods at 70°C and *ca.* 100% relative humidity.

AUGER ELECTRON SPECTROSCOPY

The Auger effect was first observed in 1925 but has only relatively recently been exploited as a surface analytical technique. Development has come about with accessibility to suitable electron spectrometers and associated electronics, and routine ultra-high vacuum systems.[11]

When an atom is ionised by removal of an inner electron, in general the filling of the vacancy by an electron of higher energy is associated with X-ray emission. However, in some cases, an electron is emitted instead. This Auger process leads to the emission of an electron having a characteristic energy which can thus be used to identify the element of origin.[12]

Auger Electron Spectroscopy (AES) is a technique in which a beam of primary electrons of low energy (typically 2 to 10 keV) is brought to impinge on the surface of interest. Both primary (elastically and inelastically diffused) and secondary electrons are emitted. A typical emission energy spectrum will contain secondary emission peaks corresponding to the Auger process which can thus be used to identify surface elements.

AES is now a well-established technique in surface physics and indeed has been used, with varying degrees of success, in adhesion studies. One major problem encountered is the charging of polymeric, non-conducting materials by the primary electron beam. Nevertheless, high surface sensitivity coupled with the possibility of depth profiling by erosion of surface layers make this technique a prime choice for the investigation of interphase regions in adhesive joints (particularly in conjunction with X-ray Photoelectron Spectroscopy (XPS)).

Gettings *et al.*[13] and, more recently, Dodiuk and Kenig[14] have used AES in investigations of the interface of fractured joints using, respectively, mild steel and maraging steel adherends, and Gettings and Kinloch have used both XPS and static Secondary Ion Mass Spectroscopy (SIMS) for investigating the effects of silane-based primers deposited onto mild steel substrates before bonding.[15] Nevertheless, most work using surface analytical technique to be found in the literature seems to treat substrates other than steel, and in particular, aluminium (*e.g.* Refs. 16–23).

In the present study, the surfaces of stainless steel cylinders used for constructing torsional joints were analysed, both before bonding and after failure, with an aim to understanding the failure mode. The primary electron beam used was of energy 2.05 keV and intensity 2×10^{-7} A. Analysis depth was of the order of 20 Å using an electron beam of diameter *ca.* 1 μm. A cylindrical mirror analyser (CMA) manufactured by Riber was employed and, during analysis, a vacuum of *ca.* 10^{-9} Torr was maintained.

An argon ion gun was used to erode the cylinder surfaces. The erosion rate is of the order of 5 to 10 monolayers per hour, in the case of a metallic surface, using a pressure of 10^{-5} Torr of argon.

RESULTS AND DISCUSSION

Gravimetric analysis of bulk samples of the epoxy resin exposed to *ca.* 100% RH at 70°C was continued until (apparent) equilibrium was attained. By plotting water uptake against the square root of time, t, it was observed that the relationship was acceptably linear up to about half of the equilibrium value, thus indicating Fickian behaviour.[24] Using the equation:

$$\frac{m_t}{m_\infty} = \frac{4}{h}\left(\frac{Dt}{\pi}\right)^{1/2}; \quad \frac{m_t}{m_\infty} \leqslant 0.6 \tag{1}$$

where D is the diffusion coefficient of water into the polymer, t is time, h is specimen thickness and m_t and m_∞ are, respectively, the masses of water absorbed at time t and saturation, D was found to be *ca.* 1.5×10^{-12} m^2 s^{-1} for a value of m_∞ taken to be 4%.

Changes in both Young's modulus, E, and the loss factor, tan δ, of the polymer as a function of temperature during the ageing process at 70°C and *ca.* 100% RH were followed using viscoelastometry. Figure 1 gives results corresponding to the adhesive in its initial, unaged state and after *ca.* 3000 hours ageing (about 4 months). It may reasonably be supposed that, after this period, the polymer is saturated (although in some cases, fluctuations in sorption figures have been observed and cannot, as yet, be accounted for). Figure 1 shows clearly that water ingress severely modifies the mechanical properties of the resin. Not only does T_g fall from *ca.* 140°C before exposure to humidity to *ca.* 130°C at saturation, but also Young's modulus at ambient temperature drops from *ca.* 2.5 GPa to *ca.* 1.9 GPa. These data show that, after water sorption, the temperature at which Young's modulus starts to decrease rapidly is much reduced, thus limiting the upper extent of the useful temperature range of the adhesive in service. A second peak in tan δ appears at

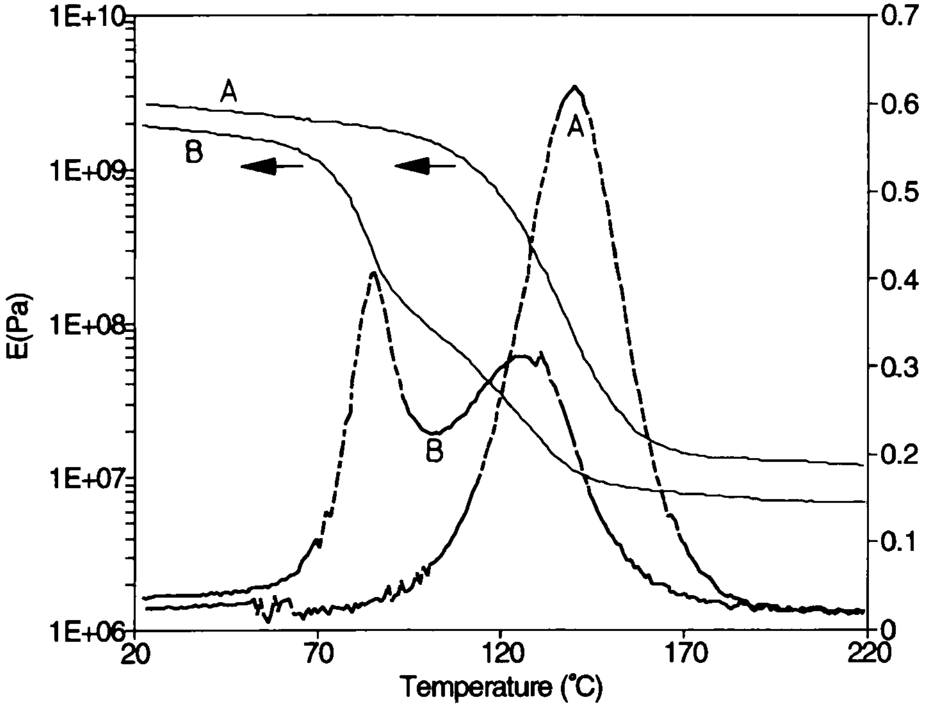

FIGURE 1 Young's modulus, E, and loss factor, tan δ, of the epoxy resin as a function of temperature, in its initial state, A, and after *ca.* 3000 hours ageing, B.

about 85°C. The appearance of two peaks is not fully understood but two possible explanations are evoked. It is possible that the presence of water in the polymer may lead to a "copolymer" structure characterised by two T_gs. Subsequent drying leads to disappearance of the peak at 85°C suggesting that its presence is related to physically, rather than chemically, bound water. Alternatively, Morgan[25] *et al.* have identified heterogeneous distributions in the crosslink density of epoxy systems. We may, therefore, postulate that water diffusion may facilitate molecular motion in phases of lower crosslink density and new transitions result.

As expressed earlier, it has been shown that the torsional test is capable of giving results leading to a satisfactory evaluation of the shear modulus, G, of the unaged adhesive.[10] After ageing for various periods at 70°C and 100% RH, torsional joints were tested to failure. Due to the kinetics of water ingress into the joint, until the joint is entirely saturated the annular adhesive layer will represent a "composite" material. Zones near water vapour contact surfaces will become rapidly saturated whilst those further away will contain less diffused liquid. There will, thus, be a gradient of modulus along the radius of the joint. Nevertheless, we may calculate an effective, or apparent, value of the adhesive shear modulus from:

$$G = \frac{2\,M\,e}{\pi\,\theta\,[r_e^4 - r_i^4]} \tag{2}$$

where M is applied couple, e is glueline thickness, θ is angular displacement and r_e and r_i are, respectively, external and internal radii of the annulus. (Equation (2) is obtained simply from the expression for shear stress,[26] *viz.* equation (3) below, and the fact that (maximum) shear strain is given by $r_e\,\theta/e$.) This effective value of G, at ambient temperature, is plotted in Figure 2 as a function of ageing time, t. Clearly the value of G given between zero ageing and saturation is of dubious value, as it stands, for the reason evoked above, but after *ca.* 250 hours of ageing, saturation is apparently attained. Equation (2) then gives the true modulus. It can be seen that the ratio of shear modulus at saturation to that of the unaged adhesive is close to 0.75. This is in satisfactory agreement with the equivalent ratio of values of Young's modulus for the aged and unaged adhesive as found on bulk samples by viscoelastometry. Assuming Poisson's ratio to be little altered by the ageing process, there is, thus, good agreement between mechanical properties as obtained from tests on the bulk polymer and in bonded joints.

However, if one considers failure behaviour, results show that ageing leads to premature failure. Figure 3 shows examples of applied couple, M, as a function of maximum strain, γ (*i.e.* shear strain at the outer radius, r_e, of the annular glueline), for an unaged torsional joint and for two ageing times (140 and 1500 hours). Couple, M, rather than maximum stress, τ, (at $r = r_e$) is used as the ordinate since although for the initial linear parts of the behaviour we may employ the elastic expression:

$$\tau = \frac{2\,M\,r_e}{\pi\,[r_e^4 - r_i^4]} \tag{3}$$

in the non-linear regions this equation is invalid.

If we assume the behaviour of the unaged polymer to be essentially plastic near the zone corresponding to the maximum couple, the stress, τ_p, will be given by:

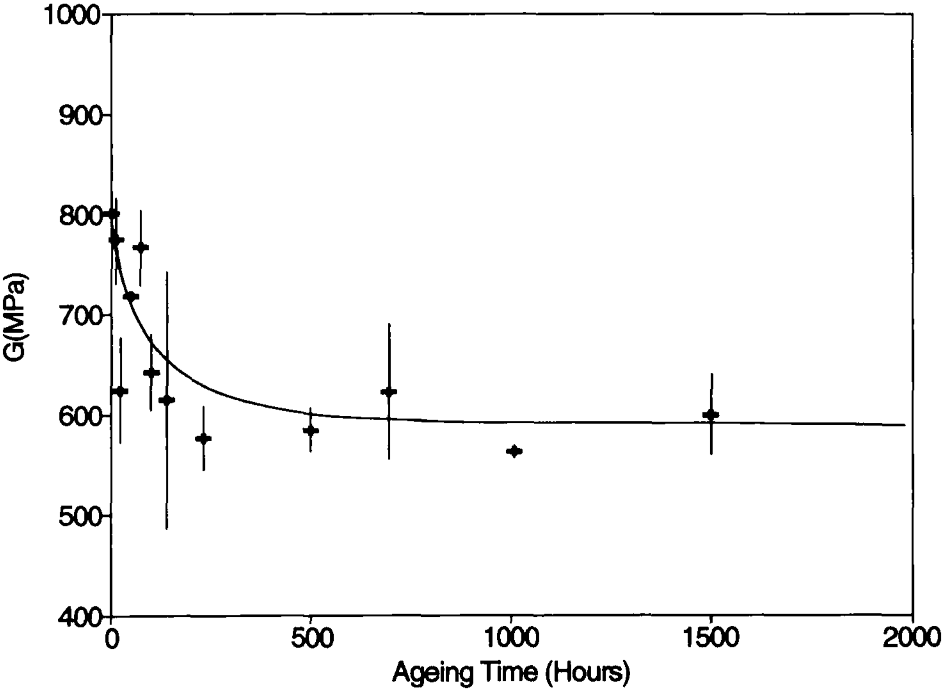

FIGURE 2 Effective value of shear modulus of the adhesive, G, at ambient temperature, *vs* ageing time.

$$\tau_p = \frac{3\,M}{2\pi\,[r_e^3 - r_i^3]} \tag{4}$$

For a maximum of M~75 Nm, equation (4) leads to τ_p~41 MPa. Assuming that the response is still linearly elastic at failure and, therefore, adopting equation (3) for the joints aged for 140 and 1500 hours, we find maximum failure stresses of, respectively, *ca.* 21 MPa and *ca.* 10 MPa.

We can thus see that stresses at failure are considerably reduced by water absorption but what is perhaps more noteworthy is the reduction in failure strain. Indeed, whereas unaged joints finally fail after considerable non-linear behaviour, highly aged joints fail shortly after the elastic domain. It is unlikely that the intrinsic behaviour of the polymer becomes more brittle after water absorption because of plasticisation effects. Failure in the interfacial or interphase zone must, therefore, be suspected. In addition, whilst unaged joints generally lead to a mixed (apparently) adhesive/cohesive (within the adhesive) type failure, aged joints tend to show (apparently) adhesive failure.

Bearing in mind the possibility of a weak interphase zone[2] and the theory of weak boundary layers,[3] use of AES was made to investigate failure surfaces obtained on the cylindrical substrates. Zones analysed were of area equal to *ca.* 20 μm^2. At this stage, the elemental analysis has been restricted mainly to carbon and iron. As far as the adhesive is concerned, the KLL carbon peak at 270 eV obtained closely re-

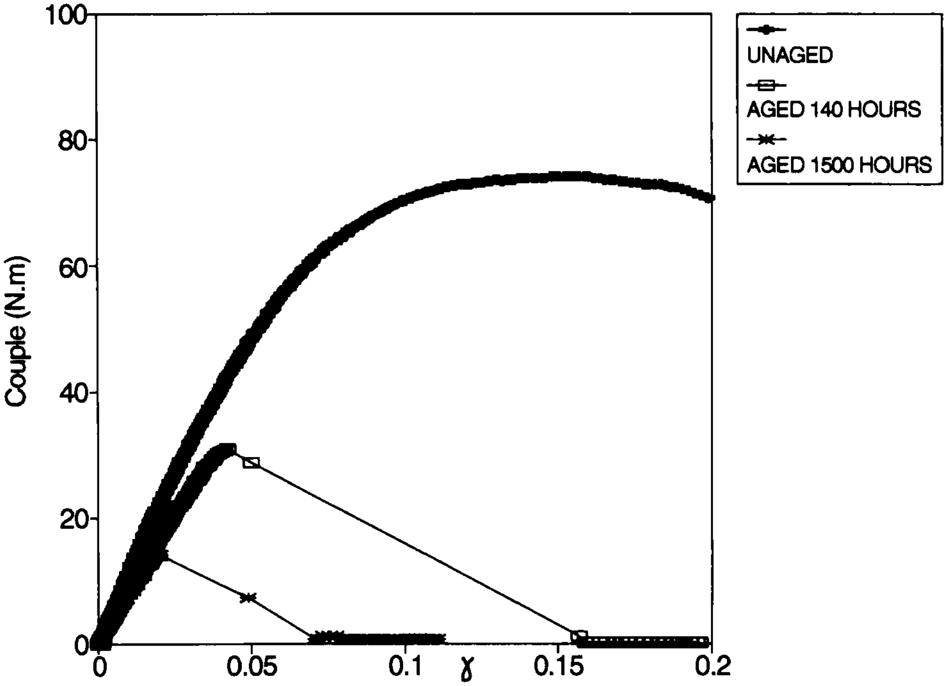

FIGURE 3 Applied couple, M, *vs* maximum strain, γ, of adhesive in torsional joint for different ageing times, t.

sembles that described by Guttman,[27] corresponding to amorphous carbon. After ageing, surface spectra suggested the presence of carbonates partially obscuring the carbon peak and thus rendering somewhat difficult identification of the type of carbon present.

Several methods of interpretation of AES spectra exist, but the one adopted here corresponds to assigning a sensitivity factor f_i to each element i present.[28] The concentration of a given element, C_i, is defined as:

$$C_i = \frac{h_i/f_i}{\sum_i h_i/f_i} \tag{5}$$

where h_i is the amplitude of the peak corresponding to element i. Nevertheless, such interpretation should be considered as semi-quantitative.

In the case of surface-treated but unbonded cylinders, it was found that the atomic percentage of iron, C_{Fe}, remained essentially constant even after argon erosion for up to 10 hours, corresponding to the removal of *ca.* 50 to 100 monolayers. There was, however, some increase in C_{Fe} for aged cylinders with erosion time and the initial value of C_{Fe} was higher before hygrothermal exposure. Unaged cylinders showed a virtually constant value of atomic percentage of carbon, C_C, of *ca.* 10 to 15% whilst in the case of aged specimens, three to four hours of erosion were sufficient to reduce C_C from the order of 40 atomic % to about 10 to 20 atomic %.

Henceforth, the carbon concentration stabilised. These effects are presumably due to surface contamination.

By contrast, the apparently metallic surface exposed after failure of an unaged joint showed a value of C_C greater than 20% up until 6 or 7 hours of erosion whilst C_{Fe} increased from *ca.* 10% to *ca.* 25% (see Figures 4 and 5). This result, whilst not being entirely conclusive, strongly suggests the presence of a non-negligible quantity of polymer remaining on the (apparently) interfacial failure surface. Unfortunately, the actual quantity is at present inaccessible since the erosion rate of the carbon material is unknown. Although more work is required to ascertain the quantity of polymer remaining, we may hazard a rough guess at its thickness by assuming erosion rate to be of the same order of magnitude as for the steel (in fact it is probably greater), in which case we obtain an estimate of a few hundreds of Angstroms. Notwithstanding the very approximate nature of this figure, clearly we may gather that the amount of polymer present after failure was relatively small and thus failure occurred, at least partially, in the polymeric phase close to the substrate surface. Two possible explanations can be evoked. Since the substrates were sand-blasted prior to bonding, the topography was irregular. It may be that the failure path ran essentially parallel to the (macroscopic) interface and, in the main, followed the

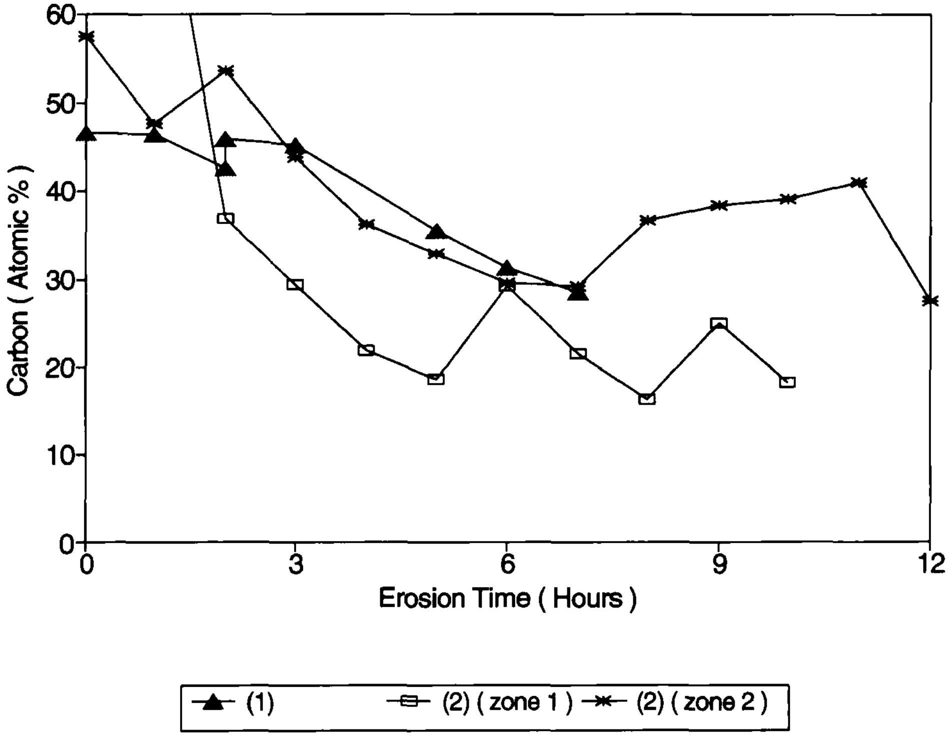

FIGURE 4 Evolution of carbon concentration on cylinder substrates after failure of unaged joint *vs* argon ion erosion time in AES. (1) and (2) refer to different cylinders and zones 1 and 2 to separate regions of cylinder (2).

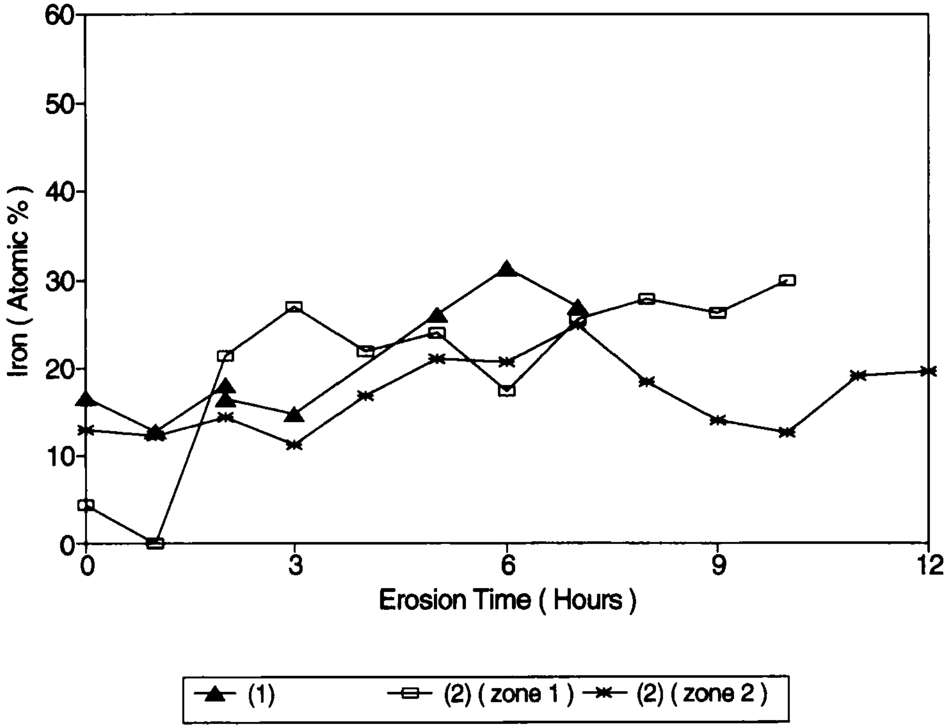

FIGURE 5 As for Figure 4, but iron concentration.

tops of the asperities of the metallic surface. In this case, some adhesive will have remained trapped between asperities and it is these "islands" of polymer which were detected by AES. The fact that some iron was detected initially suggests that at least some zones of polymer were surrounded by virtually, or even totally, bare metal. A similar explanation was proposed by Gettings *et al.* in a study of adhesion using mild steel adherends.[13] An alternative explanation is that failure took place close to, but not at the interface, in a Bikerman weak boundary layer, or weak interphase. This relatively low-strength zone could perhaps be a result of over-crosslinking of the adhesive in the immediate vicinity of a metal oxide on the substrate. It is plausible that the metal oxide may act as a "catalyst" during cure, leading to local fragilisation of the polymer.[29] Indeed, this phenomenon may equally apply, at least to some extent, in the case of the earlier proposed mechanism. The propensity to failure will be exacerbated by an effective reduction in the toughness of the adhesive.

Similar results were obtained with the failure surfaces of aged joints, but with some differences. Whilst unaged joints demonstrated mixed failure surfaces, those that were aged significantly led to predominantly (apparent) interfacial separation. Figure 6 shows examples of the evolution of the atomic percentage of carbon, C_C, as a function of erosion time for various hygrothermal exposure times. Although no definite, quantitative conclusions may yet be reached, the indications are that

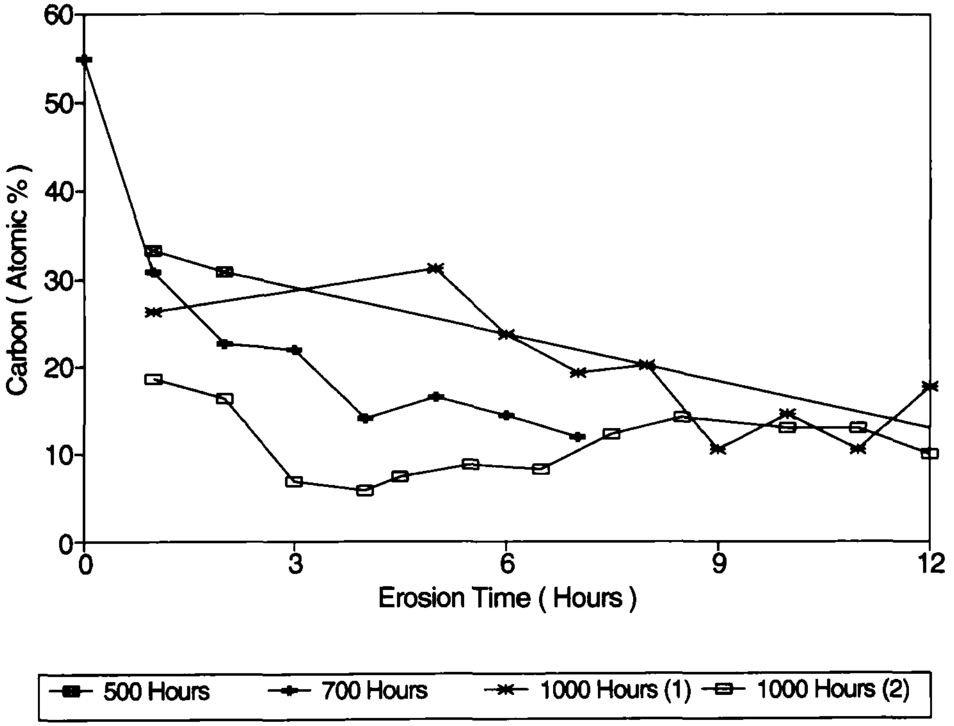

FIGURE 6 As for Figure 4, but for joints aged for various periods.

initial values of C_C are in general lower after ageing and indeed tend to decrease with ageing time. In addition, less erosion time would seem to be required to reduce C_C to values comparable with those obtained with unbonded cylinders. Iron could be detected after only a brief spell of erosion in some cases corresponding to prolonged ageing. In the light of the above discussion on unaged joints, we may postulate that swelling of the adhesive on water ingression induces differential stresses between the polymer and the stainless steel adherends. (Exposure to elevated temperature may lead to similar effects due to differential expansion, but this effect is believed to be relatively minor since unaged joints will have also undergone a more significant temperature change than this after crosslinking.) In addition, the presence of water near the adhesive/substrate interface may disrupt van der Waals bonds, and possibly weaken metal oxides in the vicinity. Such effects, either alone or combined, may well lead to a larger proportion of the adhesive being detached from the substrate and remaining on the bulk polymer, in agreement with generally lower values of C_C observed.

Alternatively, the lower values of C_C could be attributed to the existence of a thinner pellicle of adhesive remaining on the substrate after longer times of exposure to humidity. It is possible that, in the case of aged joints, the presence of water leads to chain scission (by hydrolysis) in the interphase zone. It has, in fact, been shown that the ageing process of the adhesive due to water uptake is not entirely reversible[9] (although the peak of tan δ at 85°C disappears after drying, T_g does not return to its initial value). Chain scission occurring near the polymer/metal boundary could account for failure taking place within the adhesive but nearer to the metallic surface, leaving smaller quantities of the polymer on the adherend. Of course, it is quite plausible that such degradation of the polymer aggravates the situation by adding to the previously-mentioned effects of swelling and secondary bond failure.

It is believed that these various mechanisms all participate to some extent in the failure of the epoxy/stainless steel joints studies—the exact locus of failure depending probably also to some extent on the details of the local stress field. For a given torsional joint, it was found by AES after ion erosion that evolution of the quantity of carbon depended on the zone analysed, thus suggesting the inhomogeneity (and in some cases discontinuity) of the adhesive pellicle. However, whichever mechanism(s) predominate(s), it is clear that failure after ageing occurs to a large extent within the adhesive but very close to the interface polymer/metal.

Failure of these epoxy/stainless steel joints whilst being of a mixed cohesive in the adhesive/(apparently) adhesive mode in the unaged condition evolves with humid ageing to a mainly (apparently) adhesive mode. AES analysis strongly suggests the existence of a weak interphase between the metal and the bulk adhesive. Although failure occurs to some extent in this region even for unaged joints, prolonged exposure to humidity appears to lead to a lower quantity of adhesive being left on the substrate for various reasons discussed above.

CONCLUSIONS

A modified epoxy resin has been subjected to accelerated ageing at 70°C and *ca.* 100% RH both in its bulk (crosslinked) state and in torsional stainless steel joints. Water diffusion was found to be essentially Fickian and its presence leads to lowering of the T_g of the polymer and a decrease in Young's modulus at ambient temperature. A corresponding decrease in shear modulus has been shown to occur in torsional joints once saturation has been attained. Failure occurs prematurely in aged joints but cannot be reasonably accounted for by modifications to the bulk properties of the adhesive. Whereas fracture is mixed in unaged joints, it is predominantly (apparently) interfacial in aged assemblies.

Since the mechanisms of failure of an adhesive joint depend to a large extent on the details of the system and the environment, AES analysis has been used to investigate the fracture surfaces of torsional joints. AES has indicated the presence of organic matter on the apparently bare metallic failure surfaces. This probably corresponds to deposits of the adhesive remaining on the substrate in discontinuous patches. Failure is thought to occur in a weak interphase near the polymer/metal substrate and facilitated either by the local topography or by possible modification of the adhesive near the interface during cure (or both). After humid ageing, less organic matter is apparent on the substrate. Failure presumably occurs closer to the metal surface. Various causes, or combinations thereof, are conceivable. The presence of water may lead to local swelling and, thus, differential stresses near the polymer/metal interface. Secondary bonds across the interface may also possibly be disrupted. The irreversible nature of the ageing process of the adhesive could be linked to hydrolysis and chain scission. Any of these effects would tend to make the locus of failure follow a path nearer the stainless steel adherend.

Acknowledgements

The authors thank the Société Nationale d'Etudes et de Constructions de Moteurs d'Aviation (SNECMA) for their financial and material aid in this study. The help of Y. Auriac during the development of the torsional apparatus and the invaluable assistance of T. T. Nguyen with the AES analysis are acknowledged.

References

1. R. A. Gledhill and A. J. Kinloch, *J. Adhesion* **6,** 315 (1974).
2. L. H. Sharpe, *J. Adhesion* **4,** 51 (1972).
3. J. J. Bikerman, *The Science of Adhesive Joints, 2nd Ed* (Academic Press, New York, 1968), chap. 6.
4. A. J. Kinloch, *Adhesion and Adhesives: Science and Technology* (Chapman and Hall, London, 1987), p. 362.
5. T. Gillespie and E. Rideal, *J. Colloid Sci.* **11,** 732 (1956).
6. H. Foulkes and W. C. Wake, *J. Adhesion* **2,** 254 (1970).
7. R. D. Adams and N. A. Peppiatt, *J. Adhesion* **9,** 1 (1977).
8. R. D. Adams, J. Coppendale and N.A. Peppiatt, *J. Strain Analysis* **13,** 1 (1978).
9. M. P. Zanni-Deffarges and M. E. R. Shanahan, Structural Adhesives in Engineering III, P. R. I., paper 28 (1992).
10. M. P. Zanni-Deffarges and M. E. R. Shanahan, *Key Engineering Materials* **72–74,** 287 (1992).
11. O. S. Heavens, *5e Ecole d'Eté Méditerranéenne, Adsorption et Adhesion* (Les Editions de Physique, Paris, 1983), p. 275.
12. N. A. Gjostein and N. G. Chavka, *J. Testing Evaluation, JTEVA* **1,** 183 (1973).
13. M. Gettings, F. S. Baker and A. J. Kinloch, *J. Appl. Polym. Sci.* **21,** 2375 (1977).
14. H. Dodiuk and S. Kenig, *Surface Interface Analysis* **17,** 503 (1991).
15. M. Gettings and A. J. Kinloch, *J. Mater. Sci.* **12,** 2511 (1977).
16. J. S. Noland, in *Adhesion Science and Technology 9B*, L. H. Lee, Ed. (Plenum Press, New York, 1975), p. 413.
17. J. S. Solomon and D. E. Hanlin, *Appl. Surf. Sci.* **4,** 307 (1980).
18. T. S. Sun, D. K. McNamara, J. S. Ahearn, J. M. Chen, B. Ditchek and J. D. Venables, *Appl. Surf. Sci.* **5,** 406 (1980).
19. A. J. Kinloch and N. R. Smart, *J. Adhesion* **12,** 23 (1981).
20. G. D. Davis and J. D. Venables, *Durability of Structural Adhesives,* A. J. Kinloch, Ed. (Applied Science Pub., London, 1983), p. 43.
21. J. D. Venables, *J. Mater. Sci.* **19,** 2431 (1984).
22. A. J. Kinloch, L. S. Welch and H. E. Bishop, *J. Adhesion* **16,** 165 (1984).
23. P. Poole and J. F. Watts, *Int. J. Adhesion Adhesives* **5,** 33 (1985).
24. J. Crank, *Mathematics of Diffusion, 2nd Ed.* (Oxford University Press, 1975).
25. R. J. Morgan and J. E. O'Neal, *Polym. Plast. Technol. Eng.* **10,** 49 (1978).
26. R. D. Adams and W. C. Wake, *Structural Adhesive Joints in Engineering* (Elsevier Applied Science Pub., London, 1984), p. 93.
27. M. Guttman, *Métaux, Corrosion Industrie,* n° 627, 373 (1977).
28. L. E. Davis, N. C. Donald, P. W. Palmberg, G. E. Riach and R. E. Waber, *Handbook of Auger Electron Spectroscopy, 2nd Ed.* (Physical Electronics Industries, Edina, Minnesota, USA, 1978).
29. J. Comyn, C. C. Horley, D. P. Oxley, R. G. Pritchard and J. L. Tegg, *J. Adhesion* **12,** 171 (1981).