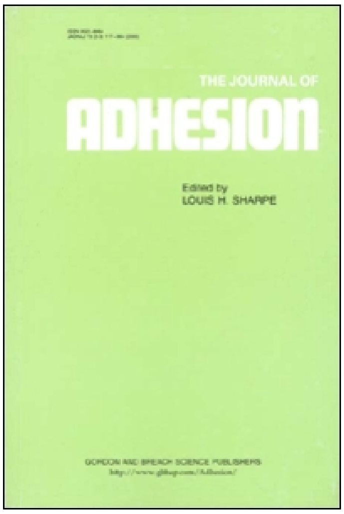

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A Comparison of Laboratory-conditioned and Naturally-weathered Bonded Joints*

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Adhesive bonding is often the most desirable joining method in terms of structural efficiency and cost and is being used in an increasing number of civil and military applications. One of the main stumbling blocks to the further use of adhesive bonding is the lack of confidence in long-term durability, particularly in humid environments. When designing bonded joints, the effect of ageing is usually accounted for by subjecting the joints to artificially high levels of loading or extreme environmental conditions for short times prior to testing. However, the relationship between the results from these accelerated tests and actual long-term ageing is poorly understood. The Defence Evaluation and Research Agency (DERA) has what is probably a unique set of experimental data for a wide range of adhesively-bonded joints subjected to both accelerated ageing in the laboratory and long-term outdoor exposure. In this paper the relationship between the naturally aged and accelerated aged joints is explored. It is concluded that no simple correlation can be made between joints aged in different environments. The best that accelerated ageing can achieve is to eliminate those adhesives likely to perform badly in conditions of high humidity and to indicate those systems likely to perform well.

Keywords: Exposure tests; Adhesive; Lap joints; Durability; Ageing

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INTRODUCTION

Adhesive bonding is now a well-established method of joining aluminium parts in aircraft applications and with the increasing use of advanced polymer composites it is envisaged that adhesive bonding will be used extensively in future aerospace structures. A persisting problem with adhesively-bonded joints is the perceived durability problem in hot/wet conditions and the difficulty in predicting a safe life. At DERA this problem is being tackled by looking at improved surface treatments [1, 2], the development of moisture-resistant adhesives [3] and self-repairing adhesives [4] and by looking at methods of predicting the ageing behaviour of joints [5, 6].

As it is known that environment can affect adhesive bond strength over long periods of time, the designer must take this into account by considering the loads and environments the joint will meet in service. As long-term test data are seldom available, and the time to market for a product is relatively short, the effects of environmental ageing are usually assessed by conducting accelerated ageing tests. In these tests the joints are subjected to conditions more extreme than those that would be expected in service in order to accelerate strength decay. As there is no way of reliably using this data to predict actual long-term ageing in more realistic conditions, the accelerated ageing tests, in effect, become a series of hurdles that an adhesive must pass before being considered fit for service. Accelerated ageing tests are also commonly used to compare adhesives and surface treatments in order to select an optimum system or process. The danger in applying the data from accelerated tests to joint design is that the acceleration method will produce an excessively high combination of moisture and temperature in the joint, resulting in unrealistic degradation patterns.

More realistic design data can be obtained by exposure trials in "real" environments. However, these trials only provide information specific to a particular adhesive/adherend/surface treatment combination in a particular environment and inevitably at an extremely slow rate. Long-term ageing trials are less commonly used than accelerated testing in research programmes because of the long time scales involved. Previously published work on outdoor ageing trials for adhesively-bonded joints can be found in Refs. [7 – 13].

A means of accurately predicting in-service ageing behaviour from laboratory tests capable of being conducted in relatively short periods of time is, therefore, highly desirable. Crucial to the development of such a capability would be the availability of long-term durability data that could be correlated with accelerated laboratory tests. Long-term, outdoor ageing trials have been undertaken at DERA for stressed and unstressed double-lap joints and peel joints. Aluminium alloy adherends were bonded with a variety of film adhesives and the joints aged at a range of outdoor sites. Similar joints were also laboratory conditioned in a variety of environments. This is probably a unique set of data, which allows a direct comparison to be made between the behaviour of joints aged in a number of different natural and accelerated ageing conditions. This paper describes recent attempts at correlating results from these two approaches to joint degradation assessment.

EXPERIMENTAL

Sample Manufacture

Three test configurations have been used in these trials: the double-lap joint, the 90°-peel test and the wedge test. The dimensions of these joints are shown in Figures 1–3. Both aluminium and titanium adherends were used in the DERA trials; however, in this paper, only the aluminium results will be presented. A clad aluminium alloy (L165)

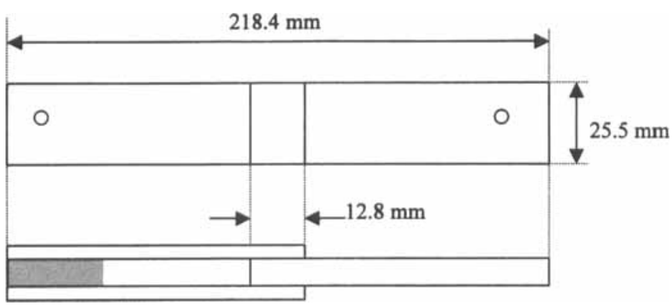

FIGURE 1 Double-lap joint.

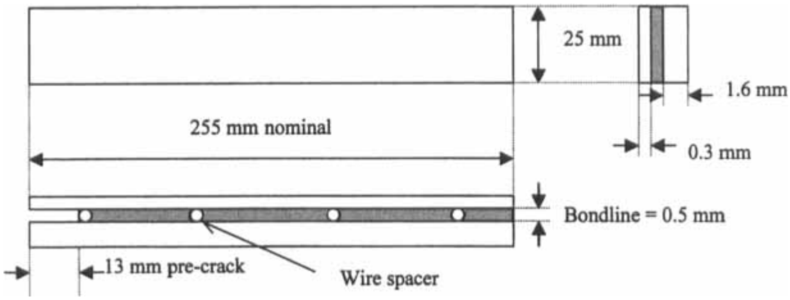

FIGURE 2 Peel joint.

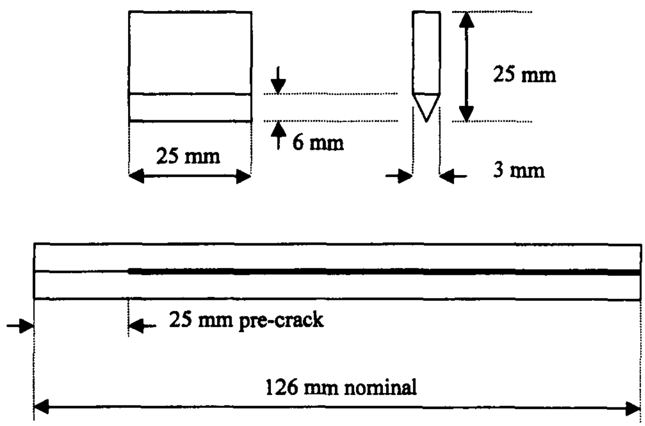

FIGURE 3 Wedge test, sample and wedge dimensions.

was used to make the double-lap joints. 4 mm sheet was used for the central adherend and 2 mm sheet for the outer adherends. The 90°-peel specimens were also made with clad aluminium alloy adherends (L61). The peel arm was made from 0.5 mm sheet and the base adherend was made from 2.6 mm sheet. The wedge test specimens were prepared from 3 mm thick L165 material. Although a number of pretreatments were studied in the trials only the chromic acid etched results are presented in this paper as these represent the most complete set of data. The etching was carried out in accordance with DEF-915B. It should be noted, however, that anodising treatments have often been shown to result in better joint durability than acid etching [12, 14, 15].

The adhesives used in the trials are described in Table I. A variety of the types of adhesive used in the aerospace industry were included in the trials. It should be noted that ME170 and ME170g are the same adhesive, the sole difference being the addition of glass beads for bondline thickness control in the latter. ME120w and ME120k are different adhesives; however, they are of a similar type and specification.

Natural Ageing of Joints

In 1966–67 the Adhesives Panel of the Joint Airworthiness Committee of the Ministry of Technology initiated a long-term outdoor weathering programme for adhesively-bonded joints. This programme centred on stressed and unstressed double-lap and peel joints, bonded with a variety of adhesives and subjected to exposure in a range of environments. Since its inception this programme has been considerably expanded to include a wide range of adhesive/adherend/surface treatment combinations. Six trials have now been completed and full experimental details of the trials have been presented by Parker and Shaw [16]. In this paper, only those results that can be directly compared with the accelerated ageing tests will be discussed. Standard deviations have not been presented in the figures to maintain clarity; however, these can be seen in Parker and Shaw's report.

Three outdoor exposure sites were used in the trials. Two sites in Australia were used to represent hot/wet (Innisfail) and hot/dry (Cloncurry) environments. Ageing in temperate conditions was conducted at Farnborough on the old RAE site. Average climatic data for these three sites are shown in Table II. The monthly variations

TABLE I Key to adhesives used in durability trials

Adhesive	*Primer*	*Type*	*Cure temp.*	*Description*
E-P		Epoxy-polyamide	170°C	Unsupported film, high-peel
V-P		Vinyl-phenolic	150°C	Supported film, durable
E-N	✔	Epoxy-novolac	170°C	Supported film, high-temp
ME170		Modified epoxy	170°C	Unsupported film, high-temp.
ME170g		Modified epoxy	170°C	Glass beads, high-temp.
N-P	✔	Nitrile-phenolic	177°C	Unsupported film, high-peel
ME120w	✔	Modified epoxy	120°C	Film with woven nylon carrier
ME120k	✔	Modified epoxy	120°C	Film with knitted nylon carrier

TABLE II Average climatic conditions at outdoor ageing sites

	Hot/wet site	*Hot/dry site*	*Temperate site*
Average temp.	23°C	25°C	10°C
Average R.H.	83%	55%	78%
Average monthly rainfall	297 mm	39 mm	49 mm

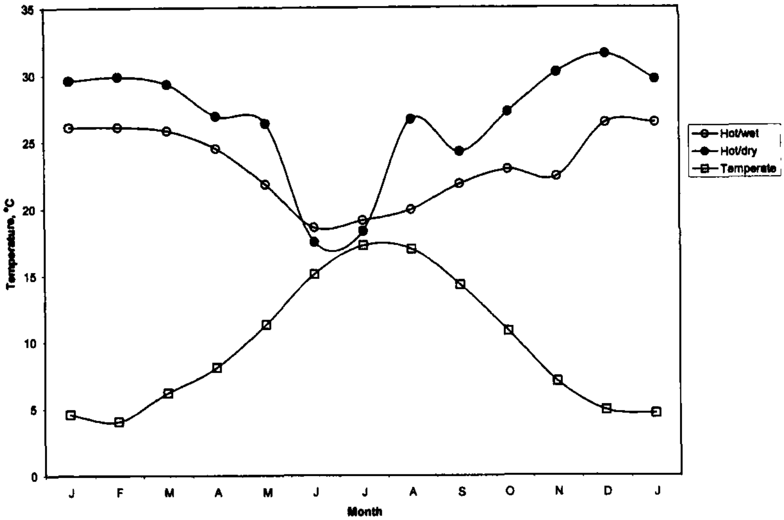

FIGURE 4 Average monthly temperature at outdoor test sites.

can be seen in Figures 4 and 5. In Figure 4 it can be seen that the hot/wet and hot/dry sites have similar temperatures, although the latter shows a greater seasonal variation. In comparison, the temperate site experiences substantially lower temperatures for most of the year. Figure 5 shows that the hot/wet site has the highest humidity levels for most of the year; however, the temperate site also has relatively high humidity levels for much of the year. The hot/dry site has much lower humidity levels and much greater seasonal variations in humidity than the other two sites. Not shown are the daily changes in temperature and humidity; however, it can be envisaged that these variations can also be quite significant.

During exposure the double-lap joints were held in purpose-designed frames to enable samples to be stressed at 5, 10 and 20% of their initial strength. After periodic exposure times 12 samples were removed and tested. The double-lap joints were tested by loading the

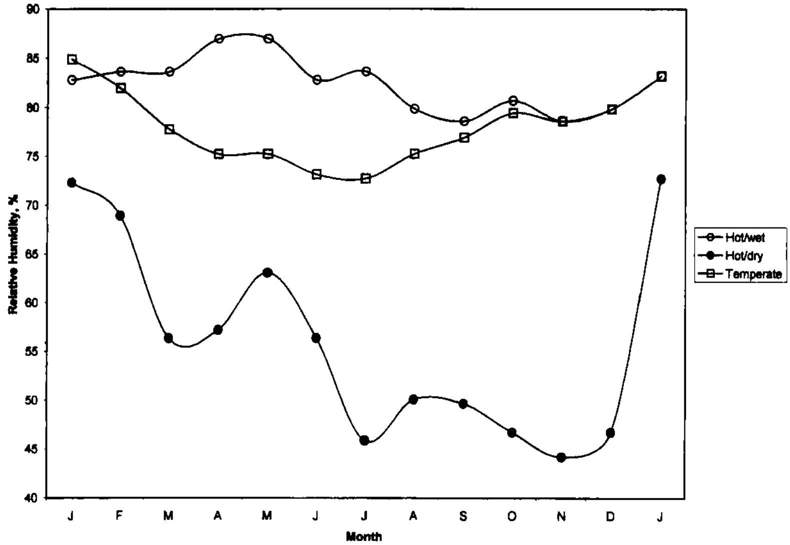

FIGURE 5 Average monthly relative humidity at outdoor test sites.

joint in tension at a loading rate of approximately 15 N/s until failure. In the peel test, the flexible adherend was peeled from the more rigid adherend at an angle of 90°. The load was monitored during the test in order to obtain a plot of load against time. After an initial period of high peel resistance, an approximately constant load is attained which was divided by the sample width to define the peel strength. Testing of both double-lap and peel joints were conducted in ambient laboratory conditions (approximately 23°C).

Accelerated Ageing of Joints

The accelerated ageing tests undertaken in this work were the laboratory ageing of double-lap joints and the wedge test. The double-lap joints were aged in humidity chambers at nominally constant temperature and relative humidity (R.H.). The results presented are for samples aged at 20°C/60% R.H. and at 35°C/85% R.H. The former condition represents a typical laboratory environment and would be expected to be fairly benign for the adhesive joints. The latter represents a high-humidity environment, with a temperature selected to be high enough to accelerate water diffusion into the adhesive joint but still well below the glass transition temperature, T_g, of the adhesive is an attempt to reduce the occurrence of unrepresentative degradation mechanisms. Testing was carried out in ambient laboratory conditions, as with the naturally-aged joints.

In the wedge test, a wedge is driven into the sample and the length of crack measured. Durability is measured by the increase in the crack length with time on environmental exposure. In these trials, the wedge test samples were aged in a humidity chamber at the nominally constant environment of 50°C/95% R.H. This is considerably more aggressive than the environments to which the double-lap joints were subjected. The crack lengths were measured using a calibrated travelling optical microscope. If the adherends do not plastically deform in the wedge test, the fracture energy (G_{Ic}) can be calculated from the crack length (a) using Eq. (1).

$$G_{Ic} = \frac{3Eh^3v^2}{16a^4} \tag{1}$$

where E is the modulus of the adherend, v is the wedge height and h is the adherend thickness. In all cases, fracture energy values were calculated for all joints and the results plotted as a function of ageing time.

Fractography

In most cases, selected examples of failure surfaces from both the exposure trials and accelerated tests were examined by optical microscopy. The failure mode was monitored by estimating the proportion of apparent interfacial failure in the samples. The amount of porosity in the adhesive was also estimated. As these trials were carried out over many years, there is some variation in the scope and detail of these optical examinations and in some of the earlier trials little information on the failure modes is available.

RESULTS

Naturally Aged Joints

If we look at the initial joint strengths in Figure 6, it can be seen that the epoxy-polyamide (E-P) joints are the strongest, followed by the

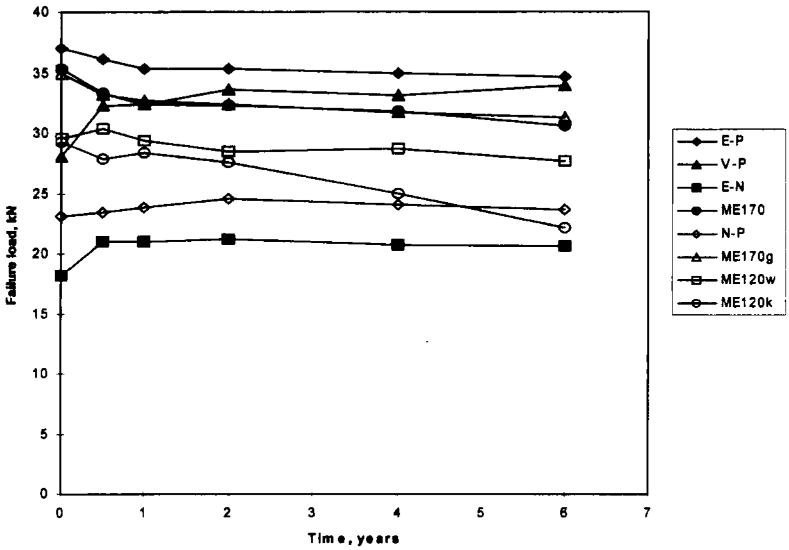

FIGURE 6 Unstressed double-lap joints exposed to hot/dry climate.

ME170 adhesives. These are all epoxy-based adhesives, cured at 170°C and modified to increase peel resistance. The 120°C-cured epoxy adhesives (ME120k and ME120w) are the next strongest, followed by the vinyl-phenolic (V-P) adhesive. A nitrile-phenolic adhesive (N-P) is the next strongest and the epoxy-novalac (E-N) adhesive has the poorest initial strength. The latter was developed specifically for high-temperature performance and is relatively brittle compared with the other epoxy-based adhesives. Thus, a relatively low joint strength was not unexpected.

It can be seen in Figure 6 that none of the adhesives exhibit a significant deterioration in strength when aged outdoors in the hot/dry environment. The E-P joints are still the strongest after 6 years exposure. There is a small initial increase in strength in the V-P and E-N joints. Most other adhesives show a small initial drop in strength followed by fairly constant performance. The ME120k joints are the only ones to show a significant decrease in strength in this environment.

Figure 7 shows that the strength of the E-P joints decrease significantly in the temperate conditions. The V-P joints show an

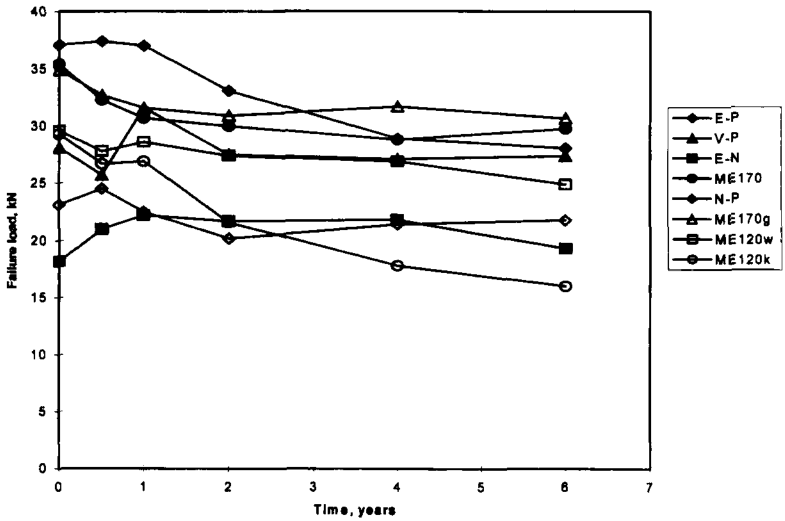

FIGURE 7 Unstressed double-lap joints exposed to temperate climate.

initial drop in strength followed by an increase before reaching a practically constant strength level. An initial increase in strength is seen with the E-N joints, after which strength is fairly constant until a small decrease is seen at the 6-year point. The ME170 joints show an initial decrease in strength, which then appears to level out and they are the strongest joints after 6 years exposure. In this environment there is little difference between the two ME170 variants. ME120k appears to be a poor performer in this environment, becoming the weakest joint after the 6 years exposure, whereas the ME120w joints only show a small reduction in strength. It should be noted that standard deviations are not shown on the figures in order to maintain clarity. However, these can be found in [16]. The standard deviations for the joints are typically 5 – 10% for initial strength and tend to increase with applied stress and on ageing in hot/wet conditions.

In Figure 8 it can be seen that the E-P joints are the worst affected by the hot/wet conditions. Initially the strongest joints, they are the weakest after only 2 years exposure. The ME120k joints are also badly affected by ageing in this environment and, like the E-P joints, strength is still on a downward trend after 6 years ageing. The ME120w joints also exhibit a significant deterioration; however, after 6 years exposure

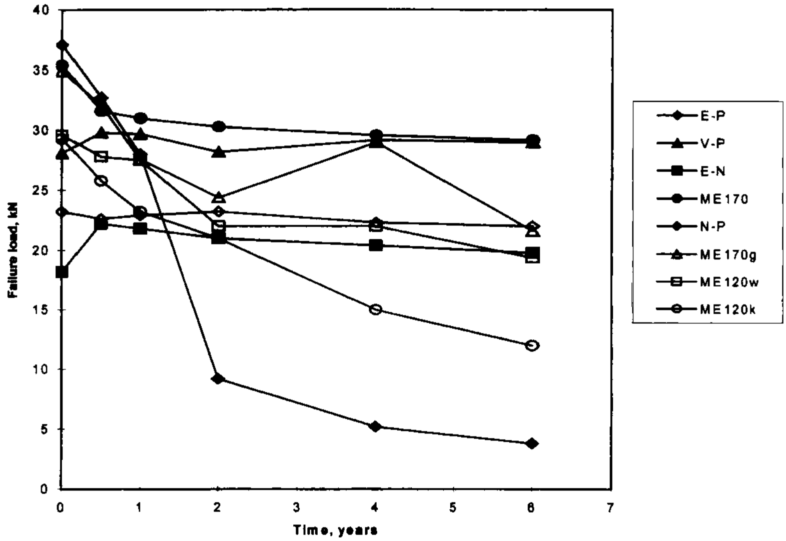

FIGURE 8 Unstressed double-lap joints exposed to hot/wet climate.

the strength of these joints is considerably higher than the ME120k joints. The V-P and E-N joints show an initial increase in strength followed by a fairly constant level. The N-P joints exhibit excellent durability, although strength is not particularly high. The ME170 joints show a small initial decrease in strength after which strength is fairly constant, resulting in the best performance after 6 years exposure. By comparison, ME170g demonstrates a significant reduction in strength after 6 years exposure, with an anomolously high strength after 4 years.

The results of the peel joints exposed to the hot/wet conditions are shown in Figure 9. It can be seen that there is a wider spread of initial strength than was seen with the double-lap joints. As expected, the E-P adhesive, designed for high peel resistance, performs particularly well in terms of initial strength, whereas the more brittle adhesives (V-P and E-N) have a low peel strength. It is also obvious that the only adhesive that deteriorates significantly in this environment over the 6 years of the trial is the E-P adhesive. The results from the hot/dry and temperate sites are not shown as there is little change in the peel strength of any of the adhesives, except E-P, over the 6 years of the

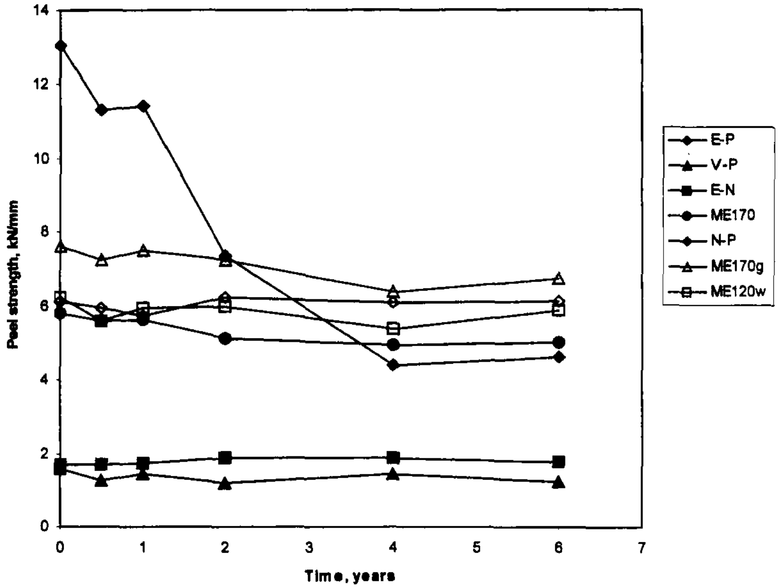

FIGURE 9 90° Peel joints exposed to hot/wet climate.

trials. The E-P joints, however, show some strength reduction in all three environments.

Effect of Stress

The effect that a constant load has on the residual strength of naturally aged double-lap joints is shown in Figures 10–12. The loads applied represented 5, 10 and 20% of the initial strength of the joint and the results are presented as the residual strength after 6 years ageing normalised against the strength of the unaged joints.

The results for the joints aged in the hot/dry climate are shown in Figure 10. It can be seen that the E-P joints are the most affected by the applied stress in this environment. The V-P joints also appear to be affected by the applied load; however, the strength of the unstressed joints increases in this environment with time; the residual strength even with the 20% loading is still high after 6 years exposure. The E-N joints appear to be unaffected by stresses up to 20%, and with all loadings the strength after 6 years exposure was substantially

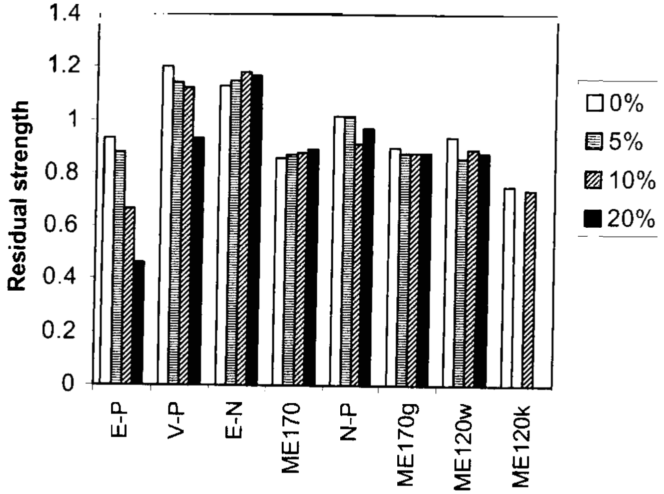

FIGURE 10 Effect of stress on double-lap joints exposed to hot/dry climate for 6 years.

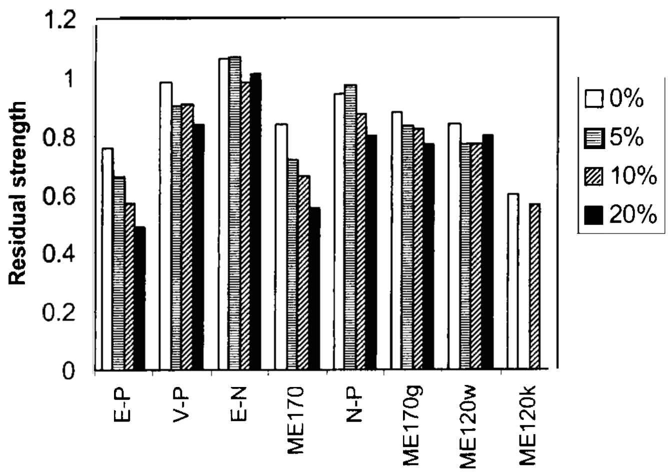

FIGURE 11 Effect of stress on double-lap joints exposed to temperate climate for 6 years.

greater than the strength of the virgin joints. The N-P joints are little affected by either the environment or the loading level in these conditions. The ME170 and ME120 adhesives showed some drop in

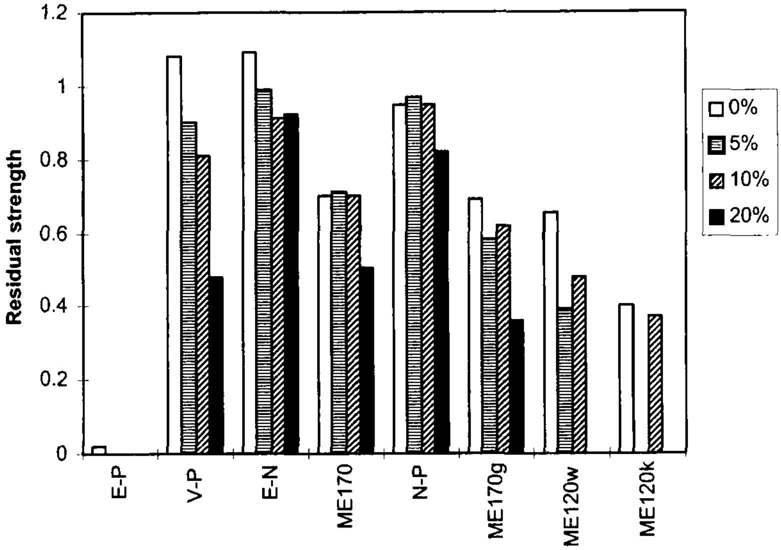

FIGURE 12 Effect of stress on double-lap joints exposed to hot/wet climate for 6 years.

strength due to the environment but no significant effect due to the applied load.

Figure 11 shows the effect of stress on joints aged in the temperate climate. In this environment the E-P joints are sensitive to the applied load. A small effect due to the applied load can be seen with the V-P joints; however, the E-N joints are, again, little affected by either the environment or the applied load. The ME170 and N-P joints now appear to be affected by both the environment and the applied load, although there is still no obvious effect of the load on the ME120 adhesives.

The effect that stress has on ageing in the hot/wet climate can be seen in Figure 12. The E-P joints exhibit an extremely low residual strength after 6 years ageing unstressed in this environment and the stressed samples fail before 6 years is reached. It can also be seen that the applied load has a much greater effect on residual strength for the V-P adhesive in this environment. The ME170 and N-P adhesives appear to be unaffected by the stress until a loading of 20% is applied. With the ME120k and ME120w joints, we can now see an apparent effect of the stress on the residual strength. With the ME120w joints, the 10% loaded joints appear anomalously high compared with the 5% loaded joints and none of the 20% loaded joints lasted 6 years in this environment.

Accelerated Ageing

Figure 13 shows the results for the double-lap joints aged at 20°C, 65% R.H. This is considered a fairly benign environment for the bonded joints and was designed to be a control environment for comparison with the joints aged in more aggressive environments. It is interesting to note, however, that these conditions are not dissimilar to those joints exposed to the hot/dry climate (average conditions 25°C, 55% R.H.). There is, then, a surprisingly large decrease in the strength of the E-P joints compared with the good durability of this adhesive in the hot/dry natural climate. As adhesive E-P is extremely sensitive to moisture, this would indicate higher overall moisture levels are achieved with the laboratory testing at 20°C, 65% R.H. than at the outdoor hot/dry site. This demonstrates the potentially damaging effect that relatively small increases in the humidity of the environment can have on the strength of some bonded joints. The other joints tend to behave similarly to those aged outdoors in hot/dry conditions, *i.e.*,

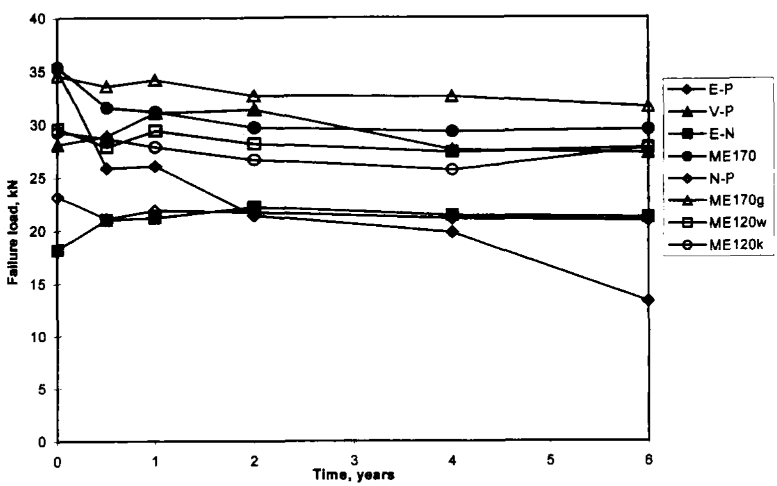

FIGURE 13 Unstressed double-lap joints aged at 20°C/65% R.H.

little change in strength with time, with some adhesives showing an initial increase in strength.

The results of the double-lap joints laboratory aged at 35°C with a R.H. of 85% are shown in Figure 14. This environment has a similar humidity level to the hot/wet site with a somewhat higher temperature and, therefore, might be expected to be a good accelerated test for long-term hot/wet performance. However, Figure 14 shows that all the adhesives seem to show an initial decrease in strength greater than that seen in the long-term testing. The plateau levels reached also appear to be lower than those seen in the hot/wet outdoor exposure trials.

The results from the wedge tests are shown in Figures 15 and 16. These samples were aged at 50°C/95% R.H., which is a far more aggressive environment than that to which the double-lap joints were subjected. This, and the stressed nature of the test, allows changes in strength to be observed over much shorter time-scales. The predominantly Mode I loading in the wedge test would appear to indicate a similarity to the peel test. However, there are some critical differences between the peel test and the wedge test. In the wedge test the joint is cracked and has a load applied throughout the ageing. Also, the adherends remain elastic (ideally) in the wedge test, whereas

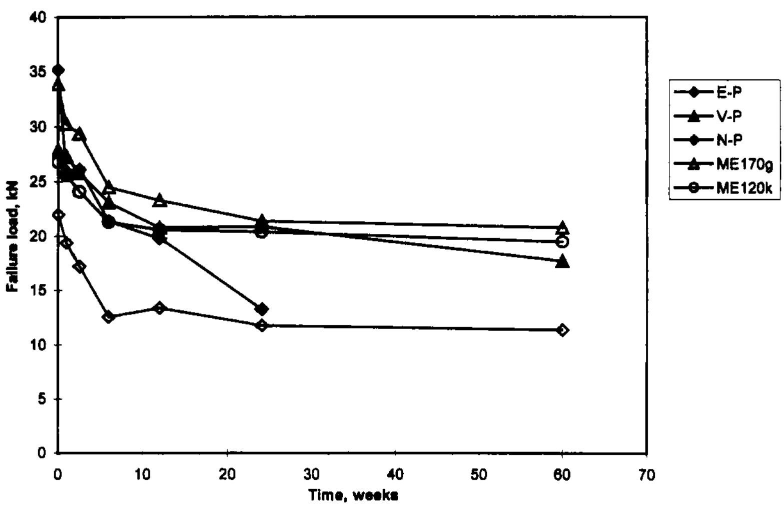

FIGURE 14 Unstressed double-lap joints aged at 35°C/85% R.H.

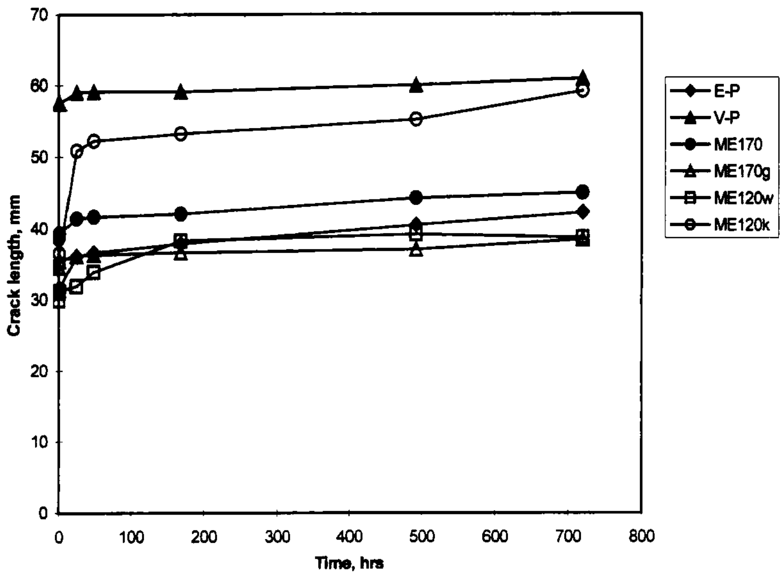

FIGURE 15 Wedge test samples aged at 50°C/95% R.H.

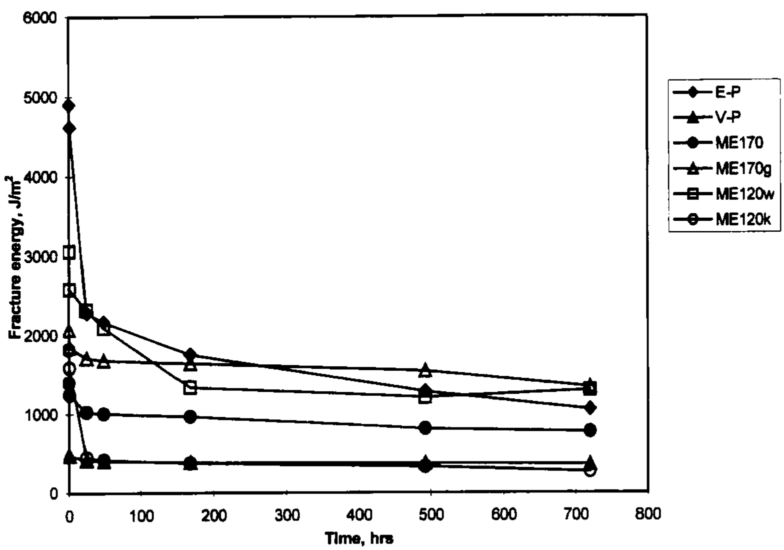

FIGURE 16 Wedge test samples aged at 50°C/95% R.H.

in the peel test the upper adherend deforms plastically to maintain the peeling angle.

Figure 15 shows the increase in crack length as the wedge samples are aged. In most cases, the crack length increases on initial exposure, then fairly quickly reaches a reasonably constant level. The initial crack length is an indication of the fracture toughness of the virgin adhesive, as all initial failures were cohesive failure of the adhesive. This is illustrated more explicitly in Figure 16, which shows the variation in fracture energy as a function of exposure time, calculated using Eq. (1). The fracture energy in the wedge test depends on the resistance of the adhesive to Mode I fracture, as in the peel test. Not unexpectedly, E-P has the highest fracture energy; however, some of the adhesives appear in a ranking different from the peel tests, *e.g.*, the fracture energy of ME120w seems surprisingly high. The magnitudes of the fracture energies are comparable with those reported from other fracture mechanics tests, such as the double cantilever beam test [*e.g.*, Refs. 17–20]. However, the fracture energies from the wedge tests should only be considered as an approximation. In Eq. (1) it can be seen that the calculated fracture energy is highly dependent on the accuracy of the crack length measurement. This length can be difficult to measure accurately, as it is often difficult to identify the crack tip, especially after ageing. It should also be reiterated that the use of Eq. (1) assumes plasticity is restricted to the crack tip and any plastic deformation of the adherends will result in an overestimation of fracture energy.

The wedge test results tend to be characterised by a steep initial drop in fracture energy followed by a constant value, which may be assumed to be the fracture energy in the presence of water. The fracture energy of the E-P joints, however, appears to be still decreasing after 60 days of exposure, whereas V-P shows only a very small initial decrease in strength. With the exception of the V-P joints, fracture migrates from the adhesive to the adhesive/adherend interfacial region on ageing. It should be noted that an increase in fracture energy cannot be seen in these tests, as that would require closing of the crack. Therefore, we cannot see an improvement in the properties as was often observed with the double-lap joints when certain adhesives were aged. The best durability in the wedge tests was seen with the ME170/170g and V-P joints.

Locus of Failure

With all the adhesives, failure of the unaged joints was primarily by cohesive fracture of the adhesive. In some cases, small amounts of apparent interfacial failure were noted which were sometimes described as failure in the oxide coating by the examiner. With most of the adhesives there was an increase in the proportion of apparent interfacial failure with both natural and accelerated ageing. This was often accompanied by significant corrosion of the adherends. Such behaviour was most apparent for the samples aged in the hot/wet conditions, and can be tentatively linked with the amount of moisture absorbed by the adhesive. Joint strength tended to decrease as the proportion of apparent interfacial failure increased; however, large amounts of apparent interfacial failure could be observed ($>40\%$) with little noticeable effect on joint strength. V-P was the only adhesive to differ significantly from the behaviour described above. In this case, only cohesive failure of the adhesive was seen, regardless of the ageing environment.

DISCUSSION

Natural Ageing of Joints

It can be seen from the results presented in Figures 6–9 that many of the adhesives exhibit excellent long-term durability even in hot/wet conditions. This is with a surface treatment not considered to be the optimum for joint durability. The notable exceptions to this are the E-P joints, which show extremely poor durability in the presence of moisture. However, this adhesive was developed for its toughness and shows excellent initial peel resistance and good durability when kept dry. The only other adhesives with questionable durability in hot/wet conditions were the 120°C-cured epoxies (ME120w and ME120k). The other high-performance adhesives tend to show a small strength reduction in hot/wet conditions, whilst the lower performance adhesives seem impervious to the environment. Two of the adhesives (V-P, E-N) show an initial increase in double-lap joint strength when aged outdoors (in all environments) and when laboratory aged at 20°C, 65% R.H. This repeatability indicates a "real" effect rather than experimental scatter. The two adhesives that exhibit this phenomenon are the most brittle at room temperature. Absorbed moisture in the adhesive reaches high levels quite quickly at the ends of the overlaps, which is also the location of the highest stresses. This will tend to plasticise the adhesive and reduce the stress concentrations at the ends of the overlap. This may prove beneficial for the more brittle adhesives, especially if failure remains predominantly in the adhesive. With the tougher adhesives this additional plasticity may be less significant and after a short while any beneficial gains are offset by the detrimental effect of the water attacking the adhesive–adherend interface. An alternative mechanism that may account for the observed increase in strength is additional curing of the adhesives during ageing. As similar recoveries in strength are observed in both the temperate (high humidity, low temperature, favouring plasticisation) and hot/dry (low humidity, high temperature, favouring further curing) environments it is not clear which mechanism predominates. Alternatively, some other (unidentified) time-dependent ageing mechanism may be responsible. These results appear to confirm the view that phenolic-based adhesives exhibit superior durability to epoxies. However, it should also be noted that stress had a severe affect on the durability of the phenolic-based adhesive joints.

Absorbed moisture can affect the strength of double-lap joints in a number of ways. Firstly, the moisture will change the mechanical properties of the adhesive, generally reducing the modulus. This will affect the stress distribution in the joint. In some cases this may be beneficial, as it may reduce the stress concentrations at the ends of the overlap, as discussed above. However, in most cases the changes in the properties will not be large at room temperature as this is well below the T_g of the adhesives in these trials. Secondly, the failure strength of the adhesive will change. The ultimate tensile strength (UTS) of the adhesive will usually decrease with increased absorbed moisture; however, the strain energy at failure may well increase for brittle adhesives. Finally, the moisture can affect the adherend oxide layer and the adhesion between the adhesive and the adherend. This can often lead to large reductions in joint strength, which explains why a reduction in strength is often accompanied by a change in the failure mode.

The peel samples appear to be less affected by environment than the double-lap joints. Failure initiates in the double-lap joint when maximum stresses are reached at the ends of the overlap, where high water concentrations can quickly be reached. Peel strength is determined by the average load as a flexible strip is peeled from a rigid adherend. In order to affect peel strength significantly we have to have high levels of moisture across the entire sample width, which would take far longer than the 6 years of the trials for most of the adhesives.

Comparison Between Long-term and Accelerated Testing

One of the simplest methods of using accelerated test results to predict long-term ageing behaviour is to calculate acceleration factors for strength degradation. In the hot/wet conditions only a few adhesives show a significant strength reduction over the 6 years of the trial, and it is only for these adhesives that it is worthwhile calculating acceleration factors. Table III shows acceleration factors that have been calculated for adhesive E-P. It can be seen that increasing temperature does accelerate degradation and that the acceleration factor varies non-linearly with time and temperature. Table IV shows acceleration factors calculated for ME120k adhesive. This shows that acceleration factors are also affected by the degree of loading.

TABLE III Acceleration factors for adhesive E-P

	25% *reduction*	40% *reduction*	50% *reduction*
Hot/wet exposure	8760 hours	10800 hours	130000 hours
35°C/85% R.H.	450 hours	1600 hours	2600 hours
50°C/85% R.H.	95 hours	270 hours	550 hours
Acceleration factor, 35°C	19.5	6.8	5.0
Acceleration factor, 50°C	92.2	40	23.6

TABLE IV Acceleration factors for adhesive ME120k

	25% *reduction*	40% *reduction*
Hot/wet exposure, unstressed	13140 hours	43800 hours
Hot/wet exposure, stressed	15330 hours	35040 hours
35°C/85% R.H., unstressed	1600 hours	7000 hours
35°C/85% R.H., stressed	850 hours	4000 hours
Acceleration factor, unstressed	8.2	6.2
Acceleration factor, stressed	18.0	8.8

If we assume that strength loss in these joints is primarily dictated by the amount of moisture absorbed by the adhesive, then we can derive an expression for joint strength in terms of time and temperature. Assuming that Fickian diffusion kinetics applies to the absorption of moisture by the adhesive, we can use the following expression to estimate the mass of water, M_t, in a semi-infinite film of thickness, h, after time, t [21, 22].

$$M_t = \frac{4M_\infty}{h}\left(\frac{Dt}{\pi}\right)^{0.5} \tag{2}$$

where D is the diffusion coefficient and M_∞ is the saturation water mass. If we assume that the failure load, P_c, is proportional to the mass of absorbed moisture, then if M_∞ and h are assumed constant:

$$P_c = \text{const.}\ (Dt)^{0.5} \tag{3}$$

It has been proposed that the diffusion coefficient of water in adhesives is related to temperature by the Arrhenius relationship in Eq. (4) [16, 23].

$$D = D_0 \exp\left(-\frac{E}{\mathrm{R}T}\right) \tag{4}$$

where D is the diffusion constant at temperature, T, D_0 is the absolute diffusion constant, E is the activation energy for absorption and R is the gas constant. Substituting (4) into (3) we can derive the following expression.

$$\log\left(\frac{P_c}{t^{0.5}}\right) = A\left(\frac{1}{T}\right) + B \tag{5}$$

where A and B are constants that can be derived empirically by plotting log $(P_c/t^{0.5})$ against $1/T$.

Equation (5), thus, gives us a method of predicting the strength of a joint at different times and temperatures as long as two empirical constants have been experimentally determined. However, there are severe limitations to the use of this equation. Firstly, the analysis is based on the assumption that the joint strength is directly proportional to the water content. This has been shown to be the case for some adhesives [16, 24, 25]; however, it is probably only true over a restricted range of conditions, which need to be determined experimentally. Non-linear relationships between water content and joint strength have also been suggested [26, 27]; however, these are of less use in strength prediction due to the reliance on empirical curve-fitting to obtain a suitable relationship. It should also be noted that Eq. (2) is only accurate for the early stages of water uptake (up to approx. 60% saturation) and, therefore, Eq. (5) is only applicable in the early stages of strength loss. Equation (3) is only correct if M_∞ and h remain constant. Therefore, the method can only be applied to samples with the same materials and geometry aged in environments with similar levels of humidity. Finally, the ageing environment should have constant temperature and humidity.

In order to validate Eq. (5), we require a set of data for samples aged at different temperatures but with the same relative humidity. As this is not available in this programme, an attempt at validating Eq. (5) has been made using a combination of laboratory-aged and outdoor-aged results. With the outdoor-aged samples, the average temperature has been used in Eq. (5). It should also be noted that humidity is far from constant in these conditions. The results are shown in Figure 17 for adhesives E-P and ME120k. Not unexpectedly, there is considerable

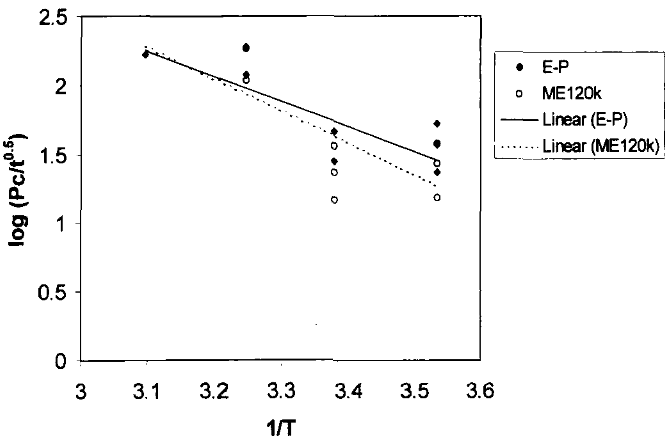

FIGURE 17 Relationship between joint strength and temperature based on water content.

scatter and it is impossible to prove a linear fit to the data with these results. However, it is interesting that the two adhesives show similar trends. This indicates that the trends are real and the scatter is probably an artefact of the simplification of using annual averages for the outdoor temperatures and assuming constant humidity.

It is apparent from the above that obtaining a quantitative measure of the rate of in-service joint degradation from accelerated test results is difficult and likely to involve large errors. It is a feature of many of the plots of strength against ageing time that there is a rapid drop in the strength, after which an approximately constant level is maintained; this may be viewed as the equilibrium level for the environment. In order to evaluate the capability of accelerated ageing tests to predict such an equilibrium level, the reduction in strength at the ends of the ageing periods for the natural- and laboratory-aged samples are shown in Tables V and VI, respectively. Although these times are rather arbitrary, in most cases the joints have reached a fairly constant level of strength at this point. The main exceptions are E-P and ME120k joints, which are still losing strength at the end of the trial period in a number of environments. If we compare the temperate

TABLE V Strength reduction, natural ageing

	Hot/dry		*Temperate*		*Hot/wet*	
	*% reduction**	*Ranking*	*% reduction**	*Ranking*	*% reduction**	*Ranking*
E-P	7	2	24	4	90	5
V-P	−16	1	2	1	−3	1
ME170	14	4	16	3	18	2
ME170g	10	3	12	2	38	3
ME120k	28	5	42	5	67	4

* After 6 years ageing.

TABLE VI Strength reduction, laboratory ageing

	DLJ 20°*C*/60% *R.H.*		*DLJ* 35°*C*/85% *R.H.*		*Wedge* 50°*C*/95% *R.H.*	
	% reduction[a]	*Ranking*	*% reduction*[b]	*Ranking*	*% reduction*[c]	*Ranking*
E-P	62.2	5	100	5	78	4
V-P	3	1	37	2	25	1
ME170	10	4	48	4	45	3
ME170g	9	2=	39	3	35	2
ME120k	9	2=	27	1	85	5

[a] 6 years ageing; [b] 60 weeks ageing; [c] 720 hours ageing.

and hot/wet naturally aged samples with those aged at 35°C/85% R.H., we can see that although the average humidity is similar there are large differences in the strength reduction in the different environments. In most cases, the strength reduction increases with ageing temperature. This indicates that increasing temperature not only accelerates ageing but also changes the residual strength at equilibrium. The fact that the accelerated ageing usually predicts a lower residual strength means that the accelerated ageing will result in over-design of joints. It is worrying, however, that in the case of the ME120k joints the accelerated ageing predicts a higher residual strength than that achieved in two of the outdoor environments.

We may finally consider whether the accelerated tests provide a good qualitative indication of how an adhesive will perform in service. In order to do this, the joints have been ranked in Tables V and VI based on the percentage of strength retention at the end of the ageing trials. If we compare the joints aged in high-humidity environments in the laboratory and outdoors, we can see that there is a broad agreement of the ranking of the different adhesive systems. In general, the V-P joints are the most durable, followed by the 170°C-cured epoxies with the ME120k and E-P joints proving least durable. The only exceptions to this are the ME120k double-lap joints aged in the laboratory, which have anomalously good durability. The reason for this is unknown; however, it should be remembered that these tests were conducted at different times, by different personnel and with different batches of adhesive, and this, rather than a real environmental effect, may be the answer.

CONCLUDING REMARKS

It can be seen from this work that there is no simple method of determining long-term durability from accelerated tests. A semi-empirical method has been suggested by which accelerated ageing tests may be used to predict longer term ageing at lower temperatures. However, this method requires a substantial test programme for validation and, when applied to naturally-aged joints with varying climatic conditions, the necessary simplifications may result in considerable errors. It should also be noted that it was difficult to assess the ability of the accelerated tests to predict long-term degradation in many of the systems as they showed such little strength loss in the long-term tests.

It was seen in both laboratory and natural ageing trials that "hot/wet" environments had the most detrimental effect on the strength of the bonded joints. This appears to justify the use of these conditions in accelerated tests to prove the joints in a "worst-case" scenario. The danger, of course, is that excessive temperatures and humidities will trigger unrepresentative degradation mechanisms or cause degradation at rates far greater than that likely to be seen in any natural environment, thereby distorting the perceived worth of the adhesive. In general, the accelerated tests tend to overestimate the degradation of joint strength and, therefore, as screening methods are more likely to eliminate potentially adequate adhesive systems than pass adhesives with poor durability.

As a means of ranking the durability of adhesives in natural environments, the accelerated tests had some success, tending to identify correctly the best and worst ranking systems. However, exact ranking varies with environment and the accelerated tests should be considered as a coarse, rather than a fine, screening tool.

Although not capable of providing a safe and meaningful measure of joint longevity, accelerated tests allow insights into the bond components (adhesive, interface, oxide layer, *etc.*) which would be vulnerable to potentially harsh service conditions. It was a feature of the joints in all environments that significant reductions in strength were accompanied by a change in failure locus from the adhesive towards the interfacial region and the adherend oxide layer.

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