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**Review of Surface
Characterisation
Techniques for
Adhesive Bonding**

W R Broughton and M J Lodeiro

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W R Broughton and M J Lodeiro
NPL Materials Centre
National Physical Laboratory
Teddington, Middlesex
TW11 0LW, UK

ABSTRACT

This report examines analytical and chemical analysis techniques that can be used for surface characterisation of metals, plastics (including fibre-reinforced plastic composites) and other substrates. The report examines physical and analytical techniques available for evaluation of surface treatments to ensure optimum bond strength and environmental resistance for specific service conditions. Techniques range from optical (or non-contact) methods to X-ray photoelectron spectroscopy (XPS). The report covers measurement of physical characteristics (surface roughness and morphology, hardness and oxide layer thickness) and chemical characteristics (functional groups and contaminants on substrate surface). Physical techniques, such as surface roughness, hardness and scratch tests, contact angle (for wettability), gloss/reflectivity, ellipsometry and colorimetry, and surface resistivity are discussed in terms of fitness for purpose for on-line inspection (i.e. quality control) and limitations. Data are provided to demonstrate the effectiveness of the techniques in differentiating between poor and good surface treatments and for assessing the maximum allowable time between surface preparation and bonding or priming the substrate. The report includes a review of key parameters and surface characteristics associated with mechanical abrasion, solvent cleaning, chemical and electrochemical (i.e. anodising), corona discharge, plasma, flame and laser surface treatments.

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National Physical Laboratory
Teddington, Middlesex, UK, TW11 0LW

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Approved on behalf of Managing Director, NPL, by Dr C Lea,
Head of NPL Materials Centre.

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1 INTRODUCTION

Surface preparation is recognised as the most critical step in the adhesive bonding process and considerable effort is often expended in optimising the surface treatment. The selection of surface treatments is usually on the basis of manufacturers recommendations, although technical, environmental and economic considerations, such as costs and time involved in preparation, also play a role in the selection process. Correct surface preparation is essential for good bond strength and maintaining long-term structural integrity of bonded joints. Unsatisfactory surface preparation will result in the bond failing adhesively and unpredictably at the adhesive/adherend interface. An essential part of this exercise is the ability to monitor and control changes in surface morphology and chemistry in order to ensure reliable performance of the bonded component.

This report examines analytical and chemical analysis techniques that can be used for surface characterisation of metals, plastics (including fibre-reinforced plastic composites) and other substrates. Techniques range from simple, inexpensive methods (e.g. gloss or hardness tests) to specialised, high cost techniques (e.g. X-ray photoelectron spectroscopy). The report covers measurement of physical characteristics (roughness, wettability, hardness, reflectivity and resistivity) and chemical characteristics (functional groups and contaminants on substrate surface). The report was prepared as part of the research undertaken at the National Physical Laboratory for the Department of Trade and Industry funded project on “Measurements for Materials Systems (MMS) Programme – Interfacial Adhesion Strength”.

The report consists of five sections (including the Introduction). Section 2 briefly discusses the primary mechanisms of adhesion. Section 3 provides an overview of various methods that have been developed to control the surface and promote good adhesion. The techniques are examined in terms of material compatibility, equipment requirements and critical processing factors (i.e. time, temperature, concentration, voltage, etc.) influencing adhesion. Surface characterisation techniques are examined Section 4 with concluding remarks in Section 5.

2. ADHESION

The primary mechanisms involved in the development of an efficient bond are:

Mechanical Adhesion: Related to the degree of roughness and as a consequence friction of the adherend surface. A certain amount of bonding can be expected purely from the mechanical interlocking of the two contacting surfaces, increasing the total surface area available for chemical bonding and creating a convoluted failure path where the adhesive penetrates crevices on the adherend surface. Although the tensile strength of the bond can depend on the re-entrant angles on the adherend surface, shear strength increases significantly with increased roughness.

Intrinsic Adhesion: This is a measure of the interatomic and intermolecular forces acting in the bulk and surface layers of liquids and solids, and across interfaces between phases. It is these forces that are generally responsible for physical-chemical bonding between an adhesive and a substrate. Provided sufficient intimate molecular contact occurs at the interface then the two materials will adhere (i.e. formation of physical-chemical bonds) because of the short-range interatomic and intermolecular forces acting between atoms and molecules in the surfaces of the adhesive and substrate [1-2].

These interfacial forces can consist of secondary bonds, such as van der Waals forces (dipole-dipole and dispersion) and hydrogen bonding, or chemical bonds (i.e. ionic, covalent or metallic), also referred to as primary bonds. Chemical bonding that occurs across the interface is termed chemisorption. The formation of covalent bonds, resulting in stable linkage, can occur through the reaction between a functional grouping on the adherend surface and a compatible group in the adhesive. Adhesives that have surface energies less than that of the adherend will readily wet the surface and yield good bonds. The extent of wetting depends on the differences in surface free energies of the solid, liquid and subsequent interface. Adherend surfaces are usually given surface treatments (e.g. chemical etching, corona discharge and plasma treatments) to create compatible groups (see Section 3). These treatments serve to increase the concentration of oxygen and nitrogen containing functional groups on the adherend surface since these species are considered to enhance adhesion by encouraging the formation of strong covalent or hydrogen bonds.

3. SURFACE TREATMENTS

The “surface” of metal and plastic substrates is generally complex, consisting of several layers with ill-defined boundaries and properties different from the bulk material. For example, the surface of a metallic substrate consists of a segregation layer directly in contact with the bulk metal, a metal oxide layer, a hydroxide and water layer, a layer of absorbed contaminants and finally a layer containing oil, grease and dust (Figure 1). Although, the segregation layer is metallic in composition, the chemical composition of the layer differs from the bulk metal due to migration or segregation of alloying element and impurities. The absorbed contaminants may include sulphur, nitrogen, carbon compounds or other pollutants from the atmosphere or manufacturing environment. The outer layer may include rolling oils, lubricants, corrosion inhibitors, etc. Most metallic surfaces (e.g. stainless steel, aluminium, titanium and nickel) are coated with metal oxides to which a layer of water is attached. Surface layers may be poorly attached forming a weakness in the joint. The surface characteristics will depend on material processing, storage and handling.

Process Oil/Dust

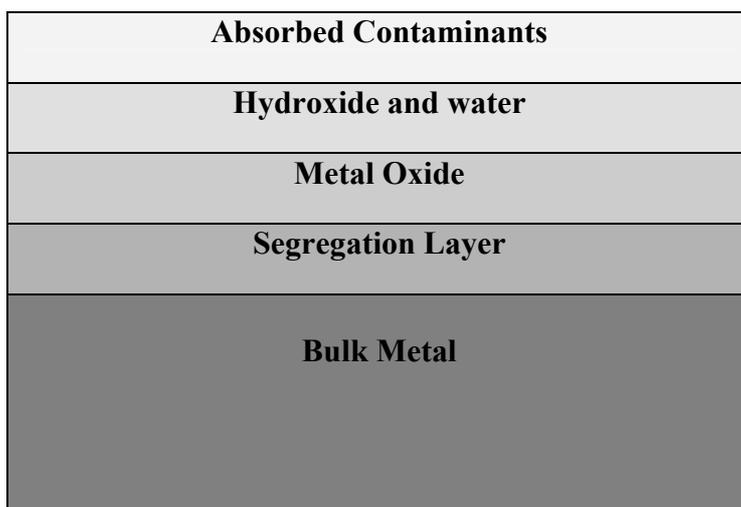


Figure 1: Schematic representation of a metal surface [2].

It may be necessary to modify the surface layers (i.e. surface characteristics) in order to ensure optimal adhesion and long-term durability. A number of different surface treatments have been developed for this purpose. Surface treatments can be classified as either passive or active [2]. Passive surface treatments (e.g. solvent washing and mechanical abrasion) clean the surface, alter topography and remove weakly attached surface layers without altering the surface chemistry. Active surface treatments (e.g. anodising, chemical etching, corona discharge and plasma treatment) alter the surface chemistry (i.e. introduction of functional groups). This section examines passive and active surface treatments used for metals, plastics and other substrates.

3.1 SOLVENT CLEANING

Mechanically abraded surfaces are usually cleaned with a polar solvent (e.g. acetone, methanol, isopropanol and methyl ethyl ketone (MEK)) before and after mechanical abrasion. Solvent cleaning methods include wiping, immersion, spraying, vapour degreasing and ultrasonic scrubbing. Solvent wiping is the most common method and is adequate for removing most of the organic contaminants. Substrates are often initially degreased to remove gross organic contamination and process films. This is necessary to prevent imbedding of contaminants into the substrate by the mechanical abrasion process and to avoid contamination of the abrasive medium. Mechanically abraded surfaces are usually cleaned with a solvent to remove residue and possible contaminants remaining from the abrasion process. Sufficient time is required between solvent wiping and mechanical abrasion to allow the surface to dry.

Immersing the substrate in an ultrasonic bath containing the solvent can enhance the cleaning process. Ultrasonic scrubbing uses high frequency sound waves to agitate the solvent with the formation and collapse of tiny bubbles on the substrate enhancing the cleaning mechanism. It is an effective method of removing strongly adherent contaminants and insoluble materials. After immersion, substrate surfaces are rinsed to remove organic contaminants.

Solvent cleaning can result in surface roughening and if excessive can weaken the surface layers of certain plastics, and possibly degrade the bulk material. Thermoplastics are particularly sensitive to solvent attack, swelling and softening can occur on contact with certain solvents. It is essential that the substrate is not soluble in the solvent.

Note: Many of these solvents are potentially hazardous or environmentally damaging chemicals. All preparation should be carried out to COSHH specifications.

3.2 MECHANICAL ABRASION

It may be necessary to remove the outer layers of the substrate surface to expose the bulk adherend material directly to the adhesive or to enable the formation of a suitable oxide layer. Residual particles remaining after mechanical abrasion are generally removed by blasts of clean, dry air and solvent wiping. Mechanically abraded surfaces are usually cleaned (i.e. solvent wipe) before and after mechanical abrasion to prevent contaminants spreading. The combined effect of solvent and mechanical abrasion treatments is to remove most contaminants and alter the surface topography (increase in surface roughness or bond area). Mechanical abrasion methods include grit blasting (wet or dry), abrasive disks, emery cloth, sand paper and wire brushes.

Grit blasting is generally the preferred method for removing rust, oxide layers, old coatings and heavy contamination from metallic surfaces, and is widely used for preparing surfaces of polymer matrix composite (PMC) materials. The technique is not suitable for thin delicate parts or surfaces highly sensitive to surface damage (e.g. plastics) and may also remove protective layers (e.g. galvanised coatings). The technique is fast and efficient, and easily controllable. Simple surface treatments, such as grit blasting are less prone to human error and therefore the variation in bond strength is unlikely to exceed $\pm 20\%$. Grit blasting can also be automated. Wet blasting is increasingly being used in preference to dry blasting, as the method is more efficient, combining abrasion and cleaning to provide more consistent surface properties [3]. A spray rinse automatically removes the blasting residue.

Grit blasting in addition to removing surface debris and roughening the surface may cause physico-chemical changes, which affect surface energy and wettability [2-3]. Coarser grit produces rougher surfaces, resulting in lower surface energies, thereby increasing environmental durability of the bonded joint. Differences in initial strength between fine and coarse grits, and types of grit are negligible. The surface energy and adhesion characteristics of a surface are dependent not only on surface texture, but also on the purity of the grit blasting media. Harris and Beevers [3] observed that finer grits deposit a higher percentage of contaminating residues on the surface, although this effect can be masked by other sources of contamination (i.e. airline contamination).

Grit-Blasting – Key Parameters
<ul style="list-style-type: none"> • Adherend type (metal, plastic or polymer matrix composite) • Surface hardness, composition (including contaminants) and reactivity • Grit type (e.g. aluminium oxide, silica, glass beads and plastic) • Grit or abrasive size, hardness, geometry and purity • Spot size (i.e. diameter of particle beam at surface) • Degree (i.e. blast time) or scan rate (mm/min) • Air pressure and angle of inclination of beam • Separation distance between substrate surface and nozzle outlet • Exposure time (time between surface treatment and bond closure) • Contamination of grit blasting media or equipment
Surface Characteristics
<ul style="list-style-type: none"> • Surface roughness/texture • Surface energy/tension • Surface composition/contamination • Surface reflectivity/gloss

The effects of grit blasting on the surface characteristics of metallic and non-metallic substrate surfaces can be assessed using a number of techniques, including:

- Visual appearance, including gloss and colour.
- Contact (e.g. stylus) and non-contact (e.g. three-dimensional laser) profilometry for characterising surface roughness/texture.
- Static and dynamic contact angle measurements for determining surface energy/wettability.
- X-ray photoelectron spectroscopy (XPS) to determine the chemical composition of the surface and to identify contaminants.

Changes in joint properties due to different surface treatments can be assessed by carrying out mechanical tests on adhesive joints (e.g. cleavage (Boeing) wedge test) following accelerated environmental conditioning (i.e. hot/wet conditions).

3.3 CHEMICAL TREATMENT

Chemical treatment involves a transformation in the chemistry and morphology of the adherend surface to improve adhesion characteristics (i.e. bond strength and environmental durability). Common chemical surface treatments include [1-11]:

- Acid etching (e.g. chromic acid etch (CAE))
- Anodising (e.g. phosphoric acid anodisation (PAA))
- Primers (e.g. organosilanes)
- Plasma discharge, corona or electrical discharge, flame, ultraviolet irradiation or laser

All the above-mentioned processes are considered active surface treatments, which either improve wettability or modify the boundary layer surface. Chemical treatments may also alter the surface morphology. Chemical surface treatments of metal substrates are intended to produce a strong, stable and receptive oxide layer, whereas for polymeric materials the objective is to increase wettability. Chemical surface treatment is performed subsequent to mechanical abrasion and solvent cleaning, the final stage in the surface preparation process.

Chemical surface treatments improve bond strength and environmental durability through the following actions [2]:

- Removal of weak boundary layer or transformation of the boundary layer to provide a cohesively strong, stable oxide layer that is strongly bonded to the underlying substrate.
- Increase the surface energy (i.e. wettability) of the substrate surface.
- Improve surface topography to enhance mechanical keying.
- Protect the surface or improve environmental resistance of the surface against environmental effects.

Bonded joints with chemical surface treatments can be more prone to large variations in bond strength, particularly as there are often numerous controlling variables, which need to be strictly controlled. Stability of the surface after treatment also needs to be considered.

3.3.1 Chemical Etching

Common chemical etching treatments are either acidic (e.g. phosphoric acid for treating steel) or alkaline (e.g. alkaline chlorite for treating copper alloys). Chromic, nitric, sulphuric and formic acid solutions are used to treat polyolefins, polypropylene and nylon [2]. Chemical etching treatments are multiple stage processes with the etching solution consisting of two or more chemicals. Many proprietary treatments have been developed for treating metallic and non-metallic substrates (e.g. FPL (Forest Product Laboratory) chromic-sulphuric acid etch treatment for aluminium alloys). Hexcel Composites (formerly Ciba composites) [6] developed an acid etch treatment for aluminium alloys based on a mixture of chromium trioxide (or sodium dichromate), sulphuric acid and water. The solution is heated to a temperature between 60 and 65 °C. UK Ministry of Defence (MoD) specification DTD 9158 provides a similar process to that developed by Hexcel Composites [6].

Chemical Etch Treatments - Key Parameters

- Adherend type (metal, plastic or polymer matrix composite)
- Initial surface treatment (i.e. mechanical abrasion/solvent cleaning)
- Solution type, pH and concentration of chemical agents
- Minimum volume required to treat a surface
- Solution temperature (typically 20 to 100 °C)
- Immersion time (seconds to hours)
- Method of rinsing (immersion or running water)
- Method of drying (air or elevated temperatures)
- Exposure time (time between surface treatment and bond closure)

Surface Characteristics

- Surface roughness/texture
- Oxide layer morphology and depth
- Surface composition/reactive groups/crystallinity/contamination
- Surface energy/tension
- Surface hardness/cohesion strength
- Surface reflectivity/gloss
- Surface resistivity

The effects of alkaline or acid etching on the surface characteristics of metallic and non-metallic substrate surfaces can be assessed using a number of techniques, including:

- Contact and non-contact profilometry for characterising surface roughness/texture.
- Scanning and scanning stereo transmission electron microscopy for determining surface morphology and oxide or boundary layer thickness.
- Static and dynamic contact angle measurements for determining surface energy/wettability.
- X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) to determine the chemical composition of the surface and to identify contaminants, and for profiling chemical and elemental composition within the oxide or boundary layer.

As previously mentioned, mechanical tests on accelerated aged adhesive joints can be used to determine the effectiveness of different surface treatments.

3.3.2 Electrochemical Treatments

Chromic acid anodising (CAA) and phosphoric acid anodising (PAA) surface treatments are widely used throughout the aerospace industry to protect aluminium and titanium alloys [7, 9-10]. Other electrochemical treatments include sodium hydroxide anodisation (SHA) and cathodically deposited aluminium oxide [10]. Both anodising processes are used to treat titanium for adhesive bonding. CAA and PAA treatments result in thick, highly porous, stable oxide layers. The surface oxide layer thickness produced on aluminium alloys using CAA and PAA treatments is typically 1500 to 3,000 nm and 400 to 800 nm, respectively. The oxide layer enhances environmental durability (i.e. moisture resistance), although hydration is known to occur under hot/wet conditions. Surface fibrils (~100 nm in length) protruding from the oxide layer enhance mechanical keying with adhesives. Figure 2 shows typical oxide morphology resulting obtained with PAA surface treatment.

Anodising is often followed by a subsequent surface treatment, such as chromic acid or phosphoric acid immersion in order to seal the surface by blocking the pores. Sealing the oxide layer is ill advised as the durability of the joint is compromised [2].

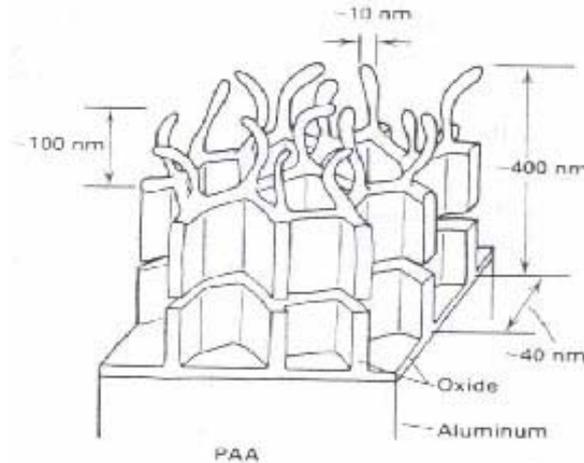


Figure 2: Typical oxide morphology for PAA treated aluminium alloy surface.

Fracture toughness of PAA treated joints (i.e. cleavage (or Boeing) wedge test) is generally higher than those joints treated using CAA or chemical etch treatments, such as CAE. However, lap joint durability performance is considered on a par with the best of these other treatments.

The physical and chemical properties of the oxide layer are dependent upon the electrolyte, anodisation voltage, time and temperature, etc (see below). Coating formation rates on aluminium alloys are typically 1 $\mu\text{m}/\text{min}$ at a current density of approximately 250 Amp/m^2 . Techniques for assessing surface characteristics and durability performance are essentially identical to those employed for assessing chemical etching (see Section 3.3.1).

Anodising Treatments - Key Parameters

- Adherend type (metal, plastic or polymer matrix composite)
- Initial surface treatment (i.e. mechanical abrasion/solvent cleaning)
- Electrolyte (pH, chemical composition and concentration)
- Solution temperature (typically 20 to 100 °C)
- Anodisation voltage/current levels
- Immersion time (seconds to hours)
- Method of rinsing (immersion or running water)
- Method of drying (air or elevated temperatures)
- Subsequent surface treatments
- Exposure time (time between surface treatment and bond closure)

Surface Characteristics

- Surface roughness/texture
- Oxide layer morphology and depth
- Surface composition/reactive groups/crystallinity/contamination
- Surface energy/tension
- Surface hardness
- Surface reflectivity/gloss
- Surface resistivity

3.3.3 Primers

Primers and adhesion promoters are organic liquids that are applied to substrates in order to promote adhesion between the substrate and the adhesive. These low viscosity substances are able to penetrate porous and rough surfaces, thereby providing improved mechanical interlocking and sealing the surface from hydrolysing effects caused through moisture ingress. Primers, such as aminopropyltriethoxysilane (or γ -APS) or glycidoxypropylmethoxysilane (or γ -GPS), are often applied to [2, 9, 11]:

- Protect the substrate surface prior to bonding and extend the time between adherend preparation and bonding.
- Increase surface energy (or wettability) of the adherend surface.
- Dissolve low levels of organic contamination, which would otherwise result in a weak boundary layer.
- Inhibit corrosion of the substrate during service.

Primers also act as a coupling agent, forming covalent bonds with the adherend and adhesive, thus improving bond strength and environmental durability.

Silane coupling agents (e.g. γ -APS) [9, 11] are known to improve durability in the presence of moisture by increasing the corrosion resistance (hydrolytic strength) of the oxide layer on the adherend surface. These substances offer a non-toxic alternative to chromate and phosphate surface treatments. Silane treatments are increasingly being used to protect metallic materials (e.g. steel and aluminium) and polymeric composites. Bond strengths can be very low, however in cases where the silane treatment is poorly controlled. Incorrect application can result in interfacial failure or cohesive failure within the silane coating. Care is needed to ensure a uniform coating, a monomolecular layer thick, is produced across the entire surface area of the adherends to be bonded.

Silane Treatments - Key Parameters
<ul style="list-style-type: none"> • Adherend type (metal, plastic or polymer matrix composite) • Initial surface treatment (i.e. mechanical abrasion/chemical) • Chemical composition, concentration and miscibility • Coating thickness • pH and temperature dependence of reaction rate • Hydrolysis (aqueous and water/ethanol solutions) • Method of application (i.e. immersion, spray or brush) • Immersion time (seconds to hours) • Method of rinsing (immersion or running water) • Method of drying (air or elevated temperatures) • Exposure time (time between surface treatment and bond closure)
Surface Characteristics
<ul style="list-style-type: none"> • Surface roughness/texture and morphology • Surface layer composition, thickness and uniformity • Surface energy/tension • Surface hardness • Surface reflectivity/gloss • Surface resistivity

3.3.4 Corona Discharge

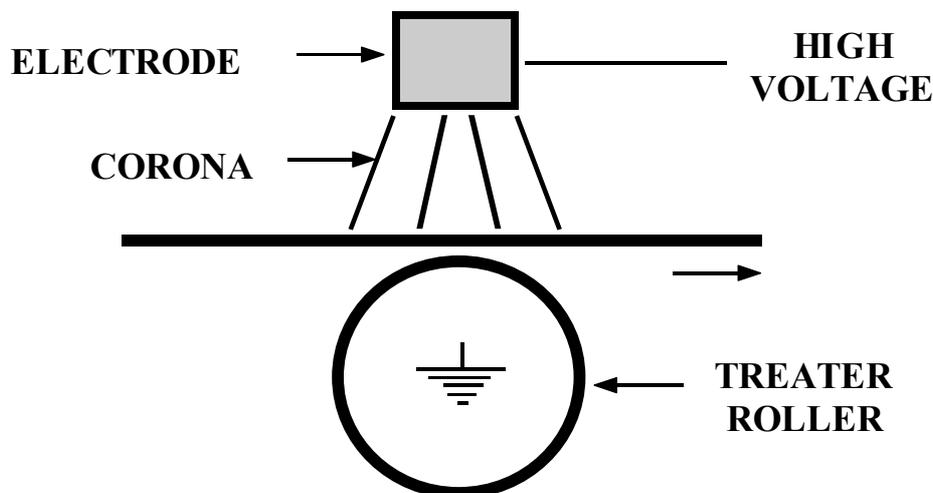


Figure 3: Corona discharge method.

Electrical corona discharge is a dry surface preparation method used for preparing polymer film surfaces to enhance adhesion of inks or coatings to the polymer surface, and for preparing GRP laminate sheet (e.g. skins or facings of sandwich panels in large refrigerated vehicles) for bonding and painting. Corona discharge surface treatment is widely used in the medical industry for applications, such as syringe barrels, pill bottles, catheters and intravenous tubes. Figure 3 shows the basic principal of electrical corona discharge treatment of sheet or film material. The process, which can be automated (i.e. on-line processing), consists basically of a developing a high potential (typically 20 kV) between a stationary electrode electrically connected to the high frequency (10-20 kHz) generator and an earthed treater roll, electrically insulated with a dielectric covering serving as the other electrode.

The result is an intense electrical field that ionises the air in the air gap (i.e. corona), which chemically modifies the surface of the material to improve wetting of the adhesive and also increases the intrinsic strength of the substrate/adhesive interface. The ionised particles (i.e. free electrons and ions) in the air gap bombard and penetrate into the molecular structure of the substrate. Free electrons and ions generally have sufficient energy to break the molecular bonds on the surface of most polymers, creating free radicals that rapidly react with oxygen to form polar chemical groups on the substrate surface. Surface energy may increase to the point that most inks, coatings and adhesives will readily wet the surface. Most film and sheet materials have a smooth, slippery surface (low surface friction). Corona treatment, in effect, chemically roughens the surface, increasing the area for bonding and intimate interlocking, and promoting capillary flow of low viscosity fluids. The resulting physical-chemical interaction increases above that for a mechanically abraded surface. Although corona treatment is stable in air, solvent wiping will render the treatment ineffective and hence should be avoided.

Corona treatment is generally less hazardous and more cost effective than other forms of surface treatment and can be readily adapted to complex configurations. In some cases, corona treating of an entire part can be done in a single split-second operation, with up to four discharge heads positioned to provide complete coverage of the surface of the part to prepare it for the application of labels, coatings, or direct printing of text or graphics. Sheet and film materials up to 3.0 metres wide can be treated at speeds up to 3 metres/minute.

Corona Discharge Treatment - Key Parameters

- Adherend type (metal, plastic or polymer matrix composite)
- Surface chemistry and morphology
- Initial surface treatment (i.e. mechanical abrasion/chemical)
- Air gap distance, spot size and treatment time (or scan rate)
- Generator voltage/current/frequency
- Temperature and humidity
- Exposure time (time between surface treatment and bond closure)

Surface Characteristics

- Surface roughness/texture and oxide morphology
- Surface composition/reactive groups/crystallinity/contamination
- Surface energy/tension
- Surface hardness
- Surface reflectivity/gloss
- Surface resistivity

A number of key points are listed below:

- Equipment is inexpensive, clean and readily adaptable to on-line processing.
- Particularly suitable for treating thin films (typically 0.635 mm or 0.025" thick), but can be used for thicker substrates (e.g. GRP laminated sheet and thin-walled containers and tubing (up to 3 mm thick)).
- Critical factors include power input (i.e. voltage and current), temperature and humidity, substrate, surface contaminants, and speed for on-line processing. Humidity will have a negative effect on the effectiveness of the treatment. Surface contaminants impede the efficiency of treatment.
- Significant bond strength improvements have been achieved for polypropylene and polyethylene. Moderate success has been achieved with metallic foils.

3.3.5 Plasma Treatment

Plasma treatment, in the form of glow discharges or plasma sprays, has proved effective in preparing the surfaces of metallic and polymeric materials for bonding. This method of surface treatment produces clean and reproducible results, depending on the degree of treatment [5, 10]. Plasma spray treatment has been successfully applied to titanium alloys, producing a surface oxide layer of uniform thickness and composition. The technique of treating titanium involves rapidly heating TiO₂, TiSi₂, MgO or SiO₂ powder to a molten or semi-molten state and then spraying the molten oxide onto the substrate at high velocity [10]. Silicon sputtering has been shown to increase bond strength and environmental durability. The improved properties were attributed to an increase surface tension and surface roughness.

Plasma glow discharge treatments have been shown to improve adhesion of polymeric materials (e.g. polyester, polyethersulfone, fluoropolymers and nylons) and thermoplastic-based composites with epoxy adhesives. Oxidising (i.e. oxygen or air) and inert (i.e. nitrogen or argon) gas mixtures have proved successful in enhancing adhesion and promoting cohesive failure of carbon fibre-reinforced polyetheretherketone (PEEK) joints [12]. The improved adhesion is attributed to the increased surface roughness and formation of oxygen and nitrogen containing functional groups on the composite surface, resulting an increase in wettability.

Plasma Treatment of Polymeric Materials - Key Parameters

- Polymer chemistry and morphology (amorphous and/or crystalline)
- Gas mixture (i.e. oxygen, air, nitrogen or argon)
- Excitation frequency and RF power
- Pressure and gas flow
- Dwell (or treatment) time and working distance
- Temperature and humidity
- Exposure time (time between surface treatment and bond closure)

Surface Characteristics

- Surface roughness/texture and morphology
- Surface composition/reactive groups/crystallinity
- Surface energy/tension
- Surface hardness
- Surface reflectivity/gloss
- Surface resistivity

Plasma treatment offers a number of advantages over chemical treatments:

- Uniform and stable oxide layer (thickness and composition).
- Insensitive to surface contamination.
- Long shelf life prior to bonding
- Low processing costs.
- No-hazardous chemicals or pollutants involved (i.e. environmental friendly).

Deposition rates of metals are typically 1 mm/hour over a square metre of material. Plasma treated parts can be stored for considerable periods of time (weeks to months) in clean, dry environments without the surface deteriorating. However, exposure to elevated temperatures or moisture will compromise the effectiveness of the treatment. Continuous treatment equipment has been developed for processing films and fibres. The high capital outlay required has limited the use of plasma treatment to these speciality markets.

3.3.6 Flame

Flame treatment is widely used to promote good adhesion between thermoplastic substrates (e.g. polypropylene, polyethylene, polyolefins and nylon) and adhesives, paints and inks. Flame treatment uses an oxygenated flame to burn-off contaminants and oxidise the polymer surface. This creates free oxygen, which reacts with the surface forming oxygen containing functional groups, thus increasing the surface energy. The treatment is suitable for film and shaped products and can be used for continuous on-line processing. Automated processing equipment is available. Hand-held torches or bunsen burners can also be used, although it is more difficult to achieve uniform treatment. The treated component may also warp or suffer other forms of thermal damage (including melting and charring) if the process is not carefully controlled. As with corona treatment, this method is not long lasting and can disappear within weeks. The flame is generated by gas burners supplied with either methane, butane or propane gas. Key factors, which are similar to plasma treatment (see Section 3.3.5), include:

- Air/gas ratio – flame characteristics are highly dependent on this factor.
- Distance between surface and flame.
- Dwell (or treatment) time.

3.3.7 Laser

Although laser treatment is a recent introduction, the treatment has proved successful in treating polymer composite surfaces [10, 13]. Improvement in bond strength and durability of composite joints is attributed to an increase surface roughness and surface tension. The increase in surface roughness is due to surface erosion through a process known as photoablation (i.e. combination of thermal and photochemical damage). The technique is particularly suited to treating composite materials for automotive applications (e.g. sheet moulded compound (SMC)). An excimer laser source (i.e. ultraviolet radiation) is favoured with these materials for a number of reasons: (i) higher photon energy, (ii) the effect of the treatment is limited to a thin layer on the surface; and (iii) surface changes are mainly photochemical. The bulk substrate remains virtually unaffected. Laser treatments have been applied to metallic surfaces, although with mixed results. Good bond strength has been achieved with titanium, however the durability performance was poor [13].

Treatment speeds tend to be slow (typically 100 mm²/sec) in comparison with other dry techniques, such as plasma and corona discharge. Consistent and high quality surfaces can be produced using laser processing.

Laser Treatment of Polymeric Materials - Key Parameters
<ul style="list-style-type: none"> • Polymer chemistry and morphology (amorphous and/or crystalline) • Wavelength and frequency of beam • Pulse duration and energy/power • Beam shape and divergence • Dwell (or treatment) time • Temperature and humidity • Exposure time (time between surface treatment and bond closure)
Surface Characteristics
<ul style="list-style-type: none"> • Surface roughness/texture and morphology • Surface composition/reactive groups/crystallinity • Surface energy/tension • Surface hardness • Surface reflectivity/gloss • Surface resistivity

3.4 DISCUSSION

It is important that the process of surface preparation only affects the chemistry and morphology of thin surface layer of the adherend(s) and does not alter the mechanical and physical properties of the underlying substrate. A brief description of general procedures used for preparing different substrates for adhesive bonding is provided in Measurement Good Practice Guide No 47 [14] (see also [15]). Specific surface treatments can be obtained in BS 7079, BS EN 12768, ASTM D2651, ASTM D2093 and BS EN 1840 [16-20].

Table 1: Maximum Exposure Time Between Surface Preparation or Priming Metal Substrates, and Associated Variation in Tensile Shear Strength

Surface Treatment	Maximum Exposure Time	Strength Variation (%)
None	1-2 hrs	± 20
Solvent Degrease	1-2 hrs	± 20
Vapour Degrease	1-2 hrs	± 20
Dry Grit-Blasting (Steel)	4 hrs	± 20
Wet Grit-Blasting (Steel)	8 hrs	± 20
Wet Grit-Blasting (Aluminium)	72 hrs	± 20
Chromic Acid Etch (Aluminium)	6 days	± 10
Sulphuric Acid Etch (Stainless Steel)	30 days	± 10
Anodising (Aluminium)	30 days	± 10
Corona discharge/plasma	1-2 months	± 10
Dry Grit + Organosilanes (Aluminium)	2-5 hrs	± 5

After completion of the surface preparation process, the adherends must not be exposed to physical handling or uncontrolled atmospheric environments in order to prevent surface contamination prior to bonding. It is advisable that bonding be performed immediately following surface treatment to maximise performance. The maximum allowable time between surface preparation and bonding or priming the substrate is dependent on the substrate and the surface treatment (see Table 1).

A number of factors in addition to those identified in Section 3.3 may influence the effectiveness of a chemical treatment. For example, chemical treatment solutions may react during preparation or storage with the containing vessel. Checks should be made to ensure that the containing vessel and stirring rods used in mixing are resistant to chemical attack from would be contents (e.g. hydrofluoric acid attacks glass). Quality assurance tests are usually carried out to check concentrations, and levels of contamination (e.g. opacity for checking particulate content, colour, dielectric conductivity for ion content and pH for acidic and alkaline solutions).

Treatment tanks or containers for chemical etching solutions (e.g. chromic acid) are required to be of sufficient size to accommodate the specimens to be treated (i.e. volume of chemical solution should be well in excess of the volume occupied by the component in solution). Tests may need to be carried out to determine the minimum volume required to treat a component. Surfaces to be treated should be completely immersed in all solutions. Treatment tanks used in chemical etching processes should be equipped with temperature controls and should be regularly agitated or stirred to prevent local overheating and to ensure uniform concentration of the chemical etching solution. The tanks should be suitably lined to prevent reaction between the tank and the chemical solution, thus ensuring no adverse effect on the solution used or the surfaces being treated. Rinse tanks should be large enough to accommodate the specimens that have been treated and should be equipped to allow for circulation of clean water to prevent build-up or carryover of materials between batches of specimens.

In many cases, it is possible to apply the Wagner or parabolic film growth law for determining the growth rate of an oxide layer on a metallic surface. The controlling equation of oxide film growth according to the Wagner law is given by the following relationship [21]:

$$\frac{\delta D}{\delta t} = \frac{K}{D} \tag{1}$$

$$D^2 = Kt + C$$

where **D** is the oxide film thickness, **t** is time and **K** is a film growth coefficient, which is the product of the concentration difference in diffusing ions across the film and the diffusivity of ions in the oxide film. **C** is an empirically determined constant, which is usually assumed to be zero (since film thickness is initially zero). It is assumed that a uniform surface film is formed free of voids and fissures.

4. SURFACE CHARACTERISATION

Surface characterisation is an essential part of the evaluation of surface treatments to ensure optimum bond strength and environmental resistance for specific service conditions. These techniques can provide important information on:

- Failure modes and mechanisms
- Chemical composition and morphology (e.g. surface roughness) of surface layers
- Effects of surface preparation on surface chemistry
- Stability of surfaces and interfaces
- Surface contaminants
- Chemical and physical degradation of both the adhesive and oxide layers.

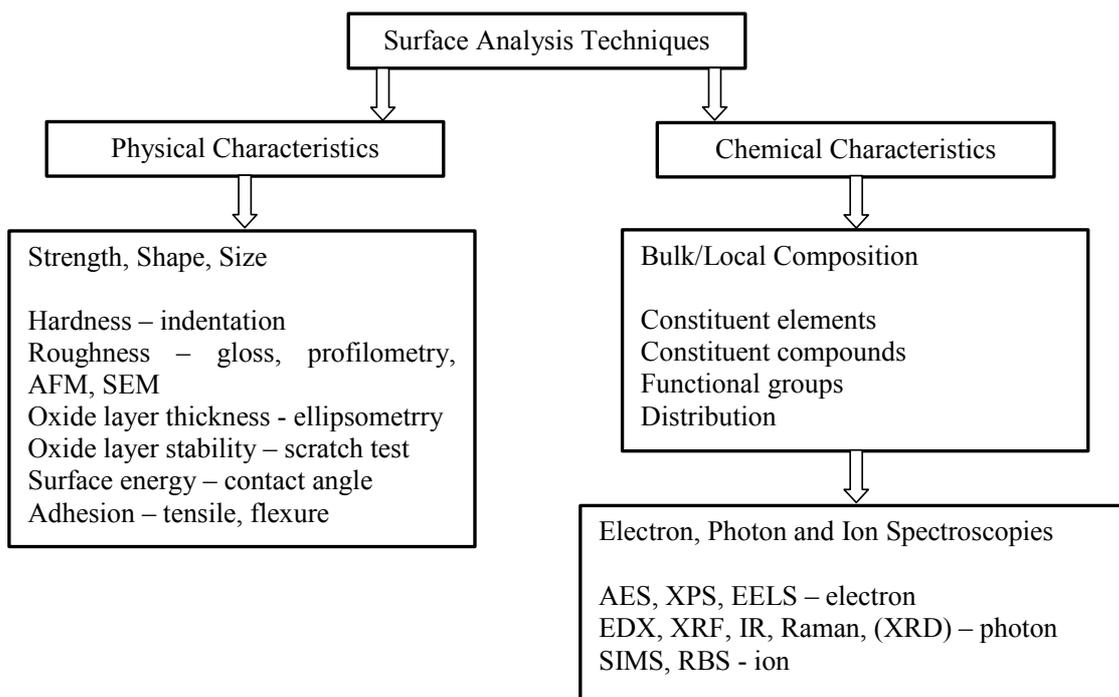


Figure 4: Surface analysis techniques.

Surface and chemical characterisation techniques can provide qualitative and quantitative information relating to the strength and durability of bonded joints [1-6]. A major concern is that a number of these techniques are carried out under high-vacuum conditions, which may result in the removal of species of interest (e.g. loosely attached moisture or contaminants) or alter hydroxide structures prior to analysis. The interrogating beam may also interact with the surface layer altering the chemical composition and structure of the surface layer. Insulators often need to be coated with a thin conductive layer (e.g. gold sputtered) in order to prevent electrical charging. This process can alter or mask the chemistry and morphological characteristics of the surface layer(s). This section examines physical and chemical techniques that can be used to characterise surfaces with particular attention given to those techniques that can be used for on-line inspection (i.e. quality control) and are accessible by small industrial concerns. The practicality and limitations of these techniques are discussed and relevant data are provided to demonstrate the effectiveness of the technique for different substrate/surface treatment systems.

4.1 SURFACE ANALYTICAL TECHNIQUES

Chemical characterisation can be achieved at either, elemental and functional group levels using spectroscopic analysis techniques. The former provides qualitative and quantitative information on chemical composition whilst the latter provides detailed information on molecular structure, conformation, surface morphology and physical-chemical characteristics. Optical microscopy and SEM are useful for studying physical surface characteristics. Surface roughness and adherence are particular properties for which topographic SEM and surface energy techniques are suitable. This section provides a brief summary of surface and chemical techniques (see also Appendix 1).

4.1.1 Scanning Electron Microscopy (SEM)

This is the most widely used of the surface analytical techniques. High resolution SEM has proved an invaluable tool for studying surface topography, oxide growth and failure analysis. The technique enables qualitative three-dimensional (3-D) imaging of surface features, however, it does not easily lend itself to quantitative surface roughness characterisation. This can be overcome by complementing SEM investigations with atomic force microscopy (AFM). In SEM, a highly focused scanning electron beam bombards the surface causing large numbers of secondary electrons to be generated, the intensity of which is governed by surface topography. The method is suitable for all materials, but non-conducting materials must be given a thin conductive coating (e.g. gold sputtered), which can alter or mask the true surface morphology. The resolution of topographical features is approximately 5 nanometres. SEM is often used to survey a surface before more specialised techniques are employed.

4.1.2 Atomic Force Microscopy (AFM)

AFM measures the morphology and topography of surfaces on the atomic scale. A small tip mounted on a cantilever is used to analyse the vertical movements of the probe as it travels over the contours of the surface of the sample (similar principle of operation to the stylus profilometer (see Section 4.2.1)). There are two modes of operation: contact and dynamic (non-contact), which maintain a constant force or separation to the sample surface respectively. This allows a quantitative assessment of surface roughness in terms of amplitude and wavelength, although data interpretation can be difficult because at the atomic level the concept of a smooth surface is meaningless. Almost all materials can be studied without the need for sample preparation.

For conducting materials, scanning tunnelling microscopy (STM) can be used, but this closely related technique can confuse between electrical and structural features. There is usually high scatter in roughness data, but significant differences are easily observed. Typical spatial resolution is 3 nm with a vertical feature resolution of <0.1 nm. Investigated areas are limited to approximately 10 nm square. As well as quantifying surface roughness, this method can produce a 3-D image of a real surface for visual inspection and can also measure relative surface stiffness giving local hardness and modulus information. (i.e. contact mode)

4.1.3 Energy Dispersive X-Ray Analysis (EDX)

This involves the emission of X-rays from a surface of a material upon exposure to a primary beam of electrons. The X-rays emitted are characteristic of the atom from which they originated. Detection and analysis of the characteristic X-ray lines of various elements can be obtained using an EDX system attached to an SEM. The maximum operational depth of EDX is typically 2 to 10 μm and the volume analysed can be as large as several cubic microns. The actual penetration depth depends on the type of material being analysed and the acceleration potential used in the SEM.

The technique can be used to generate elemental distribution maps of the area of interest, enabling both qualitative (boron to uranium) and some quantitative (sodium to uranium) elemental analysis from the same area of sample, which is under observation. The technique cannot provide information on chemical bonds. It is applicable to all materials, provided specimens are flat and polished.

4.1.4 X-ray Photoelectron Spectroscopy (XPS)

This is an analytical technique that measures the energies of photoelectrons emitted from atoms of a sample when it is irradiated with soft (or low energy) X-rays. XPS is surface-sensitive and is frequently used for quantitative elemental analysis of fracture surfaces, to determine the effect of surface preparation on surface chemistry and for monitoring chemical changes in adhesive samples. The technique, which is capable of detecting all elements with the exceptions of hydrogen and helium, can provide information on chemical structure and bonding and element distribution present on the surface of any solid material (including polymers) as well as structure thickness (through determination of the mean free path).

One of the major strengths of XPS is its ability to discriminate between different oxidation states and different chemical environments for any element. It is the most widely applicable technique with a reasonable capacity for quantification, which is reliable and easy to interpret. The maximum operational depth of XPS is less than 10 nanometres with a spatial resolution of less than 10 μm . Unfortunately, many polymeric material samples are sensitive to ion beam damage. The technique can be used in conjunction with inert gas ion sputtering to determine the variation in chemical composition with depth.

4.1.5 Auger Electron Spectroscopy (AES)

AES is a surface sensitive, non-destructive technique for identifying the elements in the first few atomic layers (~1 to 5 nanometres) on a specimen surface and is able to provide quantitative data on the detected elements (by comparison with known standard samples). High-energy electron beam bombardment of the surface results in the emission of Auger electrons at characteristic discrete energies.

Combined with inert gas ion sputtering, AES can be used to obtain depth composition profiles and, by scanning AES, to map the distribution of elements present on a specimen surface at a spatial resolution of 0.5 μm . The technique is capable of detecting all elements with the exception of hydrogen and helium. Ultra-high vacuum conditions are required to prevent contamination and oxidation of the sample surface.

AES is not particularly suited to the examination of polymers or glasses (i.e. insulating materials) due to the possibility of beam damage and electrical charging of the sample, which can complicate data interpretation. Combined with inert gas ion sputtering, AES can be used to obtain depth composition profiles. AES is a useful and complementary technique to XPS as it has better spatial resolution (smaller spot size is possible) but exhibits more sample damage and is less suited to determining chemical bonding or oxidation state.

4.1.6 X-ray Fluorescence Spectroscopy (XRF)

The target material is irradiated with X-rays, which results in the release of a photon of characteristic energy, each element having its own set of characteristic emissions. This is a non-destructive method for qualitative and semi-quantitative elemental analysis in a wide range of materials. It is sensitive to elements above aluminium in the periodic table. Minimal sample preparation is required.

A variant, total reflection X-ray fluorescence uses X-rays impinging on the surface of a sample at glancing incidence such that total reflection occurs. This excites photon emission from atoms in only the topmost layers of the material. Whilst this technique is very sensitive it does require very flat samples.

4.1.7 Infrared Spectroscopy (IR)

IRS provides information on molecular structure based on specific frequencies associated with internal vibrations of groups of atoms in molecules using a laser in the infrared region to excite the target material and analysing the frequencies absorbed. IRS provides both qualitative and quantitative chemical analysis data and is particularly useful for assessing polymer chemistry. The technique provides a fingerprint of the adhesive or coating composition in any physical state. Computerised databases of spectra for common polymeric materials are available to enable characterisation of molecular structure by observing spectral differences between known materials and the test sample. Since it is an optical (photon in/photon out) technique it is not necessary for such studies to be carried out in vacuum.

IRS is often used in conjunction with Raman spectroscopy (see Section 4.1.8) as a complementary identification technique. Some quantitative analysis is possible by analysing the magnitude of the characteristic absorption peaks. It requires minimal sample preparation but samples need to be transparent to infrared, the method is less useful for inorganic materials. Water is problematic as it obscures the spectrum. IRS is not inherently surface-specific but variants improve this aspect. One variant, attenuated total reflectance uses a prism in optical contact with the sample resulting in total internal reflection after penetrating a small way into the sample surface and is particularly useful for investigating adhesion problems and surface treatment for strong IR absorbers provided the surface is flat. Analysis is possible to within 0.5 to 3 μm of sample surface. Another variant, grazing incidence reflectance spectroscopy, uses a photon beam impinging on the surface at a high angle of incidence giving good surface sensitivity. However this technique is only applicable to metallic surfaces.

4.1.8 Raman Spectroscopy

Raman is based on the inelastic scattering of monochromatic light. A laser excites the material, which is usually in the visible region of the spectrum. The frequency of scattered light is analysed compared to incident values. The technique is similar to IR in determining the nature of molecular structures and is a complementary technique to IR when characteristic frequencies are weak or for highly absorbing materials. Samples require minimal preparation, but need to be stable to high intensity light and contain no species that fluoresce when excited by visible radiation. Raman is used to study the surfaces of polymeric materials (i.e. residual stresses), but the Raman effect is weak and samples may fluoresce, obscuring the spectrum.

4.1.9 Electron Energy Loss Spectroscopy (EELS)

This technique uses the inelastic scattering of low energy electrons in order to measure the vibrational spectra of surface species (electron-analogue of Raman spectroscopy). Since the technique employs low energy electrons, it is necessarily restricted to use in ultra-high vacuum environments, however, the use of low energy electrons ensures that it is a surface specific technique. The energy loss of a beam of electrons of fixed incident energy is analysed. This method has high sensitivity but requires flat, preferably conducting samples and has lower resolution than IR techniques.

4.1.10 X-ray Diffraction (XRD)

Monochromatic X-rays are diffracted through an angle dependent on the crystal structure. Identification of unknown compounds is achieved by comparing angles and intensities of the diffraction pattern with references. The surface enhanced variant of XRD uses X-rays incident at a shallow angle to increase the surface sensitivity and can be used to analyse structures of a few microns thickness. However, this technique is suitable only for crystalline phases and is less applicable to polymeric compounds because of the existence of amorphous and multiple crystalline phases. It is unsuitable for determining the structure of amorphous oxide films.

4.1.11 Secondary Ion Mass Spectrometry (SIMS)

In SIMS the surface is bombarded with a beam of high-energy ions resulting in the ejection of molecular fragments, atoms and ions from the surface, which are subsequently analysed (traditionally only the positive ions). It is capable of providing surface elemental analysis and depth concentration profiles on areas from several mm to sub micron. It can detect all elements and isotopes including hydrogen and hydrogenated compounds with very high sensitivity (parts per billion). It is, however, not readily amenable to quantitative analysis (complex and requires reference standards). The depth resolution is under 200nm and areas of up to 500 μm can be studied. Whilst SIMS is suitable for all materials, flat sample surfaces are required to give the best spatial and depth resolution. There are a number of different variants of the technique including static SIMS (sub-monolayer elemental analysis), dynamic SIMS (depth composition profiles) and imaging SIMS (elemental mapping) analysis.

4.1.12 Rutherford Backscattering Spectrometry (RBS)

This is one of a number of ion scattering techniques, which provide different information on an elemental level, depending on the primary ion energy (typically 1-3 MeV) and the scattered ion that is detected. A beam of positive helium ions (He^+) is directed at the target surface and the ions, which are scattered by the sample nuclei, are measured and analysed. RBS is a non-destructive technique since the erosion and the radiation degradation of the sample material by the particle impact is negligible. As a result RBS is used for the quantitative, non-destructive compositional depth profiling and thickness measurements on thin films. The depth distribution of constituents can be reconstructed with a depth resolution of 10 to 20 nm. This method can probe several thousand atomic layers and is ideal for surface analysis up to 2 μm depth.

4.2 SURFACE ROUGHNESS

Surface topography is defined as that which distinguishes a real surface from a perfectly flat, featureless one (i.e. polished) and is an important factor contributing to mechanical adhesion [2]. Once numerical representations of a surface have been determined, analysis to characterise and differentiate surfaces can be performed. Filters are used to separate the long-wave (waviness) components from the short-wave (roughness) components of the surface profile (Figure 5). Waviness is defined as the more widely spaced component of the surface texture. Roughness features are $<10 \mu\text{m}$ in size and are superimposed on the waviness. Typically data at the beginning and end of each profile are discarded to remove any potential edge errors. Statistical parameters are then obtained from these profiles, which help to characterise the surface. The most common parameters used are: R_a and R_q , the average roughness deviation and root mean square (RMS) roughness deviation, respectively. Roughness parameters are calculated relative to a reference line established as the position at which half the trace lies above and half below.

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

$$R_q = \sqrt{\frac{1}{L} \int_0^L |y^2(x)| dx} \quad (3)$$

Where L is the sampled length, x is the position along the sampled length and $y(x)$ are the roughness profile values (see Figure 5).

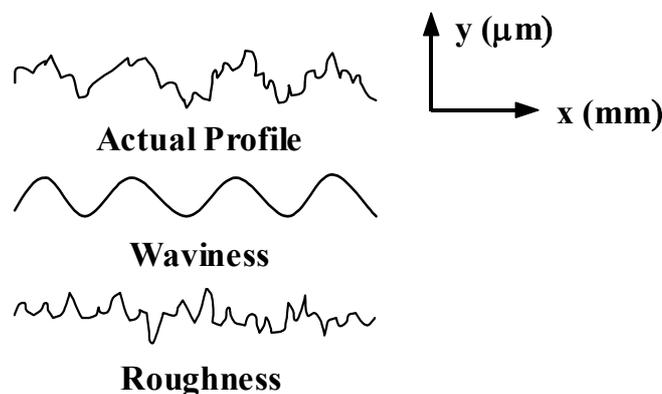


Figure 5: Surface profiles.

Another useful measure that is occasionally used is peak count, given in peaks per unit length where a peak is any maximum to minimum which extends through a given region around the reference line.

4.2.1 Surface Profilometry

Surface profilometry is a term used to describe a number of techniques, which measure surface deviations from a nominal line or plane and produce a trace or profile of the surface. These are either contact or non-contact measurements using stylus or laser profilometers respectively. These devices are usually vibration sensitive and require numerous scans to characterise large areas.

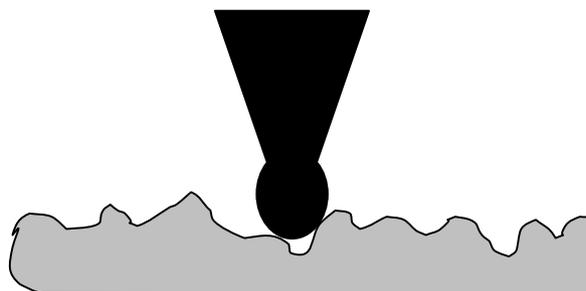


Figure 6: Contact profilometry.

Contact (Stylus) Profilometer: This instrument moves a loaded probe (usually a diamond tip) across the target surface and records the vertical movement caused by the irregularities. This 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 6) and angle (60° or 90°), stylus tip radius (typically $5\ \mu\text{m}$ - 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 and will not resolve roughness at nano-scale (see Section 4.1.2 for AFM). Truncated pyramidal, or chisel shaped small tip stylus $5\ \mu\text{m}$ are available for specialised measurements (see [22]).

Non-Contact Profilometers: Recent developments have seen the emergence of non-contact (or optical) profilometers, such as laser triangulation systems and optical interferometers for measuring 3-D surface topography. These instruments are being used to measure roughness, finish and texture of surfaces ranging from polished optics to rough surfaces, such as rolled steel and aluminium, plastics and ceramics. Spatial and depth resolution of optical instruments vary from 0.25 to $150\ \mu\text{m}$ and 0.1 to $60\ \text{nm}$, respectively. The cost of the instrument increases with resolution. High-resolution equipment is relatively expensive. Scan speed ranges $0.25\ \mu\text{m}/\text{min}$ to $25\ \text{mm}/\text{min}$. There are high-resolution systems capable of inspecting areas $300\ \text{mm} \times 300\ \text{mm}$. These instruments include a camera and PC for data collection and analysis. Currently there are no supporting standards for optical systems, although there is a plethora of instruments on the market.

Surface shape is computed from optical measurements. A collimated beam of light (often laser) is split and focused to a spot on the target and reference surfaces. Height differences result in fringes, which can be analysed to yield information about the shape and roughness of the target surface. These profilers can offer better lateral resolution, around 1 μm , than stylus profilometers, rapid large area measurements and are non-destructive. Vertical resolution is down to tenths of nanometres. Portable stylus instruments are commercially available. Relevant standards are ISO 3274, ISO 4287, ISO 5436 and ISO 12179 [23-26].

AG Electro-Optics carried out, on behalf of NPL, non-contact 3-D surface profile measurements on “as received” (or untreated), grit blasted (Figure 7) and chromic acid etched (CAE) aluminium specimens. The results presented in Table 2 show distinct differences in the values of R_a and R_q for the various surface treatments. In the case of grit blasted surfaces, the general trend was for these two parameters to increase with the level of treatment (i.e. exposure time).

Table 2: Surface Roughness Measurements on Surface Treated Aluminium

Surface Treatment	R_a (μm)	R_q (μm)
Untreated	0.20	0.25
Grit Blasted		
10 seconds	2.05	2.67
30 seconds	2.36	3.03
60 seconds	2.60	3.30
120 seconds	2.37	3.01
Chromic Acid Etching (CAE)		
10 minutes	0.26	0.35
20 minutes	0.31	0.42
30 minutes	0.26	0.35
60 minutes	0.28	0.40

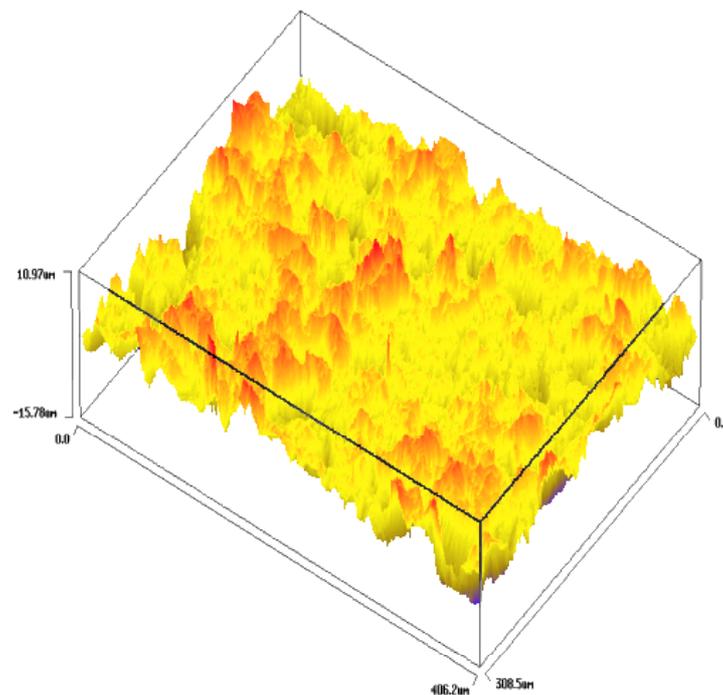


Figure 7: 3-D surface map of a grit-blasted aluminium (courtesy of AG Electro-Optics).

Optical techniques are sensitive to the effects of phase change on reflection and contaminants present on the surface. These can give rise to apparent height changes (typically 1-10 nanometres). Phase changes vary as a function of the incident angle. Optical techniques are faster than the stylus method. Studies carried out at NPL have shown that measurements obtained by stylus and optical instruments give different results in excess of their reported uncertainties. There are on-going initiatives to put in place international standards for all methods for surface roughness/texture measurement.

4.3 REFLECTIVITY

Surface reflectivity is usually measured using a reflectometer. The instrument projects a beam of light (either filtered white light as used for gloss meters or laser) onto the target surface at a specific angle and measures the amount of light reflected at the same angle (Figure 8). Surface roughness causes incident light to be scattered at angles other than that of specular reflection, such that the scatter increases with roughness. Analysis of the angular distribution and intensity of the reflected and scattered light allows parameters related to the surface roughness to be defined. These parameters include the total integrated scatter (ratio of total scattered power to total reflected power, which is related to RMS roughness R_q) and the bi-directional reflectance distribution function (scatter density normalised to incident power which contains valuable information on the distribution and size of surface features). In order to achieve this an array of detectors or a detector moving in an arc relative to the surface are used. These instruments can control the angle of incident beam and the spot size, and are capable of scanning large areas (see ASTM D523 and ISO 2813 [27-28]) and also [29-30]). A standard black glass is commonly used as a reference for comparisons.

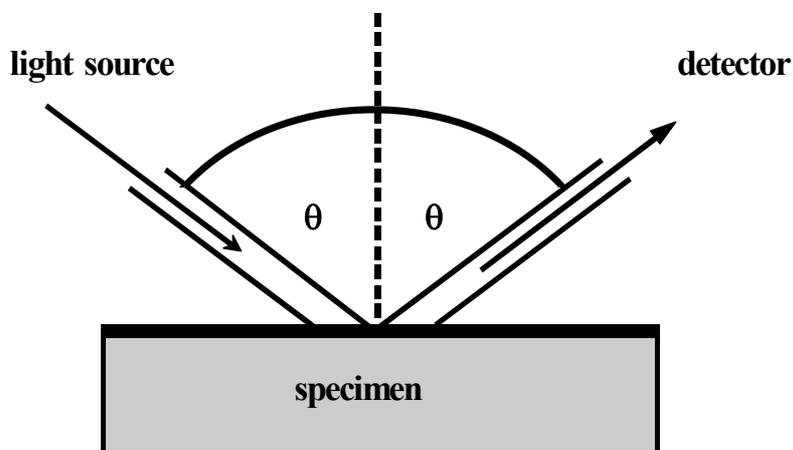


Figure 8: Geometry of a gloss meter.

Gloss Meters: Gloss is the specular or mirror-like reflection of white light from a surface and is a specific property of the surface [29-30]. The white light source is filtered to give a spectrum similar to the response of the human eye. Simple, hand-held gloss meters have been successfully used with flat and curved surfaces for determining the surface finish of polymer products and painted surfaces for quality control purposes. These instruments provide quantitative data on the uniformity and quality of surface treatments and are relatively insensitive to vibrations. The technique can be used to differentiate between surface treatments and the quality of the surface treatment. Commercial hand held instruments measure reflectivity at fixed angles to the substrate (20° , 60° or 85°). The technique can be automated for on-line inspection. Details on the operation of these devices are given in NPL Report DMM(A)111 [30].

Laser Reflectometry: Laser reflectivity has been shown to be effective in differentiating between different surface treatments. Table 3 compares average laser reflectivity for different surface treatments applied to an aluminium alloy with the untreated (or “as received”) material [31]. Although laser reflectometry techniques are capable of detecting small features, these instruments are highly sensitive to vibrations. Reflectivity measurements may also be affected by contaminants present on the surface of the sample.

Table 3: Average Laser Reflectivity for Surface Treated Aluminium [31]

Surface Treatment	Average Reflection (%)
As received (untreated)	65.2
Phosphoric acid anodising (PAA)	42.7
Chromic acid anodising (CAA)	12.7
Standard FPL etch	53.5

4.4 COLORIMETRY

Colour measurements 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.

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 the 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 occurs when [21]:

$$2\xi = \frac{\lambda}{n}, \quad \frac{3\lambda}{n}, \quad \frac{5\lambda}{n} \dots \text{etc} \quad (4)$$

where ξ is the thickness of oxide film, λ is the wavelength of the light in air and n is the refractive index of the oxide film (measured using ellipsometry). If there is a difference in the phase-change produced by the two reflections then this can be regarded as an additional path difference c and the film thickness is defined by [21]:

$$\xi = \frac{\lambda}{4n} - c, \quad \frac{3\lambda}{4n} - c, \quad \frac{5\lambda}{4n} - c \dots \text{etc} \quad (5)$$

A simplistic approach is to assume that the colour of the oxide film is governed only by the wavelength that experiences maximum interference. The thickness of the oxide film is obtained by determining the thickness of an air film between reflecting surfaces that produces the same colour by transmitted light as that observed for the oxide film.

The thickness of the oxide can be approximated using the following relationship:

$$\xi_{\text{oxide}} = \frac{\xi_{\text{airfilm}} n_{\text{air}}}{n_{\text{oxide}}} = \frac{\xi_{\text{airfilm}}}{n_{\text{oxide}}} \quad (6)$$

The refractive index of air is unity. Electrometric and interference measurements of oxide film thickness on copper, nickel and steel have been shown to be in good agreement [21].

4.5 ELLIPSOMETRY

Ellipsometry is an optical technique that uses elliptical polarised light to probe the dielectric properties of a sample (e.g. thin films) [32]. Ellipsometry can yield information about the thickness, morphology and chemical composition of layers that are thinner than the wavelength of the light source (i.e. less than 50 nanometres). The technique consists of directing a polarised light beam onto a surface at an oblique angle of incidence and measuring phase change and intensity (amplitude) of the reflected light.

There are various ellipsometric techniques available, including single-wavelength ellipsometry (null and phase-modulated techniques), and multiple-wavelength reflectometry and multiple-wavelength spectroscopic ellipsometry [31]. Many single-wavelength instruments are based on the null technique, which requires that polarisers and retarders be rotated until the effect of the polarisation is inverted and no light is transmitted through the instrument. The light sources used in these instruments are often fixed to a single wavelength.

Manually operated systems are less sensitive and less reliable than automated instruments. Spectroscopic ellipsometers can scan an entire range of wavelengths simultaneously. These instruments still use a rotating polariser (or analyser), but employ Fourier analysis of the detector signal to determine the ellipsometric parameters. These instruments, however suffer from low sensitivity under certain conditions, and have a poor signal-to-noise ratio, especially when the sample is not highly reflective.

Recent developments have seen increased usage of phase-modulated ellipsometry, particularly for dynamic studies (e.g. measurements on spreading liquid surfaces). Phase-modulated ellipsometers have a fast response time, superior signal-to-noise ratio and are less affected by small changes in the angle of incidence compared with null-based instruments. However, instruments having high frequency modulation and multi-channel detection for imaging and fast spectroscopic measurements are more expensive.

4.6 WETTABILITY (SURFACE ENERGY/TENSION)

Wetting is the spreading over and intimate contact of a liquid (adhesive) over a solid surface (substrate). If sufficiently intimate contact is achieved between the two phases, a physical attraction develops causing the liquid to conform to the surface on a macro and micro scale, displacing air and thus minimising interfacial flaws. Good wettability of a surface is a prerequisite for ensuring good adhesive bonding, and hence considerable effort has been expended in developing simple wettability tests to assess surface energy/tension prior to bonding (see below) [1-6, 33-34].

- Water break test (area of spread)
- Contact angle (static or dynamic, sessile drop or tensiometer)

Note: Surface energy is defined as the work necessary to separate two surfaces beyond the range of the forces holding them together and is given in units of mJ/m^2 . It is dependent on the interfacial intermolecular forces (dispersion – dipole interactions, acid-base/polar – hydrogen bonding where lone electron pairs are present) and their separation (see Section 2). The surface free energy of a solid can be indirectly estimated through contact angle measurements.

Two methods are available for measuring contact angles of solid surfaces: static (known as sessile drop or goniometry) and dynamic (known as tensiometry or Wilhelmy method). The static method requires the observation of a drop of test liquid on a solid substrate, while the dynamic method measures the forces of interaction as the solid is immersed in a test liquid. Dynamic contact angles measured at low speeds should equal static contact angles. Problems associated with the techniques include swelling of the solid surface, roughness and porosity. Surface energy will be affected by the solution pH (ionisation of surface oxides). Hydrogen bonding will reveal important polar and acid-base properties of the surface that may influence adhesion.

Water Break Test: This qualitative (go/no-go) test involves the specimen (in the form of a flat plate) being either immersed in water or water brushed or water sprayed onto the surface. The plate is then checked to determine the distribution of water on the surface (i.e. remains as a continuous film indicating good wettability or forms distinct droplets indicating poor wettability).

Contact Angle: The determination of contact angle at the solid/liquid phase boundary is one of the most sensitive methods for the surface characterisation of solid materials. 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 9) [3]:

$$\gamma_{lv} \cos \theta = \gamma_{sv} - \gamma_{sl} \quad (7)$$

where θ is the contact angle, and γ_{lv} , γ_{sv} and γ_{sl} are the surface free energies of the liquid-vapour, solid-vapour and solid-liquid interfaces, respectively.

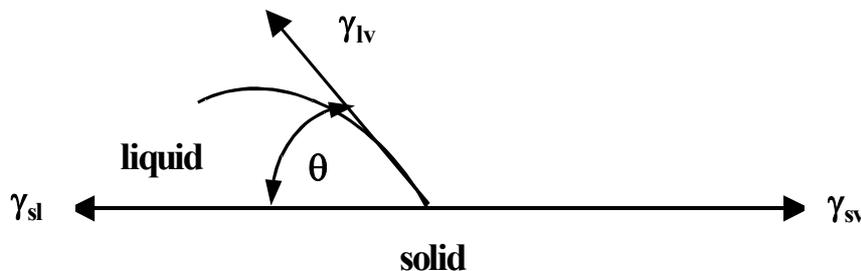


Figure 9: Contact Angle.

The lower the contact angle, the greater the tendency for the liquid to wet the solid, until complete wetting occurs at a 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. Ideally, the contact angle should be reduced to a minimum in order to enhance adhesive strength. Surface roughness will affect the shape of the droplet, complicating the contact angle measurement.

Contact angle is measured either on a goniometer or by projection (manually or video imaging). High purity liquid probes with well-known surface tension characteristics are used for measuring contact angle. Very small levels of impurities can cause large errors in contact angle measurement errors. Commonly used liquid probes, include distilled water, glycerol and methylene iodide (typical drop size is 2 to 20 μl).

Tables 4 and 5 compare contact angle measurements for different materials and substrates using sessile method. Figure 10 shows a schematic of bond strength versus contact angle (typical for increasing open time between surface preparation and adhesive bonding).

Table 4: Static Contact Angles for Surface Treated Aluminium [31]

Surface Treatment	Average Contact Angle (degrees)
As received (untreated)	61.0
Solvent Cleaned	80.0
Alkaline Etched	6.7
Standard FPL etch	<5

**Table 5: Contact Angles for Various Surface Treated Plastics
Military Handbook – 619B**

Material	Contact Angle (degrees)			
	Untreated	Plasma	Flame	Chemical
Polypropylene (PP)	87	22	87	60
Polyethylene (PE)	71	18	-	75
Poly vinyl chloride (PVC)	90	35	-	79
Polycarbonate (PC)	75	33	-	76
High Density PP	87	42	38	54

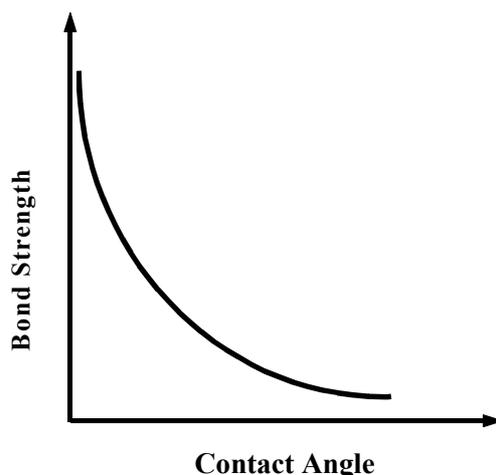


Figure 10: Schematic of Bond Strength versus Contact Angle.

Work of adhesion W_A (representing the change in the energy of the system) is given by Young-Dupre's relation [3]:

$$W_A = \gamma_s + \gamma_l - \gamma_{sl} = W_A^d + W_A^{ab} \quad (8)$$

where γ_s , γ_l and γ_{sl} are the surface free energies of the solid, liquid and solid-liquid interface respectively, superscripts **d** and **ab** denote the dispersive and acid-base components of the work of adhesion W_A , respectively.

Combining Equations (7) and (8) gives the equation below, which is used to express the strength of the interaction between the two phases:

$$W_A = \gamma_l (1 + \cos \theta) \quad (9)$$

Differences in the surface energy derived using polar or non-polar probe liquids allow the determination of the dispersion and acid-base components of W_A . Maximising acid-base interactions improves adhesion. Calculating the surface free energy of the solid surface requires testing against a series of well-characterised probe liquids (e.g. water and glycerol) with known dispersive and polar or non-dispersive components (see [2-3, 35-36]):

$$W_A = \sqrt{\gamma_s^d \gamma_l^d} \sqrt{\gamma_s^{ab} \gamma_l^{ab}} \quad (10)$$

which can be expressed as:

$$\frac{\gamma_l(1 + \cos \theta)}{\sqrt{\gamma_l^d}} = \sqrt{\gamma_s^{ab}} \left[\frac{\sqrt{\gamma_l^{ab}}}{\sqrt{\gamma_l^d}} \right] + \sqrt{\gamma_s^d} \quad (11)$$

By plotting $(\gamma_l^{ab})^{1/2}/(\gamma_l^d)^{1/2}$ versus $\gamma_l(1 + \cos \theta)/(\gamma_l^d)^{1/2}$, $(\gamma_s^{ab})^{1/2}$ is given by the slope and $(\gamma_s^d)^{1/2}$ by the y-intercept. The total free surface energy of the solid is the sum of these two component forces.

By using a suitable theory (e.g. Lewis Acid-Base theory), the polar component of the work of adhesion can be further reduced to give the individual acid and base components for the solid surface:

$$W_A^{ab} = \sqrt{\gamma_l^a \gamma_s^b} + \sqrt{\gamma_l^b \gamma_s^a} \quad (12)$$

where the superscripts **a** and **b** denote the individual acid and base components respectively of the acid-base work of adhesion.

Table 6: Surface Energy Characteristics (mJm^{-2}) of Typical Probe Liquids

Test Liquid	γ	γ^d	γ^{ab}	γ^a	γ^b
Water	72.8	21.8	51	25.5	25.5
Methylene Iodide	50.8	50.8	0	0	0
Glycerol	64	34	30	3.9	57.4
Ethylene Glycol	48	29	19	1.9	47

Dynamic Contact Angle: For porous materials, the contact angle will change with time as the probe liquid penetrates the surface. The dynamic contact angle can be measured using the Wilhelmy plate technique. This technique measures the forces exerted as the solid/liquid phase boundary is moved along the sample surface (Figure 11). If the forces of interaction, sample geometry and liquid surface tension are known then the contact angle may be calculated. This technique involves placing the sample on a balance and zeroing at the solid weight. The liquid (of known surface tension) is raised to meet the solid and the point of contact is determined and recorded as zero immersion depth. The solid continues to be lowered into the liquid to a set depth and the forces on the balance are continuously monitored. The process is then reversed and the solid is raised from the liquid.

The forces involved are:

$$F = \text{wetting force} - \text{buoyancy} \quad (13)$$

Buoyancy is accounted for by extrapolating the force back to the point of zero immersion depth.

The force is given by:

$$F = \gamma_l P \cos \theta \quad (14)$$

where P is the perimeter of the solid sample.

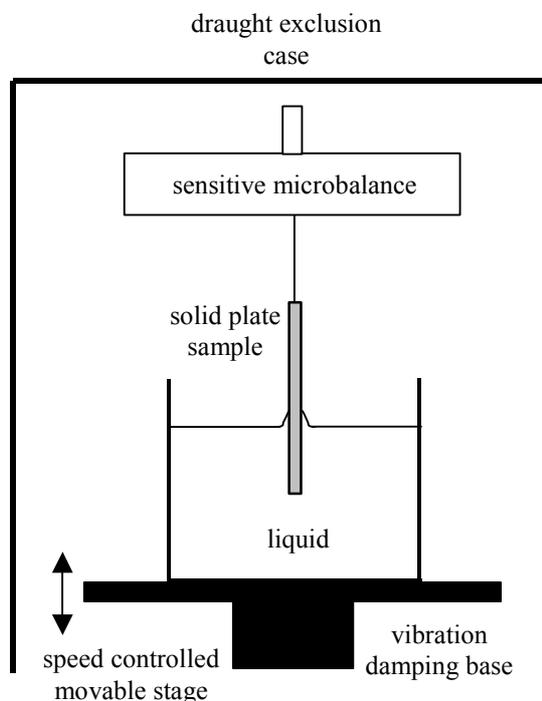


Figure 11: Wilhelmy plate method for measuring dynamic contact angle.

Using this method both the advancing (θ_{adv}) and receding (θ_{rec}) angles can be measured. The difference ($\theta_{adv} - \theta_{rec}$) is the contact angle hysteresis, which is used to characterise surface heterogeneity and roughness. In these cases, either the local surface energy (or chemistry) or local physical topography acts as barriers to the motion of the liquid contact line. Advancing and receding contact angles may be different.

The dynamic method averages the measurement over the perimeter of the solid, allows a wide range of test speeds and has no subjective error. Multiple cycles can be performed which yield information on adsorption. However, the sample geometry must be regular, having a constant perimeter over the entire length and have the same surface treatment on all sides in contact with the liquid. Table 7 presents contact angle and surface energy values for different surface treated mild steel specimens obtained by AEA Technology determined using the Wilhelmy plate dynamic method and distilled water [31]. The lower the total surface energy the more difficult to bond (see also BS EN 828 and ISO/DIS 15989 [37-38]).

Table 7: Dynamic Contact Angles and Surface Energies for Mild Steel [31]

Surface Treatment	Contact Angle (degrees)		Calculated Surface Energy (mJm^{-2})		
	θ_{adv}	θ_{rec}	γ^d	γ^p	γ^{total}
As received (untreated)	90.5	31.1	32.1	1.8	33.9
Alumina gritblast	86.9	30.2	50.4	0.5	50.9
Acid Etch	60.1	31.3	38.1	13.0	51.1
Zinc Phosphate Conversion	53.0	40.9	40.3	16.1	56.4

4.7 HARDNESS

Hardness refers to the ability of a material to resist permanent indentation or deformation (or compressive loads) when in contact with an indenter under load (Figure 12) [39]. The basic principle behind hardness testing, which includes Rockwell and Vickers indentation tests, and micro-hardness and nano-indentation tests, is to load an indenter into a surface and measure the deformed imprint after retraction of the indenter. The indenter may be spherical (Brinell test), pyramidal (Vickers and Knoop tests) or conical (Rockwell test). The indentation is generally inspected using an optical microscope attached to the hardness test apparatus. Hardness data is defined in terms of the indenter geometry and for visco-elastic materials the duration of loading. In the Brinell, Vickers and Knoop tests, hardness is the applied load divided by the unit area of the indentation and is expressed in kgf/mm^2 . In the Rockwell test, depth of indentation is measured and converted to a hardness number (no associated units), which is inversely related to depth.

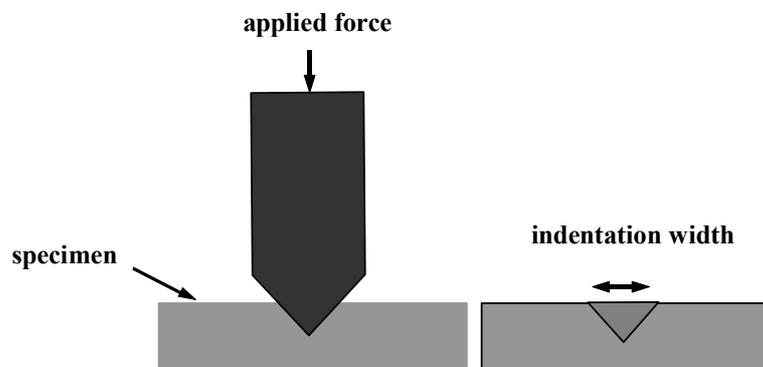


Figure 12: Indentation test.

For most hardness measurements an indentation load of 30 N (or greater) is used and the size of the indentation is approximately 300 μm in size in the plane of the tested surface. Micro-hardness testing involves smaller indenters and significantly smaller loads (10 mN to 10 N). The corresponding indentation is far smaller and is associated with local properties, whereas standard hardness tests provide bulk hardness measurements of the surface region. Indentation tests, such as micro- or nano-indentation, may provide more usable information on the mechanical properties of the near-surface material (including stiffness, plasticity and fracture). Micro-hardness tests can be used to differentiate between soft and hard surfaces. However, it is also more difficult to measure residual imprints for micro-hardness tests, as the residual imprints are relatively small. Data variability also increases with decreasing load. Most of the hardness tests have been miniaturised to enable micro-hardness measurements. The indenter penetration needs to be less than 10% of the surface layer thickness to avoid the influence of the substrate. Hardness-depth profiles can be obtained by producing tapered sections (see Figure 13).

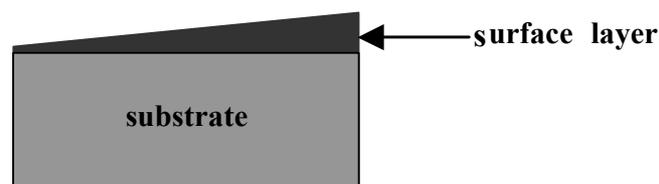


Figure 13: Taper-sectioning for hardness depth profiling.

Hardness tests can be applied to a wide range of materials and used to characterise the mechanical structure of surface layers (e.g. oxide films or coatings) [40-41]. Hardness measurements have been shown to be sensitive to surface treatment (see Table 8 [31]). The associated scatter in hardness measurements can be high, thus differentiation between the levels of treatment may be difficult. There are numerous hardness standards (see [42-47]).

Table 8: Hardness Measurements for Surface Treated Aluminium and Titanium [31]

Surface Treatment	Microhardness (Vickers Hardness Number)	Ultra-micro Hardness (N/mm ²)
Aluminium		
As received (untreated)	80-110	1,400
Phosphoric Acid Anodising (PAA)	65-84	2,900
Chromic Acid Anodising (CAA)	79-135	19,000
Titanium		
As received (untreated)	258-352	10,800
Sodium Hydroxide Anodising (SHA)	234-248	800
Chromic Acid Anodising (CAA)	322-369	12,500

4.8 SCRATCH TEST

The adhesion scratch test is a commonly used method of assessing coating adhesion (see Figure 14) [39-40]. The test is a variant on a hardness test and is designed to generate stresses at the interface between the coating and the substrate, which exceed the interfacial bond strength of thin, high adhesion coatings or films. A loaded diamond tipped stylus (10 to 60 N) is drawn across the target surface (or the sample is displaced beneath the stylus) under an increasing load (typically 100 Nmin⁻¹) until some well-defined failure occurs, usually flaking or chipping. The horizontal displacement rate is nominally 10 mm.min⁻¹ with sample size being typically 25 mm x 15 mm.

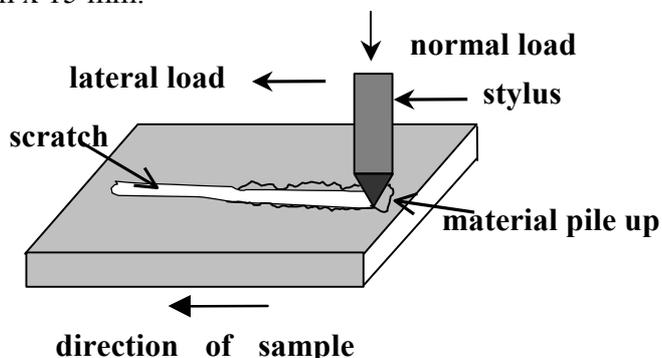


Figure 14: Scratch test.

During the test, the penetration depth and stylus position are recorded. These data can be supplemented with the vertical indenter load, the horizontal force on the indenter and acoustic emission to enable the coefficient of friction and the point of failure to be determined. The scratch can be subsequently analysed with a profilometer, SEM or optical microscopy to ascertain the scratch shape (residual depth, scratch width and pile-up height) to allow the failure mechanism to be identified. Varying the loading rate, the scratch speed and the indenter shape markedly affect the results of the test. Scratch testing equipment is commercially available. Scratches can be single or multi-pass. There has been recent collaborative work involving NPL to provide a scratch test calibration procedure, draft standards and reference materials.

4.9 SURFACE RESISTIVITY AND IMPEDANCE

Surface resistivity is defined as the electrical resistance of the surface of an insulator and is expressed in ohms (units ohms/m^2) [48-49]. The technique involves placing two electrodes on the surface of the test sample, applying an electrical potential between the electrodes and measuring the resultant current. The surface resistivity σ is determined using the following relationship [48]:

$$\sigma = K_s \frac{V}{I} \quad (15)$$

where V is the applied voltage, I is the measured current and K_s is the test cell constant for surface resistivity based on cell geometry.

A configuration for measuring surface resistivity is shown in Figure 15. The current is only measured between the bottom two electrodes as shown in the diagram. The top electrode is guarded so that only current flowing between the two lower electrodes is measured by a picoammeter. The key test parameters are applied voltage, length of electrification time, humidity and temperature. The longer the voltage is applied, the higher the resistivity. This is because the sample charges exponentially with time. Also, surface resistivity measurements decrease with increasing humidity levels. The electrical and environmental conditions should be kept constant to ensure consistent data. Poor electrical contact between sample and electrodes will also have an adverse affect on the reliability of surface resistivity measurements. The electrode area must be equal to the contact area; any discrepancies will contribute measurement errors.

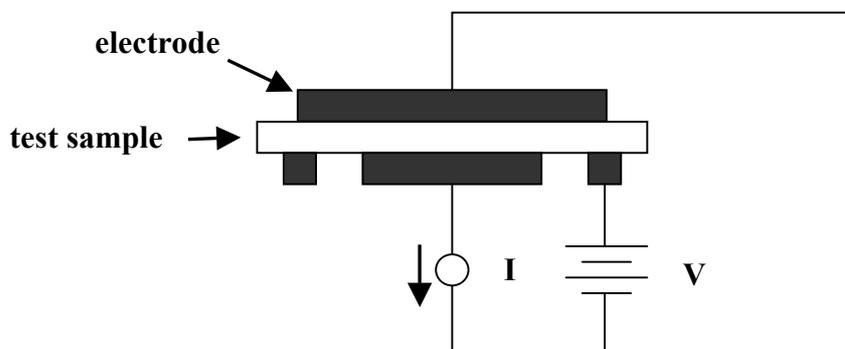


Figure 15: Surface Resistivity.

Problems can be encountered when measuring materials with high surface resistivity. Background currents due to charging, static or triboelectric charge, or piezoelectric effects, may cause measurement errors. Background currents may be of the same order of magnitude as the stimulated surface currents. Background currents of opposing polarity to the stimulated current have a cancelling effect, and the measured (resultant) current will be lower than the true current. If the polarity of the background and stimulated currents are the same then the measured current will be higher than the true current. An alternative approach is to employ the Alternative Current Method, which applies a bias polarity of positive polarity then the current is measured after a specified delay time. The polarity is then reversed and the current is then measured again using the same delay time. This process is repeated and the resistance is calculated on a weighted average of the most recent measurements. Both techniques are sensitive to surface contamination and affected by variations in composition and thickness of the surface layer and substrate.

Another approach that has proved successful for characterising oxide films and coatings is the AC impedance technique. This technique is an electrochemical method used for corrosion studies to measure oxide growth rates. In this method, the test surface is immersed in an electrolyte and an alternating voltage is applied. The resultant current is measured as a function of frequency (5 kHz to 10 MHz). The resistance, capacitance and inductance of the surface and the resistance of the electrolytic solution can be used to determine surface impedance. It is possible to relate film thickness, film composition and oxidation rate for CAA and PAA surface treatments from impedance measurements. The AC impedance technique is capable of differentiating between various surface treatments and levels of treatment for a given surface treatment. The technique is sensitive to variations in the composition and thickness of the oxide film and surface contamination. Although the technique is unsuitable for on-line inspection, there is considerable scope as a developmental tool and for modelling oxidation processes.

5. CONCLUDING REMARKS

There are a number of physical techniques that can be used for quantitative surface characterisation, which are potentially suitable for production or on-line surface inspection and development of surface treatments. For most of these techniques, it is possible to control the test parameters and in principle determine the relationship between surface characteristics (e.g. roughness, reflectivity and hardness) and test parameters, thus enabling optimisation of surface treatments and rapid on-line inspection (and possibly automated correction). It is planned to evaluate a number of physical techniques for characterising surface properties; correlating measured surface characteristics with adhesion performance. Statistical analysis (design of experiments (DOE)) techniques will be used to relate the test parameters and surface characteristics (i.e. roughness, reflectivity, wettability and hardness) for different adherend/surface treatment systems. The intention is to demonstrate the effectiveness of the techniques for different surface treatments and adherends and for optimising joint strength and durability performance. Surface characterisation measurements will be compared with durability data to ensure that the characteristics that are being measured or optimised actually translate into improved durability.

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APPENDIX 1: SURFACE ANALYTICAL TECHNIQUES

Parameter	AES	XPS	EELS	EDX	XRF	IRS	Raman	XRD	SIMS	RBS
Excitation/Probe Beam	Electron	Photon (X-ray)	Electron	Electron	Photon (X-ray)	Photon (Infra-red)	Photon (visible)	Photon (X-ray)	Ion (Ar ⁺ , O ₂ ⁺)	Ion (He ⁺⁺)
Emission/Analysed Beam	Electron	Electron	Electron	Photon (X-ray)	Photon (X-ray)	Photon (Infra-red)	Photon (visible)	Photon (X-ray)	Molecular fragments	Ion
Analysis method	Energy of Auger electrons	Energy of photoelectrons	Energy loss of scattered electrons	Energy or wavelength of X-ray	Energy of X-ray	Absorbed frequencies	Frequency changes	Diffraction angle	Mass of fragments	Energy loss of scattered ions
Depth resolution	1 - 5nm	1 - 5nm	1 μm	0.1 - 1 μm	1 nm	100 nm-5 μm	100 nm-5 μm	5 μm	1 - 200 nm	1 nm - 1 μm
Spatial resolution	1 nm - 10 μm	5 μm - 10mm	1 nm - 1 μm	1 μm	5 μm-10 mm	1 μm	1 μm	10 nm	50 nm-10 mm	1 mm
Information provided	Elemental, chemical state	Elemental, chemical state	Elemental and chemical	elemental	Elemental, chemical state	molecular	molecular	chemical	Elemental, chemical state, isotopes	Elemental, isotopes
Quantitative	Semi with standards	Semi with standards	yes	Yes (Na to U)	Semi	Semi	Semi	yes	Semi with standards	yes
Destructive technique	For some materials	no	no	no	no	no	no	no	yes	no
Chemical/elemental distribution	yes	Yes limited	yes	yes	Yes limited	no	no	no	yes	no
Depth profiling	By ion sputtering	By ion sputtering	no	By ion sputtering	yes	no	no	no	By ion sputtering	yes
Material applicability	All non-insulators	All materials	Li to U	All non-insulators	All solids	All organic	All organic	Crystalline only	All solids	All solids
Sensitivity	Not H, He	Not H, He	n/a	B to U	Al to U	n/a	n/a	All elements	All elements	Not H, He