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**Techniques for
characterising the wetting,
coating and spreading of
adhesives on surfaces**

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Techniques for characterising the wetting, coating and spreading of adhesives on surfaces

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ABSTRACT

In bonding operations it is vital that the adhesive coating is applied in the correct locations and spreads over roughened surfaces sufficiently to bond. Incorrectly applied adhesive can weaken the bond. Hardening of the adhesive, whether due to cooling, drying or cure reactions before bond formation, overspreading or over-absorption into permeable materials can weaken the subsequent joint.

This report describes techniques for characterising the properties of surfaces that influence the interactions between the substrate and adhesive during the bonding process. It describes methods for assessing substrate wettability and surface energy, surface absorbency, surface receptivity and application and spreading monitoring. Good wettability of a surface is a prerequisite for ensuring good adhesive bonding. Methods for measuring the contact angle of hot melt adhesives have been developed and compared with water drop contact angle measurements. Improvements to the Dennison wax test are also described.

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1. INTRODUCTION

Adhesive bonding is a key joining technology in many industrial sectors. Adhesives are widely used for their ability to join dissimilar materials, with joints which are durable but at the same time unobtrusive and do not detract from the aesthetics of the finished product. However, as the volumes and market values of adhesives used in industry tend to be relatively low, there are few adhesives specialists employed in manufacturing despite the financial risks of problems with the bonding operation and the consequences of failure. Project MMS9 ‘Measurements for Efficiency Improvements in Rapid Bonding Systems’ of the DTI Measurements for Material Systems programme aims to develop methods for characterising the properties of adhesives and substrates that influence dispensing and bond formation [1].

Systematic approaches, based on understanding the quantitative properties of the materials involved, are needed for designing and setting up optimised bonding processes in order to improve quality or increase throughput. However, these are rarely used as the methods for obtaining such properties are lacking. Bonding processes are normally arrived at through a combination of the bonder’s experience, material supplier’s advice and trial and error. Altering a process normally relies on the experience and skill of the production operator but problems may arise that require a more thorough approach. Adhesives suppliers are often the primary source of advice for the use of adhesives.

In bonding operations it is vital that the adhesive is applied in the correct locations and spreads over roughened surfaces sufficiently to bond. If sufficiently intimate contact is achieved between the two materials, 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. Good wettability of a surface is a prerequisite for ensuring good adhesive bonding. Incorrectly applied adhesive can weaken the bond. Hardening of the adhesive, whether due to cooling, drying or cure reactions before bond formation, overspreading or over absorption into permeable materials can weaken the subsequent joint. The condition of surfaces prior to bonding has significant implications for the quality of the bonds formed. 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 [2]. Surface measurements can focus on physical properties of the surface (e.g. roughness, surface energy or mechanical properties) or the chemical composition of the surface.

This report describes techniques for characterising the properties of surfaces that influence the interactions between the substrate and adhesive during the bonding process. There is much background information on structural adhesives (e.g. epoxies or acrylics) and metallic surfaces. Therefore, this work concentrates on non-structural materials, such as paperboard and plastic films, and hot melt adhesives typically used in packaging that have received comparatively little attention. This report describes methods for:

- Wettability and surface energy
- Surface absorbency
- Surface receptivity
- Application and spreading monitoring

2. MATERIALS

2.1 HOT MELT ADHESIVES

Packaging applications account for approximately 40% of UK adhesive usage. The adhesive bonding of packaging materials is dominated by polyvinyl acetate (PVA) based dispersion adhesives, acrylics and thermoplastic hot melt adhesives, if the starch and dextrin adhesives used for corrugated case manufacture are excluded. Hot melt adhesives are predicted to continue to gain market share, and it is these hot melt adhesive systems that are the 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.

Hot melt adhesives were first developed for commercial use in the 1950's. In the early 1960's they were first used on low speed case sealing equipment to seal the flaps of corrugated cases. Since then many advances have been made in hot melt technology and in the systems to apply them. Customers have demanded higher production speeds and wider application across a range of packaging substrates. Recently, pressure sensitive hot melt adhesives, which have permanent tack, have been introduced in packaging and garments.

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 [3]:

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

Packaging hot melts fall into the following broad applications categories:

- General purpose
- Deep freeze
- Heat/creep resistant
- Difficult substrates.

There are certain adhesive attributes which are common, and some which are specific to the market application. The common desirable attributes, applicable to all categories are included under the general-purpose heading.

General purpose

- 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.

Deep freeze

- Resists brittle failure under deep freeze conditions.

Heat/creep resistant

- Resists failure under long term applied load in warm climates.

Difficult substrates

- Able to adhere to low surface energy substrates, eg polyethylene coated and UV varnished boards.

Other considerations

- Open time and setting time are important characteristics of the adhesive, which need to be matched to the specific application.
- Universal application – manufacturing companies prefer to use a single adhesive grade for all applications to simplify housekeeping, minimise inventory levels and to avoid mistakes.

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

CM Ultra 100	Standard (low temperature application)
Cool Melt 20	Standard (low temperature application)
Instant Pak 2400	Heat resistant
Instant Pak 2500	Deep freeze
Instant Pak 2600	Standard
Novacol 90	Deep freeze (very low application temperature)
Ultra Melt 201	Standard (lighter colour)
Varnimelt X10 (134-162A)	Difficult surfaces.
Dispomelt DM727	Pressure sensitive hot melt

2.2 SUBSTRATES

A wide range of packaging substrates representing the following paper, board and plastic categories was sourced:

- 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
- printed polyethylene terephthalate coated bleached sulphate paper
- polyethylene terephthalate coated solid bleached sulphate
- polypropylene coated folding boxboard
- polyethylene coated folding boxboard
- test liners
- Kraft
- amorphous polyethylene terephthalate sheet
- polypropylene sheet.

A full description of the substrates obtained can be found in Appendix 1. Many of the substrate 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 position).

3. WETTABILITY AND SPREADING

3.1 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. Good wettability of a surface is a prerequisite for ensuring good adhesive bonding, and hence considerable effort has been expended in developing simple tests to assess surface energy/tension prior to bonding [4-6].

Surface energy is defined as the work necessary to separate two surfaces beyond the range of the forces holding them together and is given in energy per unit area. Surface energy is often referred to as surface tension and 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). It is dependent 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 significant than the other. 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 [7, 8]. 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 determining the surface energies of solid materials. However, in most cases the contact angle is 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 1):

$$\gamma_{lv} \cos \theta = \gamma_{sv} - \gamma_{sl} \quad (1)$$

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 ($\gamma_{sv} - \gamma_{sl}$). Large contact angles are associated with poor wettability.

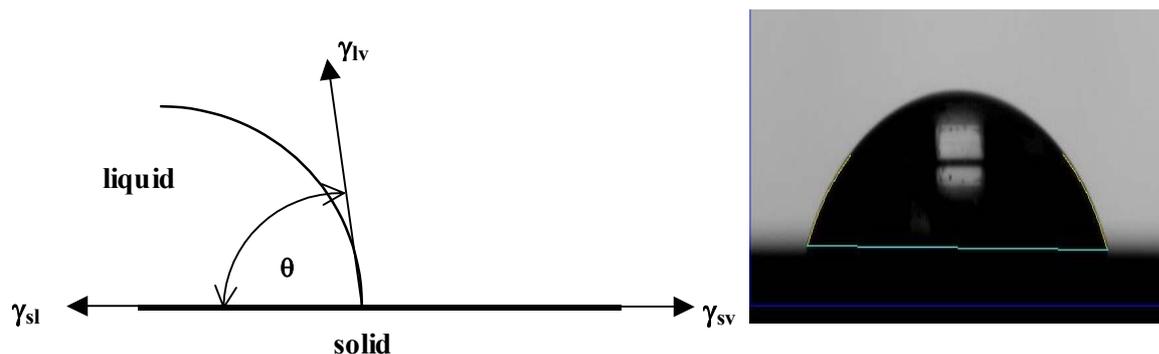


Figure 1: Contact angle of a liquid on a surface

In adhesive bonding, wettability is most 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 is less useful for the characterisation of metal or metal oxide surfaces. According to ASTM D5946 [9] 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)

In practice, water drop contact angle (WDCA) is more commonly used in the industry for looking at the relative absorption rates of uncoated papers and the printing or writing characteristics of coated or sized papers, than for assessing 'glueability'. No literature reference could be found in which hot melt adhesive had been used as the test liquid.

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 polymer based adhesives where surface tensions typically fall in the range 20 – 30 mN/m [10]. 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. Thus, water results may not always correlate with adhesive bonding performance.

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.

3.2 SIMPLE WETTING TESTS

3.2.1 Water Break Test

The water break test [11, 12] is a qualitative (go/no-go) test, involving the specimen (in the form of a flat plate) being either immersed in water or 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).

3.2.2 Dyne Pen Test

The dyne pen test for assessing the surface energy of plastic films [13, 14] 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. Dyne pen measurements were made on a subset of the substrates and the results are summarised Table 1.

Despite the widespread use of these solutions, the method has critics [15]. The shelf life of pens can be limited, particularly if in regular use, as transfer of contamination from surfaces to the ink may occur.

Both of these methods allow fairly quick assessment of relatively large surface areas and would be capable of detecting 'problem' areas much more readily than sessile drop methods that only probe small regions.

3.3 CONTACT ANGLE DETERMINATION BY SESSILE DROP

The static contact angle can be measured by observation of a drop of test liquid on a solid substrate either on a goniometer or by projection, either directly or using video imaging. Determination of the contact angle can be carried out using automated image fit techniques. In the packaging industry, contact angle is measured according to Tappi Methods for papers [18] and polymer film surfaces [19]. However, this technique tends not to be employed commonly, as it is perceived as being time consuming and requiring a degree of interpretation of the results.

3.3.1 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 [9, 16-21]. 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. 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, 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.

3.3.2 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. There are many commercially available automated contact angle measurement instruments where the image of the drop is viewed using a video camera and captured on computer. 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 will also analyse the shape of hanging pendant drops to measure surface tension of liquids. Axisymmetric Drop Shape Analysis (ADSA) is one example of a computer program that uses digital image analysis to detect the edge of a static drop and accurately determine the interfacial tension and contact angle [22]. ADSA is capable, under ideal conditions, of determining contact angles to very high accuracy with uncertainties of less than 0.1° . 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.

3.3.3 Issues in Contact Angle Measurement

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. 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. Commonly used probe liquids for measuring contact angle include distilled water, glycerol and methylene iodide (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 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);
- 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 has reached a stable equilibrium shape;
- Evaporation of the drop does not occur.

It is commonly claimed that the accuracy of the automated contact angle method is $\pm 2^\circ$. However, agreement between laboratories has been as poor as 5° [38]. ASTM D5725 suggests a repeatability of 7% within a laboratory and a reproducibility of 13% between laboratories.

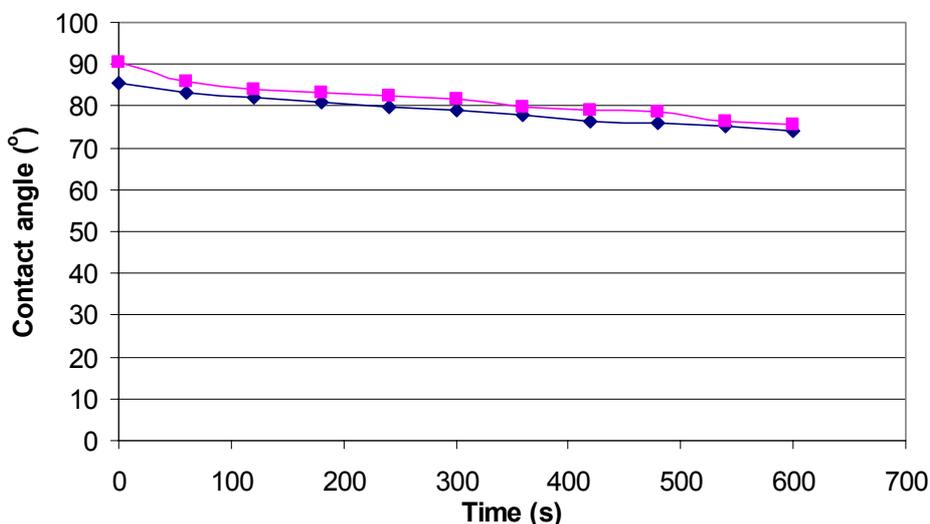


Figure 2: Time dependence of contact angle measurements

The WDCA determinations made in this study differed by more than 5° on some substrate surfaces. On closer inspection of the results these surfaces either had high absorbency, showing large angle changes with time, or were inherently variable with high standard deviations within a full set of ten separate determinations.

During contact angle measurements, drops tend to spread on the surfaces with time (as absorption of vapour alters the properties of the surface in the vicinity of the drop) and the volume of the drop may change due to evaporation or absorption of moisture. Figure 2 shows

the measured contact angle for a drop of water on a polymer surface decreasing with time. Dramatic changes in drop shape may be seen with viscous liquids after they are applied to the surface, as finite time may be needed to reach equilibrium shape, e.g. Figure 3. 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. A duration of 30s after dispensing the drop would be probably be sensible for either of the situations discussed as the rate of change in the contact angle has slowed considerably and the measurement time is not excessive.

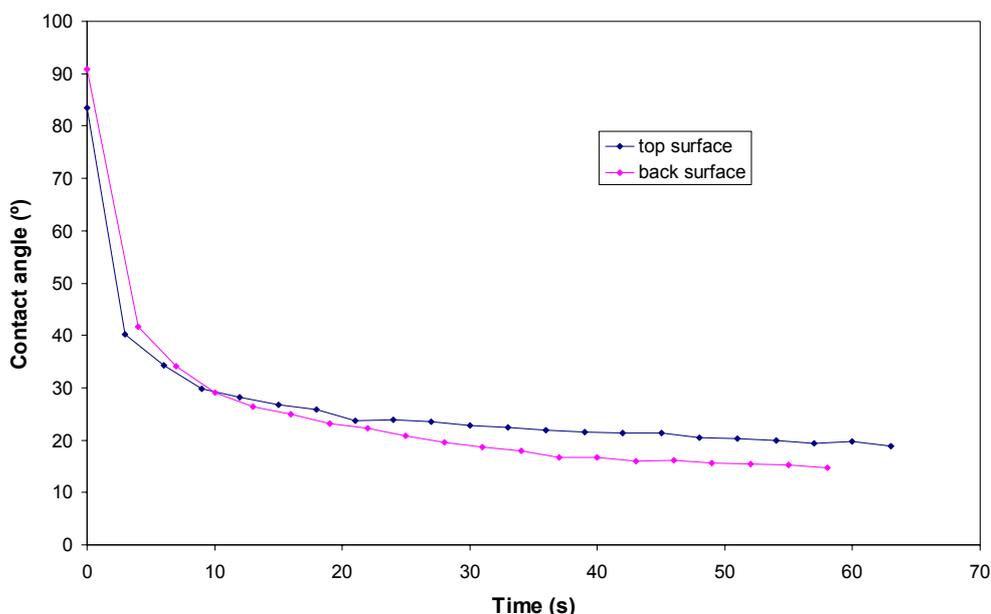


Figure 3: Contact angle measurements made for a hot melt adhesive

3.3.4 Water Drop Contact Angle Measurements on Substrates

Water drop contact angle (WDCA) measurements were made using an automated instrument as shown in Figure 4. The method is based on TAPPI method T558 [23]. The drop is imaged using the CCD camera and the shape of the drop is computed using image analysis software to calculate the contact angle. The camera image should be calibrated in orthogonal directions to ensure accurate dimensional measurement. 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.

Substrate samples with a high degree of porosity were excluded from these measurements as high absorption rates interfere with the measurement. A strip of the sample to be measured was fixed to a standard laboratory glass slide using double-sided tape and the slide placed on a platform beneath a micro-syringe. The micro-syringe was lowered to accurately place a droplet of de-ionised water ($4.00 \pm 0.09\mu\text{l}$) onto the sample surface. The silhouette of the droplet was viewed using a video camera, which captured images of the water droplet at 10 frames per second over a time interval of 15 seconds.

The contact angle was calculated using a computer programme from a measurement of the width and height of the droplet at 0.1, 1.0 and 10.0 seconds. Three droplets were measured for

each sample. The results are shown in Figure 5 and a selection of results is presented in Table 1.

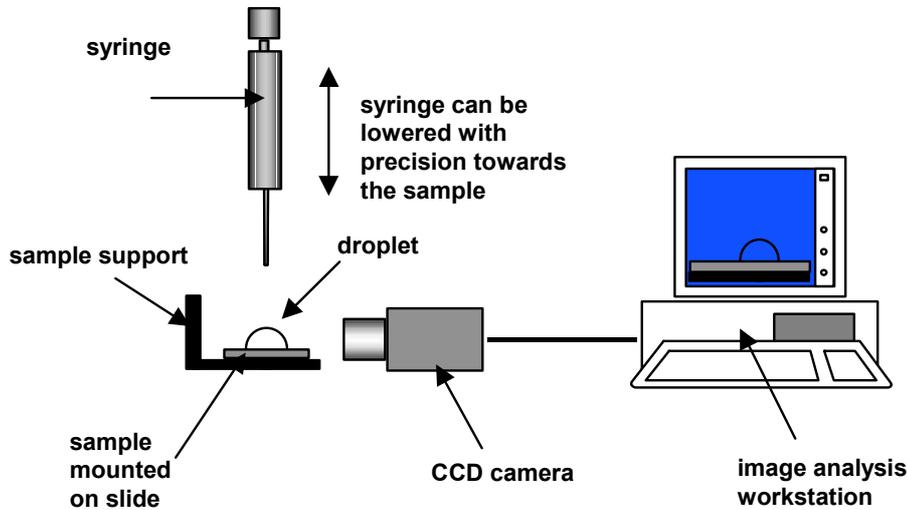


Figure 4: Contact angle by automated drop shape analysis methods

WDCA measurements were also made using an inexpensive handheld goniometer (Figure 6), which projected drop images onto an LCD screen. The results generally show a reasonable correlation with the automated image analysis techniques, Figure 6.

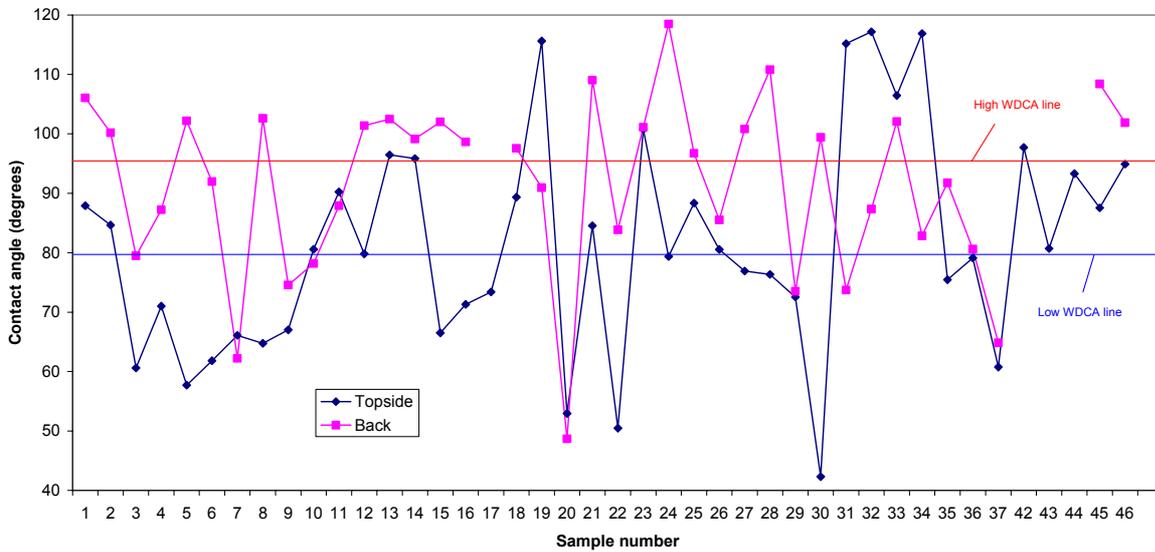


Figure 5: WDCA measurements showing the spread of results obtained for substrates.

Table 1: Relationship between WDCA and wetting tension

Board reference / Surface	Measured WDCA (°)	Wetting tension by dyne pen test (dynes/cm)		
		Theoretical [13]	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				
Sample 19 / reverse	83-91	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

*Theory according to ASTM D2578 [13] not strictly applicable for these materials

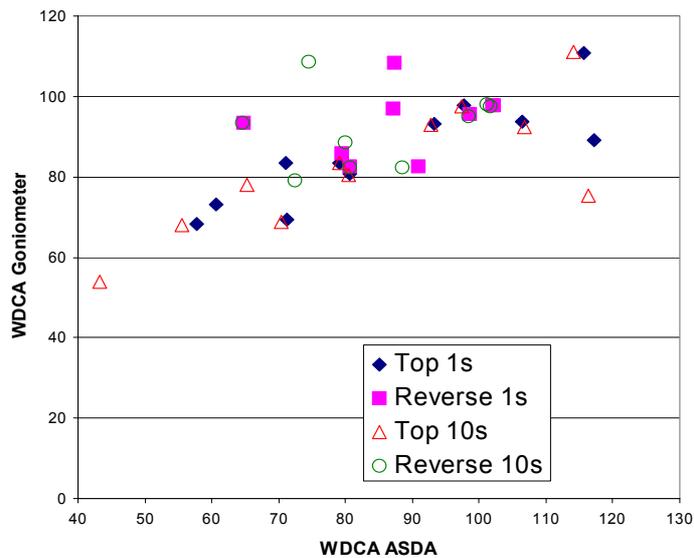


Figure 6: Correlation of WDCA techniques and handheld goniometer instrument

3.4 DETERMINING THE WETTING PROPERTIES OF HOT MELTS

3.4.1 Contact Angle of Solid Hot Melt Adhesives – Post Application Beads

Adhesives were dispensed onto different substrates using a Nordson ProBlue 4, jet applicator system fitted to the Pira Adhesive Performance Tester (PAPT), Figure 7. The air pressure setting on the Nordson unit was adjusted to achieve a nominal adhesive application weight of 1.0 g/m through a ‘Saturn’ nozzle with a 0.3 mm orifice, at a linear belt speed of 1.1 m/s. A 130 mm line of adhesive was applied to the cold surface of the substrate. Normally, after a set open time, the reverse face is brought into contact under controlled speed and held at a set pressure for a set closure time to form a bond for testing. However, in this set of experiments the upper surface was not brought into contact and the dispensed line of adhesive was allowed to set. The substrate was sectioned perpendicular to the dispense direction so that the cross-section of the dispense line could be examined. A handheld goniometer was used to determine the contact angle of the adhesive on the substrate.

Four different adhesives were dispensed onto the top and reverse sides of 8 different grades of substrate, having different wettabilities (WDCA values ranging between 60° and 120°). The size and shape of the dispensed glue beads were analysed and the results summarised in Figure 8. For each of the adhesives the measured contact angle was independent of the substrate WDCA (a typical plot of glue bead contact angle against WDCA is shown in Figure 8). The different grades of adhesive appear to have different wettabilities on the various surfaces.

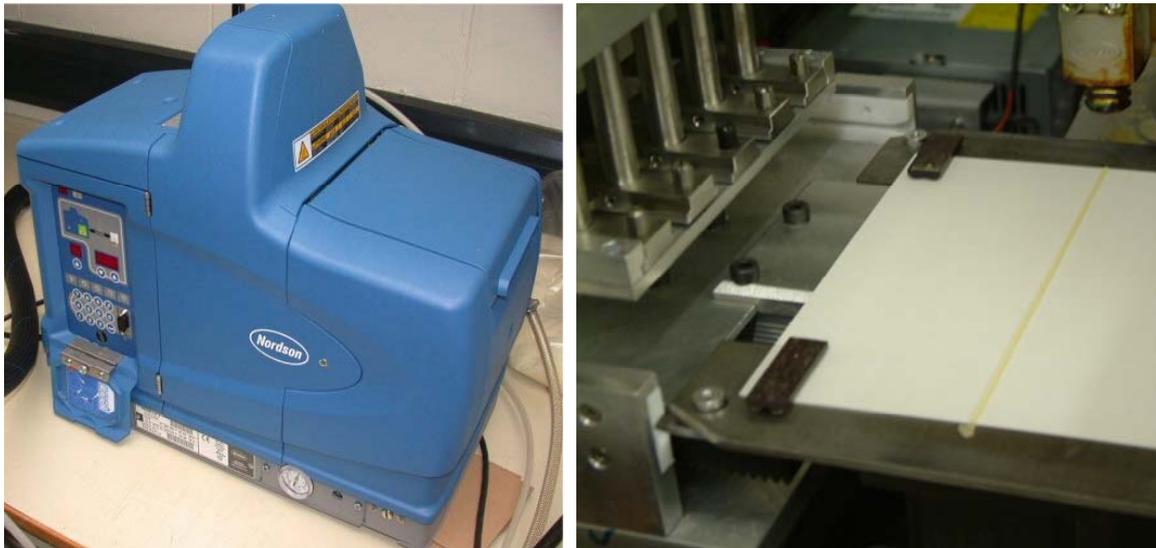


Figure 7: Hot melt applicator and dispense pattern

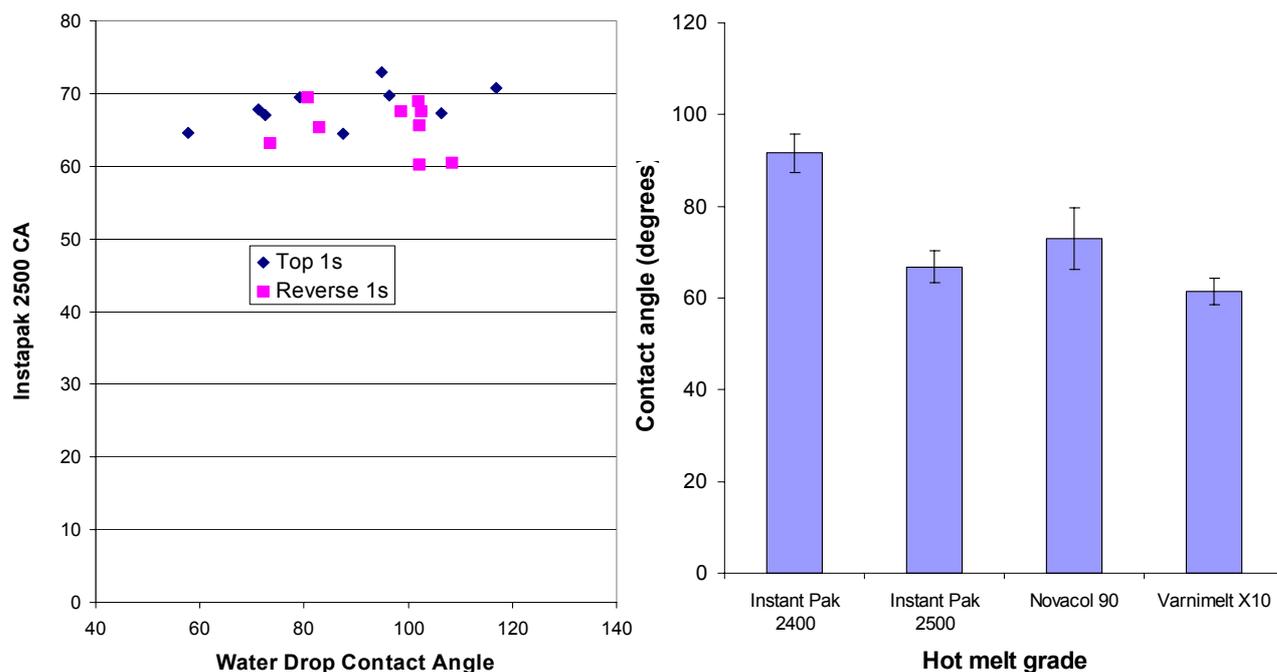


Figure 8: Glue bead contact angle results

The lack of a relationship between glue bead contact angle and WDCA substrate wettability was unexpected. The contact angles found are also higher than would be expected for a liquid that is expected to wet the substrate well. The adhesive is applied hot onto substrates conditioned at ambient temperature and therefore rapidly cools and becomes more viscous following dispense. The increase in viscosity is likely to prevent the adhesive ‘flowing’ into an equilibrium shape before it hardens. Therefore, it is much more likely that the results obtained reflect the amount (or lack) of flow before hardening (which reflect physical characteristics of the adhesive such as the heat transfer properties and the temperature dependence of the viscosity of the adhesive) rather than the surface properties of the substrate.

3.4.2 Contact Angles of Molten 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 equipment for water drop contact angles. Figure 9 shows equipment for determining contact angles and liquid surface tension under non-ambient conditions [24]. 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.

Hot melt adhesives were dispensed from disposable pipettes, as shown in Figure 10. This avoided the problem of contamination of the (expensive) micro-syringe used for water drop contact angle measurements and also enabled a thermocouple to be placed in the adhesive to monitor temperature. However, packing the adhesive into the pipette presented some practical difficulties – the adhesive tended to cool and solidify in the narrow tip if the normal ‘draw-up’

method of loading the pipette was used. Instead, cold, solid adhesive was cut into smaller pieces that could 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 Dispomelt adhesives (highly visco-elastic pressure sensitive hot melt adhesives) proved very challenging.



Figure 9: Apparatus for measuring contact angles of molten hot melts

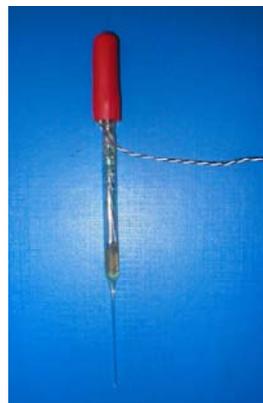


Figure 10: Pipette dispenser for hot melts

Measurements were made of 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 to higher temperatures could cause degradation of the samples. 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 [24]). The substrate surfaces had measured water drop contact angles (at ambient conditions) varying between 58° and 106°. The contact angles determined using the liquid hot melt adhesive 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 11 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.

Further measurements of the contact angle of 3 other adhesives (Varnimelt X10, Instant-Pak 2400 and Instant-Pak 2500) on one of the surfaces (amorphous polyethylene terephthalate (PET), surface No 36) were made using this apparatus. The test temperature was 100 °C. Despite all these adhesives having similar, low surface tensions the measured contact angles vary from 26° (Novacol 90) to 64° (Instant-Pak 2400), Table 2. One difference between the adhesives is that they have different recommended process temperatures, most of these adhesives are typically dispensed at higher temperatures than the Novacol 90; consequently they have a higher viscosity and are much more visco-elastic at 100 °C [25]. Figure 12 shows a correlation between complex dynamic modulus (G^*) and the measured contact angle at similar temperatures. This suggests that, at this temperature 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 findings on contact angles determined from solidified dispensed beads.

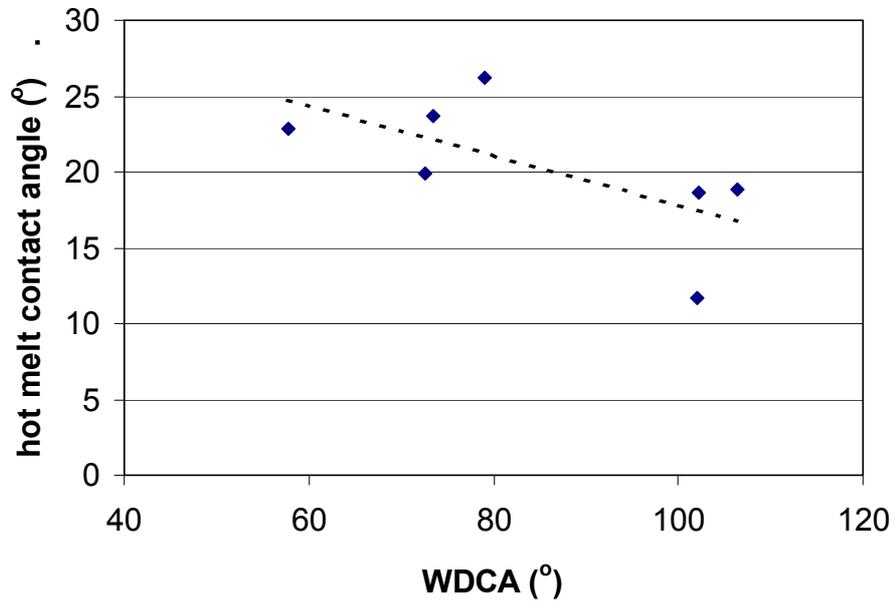


Figure 11: Relationship between measured contact angles of distilled water (room temperature) and liquid hot melt adhesive (100 °C) on a selection of packaging surfaces

Table 2: Contact angles for different hot melt adhesives on PET

Adhesive	Contact angle on PET at 100 °C (°)	Typical Process Temperature (°C)	Complex Modulus G* at 110°C (MPa)
Novacol 90	26	100	0.7
Varnimelt X10	50	180	157
Instant-Pak 2400	64	175	296
Instant-Pak 2500	40	165	147

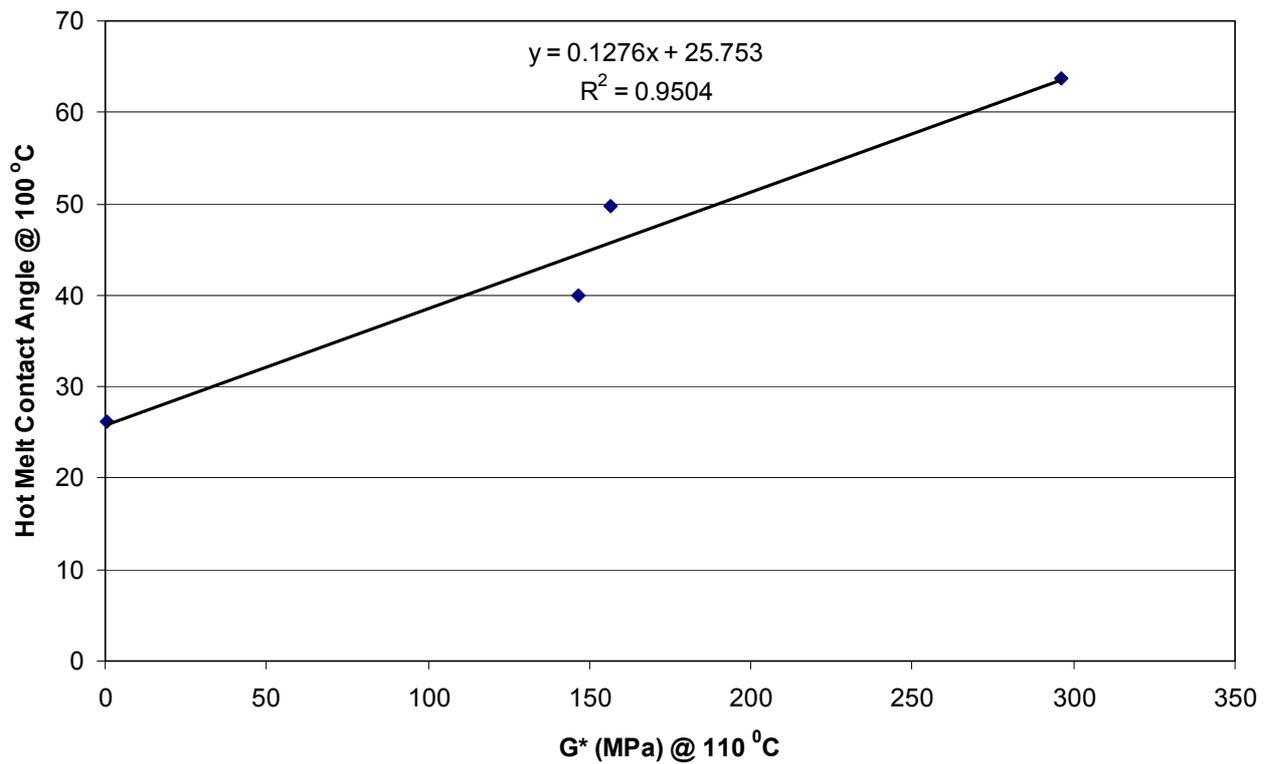


Figure 12: Apparent correlation between wetting and visco-elastic properties

3.4.3 WDCA Characterisation of Solid Hot Melt Adhesives

An indication of the surface energy of a hot melt adhesive, in the solid state, may be obtained by determining the WDCA on prepared flat samples of hot melt adhesive, treating the surface as a plastic.

A sample of hot melt adhesive granules was heated in a test tube to its recommended application temperature, and then drawn down onto a paper substrate using the edge of a microscope slide. The thickness of the drawdown (not critical) was controlled by sheets of paper at either side forming a 20mm wide central channel. The adhesive coated paper was then trimmed with a scalpel blade to 15mm wide for measurement.

This method of sample preparation was considered more satisfactory than that described in the literature [26] where EVA pellets were hot compressed between polyester sheets. This has the potential for contamination of the surface from EVA/PET interactions and any process coating applied to the pellets to prevent sticking in the hopper. The method adopted here addresses both of these issues resulting in a surface for measurement that more accurately replicates that of the hot melt in application.

The sample was measured in the goniometer that was also used for the determination of the water drop contact angle on substrate surfaces. The results for 8 hot melt adhesives used in the packaging industry are shown in Figure 13. These indicate that the surface energies are low with little variation ($< \approx 10\%$) between the adhesives.

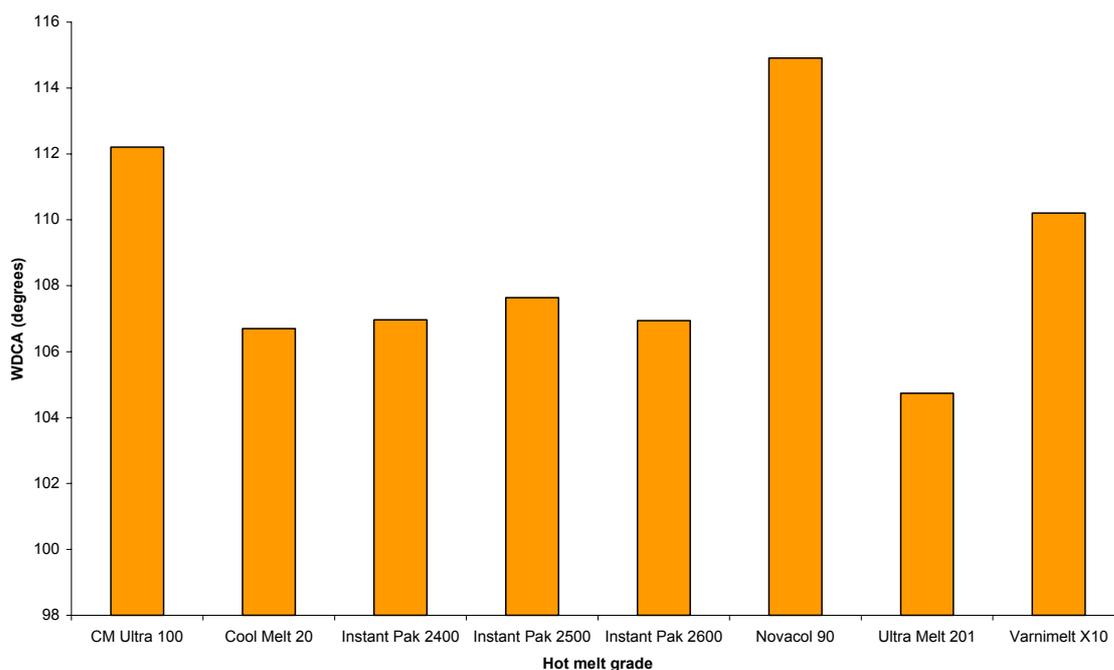


Figure 13: WDCA measurement results on prepared hot melt adhesive surfaces

The WDCA results for the solid adhesives indicating low surface energies are consistent with surface tension measurements made on a range of hot melt adhesive systems. These tests performed at elevated temperatures typical of dispense conditions using the pendant drop method, found that surface tension values fell in the range 15 mN/m – 25 mN/m [24], which are typical values for low surface energy liquids.

3.5 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. Table 1 shows a comparison between the theoretical wetting tension of the surface derived from the measured WDCA using the conversion table in ASTM D2578 [13] and the measured wetting tension. Agreement between the two methods appears limited. 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 recommended that a wider range of substrates, adhesives and process temperatures be studied to further investigate the relationship between water drop contact angle and adhesive wetting. The evidence suggests that probe liquids with surface properties that better approximate the adhesives may be more suitable for assessing wettability. These should also be investigated.

4. ABSORPTION PROPERTIES

Adhesives will tend to penetrate porous or rough surfaces. 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. The Cobb absorbency test [27] provides a method of determining the water absorptiveness of sized paper and board under standard conditions, and hence an indication of both the relative penetration and setting time of water based adhesives. Some packaging manufacturers examine porous boards using an ultrasonic method to determine the rate and depth of liquid penetration for bonding with PVA adhesives.

4.1 COBB ABSORBENCY TESTS

The Cobb test [27] 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. $\text{g/m}^2 \cdot 30 \text{ min}$). 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 14: 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. The Water

Cobb result of the top and back surfaces of each of the samples was determined in accordance with BS EN 20535 [27]. Each test piece was weighed using a calibrated digital balance, readable to 0.0001g, before being clamped with the surface to be tested uppermost in a Cobb ring having a test area of 100 cm², (Figure 14). The ring was then filled with 100 ml of distilled water. After 45 seconds the ring was drained of the water and after a further 15 seconds the sample being tested was blotted by placing between two sheets of blotting paper and rolling twice with a 10kg Cobb roller. The test piece was then immediately re-weighed. The increase in weight per unit test area (g/m²) was then calculated. The results are shown in Figure 15.

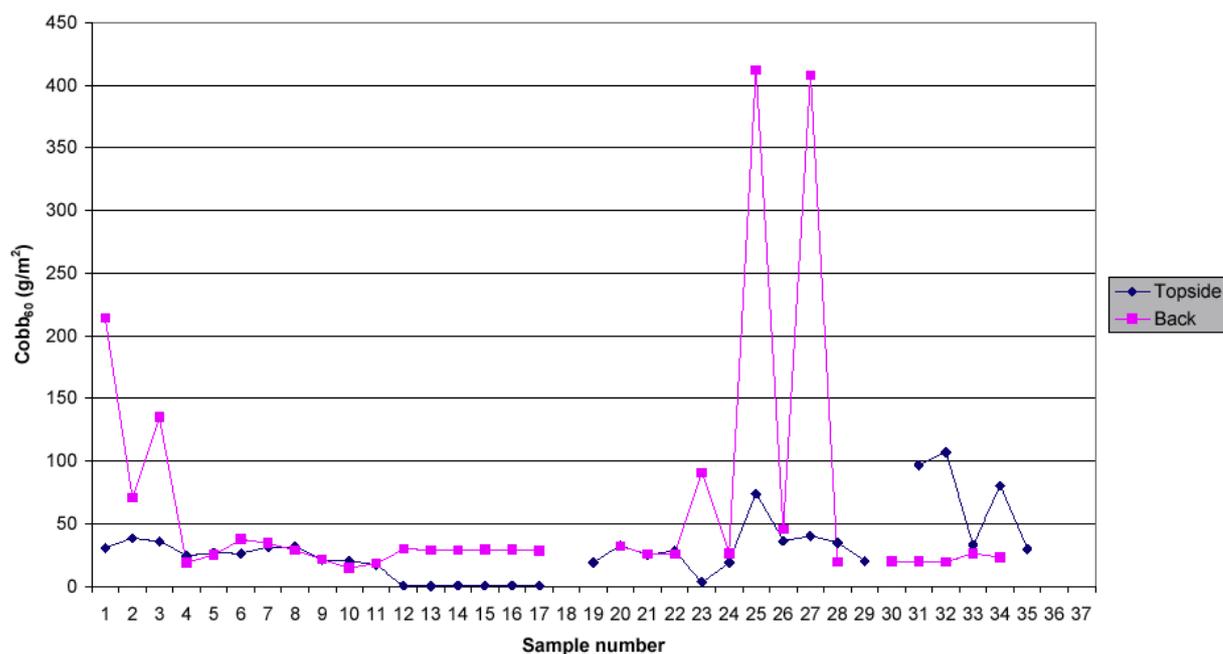


Figure 15: Cobb absorbency results

4.2 LIQUID UPTAKE BY MASS MEASUREMENT

Four substrates (substrates 1, 3, 25 and 27) whose reverse surfaces showed the highest Cobb absorbance values were investigated. Two of the substrates (1 and 3) were coated chipboards, which have similar properties. The remaining substrates (25 and 27) were coated boxboards, which have similar properties. In addition to having high Cobb absorbency, these reverse sides also had high roughness (as measured by profilometry and Bendtsen air flow [28, 29]). The chipboards have higher roughness than the boxboards but lower Cobb absorbency. The samples were conditioned at ambient conditions (23 °C and 50% relative humidity) before testing.

4.2.1 Mass Uptake Measurements

Absorption of liquids into porous materials can be followed through mass uptake (often known as gravimetric) measurements. The absorption of liquids into pores increases the mass of the system. Test methods have been standardised for studying uptake of liquids in polymers (ASTM D 570 [30] and ISO 62 [31]). Samples can be exposed to the vapour or immersed in the fluid. Mass increases of the order of a few percent of the original mass of the polymer are typical in systems with an affinity for the liquid [32]. 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 [33].

Ingress of liquid into a solid material is a diffusion process whilst ingress in to a porous system will also be driven by capillary forces. 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 dried to constant mass, m_0 (normally at an elevated temperature, depending on the thermal stability of the material) and stored in a desiccator 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 [31], 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 .

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 $m_c = m_0$.

$$m_r(t) = \frac{m(t) - m_c}{m_0} \quad (2)$$

Diffusion plots are obtained by plotting $m_t(t)/m_s$ 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 [34] to ensure that test durations do not exceed one week for typical diffusion coefficient values for polymers (ca. $10^{-12} \text{ m}^2\text{s}^{-1}$). 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. 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.

4.2.2 Mass Uptake by Immersion

The absorption test duration should simulate the length of time in which liquid adhesive absorption can take place between application and hardening. 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.



Total immersion tests were considered but it was felt that many of the samples may disintegrate during immersion. Therefore, uptake was determined through an edge absorption/desorption technique.

Specimens, 50 x 50 mm square, were cut from samples of the substrates. These were suspended from the arm of a calibrated balance (with an accuracy of 0.001 grams) over a beaker of distilled water at room temperature. One edge of the specimen was just in contact with the water surface, Figure 16. As the moisture absorbs into the specimen, the overall weight of the specimen increases and the suspended weight was recorded from the balance digital display readout at periodic intervals. The results are shown in Table 3 and Figure 17, where they are plotted against the square root of time. 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 16: Edge immersion test

The ranking of moisture uptake by edge immersion is the reverse of the Cobb ranking. Table 3 shows that, in the same time, the chipboards absorb over 5 times as much water as the boxboards. 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.

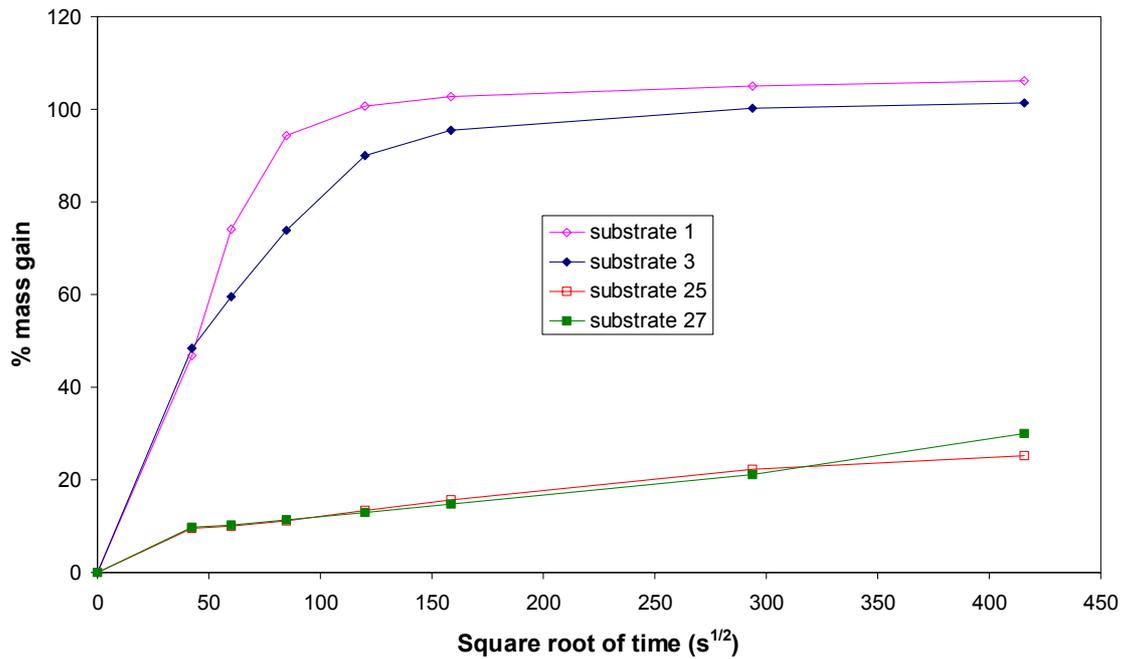


Figure 17: Edge absorption measurements

The rate at which these substrates lose absorbed moisture was also evaluated. Since the samples are thin, this process should depend mostly on the surface properties. The specimens were allowed to absorb water through one edge as before. After various fixed time periods, the beaker of water was then removed and the specimens left suspended from the balance arm to they dry out. Weight readings were taken at regular intervals until the specimens had approximately regained the same weight as they had prior to testing. The results are shown in Figure 18. The mass loss appears linear with \sqrt{t} . Unexpectedly, there is no asymptotic approach of the drying curves to zero mass gain. This suggests that if tests had been continued then 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.

Table 3: Comparison of Cobb Absorbency and Moisture Uptake

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

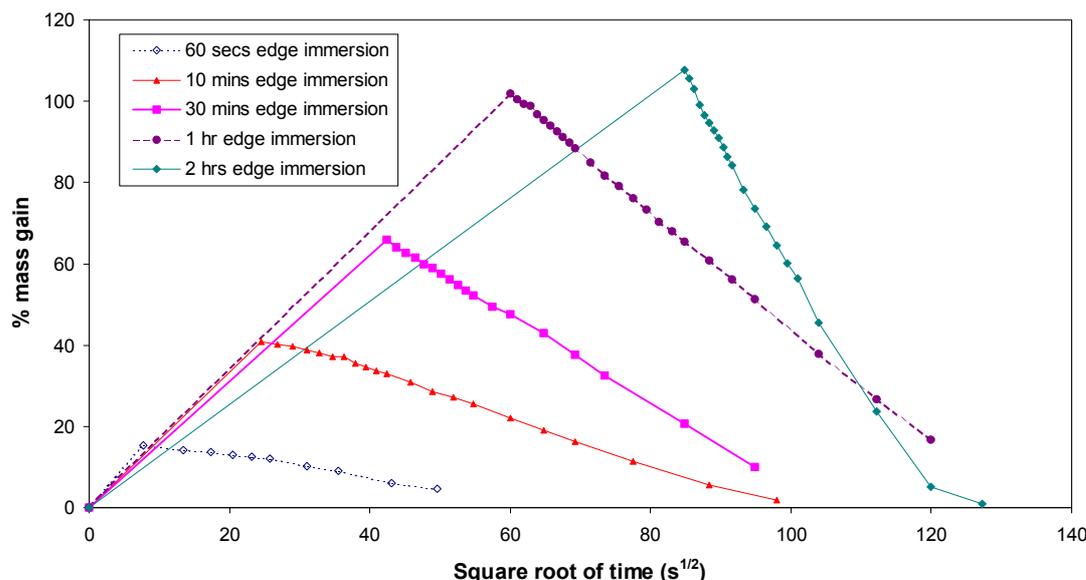


Figure 18: Loss of moisture from sample 1

4.2.3 Mass Uptake from Vapour Exposure

Samples were exposed in a Climatic Systems environmental chamber, maintaining 30 °C and 90% relative humidity. Samples 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 [31], 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 19 and summarised in Table 3. There is a rapid increase in mass followed by a peak/plateau and then a decrease in mass to an apparent constant level. The amount of moisture absorbed 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 observed in all of the tests may result from loss of material from the samples.

4.3 LIQUID VOLUME ABSORPTION MEASUREMENT

Absorption of a liquid drop or film in contact with a surface will lead to a reduction in the volume of the liquid on the surface. This can be followed through drop volume measurements or film thickness measurements. In all cases the volume of the liquid on the surface will decrease as the liquid is absorbed and as the liquid evaporates. 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.

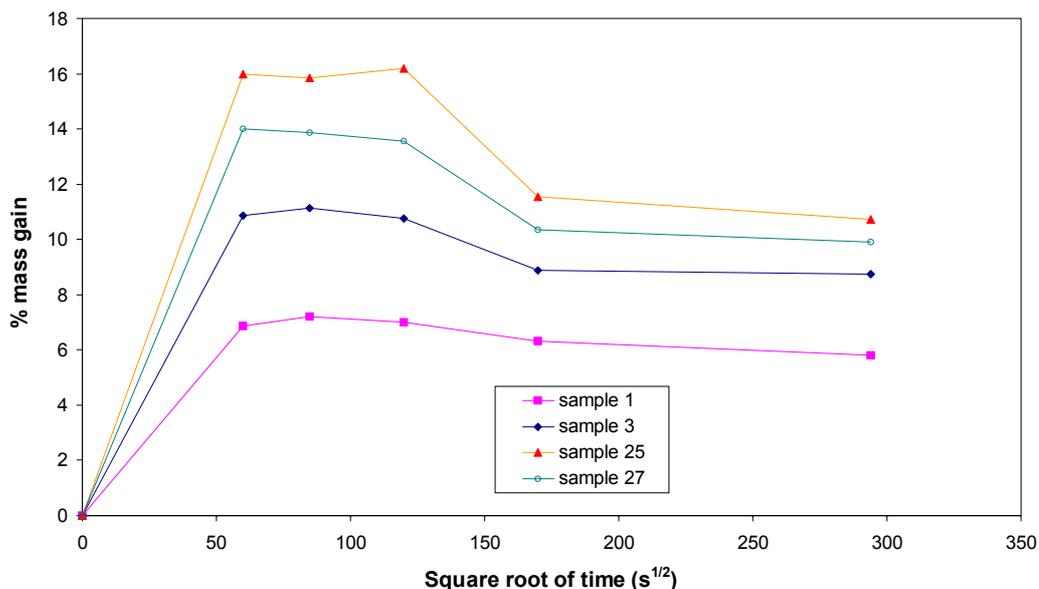


Figure 19: Moisture uptake from a humid environment

Liquids that poorly wet surfaces will form droplets on the surface. The volume of the drop can be 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. Figure 20 shows the evolution of the shape and volume of a sessile drop on a porous substrate at different times (increasing time from left to right). As time increases the contact angle decreases, the drop height decreases and the drop width increases and then decreases. 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.

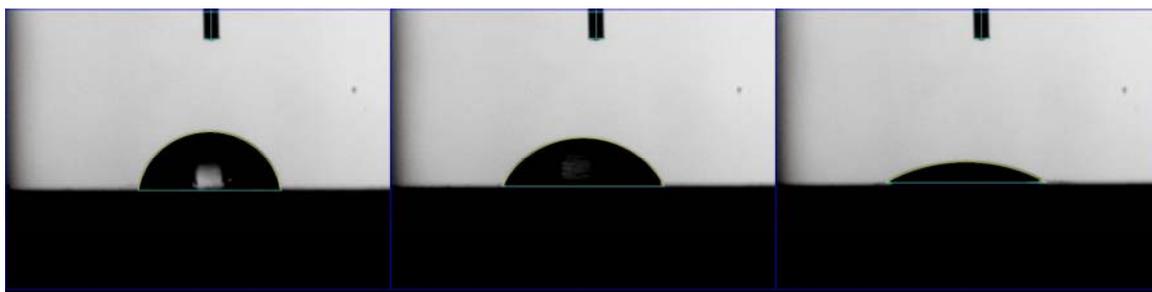


Figure 20: Timelapse photographs of a liquid drop on an absorbent surface

The magnification factor of the image must be known in order to calculate 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 – 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 change in dimensions of the drop will be a combination of two processes:

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

If the absorption of liquid into the sample is to be used to characterise the substrate then corrections need to be made for the loss of volume due to evaporation, otherwise the absorption rate will be overestimated. This may not be too much of an issue 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 absorption will depend on the area of the drop in contact with the base, which will vary with time.

The rate of evaporation of the drop will depend 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. It is obviously more appropriate to use probe liquids with low volatility (i.e. those with high boiling points and low saturation vapour pressures) in order to 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.

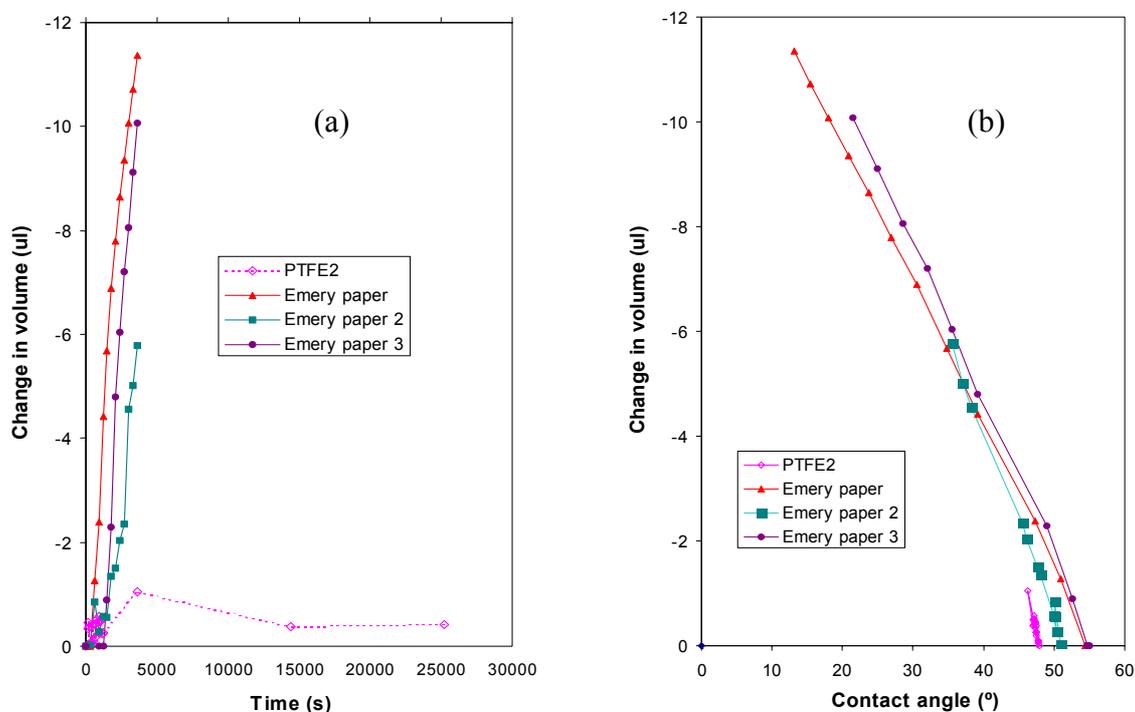


Figure 21: Change in drop volume and contact angle of paraffin

Figure 21 shows drop volume measurements made using paraffin as a probe liquid on an impermeable, low energy surface (PTFE) and a porous surface (the reverse side of emery paper). The initial volumes of the drops applied were between 14 μl and 17 μl . Paraffin has a very low rate of evaporation at room temperature and the volume of the paraffin drop remains reasonably constant with time. 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. This suggests that the rate of change of drop volume could be used as a parameter for characterising the absorbency of substrates. The surface tension of the hydrocarbon paraffin will be 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 22. 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 detections 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.

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. Possible methods include:

- *Reflection interference fringes* – 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 detection of films relies on strong reflection from the liquid/substrate interface, which is unlikely with rough or porous surfaces.
- *Ultrasonic attenuation* – the intensity of transmitted sound waves increases as the thickness of the liquid layer is reduced and commercial film thickness measurement instruments working on this principle are available. However, the measurement may be complicated by strong sound absorption in the substrate (materials such as paper and plastic have poor sound transmission properties) and the changes in ultrasound transmission of the substrate with absorption will introduce uncertainties in the thickness measurement.
- *Ultrasonic time of flight* – the speed of sound in a liquid is normally much greater than the time of flight in a gas. The time of flight between ultrasound transducers, a fixed distance apart, can be used to determine the thickness of the liquid layer, provided that

the speed of sound in the liquid is known and the effects of the substrate can be determined. Determination of film thickness from time-of-flight measurements is straightforward in a system where the properties and thickness of the substrate are constant.



Figure 22: Liquid drop spreading on a rough, porous surface

5. HOT MELT RECEPTIVITY TESTS

5.1 DENNISON WAX PICK TEST

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. Adhesive suppliers commonly use the Dennison wax pick test, TAPPI T459 om-93 [34], originally designed as a test for printing press performance, as a guide to hot melt glueability. The standard test is performed to determine the highest wax number that will not give substrate failure when pulled from the surface. A series of calibrated, hard-resin sealing ‘Dennison’ waxes with increasing adhesive ‘power’ are applied to the surface. The wax sticks are 18mm x 18mm in cross-section and numbered 2A to 26A. 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 23 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 results of Dennison wax tests on the substrates are shown in Figure 24.

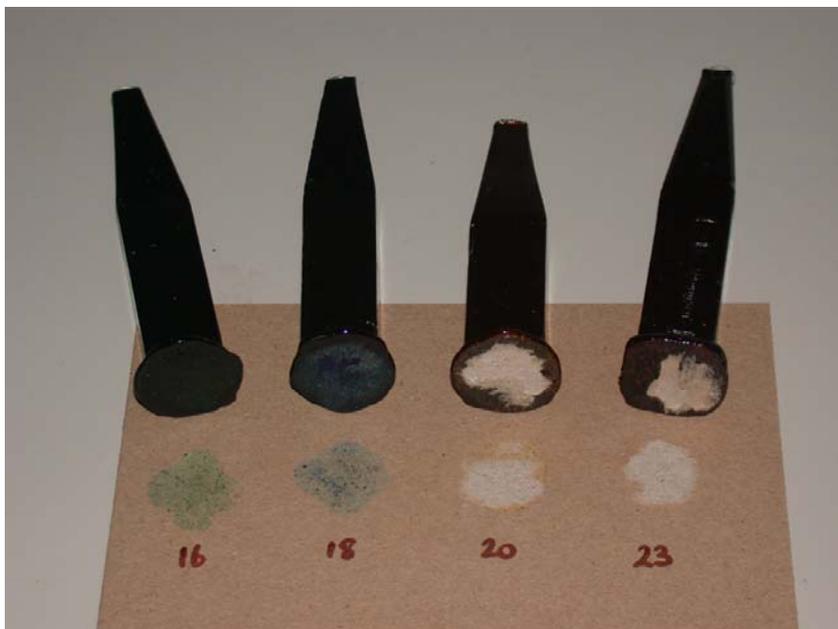


Figure 23: Dennison wax pick test

The properties of the Dennison waxes are further exploited in the hot melt receptivity test. The 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 lower viscosity or surface tension) or higher intermolecular forces.

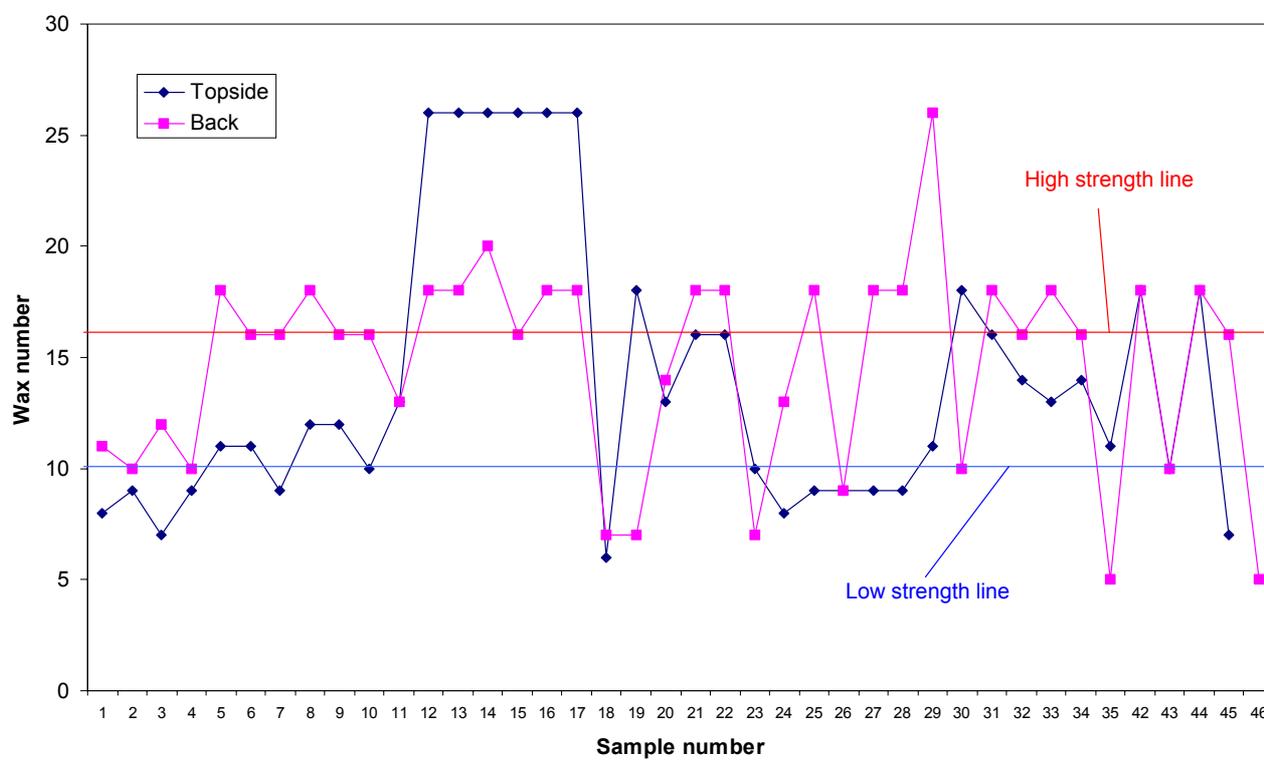


Figure 24: Dennison wax results

Since wax sticks are used as analogues for hot melt adhesives, measurements were made of their tensile strength using the pull-off test [2, 35, 36] to determine how well they replicate the properties of the adhesives. The results, shown in Figure 25, indicate that the strengths of the waxes (3-7 MPa) are not significantly different to those measured for the packaging hot melt adhesives (4 – 10 MPa [28]). 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.

As noted previously, the tensile strength of the wax appears to increase with wax number. Dynamic viscosity measurements were made on the 2A and 23A waxes at the extreme ends of the range, using a Bohlin rheometer in temperature sweep mode at a single frequency [25, 37]. The results, plotted as elastic (storage) modulus G' and viscous (loss) modulus G'' against temperature, are shown in Figure 26. 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 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 26 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 reflect the point at which the data becomes unreliable owing to the increasing stiffness of the waxes resulting in instrument compliance errors.

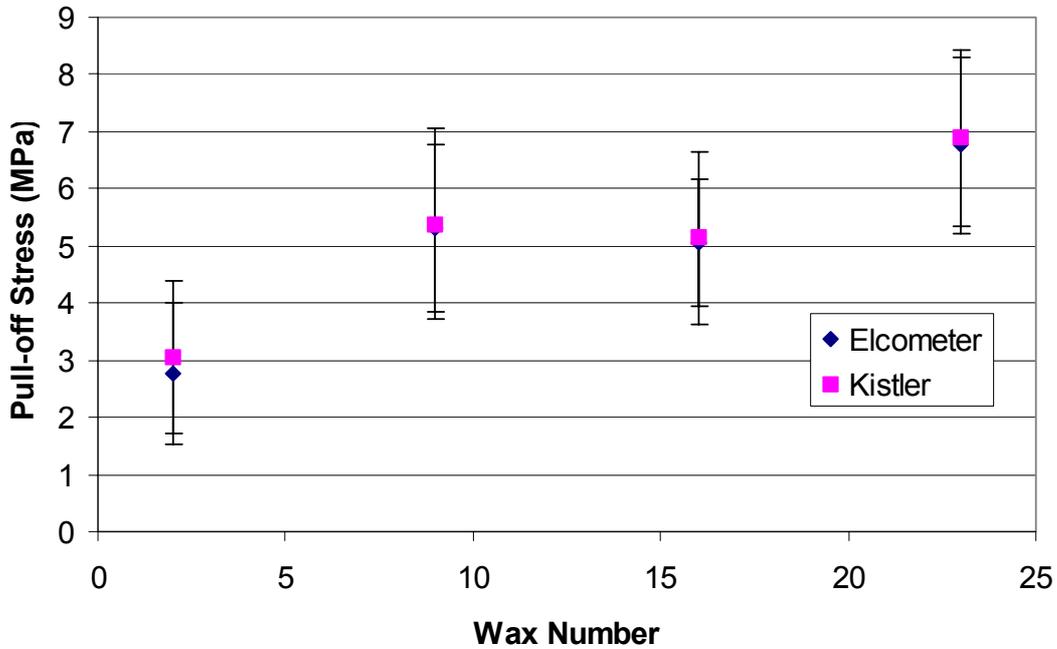


Figure 25: Pull-off tensile strength of Dennison waxes, results measured using pneumatic pressure measurements from a commercial pull-off tester (Elcometer) and piezoelectric force transducer (Kistler)

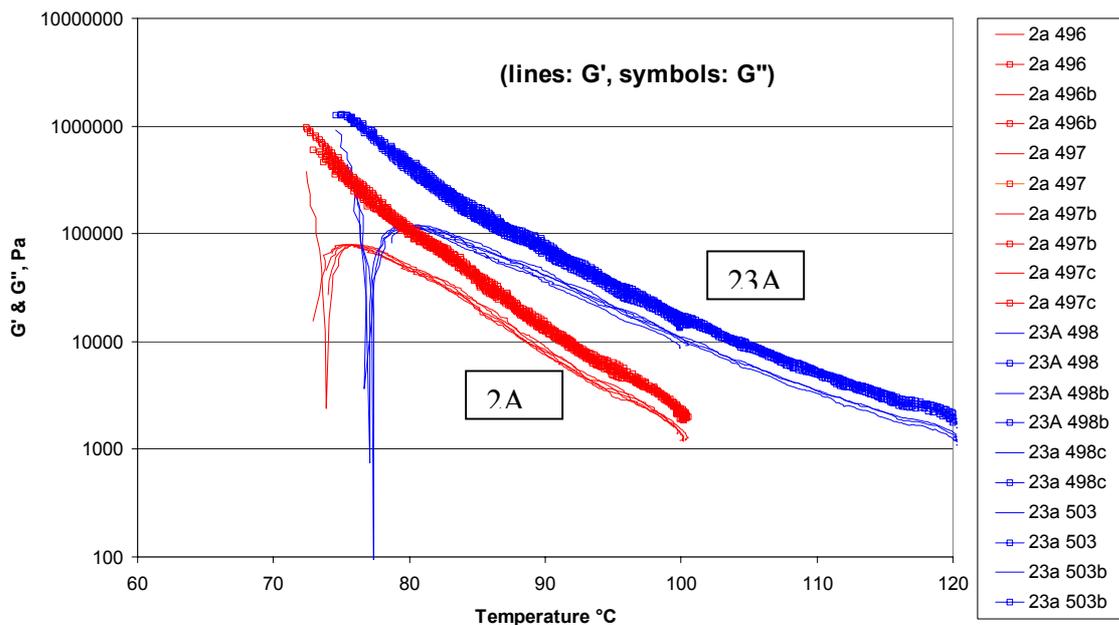


Figure 26: Visco-elastic properties of low pick (2A) and high pick (23A) Dennison waxes.

5.2 HOT MELT RECEPTIVITY TEST

This test uses the Dennison Wax system as described in TAPPI T459 [34]. The Dennison wax system test provides information on the glueability of the surface from the wax required to damage the surface but no information on the forces required to debond. Thus it is 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 ‘wettability’ of the substrate.

The test sample, approximately 100mm x 100mm, 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 spreading to an approximate 20mm diameter. The wax stick is then left to cool for 15 – 30 minutes.



The test piece is carefully placed on a compression plate of a tensometer and a wooden block with a 30mm diameter hole clamped over the stick. The clamp is attached to the load cell of the tensometer using a steel wire as shown in Figure 27. 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 28(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 27: Hot melt receptivity test

Figure 28(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. The substrate usually reaches full fibre tear around 7A – 10A with a removal force of around 40 N.

Figure 28(b) illustrates a more challenging substrate. The removal force is again progressive with wax number, but full fibre tear is achieved only at the higher wax numbers 20A – 26A.

Figure 28(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.

Figure 28(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 and no fibre tear is seen.

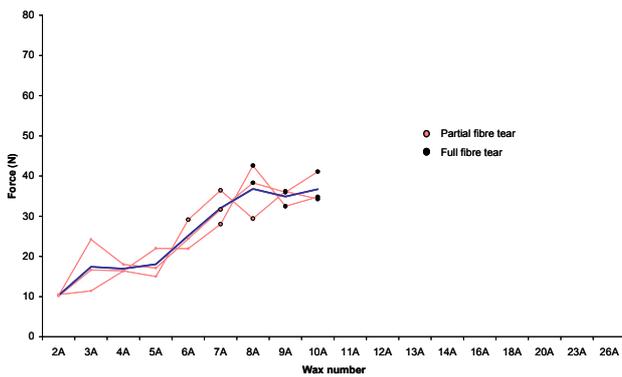
Table 4 shows a correlation between qualitative hot melt receptivity and the ease of bonding the top surface to the reverse surface for various substrates, subjectively assessed by an experienced operator. This bond simulates flap closure and bonding, an important process in sealing cartons and boxes. 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 these four surfaces. 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 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.

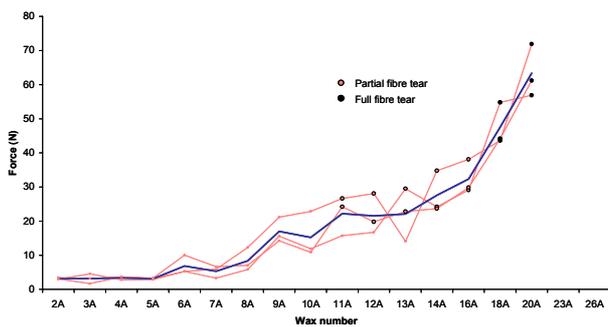
Table 4: Qualitative correlation between hot melt receptivity and ease of bonding

Sample number	Receptivity top surface	Receptivity reverse surface	Ease of bonding (top to reverse surface)
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

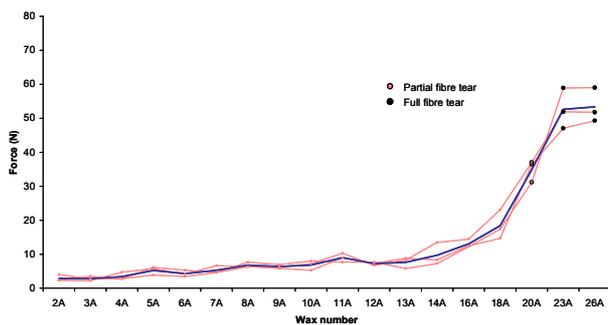
Substrate Properties



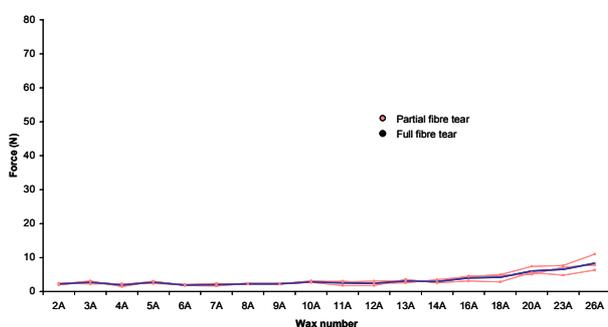
(a) Sample	46 Reverse
Roughness (profilometer)	1.6 μm
Bendtsen Roughness	47 ml/min
Wetting tension	34 Dyne
Water drop contact angle	101.9°
Wax pick value	5A
Ease of bonding	High



(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 28: (a) very easy to bond (b) moderately easy to bond (c) difficult to bond (d) extremely difficult to bond

6. APPLICATION AND SPREADING MONITORING

6.1 OPTICAL TECHNIQUES

The most basic method of checking the location of adhesive on a substrate is by visual inspection. This can be done with an operator inspecting parts or using automated image analysis. The ease of visual inspection is greatly improved if there is a high colour contrast between the adhesive and substrate. In many applications, particularly where the adhesive bond is totally enclosed after assembly, the adhesive formulator may include colouring pigments in the adhesive system to make the adhesive brightly coloured and easily visible. However, in other applications ‘invisibility’ of the adhesive (e.g. behind see-through labels or in window lamination) is a critical requirement.

The lighting and imaging systems can be adjusted to provide maximum contrast between surface and adhesive. For example, UV light sources can be used to provide fluorescence responses from the surfaces. A fluorescing material should provide a high contrast against a non-fluorescing material. Similarly, polarising filters on the illuminating light source and optical imaging system may help improve detection of deposited adhesive.

The presence of an adhesive on a substrate will alter the reflection of light from the surface. For example, a thin liquid film will provide a smooth surface and thus appear as an apparent increase in the gloss of a rough surface [2, 38, 39]. Gloss measurement can indicate gross changes of roughness but is fairly insensitive to small changes [2]. Colour measurement techniques [40] can detect changes in surfaces and the presence of liquid films (e.g. an oil coating on steel) but seems to lack sufficient sensitivity for quantifying film thickness [2].

Ellipsometry is an optical technique for probing the properties of thin films (less than the wavelength of the incident light) [41]. A polarised light beam (generally a laser) is directed onto the surface at an oblique angle of incidence. The phase change and intensity (amplitude) of the reflected light are measured. The interference of multiple reflections within surface layers provides information about the layer thickness for each layer interacting with the incident beam. Ellipsometry analysis requires a baseline set of known properties of the surface and a reflective substrate, which may not always be possible for many materials.

6.2 THERMAL IMAGING

Adhesives are often applied at a different temperature to the substrates, for example hot melt adhesives are typically dispensed at temperatures $> 100\text{ }^{\circ}\text{C}$. Therefore, since areas where adhesive have been applied will be at a different temperature to the substrate, thermal imaging or non-contact infra-red (IR) temperature measurement can be used to monitor coverage, e.g. Figure 29.

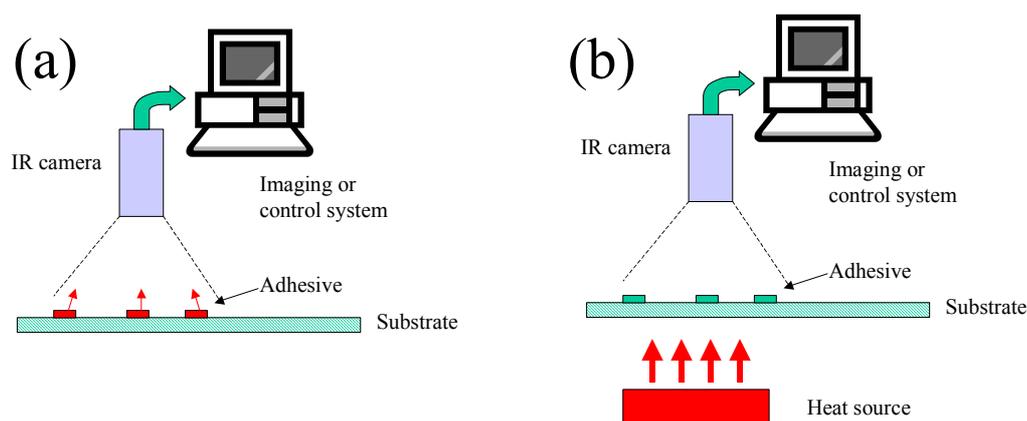


Figure 29: Schematic of thermal monitoring of (a) hot adhesive and (b) cool adhesive

Infra-red (IR) imaging uses a 2-D array of IR radiation detectors and converts the detected energy levels into an image using a colour scale, Figure 30. The energy levels are usually selected relative to the area viewed so the temperature range in the viewing frame affects the sensitivity. The IR detectors used often require cryogenic cooling to function. The advantages of this technique are that it has large area measurement capability and it is non-contacting. There is also a single point version of the technique known as IR pyrometry.

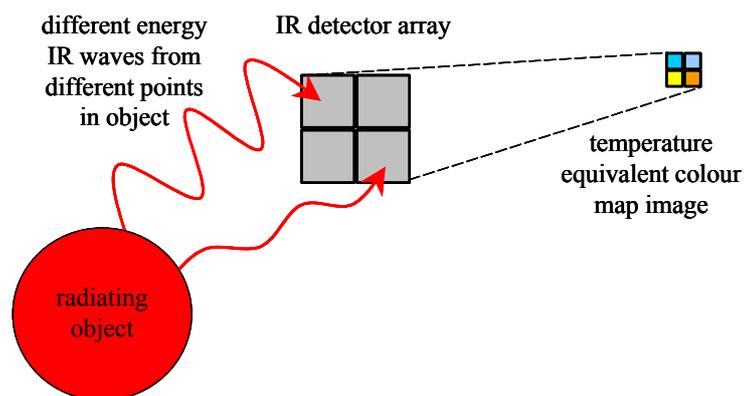


Figure 30: Basic infra-red thermography imaging process

Thermal imaging systems vary in sensitivity and response rates. The most sensitive (and most expensive) systems can distinguish temperature differences of less than $0.001\text{ }^{\circ}\text{C}$ whilst basic IR pyrometers are normally sensitive to $0.1\text{ }^{\circ}\text{C}$ temperature differences. The type of system required will depend on the temperature difference between the adhesive and substrate at the point of measurement. The temperature difference will depend on the difference between the

dispense temperature and the substrate temperature, the rate of heat transfer between the adhesive and substrate (and surroundings) and the time between dispense and measurement.

Thermal imaging can also be used in situations where there is no difference between the adhesive and substrate but where the adhesive makes a difference to the thermal transfer properties of the system. A coating of adhesive with low thermal conductivity would reduce the rate of conduction through the substrate and if heated from below, the adhesive would show up as cold spots on the thermal image.

Adhesive was dispensed through the extrusion die of a melt flow rate (MFR) instrument onto a sheet of card and transferred to the thermal imaging camera for analysis. This took approximately 30 s. A series of thermal images was taken, two of which are shown in Figure 31. The adhesive is clearly imaged in this experiment. Larger masses of adhesive are apparent as temperature ‘concentrations’. Temperature differences are clearly seen 30s after dispense and the major concentrations of adhesive are still apparent some 150s after dispense – a very long period in process terms. These results suggest that thermal imaging has considerable potential for on-line monitoring of adhesive application and spreading.

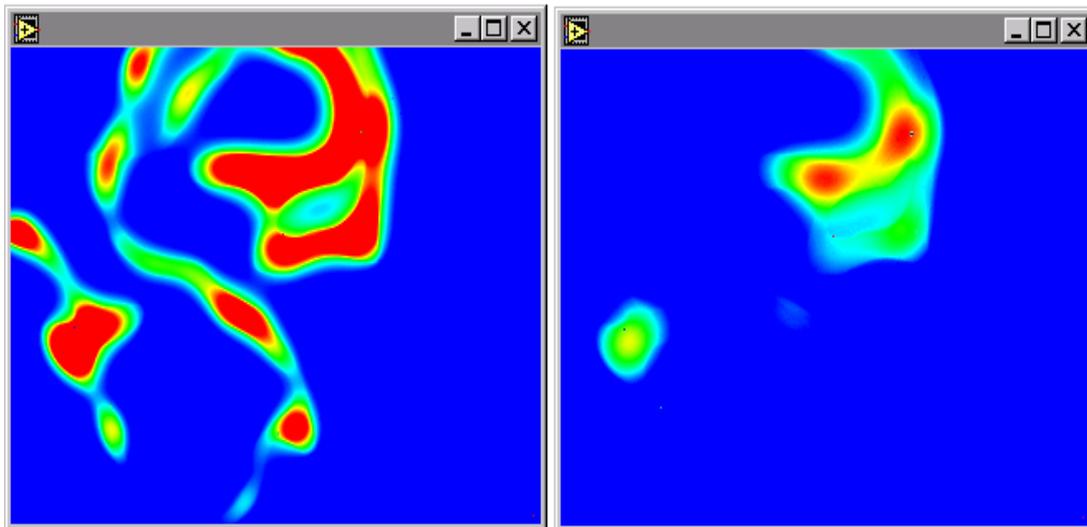


Figure 31: Thermal Images of Hot Applied Adhesive taken 37 and 152 seconds after dispense (blue regions are cold substrate, red regions are hot adhesive)

6.3 ON-LINE GLUE MONITORING

Several companies have developed on-line equipment for monitoring and detecting adhesive application, particularly for the gluing of cartons and corrugated cases. The detection system varies with the type of adhesive being applied. For example, the Nordson Corporation manufactures the ‘Seal Sentry’ Verification System for verifying the application of hot melt adhesives. Infra red detectors measure changes in temperature of the substrate and spots of hot melt as small as 1.5 x 6 mm can be monitored through the thickness of the substrate.

For water-based adhesives, two alternative systems are manufactured.

- ‘G-Net’ uses photocells to detect the adhesive pattern. This system can verify the adhesive is in the right place and volume, but prior to compression of the carton flap.

WM500 uses a capacitance technique to measure the presence and quantity of adhesive after the manufacture of the adhesive joint.

- Kurandt GmbH manufactures laser scanners and infra red glue sensors for hot melt applications. These are claimed to be able to check the accuracy of the adhesive application to within ± 1 mm at 300 m/min.

Most of these on-line glue monitoring systems can be also used to monitor or are inter-linked to carry out a number of other quality assurance checks, for example:

- barcode reading
- colour recognition
- skew detection
- overlap detection
- insert detection.

By adding an ejection system, incorrectly glued or misprinted cartons can then be automatically ejected.

The costs of such systems can vary between about £15k to £50k. Hence, in the past companies have not fitted such equipment but, with faster carton gluing operations and greater demands from packer/fillers who either are reluctant to or will not buy cartons from companies who do not possess such monitoring equipment, they are gradually becoming more common.

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APPENDIX I: SUBSTRATE MANUFACTURERS/SUPPLIERS

Sample No.	Substrate	Manufacturer/Supplier
1	Bona 400µm/300gsm - white lined chipboard	Mayr-Melnhof (UK) Ltd, Gernsbach, Germany
2	Astracolor Mirabell 390µm/280gsm - white lined chipboard	Mayr-Melnhof (UK) Ltd, Neuss Mill, Germany
3	Grafopak 380µm/250gsm - white lined chipboard	Mayr-Melnhof (UK) Ltd, Kolicevo Mill, Slovenia
4	Excellent GF 390µm/250gsm - grease freeze folding boxboard	Mayr-Melnhof (UK) Ltd, Baiersbronn Mill, Germany
5	Simcote H/S 440µm/245gsm - fully coated folding boxboard	M-Real Alliance UK Ltd, Simpele Mill, Finland
6	Simwhite 400µm/260gsm - fully coated folding boxboard	M-Real Alliance UK Ltd, Simpele Mill, Finland
7	Carta Integra 410µm/270gsm - fully coated bleached paperboard	M-Real Alliance UK Ltd, Aankoski Mill, Finland
8	Carta Solida 395µm/250gsm - fully coated bleached paperboard	M-Real Alliance UK Ltd, Aankoski Mill, Finland
9	Creaset 80gsm - coated paper	Sappi, Torraspapel Mill, Spain
10	Nikla Select 80gsm - coated paper	Sappi, Brigl Mill, Bermeister, Austria
11	Royal Parade 80gsm - coated paper	Sappi Europe SA, Maarstricht
12	Valspar lacquer 2302 coated Simcote H/S, undercured lacquer	Valspar lacquer applied by Alcan Print Finishers, Headley Road East, Woodley, Reading, Berks RG5 4UA
13	Valspar lacquer 2302 coated Simcote H/S, normal cure lacquer	Valspar lacquer applied by Alcan Print Finishers
14	Valspar lacquer 2302 coated Simcote H/S, overcured lacquer	Valspar lacquer applied by Alcan Print Finishers
15	Valspar lacquer 2436 coated Simcote H/S undercured lacquer	Valspar lacquer applied by Alcan Print Finishers
16	Valspar lacquer 2436 coated Simcote H/S normal lacquer	Valspar lacquer applied by Alcan Print Finishers
17	Valspar lacquer 2436 coated Simcote H/S overcured lacquer	Valspar lacquer applied by Alcan Print Finishers
18	Cupforma Classic 210gsm, two side polyethylene coated	Stora Enso (UK) Ltd, Imatra, Finland
19	Cupforma Classic 210gsm, one side polyethylene coated	Stora Enso (UK) Ltd, Imatra, Finland
20	Ensogloss 220gsm, fully coated solid bleached sulphate	Stora Enso (UK) Ltd, Imatra, Finland
21	Ensocoat 210gsm, coated solid bleached sulphate	Stora Enso (UK) Ltd, Imatra, Finland
22	Performa Natura 210gsm, coated paperboard	Stora Enso (UK) Ltd, Imatra, Finland
23	Pankawhite 910µm/510gsm, fully coated folding boxboard	Stora Enso (UK) Ltd, Pankakoski Mill
24	Pankabrite 740µm/425gsm, fully coated folding boxboard	Stora Enso (UK) Ltd, Pankakoski Mill
25	Tamfold 460µm/255gsm, coated folding boxboard	Stora Enso (UK) Ltd, Ingerois Mill
26	Tamwhite 410µm/255gsm, coated	Stora Enso (UK) Ltd, Ingerois Mill

	folding boxboard	
27	Tambrite 460µm/260gsm, coated folding boxboard	Stora Enso (UK) Ltd, Ingerois Mill
28	Tambrite HS 460µm/260gsm, coated folding boxboard	Stora Enso (UK) Ltd, Ingerois Mill
29	Invercote G 280gsm, 20gsm polyethylene terephthalate coating	Iggesund Paperboard Europe
30	Corona treated PP laminated folding boxboard	Alcan Print Finishers
31	Test liner II 240gsm	St Regis Paper Co. Ltd, Sudbrook Mill, Newport
32	Test liner III 280gsm	St Regis Paper Co. Ltd, Sudbrook Mill, Newport
33	Kraft 190gsm	SCA
34	Test liner II 140gsm	SCA
35	Folding boxboard 210gsm, 20gsm white PE coated	Walki Wisa Ltd, UPM-Kymmene
36	Amorphous polyethylene terephthalate sheet 240µm	Klockner Pentaplast Ltd
37	Polypropylene sheet 450µm	Klockner Pentaplast Ltd
38	1300gsm White PE / White PE Sapino	Unknown/Confidential
39	1200 gsm White test liner / Test liner	Unknown/Confidential
40	1000 gsm TK liner / Bleached Kraft	Unknown/Confidential
41	1200gsm White PE / Brown PE	Unknown/Confidential
42	1250gsm Test liner / Test liner	Unknown/Confidential
43	1100gsm White PE / Brown PE Sapino	Unknown/Confidential
44	Corrugated (Kraft)	Unknown/Confidential
45	125gsm printed PET coated bleached Kraft	Unknown/M-real
46	127gsm PE coated waste based paper	Unknown/M-real