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Environmental Degradation of Adhesive Joints Accelerated Testing

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ABSTRACT

This report evaluates environmental conditioning methods that can used for inducing accelerated moisture degradation within adhesively bonded joints. The evaluation will attempt to relate the degree of degradation (strength retention) with the level of degrading agent and exposure time, and determine any synergistic effects. The report examines durability data obtained from single-lap shear and thick adherend shear tests. Tests were conducted on bonded joints that had been either immersed in water at elevated temperatures or exposed to humid environments at elevated temperatures. Autoclave conditioning was observed to accelerate moisture absorption by a factor of 100 in polymer matrix composites and is potentially suitable for use with materials designed for hot/wet conditions. Tensile and compressive loading configurations for the thick adherend shear test have been considered. The study found that the compressive test is the more cost effective technique and potentially a faster method for generating long-term engineering data. This technique enables thinner sections to be tested.

Consideration is given to estimating the significance and limitation of the durability data generated by single-lap joint and thick adherend tensile tests and evaluates the two methods in terms of fitness for purpose in assessing environmental performance. The report provides guidance on specimen geometry, manufacture and testing, and on the validity of extrapolating data obtained from short-term accelerated tests to predicting long-term behaviour of larger bonded structures.

The report was prepared as part of the research undertaken at NPL for the Department of Trade and Industry funded project on “Performance of Adhesive Joints - Combined Loading and Hostile Environments”.

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1. INTRODUCTION

Moisture (water) degradation is probably the major cause of in-service failure in adhesively bonded structures. The ubiquitous nature of water combined with the ability to penetrate into the adhesive structure poses considerable problems. Prolonged, or even short-term, exposure to moisture at elevated temperatures will often produce irreversible chemical and physical changes within adhesives. The natural process of moisture absorption in adhesive structures is normally very slow, and this makes it very difficult to reach an adequate degree of degradation in a structural test element in practical timescales. It has therefore been necessary to speed up the moisture diffusion process by employing an accelerated conditioning technique that can produce a representative level of degradation in significantly reduced time.

The usual approach used to accelerate moisture uptake is to increase the diffusivity of the adhesive by elevating the temperature of the conditioning environment. Further acceleration can be obtained by increasing the relative humidity (RH). This report evaluates environmental conditioning methods for inducing accelerated moisture degradation within adhesively bonded joints. The evaluation will attempt to relate the degree of degradation (strength retention) with the level of degrading agent and exposure time, and to determine any synergistic effects. The report examines durability data obtained from single-lap shear and thick adherend shear tests. Tests were conducted on bonded joints that had been either immersed in water at elevated temperatures or exposed to humid environments at elevated temperatures. Consideration is given to estimating the significance and limitation of the durability data generated for each method and the validity of test conditions in relation to actual service conditions.

Tensile and compressive loading configurations for the thick adherend shear test (TAST) have been considered. The report evaluates the two methods in terms of fitness for purpose in assessing environmental performance and provides a guide to specimen geometry, manufacture and testing. Compressive loading is potentially the more cost effective and faster method for generating long-term engineering data.

The research discussed in this report forms part of the Engineering Industries Directorate of the United Kingdom Department of Trade and Industry project on “Performance of Adhesive Joints - Combined Cyclic Loading and Hostile Environments”, which aims to develop and validate test methods and environmental conditioning procedures that can be used to measure parameters required for long-term performance predictions. This project is one of three technical projects forming the programme on “Performance of Adhesive Joints - A Programme in Support of Test Methods”. **Throughout this report, statements of particular importance or relevance are highlighted in bold type**.

2 THICK ADHEREND SHEAR TEST (TAST)

The TAST was developed to overcome the weaknesses of the single-lap [1-2] and double-lap geometries. This test geometry is capable of providing shear modulus and shear strength data suitable for engineering purposes [3]. Various test geometries have been suggested, including those specified in ISO 11003-2 [4, 5] and ASTM D 3165 [6]. The

TAST is suitable for use in tension and compression. The compression specimen is a compact version of the tensile specimen and can be used to test thinner adherends (i.e. 5-6 mm total thickness), whereas the total thickness for the tensile specimen is typically 12 mm. The smaller specimen is potentially more suitable for generating long-term static strength data.

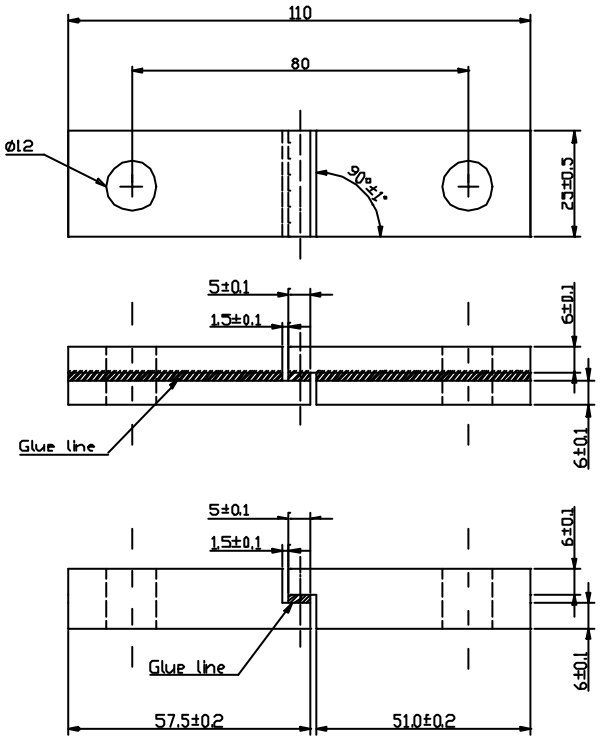
2.1 SPECIMEN GEOMETRY, PREPARATION AND TESTING

2.1.1 Principles

Tension

The shear properties of an adhesive can be determined by applying uniaxial tension load to a specimen consisting of thick, rigid adherends, with a short overlap length. The specimen can be produced by either:

(i) Bonding two pre-shaped bars together (Figure 1a); or
(ii) Bonding two sheets together and then milling two parallel slots (Figure 1b).



dimensions in millimetres

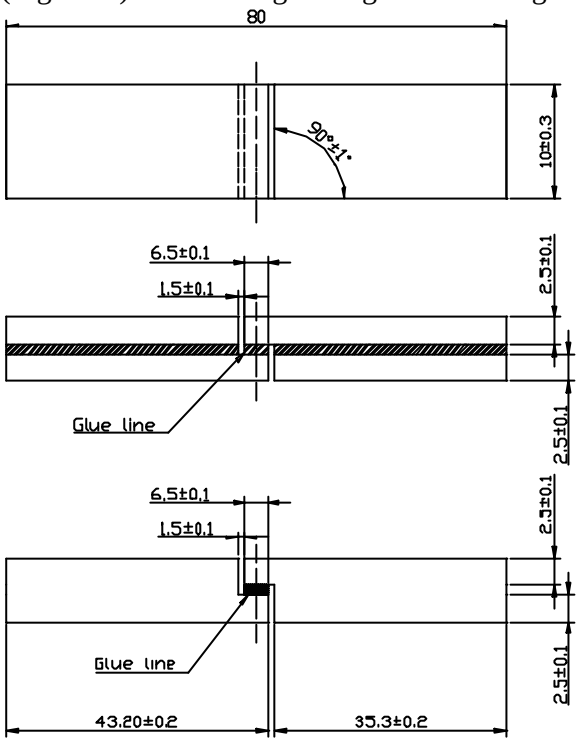
Figure 1 TAST specimen (tension): (a) bonded adherends; (b) pre-shaped adherends.

ISO 11003-2 specifies a specimen with an overall length of 110 mm, a width of 25 mm and overlap length of 5 mm. The ISO standard recommends an adherend thickness of 6 mm and a bondline thickness of 0.5 mm. Slots should be 1.5 mm wide. Load is introduced to the specimen preferably via two 12.7 mm diameter bolt holes. The hole centres are 80 mm apart. Care is needed to ensure that the holes are accurately drilled in the centre of each

adherend, since small misalignments can result in unwanted rotation and uneven loading of the joint, thus compromising the test data.

Compression

The TAST specimen can also be loaded in compression using a similar fixture to that specified in ASTM D 3846 [7]. In the ASTM standard, the specimen is supported along its entire length to minimise out-of-plane deformation. Specimens were nominally 80 mm in length and 10 mm wide. The two parallel notches are 6.5 mm apart and 1.5 mm wide. Test specimen geometry (Figure 2)and loading configuration are given in Figure 3.



dimensions in millimetres

Figure 2 TAST specimen (compression): (a) bonded adherends; (b) pre-shaped adherends.

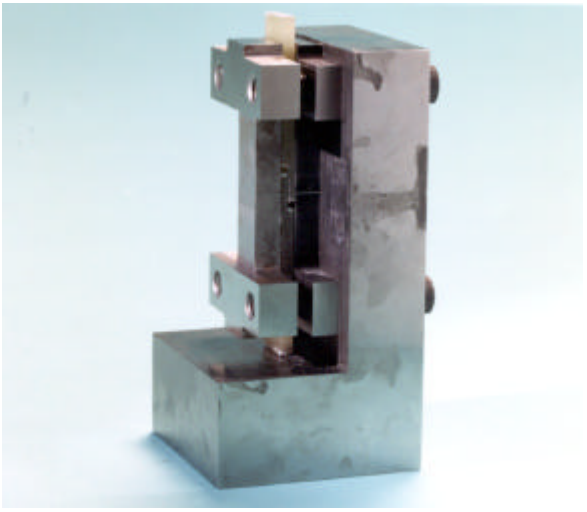


Figure 3 Compression fixture with TAST specimen.

The lap-shear strength t for both tension and compression is given by:

$$\tau = \frac{P}{bL} \quad (1)$$

where **P** is the maximum load, **b** is the joint width and **L** is the joint overlap length. The analysis assumes the adherends are rigid, and that the adhesive only deforms in shear. Shear modulus **G** may be obtained using:

$$G = \frac{\tau}{\gamma} \quad (2)$$

where t (average shear stress in the adhesive) and g (average shear strain in the adhesive) are obtained from the linear region of the stress-strain curve. Assuming that the adherends do not bend then the shear strain in the adhesive is given by:

$$\gamma = \frac{d_s}{t} \quad (3)$$

where $\mathbf{d_s}$ is the shear displacement of the adhesive and **t** is the bondline thickness. The use of two extensometers on opposing faces of the specimen is recommended for measuring shear displacement. The results are averaged and any contributions to the measurements due to bending can be minimised. Alternatively, shear deformation can be measured using video extensometry or laser speckle interferometry techniques.

2.1.2 Specimen Preparation and Testing

Tests were conducted on specimens with bonded adherends (Figure 1a and Figure 2a) and with pre-shaped adherends (Figure 1b and Figure 2b). Details on specimen manufacture can be obtained from NPL Report CMMT(A) 81 [6].

(i) Specimens with bonded adherends

Two panels were cut to the appropriate size, surface treated and then adhesively bonded in accordance with the adhesive manufacturer's instructions. The bonded panels were cut into specimens using a band saw then machined to the required dimensions. **It is important to ensure that no coolants are used when machining the edges of the specimen and the two parallel slots, as the coolant may react with adhesive or penetrate the adherend-adhesive interface.** Localised increases in temperature may also result in thermal degradation of the adhesive properties. **Care should be taken to ensure that the assembly is not heated above 50 ºC [6]. The slots must be accurately machined through only one adherend.**

(ii) Specimens with pre-shaped adherends

The adherends were machined to the required dimensions and surface treated and then adhesively bonded in accordance with the adhesive manufacturer's instructions. The adherends were bonded whilst held securely in an clamping fixture to ensure accurate alignment of the adherends. **A 1.5 mm thick strip of polytetrafluroethylene (PTFE) was**

inserted in the gaps between the adherends after the application of the adhesive and prior to curing. These spacers were removed after the adhesive was cured.

NB. Checks were made to ensure that there was no mechanical damage due to machining. For compression tests, care should be taken to ensure that the ends of the specimen (i.e. loading surfaces) are flat and parallel.

Tension

Testing was conducted at a constant displacement rate of 1 mm/min min using an Instron 8501 servo-hydraulic test frame with the specimens held by a pair of well aligned servo-hydraulic (150 bar pressure) operated wedge-action grips. Instron Series IX software was used to control the test machine and to collect the test data.

Compression

Tests were performed according to ASTM D 3846 [7] under compressive loading at a displacement rate of 1 mm/min. The supported specimen was directly loaded in compression between two hardened steel parallel platens. A four pillar die set was used to provide uniform loading to the ends of the specimen. Test equipment control and data collection was identical to that employed for tension.

2.2 EXPERIMENTAL PROGRAMME

A series of tests were conducted on unconditioned CR1 cold rolled mild steel (supplied by British Steel Plc) and 5251 aluminium alloy TAST specimens in order to evaluate the effect of adherend type (i.e. bonded or pre-shaped) and mode of loading (tension and compression) on the shear stress at failure for the different configurations. The specimens were bonded with Araldite® 2007 (also known as AV119) that was supplied by Ciba Speciality Chemicals. Prior to bonding, the adherends were degreased with 1,1,1-trichloroethane (COSHH classification - restricted use) and then grit blasted using 80/120 alumina. The surfaces to be bonded were then degreased again with 1,1,1-trichloroethane. The bondline thickness (0.25 mm) was controlled using 250 μm ballontini glass spheres (NB. Ballontini balls may cause premature failure). A small quantity of the glass spheres, 1% by weight, was mixed into the adhesive. Specimens were clamped in a special bonding jig [2] and then heated to 140°C for 75 minutes to cure the adhesive.

The results, summarised in Table 1, show noticeable differences between adherend material, adherend type and loading mode. Shear strength data obtained from compression tests are consistently higher than the corresponding values measured for the tension tests. This is due to the lateral constraint applied by the compression fixture (figure 3) on the test specimen, thus preventing out-of-plane deformation and hence minimising bending forces. **Care needs to be taken to ensure that the clamping forces preventing lateral movement are minimal.** It is possible that during testing, Poisson's effects can introduce frictional forces, thereby increasing the failure load. The data obtained from tests conducted in compression were in reasonable agreement with the Arcan test results obtained for both bulk adhesive and bonded aluminium specimens [8].

Table 1 Shear Strength Measurements for AV119 Epoxy Adhesive

Material/Loading Configuration	Shear Strength (MPa)
CR1 Mild Steel	
Bonded 2.5 mm thick adherends (T)	47.6 ± 2.9
Bonded 2.5 mm thick adherends (C)	55.1 ± 0.7
5251 Aluminium Alloy	
Bonded 2.5mm thick adherends (T)	35.1 ± 2.3
Bonded 2.5 mm thick adherends (C)	43.6 ± 3.8
Pre-shaped 5 mm thick adherends (T)	42.0 ± 2.6
Pre-shaped 5 mm thick adherends (C)	42.3 ± 1.4
Arcan Test Method [8]	
AV119 bulk adhesive	46.0 ± 2.0
Aluminium alloy adherends	47.0

Pre-shaped adherend data tends to be higher due to the presence of a small spew fillet of resin at the end of the bondline. The fillets diminish the influence of peel stresses on failure allowing the adhesive to reach its shear limit [2]. **Bondline fillets should be used in a controlled manner to ensure test data consistency**.

It is evident from the results in Table 1, that thinner sections than that recommended by ISO 11003-2 could possibly be used, provided the intrinsic stiffness of the adherend material is sufficiently high. **Steel is preferable to aluminium for measuring the shear properties of unconditioned joints**. The objective being to minimise out-of-plane bending moments, and hence minimise peel stresses at the end of the overlap, and to promote uniform shear stress distribution across the bonded area.

Three-dimensional electronic speckle pattern interferometry (ESPI) was employed to measure the shear modulus of bonded steel adherend specimens loaded in compression. The shear modulus varied from 1.03 to 1.10 GPa, which is in excellent agreement with the measured value for the bulk adhesive (1.07 GPa) obtained by Dean.et.al [8].

The smaller compact compression specimen is suitable for measuring the shear properties of bonded panels with a total thickness of 5 to 6 mm. The smaller size specimen offers the potential for rapid environmental conditioning. It should be noted, however, that smaller specimens are more sensitive to environmental attack than larger joints due to the larger bond-edge-to-bond-area ratio and therefore give a more conservative estimate of environmental resistance [9]. The compression specimen, unlike the tensile specimen, is not particularly suited to cyclic fatigue testing.

3. PERFORATED LAP-JOINT

Introducing holes within the bonded area of a single-lap joint to increase the rate of moisture and, therefore, the rate of degradation seems a logical approach. Hence, if this principle were correct, then increasing the number holes would show a systematic increase in the rate of degradation. **The results presented in NPL CMMT(A) 196 [2] showed that for moisture sensitive adhesives (i.e. material properties decrease with moisture content), the introduction of holes in an attempt to accelerate ageing has little or no effect on strength retention.** Temperature and time have a far more influential effect on joint performance than the presence of holes. Chemical and physical changes that occur within the adhesive, adherends and interface at the ends of the overlap will dominate failure. **Adhesive properties would need to be relatively insensitive to moisture/chemical attack for the method to be used for comparative studies.**

4. WATER IMMERSION CONDITIONING

4.1 SINGLE-LAP JOINT

Tensile tests were conducted on moisture conditioned single-lap joints. The single-lap joint specimens, schematically shown in Figure 4, were made from CR1 mild steel sheet and AV119. Surface treatment was identical to that employed for the TAST specimens (Section 2). The single-lap specimens consisted of two rectangular sections, 25 mm wide, 100 mm long and 2.0 mm thick, bonded together, with an overlap length ranging from 12.5 mm (Figure 4) End tabs, cut from the same material as the adherend sections, were adhesively bonded to the specimen. The end tabs were 37.5 mm in length.

The specimens were immersed in distilled/deionised water at various temperatures ranging from 25°C to 70°C. No attempt was made to optimise surface treatment as the objective of the exercise was to promote degradation in order to quantify the interactions between the key parameters that influence environmental resistance. Batches of conditioned specimens (five specimens per batch) were withdrawn at selected intervals over a 6 week period. Testing was carried out under ambient conditions (23°C, 50% RH) at a constant displacement rate of 1 mm/min min using an Instron 1196 screw-driven test frame. Instron Series IX software was used to control the test machine and to collect the test data. The strength data presented in Table 2 and Figure 5 are given in terms of load per unit width **(**N/mm).

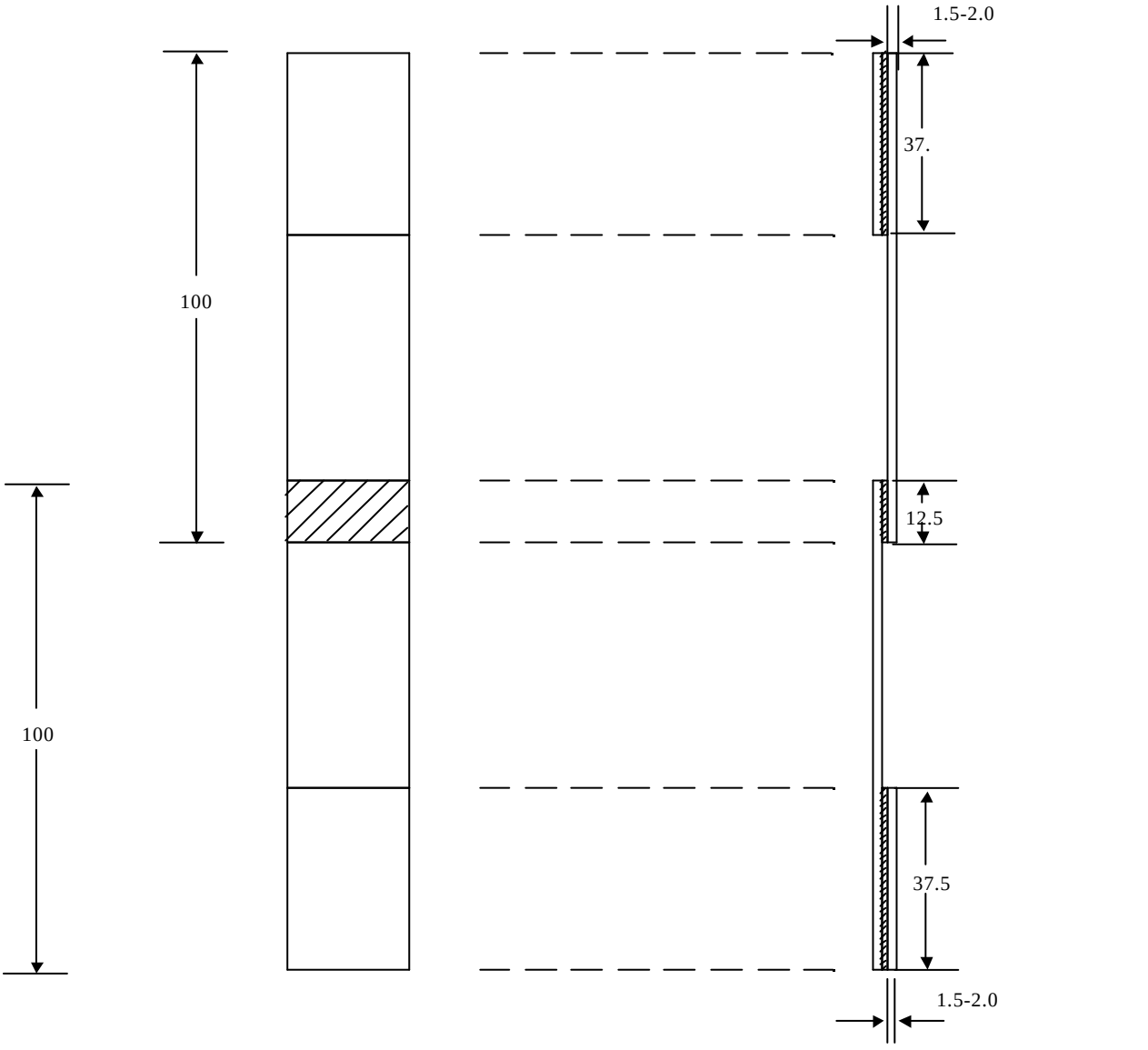


Figure 4 Schematic of single-lap joint.

Table 2 Strength (N/mm) Data for Moisture Conditioned CR1/AV119 Single-Lap Joints

Exposure Time (days)	Immersion Conditioning Temperature (°C)		
	25	40	50
0	334 ± 11	334 ± 11	334 ± 11
3	291 ± 9	228 ± 9	206 ± 12
7	272 ± 5	232 ± 7	190 ± 8
14	235 ± 6	219 ± 8	181 ± 7
21	248 ± 8	197 ± 7	171 ± 11
42	244 ± 7	213 ± 7	162 ± 7

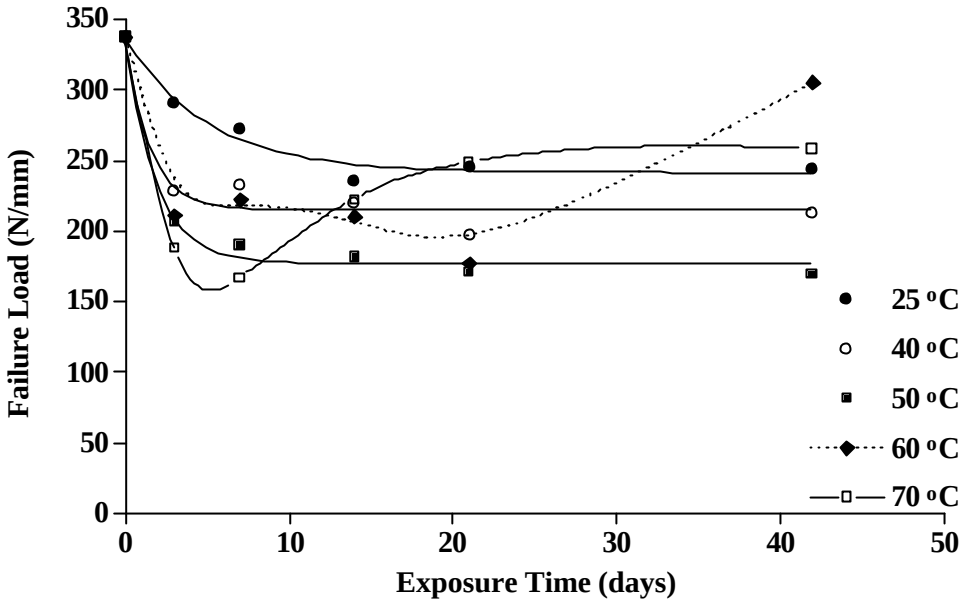


Figure 5 Strength retention of moisture conditioned CR1 / AV119 single-lap joints.

Figure 5 shows that within 42 days of water immersion, at temperatures ranging from 25 °C to 50 °C, the joint strength **P** rapidly decreases exponentially to a constant (limiting) value. The relationship between the initial rate of strength loss and the conditioning temperature, and between the limiting strength value and the conditioning temperature, can be approximated by linear functions (Figures 6 and 7). The rapid loss of strength for short exposure times is typical for adhesive joints with poor interfacial bonding. The loss of strength was attributed to interfacial failure between the adhesive and substrate.

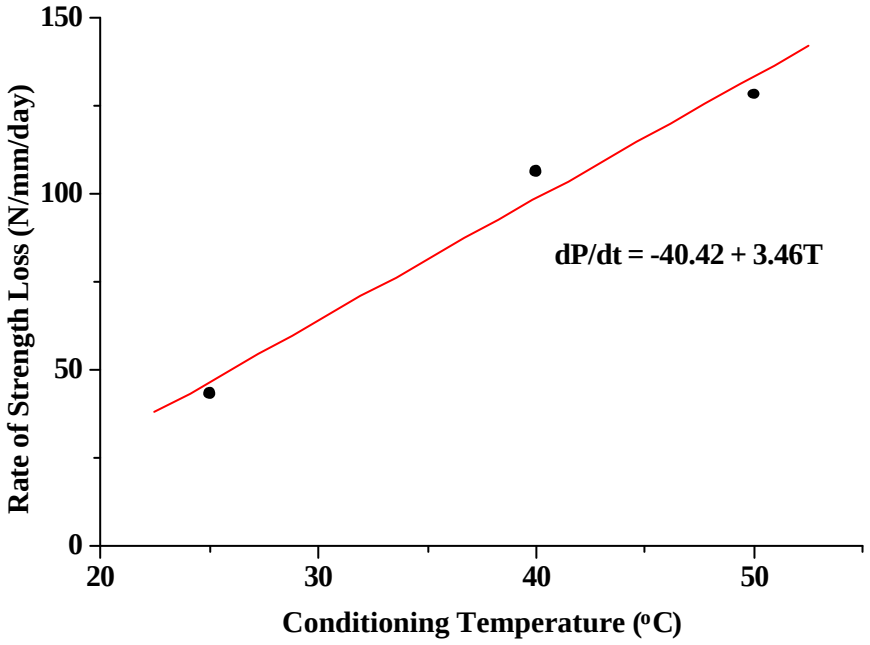


Figure 6 Rate of strength loss over first 3 days exposure for CR1 / AV119 single-lap joints.

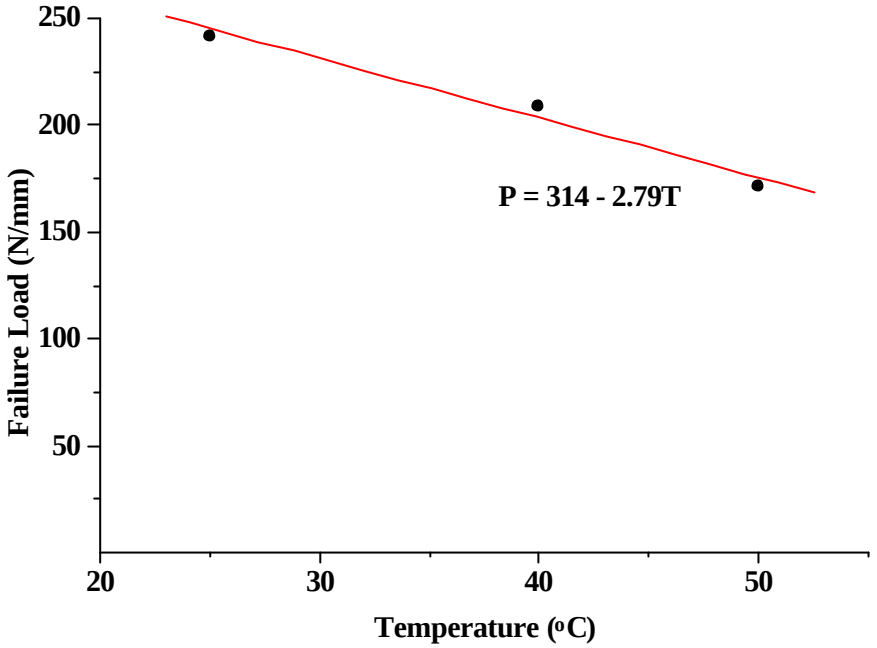


Figure 7 Strength limits for CR1 / AV119 single-lap joints.

Figure 5 also includes strength data from tests carried out on specimens that were immersed in water at 60 °C and 70 °C. A marked gain in joint strength can be observed after 21 days for those specimens that have been conditioned at 60 °C. The increase occurs within 7 days exposure for specimens conditioned at 70 °C. The increase in "apparent" strength is attributed to plasticisation of the adhesive. This results in a reduction in peel and shear stress concentrations at the joint ends to levels lower than experienced by drier specimens, thereby masking interfacial effects.

Dynamic mechanical thermal analysis (DMTA) measurements were carried out on moisture conditioned bulk AV119 adhesive specimens conditioned at 25 °C, 40 °C and 60 °C to determine the change in **Tg** as a function of moisture content (Figure 8) [2]. The results form a master curve which asymptotes to approximately 48 °C. The saturation level for AV119 conditioned at 60 °C was estimated to be 10 wt%. The maximum amount of moisture that can be absorbed by the adhesive, and hence the minimum **Tg** value attainable, was found to be temperature dependent. A sigmoidal (Boltzmann Equation) curve fit can be used to relate **Tg** with moisture content **M.**

$$Tg = \frac{A_1 - A_2}{1 + e^{(M - Mo)/dM}} + A_2 \qquad (4)$$

where $\mathbf{A_1}$ is the initial **Tg** value, $\mathbf{A_2}$ is the final **Tg** value, **Mo** is the centre and **dM** is the width. The **Tg** value at the centre **Mo** is half way between the two limiting values $\mathbf{A_1}$ and $\mathbf{A_2}$: **Tg**(**Mo**) = ($\mathbf{A_1}$ + $\mathbf{A_2}$) / 2. For AV119, $\mathbf{A_1}$ = 147.2, $\mathbf{A_2}$ = 45.7, $\mathbf{M_O}$ = 0.58 and **dM** = 1.97.

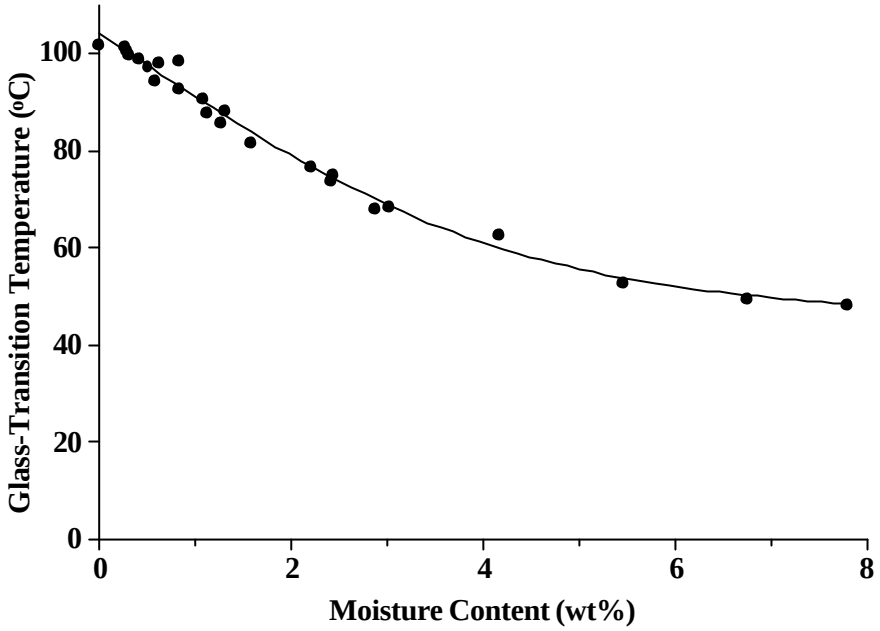


Figure 8 Glass-transition temperature of AV119 as a function of moisture content [2].

Figure 9 shows that a linear relationship exists between the minimum strength measured for dry and conditioned joints (25 °C to 60 °C) and the corresponding saturation value of **Tg** for the bulk adhesive.

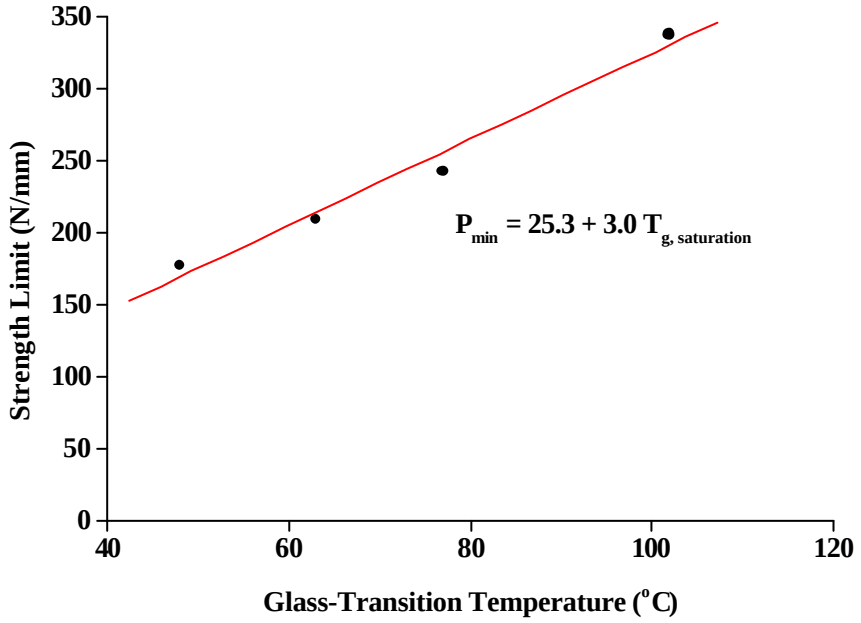


Figure 9 Minimum joint strength versus the saturation value of **Tg** for AV119 bulk resin.

The results indicate that for moisture sensitive adhesives it is possible to relate the strength reduction of bonded joints with changes in both Tg and the conditioning temperature, thus enabling intermediate strength values to be determined.

4.2 THICK ADHEREND SHEAR TESTS

Statistical analysis such as design of experiment (DOE) techniques can be used to establish the interactions between the critical factors that affect the durability of adhesive joints to hostile environments. A number of case studies have been used within the programme to demonstrate the use of these techniques in quantifying the relationship between the critical factors [10, 11].

One of the statistical analysis studies evaluated the durability performance of 5251 aluminium alloy TAST tensile specimens (Figure 1) that had been immersed in distilled / deionised water at either 25°C, 40°C or 60°C for periods of up to 6 weeks. Batches of conditioned specimens (five specimens per batch) were withdrawn at selected intervals over a 6 week period and tested at room-temperature. The TAST specimens consisted of 5 mm thick pre-shaped adherends bonded with either AV119, F241 or AF126-2. PTFE spacers were used to prevent the formation of an adhesive fillet at the ends of the overlap. Two surface pre-treatments were considered in the study. A brief description of the adhesives and surface treatment used in the assessment are provided below.

Adhesives

Araldite 2007 (AV119): A one part epoxy adhesive supplied by Ciba Polymers. The cure schedule was 140 °C for 75 minutes.

F241: A toughened acrylic adhesive supplied by Permabond Adhesives Ltd. The adhesive was cured by applying an initiator to one surface and the acrylic resin to the other surface. The adhesive was allowed 24 hours to cure at room-temperature.

AF126-2: A modified epoxy film adhesive supplied by 3M, UK. The adhesive contains a carrier fabric for bondline thickness control. The cure cycle was 120 °C for 90 minutes.

Table 3 Typical Tensile and Shear Properties for AV119, F241 and AF126-2

Property	Adhesive		
	AV119	F241	AF126-2
Tension			
Modulus (GPa)	3.05	0.60	2.03
Strength (MPa)	70	25	41
Poisson's Ratio	0.34	0.49	0.42
Shear			
Modulus (GPa)	1.10	0.20	0.71
Strength (MPa)	47	17	37

Surface Treatments

Grit Blast + Degrease (GB): Prior to bonding, the adherends were degreased with 1,1,1-trichloroethane and then grit blasted using 80/120 alumina to produce an uniform matt finish. A pressure of 85 psi was used to grit-blast the areas to be bonded. Any dust remaining after grit blasting was removed with clean compressed air. The surfaces to be bonded were then degreased again with 1,1,1-trichloroethane and dried. The time between bonding and surface pretreatment was approximately 1 hour.

Grit Blast + A187 (g-glycidoxypropyltrimethoxy) Silane (GPS): The initial surface pretreatment was identical to the procedure employed for grit blast + degrease. The grit-blasted + degreased surface was subsequently coated with A187 silane coupling agent (supplied by Union Carbide). A 1% solution of A187 silane was prepared in deionised water and allowed to stand for 90 minutes to hydrolyse. The solution was brushed onto the prepared surfaces. The coated adherends were then positioned to drain off the excess solution and allowed to dry in air for 2 to 3 hours before applying the adhesive.

Testing and data collection were identical to that previously mentioned in Section 2. The test results are presented in Tables 4 to 6.

Table 4 Failure Stress (MPa) Data for 5251 Aluminium alloy/AV119 Epoxy Joints

Condition	Exposure Time (days)					
	0	3	7	14	21	42
25 °C						
GB	24.5 ± 0.9	21.8 ± 2.5	20.8 ± 1.6	19.5 ± 2.6	21.5 ± 1.1	19.3 ± 1.0
GPS	26.0 ± 1.6	25.7 ± 0.4	25.2 ± 0.4	24.5 ± 1.4	23.9 ± 1.4	24.9 ± 1.4
40 °C						
GB	24.5 ± 0.9	17.5 ± 1.5	17.4 ± 1.8	17.1 ± 0.1	16.4 ± 0.3	16.4 ± 0.6
GPS	26.0 ± 1.6	22.1 ± 2.1	20.8 ± 0.9	19.8 ± 2.3	20.5 ± 1.3	19.9 ± 1.7
60 °C						
GB	24.5 ± 0.9	18.0 ± 0.9	21.7 ± 1.5	17.3 ± 1.0	15.4 ± 1.1	17.2 ± 1.8
GPS	26.0 ± 1.6	21.6 ± 1.8	-	18.7 ± 1.5	18.3 ± 1.7	18.3 ± 0.8

Table 5 Failure Stress (MPa) Data for 5251 Aluminium alloy/F241 Acrylic Joints

Condition	Exposure Time (days)					
	0	3	7	14	21	42
25 °C						
GB	19.6 ± 1.4	20.6 ± 1.2	22.1 ± 1.4	21.9 ± 1.1	21.2 ± 1.1	17.8 ± 1.0
GPS	19.2 ± 1.6	20.3 ± 1.3	25.0 ± 0.5	22.2 ± 1.2	19.9 ± 1.7	18.4 ± 2.1
40 °C						
GB	19.6 ± 1.4	20.3 ± 1.3	23.0 ± 1.8	20.7 ± 0.6	20.0 ± 1.0	19.7 ± 1.2
GPS	19.2 ± 1.6	22.3 ± 1.8	24.5 ± 1.1	22.7 ± 1.4	20.9 ± 0.8	20.4 ± 1.5
60 °C						
GB	19.6 ± 1.4	24.7 ± 1.1	22.2 ± 1.0	21.9 ± 1.1	20.9 ± 0.8	13.3 ± 1.9
GPS	19.2 ± 1.6	24.8 ± 1.1	21.8 ± 0.7	21.9 ± 0.7	20.2 ± 1.7	15.3 ± 1.4

Table 6 Failure Stress (MPa) Data for 5251 Aluminium alloy/AF126-2 Joints

Condition	Exposure Time (days)					
	0	3	7	14	21	42
25 °C						
GB	29.6 ± 1.6	20.6 ± 1.2	21.1 ± 1.8	19.9 ± 3.7	21.1± 3.3	20.8 ± 3.2
GPS	29.4 ± 1.8	25.6 ± 1.2	26.0 ± 2.8	23.4 ± 3.5	23.3 ± 4.4	22.3 ± 3.6
40 °C						
GB	29.6 ± 1.6	18.3 ± 1.5	17.2 ± 1.4	16.1 ± 0.8	19.5 ± 2.8	18.4 ± 1.4
GPS	29.4 ± 1.8	24.1 ± 2.1	22.4 ± 3.7	20.7 ± 3.0	20.4 ± 2.2	18.9 ± 1.1
60 °C						
GB	29.6 ± 2.1	21.5 ± 3.8	19.9 ± 2.5	16.6 ± 2.3	16.9 ± 1.8	17.5 ± 1.0
GPS	29.4 ± 1.8	23.7 ± 3.0	21.0 ± 2.0	16.7 ± 1.9	16.7 ± 1.9	18.3 ± 1.5

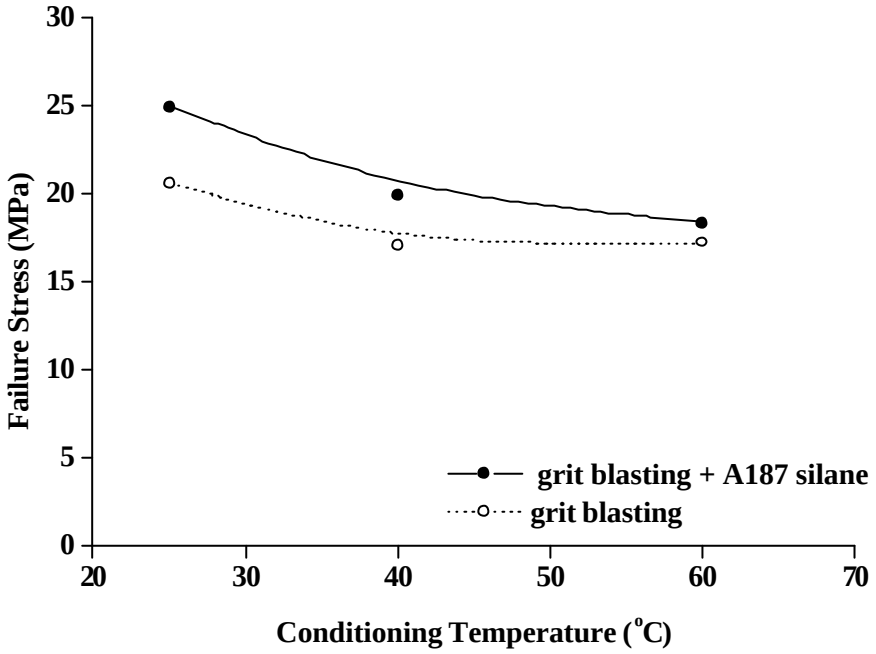


Figure 10 Failure stress after 42 days water immersion for AV119 TAST specimens

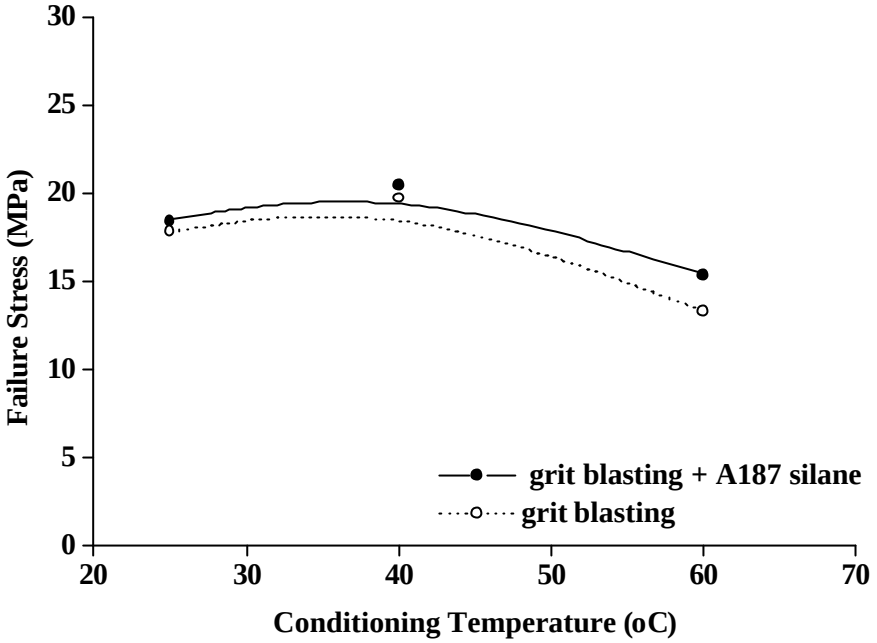


Figure 11 Failure stress after 42 days water immersion for F241 TAST specimens

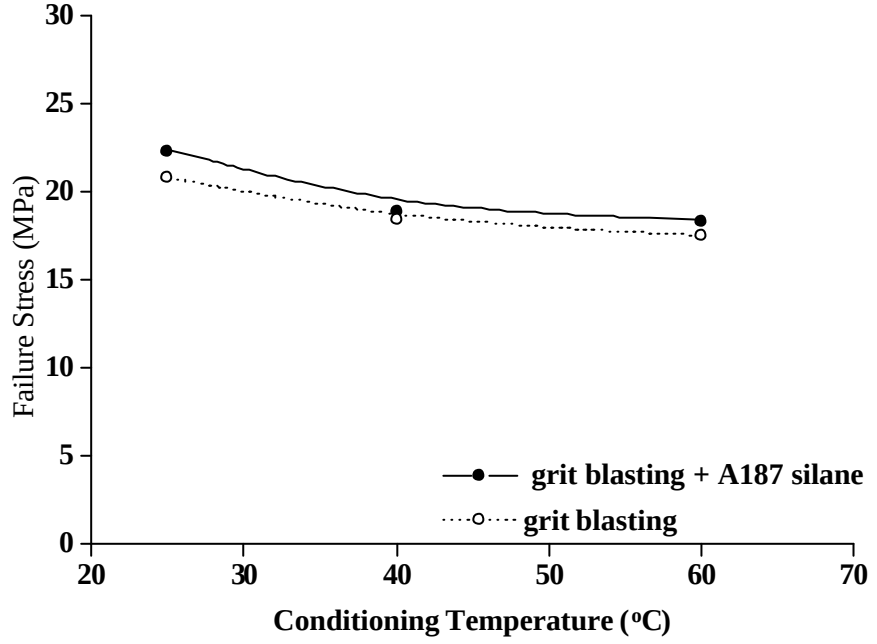


Figure 12 Failure stress after 42 days water immersion for AF126-2 TAST specimens.

Key Observations

The following observations can be made with respect to the test data generated for the three adhesive systems considered.

- **"Apparent" strength data for the unconditioned adhesive systems were considerably below that expected for these materials.** This was probably due to the prevention of a spew fillet at the end of the overlaps and the use of relative thin adherends (5 mm thick).
- There was no clear mathematical relationship that could be discerned between joint performance (i.e. residual strength) and exposure time or conditioning temperature.
- Joint strength tends to approach a limiting non-zero value in a relatively short period.
- Grit blast + silane A187 invariably provided improved environmental resistance, although the relative effectiveness of this surface treatment diminished as the conditioning temperature increases and with exposure time.
- Cohesive failure was observed for unconditioned and conditioned specimens bonded with either AV119 or AF126-2. The F241 specimens underwent interfacial failure, which always initiated at the surface on which the adhesive - not the initiator - was applied. F241 continues to cure for a longer period than allowed (i.e. during pre-conditioning).

Statistical analysis has been carried out on the test data and will be presented in a future report.

5. TEMPERATURE-HUMIDITY INTERACTION

This section evaluates the combined effect of temperature and humidity on the durability performance of single-lap joints made from 2 mm thick Ti-6Al-4V alloy sections bonded with AF126-2 epoxy adhesive film (supplied by 3M, UK). Specimens were subjected to nine combinations of temperature and humidity for periods ranging from 0 to 17 days. Table 7 shows the factors and levels used in the full matrix of tests.

Table 7 Factors and Levels used in Full Test Matrix

Temperature (°C)	Level	Humidity (% RH)	Level	Time (days)	Level
25	1	45	1	0	1
40	2	85	2	1	2
70	3	96	3	3	3
				7	4
				17	5

5.1 SPECIMEN GEOMETRY, PREPARATION AND TESTING

Specimen geometry (Figure 4), testing and data analysis were identical to that employed for the CR1/AV119 single-lap joint specimens described in Section 2.1. Tests were conducted under standard laboratory conditions (i.e. 23 °C, 50% RH). Conditioning was undertaken using Climatic System environmental chambers. The temperature and humidity were controlled to within ±2 °C and ± 5% RH, respectively. **Humidity control**

(% RH) can also be achieved at various temperatures by saturated solutions of salts and salt mixtures.

Prior to bonding, the surfaces of the titanium alloy sections to be bonded were chromic acid etched. A description of the technique is described below.

Stage 1 - Grit Blast + Degrease: The adherends were first degreased with 1,1,1-trichloroethane and then grit blasted using 80/120 alumina to produce an uniform matt finish. A pressure of 85 psi was used for grit-blasting the areas to be bonded. Any dust remaining after grit blasting was removed with clean compressed air. The surfaces to be bonded were then degreased again with 1,1,1-trichloroethane and dried.

Stage 2 - Chromic Acid Etch: The grit blasted/degreased specimens were then immersed for 30 minutes in a chromic acid etch solution at a temperature of 60-70 ^{o}C. The specimens were removed from the etch solution and washed in cold tap water and then hot tap water. Finally, the specimens were rinsed with acetone and allowed to dry in a fan oven for a few minutes at 120 ^{o}C. Specimens were inverted to enable the water to drain from the areas to be bonded. The etch solution consisted of 500 ml of distilled water with 75 ml of sulphuric acid (H_2SO_4) and 37.5 gm of sodium dichromate ($Na_2Cr_2O_7.2H_2O$).

5.2 EXPERIMENTAL RESULTS AND DISCUSSION

The test results (load per unit width, presented in Table 8 and Figures 13 to 16, clearly show that there is a synergistic effect between temperature and humidity. Figures 13 to 16 represent the average effects of temperature, relative humidity and exposure time on joint strength. No noticeable changes were observed for those specimens stored for 2-3 weeks under standard laboratory conditions.

As with the immersion tests, the joint strength exponentially declines to a non-zero limiting value, which is dependent upon the relative humidity and temperature of the conditioning environment (see Table 4). It has been observed that the diffusion coefficient and the saturation moisture contents for AF126-2 increases with temperature and relative humidity [12, 13]. The glass-transition temperature of the adhesive is sensitive to moisture. Figure 17 shows **Tg** as a function of moisture content for bulk AF126-2 specimens conditioned at 70 ^{o}C and 96% RH. The saturation moisture content is approximately 6.0 wt%.

Table 8 Effect of Elevated Temperature and Humidity on Joint Strength (N/mm)

Temperature (°C)	Relative Humidity (%)		
	45	85	96
1 day			
25 °C	368 ± 7*	281 ± 17	254 ± 17
40 °C	348 ± 28	276 ± 14	243 ± 4
70 °C	278 ± 20	273 ± 19	243 ± 7
3 days			
25 °C	368 ± 7*	270 ± 15	235 ± 10
40 °C	300 ± 6	252 ± 28	228 ± 13
70 °C	248 ± 10	240 ± 19	224 ± 21
7 days			
25 °C	368 ± 7*	276 ± 19	241 ± 13
40 °C	310 ± 17	262 ± 23	247 ± 12
70 °C	236 ± 10	244 ± 12	128 ± 19
17 days			
25 °C	368 ± 7*	187 ± 20	194 ± 15
40 °C	206 ± 15	173 ± 16	148 ± 13
70 °C	229 ± 25	195 ± 12	84 ± 9

* Joint strength assumed constant (remains relatively unaffected for 2- 3 weeks when stored at 23 °C and 50 %RH).

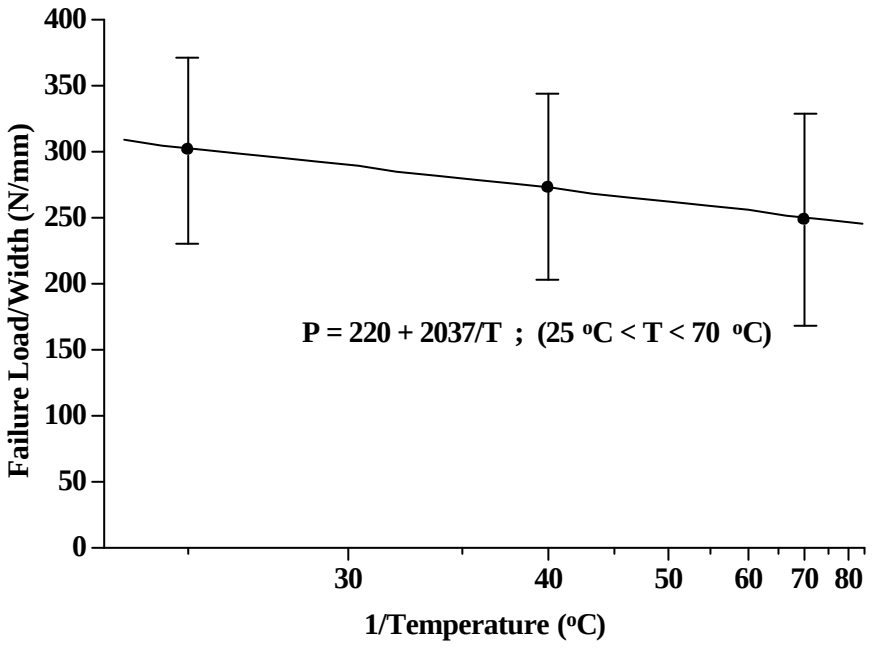


Figure 13 Effect of temperature on failure load for 6Al-4V-Ti alloy / AF126 single-lap joints.

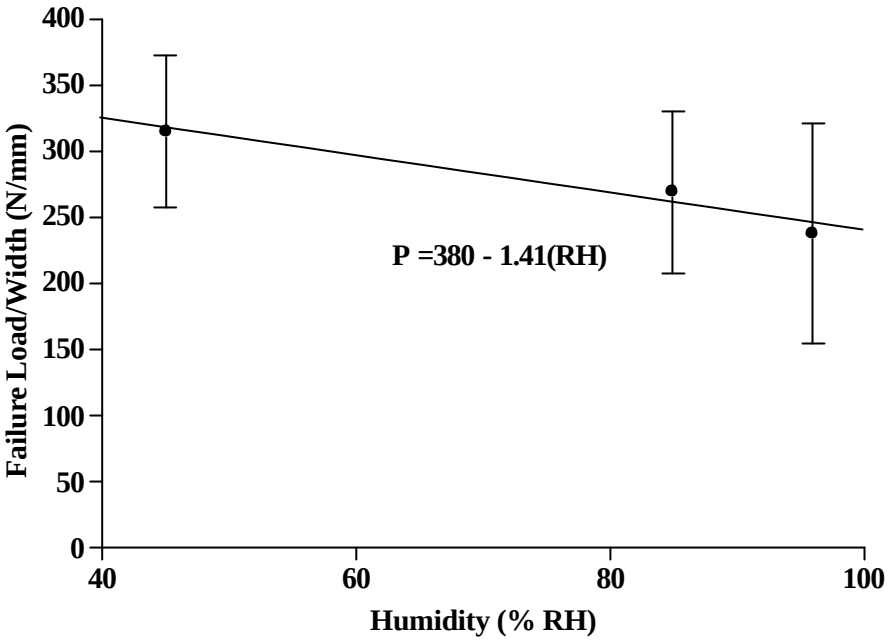


Figure 14 Effect of humidity on failure load for 6Al-4V-Ti alloy / AF126 single-lap joints.

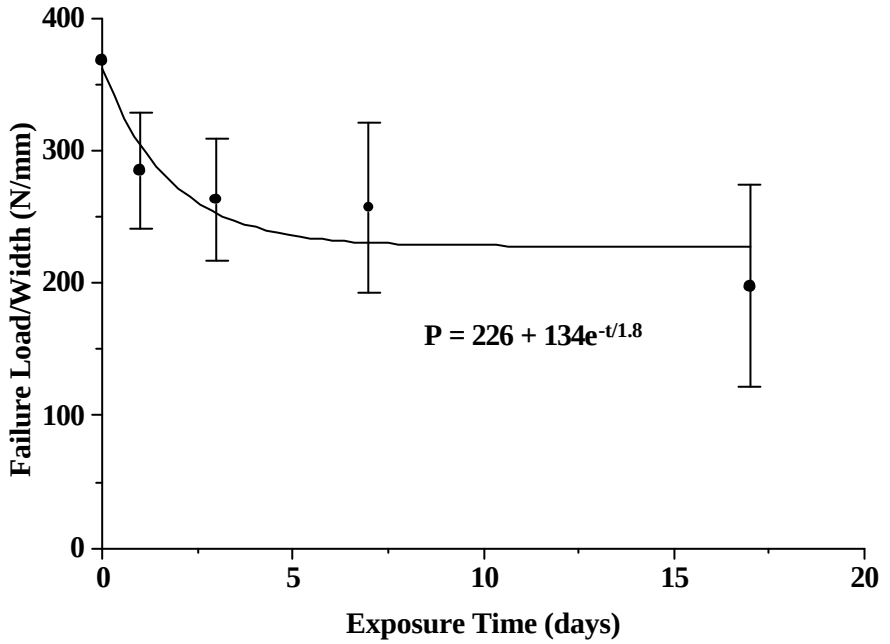


Figure 15 Effect of time on failure load for 6Al-4V-Ti alloy / AF126 single-lap joints.

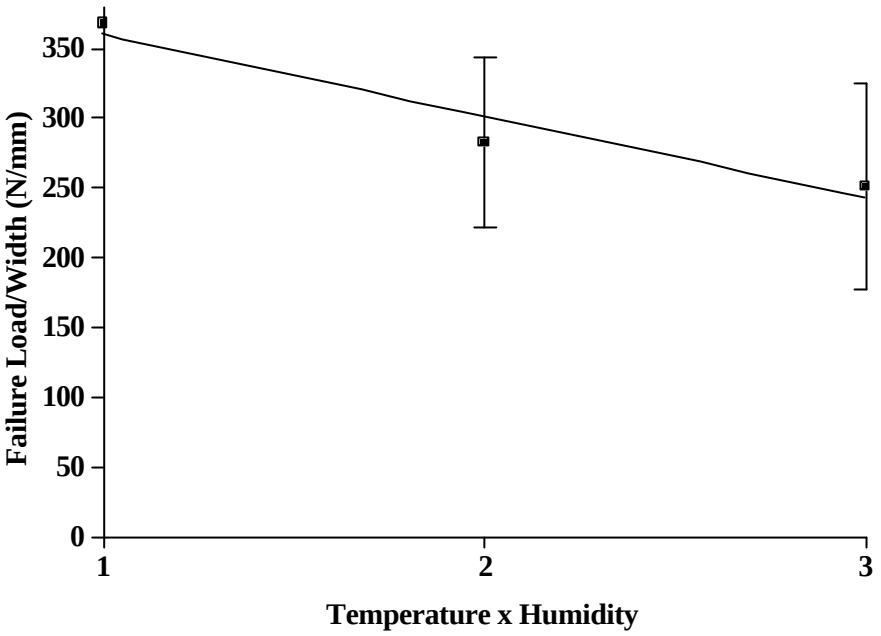


Figure 16 Interaction between temperature and humidity.

Equation (4) can be used to relate **Tg** with moisture content **M** (Figure 17) for AF126-2 conditioned at 70 °C and 96% RH. For AF126-2 conditioned at 70 °C and 96% RH, $\mathbf{A_1}$ = 113.7, $\mathbf{A_2}$ = 74.4, $\mathbf{M_O}$ = 2.20 and **dM** = 0.71.

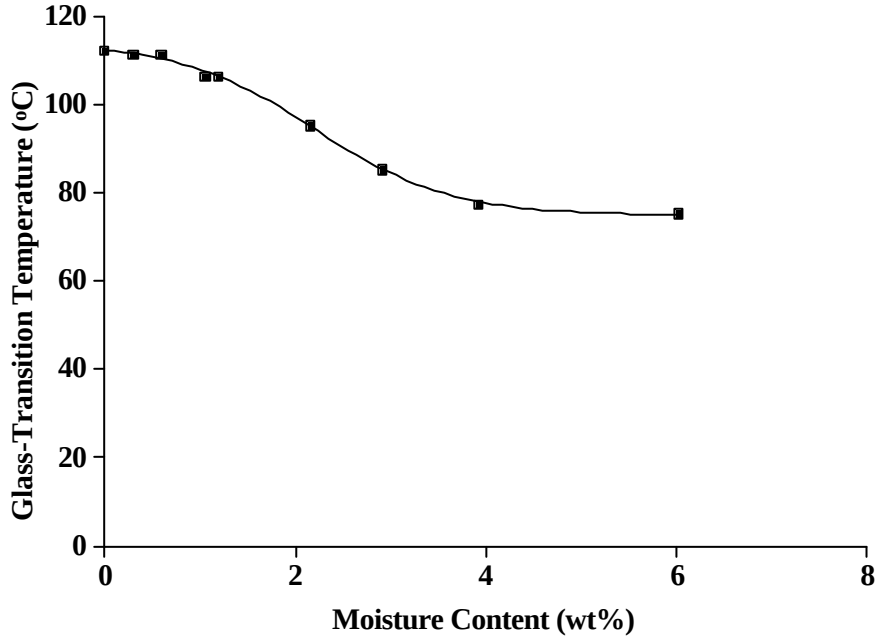


Figure 17 Glass-transition temperature of AF126-2 as a function of moisture content.

The results presented in this section show that for this particular system and joint configuration simple algebraic relationships can be used to estimate the effects of

temperature and humidity, and their interactions, on joint strength. Unfortunately, there is no universal formulation that can be applied to all adhesive systems or adhesive types. The chemical and physical complexity of adhesive materials and adherend surfaces, and the multifaceted nature of degradation mechanism(s) prevents the formulation of simple solutions.

6. AUTOCLAVE CONDITIONING

Accelerated ageing can also be carried out using a steam autoclave, although this technique is extremely harsh and can result in complete chemical and physical degradation of the adhesive. To demonstrate the possibility of employing a steam autoclave to promote accelerated ageing a series of tests were conducted using flexure specimens manufactured from cross-ply (i.e. 0/90) T300/924 carbon-fibre reinforced epoxy. Three-point flexure tests were carried out on dry and conditioned specimens under standard laboratory. The flexure tests were simply trials to ascertain the effectiveness of using a steam autoclave to accelerate ageing. Specimens were exposed to the following high temperature and pressure conditions for periods ranging from 6 to 12 hours: (i) 1.05 bar and 121 ^{o}C; and (ii) 2.6 bar and 137 ^{o}C. The results of the tests are shown in Table 4. The specimens were conditioned in a commercial autoclave unit by LTE Scientific Ltd.

Table 9 Flexural Properties of Autoclaved Conditioned Cross-Ply T300/924 Carbon/Epoxy

Condition	Moisture Content (%)	Flexural Modulus (GPa)	Flexural Strength (MPa)
Dry	0.19 ± 0.01	92.5 ± 1.1	1332 ± 78
121 ^{o}C / 1.05 bar / 6 hrs	1.10 ± 0.02	90.9 ± 1.1	1,275 ± 73
121 ^{o}C / 1.05 bar / 12 hrs	1.43 ± 0.01	90.0 ± 0.9	1,198 ±97
137 ^{o}C / 2.60 bar / 12 hrs	2.19 ± 0.06	88.9 ± 0.9	1,223 ± 21

Trials have also been carried out using an in-house autoclave unit. The preliminary results showed that within 24 hours exposure at 3.3 bar and 137 ^{o}C the transverse tensile strength of unidirectional T300/924 had been reduced by 25%.

The results in Table 9 show that moisture uptake in 12 hours was approximately 2 wt%. The corresponding reduction in **Tg** was at least 52 ^{o}C. This is equivalent to immersing the specimens in water at 60 ^{o}C for approximately 1 to 2 months. Larger coupon specimens would take 3 to 4 months and real structures 1 to 2 years to condition using current procedures. **The results strongly indicate that autoclave conditioning is a viable option for inducing accelerated ageing, particularly for those systems possessing glass transition temperatures in excess of 120 ^{o}C to 140 ^{o}C. The technique may prove far too destructive for materials possessing a low Tg value, such as polyester resins or moisture sensitive adhesives (e.g. AV119). This promising accelerated ageing procedure warrants further consideration.**

7. CONCLUDING REMARKS AND DISCUSSION

A number of conclusions can be made in respect to environmental conditioning methods that can used for inducing accelerated moisture degradation within adhesively bonded joints for inducing accelerated.

- Compression specimen is suitable for measuring the shear properties of bonded panels with a total thickness of 5 to 6 mm, and offers the potential for rapid environmental conditioning. **Smaller specimens, however, are more sensitive to environmental attack than larger joints due to the larger bond-edge-to-bond-area ratio and therefore give a more conservative estimate of environmental resistance**. **Extrapolation of short-term data from accelerated tests using small specimens needs to be considered with due caution.** The compression specimen, unlike the tensile specimen, is not particularly suited to cyclic fatigue testing.

- **The introduction of holes to accelerate ageing has little or no effect on strength retention for joints bonded using moisture sensitive adhesives (i.e. material properties decrease with moisture content).** Temperature and time have a far more influential effect on joint performance than the presence of holes. Chemical and physical changes that occur within the adhesive, adherends and interface at the ends of the overlap will dominate joint failure.

- The results indicate that for moisture sensitive adhesives it is possible to relate the strength reduction of single-lap joints with changes in both **Tg** and the conditioning temperature, thus enabling strength values to be determined at intermediate temperatures. This applies equally to water immersion and exposure to hot humid environments.

- It may be possible to relate the reduction in joint strength **P** with exposure time **t** using the the Boltzmann Equation in the form:

$$P = \frac{P_1 - P_2}{1 + e^{(t - to)/dt}} + P_2 \qquad (5)$$

where $\mathbf{P_1}$ is the strength of the unconditioned material, $\mathbf{P_2}$ is the final (or limiting) strength value, **to** is the centre value between $\mathbf{P_1}$ and $\mathbf{P_2}$, (i.e. **P**(**to**) = ($\mathbf{P_1}$ and $\mathbf{P_2}$)/2) and **dt** is the width (i.e. a measure of the transition time between $\mathbf{P_1}$ and $\mathbf{P_2}$). The following can be expected to occur with improved environmental resistance: (i) decline in strength will be delayed; (ii) differences between $\mathbf{P_1}$ and $\mathbf{P_2}$ will diminish; and (iii) **dt** will increase.

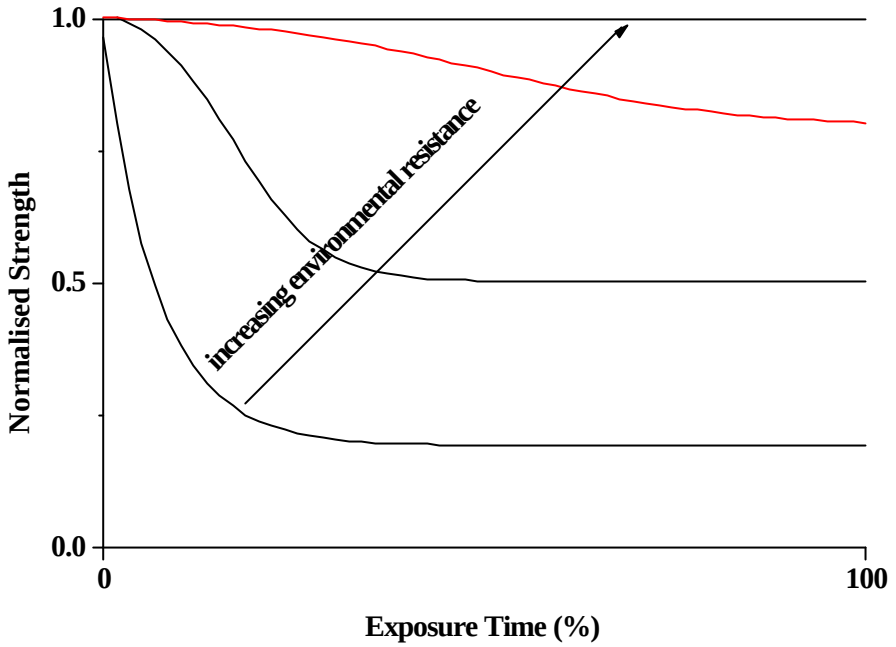


Figure 18 Schematic of typical strength reduction with exposure time curves.

- The presence of peel stresses at the ends of the overlap of a joint will increase the sensitivity of the bonded structure to environmental attack. Single-lap joints are therefore more prone to degradation than TAST specimens.

- Autoclave conditioning is a viable option for inducing accelerated ageing, particularly for those systems possessing glass transition temperatures in excess of 120 °C to 140 °C. The technique may prove far too destructive for materials possessing a low **Tg** value, such as polyester resins or moisture sensitive adhesives (e.g. AV119). This promising accelerated ageing procedure warrants further consideration.

- Boltzmann Equation can be used to relate the glass-transition temperature **Tg** to moisture content **M** for those adhesives sensitive to moisture ingress.

$$Tg = \frac{A_1 - A_2}{1 + e^{(M - Mo)/dM}} + A_2$$

  where $\mathbf{A_1}$ is the initial **Tg** value, $\mathbf{A_2}$ is the final **Tg** value, **Mo** is the centre and **dM** is the width (see Section 4.1).

The results show that the TAST is a preferable alternative to the single-lap joint. The technique can be used for quick comparison work and can often be used to generate engineering data. It cannot be assumed, however, that the variations of shear strength due to temperature and moisture for short-term tests determined with small specimens can be directly used to predict the performance of larger bonded structures Extrapolation of TAST test data to predicting joint behaviour of larger structures needs further consideration.

ACKNOWLEDGEMENTS

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APPENDIX 1 - MOISTURE DIFFUSION IN ADHESIVES

Relationships can be derived between saturation moisture content and relative humidity under different conditioning temperatures, and between the diffusion coefficient and temperature; as shown below. NPL Report CMMT(A) 204 "An Improved Modelling Approach of Moisture Absorption in Adhesive Joints using the Finite Element Method" provides a more detail coverage on the kinetics of moisture diffusion.

Diffusion coefficient D is related to the conditioning temperature by the following relationship:

$$D = Do_e^{-\frac{E}{RT}} \qquad \text{(A1.1)}$$

where **Do** is the absolute diffusion coefficient, **E** is the activation energy, **R** is the universal gas constant and **T** is the temperature (K).

Saturation Moisture Content M¥ is related to the relative humidity, f by the following equation:

$$M_\infty = a\phi^b \qquad \text{(A1.2)}$$

where **a** and **b** are measured constants. The values of **a** and **b** vary with material and conditioning temperature.