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**Adhesion Durability
Assessment**

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Summary

As part of a DTI funded Measurements for Materials Systems project, Interfacial Adhesion Strength, a number of test methods for adhesion strength have been studied as means for quantifying adhesion strength. The pull-off methods and three-point bend were evaluated, in experimental and Finite Element (FE) studies, for their ability to quantify the strength of adhesion between adhesive and adherend. In principle, these tests might be suitable for large scale screening of adhesives and surface treatments.

Durability trials have been performed, using three test systems – anodised aluminium, galvanised steel (oiled) and glass fibre reinforced polypropylene (corona discharge) – bonded with epoxy adhesives, to investigate the influence of surface treatment and measurable surface characteristics on adhesion strength performance under hot/wet conditioning (70 °C, 85% RH). Experimental matrices were chosen using design of experiments approaches and the results from the pull-off and 3-point bend measurements analysed statistically to determine any correlations with contact angle, surface roughness and colour measurements.

The study on the aluminium system indicated that there appeared to be minimal degradation of the bond strength on conditioning. The reductions in bond strength measured were most likely due to the decrease of the cohesive strength of the adhesive occurring due to moisture absorption by the adhesive. There were no correlations with surface characteristics observed.

The zinc layer on the galvanised steel corroded locally under the adhesive layer, where moisture condensed in pores in the adhesive in contact with the surface, but not where the surface was open to the environment. It is believed that the rate of corrosion depends on the rate at which moisture permeated through the adhesive – the 3-point bend sample has a much shorter diffusion path than the pull-off sample and had correspondingly higher levels of corrosion. Some correlations between bond strength and surface characteristics were observed but these must be treated with suspicion since the mode of surface degradation was different under the bond layer than it was for the exposed, travelling surfaces measured. The use of travelling specimens to observe changes in surfaces to predict bond performance is therefore questionable.

The polypropylene surfaces have very low bond strengths and failure in the bond tests was interfacial. The corona treatment reduces the contact angle (increasing surface energy for bonding) and there is a correlation between contact angle and bond strength.

Overall, the correlations between surface characteristics and interfacial adhesion strength were disappointingly poor, mainly as processes other than the surface changes are involved in the degradation of joint performance.

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1. INTRODUCTION

The mechanical response of a materials system, such as an adhesive joint, coating or composite, is influenced by the properties of the bulk materials and of the interfaces within the system. The design of adhesively bonded structures requires accurate materials data. Materials property data are often best obtained from bulk test specimens. Such data can give an indication of the cohesive strength of the adhesive but designers also need to consider debonding at an interface as a potential mode of failure. The strengths of the interfaces between the adhesive and substrates thus become part of the design process. Information on interface strengths is normally obtained from adhesives joint tests, such as lap shear. However, the complexity of stress distributions in such joints leads to difficulties in obtaining quantitative interface strengths that are applicable to other loading configurations. In many of these joint tests, observed failure modes tend to be mixed – both interfacial and cohesive – and it can be difficult to detect the point of first failure. As a result, quantitative properties of the interface are seldom considered in the design process owing to the lack of validated data and the absence of design models and tools.

Surface preparation is recognised as the most critical step in the adhesive bonding process and considerable effort is frequently expended in optimising the surface treatment. Correct surface preparation is essential for good bond strength and ensuring the long-term structural integrity of bonded structures, particularly under hostile service conditions. Unsatisfactory surface preparation will result in premature and unpredictable interfacial failure of bonded joints. An essential part of ensuring good adhesion and long-term durability is the ability to monitor and control changes in surface morphology and chemistry of the substrate materials during surface preparation and storage. Methods of assessing the surface of adherends provide a route to quality assurance of bonds.

There are many methods by which adherend surfaces are prepared prior to bonding and a very wide array of techniques available for surface characterisation [1]. High equipment cost, experimental complexity and long data acquisition times can rule out the routine use of many techniques. An experimental study was undertaken to evaluate the efficacy of various characterisation techniques for evaluating changes in surface properties of metallic materials and polymer composites resulting from changes in surface treatments and the level of treatment [2]. The techniques assessed included: contact and non-contact profilometry (surface roughness), contact angle (wettability), micro-hardness, gloss/reflectivity, colorimetry, ellipsometry, surface resistivity and optically stimulated electron emission (OSEE). The results from the study showed that most of the techniques studied were useful in determining changes in surface properties for different levels of treatment. Contact angle and colorimetry techniques proved the most suitable for relating surface changes to the level of treatment and could potentially be used to improve or optimise adhesive strength and environmental durability.

Accurate characterisation of material properties at interfaces requires sophisticated instrumentation for measuring at small scales. Studies have shown that the properties of both the adhesive and the adherend in the region of the interface may differ significantly from those of the bulk materials. The term ‘interphase’ is often used for the affected materials near the interface, although in reality the properties of the interphase will vary with position. The properties of the interphase are extremely difficult to measure or predict. From an engineering

point of view, the most important property is the 'strength' of the interface. Whether the mode of failure is due to a true interfacial failure or failure in a layer of material bordering the interface probably makes little difference in an engineering design if the materials properties in the interface region are unknown. In this report, the term interface is used to encompass the true interface, the interphase and the near surface area.

A review identified the many test methods available for characterising adhesion of coatings and adhesives to substrates [3]. An investigation was undertaken of mechanical test methods that quantify the strength of the 'interface' to assess joint strength and evaluate the effects on adhesion strength of surface pre-treatment or interface degradation. Pull-off tests, butt joint tests, pull-out tests and three-point bend adhesion tests, were evaluated as means of obtaining quantitative data on adhesion strengths. The results of experimental measurements and FE analyses using ABAQUS were described [4]. Pull-off and three-point bend tests, where sample preparation and testing are straightforward, offered the most potential for performing extensive experimental studies for assessing bond durability.

This report describes the results of durability studies on three materials systems:

- Anodised aluminium and 1-part toughened epoxy;
- Oiled galvanised steel and 2-part 'oil-tolerant' epoxy; and
- Corona treated glass fibre reinforced polypropylene and 2-part general-purpose epoxy.

Each surface was characterised using either colorimetry and/or contact angle and/or surface roughness. The adhesion strength was assessed using pull-off and three point bend tests. The objective of these studies was to evaluate these techniques for providing quantitative information on adhesion strength and bond durability. A further objective was to investigate whether correlations between surface characteristics and bond performance could be established. Such correlations would provide a valuable tool for quality assurance or the development of improved surface preparation methods.

2. MATERIALS

2.1 ADHESIVES

Three epoxy adhesives were used in this study. Their mechanical properties were determined from bulk test samples in tension and shear (Arcan notched-plate [5]). Tensile test specimens of each adhesive type were exposed to hot/wet conditions (70 °C, 85% relative humidity) to establish their moisture uptake behaviour and the influence of absorbed moisture on mechanical performance. The adsorption of moisture leads to plasticisation of the adhesives and significant reductions in modulus, yield stress and strength were observed. These findings are summarised in Figure 1.

- Adhesive A - a single-part, heat-cured, toughened epoxy with high impact resistance. The tensile modulus is 2970 MPa, the bulk tensile strength is approximately 61 MPa and the bulk shear strength is approximately 40 MPa. The modulus and tensile strength of hot/wet conditioned samples were found to be 2400 MPa and 41 MPa, respectively. Yield stress values are reduced significantly following uptake of moisture.
- Adhesive C - a two-part toughened epoxy that is formulated to be tolerant of oiled surfaces. The adhesive cures at room temperature but is formulated to undergo a high temperature post cure, which is claimed to improve the adhesion strength. The tensile modulus of the post-cured material is 2500 MPa and the bulk tensile strength is approximately 25 MPa. This adhesive is similar to Adhesive B used in earlier work but is noticeably stiffer than Adhesive B (modulus ca. 1400 MPa, strain to failure ca. 8%). Adhesive C samples failed at low strains (1.5%), in a brittle fashion around voids in the tensile test specimens. The modulus and tensile strength of hot/wet conditioned samples were found to be 1510 MPa and 16 MPa, respectively. The strain to failure increased significantly (3%) following the hot/wet exposure and the sample failed in a more ductile manner, yielding before failure.
- Adhesive D – a two-part toughened epoxy that is formulated for general-purpose application. The adhesive cures at room temperature but can be post cured at elevated temperatures. The tensile modulus of the post-cured material is 2070 MPa, the bulk tensile strength is approximately 44 MPa and bulk shear strength is approximately 26 MPa. The modulus and tensile strength of hot/wet conditioned samples were found to be 1560 MPa and 27 MPa, respectively.

2.2 ADHERENDS

Aluminium: Aluminium alloy 5754 samples were supplied by Alcan with six different surface finishes (see Table 1 in Section 5). All samples were nominally 2 mm thick. The film thickness values were confirmed by variable angle spectroscopic ellipsometer (VASE) measurements [2]. The modulus used for aluminium in various calculations was 72,700 MPa.

Steel: A hot-dip, galvanized steel sheet (1.5 mm thick Zintec supplied by Corus), typical of those used in the automotive industry, was used in studies to assess the influence of lubricant oil films. A mild steel (0.9 mm thick) strip was used as a backing for 3-point bend samples manufactured using adhesive B and galvanized steel. The modulus used for steel in various calculations was 190,00 MPa.

Composite: Injection-moulded discontinuous glass fibre reinforced polypropylene plates, 4 mm thick, with a glass fibre weight content of 50%. The (dry) modulus used for the composite in various calculations was 6,100 MPa.

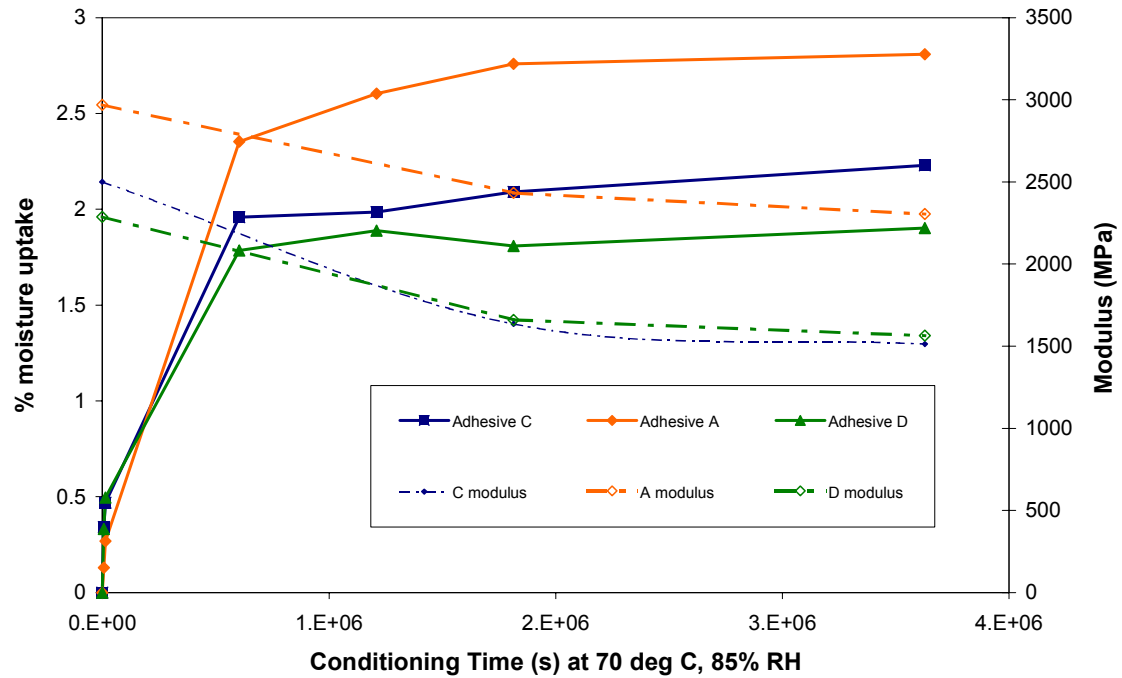


Figure 1: Effect of hot/wet conditioning on adhesive properties

3. TEST METHODS

3.1 PULL-OFF

The pull-off test [6, 7] is used widely to determine the adhesion of coatings to substrates and test adhesive bond strengths. It is simple to perform and can be carried out *in-situ* (either vertically or horizontally) on virtually any type of surface. The pull-off test is attractive as it is quick and simple to perform, requires low cost, commercially available equipment and produces a quantified measure of the adhesive strength from the maximum force applied to the sample. The test method and sample is illustrated in Figure 2.

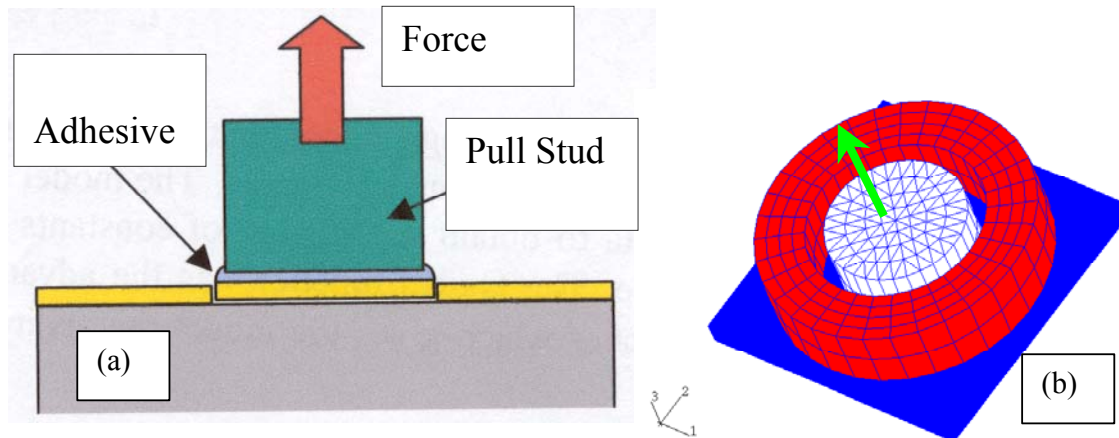


Figure 2: Pull-off test (a) schematic of substrate, interface and pull stud (b) FE model showing substrate, stud and 'restraining ring'

Adherend samples for the pull-off test were cut as 20 mm side squares. Care was taken when cutting the samples to avoid damaging the surfaces (e.g. by limiting cutting fluids to water only). The metal plates were machined after treatment; they were spark eroded and clamped flat to avoid distorting the specimens during the cutting process. The plastic adherends were cut before corona discharge. Pull-off samples were prepared by bonding cylindrical aluminium studs to the surfaces using the adhesives being tested (Figure 2a). Excess adhesive was wiped off before the samples were cured but a fillet ring was normally left behind (e.g. Figure 3). The substrate is clamped with a restraining ring and the stud pulled-off normal to the surface using a portable tester that applies force to the stud by pneumatic pressure. The force is recorded and the maximum load obtained is used to determine the failure stress.

A potential concern is that failure will occur at the weakest point of the joint – this may not be at the surface of interest. The maximum stress that can be applied may be limited by the cohesive strength of the adhesive or the strength of the adhesive-stud bond. In such cases, the test would give a minimum value for the adhesion strength for the system. FE analyses showed that stresses are similar on the top and bottom surfaces despite the considerable difference in bending stiffness of the adherends. Fortunately, experimentally no failures were observed between the stud and the adhesive. The aluminium stud was grit blasted and solvent cleaned to provide a good surface for bonding and the high rigidity of the pull stub tends to bias the failure away from the stub, Figure 2. However, most specimens failed cohesively in the adhesive layer. The FE predictions indicate that the maximum stress should occur at the

interface between the fillet and the base adherend [4]. This would tend to imply that the fillet would detach from adherend. However, in the majority of the samples tested it was observed the fillet tended to remain attached to the base when the failure mechanism was cohesive in the adhesive (Figure 3). Considerable bending of the thin substrates can also occur in the test.

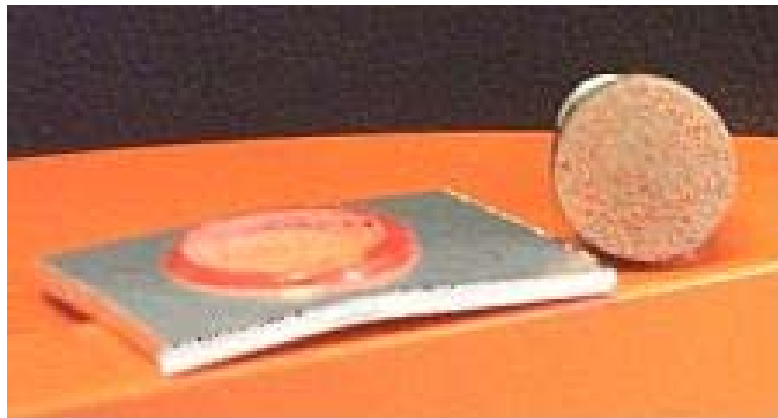


Figure 3: Magnified view of failed pull-off sample with aluminium base

FE predictions show that in each case the centre of the glue layer is under low stress. The stress increases with distance from the centre of the specimen, with the maximum value of stress occurs in the fillet. This stress concentration for the aluminium-adhesive A samples is approximately 2.5-3 times the average stress and shows little dependence on bond thickness (Figure 4). The size of the stress concentration also depends on the stiffness of the adherend, becoming lower as the adherend stiffness increases [4] and bending is reduced.

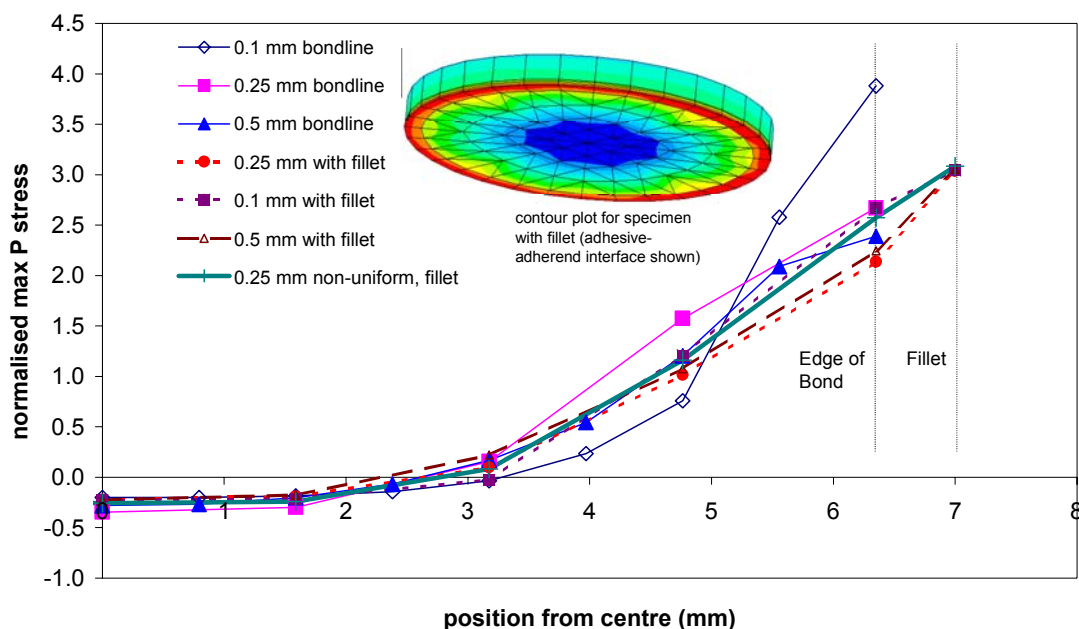


Figure 4: Distribution of stress in pull-off specimen

Preliminary measurements using aluminium-adhesive A samples demonstrated the importance of careful preparation of the adherends prior to bonding [4]. Guillotined samples produced

failure strengths of approximately 14 MPa, whereas adherends cut more carefully by spark erosion gave pull-off strengths over 20 MPa (where, if account is taken of the stress concentration factor, the strength approximates the cohesive strength of the adhesive in tension, 61 MPa). This level of maximum principle stress and the hydrostatic pressure, 35 MPa correspond to those found at failure loads in other joint configurations (e.g. butt tension, lap shear, scarf) and may be useful failure criteria for this adhesive [8].

The pull-off tester is a portable commercial instrument, which is inexpensive and simple to operate. The force is applied through pneumatic pressure and the maximum pressure to detach is indicated on the instrument display panel. This pressure is converted to strength using the calibration look-up table supplied by the manufacturers with the instrument. However, this simplicity can lead to problems. Repairs were made to the tester unit (replacement of a leaking air hose) during the period when the second work programme was carried out. Subsequent measurements appeared higher than expected. Some check samples were prepared (using unaged aluminium) and results were compared with previous measurements. The measured strength increased to 29 ± 7 MPa from 24 ± 4 MPa measured in the original tests. The increase in strength does not look statistically significant. However, one low outlier in the check samples may mask this. Excluding this result, the mean strength determined in the check tests is 31 ± 5 MPa.

Some attempts to compare the pressure measurements with the force generated on the pull off stub during the test. Bonded pull-off specimens were gripped in an assembly connected to a load cell and test carried out whilst recording the load cell output. The debonding was found to be a very fast process and the dynamic response of a standard load cell and logging system was too slow to provide a reliable representation of the load applied. A system using piezoelectric load cell from a high rate servo hydraulic test machine and high frequency digital storage oscilloscope [9] was used to obtain reliable measurements. Figure 5 shows the response of a test where a double-sided, pressure sensitive adhesive (PSA) tape was used to bond the pull-off stud to the base. The force measured was 30N, which seems reasonable for the low strength PSA. The pull-off tester recorded a value of pressure equating to nearly 40 MPa (5kN), which is far too high. Further trials are planned to investigate the accuracy of this instrument.

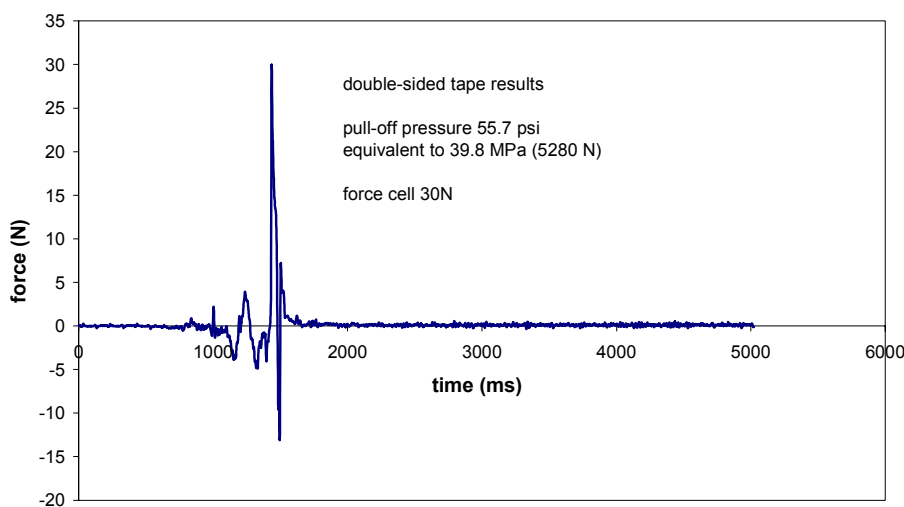


Figure 5: Force determined during a pull-off test

3.2 BEND TESTS

Bend tests are well-established techniques for assessing adhesion of coatings and paints to surfaces. The four-point bend test is often used for thin coatings and the point of failure can be detected by visual inspection or acoustic emission. However, four point bend tests may not produce failure with well-bonded, flexible coatings as peel stresses may not be sufficient to rupture the bond. The three-point bend test for adhesives, ISO 14679 [10], uses a thick rib of adhesive that increases the peel forces at the end of the bond. Figure 6a shows a three-point bend specimen and loading jig. The test sample should fail by delamination of the adhesive rib from the adherend, Figure 6b, but some initial tests using the bend techniques indicated some potential problems when testing flexible adhesives, forces at the interface were insufficient to delaminate and the samples eventually failed through cohesive rupture at the base of the rib (Figure 6c). A modification to the test, bonding a stiffener strip to the outer edge of the adhesive rib, Figure 6d, was made to increase the peel stresses at the end on the rib and thus bias failure towards the interface. In these modified samples, failure was observed to initiate at the aluminium-rib interface as desired.

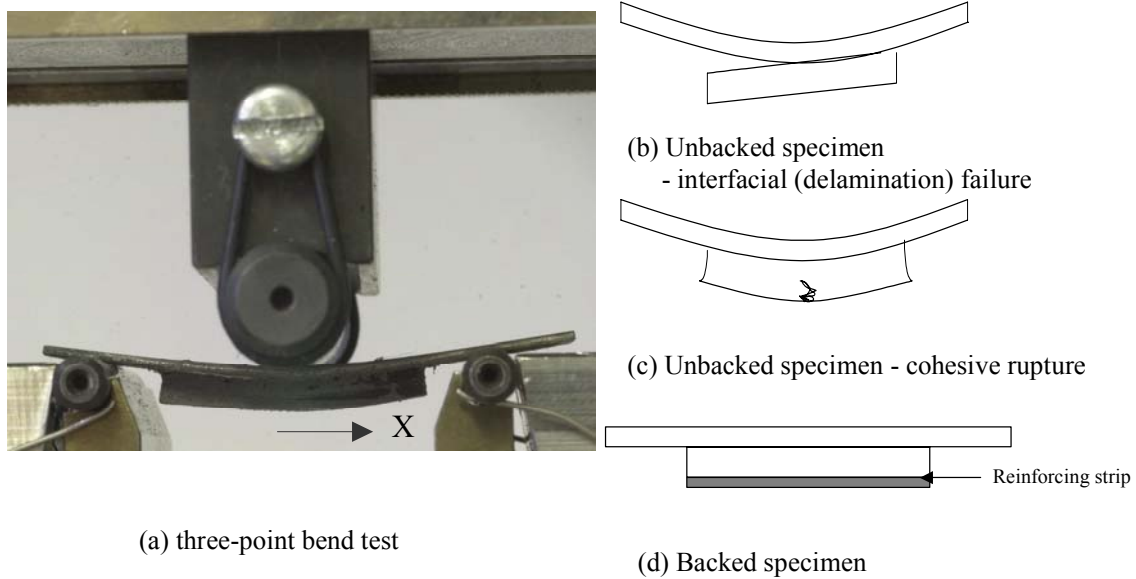


Figure 6: Three-point bend arrangements and failure modes

3.2.1 Standard Three Point Bend Test Specimen

The standard specimen consists of the adherend and adhesive rib. Analytical equations [11] have been developed to calculate the shear stress τ at the interface. These are based on the bending moments and elastic properties of the beam and rib:

$$\tau = \frac{FE_2 b(h - h_1)}{2b_1(G_2 - \frac{G_1^2}{G_0})} \left[\frac{h + h_1}{2} - \frac{G_1}{G_0} \right] \quad (1)$$

where

$$G_0 = E_1 b_1 h_1 + E_2 b(h - h_1), \quad G_1 = \frac{E_1 b_1 h_1^2}{2} + \frac{E_2 b(h^2 - h_1^2)}{2}, \quad G_2 = \frac{E_1 b_1 h_1^3}{3} + \frac{E_2 b(h^3 - h_1^3)}{3}$$

F is the applied force, b width of the adherend, b_1 the width of the rib, h total depth of the adherend plus rib, h_1 the depth of the rib, E_1 the modulus of the adhesive and E_2 is tensile modulus of the adherend.

This formulation predicts the shear stress at the interface in the centre of the beam. This will underestimate the actual stress, which will vary along the beam-direction. FE analyses predict much higher shear stress in the adhesive layer than Equation 1 [4].

3.2.2 Modified three point bend method

The addition of a metal stiffening strip to the base of the adhesive rib increases the shear and peel forces at the interface between the adherend and the adhesive rib. This has the effect of biasing the locus of failure to the interface and overcomes the difficulties in testing flexible adhesives that bond strongly to the adherend. However, the calculation of shear stress at the interface becomes more difficult. The analytical calculation for shear stress (Equation 1) was modified to account for the presence of the stiffener:

$$\tau = \frac{FE_2 b(h - h_1)}{2b_1(G_2 - \frac{G_1^2}{G_0})} \left[\frac{h + h_1}{2} - \frac{G_1}{G_0} \right] \quad (2)$$

where

$$G_0 = E_0 b_1 h_0 + E_1 b_1 (h_1 - h_0) + E_2 b(h - h_1)$$

$$G_1 = \frac{E_0 b_1 h_0^2}{2} + \frac{E_1 b_1 (h_1^2 - h_0^2)}{2} + \frac{E_2 b(h^2 - h_1^2)}{2}$$

$$G_2 = \frac{E_0 b_1 h_0^3}{3} + \frac{E_1 b_1 (h_1^3 - h_0^3)}{3} + \frac{E_2 b(h^3 - h_1^3)}{3}$$

F is the force applied, b width of the adherend, b_1 the width of the rib, h total depth of the adherend plus rib plus stiffener, h_0 the depth of the stiffener, h_1 the depth of the rib plus stiffener, E_0 the modulus of the stiffener, E_1 the modulus of the adhesive and E_2 is modulus of the adherend. This formulation predicts the shear stress at the interface in the centre of the beam.

3.2.3 Test Procedure

Moulds prepared from silicone rubber were used to control the position and shape of the rib, Figure 7. The rectangular moulds are 25 mm long by 5 mm wide by 3.8 mm deep. Adhesive is dispensed into the mould before the adherends are placed in position and pressed down using a flat plate. The samples are then cured according to normal cure schedules before they are released from the moulds. Excess adhesive is removed after the samples are cured being careful not to damage the specimen. The mould produces standard samples with a 25 mm by 5 mm by 3.8 mm thick 'rib' of adhesive bonded to the underside of a rectangular beam adherend (50 mm by 10 mm). When preparing the modified specimen thin 25 mm by 5 mm steel plates were inserted into the mould before the adhesive was dispensed. The thickness of the plates was 0.9 mm and the resulting thickness of the adhesive 'sandwich' layer was 2.9 mm.

One limitation of this method is that the adhesive layer needed is relatively thick and it may be virtually impossible to make representative samples this thick with some types of adhesive, e.g. anaerobics or cyanoacrylates. Furthermore, if the adhesive cures rapidly large temperature rises may occur in such thick adhesive samples, damaging the material. Excessive 'flash' may also occur when preparing low viscosity adhesives.

The samples were tested in a standard three point bend arrangement with supporting rollers at a 33 mm separation, as shown in Figure 6a. The crosshead is driven at a constant speed and the test concludes when failure occurs. The adhesive rib imparts stiffening to the beam and a drop in load accompanies the start of failure in the adhesive layer. Failure at the interface (Figure 6b) is the desired mode of failure to assess the interface but in certain situations failure at the outer surface of the rib, Figure 6c, may occur. This test method is potentially suitable for mass screenings as tests can be performed very rapidly. The 'open' nature of the adhesive block facilitates accelerated ageing of the interface in chemical environments.

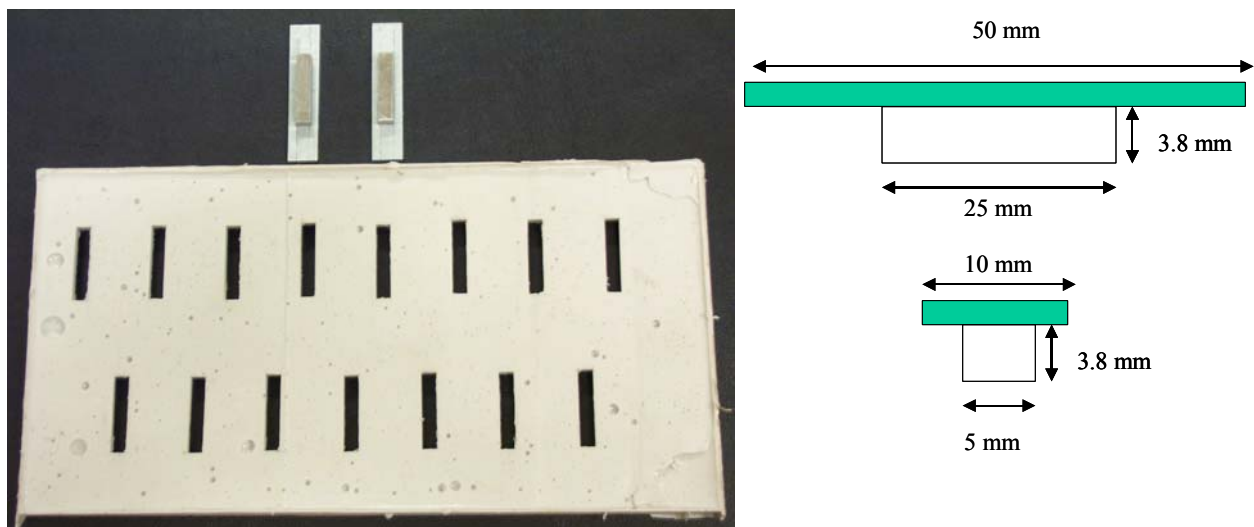
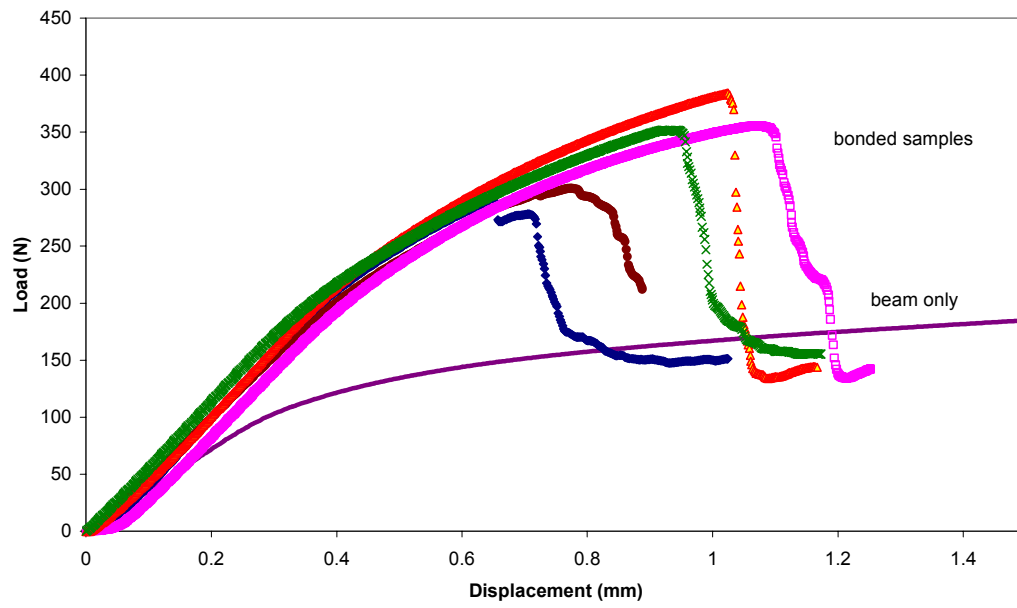
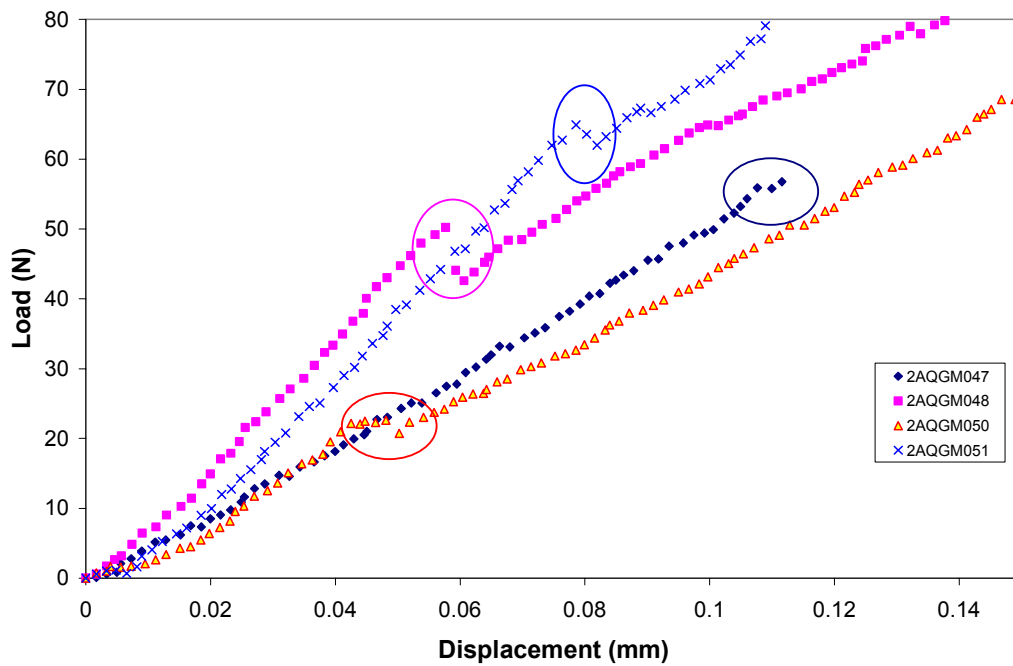


Figure 7: Sample and specimen manufacture mould

Failure in a three-point bend test is evident from a drop in the force-extension curve. This is very noticeable for high modulus adhesives, Figure 8a, but can be difficult to detect with lower modulus adhesives. In hot/wet exposure tests the absorption of water leads to plasticisation of the adhesive – reducing modulus and 'yield' stress – and a lower stiffening effect. The point of failure in some long-term exposed samples was difficult to isolate, Figure 8b. Acoustic emission monitoring was investigated as a means of identifying the point of failure. However, friction between the rollers and the adherend produced noise signals that drowned out the low acoustic energy emitted during debonding.



(a) Adhesive A-aluminium (unconditioned); Point of delamination clear



(b) Adhesive C-steel (50 days hot/wet); point of delamination (circled) unclear

Figure 8: Interpretation of onset of delamination in the three-point bend test

4. SURFACE CHARACTERISATION

Surface preparation is recognised as a critical step in the adhesive bonding process and considerable effort is frequently expended in optimising the surface treatment. Correct surface preparation is essential for good bond strength and ensuring the long-term structural integrity of bonded structures, particularly under hostile service conditions. Unsatisfactory surface preparation will result in premature and unpredictable interfacial failure of bonded joints.

Earlier studies were undertaken to evaluate the efficacy of various characterisation techniques for evaluating changes in surface properties of metallic materials and polymer composites resulting from changes in surface treatments and the level of treatment [2]. The results from the study show that most of the techniques studied were useful in determining changes in surface properties for different levels of treatment. Contact angle and colorimetry techniques proved the most suitable for relating surface changes to the level of treatment and could potentially be used to improve or optimise adhesive strength and environmental durability. Enhancement to surface roughness is an effect of some surface treatments (etching and anodising) and surface roughness measurements were included in the first trial.

4.1 SURFACE ROUGHNESS

Surface treatments are often undertaken to roughen the substrate to increase the surface area available for bonding and to provide sites for mechanical interlocking. Techniques suitable for evaluating roughness include:

- (i) Contact (stylus) profilometry
- (ii) Optical profilometry
- (iii) Atomic force microscopy (AFM).

Contact (stylus) profilometer instruments move a loaded probe (usually a diamond) across the target surface and records the vertical movement caused by the irregularities. This technique is most suitable for hard surfaces, since soft materials can be damaged and reducing the load may result in some surface features not being registered. Lateral and vertical resolution is affected by stylus shape (usually a cone with a spherical tip (Figure 9) and angle of 60° or 90°), stylus tip radius (typically 5 µm - sharper tips increase damage) and surface profile. Instruments to measure surface roughness are limited by spatial frequency, some features being too wide and others too narrow to be detected, as well as the limits on minimum height detectability of surface features. Peaks narrower than the stylus are recorded as broader and the base of narrow troughs may not be reached. This technique can also have difficulty measuring highly curved or convoluted surfaces with steep slopes.

For the purposes of these measurements, a Surtronic hand-held contact surface roughness meter was used. This instrument uses a diamond stylus with a radius of 5 µm, which follows the undulations of the roughness as it traverses the surface. Vertical movements are translated into an electrical signal, in the same way a stylus on a record player, and averaged to determine the mean roughness data. Earlier work [2] showed that stylus measurements gave comparable roughness values to optical profilometry (using a 3-D interferometric optical Phase Shift MicroXAM white light interferometer)



Figure 9: Contact (stylus) profilometry

Roughness results are presented in terms of R_a (average roughness deviation) and R_q (root mean square (RMS) roughness deviation). These show clear differences between untreated and grit-blasted surfaces, and between untreated and etched surfaces. Differences between the levels of treatment are less significant.

$$R_a = \frac{1}{L} \int_0^L |y(x)| dx \quad (3)$$

$$R_q = \sqrt{\frac{1}{L} \int_0^L |y^2(x)| dx} \quad (4)$$

where L is the sampled length, x is the position along the sampled length and $y(x)$ are the roughness profile values.

4.2 COLORIMETRY

Surface treatments will alter the appearance of substrate. There are methods available for characterising the appearance of surfaces from their optical reflectance characteristics. Gloss, or specular reflection, is sensitive to the roughness of the surface and the absorbency of the surface layer. Gloss measurements are straightforward to carry out using inexpensive, handheld instruments that quantify the intensity of white light reflected specularly from the surface (Figure 10a). Whilst gloss measurement showed sensitivity to gross changes in the surfaces, for example easily distinguishing grit blasted regions from untreated, it lacked the sensitivity to discriminate between different levels of surface treatment.

Colorimetry can be used to detect differences between surface treatments and the degree or intensity of the surface treatment (e.g. exposure time). Colour is sensitive to surface morphology and chemical composition. Although instrumented colorimetry systems are available for on-line inspection, interpretation and quantification of reflectance spectra of treated surfaces can be expected to be difficult. The equipment is basically a spectrophotometer that measures the intensity of wavelengths in the reflectance spectra (Figure 10b).

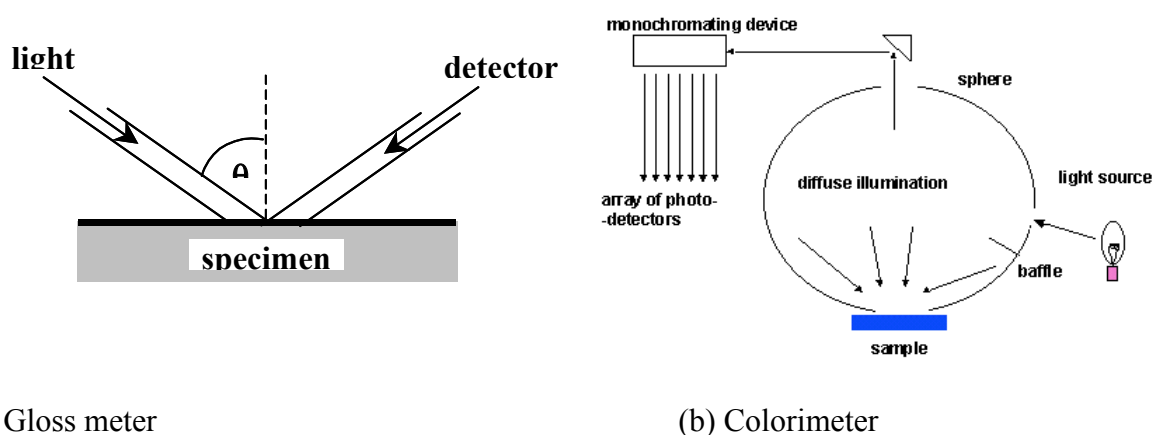


Figure 10: Schematics of reflectance measurement instruments

Colour measurement requires a spectrophotometer to illuminate the sample with white light and to calculate the amount of light that is reflected by the sample at each wavelength interval by passing the reflected light through a monochromating device that splits the light up into separate wavelength intervals. The instrument is calibrated using a white tile whose reflectance at each wavelength is known compared to a perfect diffuse reflecting surface. The reflectance of a sample is expressed between 0 and 100 (as a percentage). Reflectance values obtained are relative values and, for non-fluorescent samples, are independent of the quality and quantity of the light used to illuminate the sample. The samples were measured using a Datacolor Spectraflash 500 spectrophotometer. The spectrophotometer exposes a 10 mm diameter circular area on the surface to a light source with a daylight colour temperature and compares the percentage reflectance within the visible spectrum (360 – 750 nm wavelength, in 1 nm steps) to that of reference white and black colour tiles.

When monochromatic light falls normally on a surface with an oxide film, several phenomena occur at the interface. Some of the light is reflected back at the film-air interface and does not enter the oxide layer, while transmitted component enters the oxide layer. A portion of the transmitted light is reflected back from the metal-oxide interface. Interference of the two reflections will occur, affecting the perceived colour of the surface.

Initial colorimetry results, e.g. Figure 11, indicate that surface reflectance measurements can detect differences between levels of acid etch treatment. The reflectance increases with increasing oxide film thickness. As the oxide layer grows, the colour of the surface changes (i.e. becomes whiter).

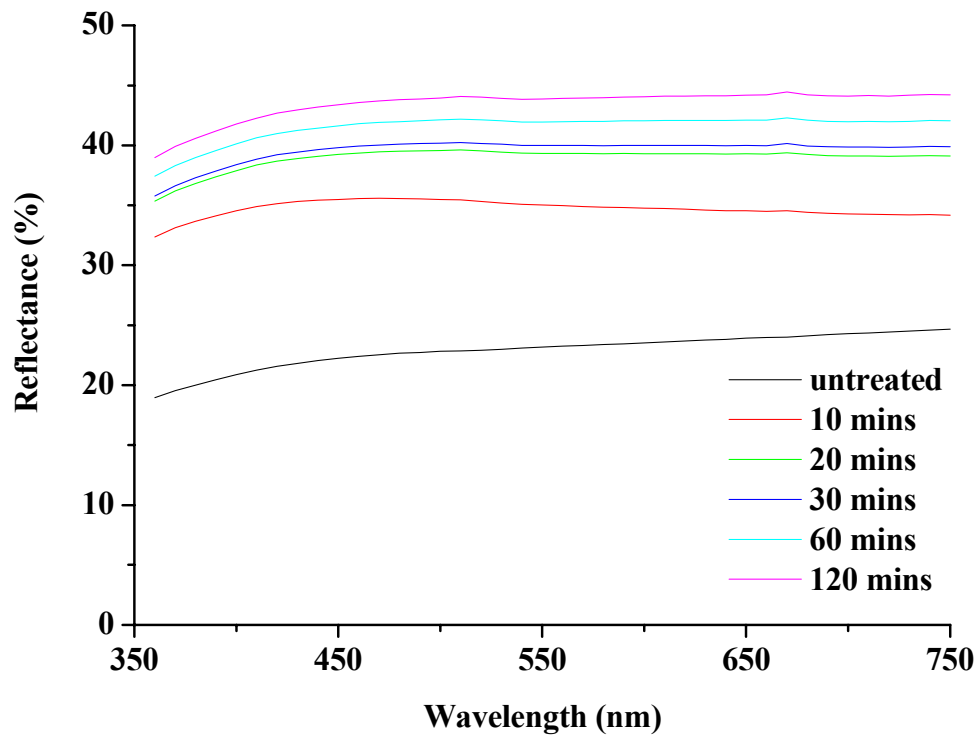


Figure 11: Reflectance spectra for untreated and CAE aluminium [2].

4.3 CONTACT ANGLE

Good wettability of a surface is a pre-requisite for ensuring good adhesive bonding. The determination of contact angle at the solid/liquid phase boundary is a sensitive method for characterising surfaces. Contact angles are closely related to wettability and adhesion, providing information on the heterogeneity and roughness of the adherend surface and the effect of surface treatments. A liquid (adhesive) will wet a solid (adherend) when its surface energy is lower than the solid surface energy. Force balance or equilibrium at the solid-liquid boundary is given by Young's equation for contact angles greater than zero (see Figure 12). The lower the contact angle, the greater the tendency for the liquid to wet the solid surface, until complete wetting occurs at a contact angle of zero. Large contact angles are associated with poor wettability.

Contact angles can be measured either on a goniometer or by projection (manually or video imaging). Goniometers are inexpensive to purchase and operate but measurements can be time consuming and prone to operator subjectivity. In this work, a FTA (First Ten Ångstroms) 200 Dynamic Contact Angle Analyser was used for sessile drop measurements by automated drop shape analysis. The automated measurement reduces measurement uncertainty. The probe liquid used for measuring contact angle was distilled water ($\gamma_{lv} = 72.7 \text{ mJm}^{-2}$).

The Young equation relates the contact angle θ , and the surface free energies of the liquid-vapour, solid-vapour and solid-liquid interfaces (γ_{lv} , γ_{sv} and γ_{sl} respectively).

$$\gamma_{lv} \cos \theta = \gamma_{sv} - \gamma_{sl} \quad (5)$$

The lower the contact angle, the greater the tendency for the liquid to wet the solid, until complete wetting occurs at an angle $\theta = 0$ ($\cos \theta = 1$). The surface tension of the liquid is then equal to the critical surface tension of the substrate. Large contact angles are associated with poor wettability.

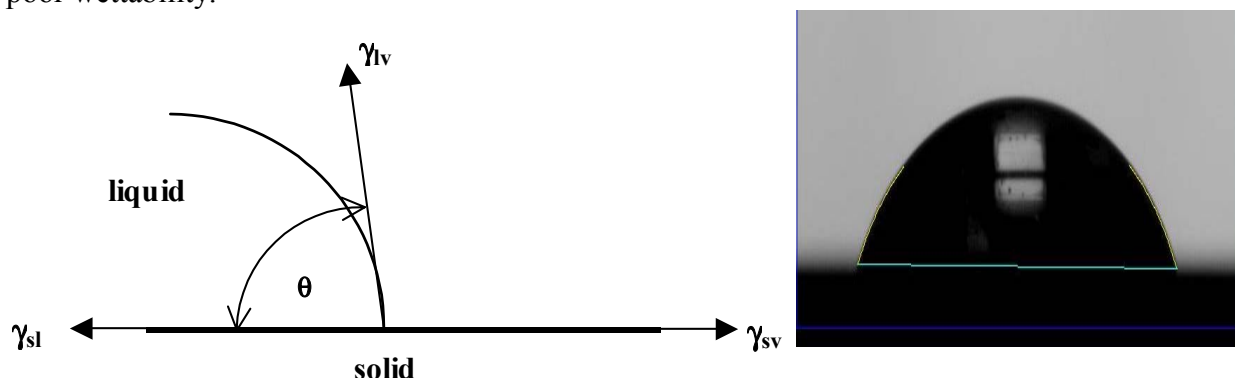


Figure 12: Contact angle by sessile drop

Trial contact angle measurements indicated that drops tended to spread on surfaces with time, Figure 13 (probably due to condensation around the edges of the drops modifying the surface, making it more wettable). The procedure of taking measurements 30s after dispensing the drop was adopted to allow the system to stabilize and thus reduce measurement variability.

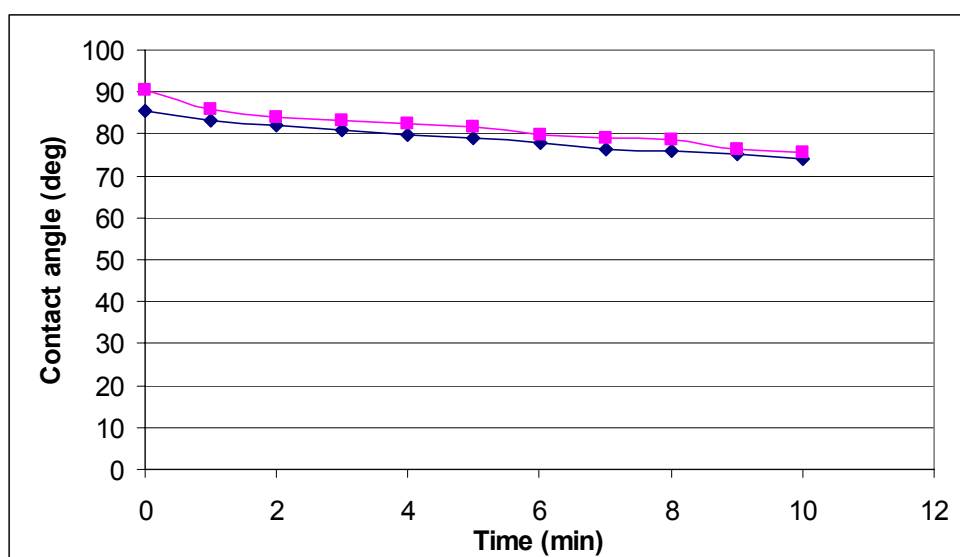


Figure 13: Change in measured contact angle with time

5. EXPERIMENTAL RESULTS

5.1 TEST PROGRAMMES

Statistical design of experiment (DOE) techniques were employed to plan the schedule of the sample manufacturing and test programme to minimise systematic effects of parameters not controlled in the procedures. For each of the three test programmes, one NPL scientist was responsible for all specimen preparation and testing to minimise variability due to the operator. Previous studies have shown that sample preparation by different operators can be a major source of experimental variability. Care was taken when cutting the samples to avoid damaging the surfaces (e.g. by limiting cutting fluids to water only). The metal plates were machined after treatment; they were spark eroded and clamped flat to avoid distorting the specimens during the cutting process. The composite adherends were cut to size before corona discharge treatment.

Mechanical tests were performed using both pull-off and 3-point bend tests in each test programme. Surface analysis was performed on traveller samples before sample bonding and throughout the conditioning (hot/wet atmosphere – 70°C/85% relative humidity – maintained in a Climatic Systems chamber). Table 1 summarises the test programmes followed. Details of the test programmes are given in Annex 1.

Table 1: Summary of Test Programmes

Test System	Treatment Variables	Conditioning Periods	Tests Used
Aluminium and adhesive A	Surface treatment – 6 different levels of cleaning and anodising	0 days 18 days 36 days Full matrix	Colorimetry Contact angle Roughness Pull-off 3-point bend
Galvanised Steel and adhesive C	Oil level 0, 1, 4, 7 and 8 µl	0, 6, 25, 44 and 50 days Partial matrix	Colorimetry Contact angle Pull-off 3-point bend
Glass fibre reinforced polypropylene	Corona discharge, untreated and 4 different treatment levels	0, 4 14, 24 and 28 days Partial matrix	Contact angle Pull-off

5.2 ALUMINIUM

5.2.1 Aluminium and Adhesive A test programme

Aluminium alloy 5754 samples were supplied by Alcan with six different surface finishes as described in Table 2. All adherends were 2 mm thick. The film thickness values were confirmed by variable angle spectroscopic ellipsometer (VASE) measurements [2]. The treated aluminium sheets were protected from the atmosphere with a plastic film, which was removed immediately before specimens were cut. Previous adhesion measurements [4] highlighted the need for care to be taken in handling and preparing specimens. Aluminium surfaces were characterised by spectral reflectance (colour), contact angle and roughness measurements.

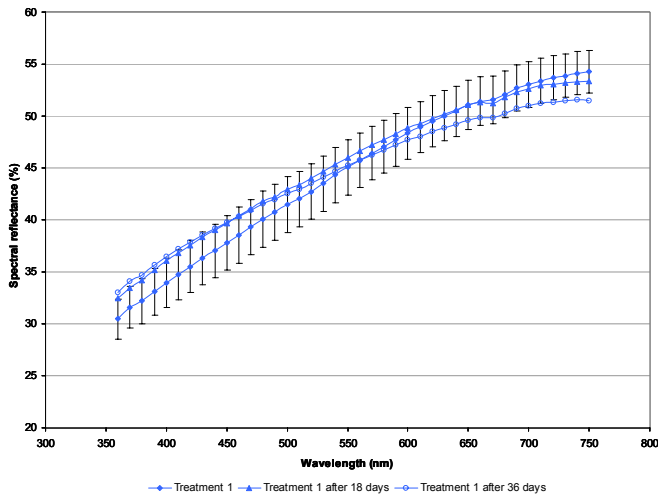
Aluminium-adhesive A samples were bonded using the procedures described in Section 3. Measurements were performed on zero day (unaged), 18 day and 36 day conditioned samples.

Table 2: Aluminium Surface Finishes

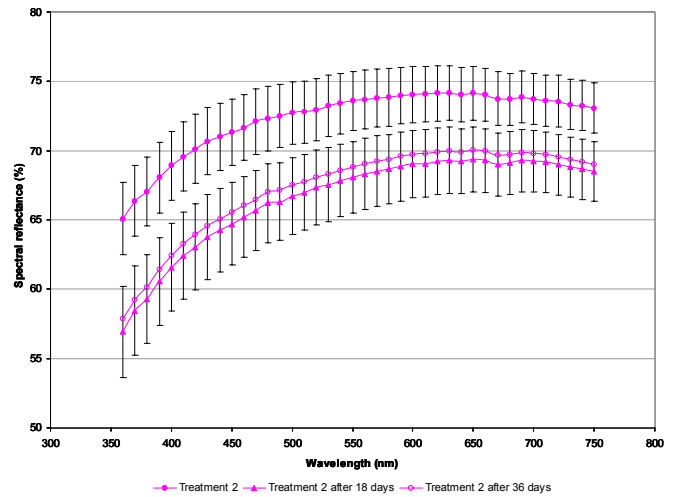
Treatment	Finish	Code	Description
1	Mill Finish	MF	Untreated aluminium
2	Light clean	PC	Lightly degreased to remove oils - most of the surface structure and oxides still remaining
3	Full clean	FC	An extensive electrolytic acid etch - equivalent of the optimized system without an anodised layer
4	Full clean + anodise	FC + 25 nm	Full clean + 25 nm barrier film ("optimised" system with a full etch and a 25 nm barrier anodised film)
5	Light clean + anodise	PC + 25 nm	Light clean + 25 nm barrier film (a variant with a lower level of etch)
6	Over anodised	FC + 25 nm + 75 nm	Full clean + over-anodised - braid (a variant with extended anodisation period to produce a 25 nm barrier + 75 nm porous anodised film,)

5.2.2 Colorimetry measurements

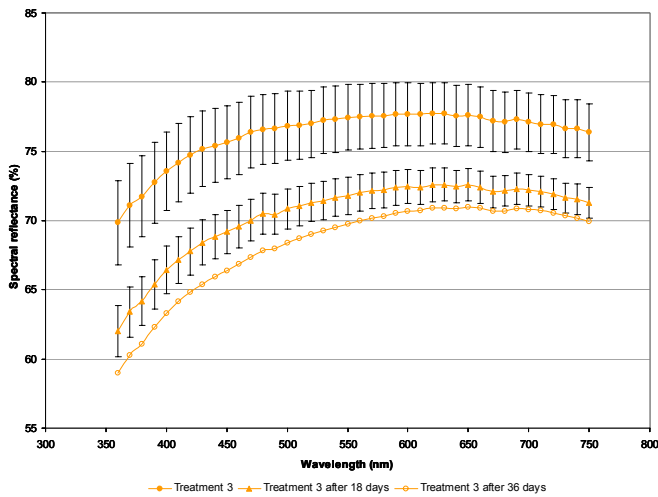
Figure 14 shows the average results for the spectral reflectance data from the surfaces of the different aluminium treatments when illuminated with white light. The data show the unconditioned treatment results and the results after 18 and 36 days at 70°C and 85% RH. In each case, data at each wavelength are averaged for 5 samples. Error bars are presented showing the standard deviation for the unconditioned and 18 days conditioning datasets, those for the 36 days conditioning are omitted for clarity. In all cases, it can be seen that the 18 and 36 days conditioning data cannot be distinguished statistically from each other, lying within the expected experimental scatter. There are, however, significant differences between the unconditioned and conditioned data suggesting that the conditioning affects the surface but that this effect does not increase with time, as characterised by the colorimeter.



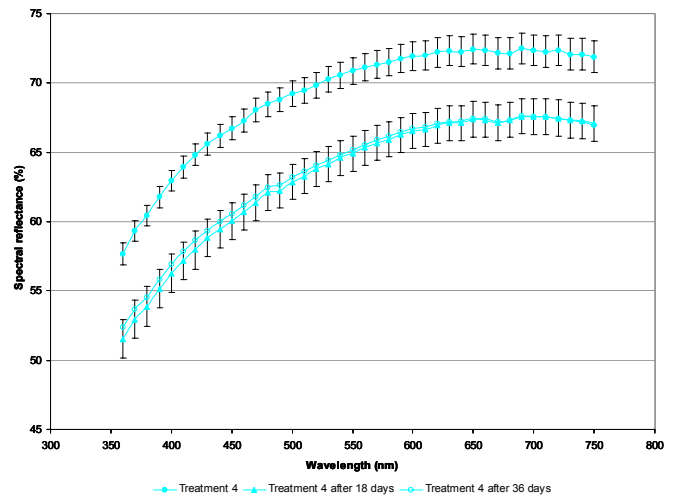
(a) Mill finish



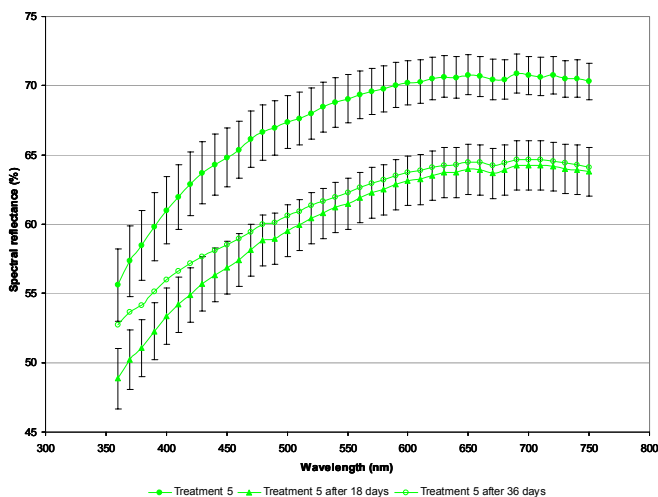
(b) Light clean



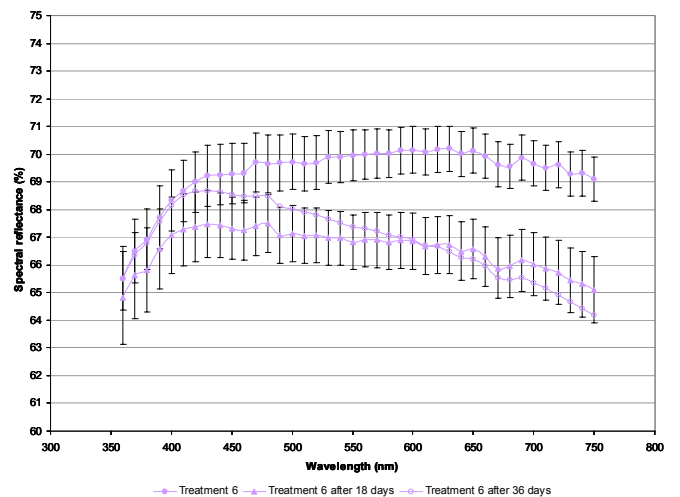
(c) Full clean



(d) Full clean + anodise



(e) Light clean + anodise



(f) Full clean + over anodise

Figure 14: Colorimetry results for different ageing durations, all surface treatments (% spectral reflectance plotted against wavelength, nm)

The mill finish (treatment 1) shows no statistically significant change in reflectance with conditioning at either level. The full clean + 25nm barrier + 75nm porous (treatment 6) shows only a slight change in spectral response after conditioning, the disparity being more apparent at higher wavelengths. All other treatments have similar spectral response curves to each other, see Figure 15, and show similar reductions in the reflectance over the spectral range investigated, after conditioning. A point to note is the smaller experimental scatter evident for treatment 4, which is nominally the optimal bonding treatment, i.e. full clean + 25nm barrier.

There is no direct correlation between the suitability of surface treatment for bonding and the spectral reflectance observed and it can also be seen from Figure 15, where error bars are similar to those shown for treatment 1, that it would be difficult to distinguish the treatments from the colorimetry data alone.

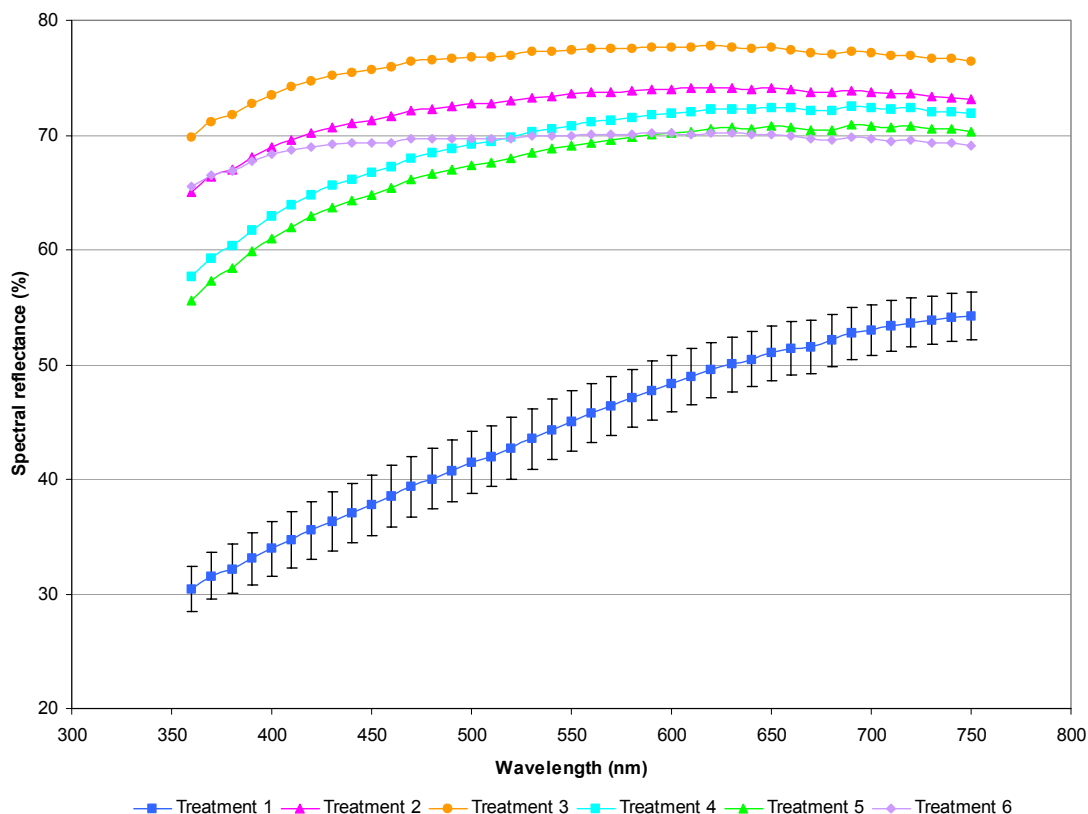


Figure 15: Colorimetry comparison of different surface treatments (unaged)

5.2.3 Contact Angle

Figure 16 shows the contact angle results using the static single drop method for each of the treatments, both unconditioned and after 18 and 36 days at 70°C and 85% RH. Each result is the average of 5 samples and error bars are presented showing the standard deviation for the unconditioned datasets only, others are omitted for clarity but show similar magnitudes.

The results are difficult to interpret due to large scatter primarily due to the variability in the local surface roughness affecting these small-scale measurements. It can be seen that there is little difference between the contact angles for the conditioned materials, probably due to hydrolysis of the aluminium oxide layer in the hot/wet environment. However, the

unconditioned material shows a significant difference between the anodised and non-anodised surfaces, with the anodised surfaces producing lower contact angles. Specifically, the lowest contact angle, i.e. the best wettability is available from the nominally optimum treatment 4.

Following further analysis, both conditioning time and treatment type were found statistically to affect the measured contact angle. An interaction existed such that the effect of conditioning time depended on the surface treatment applied, as might be expected.

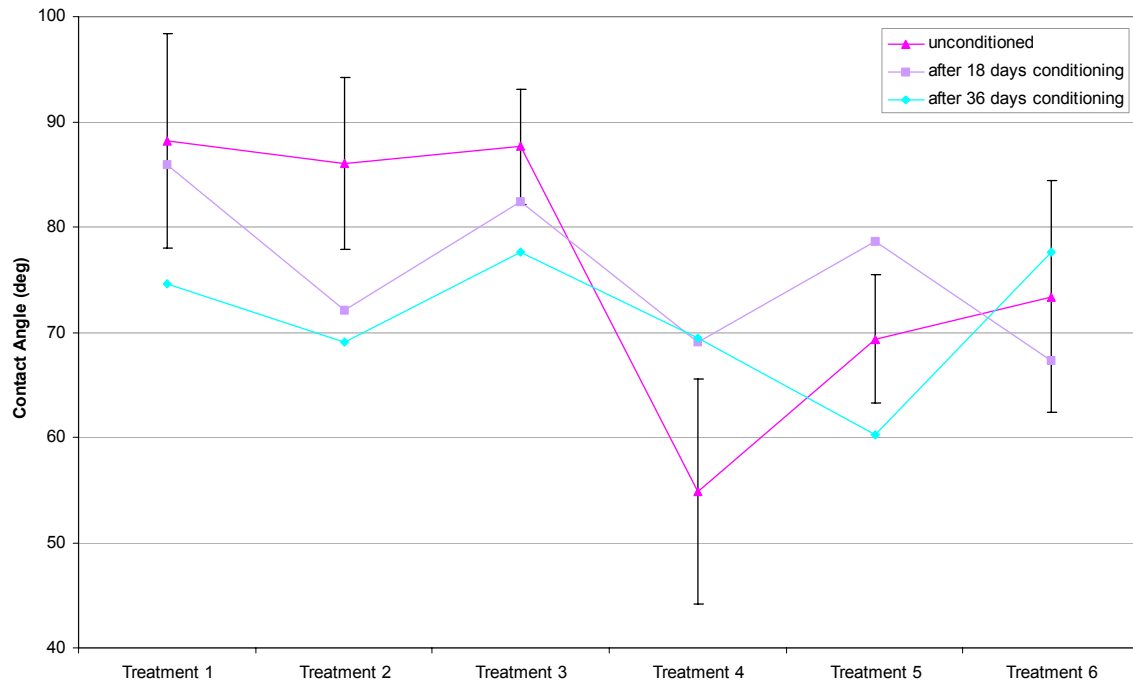
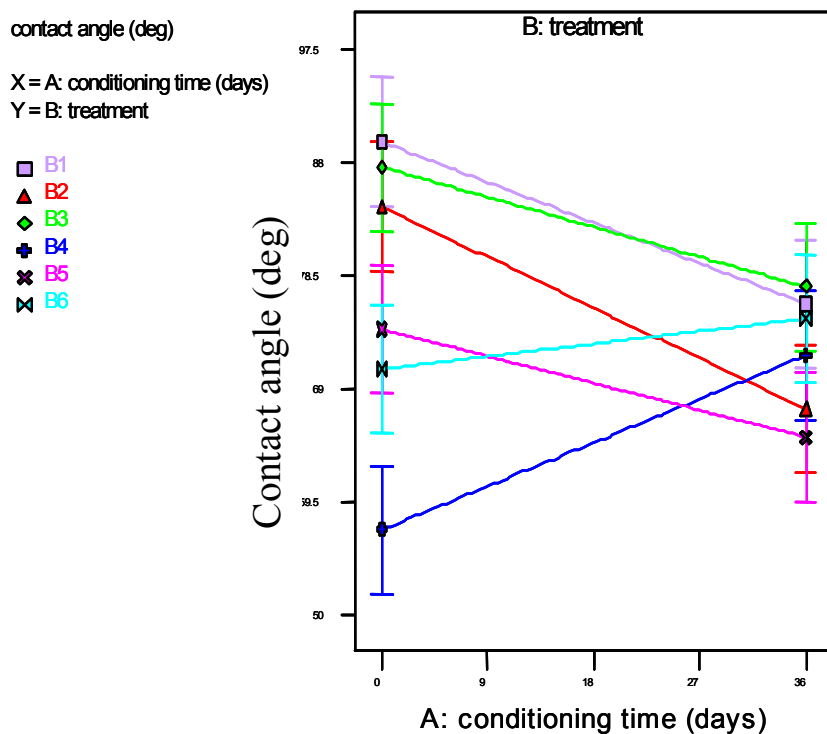
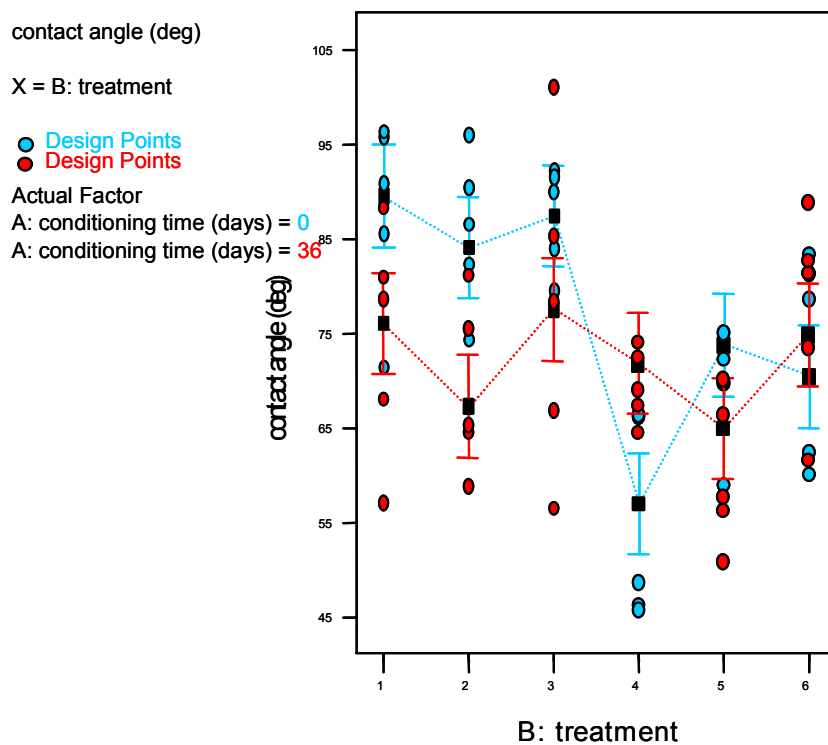


Figure 16: Contact angles results for different ageing durations, all surface treatments

The graph shown in Figure 17 shows the modelled 2-factor interaction response of contact angle with conditioning time and treatment, the experimental matrix ‘design points’ are the measured data. This again highlights that following conditioning the contact angles all tend towards a common end value, but the initial optimum contact angle is seen with treatment 4 although this surface seems more susceptible to deterioration prior to bonding. In fact some of the surfaces seems to improve in wettability with hot/wet exposure, primarily the non-anodised treatments.



(a) Contact angle and conditioning time



(b) Contact angle and treatment

Figure 17: 2-factor interaction response of contact angle with conditioning time and treatment

5.2.4 Surface Roughness

The roughness data in Figure 18 shows a higher roughness for the fully cleaned treatments compared to the lightly cleaned equivalents and similarly, anodised treatments have a higher roughness than non-anodised. Maximum roughness is seen for the nominal optimum treatment 4. Hot/wet conditioning is shown to significantly reduce roughness for all treatments except the untreated mill finish material (treatment 1) where no changes in roughness are observed. This is corroborated by the interaction graph in Figure 19 based on the modelled 2-factor interaction response.

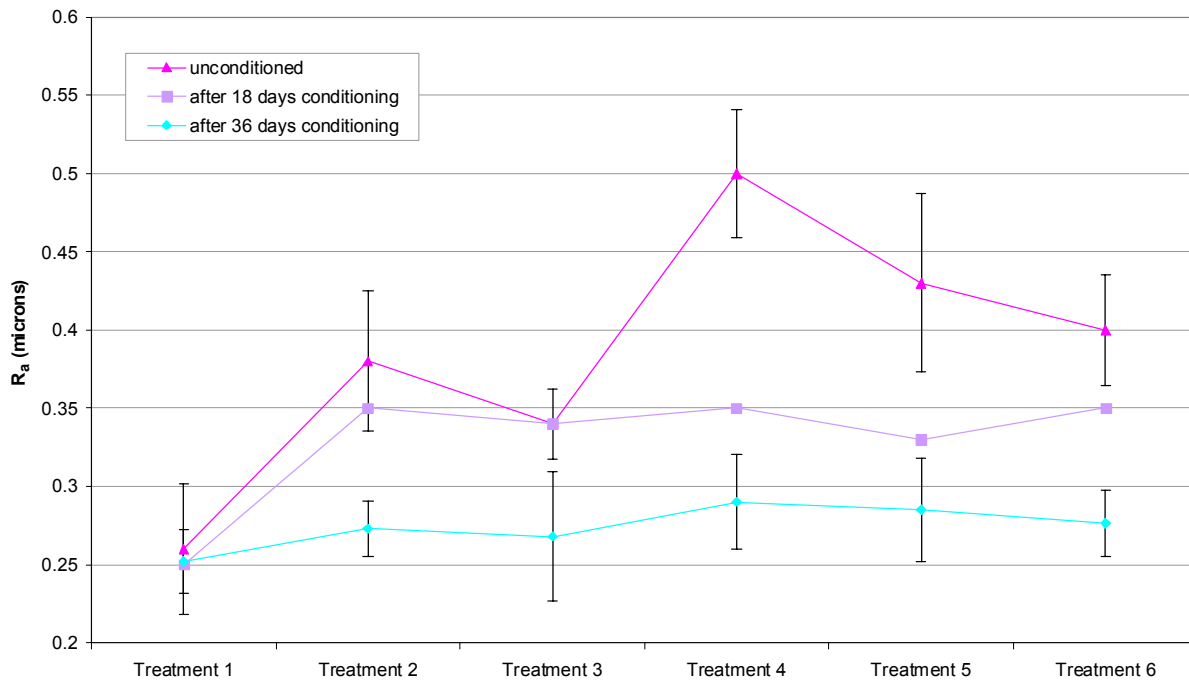
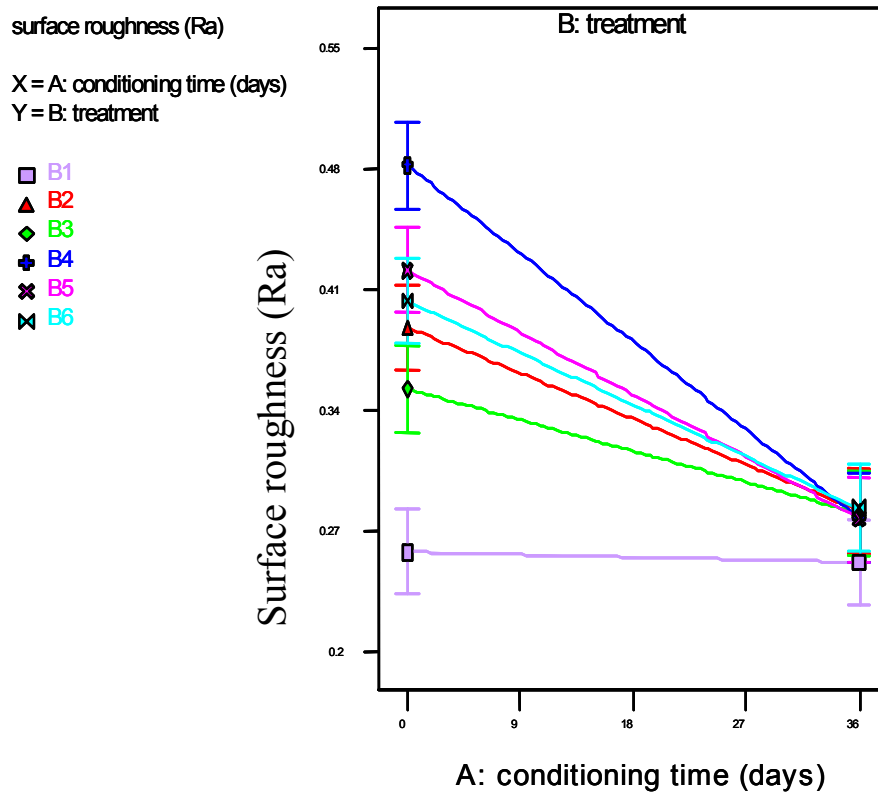
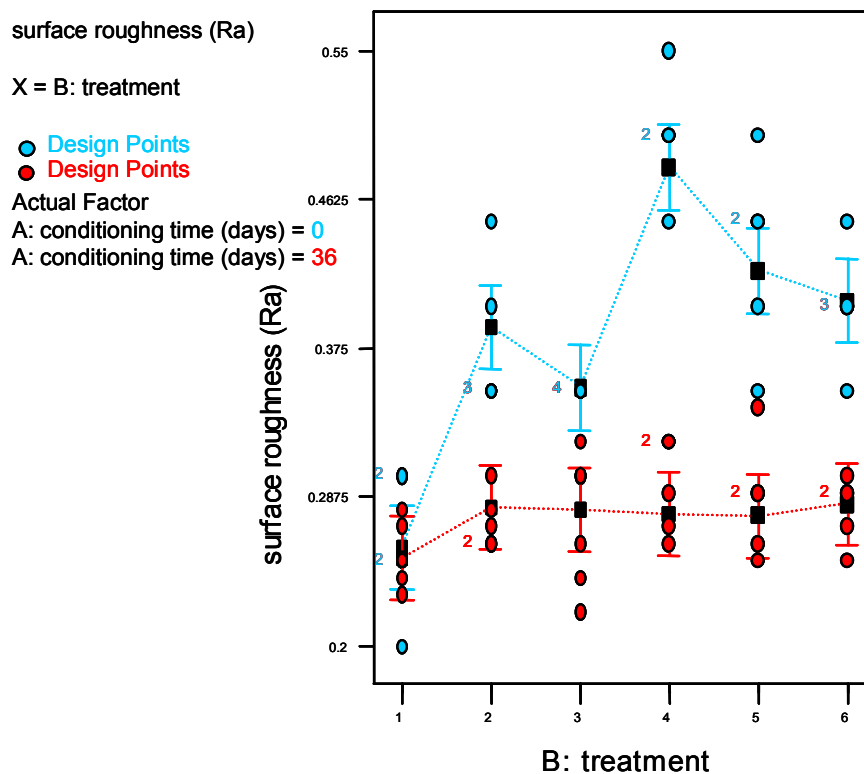


Figure 18: Surface roughness results for different ageing durations, all surface treatments

Statistical analysis showed roughness depended on conditioning time and treatment, as well as an interaction between them. Again, conditioning results in a reduction in the surface roughness, with all treatments tending towards a common end value. Whilst treatment 4 has the highest roughness, it is most susceptible to conditioning showing the largest change in roughness with time.



(a) Roughness and conditioning time



(b) Roughness and treatment

Figure 19: 2-factor interaction response of surface roughness with conditioning time and treatment

5.2.5 Aluminium pull-off test results

The raw data for the pull-off tests are presented in Figure 20. Each point shows the average and standard deviation of 5 samples. These tests produced partial cohesive failures on all samples (Figure 21a). It is unlikely that, due to the variable nature of failure, the measurements are true indicators of the strength of interfacial adhesion. This subsequently affects the accuracy of the statistical analysis. Figure 21b shows an estimate of the degree of cohesive failure in each batch of samples. The pull-off strength data are presented as 'mean' strength values. FE analyses [4] have shown that the stress distribution in the adhesive layer is non-uniform, rising along the radius from low values in the centre of the specimen to a peak value at the rim, see Figure 4. Peak values were estimated to be roughly 3 times the average stress in the bondline.

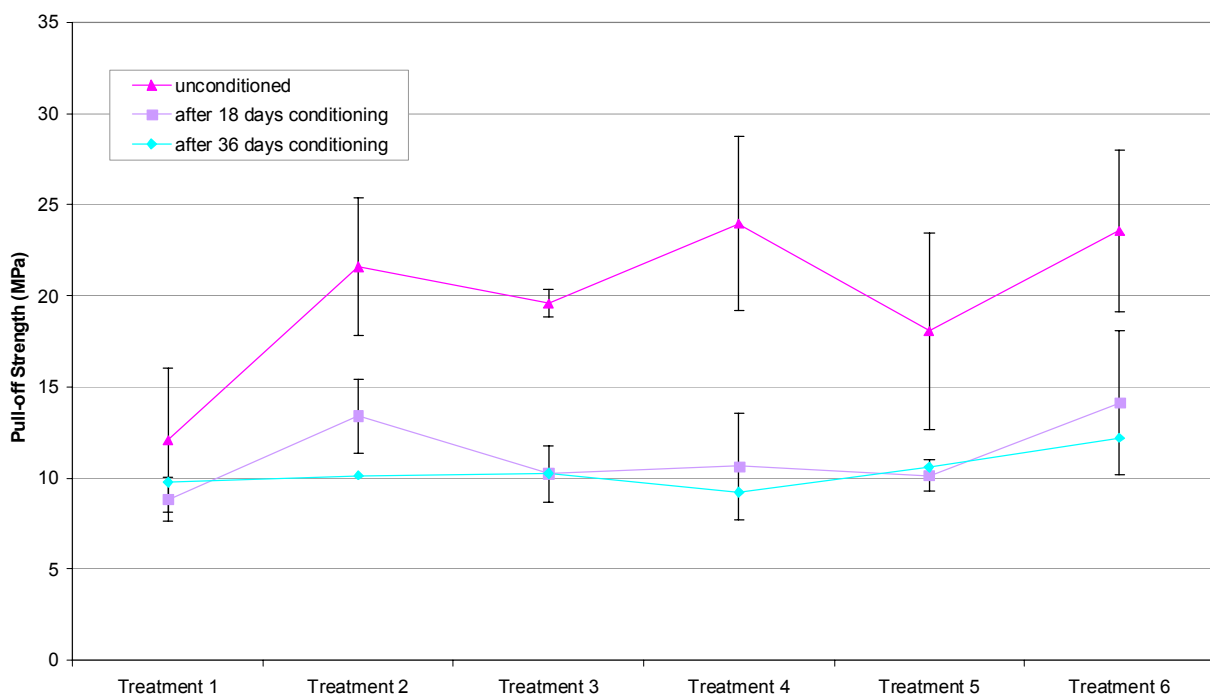
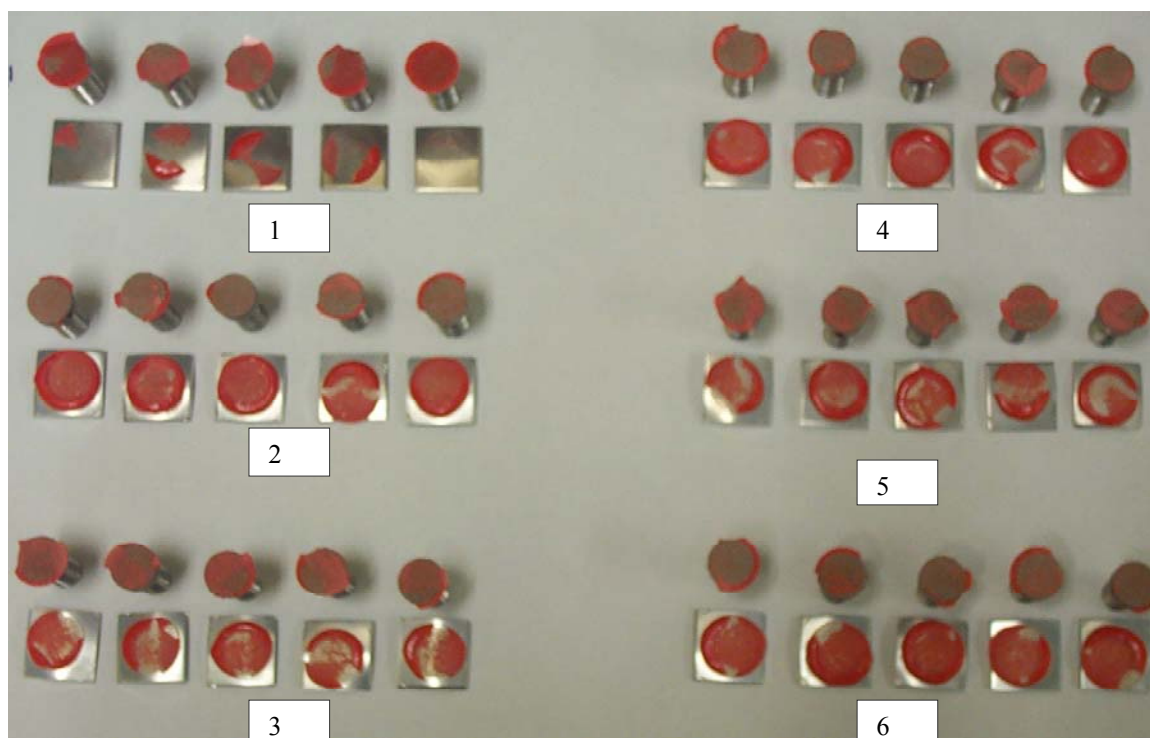
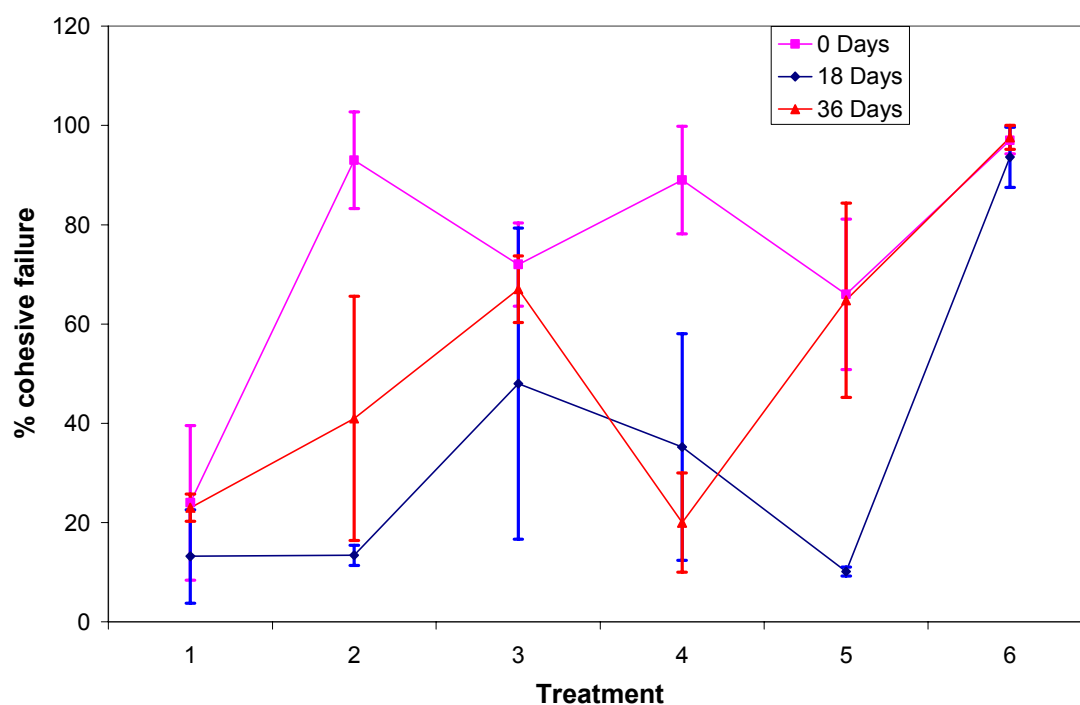


Figure 20: Raw data for the pull-off tests

In terms of failure, treatment 4 showed steadily increasing proportions of adhesive failure with conditioning, the other treatments showed strongly cohesive failure. These failure modes persisted with conditioning. The highest cohesive failure level was achieved with treatment 6 (full clean plus a porous over anodised oxide layer), where the proportion of cohesive failure remains around 90%, independent of conditioning. The base treatment 1 (mill finish only) shows low levels of cohesive failure (<30%) for all conditioning. Scanning electron microscopy (SEM) was used to examine the failed treatment 1 samples to determine whether failure was truly interfacial. The micrographs (Figure 22) indicate that the 'interfacial' failure regions appeared to be identical to 'clean' unbonded areas of the adherends indicating that no layer of adhesive remained.



(a) Pull-off specimens showing mixed modes of failure (unaged samples),



(b) Estimates of proportion of cohesive failure (from visual inspection)

Figure 21: Pull-off specimens showing interfacial and cohesive failure, treatments as listed in Table 2)

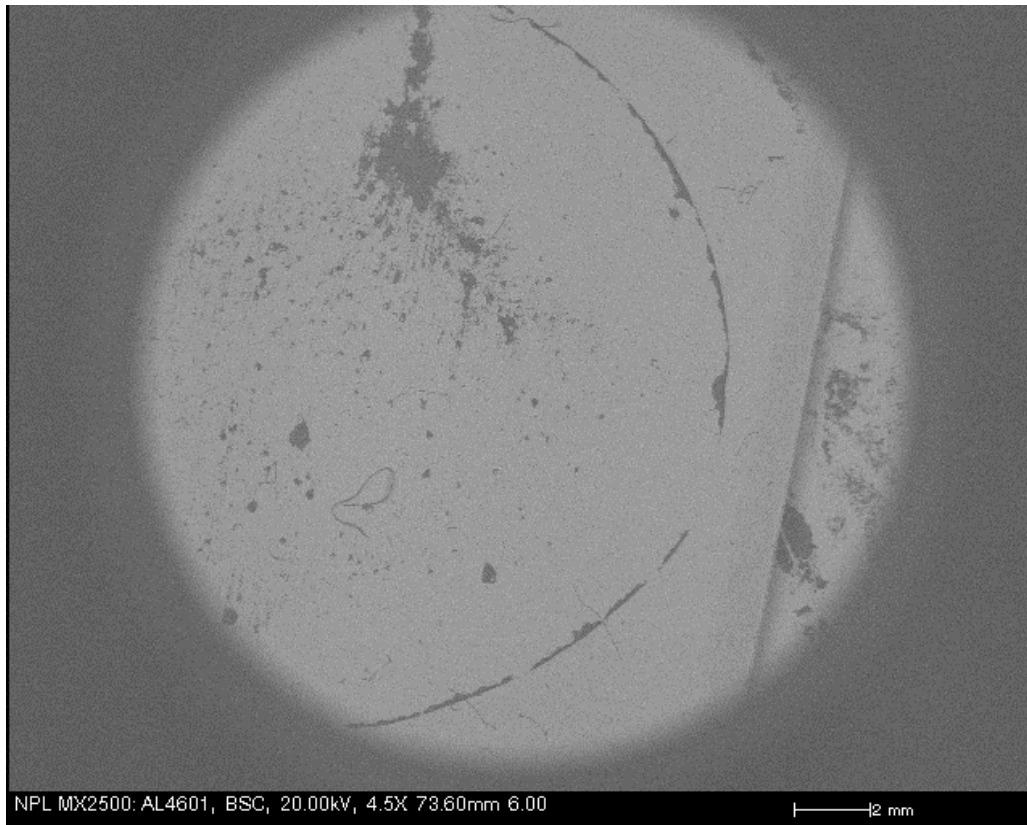
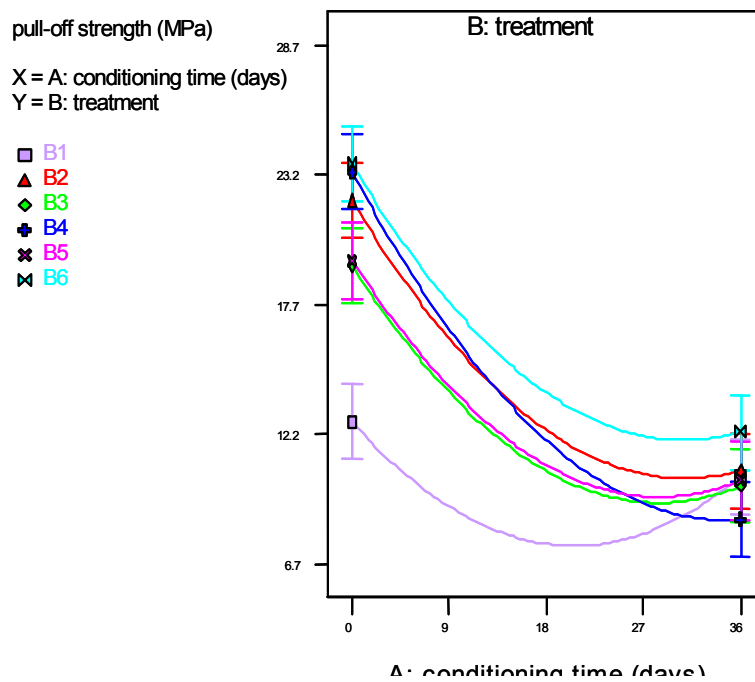
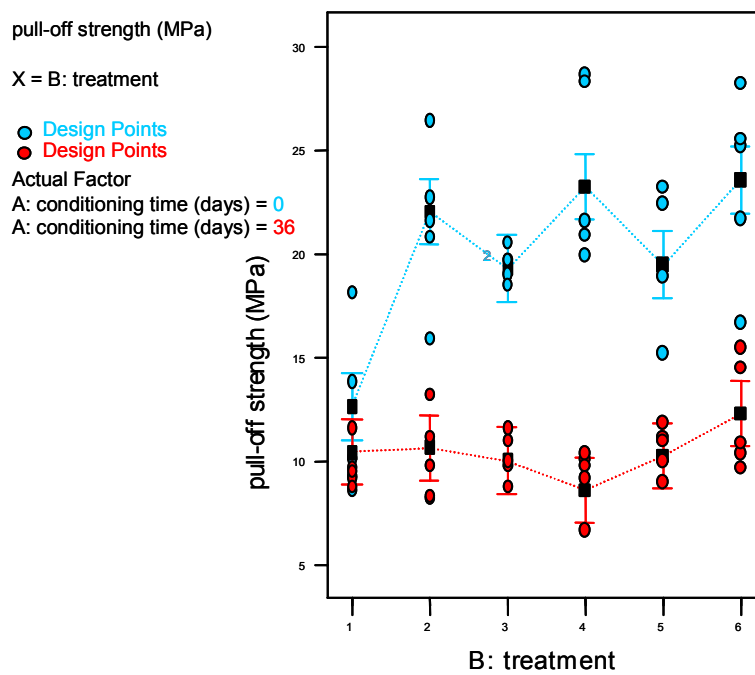


Figure 22: SEM micrograph of treatment 1 pull-off specimen (the dark arc is the remains of the fillet, the region to the left of the arc was bonded the region to the right unbonded)

Statistical analysis of the data showed the pull-off strength could be modelled using a quadratic response i.e. it depended on conditioning time (linear and quadratic dependence) and treatment, as well as an interaction between them. This is presented in the interaction graph in Figure 23. Again, treatment 4 seemed to be most susceptible to conditioning showing the largest change in pull-off strength with time and treatment 1 showing least change.



(a) Pull-off strength and conditioning time



(b) Pull-off strength and treatment

Figure 23: Interaction of pull-off strength with (A) conditioning time and (B) treatment

5.2.6 Aluminium 3-point bend test results

Figure 24 shows the raw data from the 3-point bend shear tests. Each data point is an average of 5 samples. The data are presented as interfacial shear stress values, calculated using Equation 1 from the measured dimensions of each sample and modulus values obtained from measurements on the unconditioned materials. For clarity, error bars are shown only for the unconditioned results. The scatter in the conditioned results was of a similar order. FE analyses show that this interfacial shear strength calculation significantly underestimates the true stress at the edges of the bond where failure initiates. However, data are presented in this way to account for minor variability in the manufactured specimen dimensions. These minor variations are assumed, based on FE stress analyses, to have no significant effect on failure strength. Calculations of interfacial shear strength made using the ‘dry’ and ‘conditioned’ adhesive modulus values show that the shear stress is slightly lower when the conditioned modulus is used in equations 1 and 2 (<10% difference).

There is a great deal of scatter in the data and a lack of clear trends making it difficult to draw any qualitative conclusions on the nature of the sample interface with different treatments and their suitability for good adhesion.

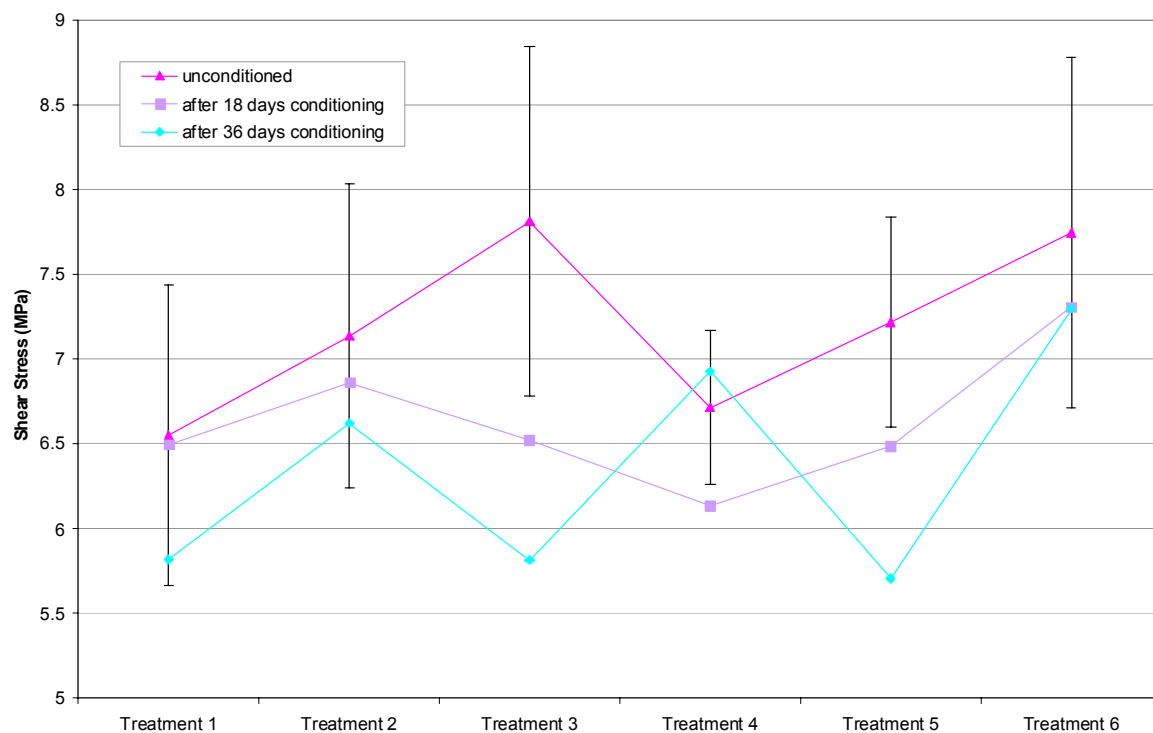
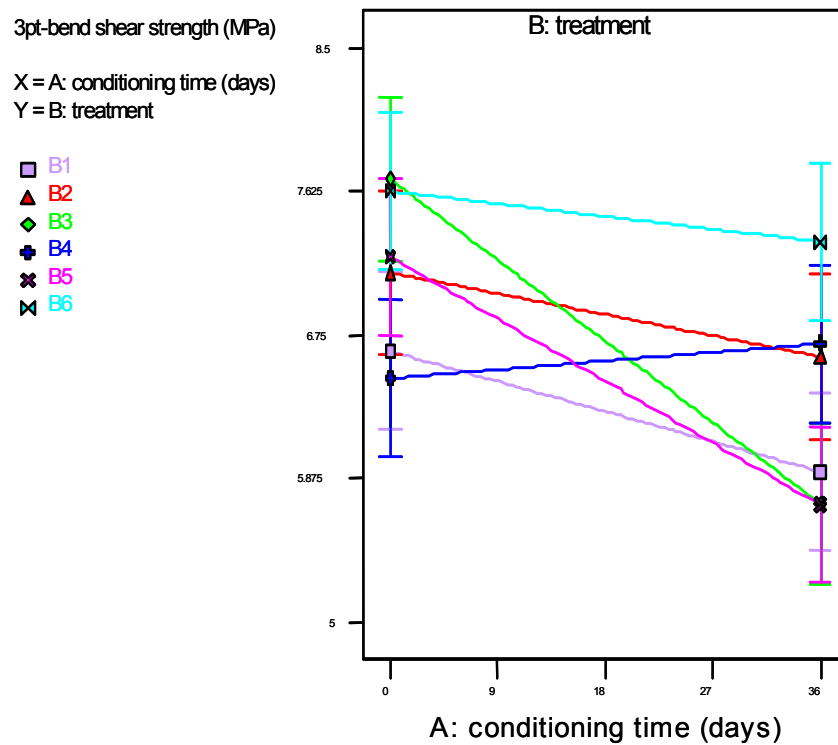
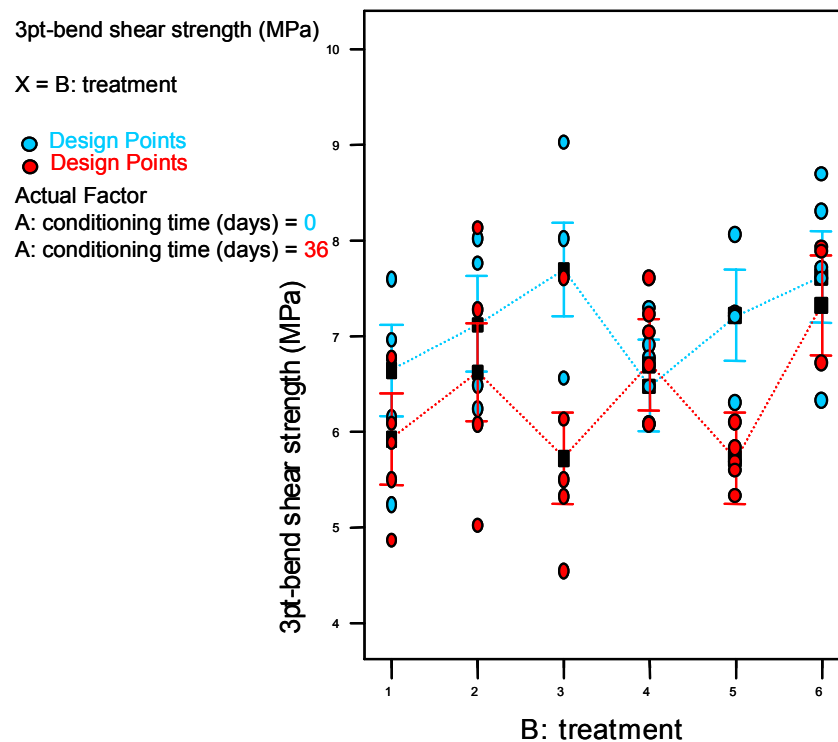


Figure 24: Raw data for the 3-point bend tests

Following statistical analysis, the interaction graph in Figure 25 is based on the modelled 2-factor interaction response; linear interactions with conditioning time and treatment were discovered. In addition, a borderline interaction between these two factors was found.



(a) 3pt bend strength and conditioning



(b) 3pt bend strength and treatment

Figure 25: Interaction of 3-point bend strength with (A) conditioning time and (B) treatment

The data still present some confusing conclusions with the optimal treatment 4 showing the lowest shear strength and which is seen to improve with conditioning time. This may be due to a change in the adhesive behaviour following hot/wet exposure leading to inaccurate strength calculations. The results for the other treatments are similarly difficult to explain, despite the statistical significance of the differences between them, presumably for similar reasons. It is clear that this test method is less sensitive to the state of the interface, even though failure is always along the interface, than to changes in other parameters hence obscuring the interfacial results.

5.2.7 Observations on the aluminium – adhesive A results

The results of the pull-off tests show surprisingly little discrimination between different surface treatments after ageing. For each treatment the mean failure stress of the aged samples is around 10-12 MPa, which is comparable with unconditioned strength of the untreated mill finished samples (treatment 1). The pull-off strengths of samples with treatment types 2-6 decrease to approximately 50% of the original unconditioned strengths on ageing.

The tensile strength of bulk specimens fell from 61 MPa to 41 MPa after hot/wet conditioning. It was remarked in Section 3.1 that the maximum principle stress calculated by finite element analysis in the unconditioned pull-off specimens was around three times the failure. Typically failure loads measure were approximately 22 MPa and applying the stress concentration factor produces a maximum principle stress value of 66 MPa, approximately equal to the bulk tensile strength (and maximum principle stress values at failure in other adhesive joint types). The same analysis was performed using material properties measured using a conditioned tensile specimen and a failure stress (11.4 MPa) corresponding to the results achieved with the conditioned pull-off samples. The calculated peak value for maximum principle stress was 39 MPa. This is close enough to the bulk tensile strength of the conditioned adhesive (41 MPa) to suggest that the maximum strength of the conditioned pull off sample is determined by the cohesive strength of the conditioned adhesive.

The 3-point bend test results show a high degree of scatter. All the mean results fall in a band between 5.5 MPa and 8 MPa. No significant decrease in strength is apparent with conditioning and it is likely given the scatter of the results that differences seen between surface treatments and conditioning are statistically insignificant.

The results from the aluminium – adhesive A tests show that the pull-off and 3-point bend tests have proved poor at discriminating between the different surfaces and their durability. With hindsight, it would have been prudent to conduct tests using a well-established test geometry, such as lap shear, to provide a basis of comparison. The strengths determined using the pull-off tests appear to be strongly related to the cohesive strength of the adhesive, which changes with conditioning. Levels of cohesive failure were high, obscuring any interfacial effects. There is a need to establish whether the plasticisation of the adhesives is reversible on drying (i.e. are the mechanical properties of bulk samples restored). If this were the case then conditioned joint samples could be dried completely before testing in order to determine the effects (if any) of irreversible changes to the interface.

The 3-point bend specimens have the advantage of generating failure at the interface and, therefore, it is expected that the reduction of mechanical properties of the adhesive on

conditioning would have less influence on the results. The force-extension response of conditioned specimens was very similar to the unconditioned specimens, with little change in bending stiffness observed. It is probable that within the scatter of the experimental results that the interfacial shear strength for this system is not affected by either surface treatment or conditioning. This is somewhat unexpected as numerous other studies indicate that the rate of decay of bond performance is determined by the quality of surface treatment. However, the pull-off tests also do not show any significant effect of surface treatment on the bond strength. The only indication of a significant dependence on surface treatment was between the unconditioned mill finished surface and the other surface treatments – pull-off strength was significantly lower and the mode of failure was predominantly interfacial.

5.3 GALVANISED STEEL

5.3.1 Test programme

A 2-factor central composite design was used for assessing the bonding surface/bond durability issues for oil coated galvanised steel. This enabled non-linearity and interactions to be studied for only 2 numeric factors. This design has the added benefit of being robust to small deviations from the set design points, i.e. deviations from the set oil levels or ageing times or even some omissions will not reduce the predictive capabilities of the design excessively. Each numeric factor is varied over 5 levels, with points being distributed within the design space as shown in Figure 26 and Table 3. 5 replicates of the centre point of the design enabled pure error to be estimated. The manufacturing schedule was arranged to make it robust to time/order effects, which could otherwise mask true data trends. Due to time constraints, however, sample batches were invariably tested in the order of ageing (correlation with this test order was checked during the diagnostic stage of the statistical analysis).

Table 3: Experimental Matrix

<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	treatment
<u>no oil</u>	<u>1μl</u>	<u>4μl</u>	<u>7μl</u>	<u>8μl</u>	oil volume
					exposure time (days)
(3)		5		(3)	0
	5		5		6
5		25		5	25
	5		5		44
		5			50

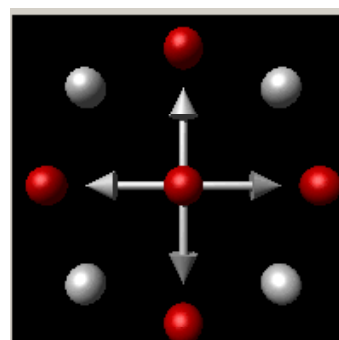


Figure 26: Design space

All steel adherends were cut to size before surface preparations. The steel samples were degreased by solvent wipe to produce a base surface for further preparation. Controlled levels of lubricant oil (Henkel MP404) were applied using a micro-pipette. Samples were 'oiled' 24 hours prior to bonding to enable the oil film to settle to a constant thickness.

Measuring the gain in mass following application made a check on the volume of sample dispensed on the sample by the pipette. The repeatability of application volume appeared reasonable but volume values (calculated from the density of the oil) did not match the dispense settings. A calibration curve was derived from mass gain measurements at different dispense settings. This is shown in Figure 27 and the slope of the best-fit line was used to correct the pipette volume setting to provide the desired oil coverage.

Test samples were prepared as outlined in Section 3. They were cured at room temperature (23 ± 2 °C) for 24 hours before being post cured for 90 minutes at 180 °C. Later discussions with the adhesive manufacturer suggested that a 30 minute post-cure at 180 °C is more usual. Hence, there is a possibility that the adhesive may have been 'over-baked' and that the performance may be less than optimal. All samples received the same post-cure treatment so variations in cure condition should not be present to influence the results.

Adhesive C is a thick, two-part paste dispensed from a cartridge. The manufacture of bulk samples indicated a high concentration of voids in the cured material. It must be assumed that the adhesion test samples would also have a high void concentration.

Adhesive C was a development of an adhesive (Adhesive B) used in an initial assessment of the test methods [4]. Adhesive B was found to bond very well to metals and had a high flexibility (large strain to failure). Consequently, 3-point bend samples could not be failed at the interface using the standard configuration. Although Adhesive C failed at relatively low strains in tension (ca. 1.5 %) this was thought to be due to the voids in the bulk specimens prepared rather than the physical properties of the adhesive. It would be expected that during exposure to hot/wet atmospheres the absorption of water would cause plasticisation and, hence, an increase in flexibility [12]. Therefore, the modified configuration, incorporating backing stiffener, was used to obtain failure at the interface for samples manufactured from Adhesive C and galvanised steel.

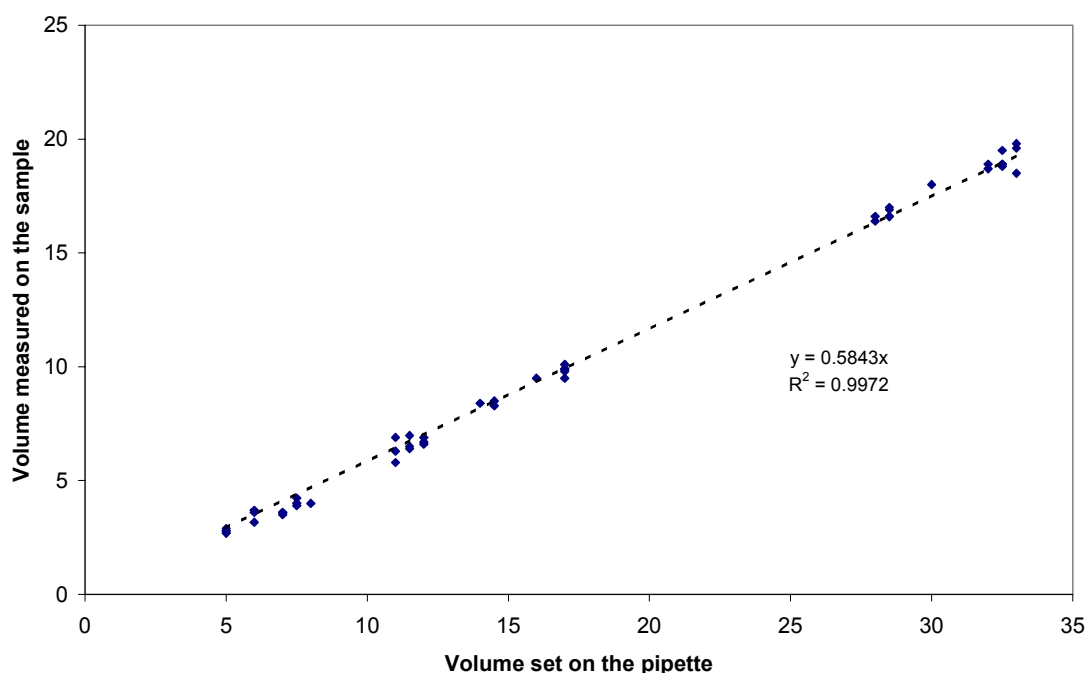


Figure 27: Calibration function for the application of oil (values in μl)

5.3.2 Colorimetry data

Graphs in Figures 28 - 31 show the averaged results for selected spectral reflectance data from the surfaces of the galvanised steel samples after treatment with different oil levels when illuminated with white light. The data show the unconditioned results and the results after conditioning at 70°C and 85% RH. In each case the data at each wavelength are averages of 3 samples. Error bars are presented showing the standard deviation for the datasets, except where magnitudes are similar to those for neighbouring datasets and error bars are omitted for clarity.

Figure 28 shows a significant difference in the amplitude and relative distribution of the reflectance spectrum for the unoled and oiled galvanised steel samples in the unconditioned state. However, different oil layer thickness levels cannot be distinguished statistically from each other, lying within the same experimental scatter. This suggests that the application of a

thin oil layer (several microns) affects the surface but that this effect does not increase with increasing oil layer thickness, as characterised by the colorimeter.

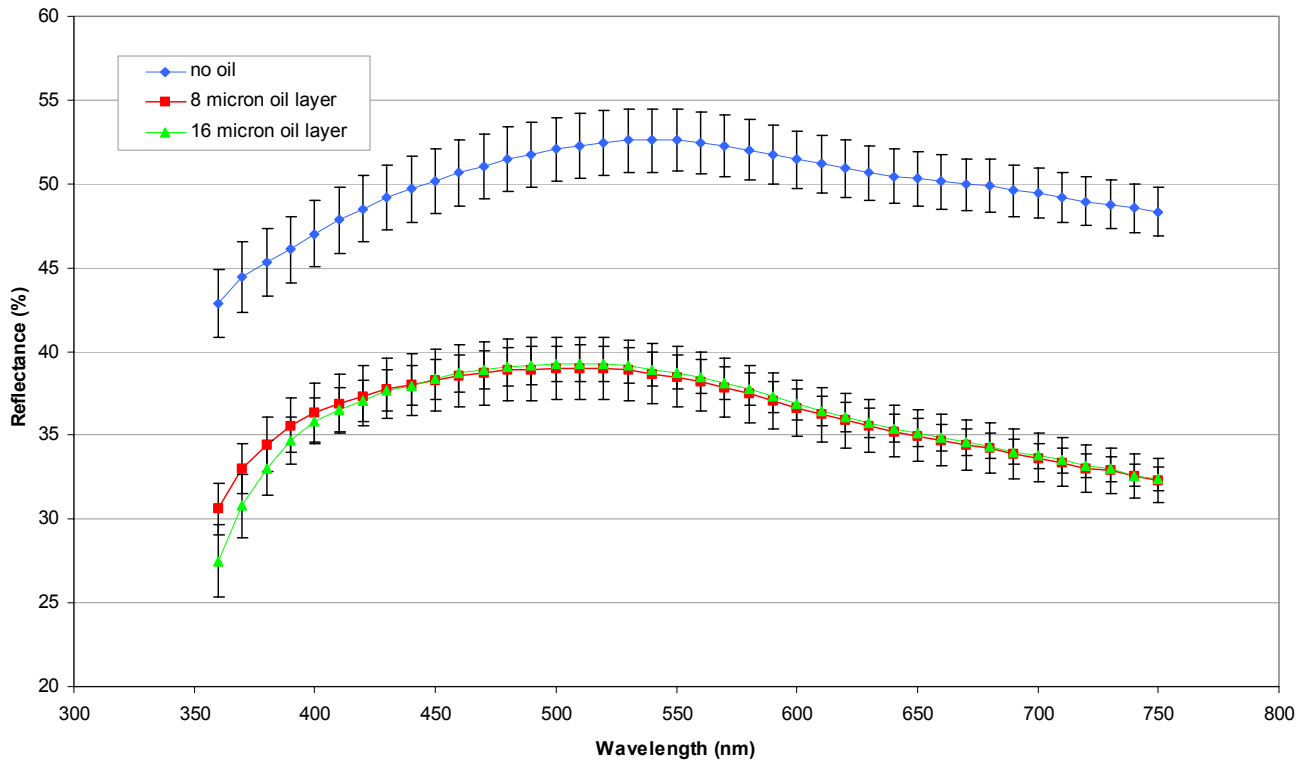


Figure 28: Reflectance of unconditioned samples with differing levels of oil

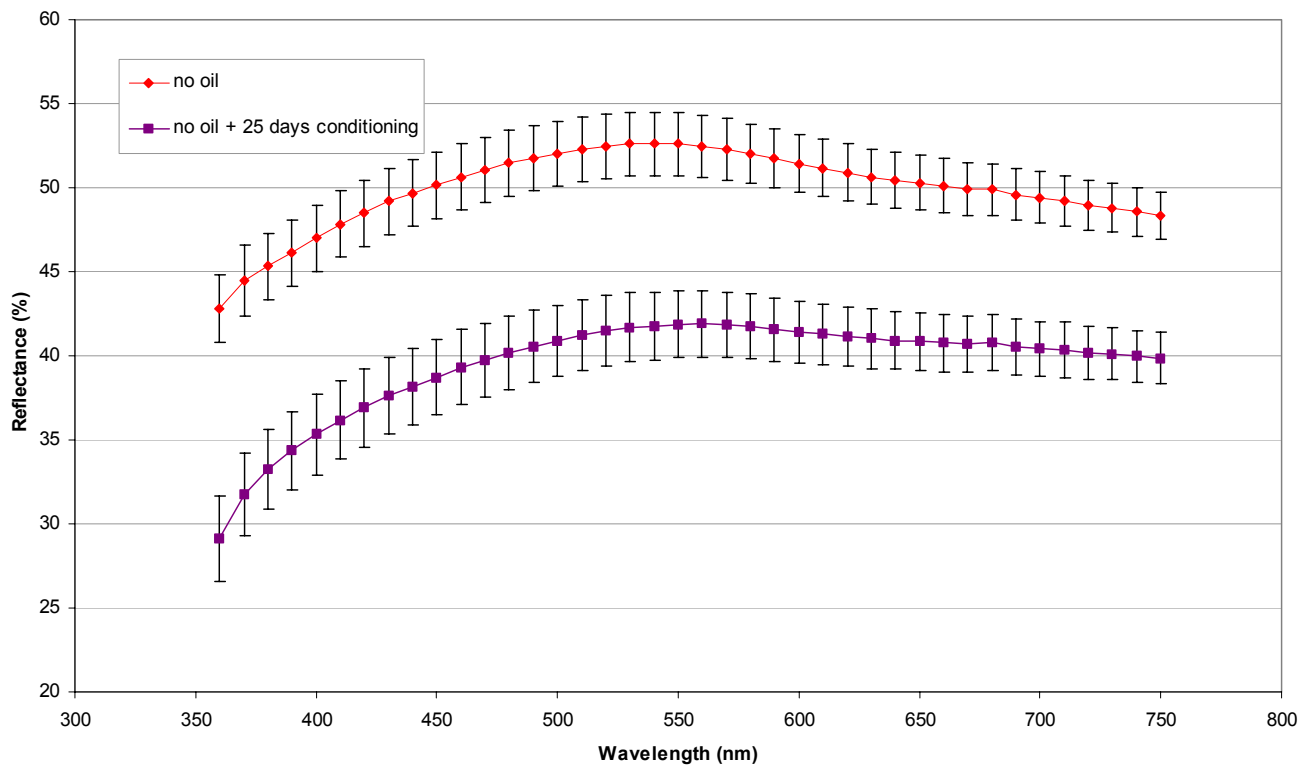


Figure 29: Effect of conditioning on reflectance spectra (no oil)

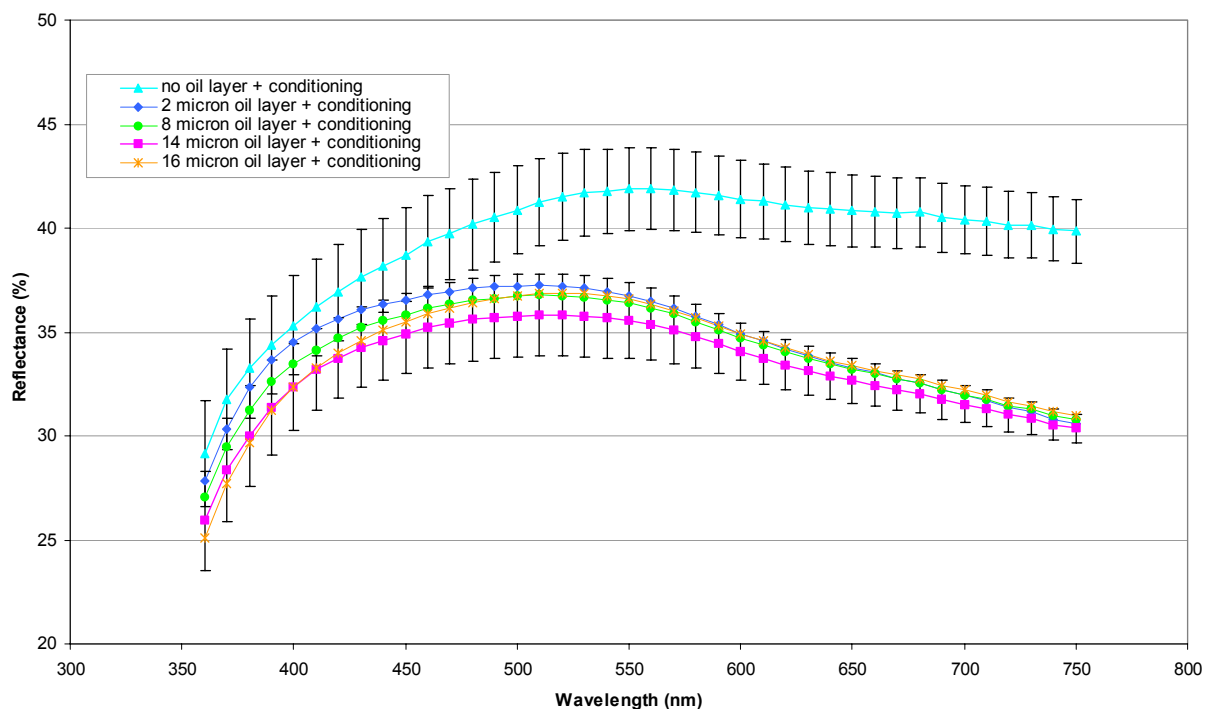


Figure 30: Effect of oil level on the reflectance spectra of conditioned samples

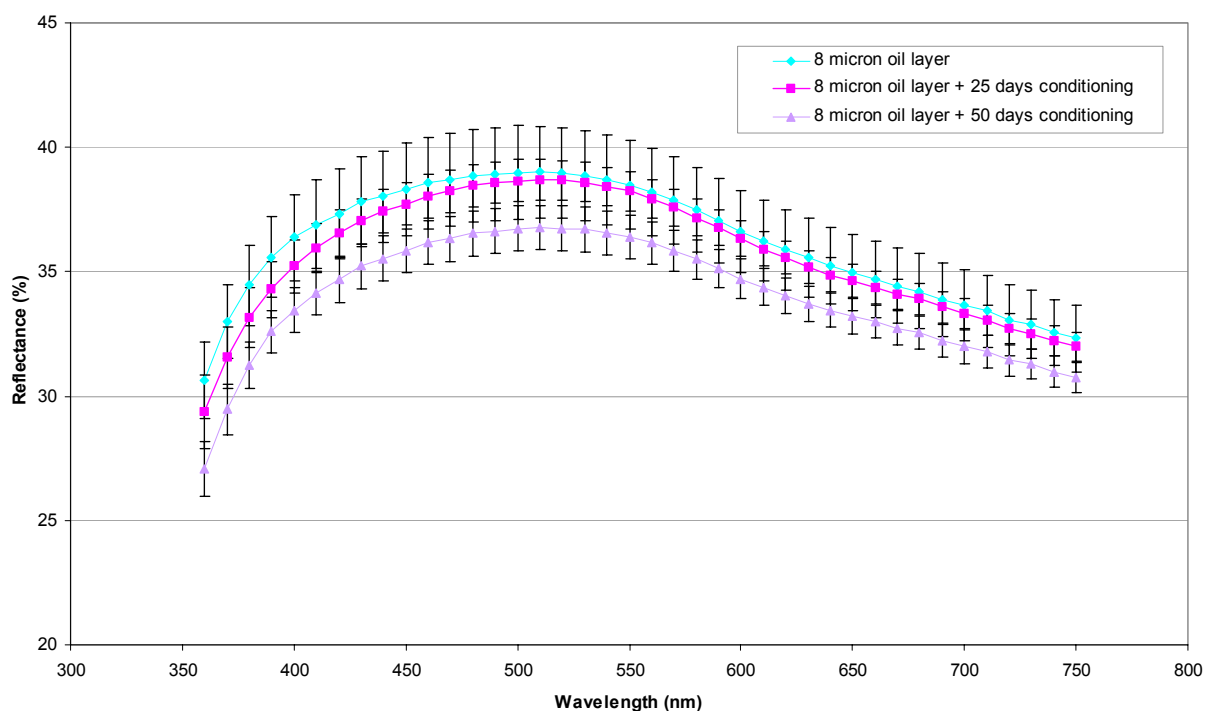


Figure 31: Effect of conditioning on the reflectance spectra of oiled samples

Figures 29 – 31 show the effects of conditioning on the bare and oiled surfaces. The ‘unoiled’ surface shows a marked change in reflectance amplitude with conditioning, although the relative spectral distribution is mostly unchanged. The conditioned oil treated surfaces show a marked difference from the conditioned bare surface, but the spectral responses for different oil levels are, as was seen with the unconditioned samples, indistinguishable from each other.

It can also be seen that the different period conditioning data cannot be distinguished from each other or from the unconditioned response for the oiled samples. Again, it would be difficult to distinguish the treatments from the colorimetry data alone, other than to specify oiled or bare surfaces.

5.3.3 Contact angle data

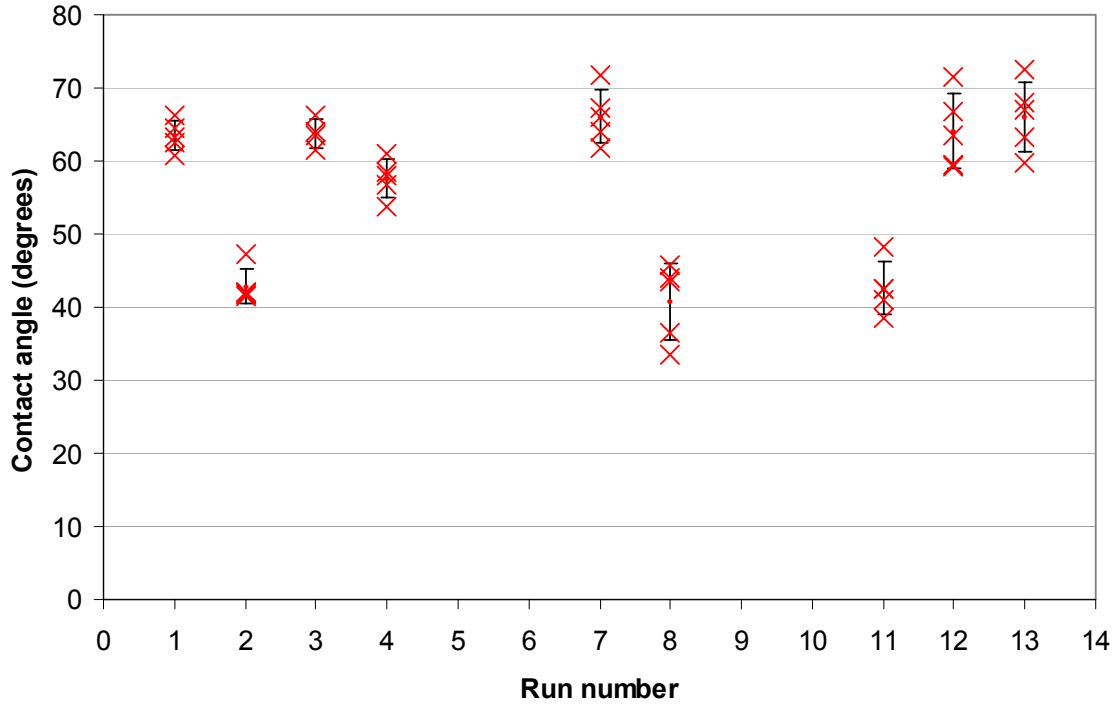


Figure 32: Contact angles determined for different experimental runs

Figure 32 shows the contact angle results using the static single drop method for each of the treatment/condition combinations specified in the design matrix. Each run consists of 5 repeat samples and error bars are presented showing the standard deviation. The combinations corresponding to each run number are specified in Table 4. Runs 5, 6, 10 and 11 are identical repeat runs of run number 1, in this instance this factor combination was measured only once.

The results are difficult to interpret due to the potentially large effect of surface roughness on the static droplet measurements, possibly greater than the effect of oil coverage. Both the ageing time and the oil layer thickness were shown to have effects on the measured contact angle as well as showing non-linearity and interactions. The predicted process model is shown below:

$$\theta = 53.24 + 0.74 * T_{age} - 0.61 * V_{oil} - 0.01 * T_{age}^2 - 0.37 * V_{oil}^2 + 0.06 * T_{age} * V_{oil} \quad (6)$$

where θ is contact angle in degrees, V_{oil} the volume of oil applied and T_{age} the ageing time.

Table 4 - Design matrix (* indicates replicates of centre design point)

Run order	Factor A Conditioning time (T_{age}) (days)	Factor B Oil volume (V_{oil}) (microlitres)
1*	25	4
2	25	8
3	44	7
4	6	1
5*	25	4
6*	25	4
7	50	4
8	0	4
9*	25	4
10*	25	4
11	6	7
12	44	1
13	25	0

Figure 33 in particular highlights the importance of the interaction term, for different levels of oil application (1 μ l and 7 μ l) the effect of ageing time on the surface contact angle is shown to be different. In this case, it seems that the thinner the oil layer the greater the contact angle and the smaller the effect of conditioning time. The contact angle increases with decreasing oil thickness and with increasing conditioning time.

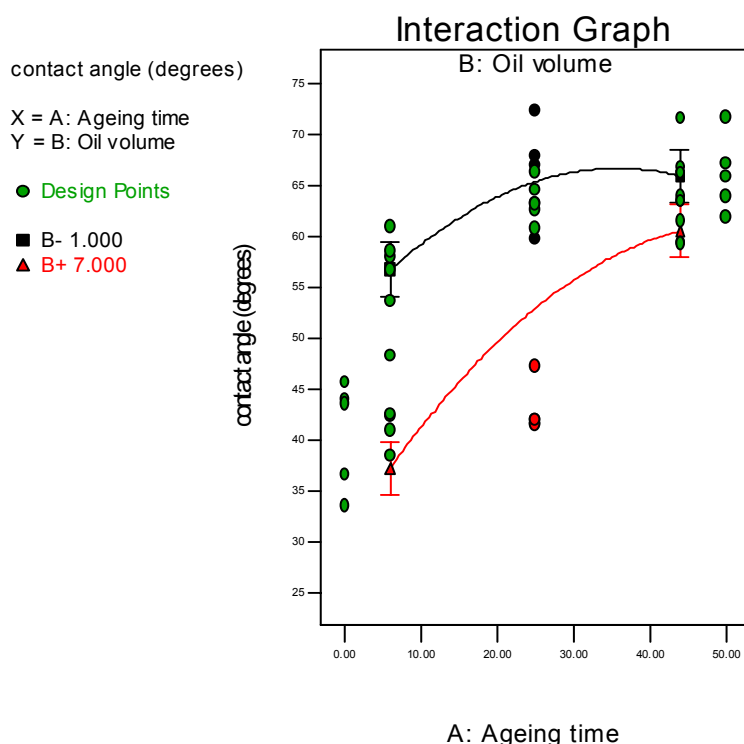


Figure 33: Interactions of oil volume, ageing time and contact angle

Figures 34 and 35 show the response of contact angle according to prediction for the combination of ageing time and oil volume, both as contour plots and gently sloping 2-D surfaces. These plots suggest the best surface wettability is achieved for unaged surfaces with thick oil layers, within the limits investigated. This is somewhat unexpected since the presence of oil would be expected to reduce wettability.

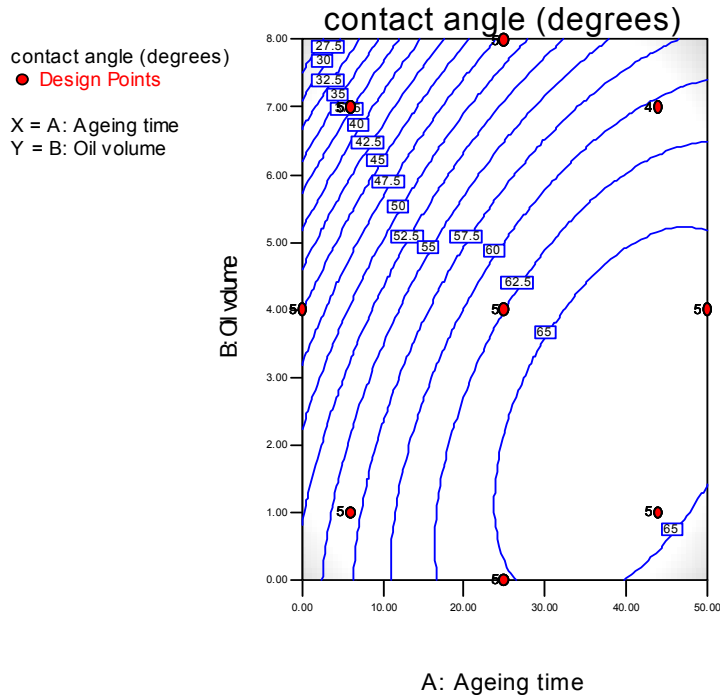


Figure 34: Contour plot of contact angle as a function of ageing time and oil volume

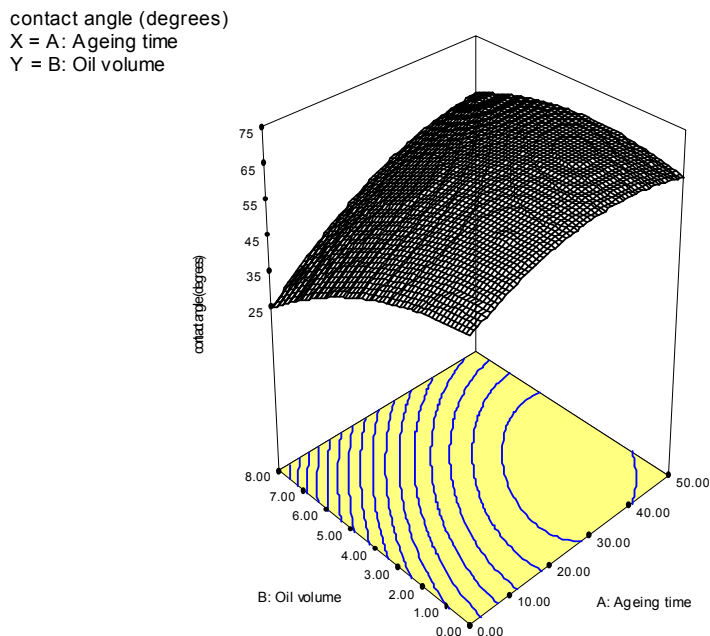


Figure 35: Saddle plot of contact angle as a function of oil volume and ageing time

5.3.4 Pull-off strength data

Figure 36 shows the pull-off strength results for each of the treatment/condition combinations specified in the design matrix shown in Table 3. Each run consists of 5 repeat samples and error bars are presented showing the standard deviation. Data for runs 7 and 12 are missing due to experimental difficulties experienced. Replicate batches were manufactured and tested for runs 1, 5, 6, 9 and 10.

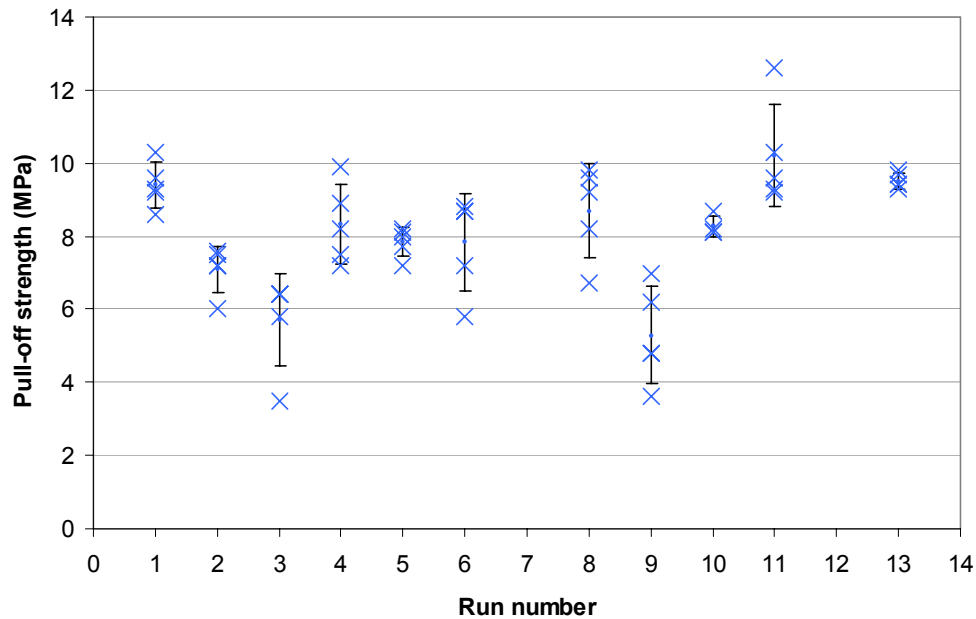


Figure 36: Raw pull-off strength data

These tests encountered difficulties with partially cohesive failures on all samples. Due to the variable nature of failure, it is unlikely that the measurements are true indicators of the strength of interfacial adhesion and subsequently affects the accuracy of the statistical analysis and design space predictions. The wide scatter in individual results seen in Figure 36 corroborates this. The predicted process model is shown below:

$$P = 7.55 + 0.05 * T_{age} + 0.38 * V_{oil} - 0.02 * T_{age} * V_{oil} \quad (7)$$

where P is the pull-off strength in MPa, V_{oil} the volume of oil applied and T_{age} the ageing time

Figure 37 shows the linear variation of each of the controlled factors and the interaction between them. Thin oil layers have increasing pull-off strength with conditioning time but the opposite is true as the layer thickness increases, even though the initial dry strength is higher for the thicker oil layer. This suggests that the mechanical performance of the dry bond increases with increased oil coating but shows a poorer performance with respect to long-term durability.

DESIGN-EXPERT Plot

pull-off (MPa)

X = A: Ageing time

Y = B: Oil volume

● Design Points

■ B- 1.000

▲ B+ 7.000

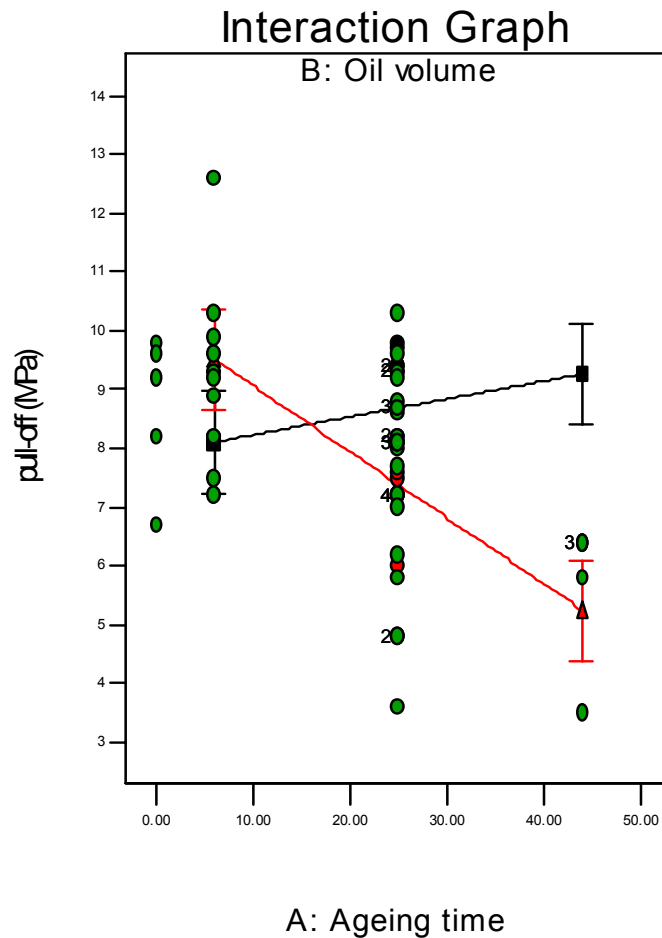


Figure 37: Interactions of ageing time, oil volume and pull-off strength

Figures 38 and 39 show the response of pull-off strength according to the statistical prediction for the combination of ageing time and oil volume, both as contour plots and 2-d saddle-shaped surfaces. These plots suggest the best mechanical performance as measured using pull-off strength is achieved for unaged surfaces with thick oil layers (or aged surfaces without oil layers) and the worst performance is produced by the same combination after prolonged conditioning, within the limits investigated.

The true tensile strength of the unconditioned adhesive C was found to be around 25 MPa (although failure was brittle before the maximum yield stress was reached). FEA suggests that the peak stress level in the pull-off sample at the typical failure load of 10 MPa for unconditioned samples is approximately 32 MPa, suggesting a high probability of cohesive failure. Hot/wet conditioning reduces the tensile strength to around 16 MPa, suggesting a maximum pull-off strength of approximately 5 – 6 MPa if the same stress concentration factor prevails. These values are consistent with failure loads observed. The adhesive would absorb oil when applied to the oiled surfaces and the absorbed oil would be likely to plasticise the adhesive. However, no data for the effect of absorbed oil on the mechanical properties of the adhesive were available. The effect of oil absorption on cohesive failure stress could be determined by manufacturing bulk samples with ‘mixed-in’ oil.

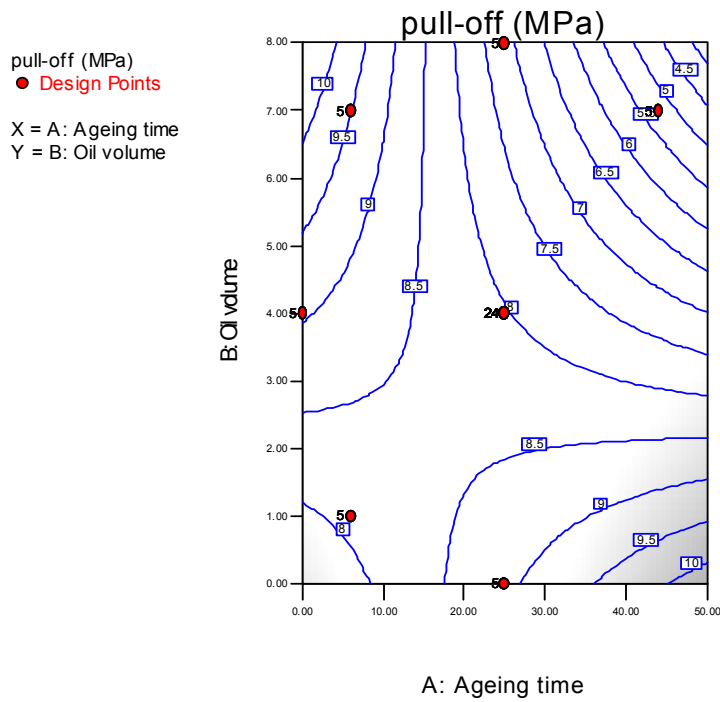


Figure 38: Contour plot of pull-off strength as a function of oil volume and ageing

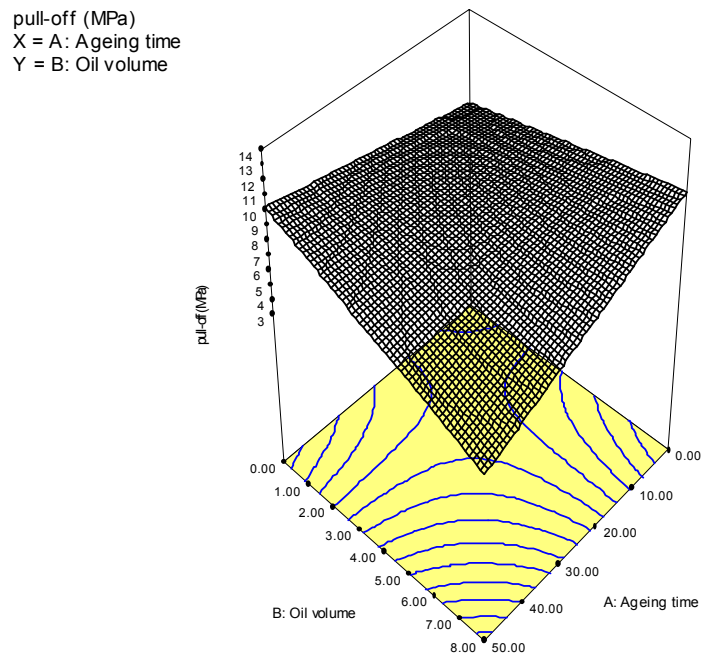


Figure 39: Saddle plot of pull-off strength as a function of oil volume and ageing

5.3.5 3-Point bend shear strength data

Figure 40 shows the results of the 3-point bend shear strength tests for each of the treatment/condition combinations specified in the design matrix shown in Table 3. Each run consists of 5 repeat samples and error bars are presented showing the standard deviation. Replicate batches were manufactured and tested for runs 1, 5, 6, 9 and 10.

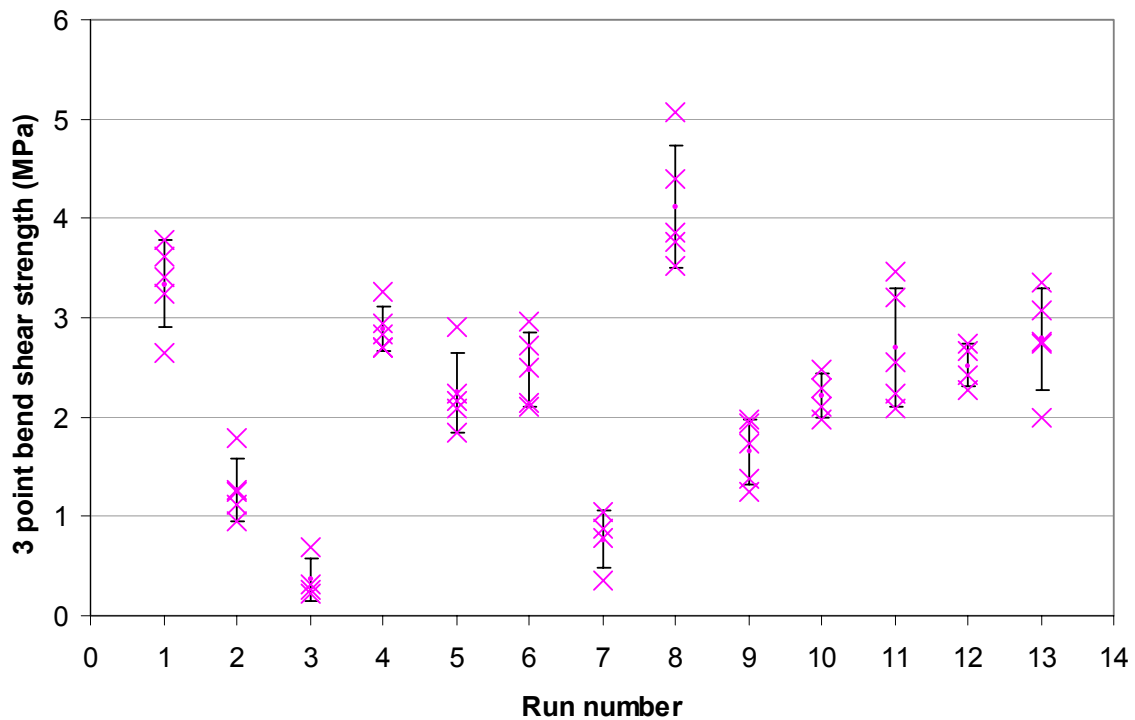


Figure 40: Raw 3-point bend test results

This test method appears to produce large scatter in the test results, as seen in Figure 40, as well as very low absolute strength values. After long durations of hot/wet ageing the surfaces under the adhesive rib appeared to corrode and several of these literally fell apart before they could be tested. The predicted process model is shown below:

$$B = 3.12 - 0.03 * T_{age} + 0.24 * V_{oil} - 0.03 * V_{oil}^2 - 0.01 * T_{age} * V_{oil} \quad (8)$$

Where B is the 3-point bend shear strength in MPa, V_{oil} the volume of oil applied and T_{age} the ageing time

Thus the interfacial shear strength as measured using 3-point bend is affected linearly by the ageing time and non-linearly by the oil volume, as well as an interaction between both factors.

Figure 41 shows the variation of each of the controlled factors and the interaction between them with respect to the measured shear strength. Thin oil layers showed similar initial dry strength to their excessively oiled counterparts but suffered less degradation following hot/wet ageing.

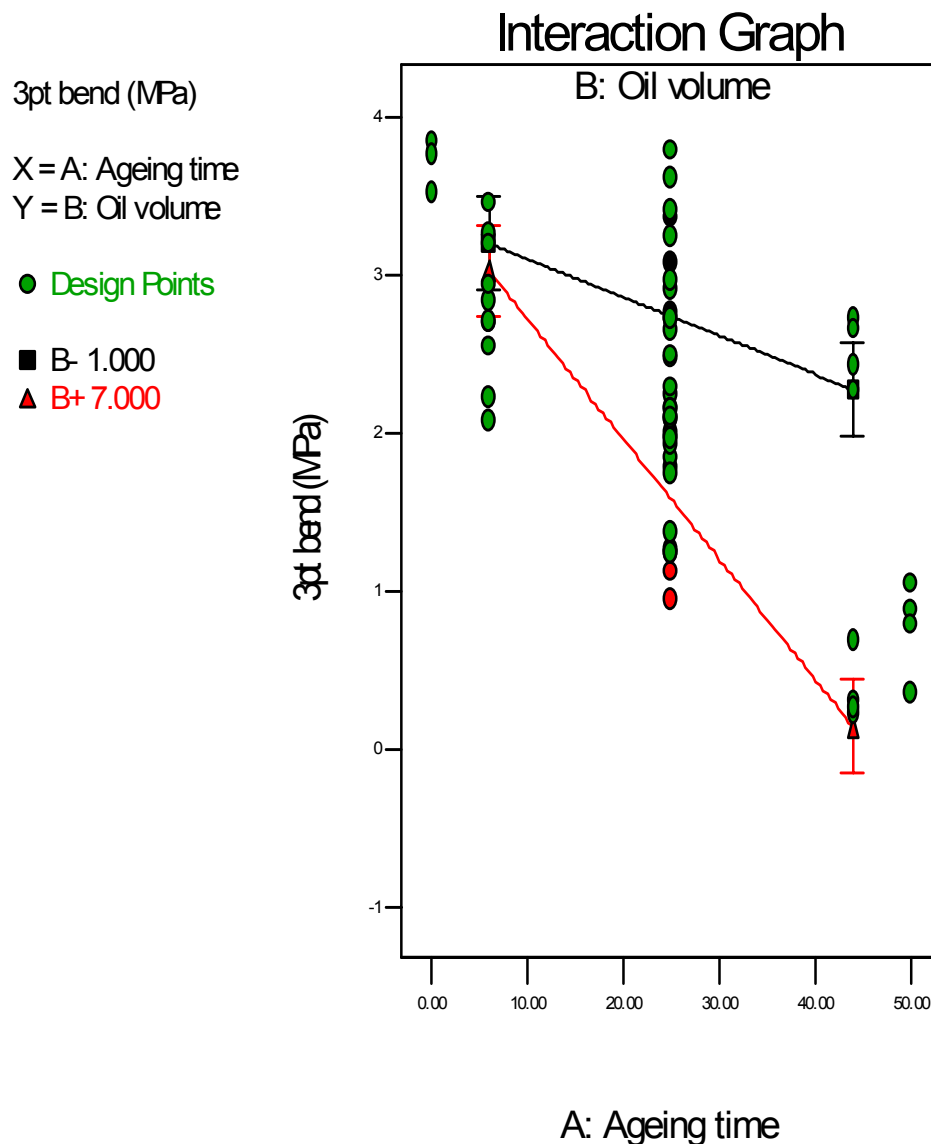


Figure 41: Interaction between ageing time, oil volume and 3-point bend strength

Figures 42 and 43 show the response of 3-point bend shear strength according to the statistical prediction for the combination of ageing time and oil volume, both as contour plots and 2-D surfaces (truncated due to impossible negative results being predicted). These plots suggest the best mechanical performance as measured using 3-point bend shear strength is achieved for mid-range oil layer thickness without conditioning. The worst performance is produced by thick oil layers after prolonged conditioning as was seen for pull-off data, within the limits investigated here.

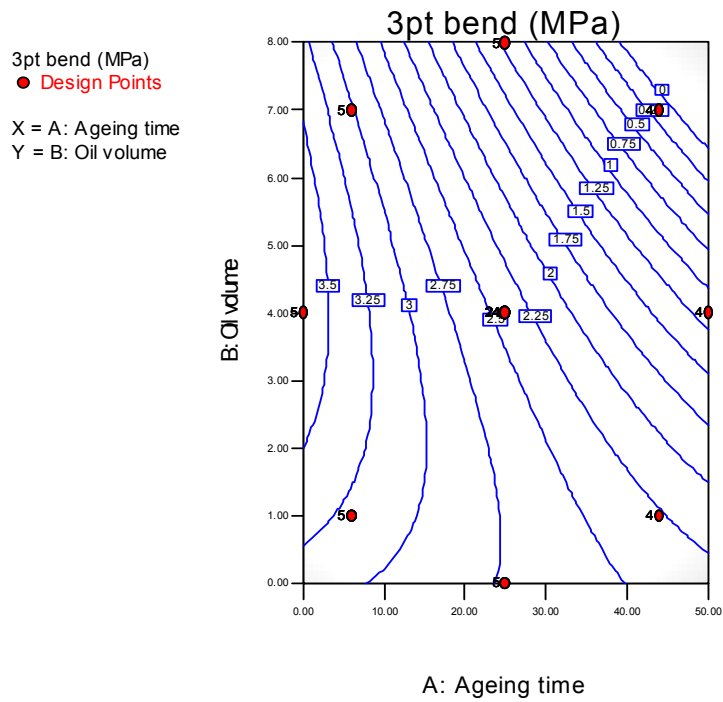


Figure 42: Contour plot of 3-point bend strength as a function of oil volume and ageing

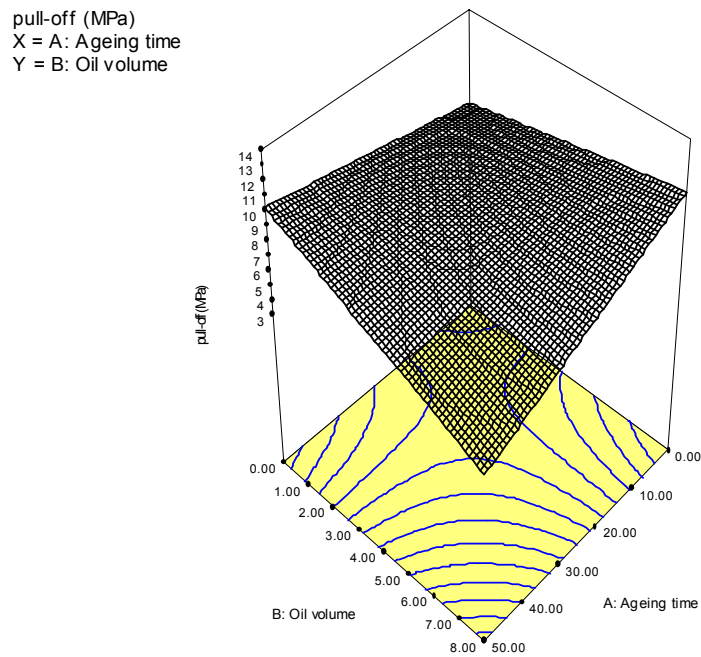


Figure 43: Saddle plot of 3-point bend strength as a function of oil volume and ageing

5.3.6 Performance predictions and check measurements

Additional data sets for the combinations of 0 days conditioning and both no oil and 8 μl oil levels were measured to check the accuracy of the predictive estimates. These are shown in Table 5.

Table 5 – Comparison of predicted to measured responses

Factor combination/test response	Predicted Values	Measured Values
0 days ageing + 0 μl oil		
Contact angle ($^{\circ}$)	53	89
Pull off strength (MPa)	7.6	11.8
3-point bend strength (MPa)	3.1	5.9
0 days ageing + 8 μl oil		
Contact angle ($^{\circ}$)	24	39
Pull off strength (MPa)	10.4	8.3
3-point bend strength (MPa)	3.3	3.9

These predictions are not as accurate as would usually be expected for a number of reasons:

- different bonding chemistry for samples with and without oil
- different conditioning degradation processes for samples with and without oil
- extremes of oil level and conditioning periods are on the periphery of the design space.

Hence, the model checks would have been more appropriate for a mid-range oil and conditioning level rather than at combinations of maxima and minima of the controlled factors, since the model is based primarily on data from the mid-ranges and the model is not as effective at extending to the far corners of the design space or to regions where different processes controlling the responses apply.

Correlations between the measured surface contact angles and the mechanical responses were investigated. It was found that the pull-off strengths showed a dependence on the surface contact angle as shown in Figure 44.

Similarly, 3-point bend strengths were found to have a non-linear dependence on the measured surface contact angle as well as an interaction between the conditioning time under hot/wet conditions and the measured contact angle, as shown in Figure 45. This shows that samples with low contact angles have a high initial dry strength but perform worse under hot/wet conditioning than the higher contact angle equivalents.

In order to optimise the mechanical response of the bond studied here, an oil volume of 6.5 μl (per 500mm² area) provided the sample would not be subject to hot/wet conditioning in-service gives the best performance. However, the best mechanical bond performance under prolonged in-service conditioning would be given by an oil free surface.

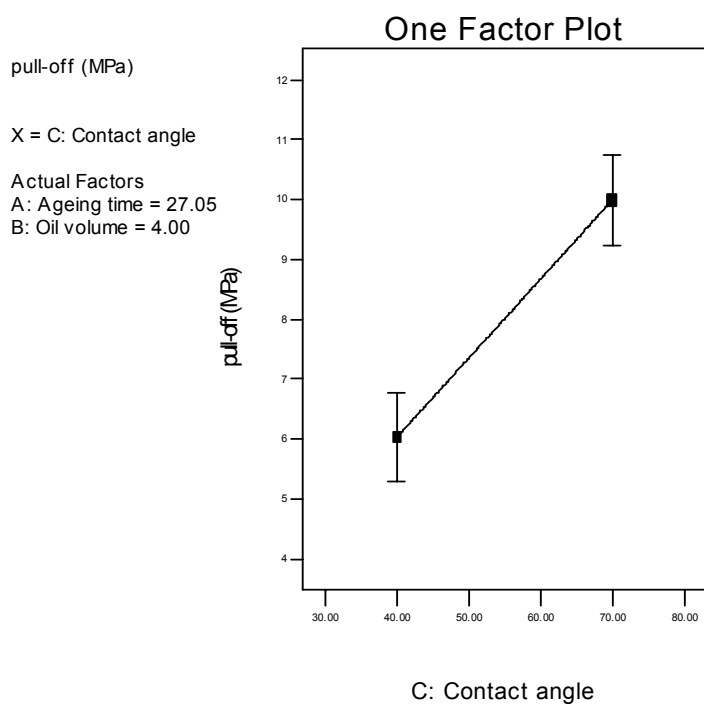


Figure 44: Dependence of pull-off strength on contact angle

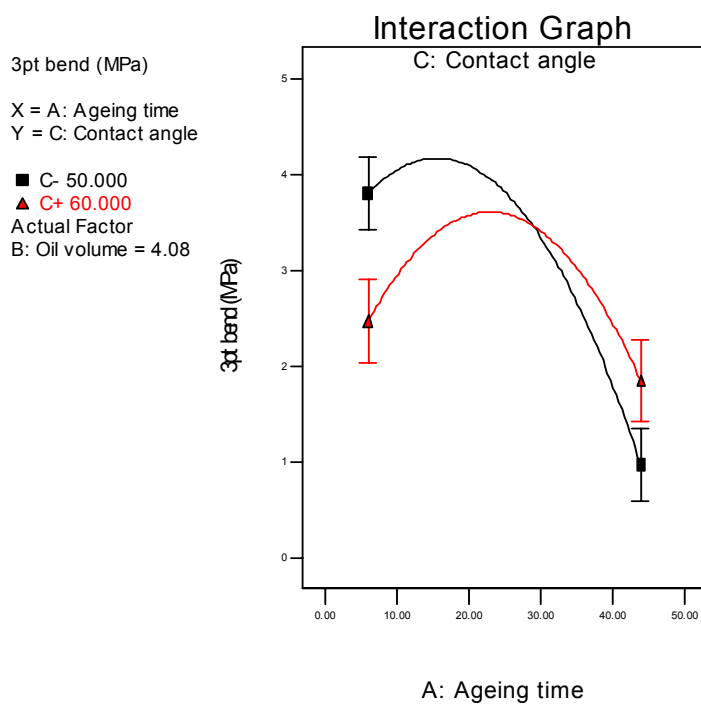


Figure 45: Dependence of 3-point bend strength on contact angle

5.3.7 Surface degradation observations

Much higher rates of bond performance degradation with conditioning time are observed from the 3-point bend tests than from the pull-off tests. The appearances of the surfaces of the samples tested after ageing indicate some major differences between the two types of test specimen. The steel surfaces under the adhesive rib of the 3-point end samples were obviously corroded following conditioning at 70 °C and 85 % relative humidity, whereas the pull-off samples appeared unaffected.

The exposed areas of galvanised steel resist corrosion well during the test. Corrosion was normally only visible near the cut edges of the samples where the protective coating has been damaged. Figure 46 shows a 3-point bend and a pull-off specimen (4 µl oil coating) that have been tested after 44 days hot/wet conditioning. The 3-point bend sample shown, typical of the longer term hot wet aged samples, has corroded under the adhesive rib. The corrosion is in the centre of the bond where it would be expected that exposure to moisture would be least, due to the time required for water to diffuse through the rib. The delamination of the rib appears to have been via interfacial failure although a patch of the corroded layer can be seen on the adhesive surface, indicating failure of the surface layer.

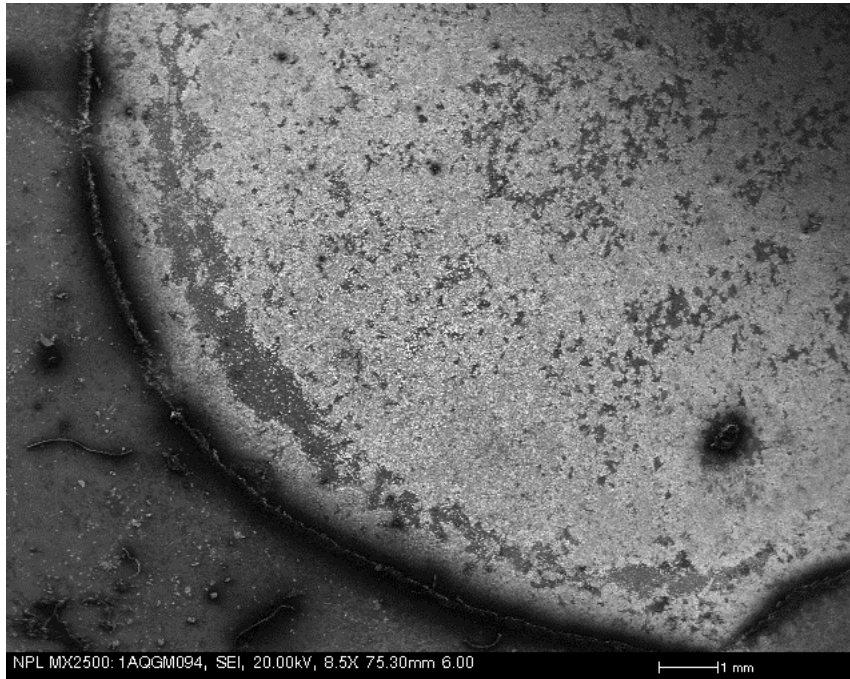
Virtually no corrosion is visible on the pull-off specimen. The region in the centre of the bond shows no sign of corrosion. There is some discolouration around the edge of the fillet region but this is more likely water marking than corrosion. Failure appears to have been mainly cohesive with obvious patches of adhesive remaining on the steel surface. There is far less surface area of adhesive exposed to atmosphere for the pull-off specimen than the 3-point bend sample. Additionally, the diffusion path length from the edge of the sample to the centre of the bond is much longer in the 3-point bend sample, which also gains protection from the circumferential fillet. Therefore, it is possible that moisture levels in the adhesive and at the interface are far lower than in the 3-point bend samples for equal exposure times.



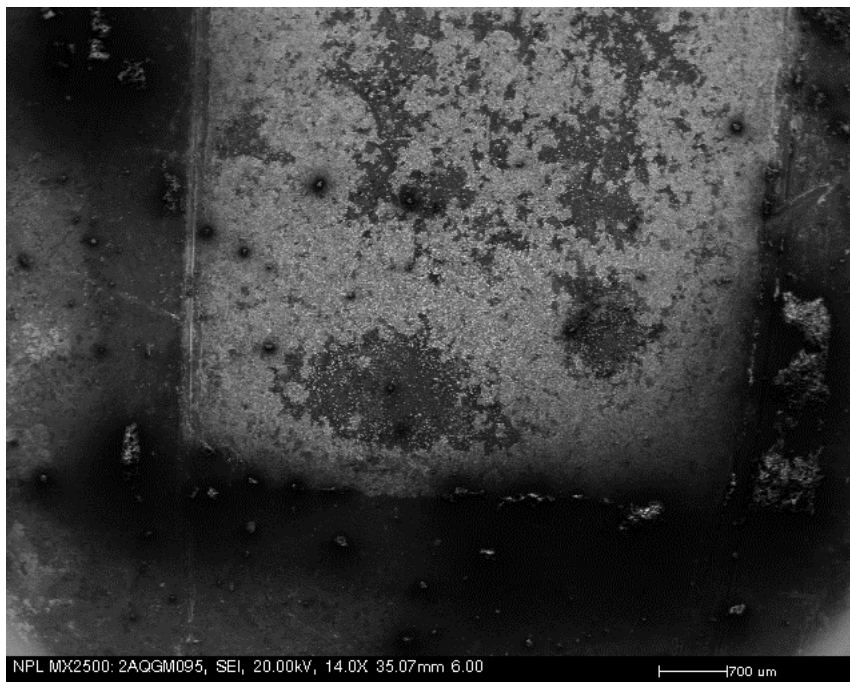
Figure 46: 3-point bend and pull-off samples tested after 44 days

Samples were examined using SEM to generate a better understanding of the surfaces after exposure. The micrographs shown in Figures 47 and 48 demonstrate that the surface under the adhesive layer appears different from the unbonded regions. The pull-off sample (47a)

shows some cohesive failure. The 3-point bend sample (47b) failed interfacially and there is evidence of changes in the surface oxide layer.

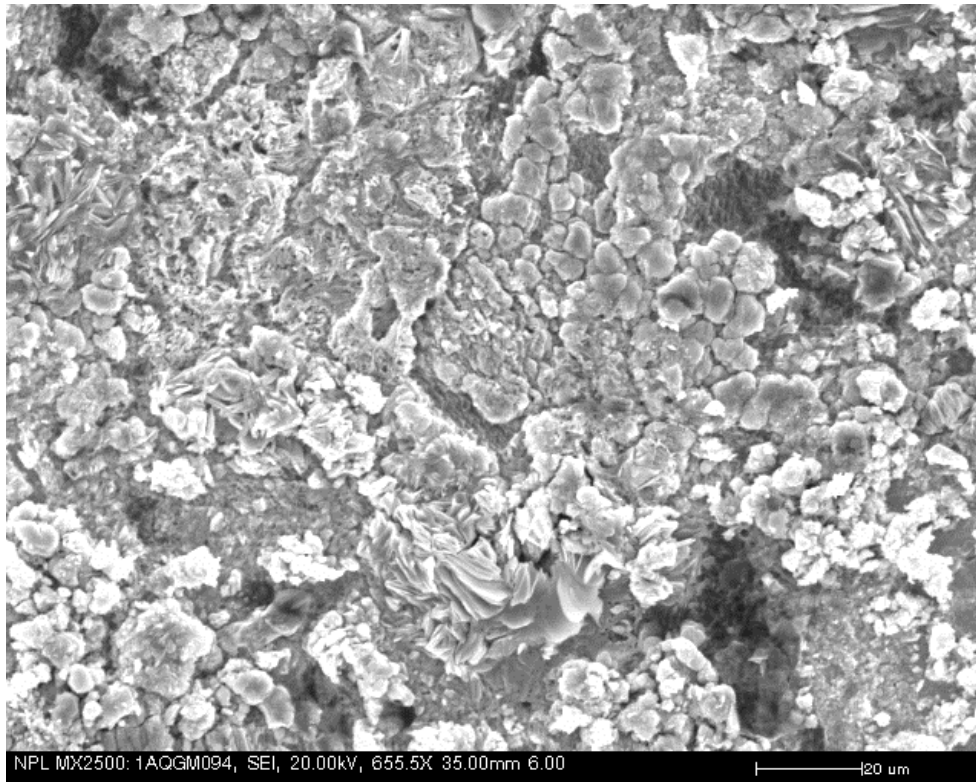


(a) pull-off sample, cohesive failure

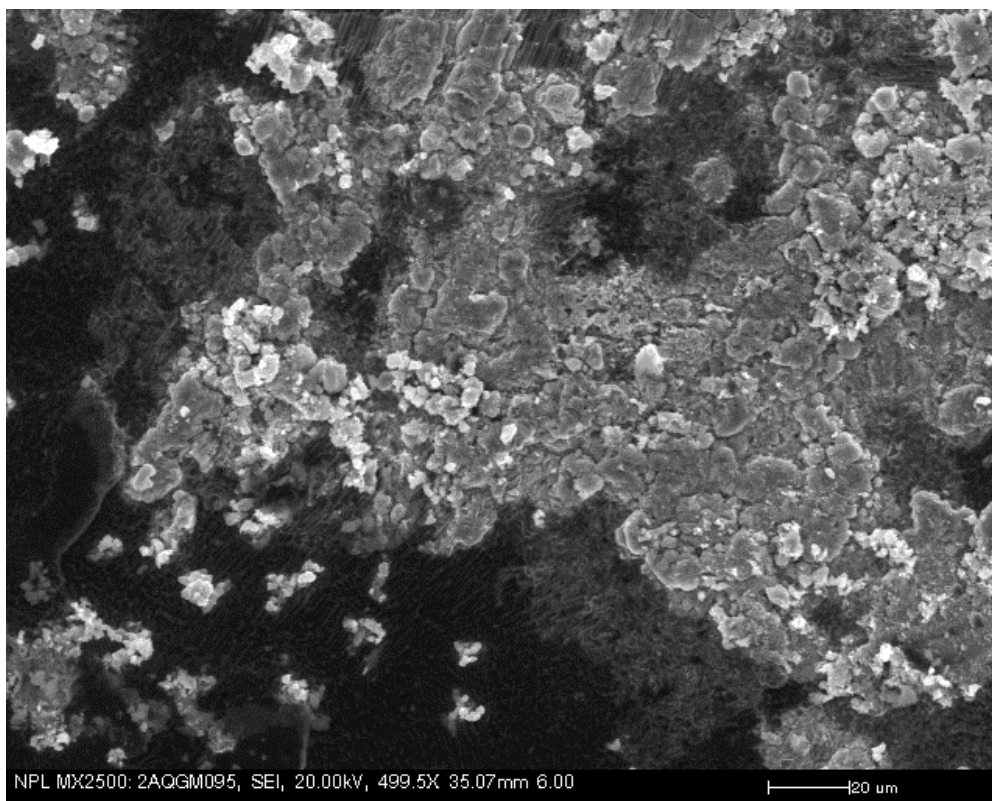


(b) 3-point bend sample, interfacial failure revealing modified surface

Figure 47: SEM micrographs of failed surfaces of exposed samples



(a) Magnified image of surface in Figure 47a (pull-off)



(b) Magnified image of surface in Figure 47b (3-point bend)

Figure 48: Magnified images from Figure 47

Zinc is more corrosion resistant than steel in most natural atmospheres, the exceptions being ventilated indoor atmospheres where the corrosion of both steel and zinc is extremely low and certain highly corrosive industrial atmospheres. Zinc owes its high degree of resistance to atmospheric corrosion to the formation of insoluble basic carbonate films. Environmental conditions that interfere with the formation of such films may attack zinc quite rapidly. The zinc layer provides good protection to atmospheric moisture (as seen from the performance of the 'open' regions of the sample and in many aqueous environments (from mildly acidic to alkaline) although strongly acidic conditions and the presence of some salts, e.g. calcium, can lead to rapid attack of the zinc layer.

Zinc normally has very good corrosion resistance in cold water. However, advice available from The Galvanisers Association [13] states that above 60°C zinc may become cathodic to steel in some aqueous solutions and no longer provide sacrificial protection if the coating is damaged. The tests were performed above this critical temperature and this may have consequences for the observed bond performance.

Voids are observed in bulk samples and in the ribs of the 3-point bend samples. It must be assumed that these voids also occur at the interface between the adhesive and the adherend. It is likely that absorbed water may condense within the pores of the adhesive. Any chemicals leached from the resin, excess oil or the fillers would concentrate in this condensate. The chemistry of the aqueous solutions in these pores may be corrosive to zinc.

In addition to producing micrographs, data on the composition of the surface of the 3-point bend specimen were obtained from the SEM, using energy dispersive x-ray analysis (EDX). The results of these are presented in Figures 49-51. The energy spectra of reflected x-rays are analysed in order to identify elements present on the surface. Results are presented as spectra, which provide a semi-quantitative measure of the concentrations of species present, and element maps, where light regions indicate increased concentrations of the elements. As expected for a galvanised surface, the major element present is zinc. However, the region under the adhesive has concentrations of oxygen not present in the unbonded region. This is indicative of the growth of zinc-oxide or zinc-carbonate films at the surface.

Figure 49 shows results for a 3-point bend sample, prepared with 7 µl oil and conditioned for 44 days. Regions under the adhesive rib and from the exposed (unbonded) region were analysed. The micrograph, Figure 49a, shows regions of the surface that were under the bond and left exposed. The line running vertically through the micrograph is the edge of the bondline. The region to the left of the line was bonded and the region to the right unbonded. The dark area on the far left was obviously corroded. The vertical lines seen on the micrograph delineating the extent of the bond are most likely scratches that were produced when the excess fillet was trimmed using a scalpel blade. The EDX detector was zoomed on three regions of the sample to produce detailed spectra of the corroded region, the uncorroded bond region and the unbonded region, Figure 49b. As the region sample moved from the unbonded region on the right to the corroded region on the left the proportion of zinc detected falls whilst the proportion of iron (from the steel) and oxygen increase. There is some evidence of calcium present on the unbonded surface but this was decreased in the corroded region. The element maps, Figure 49c, corroborate the spectra. The iron rich and zinc deficient regions correspond with the dark, corroded regions in the micrograph (and the scratches). Oxygen concentration is higher within the bonded region and appears to be slightly higher in the corroded regions. The silicon and carbon present on the unbonded

surface is likely residual material left over from the mould used to prepare the samples and from applied oil, that were not completely washed from the surface during conditioning. There are no obvious concentrations of calcium on the sample but some indications of regions with increased chlorine levels in some areas under the bond.

Figure 50 shows results from a sample (4 μ l oil, conditioned for 50 days) where a region of the micrograph, Figure 50a, was selected from the bonded region where corrosion was incomplete and regions of zinc scale and oxidation coexisted, Figure 50b. Element maps, Figure 50c, show that the central, dark region corresponds to depleted zinc and increased oxygen concentrations. Iron is concentrated in only a few specific regions. There are patches of carbon that may be residual adhesive. There are also small areas with enhanced calcium and chlorine concentrations although these do not appear to coincide nor to be associated with high iron concentrations.

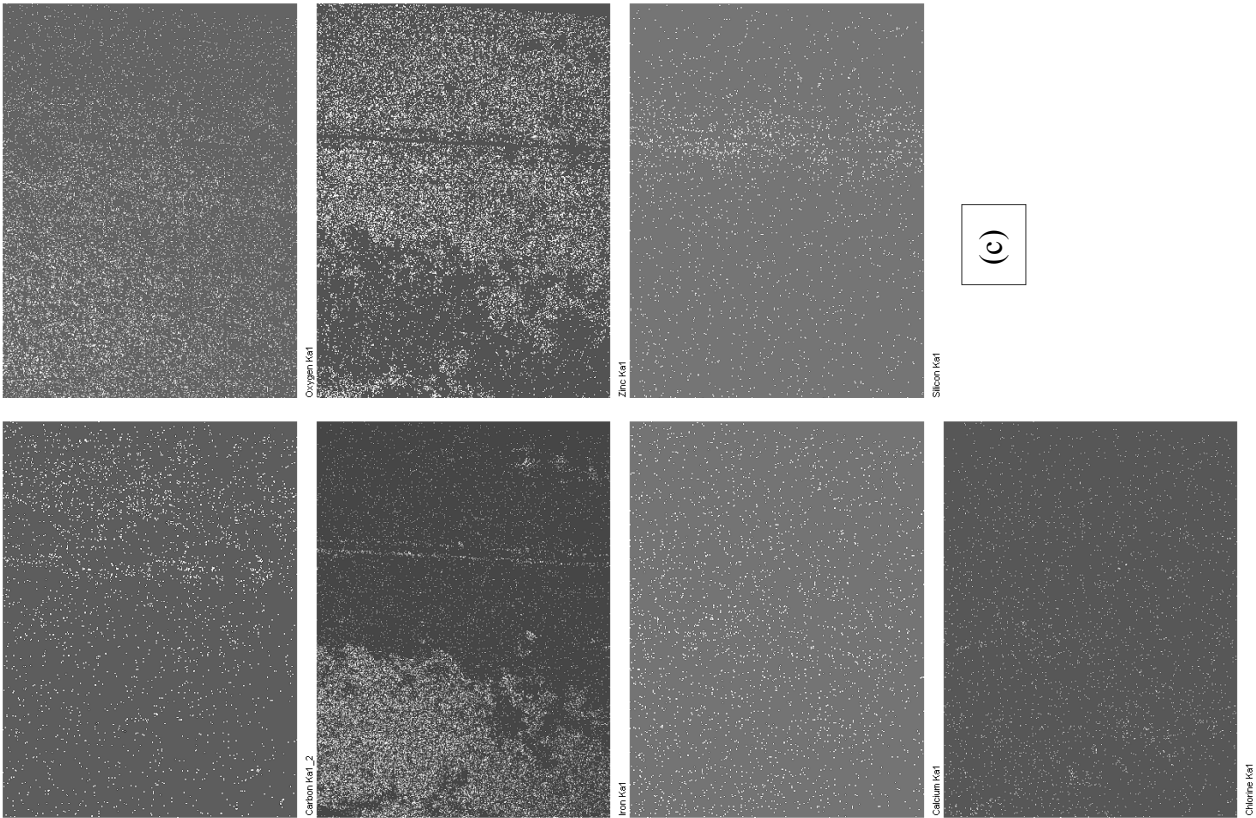
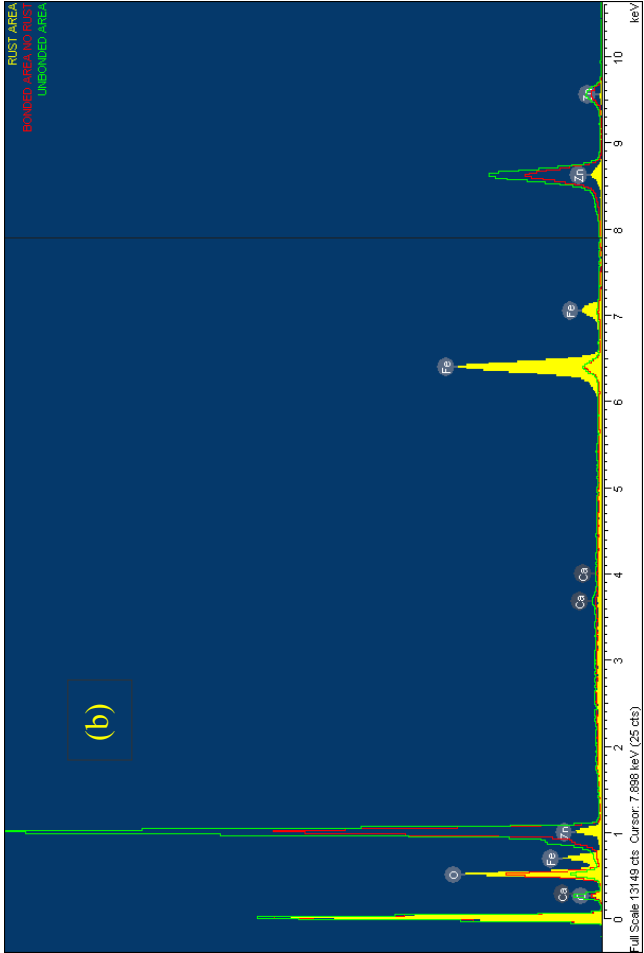
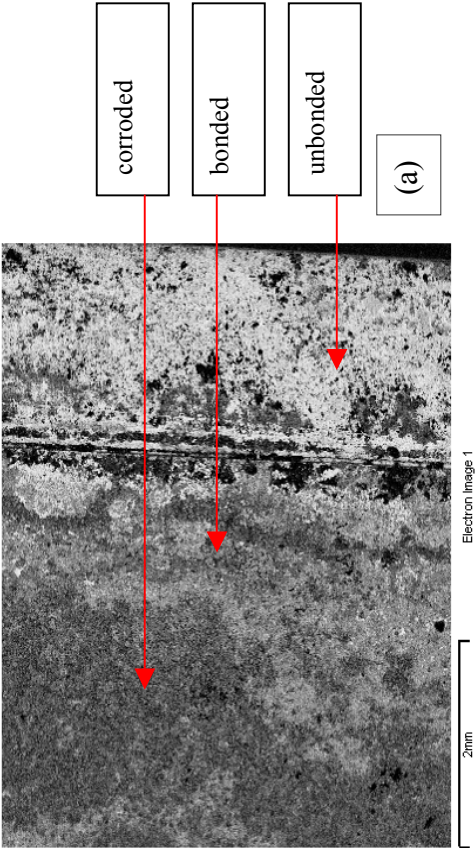
Figure 51 shows EDX analysis results for a region of the surface under the bond line of a pull-off specimen prepared with 4 μ l oil and conditioned for 50 days. The micrograph, Figure 51c, shows light and dark regions. The dark regions indicate scale formation with reduced zinc and increased oxygen concentrations. Iron levels are low overall, Figure 51b, but there are small zones with high concentrations, Figure 51c.

The results suggest that degradation of the zinc surfaces is occurring under the adhesive bondlines. These degradation processes do not occur in the unbonded regions that are exposed directly to the conditioning atmosphere. Therefore, there must be some interaction between the adhesive, absorbed moisture and surface layer that leads to degradation of the zinc layer. This degraded layer is weaker than the original surface and can promote premature failure. It is suspected that moisture condenses within voids in the adhesive and that the chemistry of the condensate is corrosive to the zinc layer. Patches of corrosion would appear first where voids containing moisture are present at the surface. There are indications from the SEM analyses that corrosion appears in patches.

The pull-off samples degrade at a slower rate than the 3-point bend samples. The EDX analyses show that changes under the pull-off layer are happening and it is suspected that the composition data are likely to represent an earlier stage of surface changes that the 3-point bend samples have already experienced. The rate of moisture ingress into the pull-off sample is likely to be slower than the rate of ingress into the 3-point bend sample as the distance from the exposed edges to the centre of the bondline are much greater. Continuing exposure of the pull-off samples might be expected to produce visible signs of corrosion in due course.

The corrosion appears to be greatest in the centre of the bondlines, furthest from the exposed edges, and, as this is the last region to reach saturation moisture content, it would have been reasonable to expect this region to have been protected for longer. It is possible that stresses induced by the differential thermal expansion of the adhesive, zinc layer and steel substrate during the post-cure cycle may have damaged the zinc layer in the centre of the samples. FEA models of stress induced on the surface of the steel by differential thermal expansion predict that the centre of the bonded region experiences the highest stress, consistent with the location of the highest levels of corrosion. Similar models for the pull-off sample showed highest levels of stress were near the centre of the specimen but slightly lower than in the 3 point bend specimen.

Figure 49: EDX data for galvanised steel, Adhesive C, 7 µl oil, 44 days



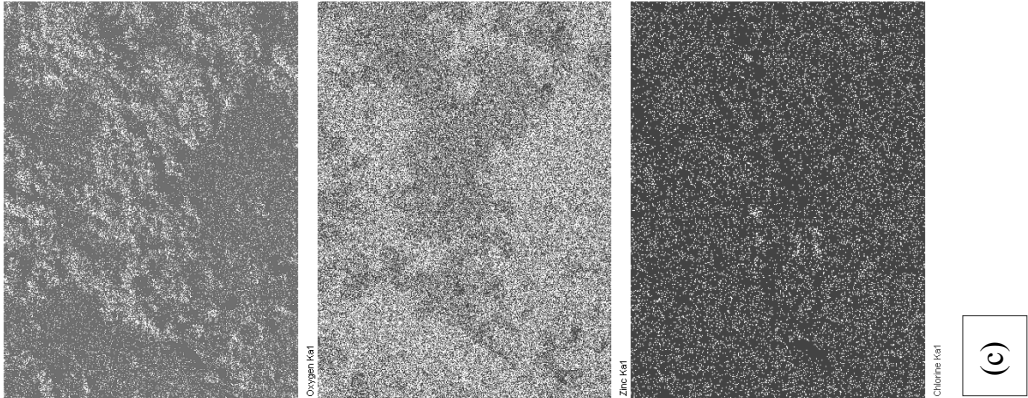
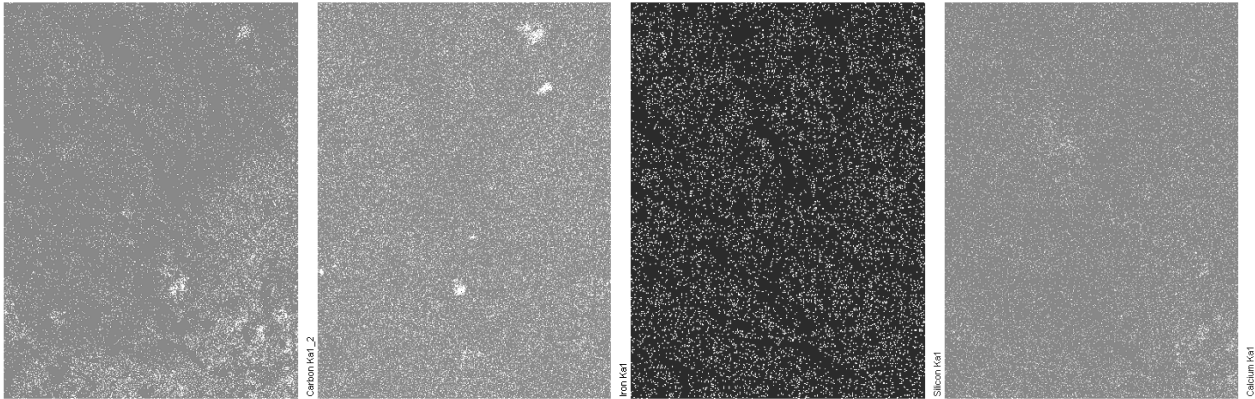
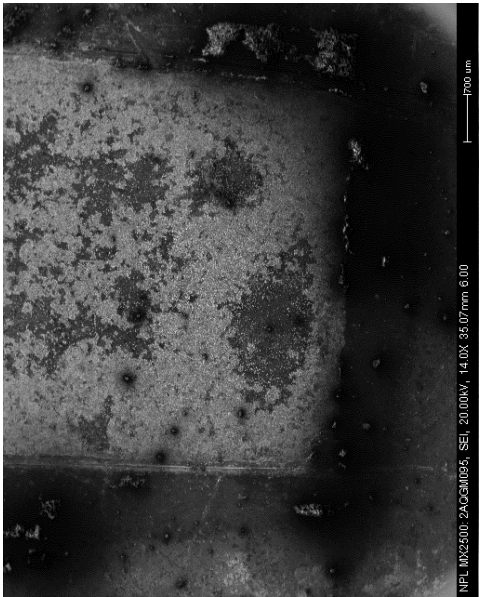
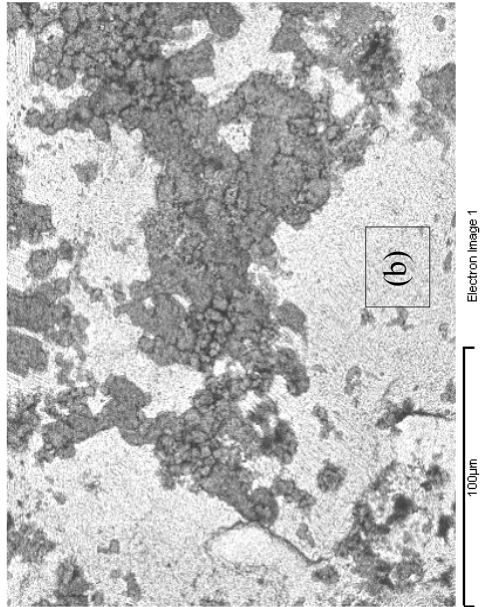
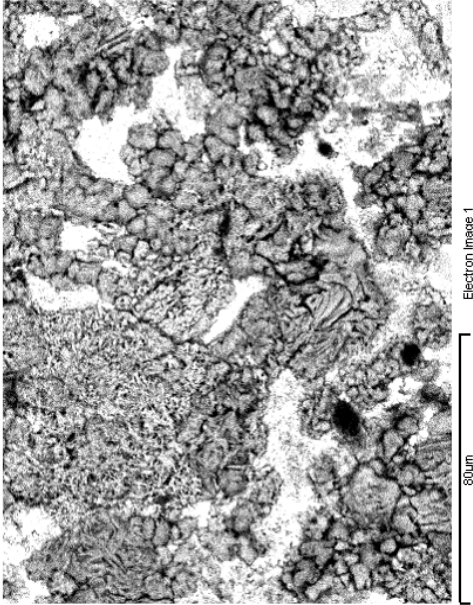
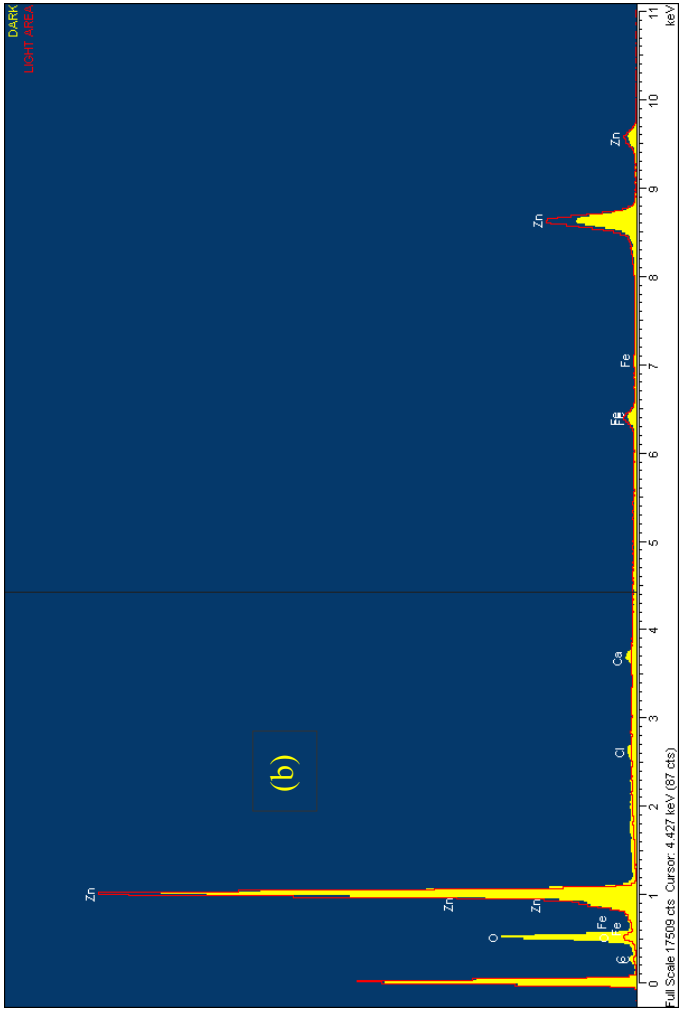


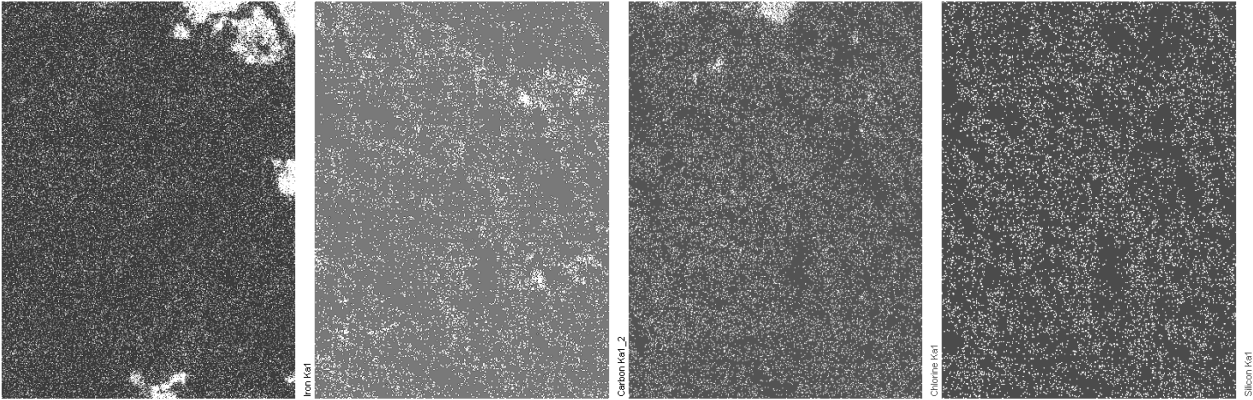
Figure 50, EDX results for 3-pt bend, galvanised steel – Adhesive C, 50 days 4 µl oil



(a)



(b)



(c)

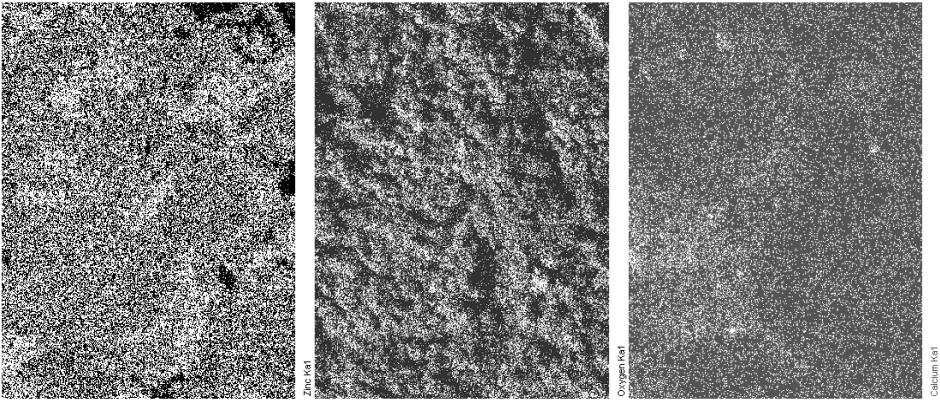


Figure 51, EDX results for pull-off, galvanised steel, Adhesive C, 50 days, 4 µl oil

5.4 GLASS FIBRE REINFORCED POLYPROPYLENE

5.4.1 Test programme

A 2-factor central composite design was used for assessing the bonding surface/bond durability issues for corona discharge treated glass fibre filled polypropylene, Table 6. The robustness of the design to deviations from the set points was particularly important since several corona treatment conditions were estimated to produce the desired surface contact angles based on previous results [14], but these would not necessarily be attained precisely in practice since there may have been electrode and set-up differences between current and previous measurements.

Table 6: Experimental matrix for plastic samples

As Received					Lab Aged					
<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	treatment
<u>90</u>	<u>84</u>	<u>70</u>	<u>56</u>	<u>50</u>	<u>90</u>	<u>84</u>	<u>70</u>	<u>56</u>	<u>50</u>	contact angle
										exposure time (days)
(3)		5		(3)	(3)				(3)	0
	5		5							4
5		25		5						14
	5		5							24
(3)		5		(3)	(3)				(3)	28

The material used was 4 mm thick injection-moulded discontinuous glass fibre reinforced polypropylene plates with a glass fibre weight content of 50%.

Polypropylene is a low surface energy material and consequently difficult to bond. It is normally treated to improve adhesion. Corona treatments were carried out using a Sherman Treaters GX10 corona laboratory bench-top unit with a 280 mm wide U-channel metallic electrode. Different settings (line speed, number of passes, power) were used to vary the surface energy of the treated plastic, Table 7. A previous trial [14] had determined relationships between settings and water contact angle on the treated plastic. This process model relating contact angle, θ , to treatment time, A , and power, B , is:

$$\theta = 94.13 - 141.22 A - 16.71 B + 198.74 A^2 \quad (9)$$

Specimens were prepared as follows 20 mm x 20 mm specimens were cut for contact angle measurement and pull-off testing. 50 mm x 10 mm specimens were cut for 3-point bend testing. Preliminary tests on untreated samples indicated that 3-point bend strengths were in the range 1.0 MPa – 1.5 MPa and pull-off strengths in the range 4.5 MPa – 6.5 MPa.

Care was taken with the handling of the specimens before and after treatment:

- Cleaned thoroughly with isopropanol before treatment
- Stored, and handled, on edge in a desiccator before and after treatment
- Treated within same region of corona treater (to avoid uncontrolled error due to varying field strength or changes in electrode separation with position).

Table 7: Plastic Treatments; expected (from Equation 9) and measured contact angles for freshly prepared samples

	Treatment	Expected Contact Angle (θ) °	Measured (θ) °
1	untreated	94	89
2	1 pass @ 25 m/min, 0.5 kW	80	70
3	1 pass @ 25 m/min, 1 kW	72	67
4	2 passes @ 5 m/min, 0.75 kW	57	63
5	2 passes @ 5 m/min, 1 kW	53	64

5.4.2 Contact angle

The measured contact angles are shown in Figure 52 and Table 7 together with the expected surface angle for the 5 different treatments. The value of using a robust design can clearly be seen, as the contact angles produced did not in most cases match the desired design value and in fact the contact angles were skewed from the originally intended linear distribution with the contact angles for the corona discharge treated samples (treatments 2-5) being grouped around 60-70°. The contact angle determined for the untreated surface (treatment 1) was around 90°, as expected, indicating no change from the original material assessed.

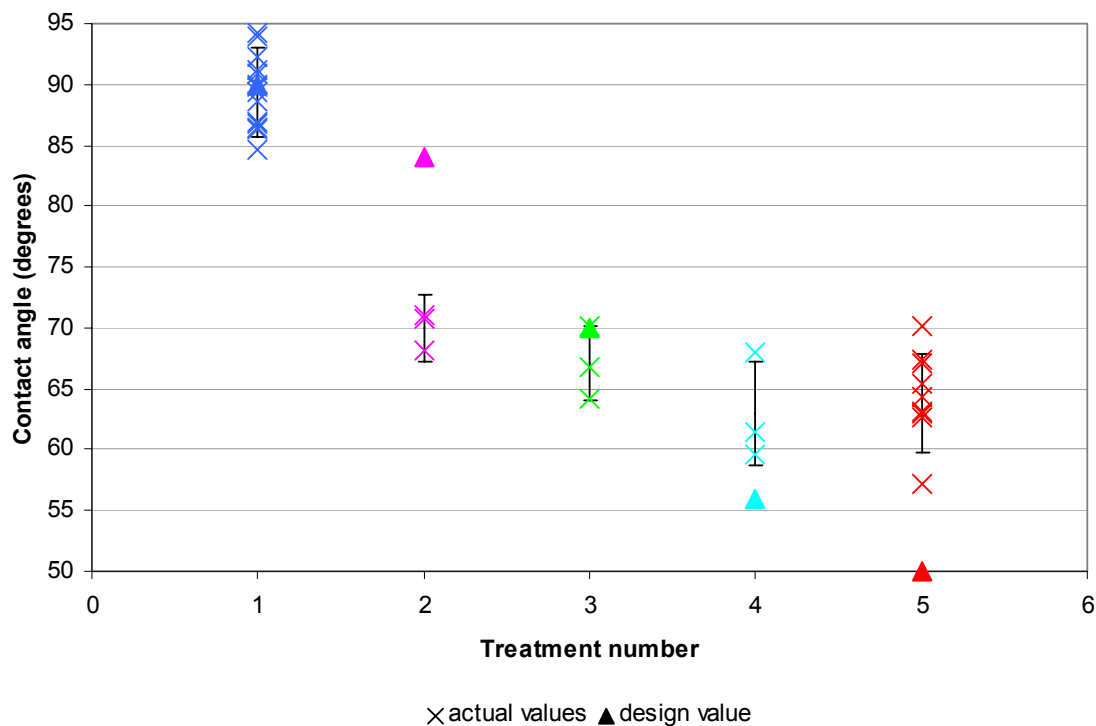


Figure 52: Measured and predicted contact angles for different corona treatments

Some additional measurements were made to investigate the deterioration of the corona treated surfaces in a laboratory environment (23°C and 50% RH) and under hot/wet conditions (70°C and 85% RH). Specimens were handled and stored with care to ensure that nothing came into contact with the treated surface during storage or exposure. Figure 53 shows the results of ageing the surfaces at moderate temperature and humidity in the laboratory. This shows no significant change in the surface contact angle with exposure time

even over a week after treatment. Similarly, the hot/wet conditioned surfaces showed only a slight deterioration in surface wettability after 6 days in an aggressive environment as can be seen in Figure 54. These results indicate the treatment is still effective after several days in uncontrolled storage conditions prior to use.

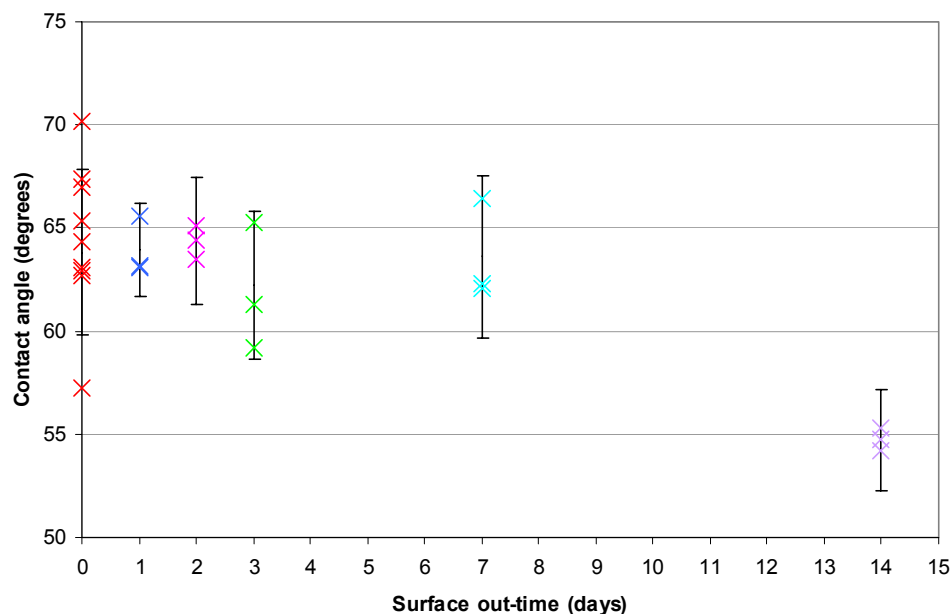


Figure 53: Effect of ageing time under ambient conditions on contact angle

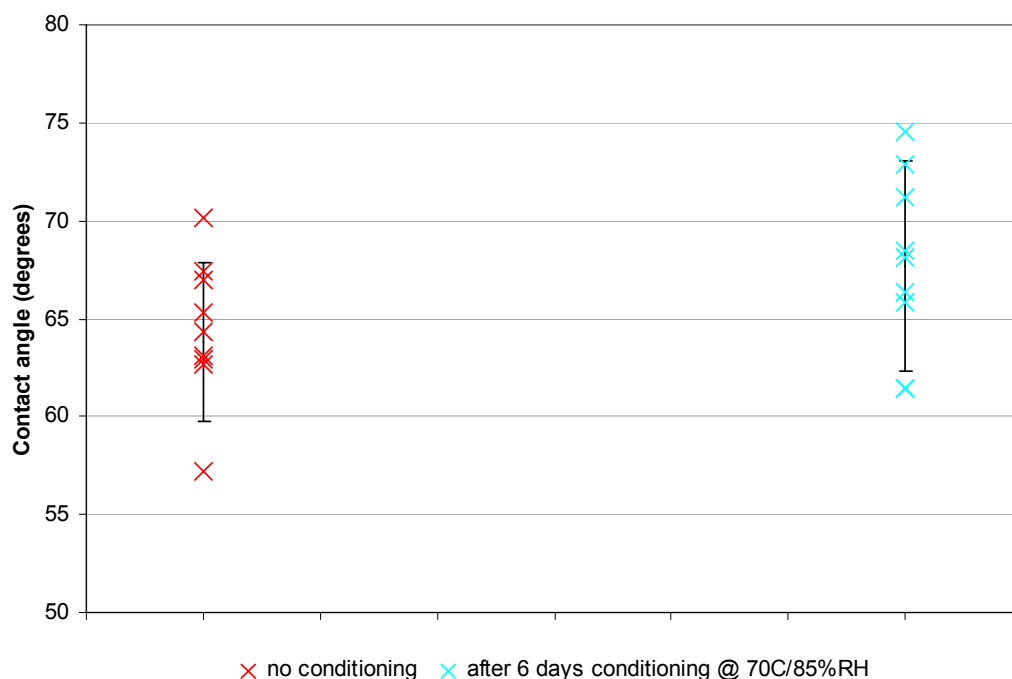


Figure 54: Effect of hot/wet conditioning on contact angle

5.4.3 Pull-off data

Figure 55 shows the pull-off strength results for each of the treatment/condition combinations specified in the design matrix, shown in Table 8, which specifies the combinations corresponding to each run number. Each run consists of 5 repeat samples and error bars are presented showing the standard deviation. Replicate batches were manufactured and tested for runs 1, 4, 8, 10 and 12. For the analysis, the actual contact angle achieved was used rather than the intended value on which the design was based.

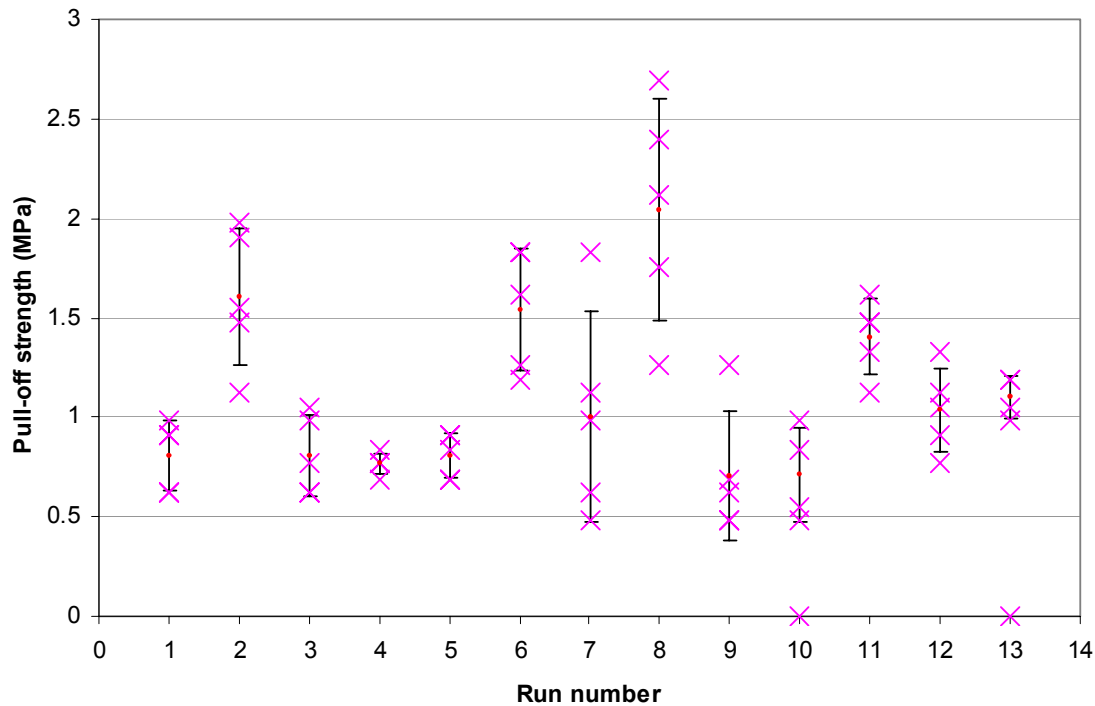


Figure 55: Raw pull-off strength values obtained for corona treated plastic

There were no difficulties with cohesive failures, unlike the other material/adhesive systems investigated, due to the very weak adhesion between the polypropylene and the Adhesive D as shown in Figure 55. Figure 56 shows that failures in these tests were interfacial. Examination of the failure surfaces also revealed that the adhesive layer between the stub and the polypropylene surface was very thin, and, although there is a complete coverage of the stub the grit blasted surface is clearly visible through the adhesive layer. FE analyses suggested that the thickness of the adhesive layer would have very little effect on stress distributions [4].

The low absolute values of strength and the wide scatter in results affects the predictive accuracy of the design. The analysis showed that the pull-off strength was non-linearly dependent on both the contact angle and the ageing time but showed no synergistic effects between the two parameters. The predicted process model is shown below:

$$P = 17.04 - 0.13 * T_{age} + 0.005 * T_{age}^2 - 0.40 * CA + 0.003 * CA^2 \quad (10)$$

where P is the pull-off strength in MPa, T_{age} is conditioning time and CA is contact angle.

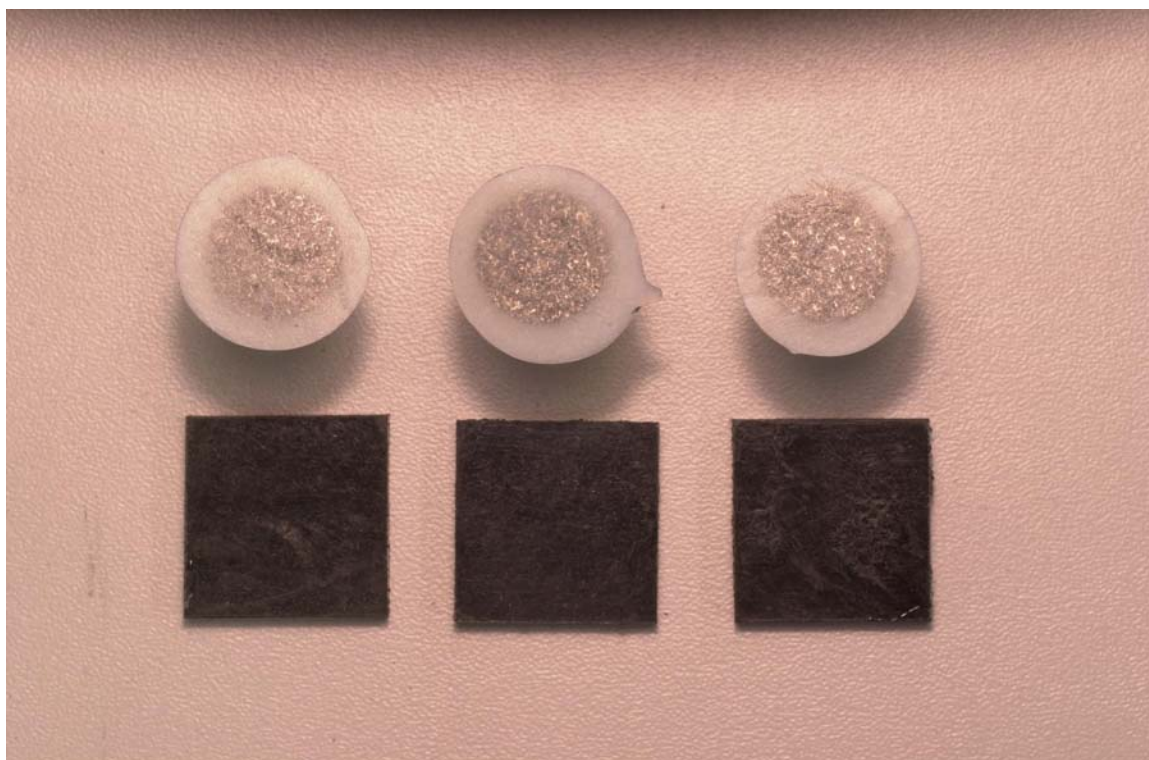


Figure 56: Failure surfaces for pull-off test samples

Table 8: Design matrix (* indicates replicates of centre design point)

Run order	Treatment number (Table 7)	Factor A Conditioning time (T_{age}) (days)	Factor B Contact angle (CA) (degrees) intended/actual
1*	3	14	70 / 67
2	4	24	56 / 63
3	2	4	84 / 70
4*	3	14	70 / 67
5	5	14	50 / 64
6	3	28	70 / 67
7	3	0	70 / 67
8*	3	14	70 / 67
9	4	4	56 / 63
10*	3	14	70 / 67
11	2	24	84 / 70
12*	3	14	70 / 67
13	1	14	90 / 89

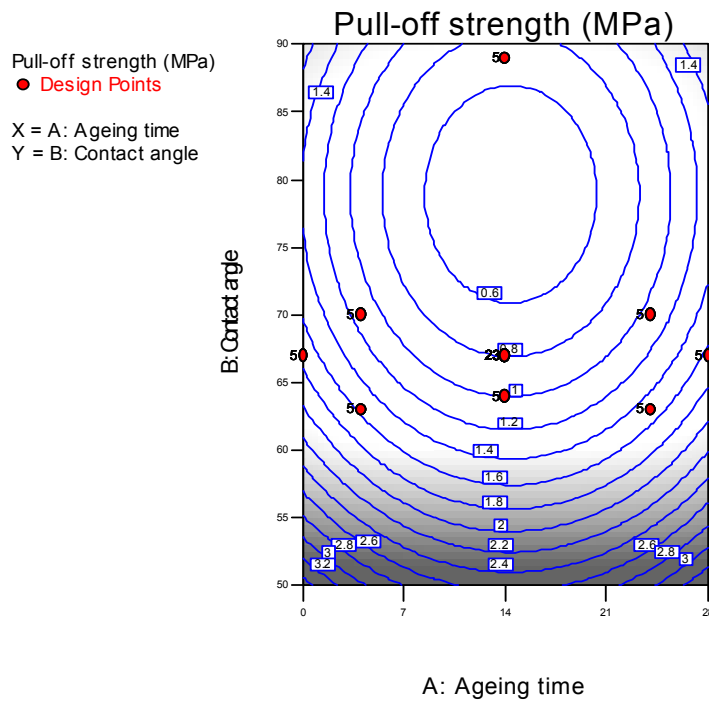


Figure 57: Contour plot of pull-off strength as a function of contact angle and treatment time

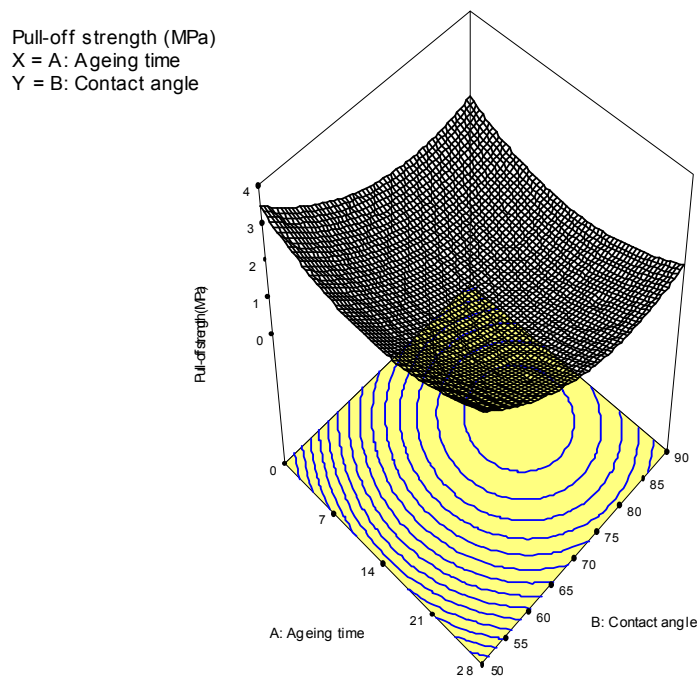


Figure 58: Saddle plot of pull-off strength as a function of contact angle and treatment time

Figures 57 and 58 show the response of pull-off strength according to the statistical prediction for the combination of ageing time and contact angle, both as contour plots and 2-D saddle-shaped surfaces. These plots suggest the best mechanical performance, as measured using pull-off strength, is achieved for unaged surfaces with low contact angles, as might be expected.

5.4.4 Laboratory ageing and check tests

Additional data sets for the combinations of 0 and 28 days conditioning, both as received and lab-aged, at the maximum and minimum treatments were measured to check the accuracy of the predictive estimates and to assess the effect if any of lab ageing on the mechanical performance. The experimental matrix is shown in Table 9. A batch of 3 samples were tested for each run listed, the raw data is shown in Figure 59. These data showed no significant effect due to laboratory ageing of the samples prior to bond manufacture.

Table 9: Additional simple 3 factor factorial design

Run order	Treatment number	Factor A Conditioning time (T_{age}) (days)	Factor B Lab ageing (L_{age}) (days)	Factor C Contact angle (CA) (degrees) intended/actual
1	5	0	0	50 / 64
2	1	0	0	90 / 89
3	5	0	7	50 / 64
4	1	0	7	90 / 89
5	5	28	0	50 / 64
6	1	28	0	90 / 89
7	5	28	7	50 / 64
8	1	28	7	90 / 89

These predictions, shown in Table 10, are not as accurate as would usually be expected due to the contact angle and conditioning periods chosen for the checkpoints being on the periphery of the design space where predictions are weakest.

Table 10: Comparison of predicted to measured responses (average values)

Factor combination/test response	Predicted values	Measured values
0 days ageing + 89°	1.64	1.64
Pull off strength (MPa)		
0 days ageing + 64°	1.94	1.43
Pull off strength (MPa)		
28 days ageing + 89°	1.54	1.22
Pull off strength (MPa)		
28 days ageing + 64°	1.85	1.15
Pull off strength (MPa)		

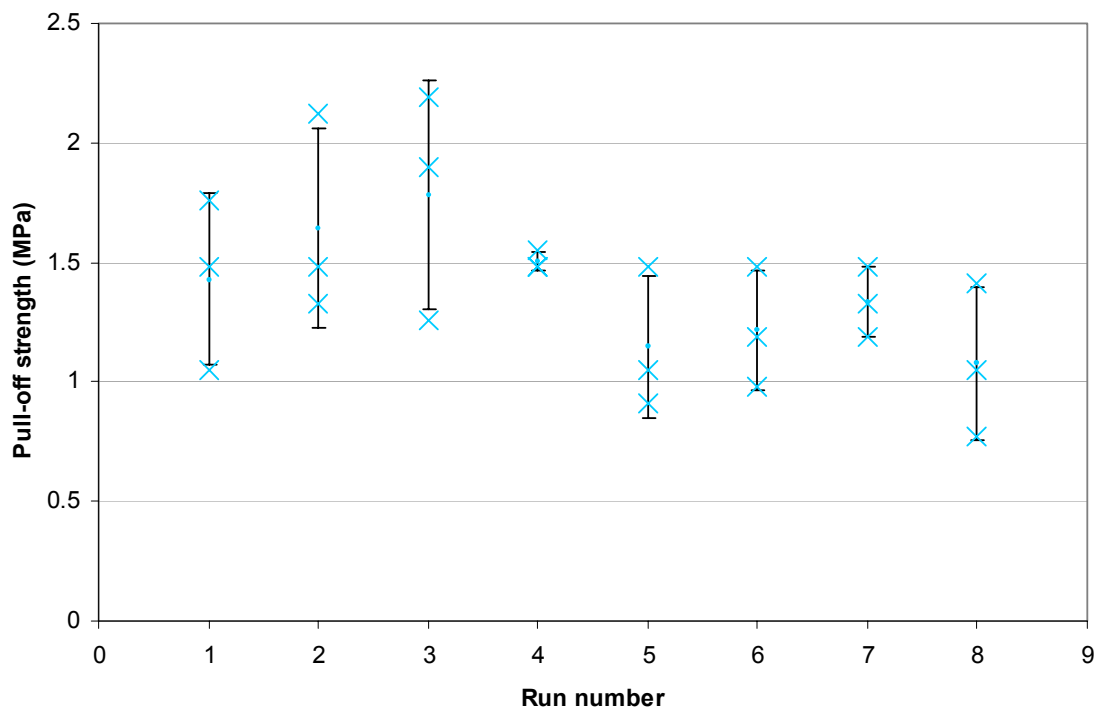


Figure 59: Pull-off data for the additional check tests

5.4.5 3-point bend tests

Bend test specimens were manufactured in parallel with the pull-off test specimens. However, the adhesive has a low viscosity. This leads to difficulties with specimen preparation as the adhesive flows out from the mould creating extensive spew fillets ('flash') around the edges of the bonded region, Figure 55. These thin fillets would have a significant effect on the initiation of failure in the tests. Attempts to remove the flash, by cutting them off using a sharp scalpel blade, tended to damage the bond at the critical end of the bond line. This often led to debonding before the sample could be tested.

The application of the 3-point bend test to this system was also complicated by the extremely poor adhesion and the low resolution of the test. The difficulty of interpreting failure from the force extension curves was such that the load at failure was virtually impossible to identify. Therefore, 3-point test data is not included in this study.

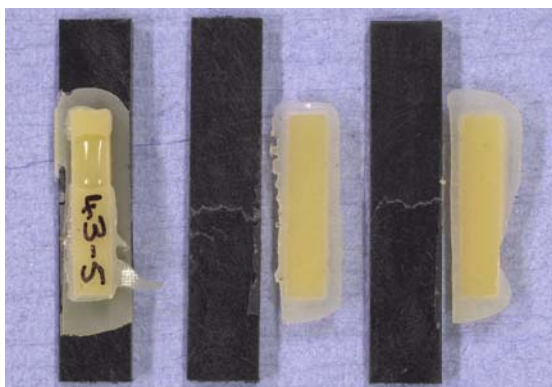


Figure 60: 3-point bend samples, polypropylene and adhesive D

6. CONCLUDING REMARKS

It is somewhat disappointing that the studies do not show stronger correlations between the surface characteristics and mechanical performance of the bonds. The measured strength of the bonds depends on the changes in both the interface strength and the cohesive strength of the adhesive. In some of the tests performed, the reduction of the cohesive strength of the adhesive masks any degradation of bond performance. With hindsight, it would have been worthwhile to include some additional tests using well-established test geometries, such as lap shear, to confirm some of the observations. Overall, there have been few correlations established between the surface characteristics studied and the bond performance.

However, several useful observations have been made:

- The aluminium surfaces studied appear to provide bond strengths that exceed the cohesive strength of the adhesive under the ageing conditions imposed – the pull-off test seems to have provided information on the cohesive strength of the adhesive rather than the interface strength of the system.
- The data from the 3-point bend tests on aluminium samples, where failure is interfacial, are scattered but indicate that the strength of the bond is not degraded significantly by hot/wet exposure.
- The surface characteristics of the different aluminium treatments have provided little correlation with bond strengths, as the interface strength seems to have degraded little whilst the cohesive strength of the adhesive was significantly reduced by uptake of moisture.
- Analysis of the exposed surface and the surface under the bond of the galvanised steel samples revealed different modes of surface degradation. The chemical environment under the adhesive is substantially different to that of the open surface. The study of travelling adherend specimens to establish changing surface properties is therefore of questionable benefit.
- Correlations were observed between the contact angle measurements and bond strengths of the galvanised steel – adhesive C samples. However, given the different local surface chemistry of the exposed and bonded regions this is more likely to be coincidence than a useful tool to predict bond performance.
- The corona treatment remains effective for several days after surface treatment as indicated by the stability of the contact angle and the pull-off strength data.
- There is a correlation between bond performance and contact angle of water on polypropylene, suggesting that contact angle is a useful property to measure in this system.
- The 3-point bend test, where moisture and other chemicals diffuses to the interface rapidly, can lead to accelerated degradation at the surface in comparison to other test geometries and, hence, offers a severe exposure test for harsh environments.

ACKNOWLEDGEMENTS

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ANNEX I TEST SCHEDULES

Anodised aluminium + adhesive A

as received						lab aged						exposure time (days)
<u>treatment</u> 1	2	3	4	5	6	<u>treatment</u> 1	2	3	4	5	6	
5	5	5	5	5	5	3-5	3-5	3-5	3-5	3-5	3-5	0
5	5	5	5	5	5							18
5	5	5	5	5	5	3-5	3-5	3-5	3-5	3-5	3-5	36

Total = 126-150 specimens for 3-point bend and 126-150 for pull off

- Treatment 1 – mill finish
- Treatment 2 – light clean
- Treatment 3 – full clean
- Treatment 4 – full clean + 25nm barrier
- Treatment 5 – light clean + 25nm barrier
- Treatment 6 - full clean + 25nm barrier + 75nm porous

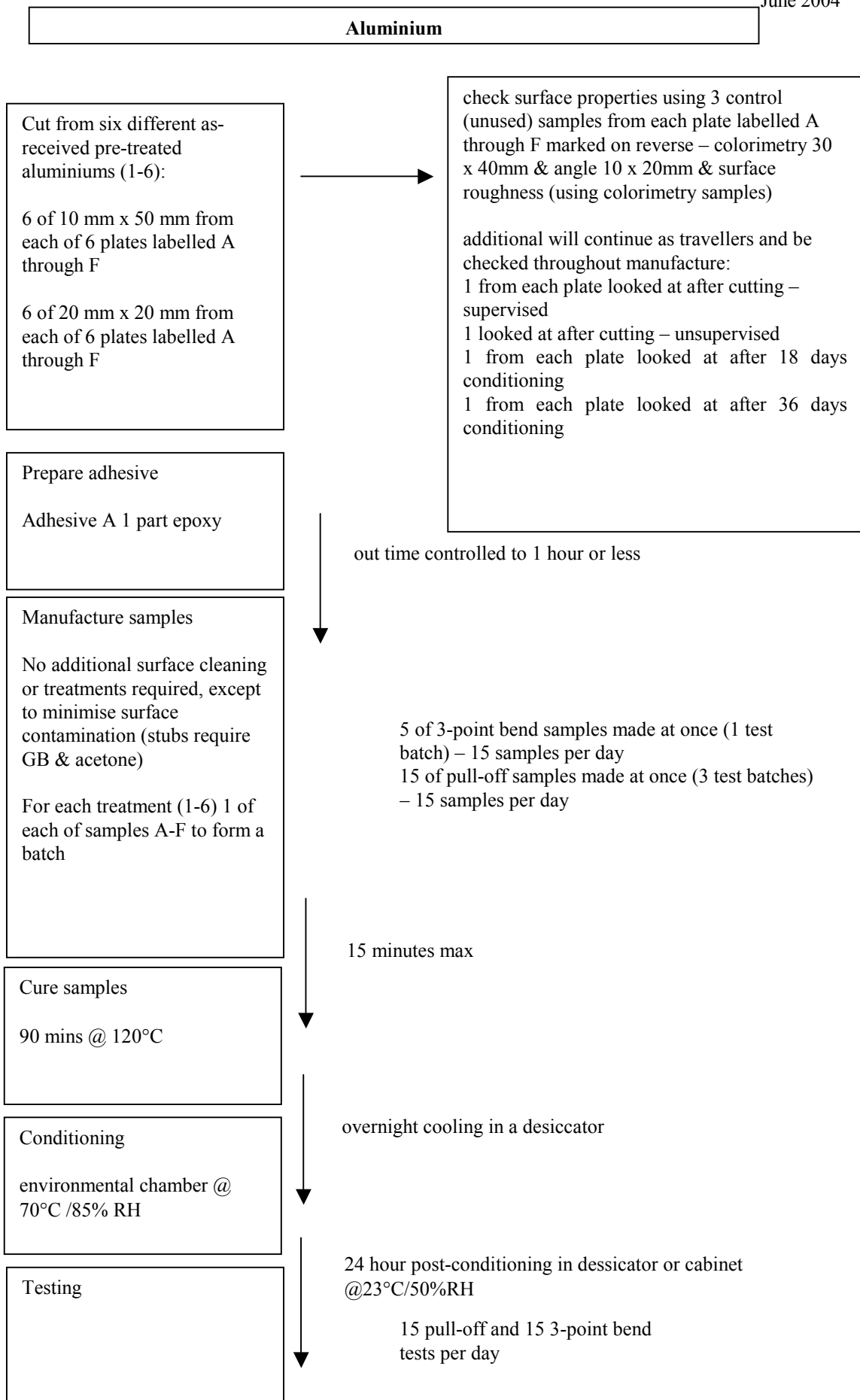
Manufacture sequence for as-received samples

Time (days)	Treatment (1-6)	Samples	Manufactured on	Placed in conditioning cabinet
0	2,4,6	3 x 5 pull-off & 3 x 5 3-point bend	Day 1 (Thursday April 24th)	
36	1,3,5	3 x 5 pull-off & 3 x 5 3-point bend	Day 6 (Tuesday April 29th)	Day 7 am (Wednesday April 30th)
18	2,4,6	3 x 5 pull-off & 3 x 5 3-point bend	Day 7 (Wednesday April 30th)	Day 8 am (Thursday May 1st)
18	1,3,5	3 x 5 pull-off & 3 x 5 3-point bend	Day 8 (Thursday May 1st)	Day 9 am (Friday May 2nd)
36	2,4,6	3 x 5 pull-off & 3 x 5 3-point bend	Day 13 (Tuesday May 6th)	Day 14 am (Wednesday May 7th)
0	1,3,5	3 x 5 pull-off & 3 x 5 3-point bend	Day 14 (Wednesday May 7th)	

Test sequence for as-received samples

Time (days)	Treatment (1-6)	Samples	Removed from conditioning cabinet	Tested on
0	2,4,6	3 x 5 pull-off & 3 x 5 3-point bend		Day 2 (Friday April 25th)
0	1,3,5	3 x 5 pull-off & 3 x 5 3-point bend		Day 15 (Thursday May 8th)
18	2,4,6	3 x 5 pull-off & 3 x 5 3-point bend	Day 26 am (Monday May 19th)	Day 27 (Tuesday May 20th)
18	1,3,5	3 x 5 pull-off & 3 x 5 3-point bend	Day 27 am (Tuesday May 20th)	Day 28 (Wednesday May 21st)
36	1,3,5	3 x 5 pull-off & 3 x 5 3-point bend	Day 43 am (Thursday June 5th)	Day 44 (Friday June 6th)
36	2,4,6	3 x 5 pull-off & 3 x 5 3-point bend	Day 50 am (Thursday June 12th)	Day 51 (Friday June 13th)

- Repeat excluding 18 day runs for 2 month lab aged samples after 2 month adherend surface out-time [require 15 template moulds and 90 pull-off stubs in use at any one time]



- Repeat process after 2 months for lab aged material

Oiled Galvanised Steel + Adhesive C

<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	treatment
no oil	1 μ l	4 μ l	7 μ l	8 μ l	oil volume
					exposure time (days)
(3)		5		(3)	0
	5		5		6
5		25		5	25
	5		5		44
		5			50

Total = 71 specimens for 3-point bend and 71 for pull off

- Additional specimens (marked by brackets) used to check model
- 1 μ l ~2 μ m oil layer, (= 2.4 μ l for 30x40mm colorimetry samples),
- 4 μ l ~8 μ m oil layer, (= 9.6 μ l for 30x40mm colorimetry samples),
- 7 μ l ~14 μ m oil layer, (=16.8 μ l for 30x40mm colorimetry samples), and
- 8 μ l ~16 μ m oil layer, (= 19.2 μ l for 30x40mm colorimetry samples).

Manufacture sequence for samples

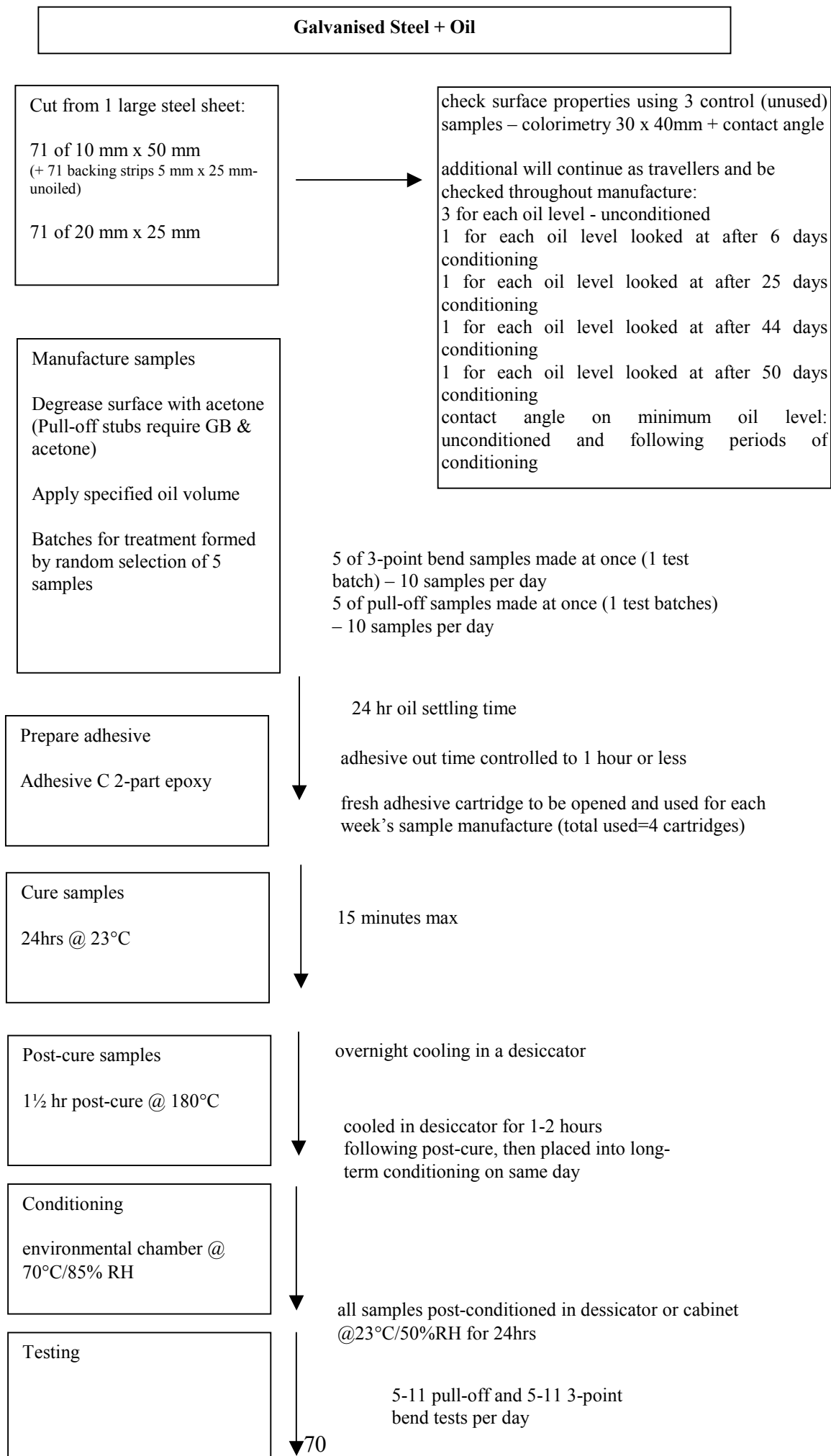
Time (days)	Oil volume (ml)	Samples	Oil applied on	Manufactured on	Post-cured, cooled and placed in conditioning cabinet
0	8	1 x 3 pull-off & 1 x 3 3-point bend	Day 1 (Tuesday Nov 11th)	Day 2 (Wednesday Nov 12th)	
25-1	4	1 x 5 pull-off & 1 x 5 3-point bend			Day 3 am (Thursday Nov 13th)
0	0	1 x 3 pull-off & 1 x 3 3-point bend			
25	8	2 x 5 pull-off & 2 x 5 3-point bend	Day 8 (Tuesday Nov 18th)	Day 9 (Wednesday Nov 19th)	Day 10am (Thursday Nov 20th)
44	7				
6	1	2 x 5 pull-off & 2 x 5 3-point bend	Day 9 (Wednesday Nov 19th)	Day 10 (Thursday Nov 20th)	Day 11 am (Friday Nov 21st)
25-2	4				
25-3	4	2 x 5 pull-off & 2 x 5 3-point bend	Day 14 (Monday Nov 24th)	Day 15 (Tuesday Nov 25th)	Day 16 am (Wednesday Nov 26th)
50	4				
0	4	2 x 5 pull-off & 2 x 5 3-point bend	Day 15 (Tuesday Nov 25th)	Day 16 (Wednesday Nov 26th)	
25-4	4				Day 17am (Thursday Nov 27th)
25-5	4	2 x 5 pull-off & 2 x 5 3-point bend	Day 22 (Tuesday Dec 2nd)	Day 23 (Wednesday Dec 3rd)	Day 24 am (Thursday Dec 4th)
6	7				
44	1	2 x 5 pull-off & 2 x 5 3-point bend	Day 23 (Wednesday Dec 3rd)	Day 24 (Thursday Dec 4th)	Day 25 am (Friday Dec 5th)
25	0				

Test sequence

Time (days)	Oil volume (ml)	Samples	Removed from conditioning cabinet	Tested on
0	8	1 x 3 pull-off & 1 x 3 3-point bend		Day 3 (Thursday Nov 13th)
0	0	1 x 3 pull-off & 1 x 3 3-point bend		
0	4	1 x 5 pull-off & 1 x 5 3-point bend		Day 17 (Thursday Nov 27th)
6	1	1 x 5 pull-off & 1 x 5 3-point bend	Day 17 am (Thursday Nov 27th)	Day 18 (Friday Nov 28th)
25-1	4	1 x 5 pull-off & 1 x 5 3-point bend	Day 28 am (Monday Dec 8th)	Day 29 (Tuesday Dec 9th)
6	7	1 x 5 pull-off & 1 x 5 3-point bend	Day 30 am (Wednesday Dec 10th)	Day 31 (Thursday Dec 11th)
25	8	1 x 5 pull-off & 1 x 5 3-point bend	Day 35 am (Monday Dec 15th)	Day 36 (Tuesday Dec 16th)
25-2	4	1 x 5 pull-off & 1 x 5 3-point bend	Day 36 am (Tuesday Dec 16th)	Day 37 (Wednesday Dec 17th)
25-3	4	1 x 5 pull-off & 1 x 5 3-point bend	Day 42 am (Monday Dec 22nd)	Day 43 (Tuesday Dec 23rd)
25-4	4	1 x 5 pull-off & 1 x 5 3-point bend		
25-5	4	1 x 5 pull-off & 1 x 5 3-point bend	Day 49 am (Monday Dec 29th)	Day 50 (Tuesday Dec 30th)
25	0	1 x 5 pull-off & 1 x 5 3-point bend	Day 50 am (Tuesday Dec 30th)	Day 51 (Wednesday Dec 31st)
44	7	1 x 5 pull-off & 1 x 5 3-point bend	Day 56 am (Monday Jan 5th)	Day 57 (Tuesday Jan 6th)
50	4	1 x 5 pull-off & 1 x 5 3-point bend	Day 66 am (Thursday Jan 15th)	Day 67 (Friday Jan 16th)
44	1	1 x 5 pull-off & 1 x 5 3-point bend	Day 70 am (Monday Jan 19th)	Day 71 (Tuesday Jan 20th)

[require 11 template moulds and 71 pull-off stubs in use at any one time]

[require < 10ml oil in total]



Corona discharge treated polypropylene + Adhesive D

as received					lab aged					
<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	treatment
<u>90</u>	<u>84</u>	<u>70</u>	<u>56</u>	<u>50</u>	<u>90</u>	<u>84</u>	<u>70</u>	<u>56</u>	<u>50</u>	contact angle
										exposure time (days)
(3)		5		(3)	(3)				(3)	0
	5		5							4
5		25		5						14
	5		5							24
(3)		5		(3)	(3)				(3)	28

Total = 89 specimens for 3-point bend and 89 for pull off

All specimens treated at constant electrode separation (5.5 mm) on one side only:

- Treatment 1 – untreated
- Treatment 2 – 1 pass @ 25 m/min, 0.5 kW
- Treatment 3 – 1 pass @ 25 m/min, 1 kW
- Treatment 4 – 2 passes @ 5 m/min, 0.75 kW
- Treatment 5 – 2 passes @ 5 m/min, 1 kW
- Additional specimens (marked by brackets and in blue) used to check model and test for lab ageing

Treatment sequence

Time (days)	Treatment (1-5)	Samples (2 from each of numbered plates, 1x3pt-bend & 1xpull-off)								
14-1	3	1	2	3	4		6			
24	4	1	2	3			6	7		
14-2	3	1	2	3	4				8	
4	2	1	2				6	7	8	
14	5	1	2	3	4	5				
28	3		2	3	4	5				9
0	3	1					6	7	8	9
14-3	3				4	5	6	7		9
4	4			3	4	5			8	9
14-4	3	1	2			5		7	8	
24	2				4	5		7	8	9
14-5	3			3	4		6	7		9
14	1 – no treatment					5	6	7	8	9
0	5		2	3	4					
28	5		2			5			8	
28L	5			3			6			9
0L	5	1			4			7		
0L ₂	1 – no treatment	1				5				9
28L	1 – no treatment						6	7	8	
0	1 – no treatment					5	6			9
28	1 – no treatment	1	2	3						

Manufacture sequence for samples

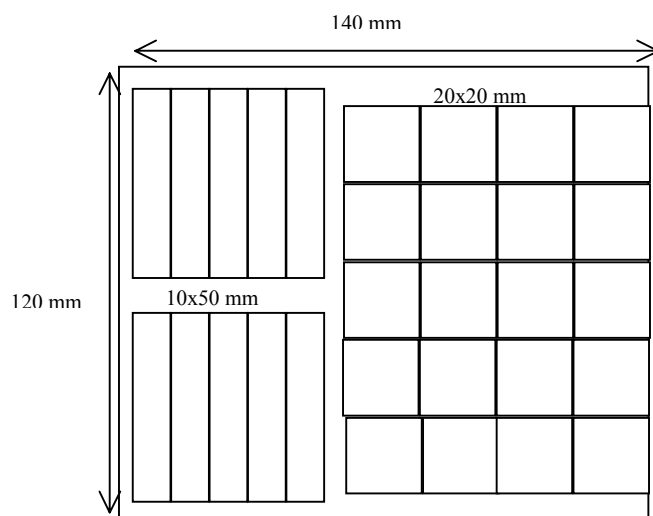
Time (days)	Treatment (1-5)	Samples	Manufactured on	Placed in conditioning cabinet
14-1	3	5 x 5 pull-off & 5 x 5 3-point bend	Day 1 (Tuesday April 27th)	Day 2 am (Wednesday April 28th)
24	4			
4	2			
14-2	3			
14	5			
28	3	1 x 5 pull-off & 1 x 5 3-point bend	Day 2 (Wednesday April 28th)	Day 3 am (Thursday April 29th)
28	(1, 5)	2 x 3 pull-off & 2 x 3 3-point bend		
14-3	3	1 x 5 pull-off & 1 x 5 3-point bend		
0	3	1 x 5 pull-off & 1 x 5 3-point bend		
0	(1, 5)	2 x 3 pull-off & 2 x 3 3-point bend		
14	1	5 x 5 pull-off & 5 x 5 3-point bend	Day 3 (Thursday April 29th)	Day 4 am (Friday April 30th)
14-4	3			
4	4			
24	2			
14-5	3			
0L	(1, 5)	2 x 3 pull-off & 2 x 3 3-point bend	Day 8 (Tuesday May 4th)	
28L	(1, 5)	2 x 3 pull-off & 2 x 3 3-point bend		Day 9 am (Wednesday May 5th)

- L – indicates lab-aged samples
- batch numbers in blue and bracketed indicate batches made up of only 3 samples

Test sequence

Time (days)	Treatment (1-5)	Samples	Removed from conditioning cabinet	Tested on
0	(5)	1 x 3 pull-off & 1x 3 3-point bend		Day 4 (Friday April 30th)
0	3	1 x 5 pull-off & 1 x 5 3-point bend		
0	(1)	1 x 3 pull-off & 1x 3 3-point bend		
4	2	1 x 5 pull-off & 1 x 5 3-point bend	Day 6 am (Sunday May 2nd)	Day 8 (Tuesday May 4th)
4	4	1 x 5 pull-off & 1 x 5 3-point bend	Day 8 am (Tuesday May 4th)	Day 9 (Wednesday May 5th)
0L	(1)	2 x 3 pull-off & 2 x 3 3-point bend		
0L	(1)			
14-2	3	3 x 5 pull-off & 3 x 5 3-point bend	Day 16 am (Wednesday May 12th)	Day 17 (Thursday May 13th)
14	5			
14-1	3			
14-3	3	1 x 5 pull-off & 1 x 5 3-point bend	Day 17 am (Thursday May 13th)	Day 18 (Friday May 14th)
14-5	3	3 x 5 pull-off & 3 x 5 3-point bend	Day 18 am (Friday May 14th)	Day 21 (Monday May 17th)
14	1			
14-4	3			
24	4	1 x 5 pull-off & 1 x 5 3-point bend	Day 26 am (Saturday May 22nd)	Day 28 (Monday May 24th)
24	2	1 x 5 pull-off & 1 x 5 3-point bend	Day 28 am (Monday May 24th)	Day 29 (Tuesday May 25th)
28	(1)	1 x 3 pull-off & 1x 3 3-point bend	Day 31 am (Thursday May 27th)	Day 32 (Friday May 28th)
28	3	1 x 5 pull-off & 1 x 5 3-point bend		
28	(5)	1 x 3 pull-off & 1x 3 3-point bend		
28L	(5)	2 x 3 pull-off & 2 x 3 3-point bend	Day 37 am (Wednesday June 2nd)	Day 38 (Thursday June 3rd)
28L	(1)			

[require 27 template moulds and 89 pull-off stubs in use at any one time]



Cutting Plan Per Plate

Additional surface measurements

Sample type	Plates									
	<i>P1</i> <i>highest θ</i>	<i>P2</i> <i>mid θ</i>	<i>P3</i> <i>lowest θ</i>	<i>P4</i>	<i>P5</i>	<i>P6</i>	<i>P7</i>	<i>P8</i>	<i>P9</i>	<i>P10</i> <i>(spare)</i>
3 pt bend	10	10	10	10	10	10	10	9	10	
pull-off	10	10	10	10	10	10	10	9	10	
θ pre-treatment	1	1	1	1	1	1	1	1	1	4
θ post-treatment 5	1	1	1	1	1	1	1	1	1	4
θ post-treatment 4	1	1	1							4
θ post-treatment 3	1	1	1							4
θ post-treatment 2	1	1	1							4
θ post-treatment 5 + 6 days conditioning	1	1	1	1	1	1	1	1	1	
θ post-treatment 5 + 1 day lab ageing				1	1	1				
θ post-treatment 5 + 2 days lab ageing				1	1	1				
θ post-treatment 5 + 3 days lab ageing				1	1	1				
θ post-treatment 5 + 7 days lab ageing				1	1	1				
θ post-treatment 5 + 14 days lab ageing				1	1	1				

