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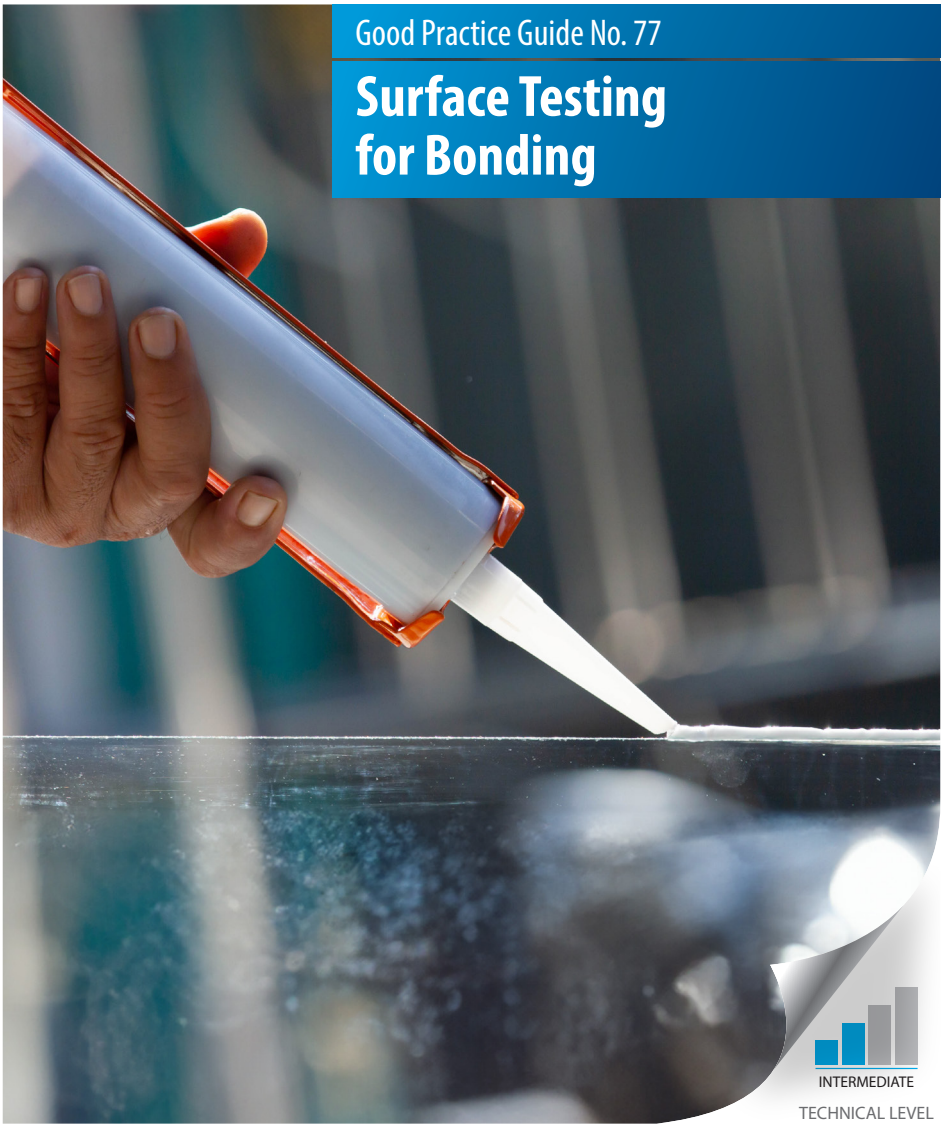
Good Practice Guide No. 77

Surface Testing for Bonding



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NPL Authors and Contributors
Bruce Duncan*
Antony Maxwell*
Doug Leatherdale**

*National Physical Laboratory, Teddington, TW11 0LW
**Pira International, Leatherhead, KT22 7RU

Find out more about NPL measurement training at **www.npl.co.uk/training** or our e-learning Training Programme at **www.npl.co.uk/e-learning**

National Physical Laboratory
Hampton Road
Teddington
TW11 0LW
Middlesex
United Kingdom

Telephone: +44 (0)20 8977 3222
e-mail: training@npl.co.uk
www.npl.co.uk

Abstract

The manufacture of adhesive bonds requires suitably prepared substrates. Methods for determining roughness, wettability, absorbency and bonding performance are presented in this Good Practice Guide. Methods need to be selected on the basis of the materials (adherend and adhesive), bonding process, loading and service conditions, degree of accuracy required and budget (time and cost) for the assessment.

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Chapter 1: Introduction

- Scope
- Materials

1. Introduction

1.1 Scope

The performance of a materials system, such as an adhesive joint, coating or composite, is influenced by the properties of the bulk materials and of the interfaces within the system. The design of adhesively bonded structures requires accurate materials data and knowledge of the performance of the interfaces. Surface preparation is recognised as a critical step in the adhesive bonding process and considerable effort is frequently expended in optimising surface treatments for bond strength and performance, since unsatisfactory surface preparation will result in premature and unpredictable interfacial failure of bonded joints. Whilst the preparation of engineering materials, such as metals or polymer composites, for structural bonding is extensively covered in the scientific literature, non-structural materials such as paper, board, polymers, leather, glass and fabric used in a vast range of consumer products have received comparatively little attention. There are many types of adhesives and bonding processes used for joining and these have a wide range of potential measurement needs [1].

This Good Practice Guide describes a selection of methods for assessing surface properties in a manufacturing environment. This Guide is one of a series of Measurement Good Practice Guides covering various areas of adhesive technology [2-8]. The Guide aims to provide guidance to technologists, laboratory staff and quality assurance personnel on how to characterise the substrates in order to achieve satisfactory adhesion in bonding processes. A general familiarity with laboratory operations and mechanical testing, but not specifically adhesives testing, is assumed. The objective of this Guide is to familiarise the operator with the options available for characterisation of surfaces.

Section 1.2 describes materials used in the project that developed this guide. Section 2 outlines surface preparations and describes methods that can be used for assessing and quantifying surface conditions. Section 3 describes methods that could be used for determining the roughness of substrates. Section 4 covers methods for assessing wettability and surface energy. Section 5 describes techniques for characterising absorbency of substrates. Section 6 summarises some useful bond test methods. Adhesion mechanisms are discussed in Appendix I. A glossary of terms is provided in Appendix II. Appendix III describes surface chemical analysis methods.

Further information and guidance on the testing of adhesives and adhesive joints may be obtained from other NPL Good Practice Guides [2-8] and various textbooks [9-16].

1.2 Materials

Many of the methods outlined in this guide were used to evaluate a range of substrate materials and hot melt adhesive systems that are typically used in the packaging industry. Further information on these materials can be obtained in the project reports [17-19].

1.2.1 Substrates

Approximately 40 substrate materials were obtained and sets of these were studied using the techniques outlined. Many of the substrates were coated or treated on one surface (the 'top' surface). Adhesive may be applied to either surface of these substrates, e.g. carton sealing often involves bonding the top of one flap to the reverse surface of another. Therefore, all of those packaging substrates were separately characterised on the top and reverse sides using the techniques. All substrate samples were conditioned under ambient conditions (23 °C and 50% relative humidity). The range of packaging substrates represented the following paper, board and plastic categories:

- white lined chipboard (WLC)
- folding boxboard (FBB)
- grease freeze folding boxboard
- bleached paperboard
- label paper
- UV lacquer coated board
- solid bleached sulphate (SBS)
- polyethylene coated solid bleached sulphate
- polyethylene coated printed waste based paper
- polyethylene terephthalate coated solid bleached sulphate (printed and unprinted)
- polyethylene and polypropylene coated folding boxboards
- test liners
- Kraft (jute) board
- plastic (amorphous polyethylene terephthalate and polypropylene) sheets

1.2.2 Adhesives

The bonding of hot melt adhesives was a major focus of this study. Hot melt adhesives are thermoplastic polymer based compounds. They are applied as molten liquids, which increase in viscosity as they cool before freezing and becoming more rigid. Two common base polymers are ethylene vinyl acetate (EVA) copolymers and polyethylene (PE) homopolymers, with metallocene based hot melts now entering the market. A tackifier resin is added to achieve good hot tack, waxes to reduce viscosity (viscosity must be low at application temperature to allow good substrate

wetting, but not too low to allow excessive spreading) and control setting speed, and stabilisers to prevent charring.

A typical formulation for a hot melt packaging adhesive would be:

- Tackifier resin 35-50%
- Polymer 25-35%
- Wax 20-30%.

Recently, pressure sensitive hot melt adhesives, which have permanent tack, have been introduced in packaging and garments. A further trend is the introduction of low process temperature (cool running) adhesives that can be dispensed around 90°C-100°C, allowing more energy efficient and safer processes than traditional systems where dispense temperatures are typically over 150°C. Hot melt adhesives are formulated for many different purposes with properties that are specific to the market application but there are certain adhesive attributes that are common:

- Low cost
- Clean running (absence of stringing or dripping)
- Long pot life (thermal stability – resistance to viscosity change and charring)
- Low temperature application – mainly desirable to reduce worker exposure to fumes and lessen the burn hazard
- Wide temperature application window
- Taint free – food packaging applications
- Generates substrate failure – fibre tear is a universal measure of satisfactory bond performance in the packaging industry

Several hot melt adhesive grades were supplied by National Starch and Chemical, representing the broad application categories used in the packaging industry.

- General purpose
- Deep freeze
- Heat/creep resistant
- Difficult substrates
- Low temperature application
- Pressure sensitive

Most of the hot melt adhesives were supplied as bags of solid pellets from which sub-samples could be taken. However, the pressure sensitive adhesives were supplied in 1 kg blocks of soft, tacky solid present a particular challenge for testing. In normal production

use the whole block would be melted in the tank of the dispensing machine before application but for testing smaller quantities are desired. It is extremely difficult to separate small pieces of adhesive from the block due to the high tack of the adhesive – it tends to re-bond as it is cut. Cooling in a deep freeze (to increase rigidity and reduce tack) and heating in an oven to over 100 °C (to make it more liquid) made little difference to the ease of cutting of the particular adhesives studied.

Chapter 2: Surface Characterisation

- Surface preparation
- Surface assessment
- Surface imaging and inspection
- Reflectance and qualifying appearance

2. Surface Characterisation

2.1 Surface Preparation

Good surface preparation is crucial to ensuring sufficient bond strength and reliable performance of bonded joints, particularly under hostile service or manufacturing conditions. Unsatisfactory surface preparation will result in premature and unpredictable bond failure at the adhesive/adherend interface either in service or at some further stage of the bonding process. Surface preparation is recognised as a most critical step in the adhesive bonding process and considerable effort may be expended in optimising the surface treatment.

The purposes of surface treatments are to:

- Remove contaminants that may interfere with bond formation;
- Remove weak surface layers;
- Produce a surface morphology that enhances the surface area available for bonding and/or allows mechanical keying;
- Chemically modify the surface to increase surface energy and chemical compatibility with the adhesive.

The selection of surface treatment is largely dependent on the substrate, the required strength and durability of the joint and economic considerations (such as costs and time involved in preparation). Surface treatment processes often consist of a series of different steps. Surface treatments can be classified as either passive or active. Passive surface treatments (e.g. solvent washing and mechanical abrasion) clean the surface, remove weakly attached surface layers and alter the surface topography without altering the surface chemistry. Active surface treatments (e.g. corona discharge or plasma treatment) alter the surface chemistry (i.e. introduction of functional groups). After completion of the surface preparation process, the adherends should be handled and stored carefully in order to prevent surface contamination prior to bonding. It is normally advisable that bonding be performed immediately following surface treatment to maximise performance.

It is normally important that the process of surface preparation only affects the chemistry and morphology of a thin surface layer of the adherend(s) and does not alter the mechanical and physical properties of the underlying substrate. There are many procedures available for engineering surfaces [e.g. 16, 20–24] but comparatively few for materials used non-engineering applications. Advice is usually sought on surface preparation from the adhesive manufacturer.

Surface preparation procedures may often require potentially hazardous or environmentally damaging chemicals. All preparation should be carried out to COSHH specifications.

2.2 Surface Assessment Methods

Surface characterisation of the adherend prior to bonding 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 surface layers.

Surface and chemical characterisation techniques can provide qualitative and quantitative information relating to the strength and durability of bonded joints. There are many physical measurement and chemical analysis techniques that can be used for surface characterisation of metals, plastics (including fibre-reinforced plastic composites) and other substrates [see e.g. 1, 3, 4, 7, 25, 26]. The techniques available to the researcher range from the inexpensive and simple (e.g. visual inspection) to the expensive and specialised (e.g. photoelectron spectroscopy).

Chemical characterisation, either elemental or functional group analysis, can be achieved using spectroscopic techniques, see Appendix III. The various techniques can provide qualitative and quantitative information on chemical composition and varying information on molecular structure and physical-chemical characteristics, which determine the attractive forces towards adhesive molecules and, hence, bonding performance. The techniques have different levels of capabilities for scanning areas or providing depth profile information. With the exception of the optical techniques (IR and Raman), the measurements are performed with samples in an evacuated chamber, which adds to the cost and complexity of the technique. Many techniques require ultra high vacuum (UHV) conditions to avoid scattering or generation of secondary x-rays or electrons from gas molecules. Under UHV, there may be loss of volatile material from the surface and alterations to the microstructure of the surface being investigated.

With the possible exception of infra-red (IR), these techniques are generally only available at large manufacturing and research facilities. Although many research technology organisations (RTOs) and academic institutions offer spectroscopic measurement services, many adhesive bonders are discouraged from regular use by the costs and need to schedule/transport samples. Therefore, such techniques are not considered further in this guide.

2.3 Surface Imaging and Inspection

The appearance of the surface immediately before bonding is the simplest quality control check that can be undertaken of a surface. The human eye is able to detect a wide range of surface features and in most cases the whole of a surface can be inspected in one go whereas many instrumented approaches tend to focus on reduced areas and detect one type of feature. A simple visual inspection will reveal potential problems, such as:

- Presence of grease or finger marks;
- Accumulation of dust;
- Damage to the surface (e.g. scratches, burns, fraying);
- Variations in surface quality or treatments (e.g. roughness or colour);
- Wrong materials.

The first check of surface condition is usually by visual inspection to detect signs of any problems that might compromise bonding, such as damage (e.g. scratches) and contamination (e.g. grease, marks). The surface appearance and morphology will also be assessed to determine whether surface treatments have been applied uniformly (e.g. the roughening caused by grit blasting a smooth surface). Many surface treatments affect the surface morphology at scales too fine to be resolved by the human eye and there are techniques available to view surfaces at higher resolution.

Often the use of visual inspection requires an experienced operator who can detect the problem and assess the likely significance of the observation. This approach works well in a relatively low volume 'craft' type manufacturing environment but in high production rate plants the volume of checks required may be excessive leading to possible errors in fault identification.

The approaches to overcoming the speed/time limitation with visual checks include:

- Batch checks on materials, the frequency of which are chosen based on the required statistical reliability of the process, the believed rate of occurrence of problems in the material or process (often from previous experience) and the economic between the cost of performing checks and the cost of resolving end of line problems (in most cases the earlier a problem is discovered the less costly the rectification).
- Automated inspection using computer image analysis, this requires that the surface can be imaged accurately and that algorithms to identify off-specification surfaces which would then trigger remedial action (e.g. further inspection by an operator).
- Reliance on quality inspections performed by the supplier.

Visual inspection is subject to interpretation by the observer and often relates to experience, one person's pass inspection may be another's fail. Automated systems may remove subjectivity but rely on the skill and knowledge of the system programmer and may not be able to cover all eventualities. There are many measurement methods that quantify aspects of surface appearance that could help with surface inspection.

Table 1 summarises various microscopy and imaging techniques that may provide higher resolution or information additional to what can be achieved with the naked eye. These techniques produce images, which give qualitative information of the surface. Often these images are compared with reference images to aid interpretation.

With the possible exception of optical microscopy, these techniques involve considerable investment in equipment and expert personnel. Often the time required to prepare and investigate a samples can be considerable. Hence, they are uncommon in production facilities but may be used in the research and development of new products/processes or forensic investigation of manufacture or service failures.

Technique	Description	Use/Limitations
Optical Microscopy	Observation of the surface through magnifying lenses.	Optical microscopes are commonly available laboratory equipment. Resolution is limited by the wavelength of light to ca. 1 μm, which is not sufficient to view many surface features. Illumination conditions can be altered (e.g. to generate fluorescence) and light signals filtered (e.g. polarising filters) to enhance images.
Scanning Electron Microscopy (SEM)	A highly focused scanning electron beam bombards the surface causing large numbers of secondary electrons to be generated and formed into an image, the intensity of which is governed by surface topography.	Qualitative three-dimensional (3-D) imaging of surface features. Resolution of SEM is approximately 100 times greater than for optical microscopy and features can be seen to approximately 5 nm. SEM is suitable for all materials, but non-conducting materials must be given a thin conductive coating (e.g. gold sputtered), which can mask the true surface morphology. To avoid degradation of the signal by scattering of the secondary electrons SEM measurements are normally performed under vacuum.

Transmission Electron Microscopy	TEM focuses a beam of electrons on the specimen. The transmitted signal is projected onto a phosphor screen and an image is created.	Extremely high resolution (0.2 nm) is possible. However, electrons cannot penetrate a specimen very deeply so sample thickness is a major problem. Ultra high vacuum (UHV) is needed in the sample chamber.
Atomic Force Microscopy (AFM) and Scanning Tunnelling Microscopy (STM)	AFM/STM measures the morphology and topography of surfaces on the atomic scale. A sharp tip, mounted on a cantilever, is scanned across the surface (in contact or non-contact modes) using interaction forces. The vertical movements of the cantilever are analysed.	Atomic force microscopy is a popular method used by many industrial R & D sectors to measure surface topography and materials properties with spatial resolutions of 5 - 20 nm and height dimensions in the range from 100 nm down to 5 nm and exceptionally to 0.2 nm. STM can produce a 3-D image for visual inspection of conductive surfaces and also measure relative surface stiffness giving local hardness and modulus information. However, investigated areas are small and scans take significant time to perform. No special atmosphere is required for AFM but the technique is sensitive to vibrations.
Thermal Imaging (or Thermography)	Infra-red (thermal) imaging cameras can be used to provide a heat map of a surface.	Thermal cameras can be used to view the flow of heat through a substrate from a heat source or the surface can be heated and the decay of heat determined. Thermal images will show hot or cold regions where the temperature differs from the surface average, which may indicate for example surface contamination, variations in thickness or density or the presence of flaws/delaminations within the substrate.

Table 1: *Imaging Techniques*

2.4 Reflectance Measurements for Quantifying Appearance

2.4.1 Gloss Measurement

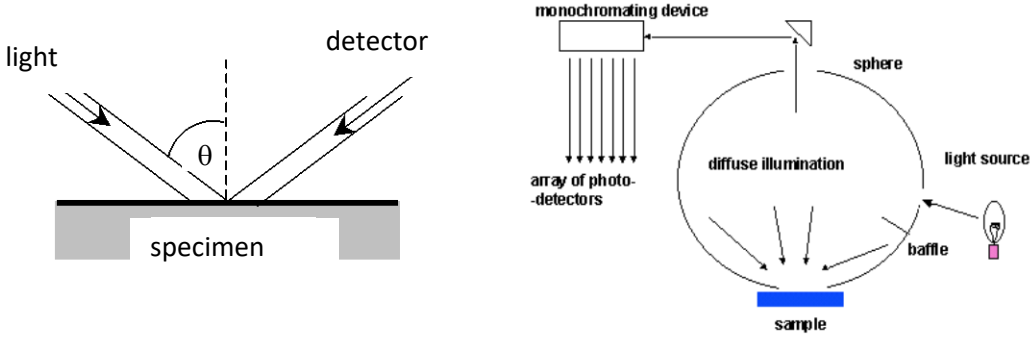
Gloss is a measure of the reflectiveness or 'shininess' of a surface. It is an important property of many everyday products, such as paints, plastics or papers, and simple, standardised measurements methods have been developed to determine gloss to enable material specification and quality assurance. Terms such as gloss or matt finish are well understood in everyday use and gloss attributes are commonly specified for many grades of materials. The gloss of a surface will be affected by the coatings, surface roughness, contaminants (such as dust or fingerprints), damage (e.g. scratches or thermal degradation) and material changes. Therefore, gloss is sensitive to many of the surface factors affecting bond performance.

Gloss is defined as the proportion of light reflected from the surface at the specular or 'mirror' angle in relation to a surface having a standard gloss value. A beam of light, normally filtered to produce a standard spectrum, is projected onto the target surface at a specific angle and the amount of light reflected is measured. For a perfectly smooth, mirror surface all the light is at the same angle, the specular angle. Surface roughness causes incident light to be scattered at angles other than that of specular reflection, such that the scatter increases with roughness, and absorption of light will reduce the amount reflected. Many simple hand-held fixed angle instruments are available that comply with the relevant international or industry gloss standards [27, 28], (Figure 1a). These instruments follow standards specifying the illumination, the angle of the incident beam (20°, 60° or 85°) and the spot size. A standard black glass tile is used as a reference for comparisons. The calibration should be checked before use and the gain of the instrument adjusted so that the measured reading corresponds with the calibrated value of the tile. The calibration should be checked regularly when performing tests and adjusted to account for instrument drift. Samples generally should be free of contaminants such dust, debris and grease are these will interfere with the measurement or possibly penetrate into the instrument. Since the gloss meter is placed in contact with the surface, transfer of contaminants between samples is a risk and procedures (such as blowing debris off the sample surface with a gentle air blast and wiping the meter surface between samples) should be used to avoid this.

Gloss measurements can provide quantitative data on the uniformity and quality of surface treatments and show sensitivity to gross changes in surface roughness and markings. Gloss will vary on surfaces having oriented features and it is good practice to take measurements in orthogonal directions to assess this. Values can vary from approximately 3 gloss units for untreated cardboards to over 100 for smooth plastic films. Polished metal or mirror surfaces will have even higher gloss values. Gloss measurement can be used in metal finishing to distinguish grit blasted regions from

untreated areas, but the technique lacks the sensitivity to discriminate between different levels of surface treatment [29]. Gloss measurements made on the coated and uncoated surfaces of a selection of paper, board and plastic film substrates used in packaging showed a general correlation between gloss and surface roughness – i.e. the gloss reading reduced as the surface roughness increased. However, as Figure 2 shows, the correlation (particularly for smooth surfaces) is not sufficiently good to determine a quantitative relationship between gloss and roughness.

The standard instruments use defined illumination spot sizes and therefore provide only point measurements of gloss, which may be insufficient to check large surface areas although systems to automatically scan gloss measurements over larger areas can be installed but at a cost. Gloss measurement is normally carried out on flat substrates but a degree of gentle curvature can be accommodated.



(a) Gloss meter (b) Colorimeter

Figure 1: *Schematics of reflectance measurement instruments*

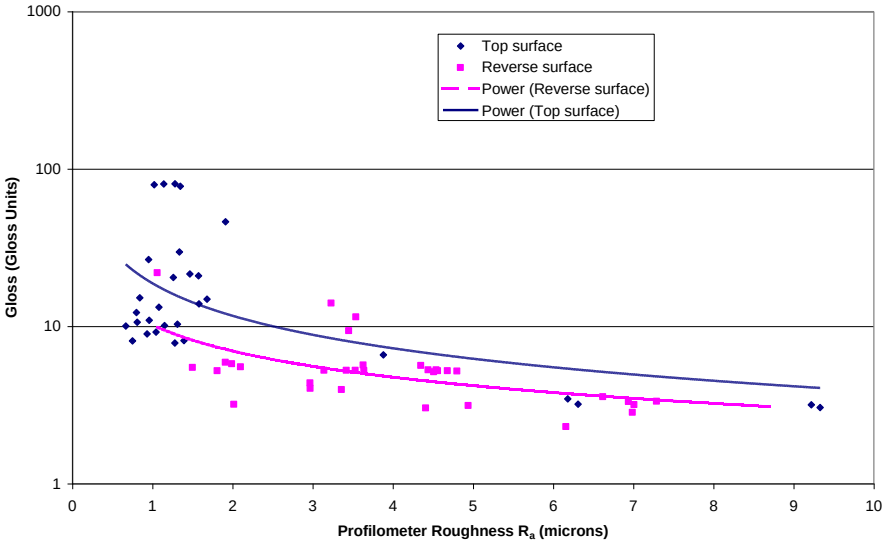


Figure 2: *Relationship between gloss and roughness*

2.4.2 Colour Measurement by Reflectance Spectroscopy

Colour measurement provides more information on the surface than gloss measurement but requires more sophisticated measurement equipment. Colour may be a specification the substrate, particularly if appearance is a critical factor for the component, but this may be more likely to be judged by comparison with reference colour charts. Colorimetry can often be used to detect differences between surface treatments and the degree or intensity of the surface treatment (e.g. exposure time), since colour is sensitive to surface morphology and chemical composition. Colour measurement [7, 30] requires a spectrophotometer to illuminate the sample with white light and to measure the amount of light reflected by the sample, Figure 1(b). The intensity at each wavelength interval is determined by passing the reflected light though a monochromating device that splits the light up into separate wavelength intervals. The instrument is calibrated using a white tile with a known reflectance at each wavelength. Reflectance values obtained are expressed between 0 and 100 (as a percentage).

Colorimetry results have shown that surface reflectance measurements have some promise and can detect differences between some metal surface treatments such as anodisation [25]. Generally, it is observed that there is a large change between the untreated surface and the treated surface but the differences between different levels of treatment are less significant. When the repeatability and measurement uncertainty of the colour measurement are take into consideration, it may be extremely difficult to distinguish between different anodisation treatments.

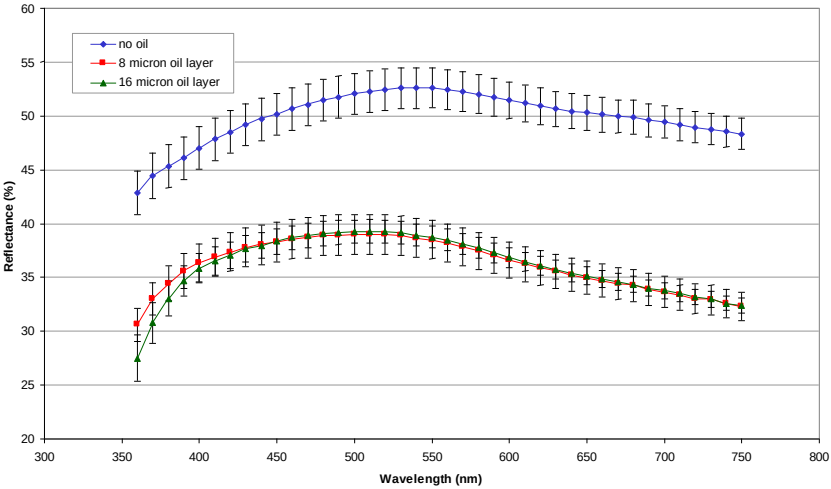


Figure 3: *Effect of oil film thickness on spectral response*

Colour reflectance measurements can also show the presence of a contaminant on a surface. For example, the results shown in Figure 3 indicate that reflectance shows a good discrimination between clean and oiled surfaces but there are no significant differences evident between the different levels

Chapter 3: Surface Roughness & Friction

- Stylus profilometers
- Optical profilometers
- Roughness Measurements for quantifying appearance
- Coefficient of friction

3. Surface Roughness and Friction

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

- Contact (stylus) profilometry: hand held roughness meters typically have a measurement range of 100 nm to 4,000 nm.
- Optical profilometry; phase shift white light interferometers have typical measurement ranges of 0.2 μm to 100 μm.
- Atomic force microscopy (AFM); typical measurement range 10 nm to 7,000 nm.
- Air flow methods, provide a relative measure of roughness.

The reliability of any measurement technique will decrease as the lower limit of resolution is approached (i.e. where the surface is smooth according to the depth scale of the instrument).

Surface topography [31] is defined as that which distinguishes a real surface from a perfectly flat, featureless one (i.e. polished). Filters are used to separate the long-wave (waviness) components of the measurement from the short-wave (roughness) components of the surface profile. Waviness is defined as the more widely spaced component of the surface texture. Roughness features are <10 μm 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.

$$R_a = {}^{1}/_{L} \int_0^L |y(x)| \, dx \tag{1}$$

$$R_q = \sqrt{{}^{1}/_{L} \int_0^L |y^2(x)| \, dx} \tag{2}$$

Where L is the sampled length, x is the position along the sampled length and y(x) are the roughness profile values (see Figure 4).

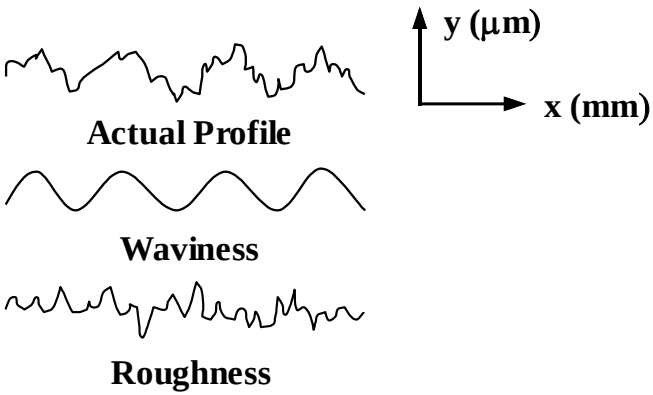


Figure 4: *Surface topography definitions*

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.

The roughness of a surface also influences the friction between the surface and a second surface. However, the level of friction is not due solely to the roughness but also to the physical nature of the surface and interaction forces between the surfaces. Furthermore, friction measurements test a much larger area of the surface than roughness measurements. It is therefore possible that the sliding friction coefficient may provide a better correlation with bonding than roughness alone.

3.1 Stylus Profilometers

Contact (stylus) profilometer instruments move a loaded probe (usually a diamond) across the target surface and record the vertical movement caused by the irregularities [31-34]. These measurements are analysed automatically using Equations (1) and (2) to produce a roughness value. A typical instrument is shown in Figure 5. The normal track length is 12.5 mm. The instrument can produce a number of roughness parameters of which the average roughness amplitude, R_a (microns), is most commonly quoted. This technique is most suitable for hard surfaces, since soft materials can be damaged, and reducing the load may result in some surface features not being registered. Lateral and vertical resolution is affected by stylus shape (usually a cone with a spherical tip, Figure 5, and angle of 60° or 90°), stylus tip radius (typically 5 μm - sharper tips increase damage) and surface profile. Instruments to measure

surface roughness are limited by spatial frequency, some features being too wide and others too narrow to be detected, as well as the limits on minimum height of surface features that is detectible. 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.

As the profilometer stylus moves in a straight line, stylus profilometry produces measurements of roughness that depend on the direction of measurement. Many surfaces may have different roughness values in different directions (e.g. due to machining or processing conditions) and measurements in different directions may be needed to fully characterise the surface.

Figure 5: *Stylus profilometer*

Even when using calibrated, standard profilometers, there may be considerable uncertainty in surface roughness values owing to variability in materials and measurement procedures. Standard deviations in the roughness values obtained on a range of packaging substrates ranged from 10% to 40% of the roughness value. Measurements made on the same sets of materials by two organisations using their own instruments and procedures typically varied by 20%.

3.2 Optical 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. The cost of the instrument increases with resolution and high-resolution equipment is relatively expensive. Currently there are no supporting standards for optical systems, although there is a plethora of instruments on the market. It has been shown

that stylus measurements gave comparable roughness values to optical profilometry techniques (e.g. a 3-D interferometric optical phase shift white light interferometer).

3.3 Roughness by Air Leakage Measurement

In the evaluation of packaging materials, roughness is often characterised through air leakage measurements. Three air leak methods are commonly used for testing roughness in the paper and board sector. Each operates on the principle that air flows between parallel surfaces at a rate proportional to the cube of the gap between them. This can be used to estimate the mean distance between the material test piece and a polished metering head. The advantage of this system is that results are weighted strongly by deeper pits in the surface, which may affect print or bond quality. The results will also be affected by the flatness of the surface as curvatures or undulations will also provide air leakage pathways and erroneously indicate a higher roughness. The softness of the surface will also affect the roughness results as features may be crushed by the weight of the sensor head decreasing the apparent roughness.

Three principal instruments/methods are commonly used, conforming to different international standards.

a) Bendtsen roughness measurement [35] is performed by clamping the test piece between a flat glass plate and a circular metal head and measuring the rate of airflow in ml/minute between the paper and head (see Figure 6 below) under a defined pressure (typically 1.47 kPa). The technique is designed to work in the air flow range 30-1500 ml/minute. Values outside this range are used as indicative only.

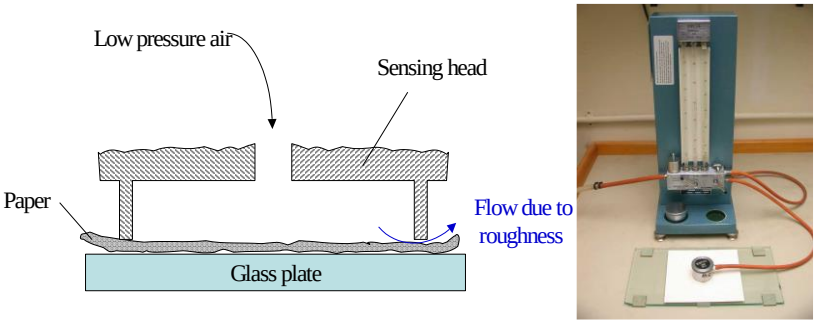


Figure 6: *Bendtsen method*

b) Bekk smoothness [36] is measured with air drawn across the surface of the test piece under a partial vacuum.

c) Parker print-surf [37] was designed specifically for measuring the surface roughness of printing papers under simulated printing press conditions. The 'Surfside' instrument contains an internal gas flow restrictor whose pressure drop versus flow characteristics is closely controlled. The air flow is calculated by comparing the pressure drop across the measuring

head and the paper test surface with that across the flow restrictor. The mean roughness of the test piece is calculated from a formula proposed by Parker.

Air leakage measurements provide a measurement of roughness that averages the roughness in all directions of the surface. Conventional roughness measurement (profilometry) provides data in units of length whilst air flow measurements are expressed in volume flow per time. There is no obvious theoretical function linking the two quantities. Roughness measurements were made on a range of different substrates used in packaging. Many of the materials are coated on one face and measurements were made on both the top (coated) and reverse (uncoated) faces. The coated surfaces are normally smoother than the uncoated surfaces. Figure 7 shows a plot of air leakage (Bendtsen) against stylus profilometry measurements. The profilometry measurements are the average of measurements that were taken in orthogonal directions on each face of the substrate samples, none the surfaces showed any significant dependence of roughness with direction.

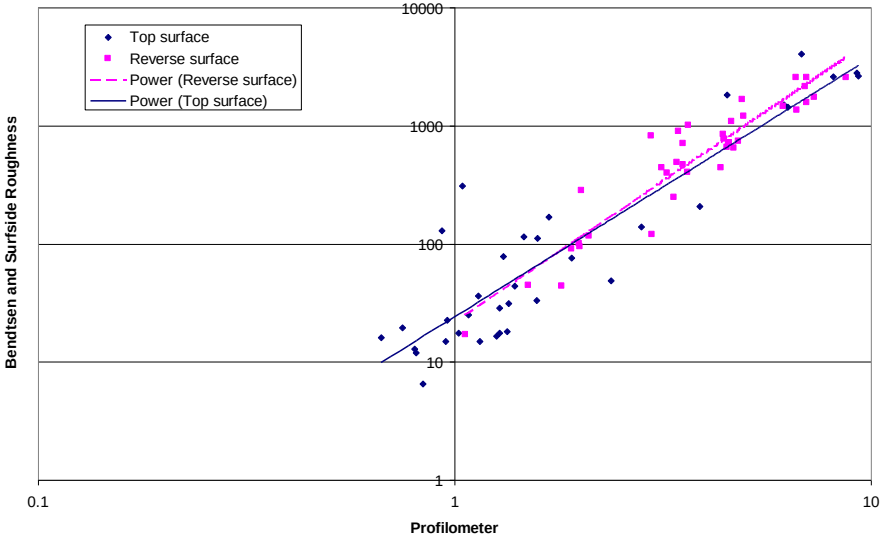


Figure 7: *Correlation between stylus and air leakage roughness measurements*

Figure 7 shows that the Bendtsen measurements results increase with the profilometry roughness. The rate of air leakage is proportional to the cube of the mean distance between the substrate and the polished metering head. There is a reasonable linear relationship between the cube root of the Bendtsen measurements and the profilometry data. The degree of scatter is relatively high (and many of the Bendtsen measurements are above 1500 ml/min, where the accuracy of the results becomes more questionable), but both the top and reverse face measurements lie close to the same best fit line.

3.4 Coefficient of Friction

The coefficient of friction between two surfaces depends on characteristic parameters such as roughness, adhesion forces and the mechanical properties of the surface layer, all of which are believed to influence bonding. Friction is reduced by the presence of lubrication layers between the surfaces that would have a detrimental effect on bond strength. Coefficients of friction can be classified as static (i.e. defined from the frictional force that must be overcome to initiate motion) or kinetic (i.e. the frictional force between two surfaces in relative motion). Various methods for measuring friction are described in ASTM G 115 [38], including inclined plane and sled methods, Figure 8. Friction measurement methods should closely simulate the sliding system of interest and this will normally guide the selection of test method.

Friction between two surfaces can be quantified by a friction coefficient μ:

$$\mu = \frac{F_f}{F_v} \tag{3}$$

where F_f is the in-plane frictional force and F_v is the vertical or normal force. In the inclined plane method, the coefficient of static friction (μ_S) is determined from the angle of incline (θ) at which the sled starts to slide:

$$\mu_S = tan(\theta) \tag{4}$$

A newer approach is to build the force sensing devices into the base. A schematic of friction measurement apparatus developed by NPL is shown in Figure 9. This system was originally designed to determine the friction properties of soft touch materials [39]. The system uses a series of strain gauged flexure elements to simultaneously detect forces in both the X and Y planes and the applied normal force in the Z direction.

Pulling an object across a sample attached to the table surface generates frictional drag between the moving object and the surface, which leads to deflections in the flexure arms that generate signals from the strain gauge bridges. The partitioning of forces between the sensors in each plane is used to calculate the position of the application of force on the sample table. These data are captured and using applications written in Labview® software [40]. The signals from each flexure element are analysed to produce a set of values. (X-Y Position, test speed,

frictional load and normal load) that can be used to calculate the friction coefficient.

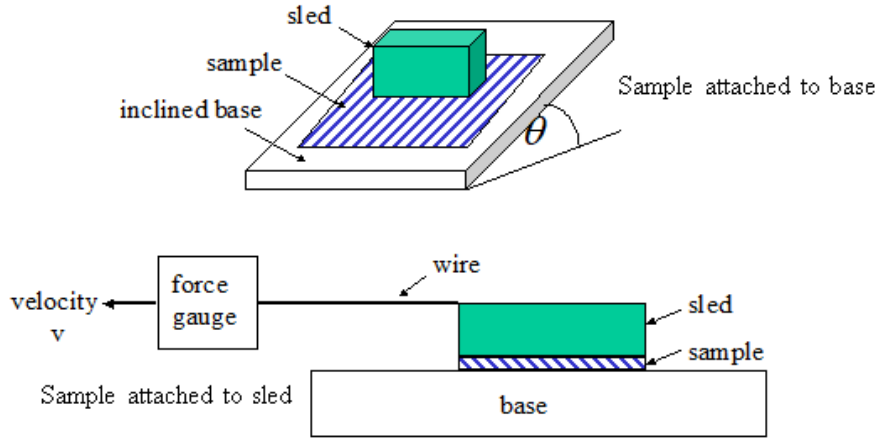


Figure 8: *Inclined plane and pulled sled methods for determining coefficients of friction (not to scale)*

The coefficient of kinetic friction between a square plate of aluminium (63.5 mm by 63.5 mm by 5 mm) with a ground surface and a mass of 65.9 g and a series of packaging substrates was evaluated using this method. The sled, weighted with an additional 2 N or 4 N mass, was pulled across the friction table using a motor at a constant speed. The coefficient of friction was calculated from Equation (3) using the components of forces in the X and Y planes and the normal force (Z plane) component. Force or friction plots typically contained noise as shown in Figure 9 and recorded values were averaged over stable regions (e.g. 15s –25s in the trace shown).

The coefficients of friction for the various substrates tested were found to vary between 0.14 and 0.35. However, there was no obvious correlation with roughness. Many of the smooth coated surfaces showed higher friction than the rougher uncoated materials. Although appearing implausible, this may due to the rigid, smooth metal sled sitting on the 'peaks' of the rough surfaces giving a decreased area of contact in comparison to the smoother samples.

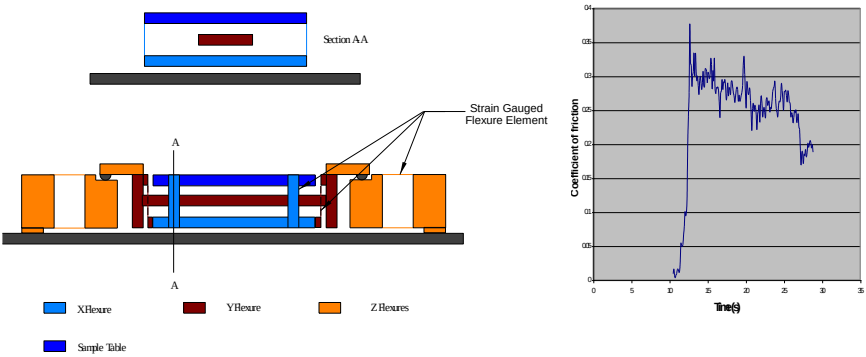


Figure 9: *Friction test apparatus and typical force trace*

Chapter 4: Surface Energy & Wettability

- Wettability, surface energy and contact angle
- Simple wetting tests
- Contact angle by sessile drop
- Wetting properties of hot melt adhesives
- Wetting balance method
- Comparison of wettability techniques

4.1 Wettability, Surface Energy and Contact Angle

Wetting is the spreading and contact of a liquid (adhesive) over a solid surface (substrate). If sufficiently intimate contact is achieved between the two phases, a physical attraction due to inter-molecular forces develops causing the liquid to conform to the surface on a macro and micro scale, displacing air and thus minimising interfacial flaws. The wettability of a surface by a liquid depends on the surface energies of the solid surface and the liquid. Good wettability of a surface is a prerequisite for ensuring good adhesive bonding, and hence tests have been developed to assess surface energy/tension prior to bonding. These tests include:

- Simple wettability tests;
- Contact angle measurement; and
- Wetting balances.

The surface free energy per unit area is the work necessary to separate two unit area surfaces beyond the range of the forces holding them together and is often referred to as surface energy or surface tension. Surface tension is often expressed in dynes/cm (a surface tension of 1 dyne/cm or 1 mN/m is equivalent to a surface free energy of 1 mJ/m2). Strictly speaking all surface tensions or energies are actually interfacial tensions or energies – i.e. the surface tension of a liquid is actually the interfacial tension between the liquid surface and air and the surface energy of a solid is the interfacial energy between the solid surface and air.

Surface energy depends on the interfacial intermolecular forces and can be split into contributions from non-polar (e.g. van der Waals) and polar (e.g. hydrogen bonding) components. The polar components can be further broken into electron acceptor or electron donor components (or Lewis acid/base components). Polar molecules have varying proportions of acceptor/donor components and in many cases one component will be much more dominant. Water is fairly unusual in having both strong acceptor and strong donor properties. The quantitative determination of the various components of surface energy of both substrates and adhesives would allow selection of appropriate substrate/adhesive pairs for bonding. However, this would require considerable effort and would not provide a full answer to the selection of materials since wetting is only one factor in the bond performance.

The surface free energy of a solid can be indirectly estimated through contact angle measurements using the approach of Zisman [41, 42]. The surface energy (and the split between different components of the surface energy) can be quantitatively determined from the interactions between the surface and a series of probe liquids of different (and known) interfacial properties. The determination of contact angle at the solid/liquid phase boundary is one of the most sensitive methods for assessing the surface energies of solid materials and the contact angle is commonly used as a relative measure of the surface energy. Contact angles are closely related to wettability, the lower the contact angle the greater the wettability.

A liquid (adhesive) will wet a solid (adherend) when its surface energy is lower than the solid's 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 10):

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

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. The lower the contact angle, the greater the tendency for the liquid to wet the solid, until complete wetting occurs (contact angle $\theta = 0$, $\cos\theta = 1$). For complete wetting to occur the surface tension of the liquid should be less than or equal to the critical surface tension of the substrate (γ_{sv}-γ_{sl}). Large contact angles are associated with poor wettability.

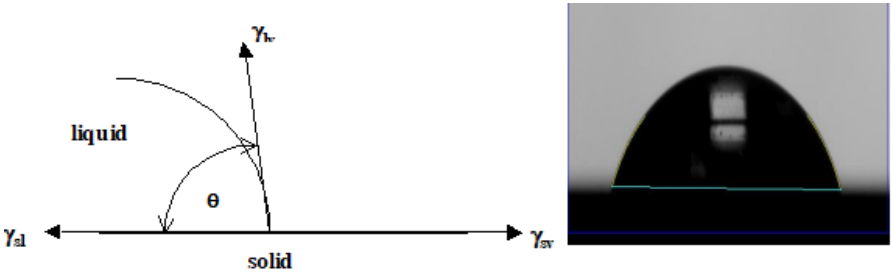


Figure 10: *Contact angle of a liquid on a surface*

In adhesive bonding, wettability is often used to determine the suitability of a plastic surface for bonding. Plastics are often surface treated to increase their surface energy (improve wettability). Surface energy approaches are likely to be useful for coated papers and boards but of less relevance to uncoated, porous substrates or metal or metal oxide surfaces. According to ASTM D 5946 [43] the following ranges of water contact angle values can be used as a guide for defining the level of surface treatment of polyolefins and many other polymer films with initial low surface energies:

- Marginal or no treatment >90° (under approximately 34 dynes/cm)
- Low treatment 85-90° (approximately 36-34 dynes/cm)
- Medium treatment 78-84° (approximately 39-36 dynes/cm)
- High treatment 71-77° (approximately 43-40 dynes/cm)
- Very high treatment <71° (above approximately 43 dynes/cm)

The wettability of a surface is often characterised through the use of a probe liquid and used to infer the suitability of a surface for bonding, rather than direct testing using the adhesive as the high viscosities of adhesives complicate testing. This simplification greatly reduces the cost of testing. However, the interfacial properties of the probe liquid may differ considerably from those of the adhesive. Water, commonly used as a probe liquid has a very high surface tension

(72 mN/m) in comparison with many hydrocarbon liquids where surface tensions typically fall in the range 20 30 mN/m [44]. In addition, water is a highly polar material that can form strong hydrogen bonds with polar groups in the substrate molecules, interactions that may not occur with weakly polar molecules where the principle inter-molecular forces are dispersive or van der Waals forces. Non-polar liquids have surface tensions around 20 mN/m. It has been determined that the non-polar component of the surface tension of water is also around this level and the bulk of the surface tension (51 mN/m) arises from the polar components.

Surface energy is sensitive to the chemistry of the surface, the morphology and the presence of adsorbed materials. The adsorption of chemicals on a surface lowers its surface free energy (wettability). Surfaces with high surface energies will have a strong tendency to adsorb materials (e.g. moisture or dust particles) from the atmosphere, reducing wettability. Therefore, contact angle measurements offer a means of studying the ageing of surfaces.

4.2 Simple Wetting Tests

These methods allow fairly quick assessment of relatively large surface areas and are capable of detecting 'problem' areas.

4.2.1 Water Break Test

The water break test [45, 46] is a qualitative (go/no-go) test. The specimen is either immersed in water or has water brushed or sprayed onto its surface. The plate is then checked to determine the distribution of water on the surface (i.e. whether it remains as a continuous film indicating good wettability or forms distinct droplets indicating poor wettability).

4.2.2 Dyne Pen Test

The dyne pen test for assessing the surface energy of plastic films [47, 48] is a semi-quantitative test. A series of mixtures of formamide and 2-ethoxyethanol of incrementally increasing surface tension are applied to the plastic or varnished surface using a solution soaked cotton wool bud until a mixture is found which just wets the surface. This is judged visually by examining for break up of the applied liquid into drops. 'Dyne solutions' (often referred to as Sherman pens) are available in sets of different surface tensions and systematic use can quickly provide an estimate of surface energy. The critical surface tension of the surface is approximated by the surface tension of that particular solution. A higher dyne value indicates a more wettable surface.

Despite the widespread use of these solutions, the method has its critics [49]. The shelf life of pens can be limited, particularly if in regular use, as transfer of contamination from surfaces to the ink may occur. There are also health and safety concerns with the use of these solvents.

4.3 Contact Angle Determination By Sessile Drop

4.3.1 Goniometer Methods

Contact angles between liquid drops and surfaces can be measured directly from the angle formed at the contact between the liquid and the flat surface [43, 50-55]. Measurements can be made using a manual goniometer, an inexpensive instrument. The drop is illuminated from behind and viewed through a lens focussed on the silhouette of the drop, e.g. Figure 10. A reference line is manually positioned to read the contact angle. The drop may also be projected onto a screen to view the contact angle. Low cost hand held instruments are available, e.g. Figure 11, based on digital camera technology, where the drop is imaged onto a built-in LCD screen using a CCD chip to produce an image that is easier to measure than the traditional magnifying eyepiece instruments.

Figure 11: *Handheld goniometer*

4.3.2 Automated Contact Angle Measurement

Manual goniometer measurements can be prone to operator subjectivity but this can be removed from the process by image analysis of the drop shape and contact using a computer programme [54]. There are many commercially available automated drop shape analysis (ADSA) and contact angle measurement instruments where the image of the drop is viewed using a video camera and captured on computer. A typical measurement system is shown in Figure 12. An image analysis

programme detects the edge of the drop and the surface. Numeric algorithms are run to establish the 'shape' of the drop and the slope of the edge in contact with the surface. The software can also analyse the shape of hanging pendant drops to measure surface tension of liquids. ADSA is capable, under ideal conditions, of determining contact angles to very high accuracy with uncertainties of less than 0.1° [55]. Through careful control of the position of the syringe plunger it is possible to make the drop advance and recede on the surface. Images of the drop can be captured in real-time allowing measurement of contact angle hysteresis through the advancing and receding contact angles.

Provided the magnification of the image is known (e.g. by placing a calibrated object in the focus plane of the image – the most simple means is to use an accurately measured syringe tip) then the drop height, width and thus volume can also be determined.

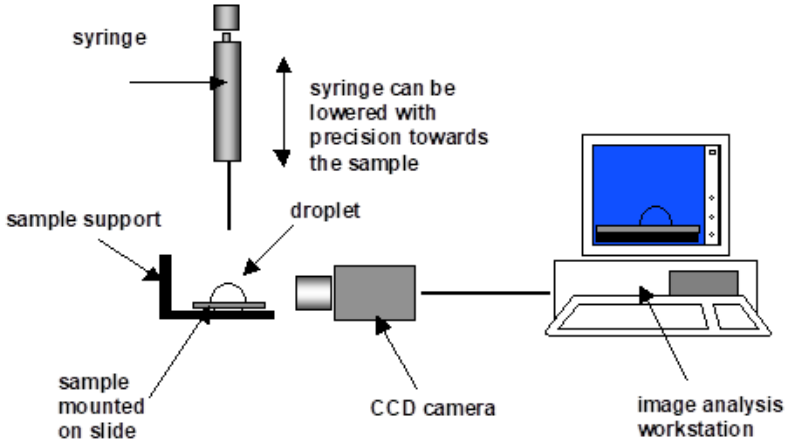


Figure 12: *Contact angle by automated drop shape analysis methods*

4.3.3 Contact Angle Measurement Issues

The sessile drop method requires the observation of a drop of test liquid on a solid substrate. Problems associated with the technique include swelling of the solid surface, roughness and porosity, which will tend to obscure the point of contact of the liquid and the surface. Cohesive hydrogen bonding within the test liquids and the solution pH may also influence the measured surface energy. The surface tensions of many liquids (particularly water) change dramatically with the absorption of small quantities of surface-active impurities (from surfaces or the atmosphere). Care must be taken with the handling and storage of probe liquids. Water is

normally freshly de-ionised or distilled before use. The surface tension of the probe liquid should be checked regularly to detect the presence of impurities. Commonly used probe liquids for measuring contact angle include distilled water, glycerol and methylene iodide. A typical drop size is 2 to 20 μl. For porous materials, the observed contact angle will reduce with time as the probe liquid penetrates the surface.

With modern automated contact angle measurements the determination of contact angle should be straightforward provided that:

- The camera image should be calibrated in orthogonal directions to ensure accurate dimensional measurement;
- The background illumination is of the appropriate intensity to achieve a good contrast between the drop and the background;
- The background illumination level is uniform in the field of view and stable during the measurement;
- The camera achieves a sharp focus on the drop and base;
- The surface is flat and level (e.g. checked using spirit levels in two orthogonal directions), thin substrates may be glued or taped to a microscope slide to ensure they do not wrinkle;
- The plane of the surface is normal to the plane of the camera, i.e. the surface should not slope from left to right or from back to front in the image;
- The surface roughness is not significant (local topography at the junction of the drop and surface can lead to interpretation errors);
- The probe liquid is of well characterised composition (e.g. distilled water, high purity solvents);
- Absorption of the liquid into the surface (and consequences such as osmotic surface swelling) are not significant;
- The drop is static and has reached a stable equilibrium shape;
- The test is performed in a 'clean' environment so that the probe liquid does not absorb impurities from the atmosphere, the equipment or the surface;
- Evaporation of the drop does not occur.

It is commonly claimed that the accuracy of the automated contact angle method is $\pm 2°$. However, agreement between laboratories has been as poor as $\pm 5°$ [56]. Variation in results will be high if the substrate surfaces are heterogeneous or if significant absorption into the substrate occurs.

A further source of uncertainty may be variation in the time between depositing the drop and recording the image to make the measurement. As Figure 13 shows, there is apparent time dependence in the contact angle measurement of water on a plastic surface. Some initial changes would be expected in the observed contact as the drop comes into equilibrium after being deposited. The time taken to reach equilibrium will depend on the rheological properties of the liquid and the interfacial tensions between the different phases. A liquid with a low viscosity is likely to reach equilibrium quickly (e.g. Figure 13a showing water) but a high viscosity may take considerable time to reach an equilibrium shape (e.g. Figure 13b shows measurements for a liquid hot melt adhesive). Longer term changes in contact angles are likely to result from absorption of the liquid in the surface making the surface next to the drop easier to wet or from absorption of surface active species (either from the atmosphere or from the substrate) that reduce the surface tension of the liquid. Chemical changes to the surface may also occur with time, particularly soon after surface treatment or a change in environmental conditions (e.g. removal from a different conditioning environment).

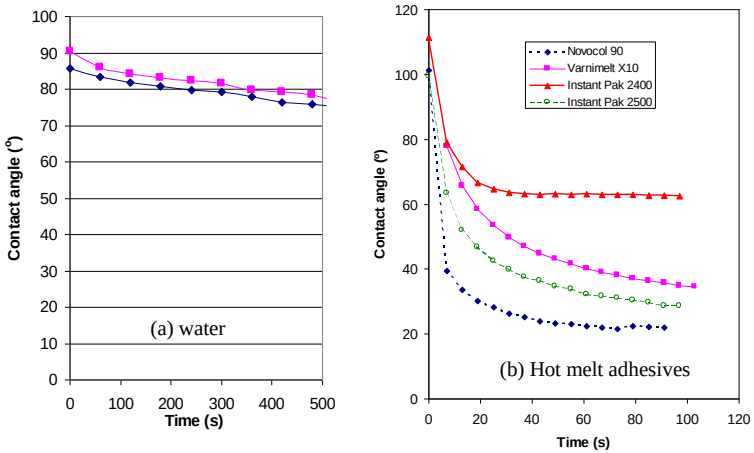


Figure 13: *Time dependence of contact angle measurements*

The procedure for taking measurements needs to specify the time after dispensing the drop at which the measurement should be made, to reduce the measurement variability. In the two cases illustrated in Figure 13, a duration of 60s after dispensing the drop would be probably be sensible as the rate of change in the contact angle has slowed considerably and the measurement time is not excessive.

Water drop contact angles (WDCA) measurements made using an inexpensive handheld goniometer, which projects drop images onto an LCD screen, generally showed a reasonable correlation with the automated image analysis techniques, Figure 14. The quality of agreement between the dyne pen method and water drop contact angle measurements is variable, Table 2.

Board reference / Surface	Measured WDCA (°)	Wetting tension by dyne pen test (dynes/cm)		
		Theoretical [47]	Measured	Agreement
Sample 13 / top	96	<34*	<34	✓
Sample 16 / top	66-73	≥43*	34	x
Sample 18 / top	89	34-36	37	✓
Sample 18 / reverse	98	<34	34	?
Sample 19 / top	83-9	34-36	37	✓
Sample 19 / reverse	83-9	34-36	37	✓
Sample 29 / reverse	74	40-43*	>48	x
Sample 30 / reverse	42	>43	>48	✓
Sample 30 / reverse	92	<34	33	✓
Sample 36 / top	79-84	36-39*	34-35	?
Sample 37 / top	61-65	>43	41	x

Table 2: *Relationship between WDCA and wetting tension*

* Theory according to ASTM D 2578 [47] not strictly applicable for these materials

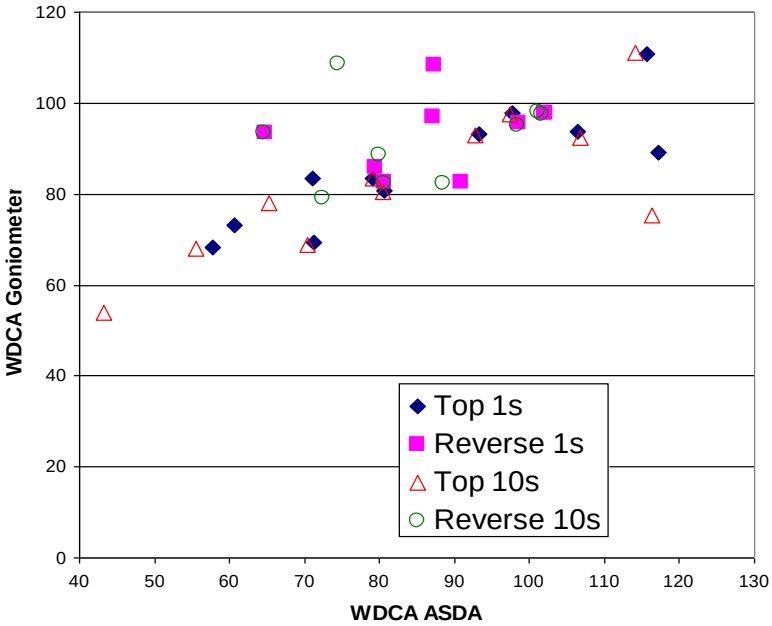


Figure 14: *Correlation of WDCA techniques and handheld goniometer instrument*

4.4 Wetting Properties of Hot Melt Adhesives

The properties of liquids can be difficult to measure at elevated temperatures. However, contact angle measurements can, in theory, be made using any liquid-surface combination provided that the sessile drop can be imaged accurately. Thus, provided that the system can be maintained at temperature, it is possible to directly measure the contact angle of hot melt adhesives on hot substrates using ADSA equipment for water drop contact angles. Figure 15 shows equipment for determining contact angles and liquid surface tension under non-ambient conditions [57]. The sample is placed inside a temperature chamber that maintains the temperature of the system. The drop is backlit and imaged using a CCD camera that views the sample through a window in the box.

The recommendations in Section 4.3.3, for standard ambient temperature automated contact angle measurements, apply to elevated temperature measurements and in addition:

- The temperature in the box should be controlled and stable during measurements.
- The sample should be allowed to stabilise at the measurement temperature prior to dispensing drops.

- The temperature box should be designed to avoid excessive air movements, whether due to convection or fans, around the sample that could deflect the drop shape.
- It is preferable to measure the substrate temperature and both the air temperature close to the syringe tip and within the adhesive during measurements to ensure all are comparable.
- Illumination and imaging to obtain a clear outline may be more problematic owing to the presence of the box.
    - A higher intensity light source may be needed.
    - Interior surfaces may need to be masked to reduced reflections on the sample or windows.
    - Window thickness should be minimized as far as possible and windows should not act as a lens, which could distort the magnification.
    - Windows should be cleaned.
- Variations in temperature in the box and the resulting air density differences may produce 'mirage' effects that distort the image. A visual check of the image may be needed to determine if this is occurring and improvements to ensure better uniformity of temperature in the box may be needed.

Hot melt adhesives may need to be dispensed from disposable pipettes, as shown in Figure 16 to avoid the problem of contamination of the (expensive) micro-syringe used for water drop contact angle measurements. The outer diameter of the tip of the pipette should be carefully measured using a micrometer so that it can be used as a reference distance in the image analysis. It is also recommended that a thermocouple to be placed in the adhesive to monitor temperature. Packing the adhesive into pipettes presents some practical difficulties – the adhesive tends to cool and solidify in the narrow tip if the normal 'draw-up' method of loading the pipette is used. Thus it may be simpler to cut the adhesive into smaller pieces that can be 'packed' into the pipette via the wider top opening and melted in-situ. This method worked well with standard EVA hot melts adhesives but the highly visco-elastic pressure sensitive hot melt adhesives proved very challenging. The loading of the pipette may introduce air bubbles into the melt that may affect the measurement. These can be seen clearly in the glass pipette and adhesive may need to be discarded until an air-free section of the sample is in the pipette tip.

Figure 15: *Apparatus for measuring contact angles of molten hot melts*

Figure 16: *Pipette dispenser for hot melts*

This method was demonstrated through measuring the contact angle of Novacol 90 hot melt adhesive on several different surfaces (top and reverse faces). The temperature used (100 °C) was chosen as there were concerns that long-term exposure of the substrate samples to

higher temperatures could cause degradation. The Novacol 90 adhesive is a low process temperature adhesive that has a low viscosity at 100 °C and a low surface tension (19.9 mN/m at 110 °C [56]). The substrate surfaces had measured water drop contact angles (at ambient conditions) varying between 58° and 106°. The contact angles for the liquid hot melt adhesive on these substrates were found to be between 12° and 26°, implying good wetting on all surfaces. The plot of hot melt contact angle against water drop contact angle (WDCA), Figure 17 shows, if anything, a negative correlation between the two that suggests that WDCA values may be misleading as a method for characterising the wettability of surfaces to hot melt adhesives at typical processing temperatures.

The rheological properties of the adhesive will influence the measured contact angle; this was shown by further measurements of the contact angle undertaken at 100 °C with three other adhesives (Varnimelt X10, Instant-Pak 2400 and Instant-Pak 2500). These measurements were made on amorphous polyethylene terephthalate, which had a water drop contact angle = 79°. These adhesives have different recommended process requirements, typically dispensed at higher temperatures, than the Novacol 90. Consequently they have a higher viscosity and are much more visco-elastic near 100 °C [17]. All these adhesives have similar, low surface tensions at 110 °C, since the temperature dependence of surface tension is not particularly strong the values would be expected to be similar at 100 °C and, therefore, the contact angles measured for each adhesive could be expected to be similar. However, the measured values varied from 26° (Novacol 90) to 64° (Instant-Pak 2400), Table 3.

Figure 18 shows a correlation between complex dynamic modulus (G*) and the measured contact angle at similar temperatures. At these temperatures, where the viscosities of some of the adhesives are relatively high, the wetting behaviour may be dominated by the visco-elastic properties rather than the surface tension of the adhesives. This is in agreement with the observations of the spread of adhesive beads deposited on various cold substrates and allowed to cool, which found that the spread (and contact angle) depended on the adhesive type but were independent of substrate.

These findings imply that, to help predict performance, measurements should be done at the appropriate dispensing temperature. Contact angles at different temperatures may help determine appropriate processing temperatures for bonding systems – the temperature at which sufficient adhesive spread is obtained may correlate with optimum bonding conditions. Lower contact angles would be expected at higher temperatures where the adhesive is more liquid-like. These findings also suggest that any contact angle measurements for the highly visco-elastic pressure sensitive hot melt adhesives should be treated with caution.

Adhesive	Contact angle on PET at 100 °C (°)	Typical Process Temperature (°C)	Surface tension at 110 °C [56] (mN/m)	Complex Modulus G* at 110 °C [17] (MPa)
Novacol 90	26	100	19.9	0.7
Varnimelt X10	50	180	20.1	157
Instant-Pak 2400	64	175	21.3	296
Instant-Pak 2500	40	165	20.8	147

Table 3: *Contact angles for different hot melt adhesives on PET*

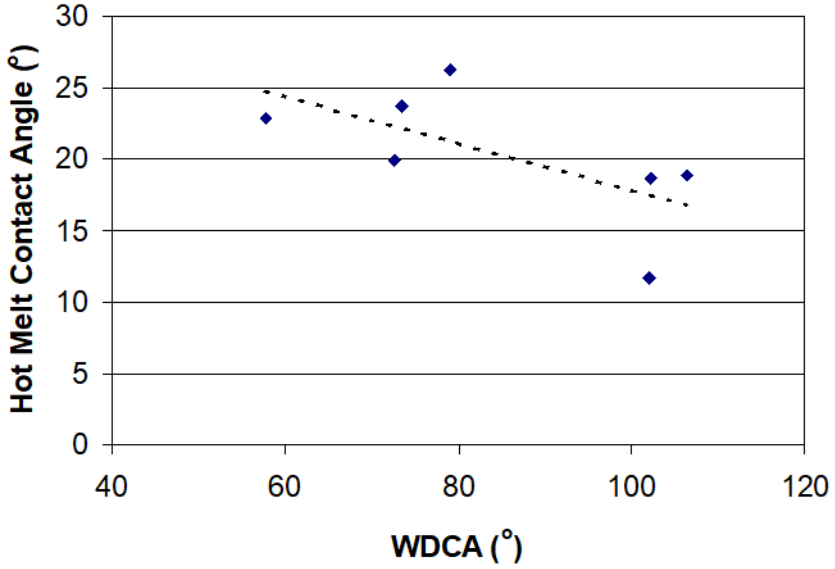


Figure 17: *Relationship between measured contact angles of distilled water (room temperature) and liquid hot melt adhesive (100 °C) on a selection of packaging surfaces*

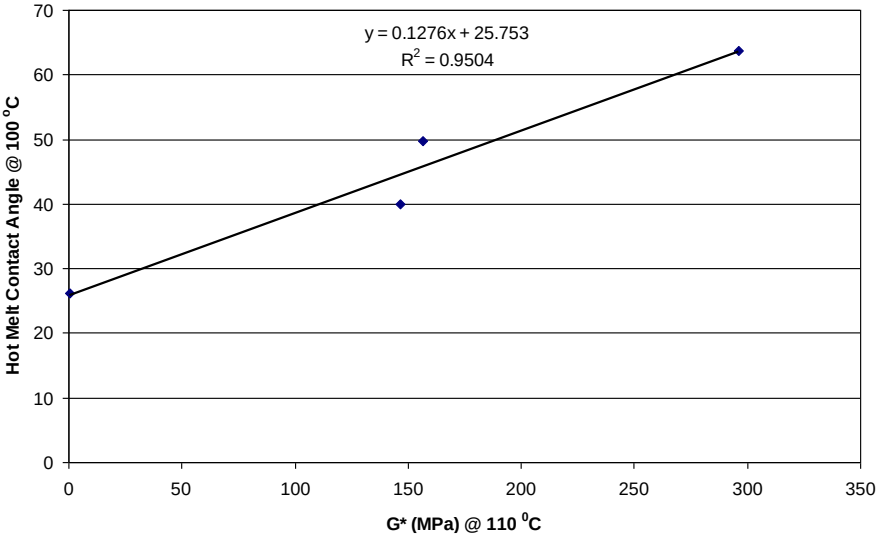


Figure 18: *Apparent correlation between wetting and visco-elastic properties*

4.5 Wetting Balance Method

Contact angle can be measured using the Wilhelmy plate technique [58-61]. This technique measures the forces exerted as the solid/liquid phase boundary is moved along the sample surface as the plate is withdrawn from the liquid (Figure 19). The sample is attached to the balance (with a resolution of 1 μg) and the balance tared to remove the weight of the sample. 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 plate 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 contact angle (θ) may be calculated from the interaction force (F), sample geometry (perimeter of the edge, P = 2 x length + 2 x thickness) and liquid surface tension (γ_l).

The forces involved are:

$$F = wetting\ force - buoyancy \tag{6}$$

Buoyancy is accounted for by extrapolating the force back to the point of zero immersion depth. The wetting force F_w is related to contact angle θ by:

$$F_w = \gamma_l\ P \cos\theta \tag{7}$$

When the contact angle is zero (i.e. perfect wetting) the value of F/P should reduce to the surface tension of the liquid. This method can be used to measure surface tension of liquids. Often a de Nouy ring will be used in place of the plate for surface tension measurements as it more readily provides perfect wetting.

Both the advancing (θ_{adv}) and receding (θ_{rec}) angles can be measured. The difference (θ_{adv} - θ_{rec}) is the contact angle hysteresis, which depends on surface heterogeneity and roughness since the local surface energy (or chemistry) and local physical topography act as barriers to the motion of the liquid contact line. Multiple cycles can be performed which yield information on adsorption. The sample geometry must be regular, have a constant perimeter over the entire length, have low mass, be suspended perpendicular to the surface of the liquid with the bottom edge parallel to the liquid surface and have the same surface treatment on all sides in contact with the liquid.

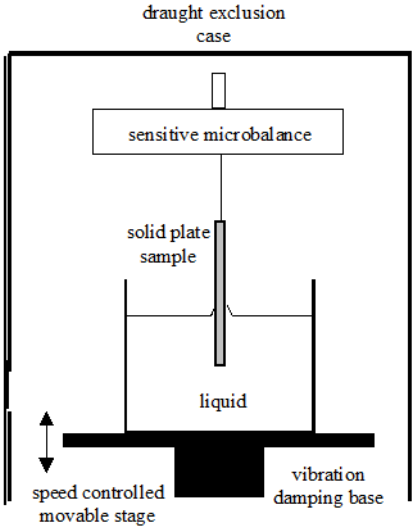


Figure 19: *Wetting balance (Wilhelmy plate) technique*

Methods for wetting balance tests have been produced for determining the efficiency of the wetting of wires by solders [60, 61] but have yet to be standardised for the evaluation of substrates. The apparatus for solder wetting test methods could be used for the evaluation of hot melt adhesives since the sample can be kept molten throughout the measurement. Visco-elastic properties would need to be considered when measuring liquid polymers, as viscous forces would be superimposed on the wetting and buoyancy forces. These viscous forces will depend on the rate of immersion/withdrawal of the plate, being higher at faster speeds.

When carrying out Wilhelmy plate measurements the following points should be considered:

- The edges of the plate immersed should be straight and meet at right angles;
- The plate should be attached vertically so that it meets the surface perpendicularly;

- There should be no bubbles adhering to the surface of the plate when immersed;
- The sample should not deform during the test; and
- The plate should not float in the liquid.

Many substrates of interest for bonding in non-structural applications, such as packaging, may lack rigidity and/or have a low density and therefore struggle to meet all of these criteria. Absorption of the liquid on will lead to changes of properties and thus measured contact angle on each immersion cycle. This may be used to characterise absorption. Interpretation of contact angle from the wetting force will be difficult for materials where the faces are different (e.g. coated samples).

4.6 Comparison of Wettability Techniques

Wettability information can be obtained using a variety of methods. One of the key concerns is how consistent are the results from different methods and how well these relate to actual bonding performance. Direct measurement of the wettability of an adhesive on surfaces is possible but may require specialist apparatus. Therefore, routine measurements will tend to require the use of substitute probe liquids, such as distilled water. Table 2 shows a comparison between the theoretical wetting tension of the surface derived from the measured WDCA using the conversion table in ASTM D 2578 [47] and the measured wetting tension from Dyne pen measurements and indicates that agreement between the two methods appears to be limited.

Wetting balance methods are probably inappropriate for flexible, low density and strongly absorbent materials frequently bonded for non-structural use. Comparisons between sessile drop contact angle measurements and wetting balance measurements made on engineering surfaces, such as metal oxide surfaces [29], suggest that there are discrepancies between the two methods, with the sessile drop method providing much better discrimination between well and poorly prepared surfaces. The low forces involved in the wetting balance method may lead to higher uncertainty in the resolution the wetting force. In addition, the sample used for the wetting balance measurements is extremely small, often cut from a larger sample and the surface condition near the edges may differ from the interior of the surface. Thus the wetting balance method is considered to be less reliable.

One limitation of the contact angle approach is that the area of the surface probed in each measurement is limited to the area covered by the drop. Assessment of the wettability of a large area would be very time consuming using this method. Two stage processes where the area is quickly checked using water break or Dyne pen methods followed by contact angle measurements on ‘suspect’ areas may be a more efficient procedure for evaluating wettability.

Contact angle measurement also has limitations where the wettability of the surface varies on a scale that is smaller than the diameter of the drop. This may be the situation with heterogeneous materials (e.g. mixed fibre boards) or patterned surfaces. The contact angle and inferred wettability properties will be an average of the surface under the drop.

As noted earlier, the water drop contact angle measured on a surface appears to bear little relationship to the wettability of a hot melt adhesive on the substrate. Therefore, water may not be a suitable probe liquid for these substrates. However, since time was limited, a full investigation could not be completed and this conclusion is based on a limited number of tests. It is possible that probe liquids with surface properties that better approximate the adhesives, including hydrocarbons such as cyclohexane or paraffin, may be more suitable for assessing wettability with respect to hot melt adhesives and these may merit further consideration for use in routine measurements.

Chapter 5: Absorption Properties

- Cobb absorbency tests
- Liquid uptake by mass measurement
- Liquid volume absorption measurement

Adhesives will tend to penetrate porous or rough surfaces to some extent. The degree of penetration will depend on many factors including the surface energies of the adhesive and substrate, the geometry of the pores, the rheology of the adhesive and the time since application. In many cases, a degree of penetration may be advantageous (e.g. to provide 'keying' into a surface or assist the removal of carrier solvents) but in other situations excess absorption will cause problems such as insufficient adhesive for bonding or degradation of substrate properties. Assessment of adhesive penetration is often through visual observation and this can be subjective.

There are methods based on ultrasound measurement, which are used by some packaging manufacturers for examining porous substrates to determine the rate and depth of liquid penetration, e.g. for bonding with water-borne PVA adhesives. These methods detect changes due to liquid penetration in the frequency and attenuation of ultrasound waves propagating in the substrate [62]. The optical properties of substrates change as liquid penetrates the pores and cavities of the substrates, changing internal air-fibre interfaces to liquid-air interfaces, leading to different attenuation and scattering of transmitted light. The effective refractive index will also change with liquid content. These changing properties can be probed using laser transmission measurements [63]. Such methods require expensive equipment and expert staff and were not investigated for this guide, which concentrates on more accessible techniques.

Probably the most straightforward methods of assessing the likely absorbency are through mass gain measurements on immersion or exposure to a probe liquid or by determining permeation rates through the sample. There are many standard methods for determining permeation of penetrants through materials [64] but since these do not provide information about the absorption capacity of the material they are not considered in this guide. The absorption test method selected should simulate the length of time in which liquid adhesive absorption can take place between application and hardening to provide useful data. During adhesive bond manufacture the time between adhesive application and joint closure or 'open time' and the period from joint closure to joint hardening (whether by cooling or cure reactions) where the liquid adhesive interacts with the substrates are typically in the range of seconds to hours.

5.1 Cobb Absorbency Tests

The Cobb absorbency test provides a method of determining the water absorptiveness of sized paper and board under standard conditions, and hence provides an indication of both the relative penetration and setting time of water based adhesives. The Cobb absorbency may also provide an indication of the likely absorbency of the material to polymeric liquids, such as an adhesive. The Cobb test measures the water resistance of materials and is used to determine the absorption of liquid media, such as water, aqueous solutions, oils, varnishes etc. by paper, solid board and corrugated board. Results are usually expressed in g/m^2 and the length of time (e.g. g/m^2.30 min). The test provides information on the surface and internal sizing. It can be run from either the reverse side or the coated side of the paper. The test run from the reverse side measures the base sheet sizing. The test run from the coated side responds to the "openness" of the coating.

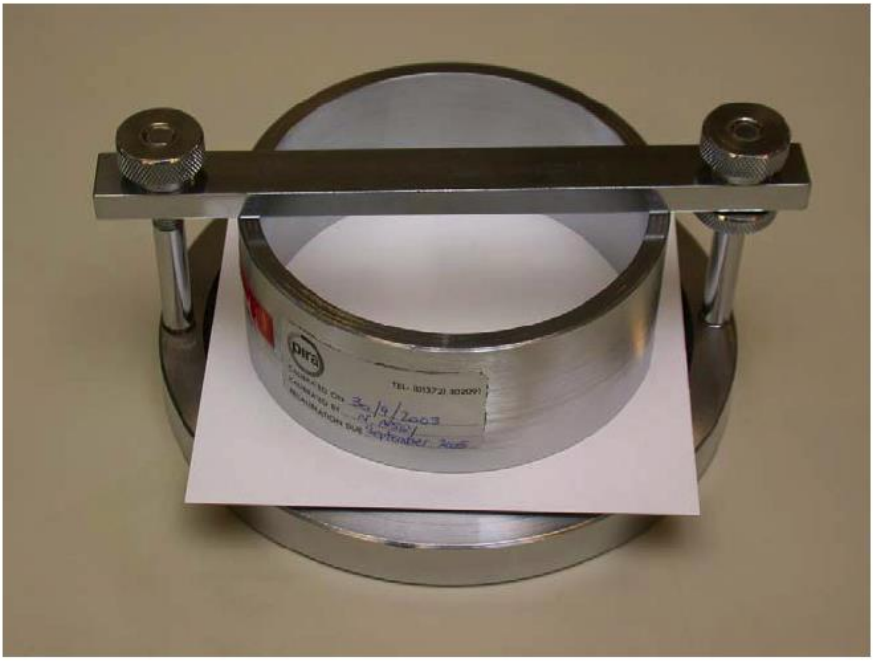


Figure 20: *Cobb absorbance test*

A column of water is placed in the ring for a set time and the amount of water absorbed by the sample is measured. More water resistance will result in a lower Water Cobb value. In accordance with BS EN 535 [65], each test piece should be weighed using a calibrated digital

balance, readable to 0.1 mg before testing. The sample should be clamped with the surface to be tested uppermost in a Cobb ring having a test area of 100 cm^2, (Figure 20). The ring is then filled with 100 ml of distilled water. It is important that water does not leak from the cylinder during tests, as this will increase the substrate contact area. The ring is drained of water after 45 seconds. The sample being tested is blotted, after a further 15 seconds, by placing it between two sheets of blotting paper and rolling twice with a 10kg Cobb roller. The test piece is then immediately re-weighed. The increase in weight per unit test area (g/m^2) is then calculated. The Cobb absorbency values for the substrates tested varied from <1 g/m^2 for surfaces with 'impermeable' plastic or lacquer coatings to >400 g/m^2 for extremely porous uncoated cards. The values obtained from most papers were typically in the range 20-50 g/m^2.

The repeatability of the Cobb measurement will be affected by several factors and these should be controlled to ensure repeatability:

- The efficiency of sealing the Cobb ring;
- The control of the contact and blotting times;
- The blotting procedures used
  - absorbency of the blotting paper;
  - evenness of rolling;
- The interval between blotting and weighing.

The Cobb test produces a single point measurement of absorbency but in some applications an uptake curve may be more useful.

It should be noted that although the Cobb test is still widely used in industry the relevant standards for the Cobb test have been withdrawn by both ISO or ASTM.

5.2 Liquid Uptake by Mass Measurement

Absorption of liquids into porous materials can be followed through periodic mass uptake (often known as gravimetric) measurements. These methods provide information on the rate of uptake and the saturation level. The frequency of measurement will depend on the rate of uptake but should also take into account practical issues such as the time required to perform the mass measurement in relation to the duration of exposure between measurements. Test methods have been standardised for studying uptake of liquids in polymers (ASTM D 570 [66] and ISO 62 [67]). Samples can be exposed to the vapour or immersed in the fluid. ISO and ASTM specify saturated salt solutions for maintaining constant humidities at set temperatures within an enclosed container. Alternatively, samples can be exposed in environmental cabinets capable of maintaining set temperatures and humidities but these systems can be expensive purchase and maintain.

Mass increases of the order of a few percent of the original mass of the sample are typical in polymer films [68] but mass gains in porous substrates may exceed 100% of the initial mass. However, if the material samples (or components of the material) are soluble in the liquid then mass loss due to leaching of material can also occur and lead to errors in the absorption measurements [69].

Ingress of liquid into a solid material is a diffusion process whilst capillary forces will also drive ingress into a porous system. However, in both cases the size and geometry of the sample will have a significant affect on the results. Therefore, when comparing materials it is important to use identically sized samples. Samples should be conditioned to constant mass, m_0 (normally samples are dried at an elevated temperature, depending on the thermal stability of the material but it may be more relevant to condition in a controlled environment to produce appropriate samples) and stored in controlled conditions (e.g. a desiccator for dry samples) before testing.

After immersion or exposure for the fixed period (at constant temperature), the sample is removed from the medium and surface liquid wiped off using a dry cloth before immediately weighing (in a weighing bottle for very thin samples). Samples can then be returned to the medium for continuing exposure provided that the time out of the medium is minimised. The balance used should be have a resolution of 0.1 mg or better [66], which can be relaxed, to 1 mg if water absorption is greater than 1%. The increase in mass divided by the initial mass, measured at regular time intervals, is plotted against time in order to define the absorption curve. Saturation mass uptake m_s is defined when the weight gain from 3 successive measurements differ by less than 1% of the overall weight gain and saturation moisture content C_s is simply m_s/m_0.

Loss of soluble matter from test samples may also affect results. This can be checked by reconditioning (drying) the sample back to constant mass m_c and comparing against the original mass m_0. If the sample contains absorbed liquid before testing (e.g. the common conditioning environment 23°C, 50% relative humidity will ensure some absorbed moisture in the sample) then this should be taken into consideration when reconditioning.

The relative mass uptake at time t is calculated from the mass m(t), initial mass m_0 and the reconditioned mass m_c. If there is no loss of water-soluble matter then $m_c = m_0$.

$$m_r(t) = \frac{m(t)-m_c}{m_0} \qquad (8)$$

Diffusion plots are obtained by plotting $m_r(t)/m_s$ against a function of $\sqrt{t}$. The time required to reach saturation depends on the square of the sample thickness. A maximum sample thickness of 1 mm is recommended for polymer films [66] to ensure that test durations do not exceed one week for typical diffusion coefficient values for polymers (ca. 10^{-12} m^2s^{-1}). With

porous materials absorption is likely to be quicker allowing thicker samples to be tested in reasonable times.

In materials with anisotropic diffusion properties (e.g. fibre reinforced plastics, board materials, coated materials) erroneous results may be obtained if absorption through exposed edges is significantly different to absorption through surfaces. For this reason the ratio of edge area to surface area of samples should be minimised. Allowances can be made in the analyses to account for edge effects but these will be tenuous if the edges have significantly different properties to the faces. Where edge effects are of concern then edges can be sealed, e.g. by bonding aluminium foil to the edges, but the additional mass of the sealing material needs to be accounted for when analysing results. Any sealing materials used should have insignificant moisture absorbance.

Standard methods for determining liquid absorption call for total immersion of the sample in the liquid. However, for many materials total immersion may not be suitable as samples may disintegrate during immersion. Uptake can also be determined through an edge absorption/desorption technique, which should reduce the risk of this happening.

Figure 21: *Edge immersion test*

In performing edge absorption measurements, suitable sized samples are suspended from the arm of a calibrated balance (with an accuracy of 0.001 grams) over a beaker of test liquid (e.g. distilled water at room temperature). One edge of the specimen is just in contact with the water surface, Figure 21. As the moisture absorbs into the specimen, the overall weight of the

specimen increases and the suspended weight is recorded from the balance digital display readout at periodic intervals.

Typical results, plotted against the square root of time, are shown in Table 4 and Figure 22. All of the substrates shown have high Cobb absorbency values. The chipboard samples (1 and 3) appear to reach saturation within the duration of the test (48 hours) whilst the boxboard samples still seem to be absorbing water.

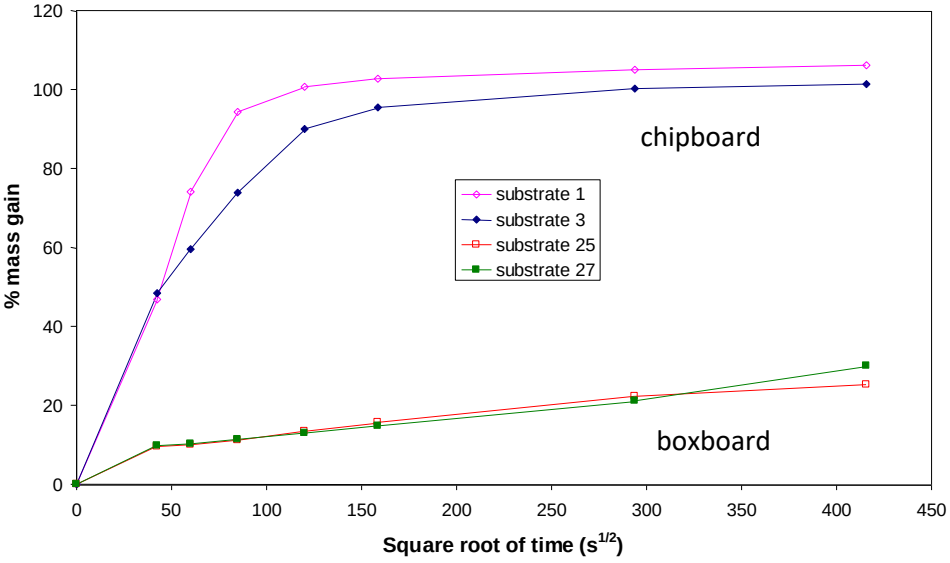


Figure 22: *Edge absorption measurements*

Another method of maintaining sample integrity during mass uptake tests is to expose the samples to vapour rather than immersing in the liquid. Mists of fine droplets have also been proposed for exposure tests [62, 63]. Atmospheric water vapour levels (relative humidity) can be simply controlled in sealed containers using aqueous glycerine or saturated salt solutions [70, 71, 72]. Water vapour can also be controlled using environmental cabinets but these, although usually allowing a greater volume for exposure and a wide range of temperature/relative humidity settings, are considerably more expensive to purchase and operate than the sealed container methods.

Illustrating this approach, samples of the materials shown in Figure 22 were also exposed in a Climatic Systems environmental chamber, maintaining 30 °C and 90% relative humidity. They were supported vertically in a rack so that the maximum surface area could be exposed to the humid air. Following the procedure of ISO 62 [67], samples were periodically removed from

the chamber and weighed. Any condensed moisture on the samples surface was wiped off with an absorbent cloth prior to weighing. The time the sample was out of the environmental chamber was minimised. The results are shown in Figure 23 and summarised in Table 4. There is a rapid increase in mass followed by a peak/plateau and then a decrease in mass to an apparent constant level.

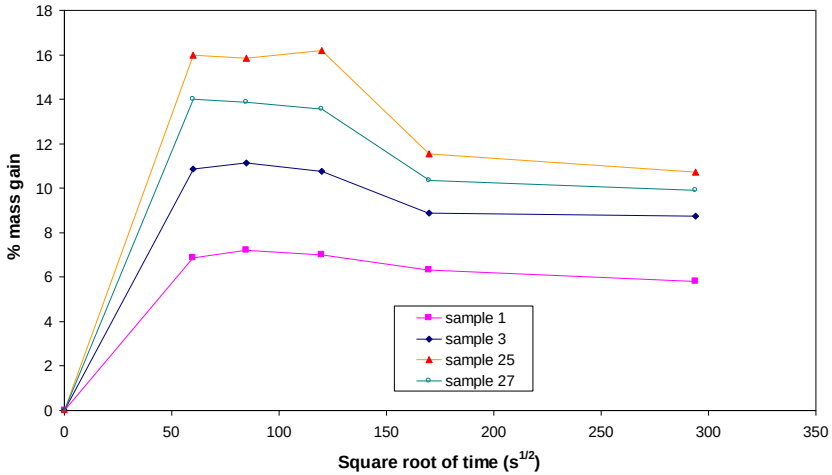


Figure 23: *Moisture uptake from a humid environment*

The rate at which materials lose absorbed moisture can also provide information on the absorbency of the substrate. Where samples are thin this process should depend mostly on the surface properties. The specimens are allowed to absorb water through one edge as described previously. After various fixed time periods, the beaker of water is removed and the specimens are left suspended from the balance arm to they dry out. Weight readings are taken at regular intervals until the specimens had approximately regained the same weight as they had prior to testing. Typical results are shown in Figure 24. The mass loss appears linear with $\sqrt{t}$. Unexpectedly, there is not an asymptotic approach of the drying curves to zero mass gain. This suggests that if tests had been continued then a net mass loss may have been found. This may be due to loss of original moisture that was in the samples following conditioning or some component of the substrate being leached by the water. The initial rate of mass loss appears to increase with the moisture level, which is consistent with diffusion processes.

It should be noted that results from different tests may not always produce the same findings as the methods may probe different mechanisms. For example, the ranking of moisture uptake found by edge immersion is the reverse of the Cobb ranking. Table 4 shows that, in the same exposure time, the chipboards absorb over 5 times as much water as the boxboards whereas the Cobb values for the boxboards are substantially higher than the values for the

chipboards. It is not unexpected that these results do not correspond with the Cobb results as the main route of moisture ingress in this test is through the cut edge of the card and this may present a very different affinity to moisture than the surface. The method of cutting, the edge used (in materials with a dominant processing or fibre direction) and the depth of immersion will have a considerable influence on the rate of moisture ingress.

Type	Substrate	Cobb Absorbency (g/m^2)		Edge Immersion (% mass gain)		Vapour Exposure (% mass gain)	
		Top	Reverse	1 hour	24 hours	Peak	Final
Chipboard	Substrate 1	31	214	74 ± 14	105 ± 3	7.2	5.8
	Substrate 3	36	135	60 ± 23	100 ± 9	11.1	8.8
Boxboard	Substrate 25	74	413	10 ± 1.5	22.3 ± 1.6	16.2	10.7
	Substrate 27	40	408	10.2 ± 0.8	21.2 ± 5.2	14.0	9.9

Table 4: *Comparison of Cobb Absorbency and Moisture Uptake*

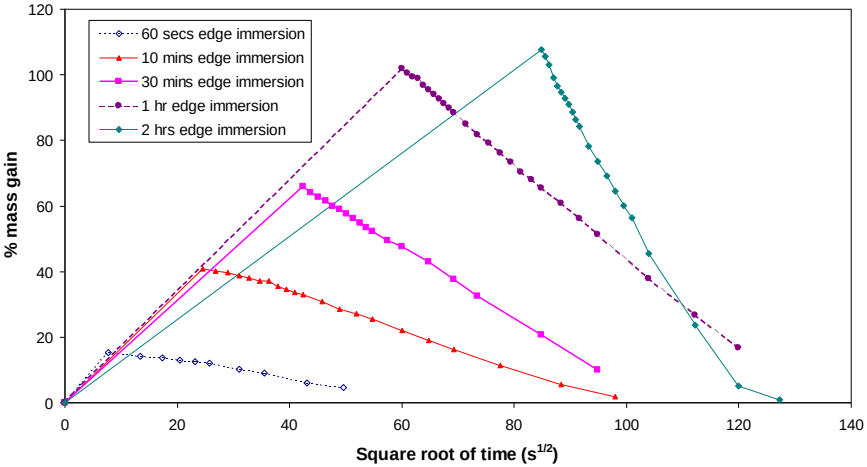


Figure 24: *Loss of moisture from sample 1*

In the vapour exposure tests, the amount of mass gained by the chipboards (1 and 3) is substantially lower than that absorbed in edge immersion experiments. The peak moisture absorption by the boxboards (25 and 27) is comparable to the edge immersion at similar times. The boxboards absorb more moisture than the chipboards, which is in agreement with the Cobb test results. The decrease in mass (from the peak) observed in all of the tests may

result from loss of material from the samples. This loss of mass is not seen in the Cobb test, as this is a single point test.

5.3 Liquid Volume Absorption Measurement

An alternative approach to mass uptake measurement for determining absorption is to measure the reduction in volume of the liquid remaining on the surface of substrates, whether in the form of liquid drops or surface films, through drop volume or film thickness measurements.

Evaporation (and/or absorption from the atmosphere) must be considered in all cases as changes in volume due to material exchange between the liquid surface and the atmosphere will be a factor in all measurements. In many cases, the rate of evaporation may be very significant in comparison to the rate of absorption. Thus all measurements need to account for material lost through evaporation. Rates of evaporation can be determined by applying the test liquid to an impermeable surface and following the loss of volume/thickness over the likely experimental duration. The evaporation correction will be large for volatile liquids in low vapour pressure environments. This correction can be reduced through using liquids with low volatility (e.g. paraffin rather than water) or testing in a saturated atmosphere.

Drop volume measurements are made using liquids that poorly wet the surface and form droplets with a large contact angle. The volume of the drop is determined, assuming the drop is symmetrical, from the shape (width and height) of the silhouette outline of the drop. Automated image analysis routines can be used to continually determine the time evolution of the drop volume. Such capabilities are available in drop shape analysis systems for determining contact angles.

The principle of a drop volume measurement method is shown in Figure 25. The evolution of the shape and volume of a sessile drop on a porous substrate at different times (increasing time from left to right) is determined. As time increases the contact angle decreases, the drop height decreases and the drop width may initially increase (as the surface becomes more wettable) and then decrease (due absorption or evaporation from the drop edges occurring faster than continuing spread). The drop width and contact angle are influenced by the changing characteristics of the surface due to the presence and adsorption of the liquid – as the ‘dry’ surface is exposed to the liquid/liquid’s vapour it becomes more easily wetted.

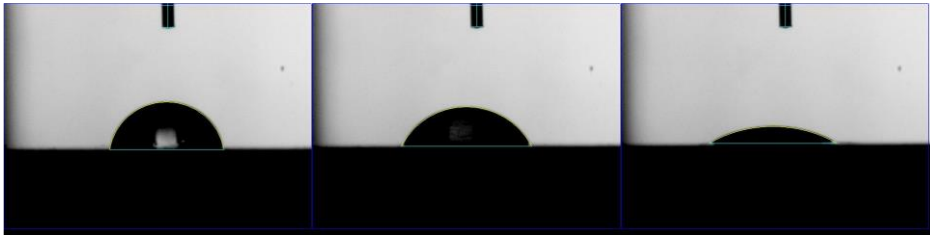


Figure 25: *Time-lapse photographs of a liquid drop on an absorbent surface*

The measurement of drop volume is influenced by the same parameters that apply to contact angle measurement. In particular, the magnification factor of the image must be known in order to calculate accurate drop dimensions from the image. The most straightforward method of calibrating the image is to include an object of known dimensions within the focal plane of the camera – as illustrated in Figure 25, having a syringe tip with an accurately measured diameter remaining in the image after depositing the drop can provide this calibration. The calculation of drop volume depends on being able to obtain a sharp image of the drop to provide a clear outline silhouette and a sharp demarcation between the base and the drop. Surface roughness creates uncertainty in the location of the interface between the drop and substrate leading to uncertainties in both the contact angle and the drop dimensions.

The changes in dimensions of the drop are a combination of two processes:

- Evaporation from the exterior drop surface
- Absorption into the sample through the base of the drop

Corrections need to be made for the loss of volume due to evaporation before absorption of liquid into the sample can be used to characterise the substrate, otherwise the absorption rate will be overestimated. The rates of absorption and evaporation will depend on the area of the drop in contact with the base and the surface are of the air-liquid interface, both of which will vary with time. Corrections for evaporation may be less critical if the measurements are being made for comparison of different materials under well-controlled conditions (e.g. constant applied drop volume, stable test temperature and atmospheric vapour concentration).

The rate of evaporation of the drop depends on many factors including the environment (temperature, vapour pressure, saturation vapour pressure), volatility of the liquid and the exposed area of the drop (volume/mass evaporation rate will be proportional to area). In an enclosed environment a build up of vapour pressure may reduce the rate of evaporation but in an open well-ventilated environment the vapour pressure may remain approximately constant. Using probe liquids with low volatility (i.e. those with high boiling points and low saturation vapour pressures) will help minimise the uncertainty in absorbency measurements

due to evaporation. A method for establishing evaporation loss rates is to apply the sessile drop to an impermeable surface and monitor the reduction of volume (or mass) with time under conditions replicated in the absorbency measurements. The resulting plot of volume against time can be used to generate curves for volume loss rate against exposed area, which can be used to correct the absorbency measurements.

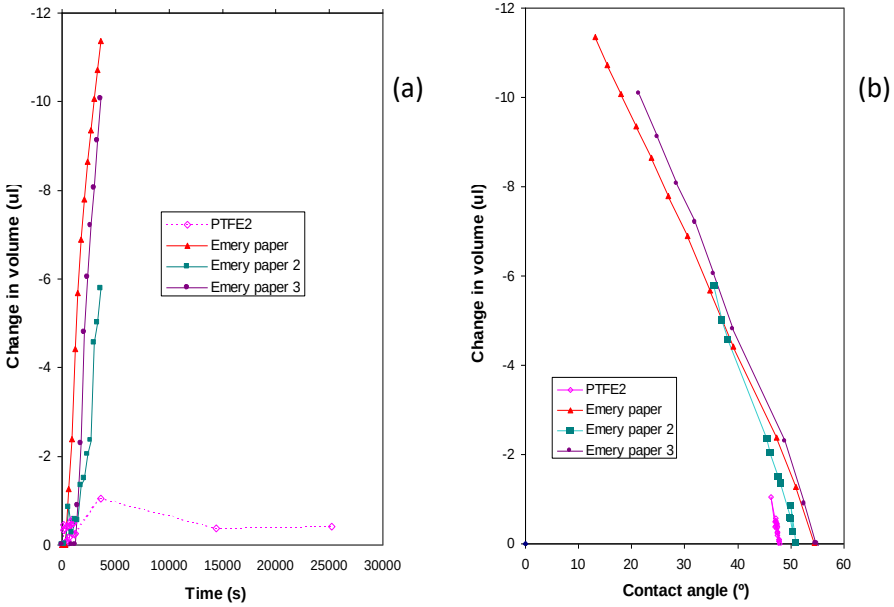


Figure 26: *Change in drop volume and contact angle of paraffin*

Measurements were made of absorption/evaporation of paraffin drops on an absorbent surface (the reverse side of emery paper) and a low energy, low permeability surface (PTFE). Figure 26 shows these drop volume measurements. Drops applied to the surfaces, with initial volumes between 14 μl and 17 μl, had initial contact angles around 50° that were sufficient to produce clearly visible drops. Paraffin has a very low rate of evaporation at room temperature and the volume of the paraffin drop remained reasonably constant with time (as shown by the results for the PTFE surface). The volume reduction of approximately 1 μl seen in the figure is believed to be an artefact of the measurement method due to uncertainties in drop edge detection. A repeat test indicated a 'gain' in drop volume of approximately 1 μl. The uncertainty in drop volume measurement is therefore around 1 μl. Three repeat measurements of paraffin drop volume on the emery paper are shown. The rate of absorption into the porous emery paper is relatively constant and much greater than the uncertainty in the measurement and any evaporation occurring. The surface tension of the hydrocarbon

paraffin is similar to those of hot melt adhesives making paraffin a useful analogue for the adhesives.

Drop absorbency can also be measured by viewing the spreading and disappearance of the drop from above, e.g. through a microscope, Figure 27. The diameter and/or area of the visible drop at different times, which may be determined using computer image analysis techniques, can be used to infer the proportion of liquid that has absorbed and/or evaporated. The extent to which the liquid has absorbed or spread can be estimated from the extent of the wet 'ring' around the drop. This spread of the drop will happen due to:

- Diffusion of liquid absorbed into the substrate from the base of the drop.
- Wicking of the liquid through channels formed by the surface. The direction of spread may be affected by any 'direction' of the surface texture or fibres.

Clear, sharp detection of the edge of the liquid drop and of the edge of the spread are required in order to use this method. Various intensities of illumination or filters (colour or polarising) may be used in order to improve contrast but since no information on drop height is available this method is not considered to be as accurate as the drop profile method described earlier.

The absorbency of a substrate can also be determined from the change in thickness of an applied liquid film. This has the advantage of maintaining a constant contact area during the measurement. The main challenge would be to monitor the film thickness. There are many optical methods, including ellipsometry, that use reflection interference fringes to measure film thickness with a high degree of accuracy. The spacing of light and dark interference fringes produced by total internal reflection on light within the liquid film depend on the incidence angle, refractive index of the liquid and the film thickness, changes in any of these will change the fringe spacing. However, the measurement of film thickness relies on knowledge of the optical properties of the liquid film and a strong reflection from the liquid/substrate interface, which is unlikely with rough or porous surfaces. There are commercial film thickness gauges available but their resolution, particularly for liquid films on rough, soft, porous surfaces is unlikely to be sufficient for this type of measurement.

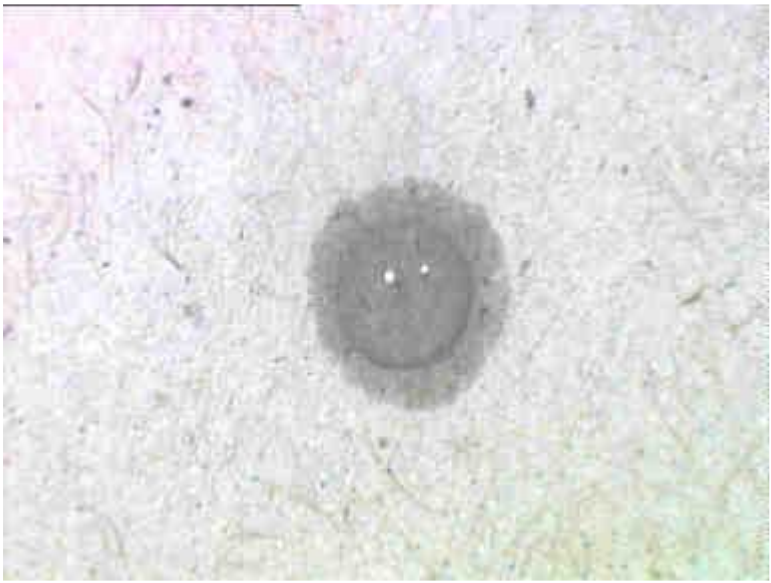


Figure 27: *Liquid drop spreading on a rough, porous surface*

Chapter 6: Bond Tests

- Hand rupture assessment
- Creep rupture tests
- Pira adhesive performance test (PAPT)
- Pull-off test
- Dennison wax pick test
- Hot melt receptivity test

6. Bond Tests

Surface inspection can provide information about the likely suitability of the substrates for testing but in many cases the validation of the materials and process will require bond tests. There are many types of bond tests used for structural adhesives, which are covered in other texts [e.g. 2-16]. In this section several tests for bond performance are described, including the simple fibre tear test and a new adhesive performance tester, which illustrates many practical issues in bond testing. Wax pick tests can be used to provide information on the glueability of surfaces. This section also covers the standard Dennison wax test and an adhesive receptivity test performed using the waxes.

6.1 Hand rupture assessment

The hand rupture or 'fibre tear test' is ubiquitous in the assessment of bonds involving board or paper in the packaging sector. Bonds are made between the materials, stored for an agreed duration in an agreed environment and then pulled apart by hand. The surfaces of the substrates are examined visually to determine the mode of failure, in particular the amount of 'fibre tear' occurring. This is a very uncontrolled test, dominated by in-house methods and operator subjectivity. The method of bond manufacture, dimensions of the substrate samples and direction of pulling may all vary. It is known that the test results can vary depending on which substrate the adhesive is first applied when bonding dissimilar materials.

Typically, substrates will be 100 mm by 25 mm strips and these will be bonded a right angles to form a cross. One 'leg' of the each of the lower and upper substrates is held and a peeling motion (diagonally from opposing corners) is used to rupture the bond. After rupture, the substrates are inspected and the mode of failure and an estimate of extent of fibre tear recorded. Some examples of rupture surfaces are shown in Figure 28. If no substrate failure is evident, then the strength of the bond can be subjectively judged (either strong, moderate or weak).

It is generally accepted that 'fibre-tear failure' is an indication of a satisfactory bond to board. This can lead to a misjudgement of bond performance where:

- The fibre structure is of lower strength than the application demands;
- Failure is not fibre tear, but the strength is nevertheless greater than the application demands; or
- Long-term response to stress on the bond is different to short term response (i.e. creep effects occur).

This measure is of no use where substrates surfaces are not paper based (e.g. plastics or coated substrates). There is considerable inherent scope for variability in this test; the

adhesive will experience a mixture of peel and shear stress that depends on the flexibility of the substrates and the manner in which the bond is pulled. The method used to make the bonds may be considerably different to the actual production line method. Automated bond test instruments, such as the Pira Adhesive Performance Tester (PAPT), considerably reduce scope for variability in bond production and rupture and provide quantitative data on the forces required to fail the bonds.

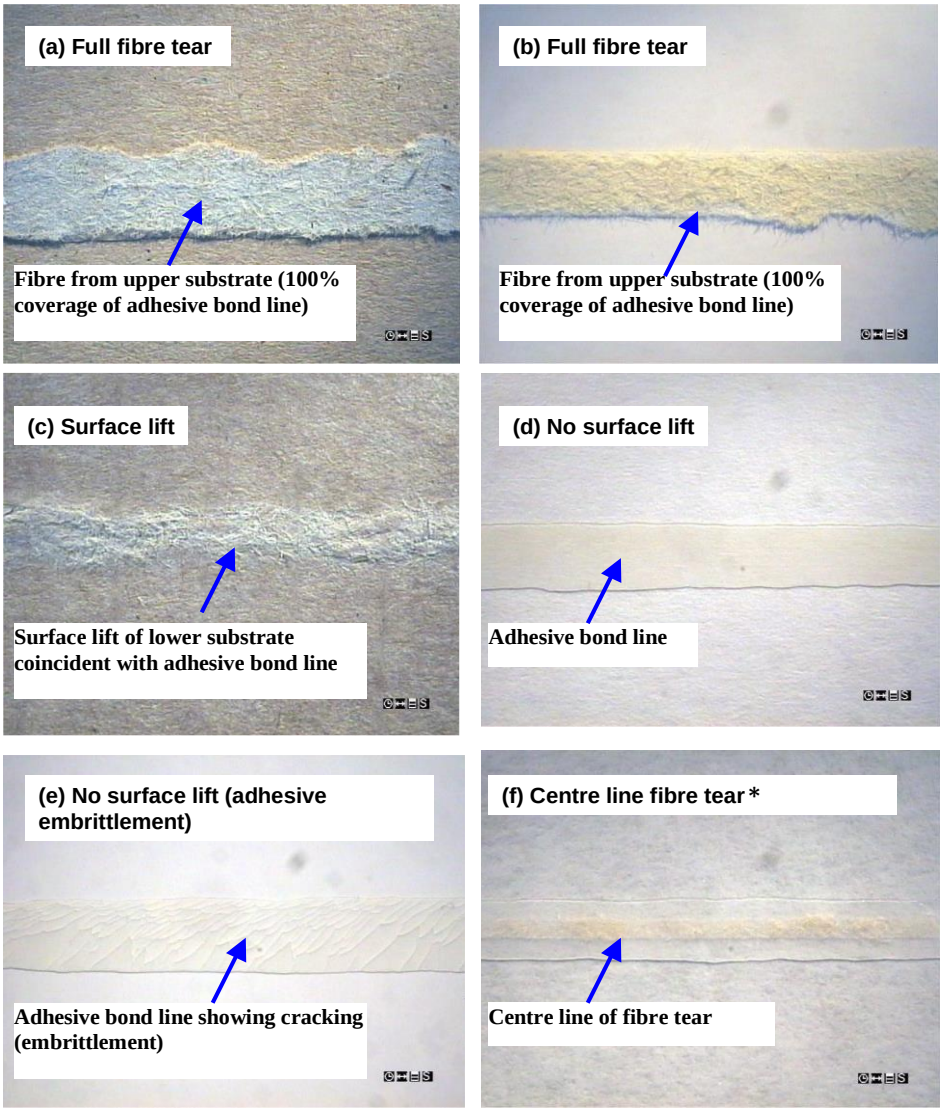


Figure 28: *Typical hand rupture failure modes (all images are of the lower substrate)*

6.2 Creep Rupture Tests

Most bonds suffer continuous stress (loading) in use. Although the levels of stress may be low, the duration of exposure is likely to be long (weeks, months or, possibly, years). The dynamic rupture of a bond demonstrating high bond strength and/or fibre tear gives no indication of the bonds durability to sustained loading. It is therefore necessary to subject bonds to creep resistance tests in order to assure long-term durability. The creep resistance of an adhesive/substrate system will be influenced by environmental conditions (temperature and humidity) and these should be controlled to be relevant to conditions the bonds are expected to endure (e.g. hot, high humidity in SE Asia, cold (or sub-zero) in N Europe or N America).

For practical reasons, a creep resistance test should satisfy the following:

- Occupies a minimum period of time.
- Can be applied equally to rigid, semi-rigid and flexible substrates.
- Is compact in design and avoids the use of heavy weights particularly so that a reasonable number of test samples will fit within an environmental cabinet.

Failure through creep tends to follow a linear relationship of Log (time to fail) to stress applied to the bond, other than at very low stress levels. The value of the constant will be influenced by both test geometry and by the creep resistance of the bond under test. The logarithmic relationship implies that small changes in 'stress' will give large changes in 'time to fail'. Thus any test that satisfies a requirement to occupy a minimum period of time must be designed with a "challenging" stress geometry. Test samples should be uniquely identified and records should contain information on the type of test, materials tested, dimensions of the substrates and bonded region, force applied and test environment. Samples can be continuously monitored using automated systems, although with multiple tests running in parallel this may be expensive. Where automatic monitoring is not used, samples should be inspected for failure on a regular basis. The frequency of checks may depend on the expected durability of the joints and many schedules will begin with fairly frequent checks (e.g. hourly) for a set duration before switching to less regular inspections (e.g. daily). In each inspection the samples that have failed should be recorded. The mode of failure should be examined and recorded for each specimen.

Commonly used creep test geometries are illustrated in Figure 29. Each of these tests suffers from limitations, which the user needs to consider both in the selection of method and in the subsequent interpretation of results.

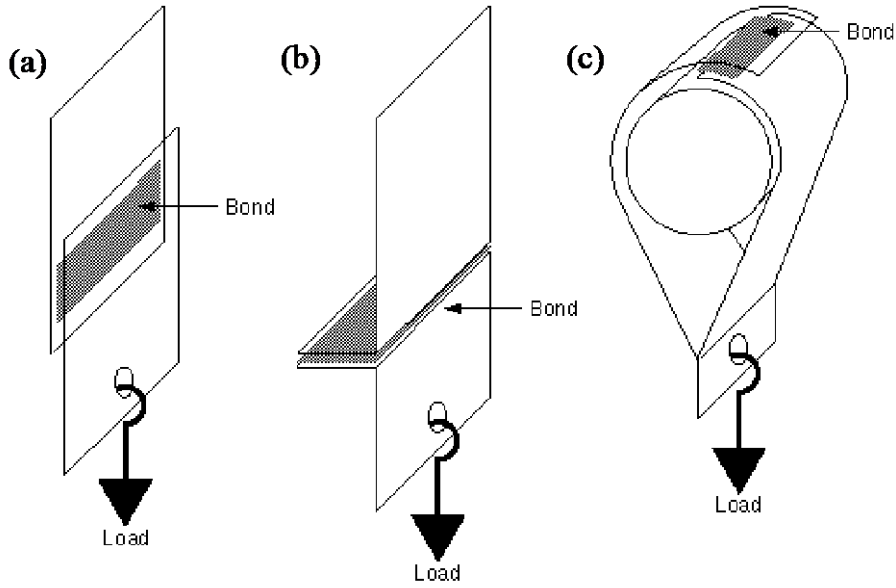


***Figure 29**: Creep rupture test methods*

In Test a, the bond is loaded in shear and the loaded area is relatively large, thus large weights and a long test period are necessary. The stress distribution changes with substrate rigidity, the ratio of peel stress to shear stress will increase as the substrates become more flexible. Test b only suits flexible materials since the substrates need to be bent in order to make the test specimen. The stress distribution near the end of the bond will depend on the rigidity of the substrates. Test c only suits semi-rigid and flexible materials. In addition, the stress distribution varies with substrate rigidity.

Figure 30 shows an improved test geometry, which is more complex than those in Figure 29 but satisfies all the requirements of the rationale. Where reinforcements are necessary (e.g. for flexible and semi-rigid materials) thin plywood has been found suitable. These can usually be well bonded to the substrates, using a PVA type adhesive (this should be selected for freedom from solvents, plasticiser, etc). Pressure sensitive materials (e.g. double sided tape) are unsuitable, as they will suffer creep failure. Performance standards that have been found appropriate to most packaging applications are shown in Table 5.

Tests are typically performed with six replicate samples prepared under the same conditions and loaded under the same stress. Samples should be inspected on a regular basis and samples that have failed recorded on each inspection until all samples have failed. The data can be presented as cumulative failure against time to facilitate comparison between systems. Although the visco-elastic properties of the solid adhesive are an important factor in

determining time to rupture, the nature of the substrate also plays a role. Tests may be performed under constant conditions but durable systems may require long test times to produce rupture. Therefore, tests may be carried out where the severity of the environmental condition (i.e. temperature) is progressively increased after preset exposure durations. These tests provide additional information on the heat resistance of the bond. For example, after a week at 23 °C the temperature may be increased by 3 °C per day until all samples have failed. This provides a more rapid qualitative assessment of the bond performance.

Application	Load (g)	Test Period (weeks)
Normal use conditions	100	1
High stress use conditions (e.g. Bag-in-box)	200	1
Low stress use conditions (e.g. light weight overwrap of light product)	50	1

Table 5: *Loading conditions for creep rupture tests*

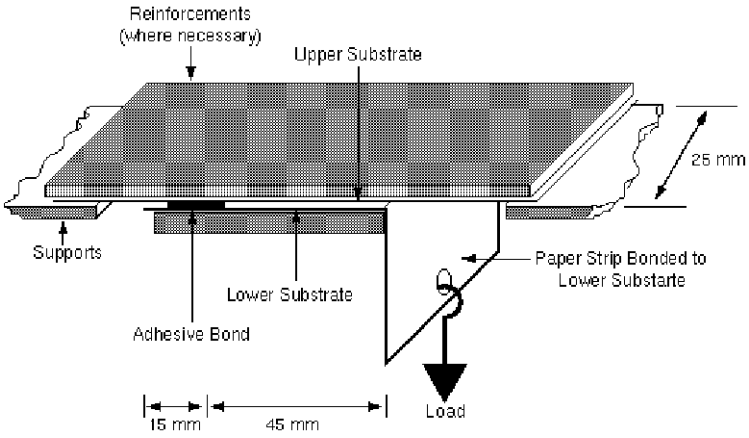


Figure 30: *Creep rupture specimen*

6.3 Pira Adhesive Performance Tester (PAPT)

The Pira Adhesive Performance Tester (PAPT), designed to allow complete control over the key bonding process parameters of open time, contact time, glue application weight, contact pressure, adhesive temperature and application speed, is described here to illustrate important considerations in bond assessment. The PAPT can measure the strength of the joint after multiple pre-set open and/or contact times, without the need to remove the test pieces from the instrument. Thus, the user is able to predict the compatibility of combinations of adhesive and substrate under simulated process conditions.

The PAPT uses a hot melt applicator to provide complete control of the tank, hose and gun temperatures when dispensing the adhesive. The gun is mounted onto a linear guide, which accelerates the gun up to the application speed (up to 1.1 m/s) before it applies glue to the test sample at the required pressure, Figure 31. The sample is then drawn onto a low deflection load cell. This provides control over the dispensing process to ensure a consistent quantity of adhesive is dispensed under well-defined conditions.

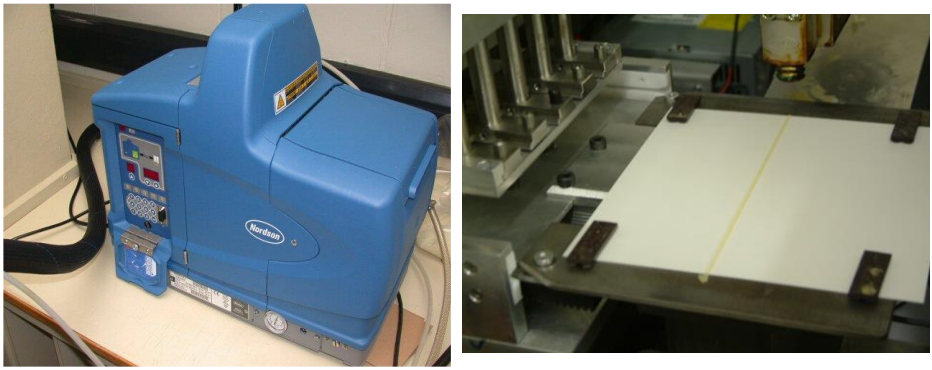


Figure 31: *PAPT Adhesive dispensing*

A second piece of substrate is mounted on each of the five feet (rupture stations), which each are then lowered onto the glue line. A stepper motor powered, constant velocity cam individually drives each rupture station. This allows accurate and repeatable control of the bonding parameters at each station. The speed (closing and rupture), contact pressure and timings (open and contact) can be set at each rupture station. The contact pressure at each station can be adjusted by changing the weight of the foot, while the open time (variable from 0.2s upwards), contact time (variable from 0.2s upwards), contact speed (variable up to 250 mm/s) and rupture speed (variable up to 250 mm/s) are changed by programming the stepper motor controllers from a computer interface. Each foot can then be sequentially ruptured which allows the measurement of the bond as it develops as shown in Figure 32.

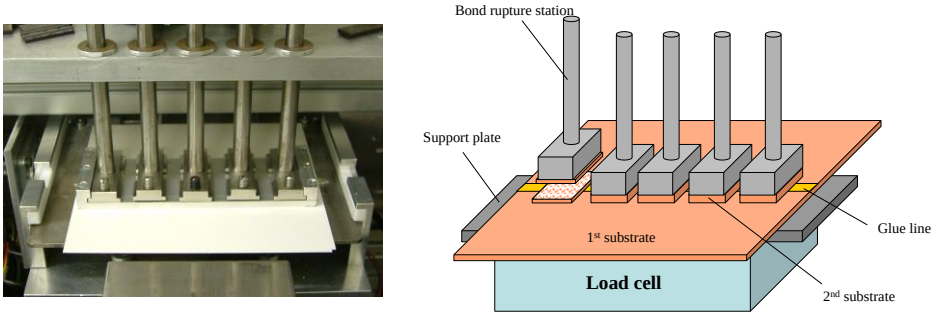


Figure 32: *Schematic multiple bond rupture stations*

The settings can be adjusted to vary both the bonding conditions and the rupture test parameters to explore the effect of materials and process parameters on bond performance. Information on the bond performance can be obtained from the failure surfaces. Figure 33a shows a series of tests where the contact time increases from left to right – cohesive failure occurs at low contact time as the adhesive has not cooled sufficiently to withstand load and fibre rupture occurs once the adhesive has cooled sufficiently to harden. Figure 33b shows the force trace for the same type of test – the rupture force increases as the contact time increases (the rupture force is defined from the difference between the plateau and the trough reading as there is a different force offset for each test).

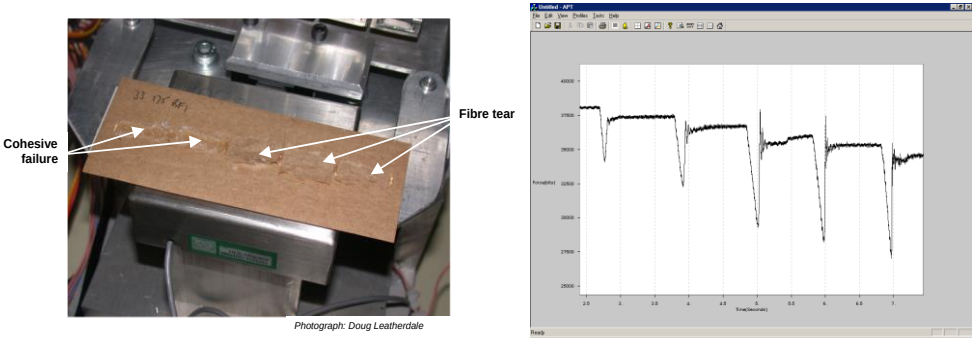


Figure 33: *(a) Failure surface (b) Force trace*

The PAPT can also be used to manufacture bonds for other tests (e.g. creep rupture tests). The upper substrates can be released from the clamps after the bond is formed so that the

bonds are not ruptured when the rupture station is withdrawn. In this way samples can be made under controlled bond formation settings, which approximate manufacturing conditions.

6.4 Pull-Off Tests

Tensile pull-off tests [73-75] are used widely to test the adhesion of coatings to substrates and to assess adhesive bonds. They are simple to perform and can be carried out *in-situ* (either vertically or horizontally) on virtually any type of surface, requires low cost, commercially available equipment and produce quantified measures of the adhesive strength from the maximum force applied to the sample.

Figure 34 shows a schematic of a pull-off test. A test pull stud is bonded to the surface under investigation. The stud is clamped in the test instrument and is pulled normally from the surface until the stud until the bond ruptures. The maximum load is recorded. These tests can be carried out in mechanical tensile test machines but many purpose built commercial instruments are available that use mechanical leverage or pneumatic pressure to apply the force. In pneumatic instruments, inflating a pneumatic bladder pushes the two platens apart and the maximum pressure applied to rupture the bond is recorded. A calibration look-up table is used to determine the failure stress from the pressure.

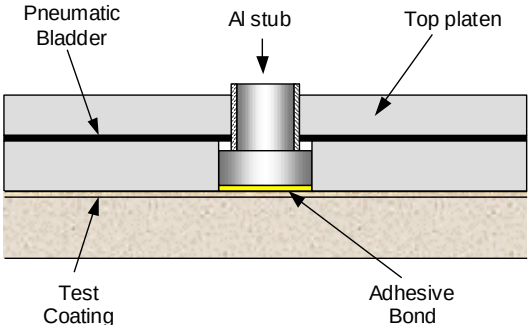


Figure 34: *Schematic of pull-off test*

Sample preparation is straightforward. Adhesive can be applied to either the substrate or the pull stud. These are then pressed together with the pull stud perpendicular to the sample and held in position whilst the bond hardens.

The test provides information about the strength of the adhesive, the adhesive bond and the substrate surface. There are features of the pull-off test that should be considered by the user:

- It is important that the sample should not fail at the interface between the pull stud and the adhesive. The adhesive and pull stud need to be compatible and the surface of the pull stud prepared to achieve sufficient bond strength. It has been found that grit-blasted aluminium provides a suitable surface for most adhesives.
- The pull-off test generally requires a rigid substrate in order that the substrate is not pulled through the platens. This could make it difficult to test many soft or thin substrates.
    - Flexible samples could be bonded to more rigid substrates to prevent this but the bond strength of the sample to the substrate would need to be greater than that of the adhesive to the sample surface.
- The pull off test takes place in a very short period of time; maximum load is reached in less than 1s. The dynamic response of the transducer may introduce measurement errors.
- The surfaces of the pull stud and the substrate should be flat and bonded so that they are parallel and the bondline thickness is constant throughput the sample. Non-uniform bond thickness will induce cleavage stress in the sample leading to premature failure.
- The adhesive layer thickness should be constant in all regions of the sample.
- A spew fillet is likely to form around the pull stud due to displacement of adhesive from the bond region when pressure is applied. It is recommended that the fillet be left as removing it may damage the bondline.
- The test provides a value of pull-off strength as a 'stress' in MPa. This is the applied force divided by the bonded area (calculated from the radius of the pull stud). However, it is recognised that the stress will vary within the bondline, as the substrate will deform during the test.
- Care must be taken when comparing the bonding performance of an adhesive on different materials since the stress distribution in the bondline depends on the bending stiffness of the substrate.
    - The stress distribution becomes more uniform as the stiffness of the substrate increases.
    - Under equal loads, adhesives bonded to substrates with low bending stiffness will experience higher stresses than they would if bonded to substrates with high bending stiffness.
- In situations where the substrate is significantly more flexible than the pull stud (most thinner gauge materials), then the maximum stress is predicted to occur at the interface between the fillet and the adherend.
- In strongly bonded systems, as Figure 35 shows, failure is often cohesive within the bondline, leaving the adhesive and fillets firmly attached to the substrate.
- The travel of the platens of pneumatic instruments is limited and may not be sufficient to rupture highly flexible adhesives.

- The calibration of the pneumatic pull-off instrument is a concern as there is no obvious way of checking for instrument drift.
  - Check samples, bonds of known strength, can be prepared and tested on a regular basis to check for drift, but this requires confidence in repeatability of the bond manufacture and stability of the materials system over time.
  - The calibration and stability of the instrument can be checked by making test samples where the aluminium pull stubs are bonded to steel bolts that can be connected to a calibrated piezo-electric force transducer. Tests are performed to simultaneously record the peak 'forces' using the load cell and pull-off tester, from which pull-off strengths can be calculated and compared. A data recorder capable of high frequency logging, such as a digital storage oscilloscope, is needed for the force transducer signal, as the time to rupture is extremely short.

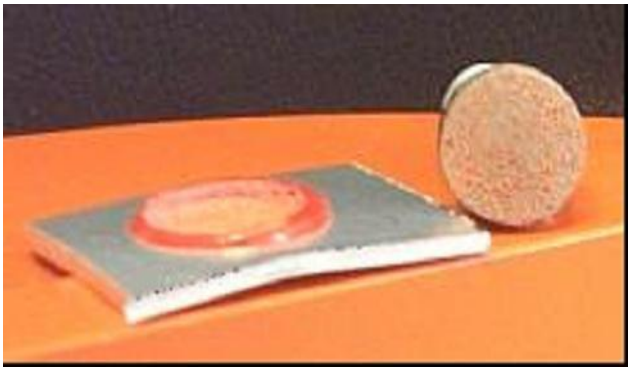


Figure 35: *Pull-off test specimen*

Tests to determine the adhesion strength of structural adhesives to metal surfaces with different treatments carried out using a commercial pull-off tester assess this method were reported in an earlier project [75]. Since wax pick tests (Section 6.5) were investigated as a means of evaluating bonds, information on the tensile strengths of both hot melt adhesives and waxes was measured using this method, in order to better understand their respective bonding performances.

Figure 36 shows tensile strength values obtained using a commercial pull-off instrument (Elcometer Patti 110) for a selection of packaging hot melt adhesives. Force measurements were made simultaneously using a Kistler force transducer to check the instrument calibration. Although there is a high degree of scatter in the average strengths measured, there does not appear to be much significant variation in strength (except for the cool-melt 20 adhesive, which is a low temperature application hot melt). The results shown in Figure 36 demonstrate

that the agreement between the pneumatic tester (Elcometer) and the force cell (Kistler) is generally good, confirming the calibration of the pneumatic tester.

Limitations in this technique were shown by pull-off tests performed using a high tack, pressure-sensitive hot melt adhesive. This adhesive was highly extensible and it proved to be impossible to rupture the bond within the maximum travel of the tester as the adhesive formed long strings when pulled.

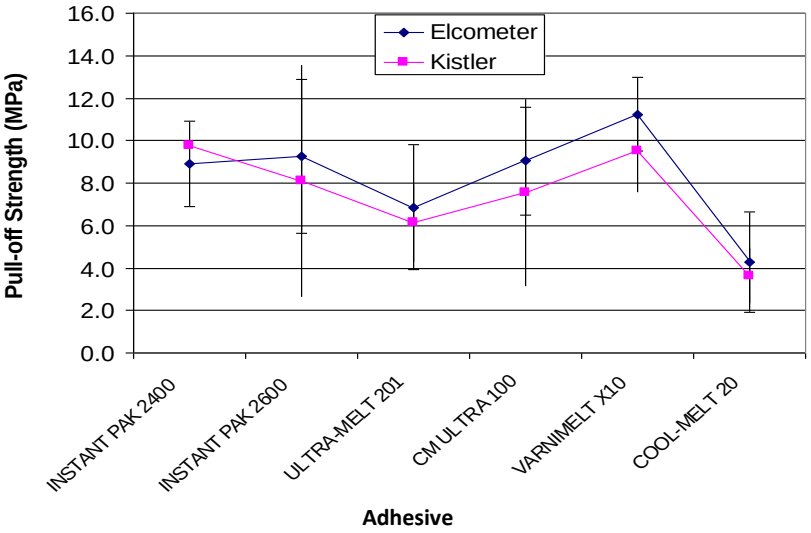


Figure 36: *Pull-off strengths of hot melt adhesives*

6.5 Dennison Wax Pick Test

Adhesive suppliers commonly use the Dennison wax pick test, TAPPI T459 om-93 [76], originally designed as a test for printing press performance, as a guide to hot melt glueability. In the standard wax pick test, the lowest wax number which does not disturb the test surface is quoted as the Critical Wax Strength Number (CWSN) and is used as a measure of the surface strength of uncoated and coated papers. A high CWSN designates a strong surface strength.

A series of calibrated, hard-resin sealing 'Dennison' waxes with increasing 'adhesive power' are applied to the surface. The wax sticks are 18 mm x 18 mm in cross-section and numbered 2A to 26A (higher numbers indicate higher 'adhesive power'. The wax stick, cleaned with a sharp blade, is heated in a low flame, rotating the stick slowly allowing several drops of molten wax to fall, but not letting the stick catch fire. The molten end is then immediately placed on the surface to be tested. The melting of the hot waxes onto the surface draws comparison with the hot melt glueing process. Once the waxes have hardened, after 15 minutes to 30 minutes after application, a wooden block with a hole 30mm in diameter is placed over the wax stick and whilst holding the wooden block firmly, the wax stick is quickly pulled from the paper, at right angles to the surface. The highest wax pick number that does not disturb the surface of the paper is the numerical rating of the paper, e.g. Figure 37 shows a surface with a wax pick rating of 18A. A high wax number designates a strong surface strength but this may not always correlate with actual bond strength. The properties of the Dennison waxes are further exploited in the hot melt receptivity test.

Waxes are supplied with wax numbers range from 2A to 26A in order of increasing 'adhesive power'. However, the physical basis of the 'adhesive power' is unclear. The increased adhesion 'power' may be a result of higher cohesive strength of the wax, better wetting (due to low viscosity or surface tension) or high intermolecular forces. Since wax sticks are used as analogues for hot melt adhesives, measurements were made of their properties to determine how well they replicate the properties of the adhesives.

Tensile strengths were measured using the pull-off test (see Section 5.3). The results, shown in Figure 38, indicate that the strengths of the waxes (3-7 MPa) are not significantly different to those of the hot melt adhesives (4 – 10 MPa). The trend is for the mechanical strength of the wax to increase with wax number. However, there is a high degree of scatter in the strength measurements and the strengths of the two mid-range waxes are not significantly different.

Figure 37: *Dennison wax pick test*

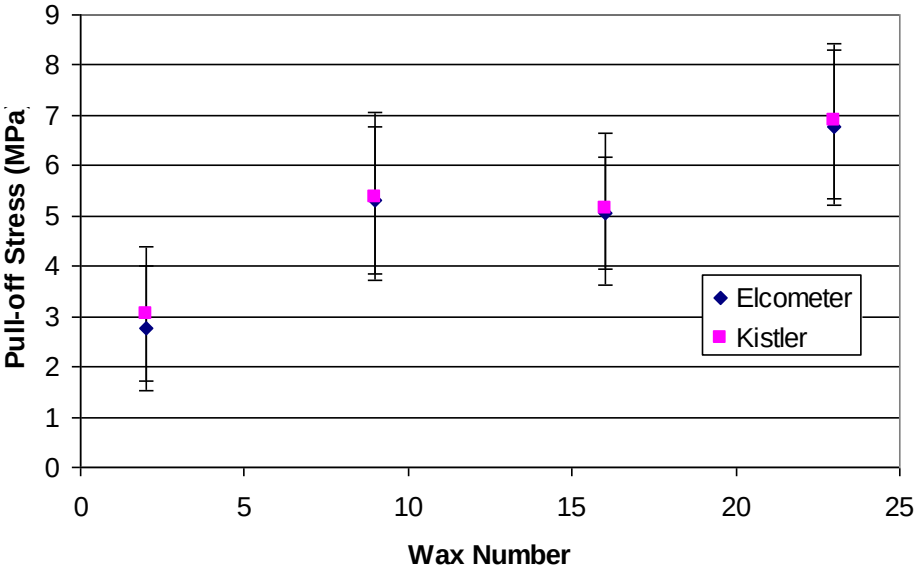


Figure 38: *Pull-off tensile strength of Dennison waxes*

Dynamic viscosity measurements were made on the 2A and 23A waxes, representative of the extreme ends of the wax range, using a Bohlin rheometer in temperature sweep mode at a single frequency [77]. The results, plotted as elastic (storage) modulus G' and viscous (loss) modulus G" against temperature, are shown in Figure 39. The waxes typically reach around 120 °C when they are heated before application. The temperature will decrease as soon as the heat source is removed and the temperature of the wax when applied to the surface will obviously be less than 120 °C, suggesting that the range of test temperatures covered is relevant to the use of the waxes. The visco-elastic properties vary over several orders of magnitude between the molten and solid states but there is not a sharply defined melting transition. Figure 39 shows that there are significant differences between the visco-elastic properties of the two waxes over the range of test temperatures. The viscous modulus (G") of the 23A wax is significantly higher than the 2A wax at high temperatures, which would suggest that it would have greater difficulty in wetting substrates than the lower 'power' wax. The higher elasticity (G') of the 23A wax suggests greater resistance to deformation and it is less likely to fail before the surface than the less elastic 2A wax. The low temperature cut off of the data reflects the point at which the data becomes unreliable owing to the increasing stiffness of the waxes resulting in instrument compliance errors.

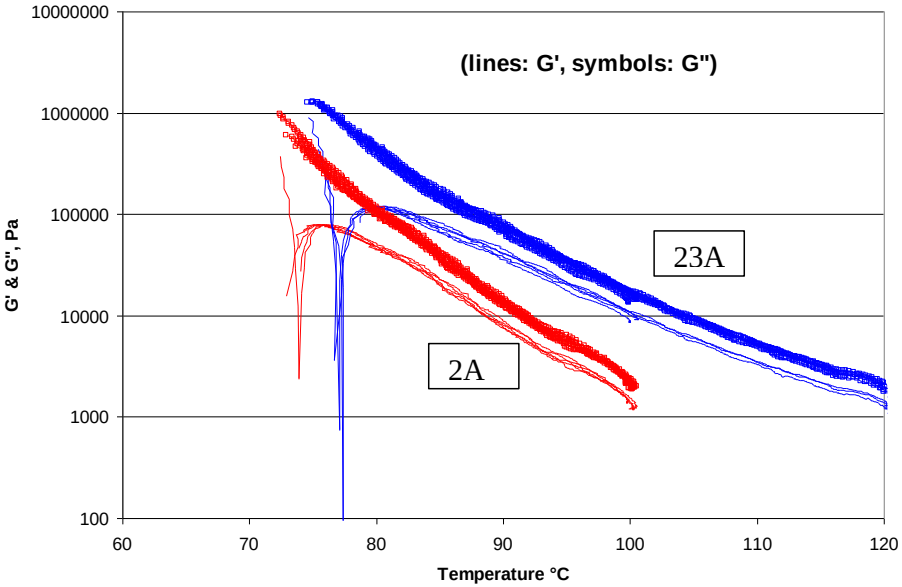


Figure 39: *Visco-elastic properties of low pick (2A) and high pick (23A) Dennison waxes*

6.6 Hot melt receptivity test

This test uses the Dennison Wax system as described in TAPPI T459 [76]. The Dennison wax system test provides information on the glueability of the surface from the wax number required to damage the surface but no information on the forces required to debond. It is therefore only useable with 'weak' fibrous materials, such as paper and cardboard and cannot provide much information on other common materials such as plastics or foils. The receptivity test can be used for all materials.

The hot melt receptivity method extends the versatility of the wax pick method through measuring the 'pull-off' force. This 'pull-off' force depends on the ability of the wax to 'wet' onto the substrate. As the wax adhesive power is graded, the result depends on the 'glueability' of the substrate.

Samples are prepared using the wax pick method. The test sample, approximately 100 mm x 100 mm, is placed on a smooth non-heat conductive surface e.g. a wooden bench, with the substrate surface of interest uppermost. A wax stick, cleaned with a sharp blade, is heated in a low flame, rotating the stick slowly allowing several drops of molten wax to fall, but not letting

the stick catch fire. The melted end of the stick is then quickly placed firmly onto the centre of the test surface. The end spreads to an approximate 20 mm diameter. The wax stick is then left to cool for 15 – 30 minutes.

***Figure 40**: Hot melt receptivity test*

The test piece is carefully placed on a compression plate of a tensile test machine and a wooden block with a 30 mm diameter hole clamped over the stick. The clamp is attached to the load cell of the tensile test machine using a steel wire as shown in Figure 40. The stick is pulled from the surface at a constant speed of 100 mm/min and the peak force to remove the stick from the surface is recorded. Three replicate measurements are made at each wax number. The results are plotted as a graph of wax stick removal force against wax number.

Figures 41(a)-(d) illustrate results of receptivity tests made on the selected substrate surfaces, chosen for their different ease of bonding. The blue line represents the mean of three replicate sets of results. Selected measured surface characteristics for each substrate are also presented.

Figure 41(a) illustrates a substrate that would be characterised as easy to bond. There is a steady progressive increase in wax removal force with increasing wax number. Full fibre tear occurs around wax number 7A – 10A with a removal force of around 40 N.

Figure 41(b) illustrates a more challenging substrate. The removal force is again progressive with wax number. Partial fibre tear occurs above wax number 11A (pull off forces 20 N to 30 N) but full fibre tear is achieved only at the higher wax numbers, 20A – 26A, where pull-off forces are greater than 30 N.

Figure 41(c) illustrates a 'difficult' substrate, where removal force is low until wax number 18A and then rises rapidly to full fibre tear at wax number 23A. Pull-off forces increase significantly from ca. 15 N to >30 N in this region.

Figure 41(d) shows the receptivity of a substrate surface that is characterised as 'very difficult'. Only a low wax removal force is achieved at the highest wax number 26A (< 10 N) and no fibre tear is seen.

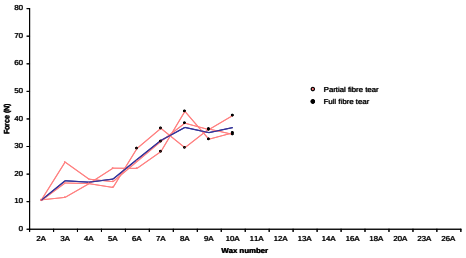
Table 6 shows a correlation between qualitative hot melt receptivity and the ease of bonding the top surface to the reverse surface for various substrates, subjectively assessed by an experienced operator. This bond simulates flap closure and bonding, an important process in sealing cartons and boxes. In any top/reverse surface pair a very low receptivity assessment for either surface corresponds with very difficult bonding. Moderate or high receptivity (provided the other surface does not have a very low receptivity) generally corresponds to 'fair' or better bonding.

There appears to be no obvious correlation between surface parameters and the bonding performance for the four surfaces illustrated. The easy to bond surface has a very similar roughness to the very difficult to bond surface. The dyne pen wettabilities of these two surfaces are also similar. The high water drop contact angle of the top surface of substrate 46 would suggest poor wetting by the adhesive but this does not correlate with either the receptivity results or the assessed ease of bonding. There appears to be an inverse relationship between wax strength and bonding performance for these four surfaces – the easier to bond surfaces have low wax pick numbers in comparison to the difficult to bond surfaces. However, the force required to achieve fibre tear is similar for each surface with the exception of the very difficult to bond surface where fibre tear does not occur and the pull-off force is low. The high wax number arises because the wax does not stick well to this substrate.

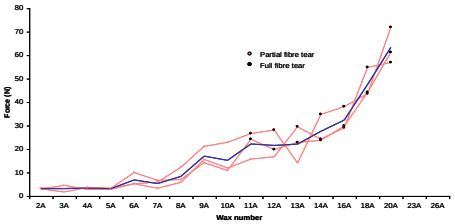
Sample number	Receptivity top surface	Receptivity reverse surface	Ease of bonding
5	moderate	low	fair
13	v. low	low	v. difficult
16	v. low	low	v. difficult
29	moderate	v. low	v. difficult
33	low	low	good
34	low	moderate	good
36	v. low	v. low	v. difficult
45	not measured	low	difficult
46	not measured	high	good

Table 6: *Qualitative correlation between hot melt receptivity and ease of bonding*

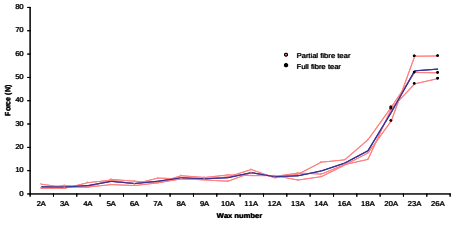
Substrate Properties



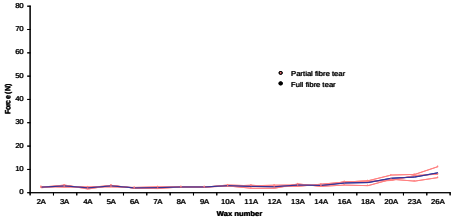
(a) Sample	46 Reverse
Roughness (profilometer)	1.6 µm
Bendtsen Roughness	47 ml/min
Wetting tension	34 Dyne
Water drop contact angle	101.9°
Wax pick value	5A
Ease of bonding	High



(b) Sample	5 Top
Roughness (profilometer)	1.3 µm
Bendtsen Roughness	16 ml/min
Wetting tension	N/A
Water drop contact angle	57.7°
Wax pick value	11A
Ease of bonding	Fair



(b) Sample	5 Reverse
Roughness (profilometer)	4.8 µm
Bendtsen Roughness	500 ml/min
Wetting tension	N/A
Water drop contact angle	101.2°
Wax pick value	18A
Ease of bonding	Fair



(b) Sample	16 Top
Roughness (profilometer)	1.7 µm
Bendtsen Roughness	8 ml/min
Wetting tension	34 Dyne
Water drop contact angle	71.3°
Wax pick value	26A
Ease of bonding	V. difficult

Figure 41: *(a) very easy to bond (b) moderately easy to bond (c) difficult to bond (d) extremely difficult to bond*

Chapter 7: Concluding Remarks

7. Concluding Remarks

A selection of measurement methods, which can be used to characterise substrates for bonding has been presented. This is by no means an exhaustive list of possible methods but concentrates on methods for examining the roughness, wettability, absorbency and surface strength of flexible, porous substrates, which are commonly used in non-engineering applications such as packaging, footwear and consumer goods.

As a wide range of material types was investigated, it is perhaps not surprising that there is no single measure of substrate properties that definitively predicts bonding performance for any substrate with any adhesive. The use of any combination of adhesive and substrates would need to be investigated using the bond test methods, such as those outlined in Section 6. The hot melt receptivity test appears to correlate well with bond performance. Good control over bonding conditions, such as achieved using the Pira Adhesives Performance Tester and a new hot melt tack tester developed by SATRA [78], allows investigation of the process conditions needed to produce strong bonds.

Many of the measurement methods outlined in this guide can be used for quality assurance measurements of substrates received for production, to check for consistency. It is also likely that many of the methods can be used for exploring the effects of surface treatments (e.g. coatings or plasma treatments, on similar substrates for optimising bond performance). Wettability is an important property of the surface-adhesive interaction and a number of methods for determining this have been described. It should be noted that the correlation between water contact angles and adhesive contact angles appears to be poor. Non-aqueous probe liquids may be better for predicting bonding properties.

Chapter 8: Useful Contacts

8. Useful Contacts

NPL
National Physical Laboratory,
Hampton Road,
Teddington,
Middlesex, UK, TW11 0LW
www.npl.co.uk

ASTM
100 Barr Harbor Drive,
P.O. Box C700,
West Conshohocken,
Pennsylvania 19428, USA
www.astm.org

SATRA
SATRA Technology Centre Ltd,
Wyndham Way,
Telford Way,
Kettering,
Northamptonshire, UK NN16 8SD
www.satra.co.uk

ISO
International Organization for Standardization,
ISO Central Secretariat,
Chemin de Blandonnet 8 CP 401,
1214 Vernier, Geneva,
Switzerland
www.iso.ch

BSI
British Standards Institution,
389 Chiswick High Road,
London, UK, W4 4AL
www.bsi-global.com

TAPPI
15 Technology Parkway South,
Suite 115, Peachtree Corners,
GA 30092 USA
www.tappi.org

TWI
Granta Park,
Great Abington,
Cambridge, UK, CB1 6AL
www.twi.co.uk

BASA
British Adhesives and Sealants Association,
24 Laurel Close,
Ely, Cambridgeshire, UK, CB6 2BN
www.basaonline.org

PSTC
Pressure Sensitive Tapes Council,
111 West Jackson Blvd.,
Suite 1412, Chicago, IL 60604 USA
www.pstc.org

Adhesion & Adhesives Group
Institute and Materials, Minerals and Mining,
297 Euston Road,
London NW1 3AD, UK
https://www.iom3.org

Chapter 9: References

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Chapter 10: Appendices

- Appendix I: Adhesion
- Appendix II: Glossary of Terms and Techniques

Appendix I: Adhesion

The term adhesive is used to describe a polymeric material that bonds two surfaces or components together to form a joint, particularly one that will bear load. A true adhesive bond to a surface is formed through inter-molecular attraction between molecules in intimate contact. Bonds form due to (in order of increasing bond strength):

- Van der Waals attractive forces
- Polar interactions and hydrogen bonding
- Covalent, chemical bonding

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.

Adsorption and Wetting: The formation of a physical bond resulting from highly localised intermolecular forces. Adhesives that have surface energies less than that of the adherend will readily wet the surface and yield good bonds. If sufficiently intimate contact is achieved between the adherend and adhesive a physical interaction develops between the atoms of the two surfaces, which results in wetting. Wetting may be due to acid-base interactions, weak hydrogen bonding or Van der Waals forces (dipole-dipole and dispersion forces). The extent of wetting depends on the differences in surface free energies of the solid, liquid and subsequent interface.

Chemical Bonding: The formation of a stable linkage by the reaction between a functional grouping on the adherend surface and a compatible group in the adhesive. Adherend surfaces are usually given surface treatments (e.g. chemical etching, corona discharge and plasma treatments) to create compatible groups. 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.

In thermodynamic terms, to break an adhesive bond energy must be applied to the system such that the input energy (ΔE) is greater than the free energy of the two new surfaces created less the interfacial energy.

$$\Delta E \geq W_A + W_S - W_{AS} \qquad \text{(A.1)}$$

Where W_A is the surface energy of the adhesive, W_S is the surface energy of the substrate, W_{AS} is the interaction energy.

In theory, all bond strengths could be calculated from these surface energy properties. Wettability (and contact angle) measurement techniques enable determination of surface energies resolved into dispersive and polar terms [79-82] and with the correct choice of probe liquid acidic and basic properties of the surfaces can be quantified. Unfortunately, the surface energy approach has only limited application to predicting the strength of a joint since, as mentioned above, true interfacial failure is unlikely. Further complications arise since the contact area, due to roughness at a molecular scale, is difficult to determine although adsorption techniques have been used [83]. Furthermore, the surface energy approach ignores any direct chemical interaction between the adhesive and adherend and also fails to consider any changes in the composition of the surface layers due to the presence of the second layer. Wettability is therefore a useful method for assessing suitability to bond but would be difficult to relate directly to bond strength. Phenomena such as mechanical keying often provide enhanced bond strengths to the physico-chemical bonds. An alternative technique for characterising energies of interaction between surfaces is the determination of detachment forces and contact radius using sensitive surface force apparatus [84]. Highly sensitive force measurement systems enable the measurement of extremely small adhesion forces. The measurements require that the surfaces are molecularly smooth. This is generally achieved through the use of cleaved mica sheet substrates. Monolayers of polymer or surfactant can be deposited on the mica surface and interactions measured directly. This type of measurement can yield accurate adhesion strengths but is limited in the types of materials that can be studied through the requirement of molecularly smooth surfaces.

Workers in the adhesives field, such as Sharpe [85] and Bikerman [79], have argued that the statistical improbability of a fracture propagating solely along a molecularly rough surface means that true interfacial failure never occurs. Thus, the phenomenon of 'interfacial failure' is more accurately described as near surface failure. However, other authors [80] have argued that failure at the interface can be thermodynamically favoured and that the surface energies can be correlated with bond strength with polar components of the surface energies playing a critical role. Whatever the terminology employed, understanding the behaviour of interfaces throws up many challenges. Stresses in the region of the interface are difficult to determine accurately owing to the difficulty in modelling load transfer between dissimilar materials. The properties of surfaces may differ both chemically and physically from those of the bulk material (e.g. oxide layers on metals). Furthermore, there is some evidence that the proximity of another surface may further modify the properties of interface layers of the adhesive through mechanisms such as molecular re-orientation, preferential diffusion/ adsorption of components or altered chemical reactions (e.g. through catalysis or differences in the thermal history during cure). The concept of an interphase region has been used to describe material characteristics near an interface [87, 88]. The properties of the adhesive in this region can be

significantly different to the bulk adhesive [86-89]. The differences between bulk and interface properties depend on the adhesive, surface material and surface preparation. Substantially higher modulus values have been reported for the near surface material, attributed to the transfer of materials from the surface oxide layers into the adhesive [86] as have decreased modulus values near the interface [87-89], thought to be due to incomplete cure and residual stresses in the near interface region. The extents of the interfacial zones in the adhesive layer have been estimated as relatively thick (greater than 0.1 mm) in comparison to bond thickness [79, 86-89]. The keying of adhesive into surface roughness features can also be considered as forming an interphase region whose properties affect the mechanical performance of the joint [90]. In this Guide the term interface is used to encompass the true interface, the interphase and the near surface area.

Appendix II: Glossary of Terms and Techniques

(Based on BSI and ASTM definitions)

Adherend: Body that is, or is intended to be, held to another body by an adhesive.

Adherend failure: Failure of a joint in the body of the adherend.

Adhesion: State in which two surfaces are held together by interfacial bonds.

Adhesive: Non-metallic substance capable of joining materials by surface bonding (adhesion), the bonding possessing adequate internal strength (cohesion).

Adhesive failure: Failure of an adhesive bond such that separation appears to be at the adhesive/adherend interface.

ASTM: American Society for Testing and Materials.

Bond: The union of materials by adhesives.

Bond line: The layer of adhesive that attaches two adherends, also called the bond layer.

Bond strength: The load - tension, compression, flexure, peel, impact, cleavage, or shear - required to break an adhesive assembly with failure occurring in or near the plane of the bond. Often quoted normalised to some dimension of the bond (e.g. area, length or width).

BSI: British Standards Institute

Butt joint: Joint in which the plane of the bond is at right angles to a major axis of the adherends.

Bulk adhesive: The adhesive unaltered by the adherend.

Cleavage: Mode of application of a force to a joint between rigid adherends, which is not uniform over the whole area, but results in a stress concentrated at one edge.

Cohesion: The ability of the adhesive to resist splitting or rupture.

Cohesive failure: Failure within the body of the adhesive (i.e. not at the interface).

Contamination-free: Absence of foreign matter, both on a treated surface (i.e. cleanliness), or which could migrate through the bulk to a bonded interface with time.

Creep: The time-dependent increase in strain resulting from a sustained load.

Cure: The process through which a liquid, film or paste adhesive hardens and becomes capable of sustaining load.

Fillet: Portion of an adhesive that bridges the adherends outside the bond line.

Fracture toughness: The resistance of a material (or interface) to crack propagation. Defined for different modes of fracture. Mode I is direct tension, Mode II is in-plane shear and Mode III is out-of-plane shear.

Glass transition: Reversible change in an amorphous polymer or in amorphous regions of a partially crystalline polymer from (or to) a viscous or rubbery condition to (or from) a hard and relatively brittle one.

Hyperelastic: Large strain elastic behaviour modelled using a strain energy potential.

Interface: The region where two materials are in intimate contact. Interfaces can be solid-solid (cured adhesive joint), solid-liquid (uncured adhesive joint), solid-gas (exposed adherend), liquid-gas (open adhesive) or liquid-liquid (insoluble liquids).

Interphase: The region near an interface where the properties of materials are altered from their bulk properties due to the presence of the interface.

ISO: International Standards Organisation.

Lap joint: Joint made by placing one adherend partly over another and bonding together the overlapped portions.

Materials model: Constitutive equations linking stress and strain properties.

Modulus: Material property denoting the stress required to extend a specimen by unit strain. (modulus = σ/ε)

Peel: Mode of application of a force to a joint in which one or both of the adherends is flexible and which the stress is concentrated at a boundary.

Poisson's ratio: The ratio between axial and transverse strains in a uniaxial tension test as defined in Equation (3), used in the definitions of elastic moduli.

Post-cure: Further treatment by time and/or temperature of an adhesive to obtain the required properties by curing.

Roughness: Micro-roughness represents the fine structure of a surface with dimensions 0.1 μm or less. Macro-roughness, which may also have a significant influence on bond performance, suggests the coarser structure of a surface with dimensions greater than this.

Scarf joint: Joint made by cutting identical angular segments at an angle less than 45° to the major axis of two adherends and bonding the adherends with the cut areas fitted together to be coplanar.

Sealant: An interlaminar layer of polymeric material applied for the purpose of filling gaps and insulating the interior of the joint from external environments. Sealants are not used to provide load bearing capacity although adhesives can also act as sealants.

Shear: Mode of application of a force to a joint that acts in the plane of the bond.

Soundness: Freedom from weak and loosely attached surface layers.

Stability: The stability of surface layers and oxides, towards water, organic compounds and elevated temperatures, as a function of time following treatment.

Strain: Unit change due to force in size of body relative to its original size (ε). Engineering or nominal strain is defined by Equation (2). True strain is defined in Equation (4).

Stress: Force exerted per unit area at a point within a plane (σ).(ε). Engineering or nominal stress is defined by Equation (5). True stress is defined in Equation (6).

Stress-strain diagram (or curve): A diagram in which corresponding values of stress and strain are plotted against each other.

Structural bond: Bond that is capable of sustaining, in a structure, a specified strength level under a combination of stresses for a specified time.

Substrate: A material upon which an adhesive is applied.

Surface preparation (or treatment): Physical and/or chemical treatments applied to adherends to render them suitable or more suitable for adhesive bonding.

Tension: Mode of application of a tensile force normal to the plane of a joint between rigid adherends and uniformly distributed over the whole area of the bond line.

Thermoset: A resin that is substantially infusible and insoluble after being cured.

Uniformity: Visible or measurable consistency of the other characteristics, and of the regularity of a treated surface area.

Visco-elastic: A material whose properties combine elastic (or recoverable) and viscous (or irrecoverable) components. Visco-elasticity leads to strain rate and temperature dependent properties and is also responsible for damping.

Wettability: A measure of the attractiveness of a solid surface towards a liquid, encompassing aspects such as energy and chemistry.

Yield stress: The stress (either normal or shear) at which a marked increase in deformation occurs without an increase in load.

Technique	Description	Use/Limitations
Infrared Spectroscopy (IR)	Absorption of IR photons (transmitted or reflected) occurs at specific frequencies associated with internal vibrations of groups of atoms in molecules.	IR provides qualitative and quantitative chemical analysis data, particularly useful polymer chemistry. IR provides a fingerprint of the adhesive or coating composition in any physical state that can be compared with databases of spectra to enable characterisation of molecular state. Since it is an optical (photon in/photon out) technique it is not necessary for such studies to be carried out in vacuum. IR is a commonly available laboratory technique.
Raman Spectroscopy	Raman is based on the inelastic scattering of monochromatic light. A laser excites the material, usually in the visible region of the spectrum. The frequency of scattered light is analysed and 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.
Energy Dispersive X-Ray Analysis (EDX)	X-rays emitted from a surface material upon exposure to a primary beam of electrons 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. EDX generates elemental distribution maps, enabling both qualitative (boron to uranium) and some quantitative (sodium to uranium) element analysis. Samples must be studied under vacuum.

X-ray Photoelectron Spectroscopy (XPS)	Measures the energies of photoelectrons emitted from atoms of a sample when irradiated with soft (or low energy) X-rays.	XPS is surface-sensitive and used for quantitative elemental analysis, capable of detecting all elements with the exceptions of hydrogen and helium. XPS can discriminate between different oxidation states and different chemical environments. XPS can be used in conjunction with inert gas ion sputtering to determine the variation in chemical composition with depth. Some polymeric material samples are sensitive to ion beam damage. Samples must be studied under vacuum.
Auger Electron Spectroscopy (AES)	High-energy electron beam bombardment of the surface results in the emission of Auger electrons at characteristic discrete energies.	AES is a surface sensitive, non-destructive technique for identifying the elements, with the exception of hydrogen and helium, in the first few atomic layers and is able to provide quantitative data (by comparison with known standard samples). Combined with inert gas ion sputtering, AES can obtain depth composition profiles. AES can scan the specimen surfaces with high spatial resolution (0.5μm). AES is not particularly suited to insulating materials. Samples must be studied under vacuum.
X-ray Fluorescence Spectroscopy (XRF)	Irradiation with X-rays results in the release of photons with element specific characteristic energies.	XPS provides qualitative and semi-quantitative elemental analysis for elements above aluminium in the periodic table. It requires very flat samples. Samples must be studied under vacuum.

Secondary Ion Mass Spectrometry (SIMS)	The bombardment of a surface with a beam of high-energy ions results in the ejection of molecular fragments, atoms and ions from the surface, which are subsequently analysed.	SIMS provides 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). Quantitative analysis is complex and requires reference standards. Samples must be studied under vacuum.
Rutherford Backscattering Spectrometry (RBS)	A beam of positive ions is directed at the target surface and produces ions, which are scattered by the sample nuclei, to be measured and analysed.	RBS is used for the quantitative, non-destructive compositional depth profiling and thickness measurements on thin films. The depth resolution is 10 to 20 nm and RBS can probe several thousand atomic layers and is ideal for surface analysis up to 2 μm depth. The erosion and the radiation degradation of the sample material by the particle impact are negligible. Samples must be studied under vacuum.