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**A Review of Adhesive Bonding
Assembly Processes and
Measurement Methods**

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Abstract

Adhesive bonding is a key manufacturing technology. However, the adhesive industry suffers from a perception within certain industries that its products are a low technology commodity item and, hence, the choice of adhesive for a given application is largely based on cost alone. This is compounded by the lack of measuring techniques available to distinguish performance differences and processability.

There are many different types of processes and materials that can be involved in the manufacture of an adhesive bond. There are also many measurement and inspection methods that could, in theory, be used to improve the bonding process but are either unsuitable in practical applications or not used for many reasons. Although there are many factors influence bonding effectiveness, there are some aspects of the adhesive bonding process that are key to nearly every bonding operation. These are in the areas of flow characteristics, substrate characterisation and inspection, wetting and adsorption on surfaces, initial bond strength and cure. Some of these aspects are interlinked (e.g. flow characteristics and wetting/adsorption).

The key areas needing to be addressed, identified in this review are:

- Techniques for characterising rheology of adhesives for high rate and intermittent dispensing processes.
- Quantitative techniques for slump properties and wet strength.
- Inspection of rough and porous surfaces for suitability to bond (e.g. for roughness, porosity, surface layer strength).
- Measurement of substrate wettability, in particular to water based and hot melt adhesives.
- Measurement of adhesive spread and adsorption on surfaces.
- Determination of tack and setting rates of adhesives with transient properties (e.g. hot melts).

To be useful to industry any measurement techniques developed to meet these needs should be suitable for use on the production line or in small workshops or industrial laboratories and should depend on robust easy to use equipment. Techniques must be cost effective in order to enable industry to justify their use.

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Approved on behalf of Managing Director, NPL, by Dr C Lea,
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CONTENTS

1.	INTRODUCTION	1
1.1	BONDING MECHANISMS	2
1.2	BONDING AND ASSEMBLY PROCESSES	3
2	PRODUCT DESIGN	4
2.1	MATERIAL SELECTION	4
2.1.1	Adhesive Types	4
2.2	JOINT DESIGN	5
3.	ADHESIVE HANDLING AND DISPENSING	6
3.1	ACCEPTANCE TESTS	6
3.2	ADHESIVE STORAGE	6
3.3	PRECONDITIONING	7
3.4	MIXING ADHESIVES	8
3.4.1	Two Component Adhesives	8
3.4.2	Work Life	8
3.4.3	In-Line Mixing	8
3.4.4	Bulk Mixing	9
3.4.5	Two-Sided Application	10
3.4.6	Assessment of Mix Quality	10
3.5	DISPENSING	10
3.5.1	Brushing and Trowelling	11
3.5.2	Roller Transfer	11
3.5.3	Spray Application	11
3.5.4	Low Precision Nozzle Dispensing	12
3.5.5	Pin Transfer	12
3.5.6	Stencil Printing	12
3.5.7	Precision Nozzle Dispensing Methods	13
3.5.8	Application Problems and Monitoring Techniques	14
3.6	FLOW CHARACTERISATION	16
3.6.1	Viscometry	19
3.6.2	Capillary Rheometers	20
3.6.3	Rotational Viscometers	22
3.6.4	Thixotropy, Creep, Sag and Slump	24

4.	SURFACE PREPARATION AND CHARACTERISATION	25
4.1	SURFACE PREPARATION METHODS	25
4.1.1	Cleaning	25
4.1.2	Mechanical Abrasion	26
4.1.3	Modification of Surface Chemistry	26
4.1.4	Primers	27
4.2	TESTS FOR SURFACES	28
4.2.1	Surface Chemical Analysis	28
4.2.2	Surface Topography	30
4.2.3	Surface Layer Properties	31
4.2.4	Wettability (Surface Energy/Tension)	32
5.	ASSEMBLY	35
5.1	DRYING	35
5.2	ABSORPTION OF ADHESIVE	35
5.3	ACTIVATION OF ADHESIVE	36
5.4	OPEN AND SETTING TIMES	36
5.5	POSITIONING	37
5.6	PRESSING AND JIGGING	38
5.7	INITIAL FIXING AND TACK	38
5.7.1	Tack	38
5.7.2	Loop Tack Test	39
5.7.3	Probe Tack	39
5.7.4	Rolling Ball	40
5.7.5	Quick Stick	40
5.7.6	Wet Strength	40
6.	CURE IN ADHESIVES AND RESINS	41
6.1	DEFINITION OF "CURE"	41
6.2	PROCESSES OCCURRING DURING CURE	42
6.2.1	Removal of solvent or dispersing medium	42
6.2.2	Cooling	42
6.2.3	Chemical reaction	43

6.3	CURE MONITORING	43
6.3.1	Available Techniques	43
6.3.2	Chemical Techniques	44
6.3.3	Electrical Techniques	46
6.3.4	Mechanical Techniques	46
6.3.5	Microstructural Techniques	47
6.3.6	Optical Techniques	48
6.3.7	Thermal Techniques	48
6.3.8	Ultrasonic Techniques	51
6.4.	INDUSTRY EXPERIENCES	52
6.4.1	Cure Monitoring Techniques used in Industry	52
6.4.2	Future Cure Monitoring Requirements and Techniques for Industry	53
7.	SUMMARY	53
8.	ACKNOWLEDGEMENTS	53
9.	REFERENCES	54
	APPENDIX I: PACKAGING SECTOR NEEDS	60
	APPENDIX II: PROCESSES AND PROCESS MEASUREMENTS FOR FOOTWEAR, CLOTHING AND FURNITURE INDUSTRIES	67

1. INTRODUCTION

Adhesive bonding is a key joining technology in many industrial sectors and usage is predicted to expand steadily over the next few years. Adhesives are widely used for their ability to join dissimilar materials, with joints which are durable but at the same time are 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. The cost of bonding failures can far exceed the value of the adhesive used. Thus, there is a need to supply adhesive users in industry with simple, robust and reliable measurement methods to help maintain efficiency in bonding operations and, particularly, support increases in production rates. For adhesives users, changes in materials impact on manufacturing processes. For example, the trend to reduce solvent use, both in adhesives and surface treatments, necessitates changes in either materials or processes in order to continue making reliable products.

The bonding process is critical to manufacturing products that will perform appropriately in service. Complex interactions between the properties of the adhesive, the characteristics of the surface to be bonded and the bonding environment determine the optimal bonding process. Rapid bonding processes are preferred, to speed up throughput and reduce work in progress. Demanding joints may require lengthy multi-step processes - from materials preparation, through adhesive application and drying, to bonding - but even here the bonding step is rapid and may depend on transient phenomena such as tack. Because of the nature of the materials and the bonding processes much of the process monitoring is subjective, and there are few quantitative measurements other than for temperature and pressure.

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 knowledge 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.

Within the Measurements for Materials Systems (MMS) programme formulation exercise it was recognized that many of the available process measurement and quality control techniques have shortcomings. Techniques tended to be developed for specific industries and processes and thus produce qualitative data that have little general applicability for other processes or for assessing major changes in materials or procedures. Project 9 "Measurements for Efficiency Improvements in Rapid Bonding Systems" of the MMS programme aims to provide improved test methods and procedures that will enable adhesive users to characterise materials and processes. Since, in many industries, users tend to operate in relatively low technology environments with low margins, and are unable to invest in sophisticated analysis equipment, simple quick methods and guidance on good practice for characterising and producing suitable surfaces for bonding will be developed in this project.

Choosing the most appropriate methods for characterising an adhesive bonding system or process can be a difficult task. A brief search of the websites [1-3] of major standards bodies such as the International Standards Organisation (ISO) [1], British Standards Institute (BSI)

[2] and American Society for the Testing of Materials (ASTM) [3] revealed several hundred standard test methods related to adhesives and many terminology documents [e.g. 4-6]. There are many manufacturers associations, e.g. Pressure Sensitive Tape Council (PSTC) [7] and Technical Association of the Pulp and Paper Industry (TAPPI), that develop methods for specific products and end users, e.g. US military, that set standard product specifications. Standard methods for many other materials, e.g. paints, inks and plastics, are also used to characterise adhesives. This report, the output for task 1 of the project, reviews the major processes and available measurement methods. Brief reviews of practices and requirements for the packaging and footwear, clothing and furniture sectors were carried out and the findings reported in Appendices I and II respectively.

1.1 BONDING MECHANISMS

There are primary mechanisms recognised as contributing to the development of an efficient bond, covered in many general texts [8-17]. Chemical bonding is normally thought to give the strongest and most durable bonds but mechanical and wetting mechanisms also contribute to bond strength even where chemical bonding does not occur.

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, increased 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 crevice 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 form 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.

1.2 BONDING AND ASSEMBLY PROCESSES

Although there are many different types of adhesives, materials and joints within the general description of bonded products, there are generic steps common to all adhesive joining processes. The steps in the design and manufacture of adhesive joints include:

- Product Design
 - Materials selection
 - Joint design
- Adhesive handling and dispensing
 - Material acceptance
 - Storage
 - Pre-conditioning
 - Mixing
 - Application
 - Inspection
- Substrate surface preparation
 - Surface preparation
 - Inspection
- Assembly
 - Drying and Absorption
 - Activation
 - Open/setting times
 - Assembly
- Curing
 - Processes
 - Monitoring/assessment

In addition there are certain characteristics of adhesive systems that are common to many different processes and materials

- Flow
- Wettability
- Tack

2 PRODUCT DESIGN

2.1 MATERIAL SELECTION

Commonly, substrates are selected to provide the engineering and aesthetic properties required by the product. Although the selection of an adhesive is a critical factor in the bonding process this is sometimes almost an afterthought at the design stage and the onus is normally placed on the adhesive supplier to provide a suitable product to bond the parts. This has led to the development of very many different formulations of adhesives (and surface treatments) to try to meet the many different requirements of users. It is not uncommon for a supplier to formulate an adhesive system for a particular user application.

2.1.1 Adhesive Types

There are many different types of adhesive (both in constituent chemistry and physical types) available to cover a myriad of joining needs [8, 9, 13-17]. There are far too many to describe here. For simplicity these can be aggregated into five general classes of adhesive: structural; hot melt; pressure sensitive; solvent-based and enclosed cured. Within these classes, there are many possible material chemistries and curing mechanisms. The most important are:

Single-part, heat-cured: The adhesive is formulated with resin and hardening agent present together but inhibited from reacting unless exposed to high temperatures. Single part adhesives include epoxy, acrylic, silicone, phenolic, polyimide and elastomer (butadiene) chemistries. Single part adhesives are commonly used for structural applications and surface component mounting in electronics. They are typically supplied as thick liquids and pastes although some are in the form of films.

Single-part, moisture-cured: Adhesives, such as single-part polyurethanes and silicones, that cure in the presence of moisture.

Two-part: The adhesive is formulated with separate resin and hardener. Once these are mixed, the cure reaction starts. Normally the formulations will cure at room temperature although cure rates can be increased by raising the temperature. Two-component adhesive types include epoxies, acrylics, silicones and polyurethanes.

Anaerobic: Enclosed cure adhesive that cures in thin gaps through the catalytic action of surface moisture in the absence of oxygen, which inhibits the reaction.

Cyanoacrylate: Enclosed cure adhesive, based on acrylic monomer, that polymerises into an acrylic polymer in contact with alkaline surfaces. The presence of surface moisture helps neutralise acidic stabilisers in the adhesive and promote the hardening reaction.

UV Curing: Adhesive where the cure reaction is initiated by ultra-violet light. Acrylic monomer polymerises into acrylic polymer.

Solvent-based: Adhesive material is carried in a solvent (either an organic solvent or water). Water dispersed adhesives are commonly known as water-based adhesives. The solvent must evaporate (dry), depositing the adhesive film, before bonding. Owing to health and environmental concerns organic solvent-based systems are being replaced by water-based systems. An activation stage (e.g. heating) may be required before bonding. Rubbery

polymers such as natural rubber, urea formaldehyde, polyvinyl acetate, polyurethane, polychloroprene or acrylics are used in these formulations.

Pressure sensitive: PSAs are semi-solid adhesive, permanently tacky due to their visco-elastic characteristics, often used on tapes and labels. PSAs may be made from film-forming elastomeric materials, such as styrene-butadiene rubber, butyl rubber, silicone rubber, nitrile rubber and acrylic rubber, or block-copolymers with the addition of small quantities of tackifiers, plasticizers, waxes or oils.

Hot melt: Thermo-plastic, solvent-free materials, characteristically solid at low temperatures, which are low viscosity fluids above 80 °C and rapidly set upon cooling. Hot melt adhesives are used in a variety of manufacturing processes, including bookbinding, product assembly, and box and carton heat sealing. There are a number of hot melt adhesives in use, with the most common being those used for hot melt pressure sensitive adhesive applications:

- ethylene vinyl acetate (EVA) copolymers, compatible with paraffin, the original hot melt;
- styrene-isoprene-styrene (SIS) copolymers;
- styrene-butadiene-styrene (SBS) copolymers;
- polyimides;
- polyesters;
- ethylene ethyl acrylate copolymers (EEA); and
- polyurethane reactive (PUR).

2.2 JOINT DESIGN

The basic design of a joint is likely to be dictated by the overall design of the product to meet the general size, cost, appearance and performance desired. Where adhesive bonding is replacing another joining technique there may be limited scope for radical changes to the joint. However, it is becoming recognised that certain basic design rules (such as loading the adhesive in compression or shear rather than peel and tension), taking account of the special properties of adhesive, may make it cost effective to tailor designs to the requirements of bonding [10, 12, 13-15].

There are many approaches to joint design. Much design is based on empirical factors (e.g. lap shear or peel strength and a ‘safety’ factor to calculate the required bonded area), users experience or trial and error – frequently a combination of all three. The adhesive properties used in this approach to design are normally obtained from manufacturers data sheets. The quantity and quality of materials data supplied by manufacturers can be variable. Even at best, the mechanical properties data available typically consist of only basic lap shear or peel strengths and are of limited value for more detailed design calculations that consider stress concentrations in the bond line.

Computerised stress analysis packages, based on the finite element method, are becoming more popular for joint design, particularly in engineering sectors such as aerospace and automotive. With accurate mechanical properties data, the correct materials models and appropriate failure criteria, predictions of joint stiffness and strength can be made using virtual simulations. Considerable research effort has been directed, in the Performance of Adhesive Joints and other programmes [18-23], towards developing the materials models

(and test methods needed to obtain material parameters) for structural adhesives. Other adhesives have been less well served.

3. ADHESIVE HANDLING AND DISPENSING

The various stages between receiving the adhesive from the supplier until deposition of the adhesive on the components being bonded can have an enormous influence on the joint manufacture process. Dispensing is an area where the physical properties of the adhesive have considerable importance. However, transport, storage, pre-conditioning and mixing are all activities where the physical properties of the adhesive can change detrimentally. The measurement of the flow (or rheological) behaviour of adhesives is described in this Section.

Adhesive dispensing – transferring the correct quantity of adhesive to the correct locations on the substrates and ensuring the adhesive remains in location until hardened – is a key process in adhesive bonding. Single part adhesives can be applied directly. Multi-component adhesives need to be mixed either before or during application. The methods and degree of advanced technology employed varies considerably between industries and applications. In lower volume and craft based industries, such as footwear or construction, adhesive is often applied manually either directly from a cartridge, e.g. using a sealant gun, or using a tool to transfer and place the adhesive. In other industries, e.g. packaging or automotive, automated dispensing is more common. Electronics provides one of the most challenging tasks for adhesive dispensing – small components must be bonded precisely in position at high production rates. In circuit board bonding, the output rates for pick and place machines are exceeding 70,000 components an hour but actual production rates are limited by adhesive dispense rates, currently around 40,000 an hour. Dispensing technology in the electronics industry is being developed to meet this need. Many of the techniques reviewed in this section originate from electronics assembly.

3.1 ACCEPTANCE TESTS

Adhesive products and substrates may need to be tested on delivery to confirm their adherence to specification and manufacturers data sheets. Typical tests may include:

- Chemical/composition tests, e.g. density [24-25]
- Viscosity measurement [26-29]
- Solid adhesives content (for solvent/water-based system) [30]
- Bond strength (e.g. lap shear [31-34] or fibre tear tests)

3.2 ADHESIVE STORAGE

Adhesives are multi-component and chemically reactive materials. Changes in their physical or chemical compositions will inevitably occur once a batch has been manufactured. These are affected by storage conditions. Changes in composition are likely to affect both the processability of the adhesive and its final structural/durability properties. Thus adhesives have ‘shelf lives’ during which their properties should, if stored correctly, remain within specification. Manufacturers normally recommend that out-of-life material be discarded. Stock control measures are usually taken to ensure that the correct material is used.

Some changes in composition, e.g. sedimentation of filler particles, are reversible by remixing but others, e.g. polymerisation or evaporation of volatiles, are not. Adhesive

manufacturers use various means of stabilising adhesive formulations but there are no means of providing infinite shelf life. Adhesive stabilisers are often added to extend the cure period but these add to cost and will tend to diminish the final properties of the adhesive. The sensitivity to environment and rate of performance decay of properties will vary from formulation to formulation. However, only a few standard methods [35, 36] exist to determine shelf lives. Thus shelf lives are normally stated conservatively.

Temperature is a critical storage requirement for many adhesives. Many adhesives, particularly single-component systems, must be stored refrigerated or frozen to ensure that changes during storage are minimised. Two part adhesives also are often stored cold to improve their shelf lives. Cold shelf life varies among adhesives, but most are quoted as between 6 and 12 months. Cold storage should follow manufacturers instructions as temperatures that are too low may degrade the adhesive, for example freezing may cause large changes in composition that affect the final properties. If adhesive is to be used within a few weeks of delivery, room temperature storage may be acceptable. However, storage and transport should ensure that exposure to higher temperatures is minimised. Prior to application, sufficient time should pass to ensure that the adhesive is brought to the application temperature. Adhesive that is stored frozen should be allowed to thaw. This should always be done at room temperature. Where records of storage and transport conditions are unknown or believed to have differed from recommended conditions, it may be necessary to test the material, using some of the acceptance tests, to ensure that the properties have not degraded below specification.

Adhesive storage conditions should also avoid exposing the adhesive to substances that can react with the adhesive or be absorbed into the system. In most cases this implies avoiding moisture. However, for some adhesives the storage may require exclusion of oxygen or catalysing substances. Adhesive should also be stored in conditions that avoid loss of substances through evaporation (e.g. volatile components or solvents). Therefore, it is preferable to store the adhesive in the original, sealed containers to minimise contamination. Transfer of adhesive to another vessel, particularly an unsealed one, increases the chances of picking up contamination (both from the atmosphere and from equipment used to transfer the adhesive) or losing material.

Standard methods for determining shelf life of adhesives are limited. Some techniques, e.g. ASTM D1337 [35], specify testing either consistency (viscosity) or bond strengths (lap shear) at regular intervals to determine whether changes are occurring. Arbitrary property changes, with little correlation with engineering performance, are defined to indicate when a material is considered out of date. Other techniques assess chemical changes or solvent levels in the adhesive.

3.3 PRECONDITIONING

The processability of adhesives is sensitive to the environment in which they are used. The flow behaviour will be temperature sensitive and the adhesive should be warmed to the recommended dispensing temperature before use. Normally, the dispense temperature for all but hot melt adhesives will be around room temperature (20-25 °C). Sufficient time should be allowed for adhesives and substrates to come to the application temperature before use. Some adhesives may be warmed further to 'thin' them, allowing easier flow. Caution must be taken when using adhesives heated above room temperature as the working life may be dramatically shortened.

Long-term storage of adhesives may lead to physical separation of the constituents. The most common mechanism for this is sedimentation of solid filler particles since the density of these materials will be greater than the adhesive resin. Sedimentation rates are much higher in low viscosity liquids than in thick paste adhesives. Sedimentation is normally reversible by agitating or remixing the system to re-disperse the particles. Adhesive should be observed visually during dispensing to ensure that the colour and consistency are uniform and that there are no aggregated solids.

3.4 MIXING ADHESIVES

3.4.1 Two Component Adhesives

Many types of adhesive are supplied as two-component systems, a resin and hardener, which are mixed in order to initiate the cure reaction to harden the adhesive. These systems will cure at low temperatures; essential where heat cannot be applied to cause cure. The performance of the bonds made from two-part adhesives depends on having the correct ratio of components intimately mixed and applied within the working life of the system. Mix ratios of adhesive components can vary enormously. Ratios of 1 part resin to 1 part hardener (1:1) are common. However, many systems are mixed in different ratios and 10:1 (or even 40:1) systems exist.

In most applications the adhesive components are mixed before they are applied to the substrates. This can be done from twin-pack cartridges or automated dispensing equipment using nozzles containing in-line mixing elements. Adhesives can also be mixed together in bulk. In some systems, often with very high mix ratios, adhesive components are applied to opposite sides of the joint and are mixed when brought into contact.

3.4.2 Work Life

The mixing of the adhesive initiates the cure reaction. The first stage of the reaction will lead to a progressive reduction in the ability of the adhesive to flow easily. Thus, the adhesive will be less capable of wetting the adherends as time passes. The time from mixing until the mixed adhesive gels and becomes too viscous to use is known as the work life. Work lives for adhesives depend on the formulation/application and can vary from seconds to hours. All mixing, application and bonding should take place within the work life of the adhesive. Standard methods for determining working life, e.g. [37, 38], are similar to those for shelf life. Working lives are determined based on when arbitrary changes in viscosity or bond strength occur. Bond strength tests require the preparation and testing of standard adhesive joints at different times after mixing. The effort involved may be considerable and there are difficulties in characterising relatively fast curing systems, e.g. those with work lives of less than a few minutes. Viscosity measurements can be performed continuously and are more suited to faster curing systems than joint tests. A commonly quoted value relating to the work life of an adhesive is the gelation time [39]. This can be determined through oscillatory rheology methods and is defined as the time where the elastic and viscous modulus values cross.

3.4.3 In-Line Mixing

In-line mixers contain mixing elements whose baffles cause the two flows to intertwine thus mixing the adhesive. Flow rates from the two parts can be balanced to ensure the correct ratio

of components is dispensed. For example, 1:1 twin packs can be dispensed using twin piston sealant guns. The mixing efficiency depends on the number of mixing elements and the viscosities of the two parts of the adhesive. Very high viscosity adhesives may be difficult to pump through the nozzle owing to large pressure requirements. Low viscosity systems can also cause problems. Large viscosity differences between the two components may lead to mixing problems, as flow rates may be unequal.

When setting up the system, the length of nozzle (and number of mixing elements) can be varied until uniform adhesive is dispensed from the nozzle. The larger the number of mixers elements the better the mixing quality but large numbers of mixers cost more and require higher pressures to maintain flow rates. Adhesive should not dwell within the mixer nozzle for times approaching the work life of the adhesive. It is advisable that if flow is interrupted for a significant period of time then the nozzle should be discarded and replaced with a fresh one. Although slightly wasteful of material, it is good practice that when a fresh nozzle is attached, the first volume of adhesive to flow through the nozzle be discarded. The initial mixing may not be to specification (differences in component rheology may lead to off specification mix ratios at the start of flow and air entrapment is more likely in an empty nozzle). In most instances, in-line mixed systems are most effective in applications where continuous dispensing occurs.

3.4.4 Bulk Mixing

For operational or cost reasons automatic mixing of adhesives may not be possible. Adhesives must then be decanted from their packaging and mixed in bulk before application. Incorrect or variable mix quality will produce off-specification material that may have deleterious consequences on joint performance (although experienced users do sometimes deliberately alter the mix ratio to produce material with different properties, e.g. reducing the hardener to produce more flexible adhesives, this is not recommended without consultation with the adhesive manufacturer). Mixing can be through manual or mechanised stirring. Off-line mixing leads to slower bonding and, unless adhesive can be repackaged for dispensing, manual application. This is not a preferred situation for rapid bonding.

The proportions of adhesives should be accurately measured out, according to manufacturers instructions, before mixing. Depending on the adhesive system the quantities of adhesive will be measured by volume or mass. Mass is normally the easier measure for high viscosity adhesives. Adhesives are normally supplied in packages containing the correct proportion of components and if whole packs are mixed then the ratios ought to be correct. However, in many applications smaller quantities than a full pack are often used, as large bulk packs of adhesive are normally more economic to purchase. Adhesives must be measured out before mixing. Where the mix ratio is around 1:1 by volume the risk of serious imbalance in proportions and the consequences of poor mixing will be lower than in high mix ratio systems.

The sub-sampling of adhesive from a bulk container for mixing may affect the properties of the adhesive. Opened containers of adhesive are likely to have shortened shelf lives in comparison with unopened containers. If the storage conditions need to be controlled then repeated decanting of adhesive might cause exposure of the material to undesirable environmental conditions. Periodic checks may be required on adhesive in opened containers. Adhesive decanted for mixing will be exposed to the atmosphere and changes in composition may occur before mixing (e.g. through moisture absorption, evaporation of volatiles or chemical reactions). It is preferable to minimise the time between decant and mixing. The mixing

vessel should be clean of any substances likely to react with or absorb into any components of the adhesive.

The components should be stirred carefully until they are thoroughly mixed. The mixing should avoid, as far as possible, the inclusion of air into the system that could lead to undesirable voids in the joint. Experience suggests that bulk mixing is more likely to entrap air than in-line mixing [18]. Post mixing processes can be used to remove air. Vacuum degassing can be used with varying degrees of success to remove air. This works best with lower viscosity systems and the rate of air removal can be increased through stirring (however, this requires specialist equipment). Vacuum degassing carries a risk of foaming the adhesive. The adhesive can also be centrifuged to remove air. Any degassing procedures need to be performed well within the work life/shelf life of the adhesive.

3.4.5 Two-Sided Application

A third method of mixing two component adhesives is through the application of the components (resin and hardener/activator) on to the different surfaces to be bonded. When the surfaces are brought into contact the components mix through diffusion and react. An example of this type of system is an acrylic adhesive where the activator is applied to one adherend and the resin to another. A very fast reaction takes place when the two are brought into contact and a strong bond is formed within a few seconds. Adhesives used in this way tend to be low viscosity systems (to allow diffusion) and are used in thin layers (to ensure that diffusion will occur sufficiently to enable all the adhesive to react). The correct proportions of each component should be used, with identical areas covered on opposite sides of the joint.

3.4.6 Assessment of Mix Quality

In order to assess mix quality, the components are often different colours and good mix quality is shown by a uniform colour without streaks. The final colour will indicate the correctness of the mix ratio (and could be checked using a colour meter or against a colour chart). Preparing and testing adhesive joint specimens for bond performance can also be done to assess mix quality. Thermal analysis methods such as DSC or DMTA (Section 6) can also be used to check mix consistency in the final cured material.

3.5 DISPENSING

Dispensing is the process whereby adhesive is applied to the surfaces being bonded. There are large number of dispensing options available whose use depends on the type of adhesive being dispensed, the rate of bond formation, the precision of adhesive dispensing required and the area of surface to be coated. Dispensing processes range from manual, craft-based methods to fully automated systems.

Commonly used methods include:

- Brushing and trowelling;
- Roller transfer;
- Low precision nozzle dispensing - sealant gun or squeeze bottle;
- Spraying;
- Precision nozzle;
- Screen/stencil printing; and

- Pin transfer.

Dispensing methods are evolving continuously often based on technologies from related industries such as printing and paints. This is especially true in electronic assembly bonding where shrinking component sizes, increased component numbers and higher production rates require continual improvement in adhesive bonding technologies.

3.5.1 Brushing and Trowelling

In many adhesive processes (e.g. footwear bonding, construction) the process of applying adhesive to the adherends is performed manually. The adhesive is transferred from the container to the adherend using tools such as brushes, trowels or spatulas. The choice of tool is determined by the consistency of the adhesive and the area to be coated. Low viscosity or shear thinning adhesives are more readily brushed than pastes. The key quality control aspects of these types of operations are:

- Levels of coverage
- Extent of coverage
- Placement of adhesive
- Wetting of surface
- Work-in on rough or porous substrates
- Open/drying times

These dispensing operations require neither capital investment nor highly skilled operators. However, application times can be long and coverage is likely to be variable leading to problems with joint quality and reliability.

3.5.2 Roller Transfer

Adhesive can be transferred to adherends using roller-coating processes (also referred to as wheel or disc coating). Adhesive, stored in a reservoir, is transferred to a roller (either directly through immersion in the reservoir or by 'pumping' onto the roller) and then (either directly or indirectly via another roller) to the adherend. This process is suitable for assembly line/conveyer belt production in applications where large areas are to be coated/bonded. Precision placement or complicated patterning is not readily accomplished using roller transfer. Production problems may arise from contamination of the adhesive either via absorption from the air or transfer from the rollers.

3.5.3 Spray Application

Spray application is suitable for covering large areas with adhesive. There are several kinds of spray guns available. The most common of these are conventional air atomisation, HVLP (high volume, low-pressure) atomisation and electrostatic atomisation. All of these spray guns perform the same function. HVLP and electrostatic methods typically have higher transfer efficiencies than conventional air atomisation. The most important factor that impacts transfer efficiency [40] is the set-up of the spray guns, e.g. orientation, distance from surface, fluid pressure and air pressure. Settings are normally arrived at through trials. The type of adhesive and its viscosity affects transfer efficiency. Switching adhesive will require changing the process settings. In an atomisation spraying process, the transfer efficiency for water-based adhesives can be very high.

3.5.4 Low Precision Nozzle Dispensing

Squeeze Bottle: Fluid adhesives can be applied directly from plastic bottles fitted with nozzle tops or “toothpaste” tubes. Adhesive can be placed as accurately as the operator is able to position the nozzle. Adhesive flows when the bottle is inverted or pressure is applied to the bottle. It is difficult to precisely control the volume of adhesive dispensed.

Sealant Gun: The sealant gun is a familiar tool to DIY and building trade users. It is a simple means of dispensing pastes from standard sized cartridges. The cartridge is secured in the gun; squeezing or triggering the handle depresses a plunger at the base of the adhesive cartridge that forces the paste out through the cartridge nozzle. Guns are available for a range of standard size one or two component adhesive cartridges. The simplest guns are manually driven but pneumatically or motor driven systems are also available. The technology can also be used in automated manufacture systems.

Adhesive can be dispensed directly from specially designed containers normally as lines or a series of ‘blobs’. The initial width is related to the diameter of the nozzle (normally >1 mm) but will spread to an extent determined by the viscosity of the adhesive. The precision is adequate for accurate joining of relatively large parts.

3.5.5 Pin Transfer

Pin transfer is one of the fastest methods of applying patterns of adhesive to surfaces (e.g. printed circuit boards). A dedicated tool with an array of pins, designed to match the adhesive dot pattern on the substrate, is dipped into a tray of adhesive, wetting the pins in predictable amounts. The pins are then touched to the substrate and adhesive transfers to the board. Thus whole boards can be done in a single operation. Since tools need to be manufactured precisely, pin transfer tends to be used in high volume applications that have long production runs. Applying adhesive using the pin transfer method is considered to be difficult for small components. The adhesive viscosity is very important – a degree of fluidity is needed to wet the pins and for transference to the board but ‘non-drip’ properties are required to hold the adhesive in place between ‘dipping’ and transfer.

3.5.6 Stencil Printing

Stencil (or screen) printing is a viable and cost-effective method of rapidly applying adhesives. A stencil patterned with apertures corresponding to the desired placement of adhesive is placed on the surface to be bonded. The adhesive is applied to the top of the stencil using a roller or ‘squeegee’ to force the adhesive into the openings, making contact with the surface below. The stencil is lifted from the surface and adhesive is pulled from the apertures to form an array of adhesive dots on the surface. Stencil printing is used as a deposition method for high-throughput assembly environments such as fixing of surface mount components on printed circuit boards where adhesive needs to be dispensed on circuit boards at precise locations with well-defined dot shapes and sizes. The size and shape of the resulting dots can be controlled through the geometry of the stencil apertures (principally stencil thickness and aperture diameter) and rheology of the adhesive. Dot height may be expected to be equal to the stencil thickness but it is known that the aperture diameter plays a role.

Adhesives for stencil printing must have the characteristics to produce reliable depositions. Since adhesive may remain in the stencil and be exposed to the atmosphere for long periods of time, the formulation must be suitable for long-term exposure to ambient humidity. Hygroscopic (i.e. absorb moisture) adhesives are unlikely to be suitable for stencil printing. The flow properties of the adhesive also need to be tailored so that the adhesive can penetrate the apertures but forms and maintains an acceptable dot profile when the stencil is removed.

Stencil printing has some drawbacks as storage space is required to store stencils and tooling when not in use, and cleaning the stencil or tooling after a production run can be time consuming. New stencils will be required each time the dispense pattern is changed

3.5.7 Precision Nozzle Dispensing Methods

Precision methods for dispensing adhesives are higher technology, more automated versions of low precision nozzle dispensing methods and include:

- Time/pressure pump
- Auger pump
- Piston pump
- Jet type pump

These application methods have advantages and disadvantages that must be taken into account when setting up the application. Capital costs are likely to be high, restricting the equipment to high volume applications. The first three methods are ‘contact’ methods and 3-D movement is needed. The adhesive at the end of the nozzle is brought into contact with the surface, the adhesive is dispensed and nozzle is raised before moving to the next point. The actual transfer of adhesive takes place during a dwell time in which the fluid contacts the board, wetting the surface. The fluid remains in place, breaking off, when the dispenser is moved away. The need to raise and lower the nozzle can limit the dispense rate. The needle standoff height when dispensing and raised are key process control parameters as they can influence the size and shape of the dots dispensed. In contrast, the jet pump is a non-contact dispensing method. The theoretical dispense rates are higher as only 2-D movement is needed. The needle-surface separation influences the size and shape of the dots dispensed.

Time/pressure dispensing was an early method for dispensing adhesives and is still widely used in surface mount applications. The adhesive is contained in a pressurized syringe and the flow is controlled using air pulsed through a nozzle valve to dispense the desired amount of adhesive. This method is simple and reliable; rates as high as 40,000 dots per hour can be achieved. Higher speeds generally lead to less consistent dots. As the adhesive level in the syringe gets lower the column of air in the syringe becomes larger and the change in pressurization time leads to the dot inconsistency. Control systems can compensate for changes in fluid level but the system is sensitive to viscosity changes.

Auger pump dispensing uses a pump with a rotating screw thread to displace the adhesive within the reservoir. Turning on and off the screw’s electric motor dispenses measured amounts of adhesive. The motion of the pump will shear thin a thixotropic adhesive, easing dispensing and possibly evening out trapped air. Once the fluid in the pump contacts the surface, a consistent flow will be maintained. This method works with a wide range of adhesives. The auger pumps dispense dots in the same approximate range of sizes and dispense rates as the time/pressure method. However, there is more consistency in dot shape

and the pump is less sensitive to viscosity changes than the time/pressure dispensing method. The flow rate is dependent on needle size selection. Smaller gauge needles develop more backpressure, leading to problems as the fluid viscosity increases over time. Since the dot is dispensed through contact with the surface the speed of the process is limited by the speed at which the dispensing head can be moved in three-dimensions. This, rather than adhesive flow rate, tends to be the limiting factor to increasing process speeds.

Piston pump is a positive displacement method of adhesive application. The movement of a piston in a closed chamber precisely determines the volume of adhesive dispensed. In normal operation, viscosity changes or needle size have little effect on the piston pump flow rate. However, the pressures developed by the relentless nature of the piston can cause other problems if internal pressures are allowed to exceed specified operating levels. In most dispensing applications the pump is set to a fixed displacement to give a specified shot size. However, continuous extrusion is possible for other applications. As with the Auger pump, the nozzle contacts the surface and three-dimensional movement speeds limit dispense rates.

Jet dispensing is a method of applying adhesive using a spring-loaded pin or 'hammer' to force adhesive through the nozzle in a rapidly cycled manner. It is similar to the fixed volume piston pump with a high velocity that 'jets' the material. Air pressure raises the pin above the fluid reservoir and when the air pressure is removed the spring drives the pin down to force adhesive through the nozzle. The adhesive is ejected from the nozzle and propelled on to the surface, forming a dot. As the nozzle does not move in the Z-axis, significant increases in dots per hour over auger and piston pumps are possible. Consistency over a production shift is at least equal to other nozzle dispense methods. Jet dispensing can give tall dot profile, which is especially advantageous for smaller components. A limitation is that the jet can only dispense one dot size without changing equipment settings. The settings on the jet must correspond to the smallest dot size required but larger dot sizes can be composed of integer multiples of shots of this size. Multi-headed jet dispensing is a potential route to alleviate this problem. Non-contact jetting provides advantages such as easy programming, fast setup and robust process control in addition to higher dispense rates.

3.5.8 Application Problems and Monitoring Techniques

Adhesive Positioning: The main requirement of the adhesive dispensing process is to put the correct quantity of adhesive in the right place. Assessment of dispensing effectiveness is often performed visually – i.e. observation of the position, size or shape of the adhesive dispensed. This is normally done by the process operator using subjective criteria but can be automated using computer image analysis methods.

Within the packaging industry 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, a system for verifying the application of hot melt adhesives uses infrared detectors to measure changes in temperature of the substrate. Spots of hot melt as small as 1.5 x 6mm can be monitored through the thickness of the substrate.

For water-based adhesives, there are several position monitoring systems available. One uses photocells to detect the adhesive pattern and can verify that the adhesive is in the right place and volume, prior to closing the joint. Another uses a capacitance technique to measure the presence and quantity of adhesive after the manufacture of the adhesive joint. A

microwave detection system is also made for cardboard package sealing equipment. This monitors the moisture content in the glue flap and is claimed to operate at up to 800m/min.

In addition, laser scanners and infrared glue sensors can be used to monitor hot melt applications. These are claimed to be able to check the accuracy of the adhesive application to within ± 1 mm at 300m/min. Most of these on-line glue-monitoring systems can be also used to carry out a number of other quality assurance checks.

By adding an ejection system, incorrectly glued or misprinted cartons can be automatically ejected. Such equipment can be expensive. Hence, in the past companies have not fitted such equipment. However, 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.

Dot Shapes: Problems can occur in adhesive dispensing that are not necessarily the fault of the adhesive, the dispensing method or the machinery for controlling the application. These problems may also arise from a combination of improper settings in one or more of these areas, out of life material or from training and handling issues. Solving these problems is usually done through trial and error. Some typical problems in dot dispensing are outlined below. Problems with the ejection of adhesive from the nozzle can also influence the dispensing efficiency. These are most likely caused by process settings unsuitable for the rheological or visco-elastic properties of the adhesive system.

'Tailing' of the adhesive is a typical needle dispensing problem. A string or tail develops on the top of the adhesive dot when the dispenser is removed. This can slump over and place adhesive in undesirable locations.

'Satellites' are small outlying dots that occur in high speed dispensing. In contact dispensing this is usually a result of tailing and needle break-off and with the non-contact jet method it is usually due to incorrect dispense height. It may also be caused by stringing or break up of the dot on impact with the surface if dispense speeds are not matched to adhesive rheological properties.

'Popcorning' is a result of air or moisture getting into the adhesive and 'popping' out during the curing stage. This usually results from improper handling of fluid or using out of date material.

'Tombstoning' occurs when a component rises at one side during cure because of uneven forces in the adhesive. This is likely to occur as a result of an inaccurate dispense or a poorly designed process. It may also possibly result from improperly handled or out of date materials.

'Stringing' or the break up of the adhesive between nozzle and substrate is likely to occur if the ejection speed is too great for the viscosity/cohesive strength of the adhesive.

'No dispense' or the failure to eject a dot occurs when the force applied in the nozzle is insufficient to force and break adhesive from nozzle end. The next dot dispensed is likely to be twice the nominal size as the undispensed adhesive is dispensed. Characteristic patterns of no adhesive then double sized dots may be deposited. This problem may occur when the elasticity of the adhesive dominates over the viscous flow of the adhesive during the duration of the applied pulse.

Adhesive coating weight: Although visual inspection can determine the area where adhesive has been applied, the bonding performance may depend on the volume/mass of adhesive requiring control of the adhesive coating thickness. The adhesive coating weight can be determined through mass measurements using standard techniques [41, 42]. These are off-line techniques, requiring sampling of parts from the assembly line, which give average adhesive weight per unit area. Since the mass of adhesive is likely to be small compared with the mass of the substrate and substrate mass may change during the application process (e.g. due to moisture absorption or loss) the substrate mass needs to be determined accurately before adhesive application. This requires that substrate samples with accurately known mass be run through the process, which may not always be practical. Wet film thickness gauges [43] can be used to check organic coating thicknesses and may have their uses for adhesive bonding. Optical methods for determining coating thickness, such as ellipsometry [44], tend to involve high capital costs and require skilled operators. Technical limitations such as the requirements for flat, smooth surfaces and for thin, transparent adhesive layers limit the types of process where such techniques can be successfully implemented.

A number of techniques can be used to measure the thickness of relatively thick cured adhesive layers including travelling microscopes and micrometers [45]. Acoustic or electrical measurements are also possible for adhesive or coating layer thickness [46]. Accurate coating thickness values can also be produced using wear tests such as ball cratering [47, 48] or electron microscopy.

3.6 FLOW CHARACTERISATION

Much of this section is based on an earlier review of rheological measurement methods for structural, visco-elastic adhesives [49]. Adhesives are usually supplied as liquids - that can vary in form between thin, watery liquids to thick, viscous pastes - that harden to form a bonded joint. The flow characteristics control the dispensing, spreading, penetration and gap filling behaviour of the adhesive. This is often a critical criterion for selecting an adhesive and is a target property for adhesive manufacturers in the formulation of new products. The flow of materials is characterised by the science of rheology [50-52]. Knowledge of these properties is necessary for the selection of adhesives and the performance of manufacturing processes. A further area where rheological testing is used is in quality control, e.g. to test batch-to-batch variation or for shelf life.

There are many methods for studying the rheology of adhesives ranging from simple tests providing qualitative properties to sophisticated techniques able to provide multi-dimensional data (covering rate, time, temperature and stress) required for flow process modelling. This section is concerned with rheological measurement methods for uncured adhesives, which range from thin fluids to visco-elastic pastes. Selection of the appropriate technique depends on the properties of the material being tested and the type of data required.

Classically, distinctions were drawn between solids and liquids. Separate physical laws were formalised for their behaviours. Solids were assumed to obey Hooke's Law of elasticity and fluids obey Newton's Law of constant viscosity (the fluid stress is directly proportional to shearing rate). A single viscosity coefficient is all that is required to define the behaviour of a non-compressible Newtonian fluid under any conditions of flow and stress. The Newtonian approach allows easy comparison between adhesives for many applications. Low viscosity

adhesives are used in applications where the adhesive is required to flow easily, e.g. thread sealing where penetration into small gaps is needed. High viscosity adhesives are used in large gap joining and sealing operations where adhesive is required to remain in position after application.

However, this is a simplistic view of liquid behaviour that may not be suitable for all applications. Polymeric materials have visco-elastic properties showing characteristics of elastic solids and viscous liquids. Their rheological properties are non-Newtonian [49-52]. Most adhesives exhibit shear-rate dependent viscosities, commonly shear thinning (i.e. the resistance to motion falls as the rate of straining increases much as when paint is stirred), and may exhibit a yield stress (below which the adhesive will not readily flow, often described as a slump resistance) or thixotropy (time dependent viscosity). Thus, high and low flow rate properties can vary significantly and bonding processes may take advantage of these. For example, an adhesive with a high yield stress but low flow viscosity could be easily applied to a surface using a high shearing process (e.g. by brushing or spraying) and then stay in place once the flow stress is removed.

Rheological measurements are used to determine the behaviour of non-Newtonian liquids in simple flow situations using suitable material functions. The measurements obtain correlations between molecular structure and material properties, and between material properties and behaviour in practical situations. They may also be used to predict material behaviour in complex flow situations. This requires sophisticated mathematical treatments using data obtained from simple rheological experiments. The rheological behaviour of paste adhesives is sometimes characterised through visco-elastic models. The Casson model [53] has been shown to be appropriate for slump resistant one-part epoxy paste adhesives used in the automotive or electronic industries. The Casson model combines a pseudo-yield stress (for low rate properties) with a plastic viscosity (high rate behaviour) to fully characterise the adhesive.

Flow regimes for visco-elastic fluids can be categorised as shear (where layers of fluid slide past each other) or extensional (where 'slugs' of fluid are drawn in tension). Most rheological measurement methods work in shear flow but some techniques have been developed for extensional flow. There is a realisation that many processing steps involve extensional flow and that knowledge of extensional properties is required to understand process behaviour.

Viscosity and rheological measurements can be divided into three classes:

1. Steady flow: for example; flow cup [54], tube [55-57] and capillary[58] viscometry, falling ball viscometry [59, 60] and rotational rheometry[29, 61, 62] techniques.
2. Oscillatory testing: where the specimen is subjected to an oscillating force or deformation. Such tests can be performed using oscillatory rheometers [63] or dynamic mechanical testing [64] depending on the physical nature of the material.
3. Transient condition testing: e.g., the variation of deformation with time after a change, usually sudden, of applied stress or the variation in stress after a deformation [65]. The magnitude of the resultant deformation or stress, respectively, is dependent upon the visco-elastic properties of the test sample. These tests can be carried out on some equipment used for steady shear flow.

It must be remembered that the properties of adhesives are likely to be sensitive to rate and temperature. When selecting a rheological technique, consideration must be given to how rate and temperature are to be controlled/monitored and how the data relate to the application in question.

Standard flow characterisation methods for adhesives cover basic viscosity determination. ASTM D1084 [26] offers four methods for characterising low viscosity or ‘free flowing’ adhesives. Brookfield viscosity results are the most commonly quoted viscosity measurements for adhesives.

1. The Ford flow cup method [54] determines Newtonian viscosities from the time for 50 ml of adhesive to flow from a vessel. Different orifice sizes are used to ensure test times are between 50 s and 100 s.
2. The Brookfield methods [29, 62] employ the principle of rotational viscometry; it measures viscosity by sensing the torque required to rotate a spindle at constant speed while immersed in the sample fluid – the resin in a liquid state. The torque is proportional to the viscous drag on the immersed spindle and thus to the viscosity of the fluid. Both Newtonian and non-Newtonian fluids can be measured. Most resins are non-Newtonian and the measured viscosity depends on the velocity gradient to which the product is subjected. For these viscometers, the velocity gradient is not the same for every point of the spindle, hence the result is not strictly the ‘true velocity at a known velocity gradient’ and therefore is conventionally called an ‘apparent viscosity’. Different sizes of measurement geometries and instrument speed settings provide a range of shear rates for characterising the adhesive. These instruments cover viscosity ranges from 50 to 200,000 cP. Adhesive technical data sheets often provide a Brookfield viscosity value although this is normally a single point value.
3. The Stormer viscometer [66] uses a falling weight to rotate a paddle immersed in an adhesive. The time to produce 100 revolutions of the paddle is recorded. This method provides qualitative information on the adhesive viscosity for quality control purposes.
4. Zahn viscosity cups are designed to measure the time taken for a sample to flow through a calibrated orifice. The cup is immersed in the adhesive and withdrawn. The time between removing the cup from the reservoir until the flow breaks is measured and converted into a viscosity using conversion methods given in the standards.

3.6.1 Viscometry

Falling Ball Viscometry: The falling ball viscometry method [59] is the oldest and simplest viscometry method. In this method, the time for the ball to fall a known distance in the fluid is measured and the terminal velocity, u , is determined from which a viscosity can be calculated. Assuming Newtonian behaviour the apparent viscosity (η) which depends on the densities of the ball and fluid (ρ_b and ρ_f , respectively) and the radius, R , of the ball and gravitational constant (g):

$$h = \frac{2(\rho_b - \rho_f)gR^2}{9u} \quad (1)$$

The falling ball technique can be sealed to prevent evaporation or even to permit measurements at high pressure. However, to avoid complex flow patterns there must be a significant gap between the falling ball and the wall, which limits the method to materials that have a reasonable degree of transparency. The range of strain rates that can be covered is low. This method is not particularly suitable for rate-dependent, visco-elastic materials such as adhesives.

A variation on the falling ball method is the rolling ball method [60] where the tube is inclined at known angles and the velocity of the rolling ball measured. As the ball is in contact with the wall even opaque liquids can be measured. Varying the angle of incline allows variation in the shear stress and shear rate. However, analysis of the flow is much more complex. The falling or rolling ball technique is well suited for quality control applications, as changes in viscosity ought to be apparent through changes in “time of flight”.

Hydrostatic Head Viscometers: Hydrostatic head viscometers rely on the pressure generated by the fluid mass to provide driving force for flow. The simplest techniques use flow cups [54] – the adhesive is put into a vessel with a drain hole and the rate at which the adhesive flows from the cup is measured, as described above. This gives a qualitative value for the relative viscosities of different materials.

Figure 1 shows three types of hydrostatic head viscometers. These are the most popular for general and high precision measurement of the viscosity of thin Newtonian fluids. The time for the fluid to fall or rise between marks A and B (which is proportional to the kinematic viscosity) determines the flow rate, Q . The pressure drop, ΔP , is calculated from the head of fluid. The viscosity can be determined from these values and the geometry of the viscometer. The use of tube viscometers such as these is covered in various standards [55-57]. These relatively cheap, easy to use viscometers are capable of high reproducibility and repeatability.

However, the pressure drops are low. Measurement of the rheology of thick, paste adhesives would be problematic, if not impossible, using such instruments. A further limitation of these types of viscometers is that they are not suitable for measuring the viscosity of non-Newtonian fluids. There are insufficient ranges of shear stress and shear rates available for the measurement of fluids exhibiting behaviour of this nature. For these reasons, hydrostatic head viscometers are unsuitable for the majority of adhesives with the exception of thin liquid adhesives such as cyanoacrylates or anaerobics.

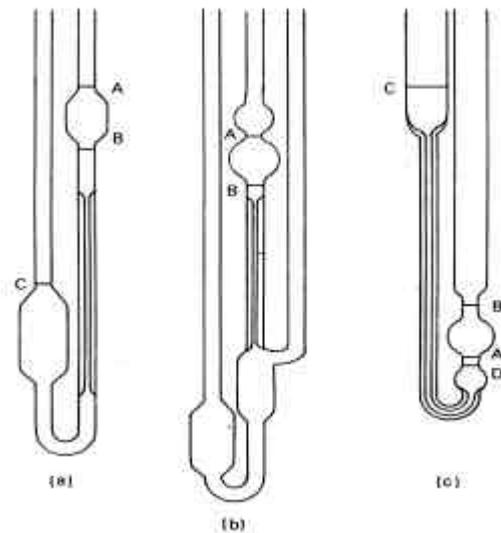


Figure 1: Three typical 'U' tube viscometers, a; Ostwald, b; Ubbelohde and c; reverse flow.

3.6.2 Capillary Rheometers

Capillary rheometry is used to characterise a fluid's shear flow properties. It also allows an understanding of the way fluids flow in variable cross-section geometries. Fluid flow lies at the centre of all extrusion processes, whether batch or continuous. This includes, the dispensing of adhesives and other paste and fluid materials. Adhesive materials used in manufacture are becoming more complex in terms of their rheology and ever more complex dispensing processes are being introduced. Therefore, there is an increasing need to fully understand general flow in a tube and the specific case of capillary flow.

For steady flow within a constant circular section, it is relatively straightforward to derive equations describing the velocity profile and pressure drop from the fundamental constitutive equations [49-52]. By measuring the pressure drop ΔP as a function of the fluid volumetric flow rate, Q , it is possible to determine the fluid's behaviour in terms of an apparent viscosity.

The pressure drop ΔP can be expressed in terms of the volume flow rate Q , the capillary length L and radius r_0 :

$$\Delta P = \frac{8hL}{pr_0^4} Q \quad \text{or} \quad Q = \frac{pr_0^4}{8h} \Delta P \quad (2)$$

Driven flow capillary rheometers [58] overcome some of the limitations of the hydrostatic head viscometers by providing sufficient pressures to measure higher viscosity adhesives. The simplest method of providing pressure is to use a mass and piston, e.g. the melt flow index (MFI) test [67] shown in Figure 2. MFI, widely used in the plastics industry for batch quality control, has been little used for adhesives for various reasons:

- A lack of reference data and, to date, a correlation with specific machine performance criteria.

- Hot melt viscosities are typically lower in viscosity than most polymers at their application temperature and hence are difficult to measure by MFI.
- These basic systems, although cheap to purchase and simple to operate, do not have the capability to fully characterise visco-elastic or rate dependent adhesives.

Recent developments of the MFI test have concentrated on varying the geometry (length and diameter) of the capillary die, thus altering the flow regime in the instrument, to enable variable shear rate and flow condition data to be obtained from this simple test instrument.

A more sophisticated type of capillary rheometer, shown in Figure 3, uses a mechanical screw to apply the piston pressure. The speed of the piston can be varied thus allowing variable flow rate tests. Shear rates in the fluid are controlled by the flow rate and the diameter of the exit die. An internal transducer measures the pressure drop. The temperature of the fluid in the barrel is controlled using the barrel heater. This measurement method most closely mimics the extrusion process.

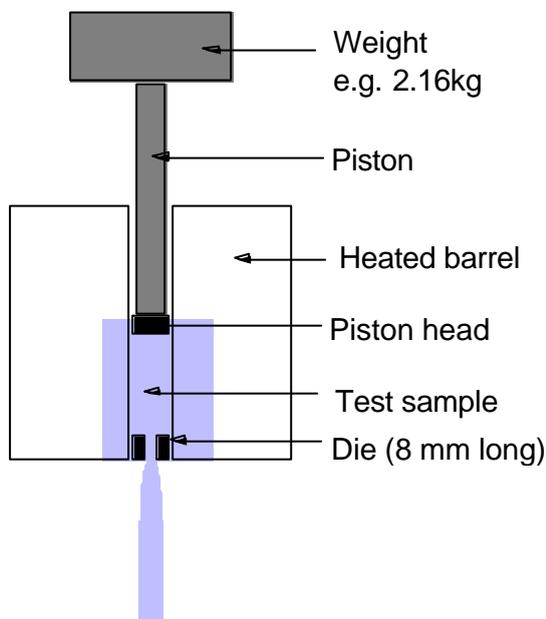


Figure 2: MFI Equipment

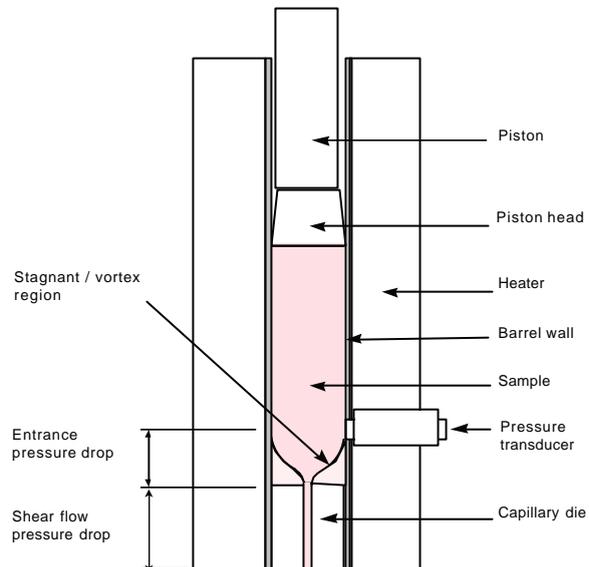


Figure 3: Screw driven capillary rheometer

This type of instrument is significantly more expensive than simple, non-mechanically driven instruments but benefits from having a wide range of shear rates available. The internal pressure transducer allows pressure measurement close to the capillary and the data can be logged to a chart recorder or PC. As part of the calibration routine for capillary rheometers, the dimensions of the capillary dies should be accurately measured, as the results are very sensitive to the die diameter [68].

In regions of the flow where the external diameter of the flow changes, e.g. at the entrance and exit of the die, the assumption of a shear flow regime is not valid. The convergence (or divergence) of the fluid adds an extensional (or tensile) component to the flow field. This is the situation in any extrusion process such as needle dispensing of adhesive. Work on polymer melts suggests that extensional rheological behaviour has a major impact on behaviour in

extrusion processes and that for some polymer formulations the extensional viscosity can differ far more than the shear viscosity. Extensional flow can be characterised [69] using filament drawing equipment such as shown in Figure 4.

Extensional flow can also be characterised in capillary rheometers through the use of step changes in channel diameters to cause converging flow [70]. Recent results suggest that, with only minor modifications to procedures and equipment, extensional viscosity measurements can be made using MFI equipment. Such findings suggest that reasonably cheap and simple methods for characterising extensional flow of adhesives could be developed.

NPL extensional rheometer

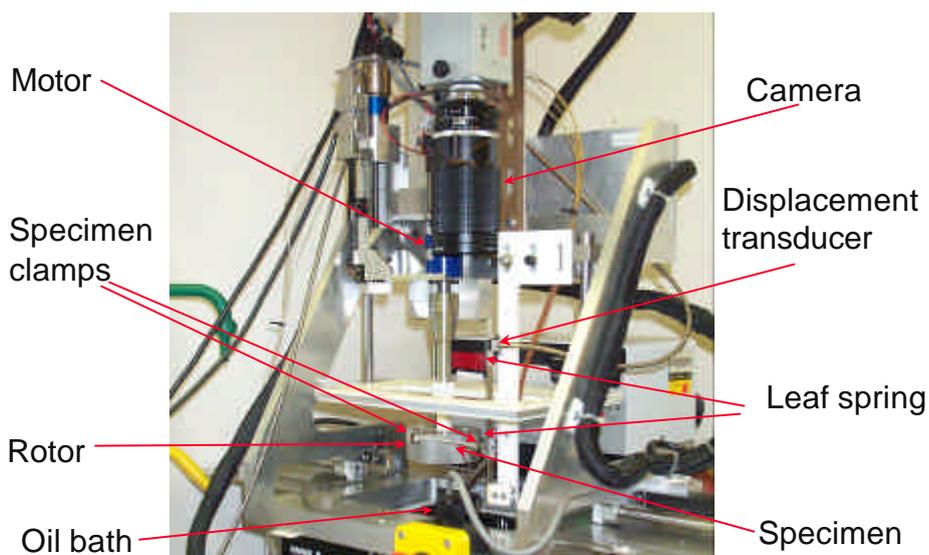


Figure 4: Stretching flow extensional rheometer

3.6.3 Rotational Viscometers

Rotational viscometers shear the test fluid between cylinders, cones or plates [29, 49-52, 61, 62] rotating about a common axis, see Figure 5. The drag of the fluid on the rotating parts provides the mechanical force used to determine the rheological information. This method of testing has advantages over capillary flow viscometers in that:

- samples can be sheared for as long as required, thus allowing the time dependent behaviour of the fluid to be determined;
- by use of suitable test geometries, a uniform shear rate can exist through the sample.
- Small sample volumes can be used.

The shear rate is proportional to the angular velocity, which can be varied over large ranges to provide information on adhesive properties under different flow rates. Thus, the flow curve can be derived more practicably than by tube viscometry. Rotational rheometers come in two main types: controlled strain (including the common Brookfield types) and controlled stress. These different types of instruments are capable of performing all the standard viscometry measurements but each has advantages for certain types of measurement (e.g. controlled stress is preferred for accurate creep or yield stress measurements). Different instruments within

each type have different operating capabilities, measurement ranges and sensitivities. High specification rotational rheometers are capable of operating in an oscillatory mode for determining visco-elastic properties [63, 71, 72].

However even the simplest rotational viscometers are considerably more expensive than cheap capillary flow systems. High shear rates cannot be achieved without an increase in the sample temperature due to shear heating effects (although with temperature control a compensation can be made). Tight tolerances in the measurement geometries and precise alignment are required to avoid inaccuracies in the measurements.

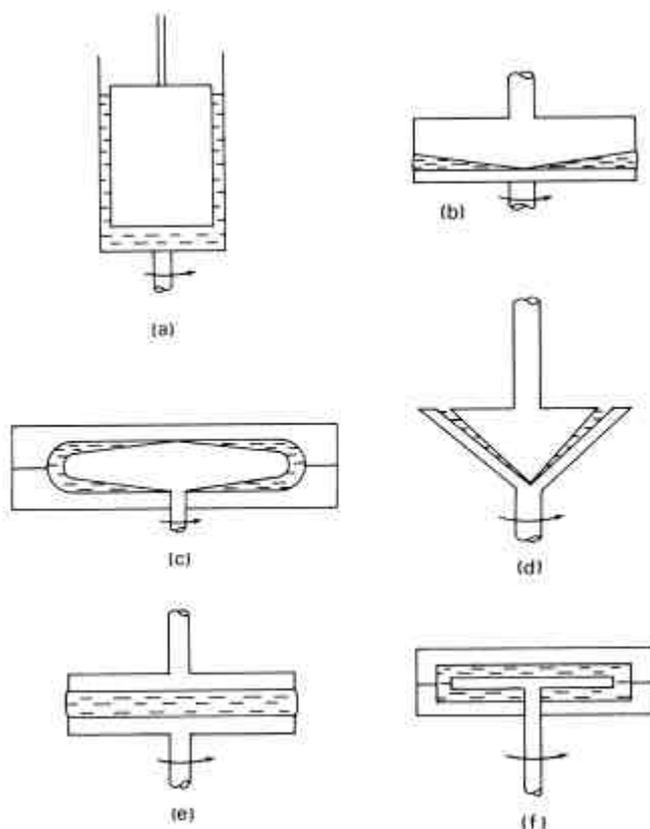


Figure 5: Geometries used for rotational rheometry.

Rotational rheometers are generally calibrated using standard reference fluids (although these are of comparatively low viscosity) but it is possible in many instruments to directly calibrate the torque and position sensors.

Early designs of rotational rheometers, for example the Brookfield type instruments [29, 62] have several user-set motor speeds and give an output as a voltage proportional to torque. The operator then uses conversion factors pertaining to the measurement geometry (normally a bob-and-cup system as shown in Figure 5a) and motor speed setting to calculate shear rate and viscosity. Instruments with computerised control, data acquisition and analysis functions provide more data and offer powerful solutions for qualitative, quality control functions in many industries and quantitative laboratory investigations of fluid properties. There are a large number of manufacturers and suppliers of rotational rheometers.

For the determination of the shear flow properties of adhesives, pastes and other ‘stiff’ materials using rotational rheometers, parallel plate geometries are recommended. The measurement gap should be set to allow the free movement of any filler materials in the test material. ‘Clogging’ problems may occur when solid particles are present and the gap is too small. If the material has a very high viscosity (e.g. highly filled adhesive pastes) then a small diameter geometry, large measurement gap system is required. This is so that torque limits for the instrument are not exceeded. Specialist testing instruments have been developed for ‘stiff’ materials. It should be noted that all rheometers will have a small but finite compliance and that at high torque settings a considerable proportion of the total deformation can be that of the rheometer shaft rather than the sample [49]. This will introduce a significant error into the measurement unless a compliance correction procedure is followed.

3.6.4 Thixotropy, Creep, Sag and Slump

One performance requirement of paste adhesives is often that they resist ‘slump’ or ‘sag’, i.e. once applied they should retain their position and shape under their own weight (in the paint business this would be referred to as non-drip). Many adhesives available on the market are described as ‘low-slump’ or ‘non-slump’ systems although there are no precise definitions.

There are several standard tests, e.g. [72, 73], to characterise slump behaviour. These are subjective assessing:

- Flow of adhesive strips on a vertical panel – furthest distance moved in set period;
- Cylindrical plug on a vertical panel – furthest distance moved in set period;
- Flow from a lap joint – assessment of sag from edge of vertically mounted slot; or
- Flow of adhesive through a hole – identify the diameter of the largest adhesive filled hole from which no adhesive has dripped within the prescribed period after inversion.

In rheological terms, slump resistance requires a high yield (or pseudo-yield) stress and low creep rates. The visco-elastic nature of polymers means that the response of an adhesive paste to an impulse, such as an applied deformation or pressure, will depend on the rate of application and the duration of the impulse. Thus, an adhesive with a high yield stress may flow or ‘slump’ given sufficient time.

Slump behaviour can be studied through creep measurements of the long-term flow of the paste under small but constant stress. Controlled stress rheometers are capable of applying constant loads needed for creep measurements on pastes or soft solids and such instruments are capable of measuring displacement to the high resolution needed to resolve low creep rates. Although paste adhesives can be fully characterised using modern rheological instruments as described there are no standards for determining slump performance using these tests, partly as they require expensive instruments and trained operators.

Slump resistant adhesives often take advantage of thixotropy - *“a decrease of viscosity under constant shear stress or shear rate, followed by a time dependant recovery when the shear is removed”*. This is the property that makes the viscosity of a liquid change with time and may be responsible for flow related problems such as sagging, sedimentation and pipeline blockages. Thixotropy is often confused with shear thinning or pseudoplasticity. Shear thinning materials show a decrease in viscosity under increasing shear loads, but they do not show a time dependant recovery of viscosity unless they are also thixotropic. Hence a thixotropic material is shear thinning, but a shear thinning material is not necessarily thixotropic. In adhesive use, thixotropy can be a benefit. The lowering of viscosity as the

adhesive is strained will aid spreading but the subsequent recovery in structure and thickness will help retain adhesive where it is desired.

Thixotropy can be characterised using rotational rheometers. However, many industries have developed their own “home made” tests to characterise thixotropy. For example, in the ketchup industry some companies characterise their materials by loading the sample into a small reservoir and allowing it to flow down a graded ramp, measuring the distance that the sample flows. This can be done after different intervals between ‘shaking’ the ketchup and opening the reservoir in order to study recovery. The resulting number is related to both the viscosity and the thixotropy of the sample.

4. SURFACE PREPARATION AND CHARACTERISATION

4.1 SURFACE PREPARATION METHODS

The preparation of surfaces prior to bonding is an important stage in most bonding processes. Generally, surfaces should be clean and free of grease to allow the adhesive to wet-out. A degree of surface roughness is normally desirable to increase the adhesive/adherend contact area and promote mechanical keying. The outer layer of the adherend should be stable and firmly attached to the bulk of the adherend so that this does not become the weak point of the joint. Many physical and chemical treatments can be used to alter the surface properties of materials for bonding [16, 75-78].

Surface treatments can be classified as either passive or active [16]. Passive surface treatments (e.g. solvent washing and mechanical abrasion) clean the surface and remove weakly attached surface layers without altering the surface chemistry. Active surface treatments (e.g. anodising, chemical etching, corona discharge and plasma treatment) alter the surface chemistry (i.e. introduction of functional groups). National and international standards give general guidance for the preparation of many surfaces. Many industries or manufacturers will have their own surface preparation procedures. Some of the most common methods are outlined below.

4.1.1 Cleaning

Surfaces are usually cleaned with an organic solvent (e.g. acetone, methanol, isopropanol and methyl ethyl ketone (MEK)) before bonding [75-78]. Many traditional chlorinated solvents have been banned for environmental reasons and there are pressures to reduce discharges of other organic solvents to the environment. Solvent cleaning methods include wiping, immersion, spraying, vapour degreasing and ultrasonic scrubbing. Solvent wiping is the simplest method and is adequate for removing most of the organic contaminants. Substrates are often degreased before other surface treatments to remove gross organic contamination. The requirement is to prepare a suitably clean surface and there are measurement issues relating to monitoring the cleanliness of the surface. Optical methods (e.g. visual inspection, gloss or colorimetry) give information on the appearance of the surface. Spectroscopic methods (e.g. UV, infrared, ellipsometry) may give information on the thickness and chemical nature of any residual contaminant films.

4.1.2 Mechanical Abrasion

Mechanical Abrasion is used to remove weakly adhering or contaminated outer layers of the substrate surface, exposing the bulk adherend material directly to the adhesive or enabling the formation of a suitable surface layer (e.g. an oxide layer on metals). Residual particles remaining after mechanical abrasion are generally removed by blasts of clean, dry air and solvent wiping. Grit blasting is generally the preferred method for abrasion of metallic surfaces, and is widely used for preparing surfaces of polymer matrix composite (PMC) materials. Wet blasting is often considered to give a more consistent surface than dry grit blasting [75, 79]. The technique is not suitable for thin delicate parts or surfaces highly sensitive to surface damage (e.g. plastics). The technique is fast and efficient, and easily controllable. Roughening using abrasive surfaces is common in many industries, e.g. the preparation of leather. Leather or coated textile upper materials are prepared by roughing with a rotary wire brush, in manual or automatic machines. The process not only serves to remove weakly bound finishes and coatings, but in the case of leather removes the outer grain layer composed of weak fibres and raises a strong fibre nap for bonding. It may be necessary to remove 25% of the leather thickness to obtain a good surface. A textured surface, which appears to be essentially split leather and is very rough at the micrometer level often gives poor adhesion. Not only the surface texture but also the roughing depth must be correct. Both are normally assessed visually, even in automatic machines.

The effectiveness of mechanical abrasion treatments is often done through a visual examination but can be quantitatively assessed through roughness measurements (using either stylus or light scattering techniques). The stability of the roughened surface may also influence bond performance but techniques for assessing this are not well established.

4.1.3 Modification of Surface Chemistry

Chemical Etching – is performed to alter the surface chemistry of the adherends. With metallic materials the aim is to form a stable, well-adhered oxide layer [16]. Treatment will also alter the surface morphology. Common chemical etching treatments are either acidic (e.g. phosphoric acid for treating steel) or alkaline (e.g. alkaline chlorite for treating copper alloys). Chromic, nitric, sulphuric and formic acid solutions are used to treat some polymers, as are sodium naphthalene solutions [80, 81]. Chemical etching treatments are multiple stage processes with the etching solution consisting of two or more chemicals. Many proprietary treatments have been developed for treating metallic and non-metallic substrates (e.g. FPL chromic-sulphuric acid etch treatment for aluminium alloys or the Hexcel acid etch treatment for aluminium alloys [82] based on a mixture of chromium trioxide (or sodium dichromate), sulphuric acid and water).

Electrochemical Treatments – anodising techniques [80, 83-87] such as chromic acid anodising (CAA), phosphoric acid anodising (PAA), sodium hydroxide anodisation (SHA) and cathodically deposited aluminium oxide surface treatments are used in some industries for the preparation of metallic surfaces (particularly aluminium and titanium alloys in the aerospace industry). CAA and PAA treatments result in thick, highly porous, stable oxide layers. The oxide layer enhances environmental durability (i.e. moisture resistance), although hydration is known to occur under hot/wet conditions. Surface fibrils (~100 nm in length) protruding from the oxide layer enhance mechanical keying with adhesives. Anodising is often followed by a subsequent surface treatment, such as chromic acid or phosphoric acid immersion in order to seal the surface by blocking the pores.

Electrochemical and etching treatments can be assessed using surface spectroscopy (e.g. SIMS or Auger) to monitor chemical changes or electron microscopy to assess changes in topography. The visual appearance of etched surfaces will change and may be quantified by gloss or colour measurement.

Electrical corona discharge - is a dry surface preparation method used for preparing polymer film surfaces to enhance adhesion of adhesives, inks, paints or coatings [81, 88]. The process, which can be automated (i.e. on-line processing), consists basically of developing a high potential (typically 20 kV) between a stationary electrode electrically connected to the high frequency (10-20 kHz) generator and an earthed treader roll, electrically insulated with a dielectric covering serving as the other electrode. The result is an intense electrical field that ionises the air in the air gap (i.e. corona), which chemically modifies the surface of the material and also increases the intrinsic strength of the substrate/adhesive interface. The ionised particles (i.e. free electrons and ions) in the air gap bombard and penetrate into the molecular structure of the substrate, reacting with oxygen to form polar chemical groups on the substrate surface. Increases in surface energies can be determined using contact angle or wetting measurements.

Plasma treatment - in the form of glow discharges or plasma sprays, has proved effective in preparing the surfaces of metallic and polymeric materials for bonding [9, 89]. Plasma treatment has been successfully applied to titanium alloys, producing a surface oxide layer of uniform thickness and composition. The technique of treating titanium involves rapidly heating TiO_2 , TiSi_2 , MgO or SiO_2 powder to a molten or semi-molten state and then spraying the molten oxide onto the substrate at high velocity. Silicon sputtering has been shown to increase bond strength and environmental durability. The improved properties were attributed to an increased surface tension and surface roughness

Flame treatment - is used to promote good adhesion between thermoplastic substrates (e.g. polypropylene, polyethylene, polyolefins and nylon) and adhesives, paints and inks [81]. An oxygenated flame is used to burn-off contaminants and oxidise the polymer surface. This creates free oxygen, which reacts with the surface forming oxygen containing functional groups, thus increasing the surface energy.

Laser Treatment – is a relatively recent treatment for metal, polymer and polymer composite surfaces [86, 90]. An excimer (i.e. ultraviolet radiation) laser source is favoured because the effect is limited to a thin layer on the surface and surface changes are mainly photochemical. The bulk substrate remains virtually unaffected.

4.1.4 Primers

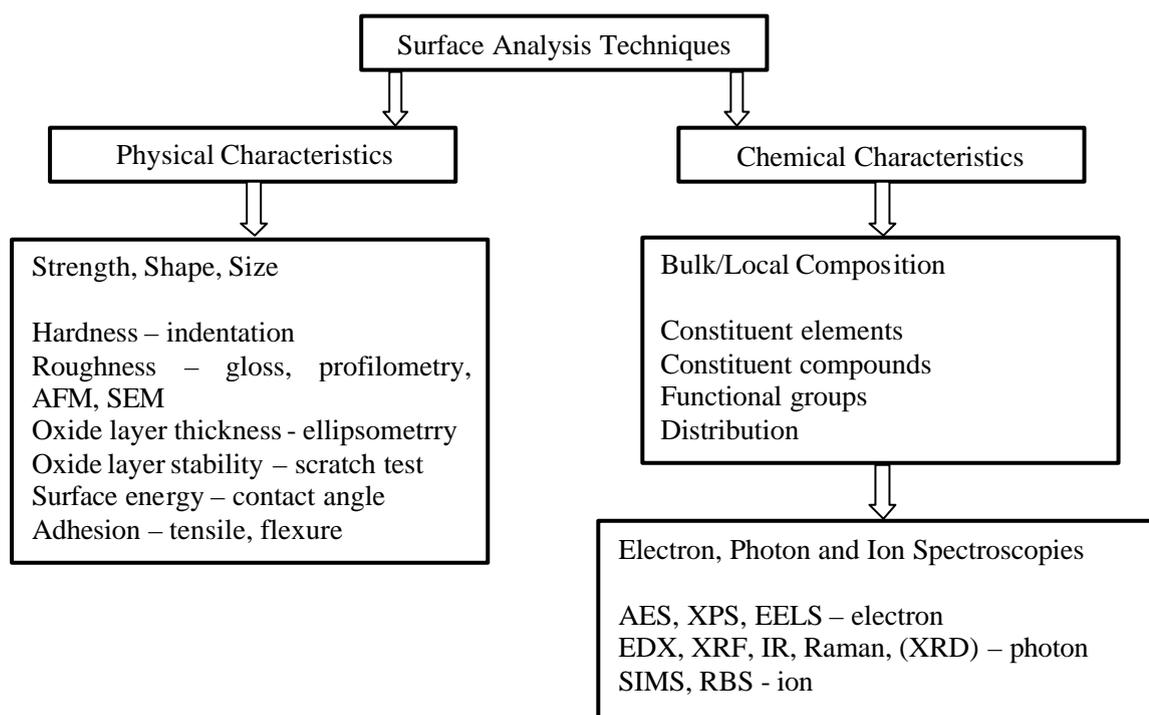
Primers are often applied to metal surfaces before bonding not only to provide corrosion protection but also to enhance adhesion by providing a compatible surface for the adhesive [85, 91]. Primers are low viscosity systems able to completely wet the substrate. Silane or epoxy primers are commonly used to improve durability when bonding to metals. Primers are also used on plastics and rubbers to modify surface chemistry, for example the surface chlorination of vulcanised (SBR) and thermoplastic (SBS) rubbers. Primed surfaces can be checked visually for completeness of *coverage*, aided by use of fluorescent additives and inspection under UV light. Sometimes changes in the material *surface condition* can be detected subjectively; an example is the reduction in friction when thermoplastic rubber is

chlorinated. In general, confirming the effectiveness of the treatment requires wetting tests, contact angle measurements or infrared spectroscopy in the laboratory, or the making of trial bonds.

4.2 TESTS FOR SURFACES

There are many physical and analytical techniques for evaluation of surface treatments to ensure optimum bond strength and environmental resistance for specific service conditions [75, 92]. Techniques range from optical (or non-contact) methods to X-ray photoelectron spectroscopy (XPS). There are methods for the measurement of physical characteristics (surface roughness and morphology, hardness and oxide layer thickness) and chemical characteristics (functional groups and contaminants on substrate surface). Physical techniques, such as surface roughness, hardness and scratch tests, contact angle (for wettability), gloss/reflectivity, ellipsometry and colorimetry, and surface resistivity are available for surface inspection although not all techniques are suitable for on-line inspection (i.e. quality control).

This section reviews methods for assessing surface characteristics associated with mechanical abrasion, solvent cleaning, chemical and electrochemical (i.e. anodising), corona discharge, plasma, flame and laser surface treatments.



4.2.1 Surface Chemical Analysis

There are many techniques to gain information on the chemistry of a substrate prior to bonding. However, even IR spectroscopy, the cheapest of these methods tends to require a significant capital outlay and a degree of user expertise. Thus only larger laboratories and users, such as aerospace, defence or automotive companies, will tend to have such equipment. These techniques tend to be used for adhesive or process development and for failure investigations. The main techniques are briefly covered below [75].

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

X-ray Photoelectron Spectroscopy (XPS): XPS can discriminate different oxidation states and different chemical environments for any element (except hydrogen and helium) by measuring the energies of photoelectrons emitted from atoms of a sample when it is irradiated with soft (or low energy) X-rays. XPS is surface-sensitive with a maximum operational depth of less than 10 nanometres. XPS is frequently used for quantitative elemental analysis of fracture surfaces, to determine the effect of surface preparation on surface chemistry and for monitoring chemical changes in adhesive samples by providing information on chemical structure and bonding and element distribution present on the surface.

Auger Electron Spectroscopy (AES): AES is a surface sensitive, non-destructive technique for identifying the elements in the first few atomic layers (~1 to 5 nanometres) on a specimen surface and is able to provide quantitative data on the detected elements (by comparison with known standard samples). High-energy electron beam bombardment of the surface results in the emission of Auger electrons at characteristic discrete energies. Combined with inert gas ion sputtering, AES can be used to obtain depth composition profiles and, by scanning AES, to map the distribution of elements present on a specimen surface at a spatial resolution of 0.5 μm . The technique is capable of detecting all elements with the exception of hydrogen and helium. Ultra-high vacuum conditions are required to prevent contamination and oxidation of the sample surface.

X-ray Fluorescence Spectroscopy (XRF): In XRF, the target material is irradiated with X-rays, which results in the release of a photon of characteristic energy. Each element has its own set of characteristic emissions and can be used for qualitative and semi-quantitative elemental analysis in a wide range of materials, above aluminium in the periodic table. Minimal sample preparation is required.

Infrared Spectroscopy (IRS): IRS provides information on molecular structure based on specific frequencies associated with internal vibrations of groups of atoms in molecules using a laser in the infrared region to excite the target material and analyse the frequencies absorbed. IRS provides both qualitative and quantitative chemical analysis data and is particularly useful for assessing polymer chemistry. The technique provides a fingerprint of the adhesive or coating composition in any physical state. IRS is not inherently surface-specific but variants, such as attenuated total reflectance and grazing incidence reflectance spectroscopy, improve this aspect.

Raman Spectroscopy: Raman is based on the inelastic scattering of monochromatic light. A laser excites the material, which is usually in the visible region of the spectrum. The frequency of scattered light is analysed compared with incident values. The technique is similar to IRS in determining the nature of molecular structures and is a complementary technique to IRS 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.

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

Secondary Ion Mass Spectrometry (SIMS): In SIMS the surface is bombarded with a beam of high-energy ions resulting in the ejection of molecular fragments, atoms and ions from the surface, which are subsequently analysed (traditionally only the positive ions). It is capable of providing surface elemental analysis and depth concentration profiles on areas from several mm to sub micron. It can detect all elements and isotopes including hydrogen and hydrogenated compounds with very high sensitivity (parts per billion). It is, however, not readily amenable to quantitative analysis (complex and requires reference standards).

Rutherford Backscattering Spectrometry (RBS): This is one of a number of ion scattering techniques, which provide different information depending on the primary ion energy and the scattered ion that is detected. A beam of positive ions is directed at the target surface and the ions, which are scattered by the sample nuclei are measured and analysed.

4.2.2 Surface Topography

The topography or local shape of the substrate can be important in the strength of an adhesive bond. Many surface preparation procedures aim to produce a roughened surface but quantitative values for the degree of roughness are rarely specified or measured. Surface roughness is usually assessed qualitatively through visual inspection. A number of techniques can give further information on topography.

Gloss Measurement: Gloss is a measure of appearance that is affected by the surface finish (e.g. gloss or matt paints). Measurements are made with a reflectometer that project a beam of light (often a laser) onto the target surface at a specific angle and measures the amount of light reflected at the same angle. Surface roughness causes incident light to be scattered at angles other than that of specular reflection, such that the scatter increases with roughness. Hand held devices (ASTM D523 and ISO 2813 [93, 94]) – see also [95, 96] can quantify the surface finish, via the proportion of light reflected at the specular angle, of polymer products and painted surfaces for quality control purposes. Quantitative data on the uniformity and quality of surface treatments can be obtained. More sophisticated, multi-angular techniques based on analysis of the angular intensity distribution of the reflected and scattered light allow parameters related to the surface roughness to be determined.

Scanning Electron Microscopy (SEM): SEM is a widely used surface analytical technique in engineering. High resolution SEM uses reflected electrons to produce qualitative three-dimensional (3-D) images of surface features. It has proved an invaluable tool for studying surface topography, oxide growth and failure analysis. The method 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. The resolution of topographical features is approximately 5 nanometres.

Atomic Force Microscopy (AFM): AFM measures the morphology and topography of surfaces on the atomic scale. A small tip mounted on a cantilever is used to analyse the vertical movements of the probe as it travels over the contours of the surface of the sample (similar principle of operation to the stylus profilometer). There are two modes of operation: contact and dynamic (non-contact), which maintain a constant force or separation to the sample surface respectively. Almost all materials can be studied without the need for sample preparation.

Surface profilometry: This is a term used to describe a number of techniques, which measure surface deviations – surface roughness - and produce a trace or profile of the surface [97]. Contact or stylus profilometers move a loaded probe (usually a diamond) across the target surface and record the vertical movement caused by the irregularities. This is most suitable for hard surfaces, since soft materials can be damaged but reducing the load may result in some surface features not being registered. Resolution is affected by stylus shape; AFM gives molecular scale resolution. Portable stylus instruments are commercially available and there are several relevant profilometry standards [98-101]. Surface shape can also be determined from non-contact optical measurements [98]. A collimated beam of light (often laser) is focused on to a spot on the target and the reflected light analysed. Height differences result in fringes, which can be analysed to yield information about the shape and roughness of the target surface. Currently there are no supporting standards for optical systems, although there are a plethora of instruments on the market.

4.2.3 Surface Layer Properties

There are many test methods for substrates that will give information on the characteristics of surfaces prior to bonding. Many of these are for engineering materials and concerned with their suitability for structural bonding.

Colorimetry: Colour is sensitive to surface morphology and chemical composition and, thus, can be used to detect differences between surface treatments and the degree or intensity of the surface treatment (e.g. exposure time) [102]. Although instrumented colorimetry systems are available for on-line inspection, interpretation and quantification of reflectance spectra of treated surfaces can be expected to be difficult. The equipment is basically a spectrophotometer that measures the intensity of wavelengths in the reflectance spectra.

Ellipsometry: An optical technique that uses elliptical polarised light to probe the dielectric properties of a sample (e.g. thin films) [44]. Ellipsometry can yield information about the thickness, morphology and chemical composition of layers that are thinner than the wavelength of the light source (i.e. less than 50 nanometres). The technique consists of directing a polarised light beam onto a surface at an oblique angle of incidence and measuring the phase change and intensity (amplitude) of the reflected light.

Indentation: Indentation techniques can be used to determine mechanical properties of surfaces and thin films. Hardness is the ability of a material to resist permanent indentation or deformation (or compressive loads) when in contact with an indenter under load [39]. The basic principle behind hardness testing, which includes Rockwell and Vickers indentation tests, and micro-hardness and nano-indentation tests, is to load an indenter into a surface and

measure the deformed imprint after retraction of the indenter. The shape and size of the indent can also provide information on the attachment of the surface layer. Recent developments in instrumented indentation testing enable determination of the modulus of a surface from the unloading curve.

Scratch Testing: The adhesion scratch test is a commonly used method of assessing coating or film adhesion [103]. The test is a variant on a hardness test. A loaded diamond tipped stylus (10 to 60 N) is drawn across the target surface (or the sample is displaced beneath the stylus) under an increasing load (typically 100 Nmin^{-1}) until some well-defined failure occurs, usually flaking or chipping. The type of failure provides information on the coating adhesion strength.

Electrical Properties: Electrical properties of surfaces can give some information about the composition and cleanliness of surfaces. However, techniques are not used routinely and interpretation presents many challenges. Surface resistivity, defined as the electrical resistance of the surface of an insulator and is expressed in ohms/m^2 [104, 105], is measured using two contact electrodes. Surface resistivity is sensitive to surface moisture and decreases with increasing humidity levels. The AC impedance technique has proved successful for characterising oxide films and coatings. It is an electrochemical method used for corrosion studies to measure oxide growth rates. The test surface is immersed in an electrolyte and an alternating voltage is applied. The resistance, capacitance and inductance of the surface and the resistance of the electrolytic solution can be used to determine surface impedance. It is possible to relate film thickness, film composition and oxidation rate for CAA and PAA surface treatments from impedance measurements. Although the technique is unsuitable for on-line inspection, there is considerable scope as a developmental tool and for modelling oxidation processes.

Dennison wax test: This method is designed to measure the surface strength or resistance to picking of a paper (or similarly weak substrate). Calibrated wax sticks of increasing adhesion are melted and pressed onto the paper surface to be tested. The numerical designation of the wax at which the paper surface breaks, picks or lifts provides a measure of the surface strength of the paper [106]. This is sometimes taken as an indication of the ease of hot melt bonding to the substrate.

Fibre Tear Test: Fibre tear is a method used in the packaging industry to assess the quality of bonds to paper and cardboard. A bond is made and then pulled apart manually. The location of failure should be within one of the adherends (e.g. a surface tear). Systems where failure is in the adhesive or cleanly at the interface are deemed to fail the test. No failure loads are determined in this test and some systems may be wrongly rejected – e.g. strong substrates may have good bond ability but fail this test as their strength exceeds that of the adhesive.

4.2.4 Wettability (Surface Energy/Tension)

Wetting is the spreading over and intimate contact of a liquid (adhesive) over a solid surface (substrate). If sufficiently intimate contact is achieved between the two phases, a physical attraction develops causing the liquid to conform to the surface on a macro and micro scale, displacing air and thus minimising interfacial flaws. Good wettability of a surface is a prerequisite for ensuring good adhesive bonding, and hence considerable effort has been

expended in developing simple wettability tests to assess surface energy/tension prior to bonding (see below) [8, 75, 107].

- Water break test (area of spread) [108]
- Contact angle (static or sessile and dynamic) [109-117]

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 (1 dyne/cm is equivalent to 1 mJ/m²). It is dependent on the interfacial intermolecular forces.

The surface free energy of a solid can be indirectly estimated through contact angle measurements. 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. Contact angles are closely related to wettability. A liquid (adhesive) will wet a solid (adherend) when its surface energy is lower than the solid surface energy. Force balance or equilibrium at the solid-liquid boundary is given by Young's equation for contact angles greater than zero (see Figure 6):

$$\gamma_{lv} \cos \theta = \gamma_{sv} - \gamma_{sl} \quad (3)$$

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

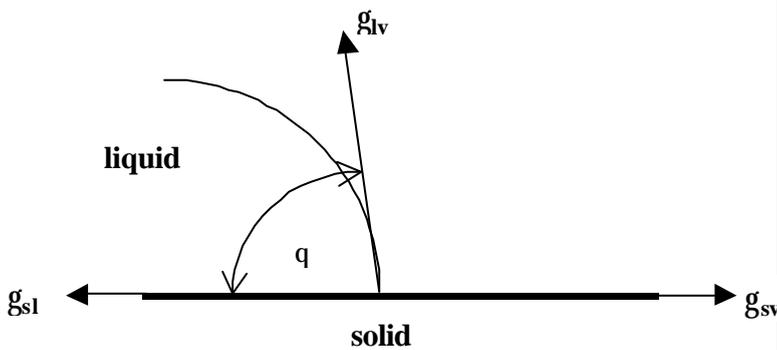


Figure 6: Contact Angle

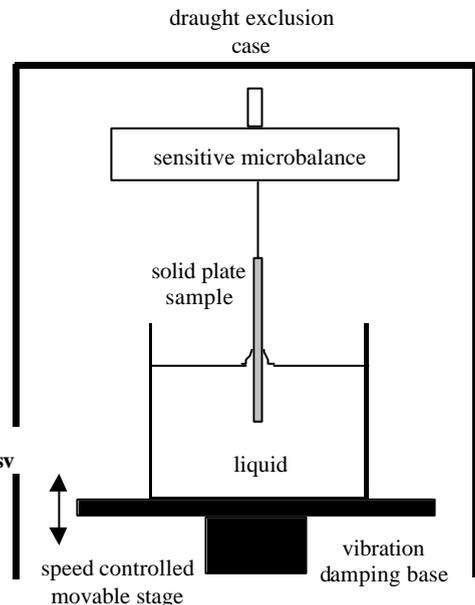


Figure 7: Wilhelmy plate method for measuring dynamic contact angle

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

Two methods are available for measuring contact angles of solid surfaces: static (known as sessile drop or goniometry) [109-115] and dynamic (known as tensiometry or Wilhelmy method) [116]. The static method requires the observation of a drop of test liquid on a solid substrate, while the dynamic method measures the forces of interaction as the solid is immersed in a test liquid. Problems associated with the techniques include swelling of the solid surface, roughness and porosity. Cohesive hydrogen bonding within the test liquids and the solution pH may 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. For porous materials, the observed contact angle will change with time as the probe liquid penetrates the surface.

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. Commonly used probe liquids for measuring contact angle include distilled water, glycerol and methylene iodide (typical drop size is 2 to 20 μl). Analytical instruments can be used to measure the contact angle of a water droplet placed on the surface of a film [112]. In the packaging industry contact angle is measured according to Tappi Methods for papers [114] and for polymer film surfaces [115]. However, this technique is not commonly employed, as it is perceived as time consuming and requiring a degree of interpretation of the results.

Dynamic Contact Angle: can be measured using the force-balance technique, using rectangular Wilhelmy plate specimens [116]. The forces exerted as the solid/liquid phase boundary is moved along the sample surface are measured (Figure 7). The contact angle may be calculated from the forces of interaction, sample geometry and liquid surface tension. This technique involves placing the sample on a balance and zeroing at the solid weight. The liquid (of known surface tension) is raised to meet the solid and the point of contact is determined and recorded as zero immersion depth. The solid continues to be lowered into the liquid to a set depth and the forces on the balance are continuously monitored. The process is then reversed and the solid is raised from the liquid until the liquid film ruptures. Dynamic contact angles measured at low speeds should equal static contact angles.

Both the advancing (q_{adv}) and receding (q_{rec}) angles can be measured. The difference ($q_{\text{adv}} - q_{\text{rec}}$) 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. However, 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.

Quicker and simpler methods exist for fast inspection of the wettability of surfaces. These are the water break test and wettability (or dyne) pens.

Water Break Test: This qualitative (go/no-go) test involves the specimen (in the form of a flat plate) being either immersed in water or water brushed or water sprayed onto the surface [108]. The plate is then checked to determine the distribution of water on the surface (i.e.

remains as a continuous film indicating good wettability or forms distinct droplets indicating poor wettability). Other liquids can be used for wetting break tests.

Wetting Pens: This semi-quantitative test [117, 118] involves marking the surface with a pen containing ink of a known surface tension and observing whether or not the initial continuous line breaks into distinct droplets (indicating that the surface energy is lower than the surface tension of the ink). ‘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. Despite the widespread use of these solutions, the method has notable critics [119]. The shelf life of pens can be limited, particularly if in regular use, as transfer of contamination from surfaces to the ink may occur.

5. ASSEMBLY

Following preparation of the surfaces and application of the adhesive the next stage is assembly. There are several process issues likely to affect this stage. Part of the quality control procedures of any bonding process is likely to include bond strength tests. These may be carried out at different points of the process, e.g. to assess initial ‘stick’ or ‘tack’, degree of cure, bond strength or even (with appropriate conditioning) durability. The testing of structural adhesive joints has received comparatively greater attention than other types of joints and thus will not be covered in this review.

5.1 DRYING

Many adhesives are dispersed/dissolved in an organic solvent or water in order to produce a low viscosity system that can be applied easily. The presence of solvent when the joint is closed can have deleterious effects on the performance of the bond. In extreme cases where heat is applied to cure the adhesive ‘boiling off’ of solvent could pop the joint open. Therefore, the adhesive must be essentially dry and free from solvent or water at bonding otherwise the green bond strength may be reduced. Residual solvent may also cause damage to thermoplastic materials if it is driven off at higher temperatures. Judging the *completeness of drying* of an adhesive coat relies on touch, smell or weighing. Smelling is not to be encouraged with solvent-based products, for health reasons. Weighing is more suited to laboratory trials than production.

One advantage of water-based adhesives is that the degree of drying can be checked very easily using a small conductance probe of the sort used to check dampness in buildings, and these are now used by adhesive technologists in shoe factories.

5.2 ABSORPTION OF ADHESIVE

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 can be subjective. The Cobb absorbency test [120] 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.

5.3 ACTIVATION OF ADHESIVE

Dry adhesive films deposited from solvent/water-based systems, common in industries such as footwear, are inert at room temperature. They must be heated to enable the adhesive films to be decrystallised and made tacky. Typically, infrared heating is used to bring the adhesive temperature to over 45°C. The film on one surface may be heated to 80-90°C, warming the second cold film when it is brought into contact. Alternatively both surfaces may be heated to about 60°C.

Measuring surface temperature after heat activation is well established, using either melting crayons or an infrared pyrometer 'gun' [121]. If a pyrometer is used it must be responsive to the correct wavelength range, about 7 -15 micrometres, otherwise misleading results will be obtained.

5.4 OPEN AND SETTING TIMES

The assembly of parts must be done in the period when the adhesive can be worked but before it sets. The open time may be limited by on-going cure reactions (e.g. in two-part systems after mixing) or cooling beneath a setting temperature in the case of hot-melt or heat activated adhesives. There are standard test methods for working life of two-component systems, e.g. [38], but as discussed earlier these tend to be subjective. Bonding or tack tests at different parts of the process cycle can be used to determine open times.

The softening temperature defines a lower working limit for hot melt adhesives. The softening point of a hot melt adhesive is usually measured by the ring and ball method [122]. The temperature at which a steel ball penetrates a pre-formed disc of resin located in a ring is determined by steadily increasing the temperature until penetration occurs. Less commonly, the Vicat softening temperature of the adhesive is determined [123]. In this test procedure, the temperature at which a flat-ended needle of 1mm² cross-section penetrates the resin to a depth of 1mm, under a specified load, is measured under a steadily increasing heating rate. Thermal analysis methods such as differential scanning calorimetry (DSC) or dynamic mechanical analysis (DMA) can also provide information on the softening and melting temperatures of polymers [124].

The softening temperature is one factor affecting the open time. The other factor is the rate at which the adhesive and substrate cool. This is determined by the materials and thermal mass of the system, the starting temperature and environment (external temperature, air flow, conductive coupling to heat sinks). Thus, cooling rates are not easily calculated. They can be determined or monitored through temperature measurements either using contact probes such as thermo-couples or resistance thermometers or through non-contact methods such as pyrometers.

For many adhesives where the setting or cure reaction is activated by an external stimulus (e.g. heat or UV radiation) open times are effectively infinite and the parts can be reworked as required although common sense dictates that it is better to avoid leaving an adhesive open

to the environment for longer than is strictly necessary. Similarly cyanoacrylates or anaerobics that cure instantly in small gaps when the joint is closed have no true 'open' times but evaporation of volatiles may limit the time between application and joint assembly.

5.5 POSITIONING

On assembly, assessing manual alignment of components tends to be subjective although digital image analysis methods offer automated methods of checking alignment. One consideration in the process is whether a component can be reworked to correct alignment or positioning problems. This is possible if there is sufficient open time.

A common process requirement is that the adhesive should fix a joint until further process operations are performed. For example, loosely combined assemblies may need to remain intact as they are handled and passed to a press or oven for final cure. This requires sufficient initial adhesion or 'tack'. In footwear assembly where tack is a critical property it is also known as 'spotting tack', as it allows part of the sole to be 'spotted' or secured locally to the upper while the remainder is aligned. Upper limits of tack are also important so that parts can be detached and re-bonded if necessary. Footwear adhesives usually have sufficient tack to allow a misaligned, incorrectly spotted, sole to be detached and the process repeated.

There are a number of different tests for permanently tacky, pressure sensitive adhesives as often used for adhesive tapes. Tack of heat activated adhesive is often measured subjectively, for example by manually spotting heated test pieces, although the SATRA/NPL tack tester allows heat activated tack to be measured in the laboratory [125].

5.6 PRESSING AND JIGGING

Assembled parts often need to be pressed or jugged to hold them in position and contact until set sufficiently. This is potentially a process rate limiting operation and can increase manufacture costs. Faster curing systems can reduce jugging time. Accurate knowledge of cure development, potentially supplied through cure monitoring, can be used to speed processes. The important factors in this stage of the operation are pressure and temperature.

Correct pressure and pressure distribution is important to ensure that all parts of the components being bonded are brought into contact with the adhesive and a sufficiently uniform bond thickness is produced. This is particularly important when bonding flexible materials or large sheets that deform under pressure. The overall pressure in the bonding press can be determined from the total thrust, pneumatic or hydraulic, which is applied. However, it is the pressure distribution that is critical and this can be checked with pressure sensitive film [125] or a pressure capsule such as SATRA Pressrite (comprising of a sensing element enclosed in a partly inflated bladder). Pressure distribution measurements in the footwear industry are carried out using simple techniques such as sheets impregnated with pressure sensitive resistive inks, carbon paper print (e.g. SATRA Pressure Pack a sandwich of a pimpled rubber sheet, carbon paper and plain paper) or dimpled aluminium sheets (e.g. SATRAFoil).

The temperature of the system is important during bonding. For heat-cured adhesives the correct temperature is needed to ensure that cure reactions proceed as expected. For hot melt or heat activated adhesives temperatures need to be controlled to ensure the correct adhesive

properties for bonding. Over-temperature may cause as many problems as under-temperature. If an adhesive is too hot, the viscosity may be too low to allow proper gap filling and it may penetrate porous materials excessively or strike through the material. If it is too cold then flow will be limited and bonding will be inadequate. Temperatures should be kept below the material limits to avoid degrading either the substrate or the adhesive. With reactive systems, large exotherms may be generated by chemical reactions and heat rises may become significant in thick bondlines, particularly over 5 mm. Temperature can be monitored by embedded thermocouples or remote infrared pyrometry.

5.7 INITIAL FIXING AND TACK

Often pressing or jiggling are inappropriate in the manufacturing process. There are many instances, such as shoe manufacture, where an adhesive is required to hold parts in place until a later part of the process. This can be achieved through 'instant' stick adhesives with a high tack or by using an adhesive paste with sufficient wet strength.

5.7.1 Tack

Tack is a measure of how 'sticky' a substance is [126]. It is the property of a material that enables it to form a bond immediately on contact with another surface, which may be an adherend or another layer of adhesive, under light pressure. Although not all adhesives (e.g. film epoxies) are tacky at room temperature, tack is of great relevance to industries such as packaging and footwear where rapid processing is essential. Control of tack is important so that the right level of initial bond strength is achieved. If the tack is too low then the bond may rupture during manufacture or if the tack is too high then repositioning of substrates may be difficult.

Tack, normally determined from the force required to separate two components, is often measured as part of the quality control procedures of an adhesive manufacturer or user. The simplest 'instrument' for determining if something is tacky is the thumb. Obviously, this is rather subjective and, depending on the adhesive or processing conditions, is potentially hazardous to the operator. The measurement of tack is normally specific to a particular application. Different measurement standards and methods have evolved within industries [126]. Tack is not a fundamental material property but depends on a wide range of factors including the method of testing. Therefore, the results from different tests are unlikely to be directly comparable.

To achieve high tack, the adhesive needs to wet the surface and spread to form a continuous interface between the surfaces. High wetting energies are associated with strong adhesion to the surface. High tack forces on separation are associated with effective wetting of the surface. Thus, tack gives an indication of how quickly an adhesive can wet and make intimate contact with a surface. The adhesive must fully wet the two surfaces to form a continuous film to achieve maximum tack strength. Therefore, the tack will depend on the pressure applied, the time history of the applied pressure and on the flow (or rheological) properties of the adhesive. These in turn imply that the rate at which the surfaces are brought together and separated will influence the measured tack force. Since the properties of the adhesive, substrate or interface may change with time, the dwell time will also be important. Results from different tack test measurements are rarely comparable [126].

The most widely used methods for measuring tack are:

- loop tack test [127-129];
- probe tack test [130, 131];
- rolling ball test [132-134].

5.7.2 Loop Tack Test

Loop tack testing involves lowering a loop of tape being tested on to a rigid plate until it makes contact over a known area (Figure 8). The direction of travel is then reversed and the force required to separate the loop from the plate is measured. Depending on the method used, the adhesive can be applied to either the tape [127, 128] or the plate [129].

A widely used tack test method in the UK is FINAT Test Method Number 9 (FTM9) [128]. The loop is made from a strip of tape 25 mm wide and at least 175 mm long. The plate is made of “Float Process” glass 25 mm wide, so that the area of contact is 25 mm square. A tensile tester or similar machine is used. The crosshead speed setting is 300 mm per minute.

5.7.3 Probe Tack

The probe tack test is based on an ASTM Standard [130]. The equipment was initially developed in the 1950s, and is commercially available [131]. The tape specimen is applied to an annular weight (to control force), and positioned above a cylindrical probe. The probe is raised to make contact with the specimen, held for a fixed time, and then the force required to cause separation is measured. The machine enables systematic studies of tack to be performed. Tack can be studied as a function of contact pressure, dwell time, probe speed and probe material.



Figure 8: Loop tack test



Figure 9: Rolling ball test

5.7.4 Rolling Ball

The rolling ball method [132-134] is simple to carry out and the equipment (Figure 9) is inexpensive. A ball is rolled down an incline on to the tape being tested. Tack is related to the inverse of the distance rolled before the tape stops the ball. The method becomes less accurate at longer travel. Choosing different incline angles, incline heights or type of ball, can vary the test to suit the type of adhesive being tested. However, results from different test equipment will not be comparable. The rolling ball test is intended primarily as a comparative method for quality control.

The backing material of the tape or the thickness of the adhesive layer can significantly influence the results from this test. A thick, 'soft' backing or a thick layer of adhesive will absorb a significant proportion of the kinetic energy of the ball and thus bring it to a stop earlier. Where the adhesive coating is thin, the area of contact between the ball and adhesive will be small (as the ball will not sink as deep) and the stopping distance will be longer.

5.7.5 Quick Stick

Quick stick tests [135-137] are similar in many ways to tack tests. They characterise the ability of an adhesive to adhere instantly to a surface through the resistance to peel tape at a 90° angle from a standard surface. Tests are carried out in a tensile test machine using a special fixture to assure that the edge of the peel is always directly beneath the grips. The initial 25 mm of peel are ignored and the quick stick is measured from the force required to peel the remainder of the tape. Some quick stick tests specify pressing on the tapes with a standard 25 g roller and in all tests the dwell time between application and removal will be longer than those commonly employed in tack tests.

5.7.6 Wet Strength

In some applications, e.g. circuit board assembly, the part will move around several stations before the adhesive used is finally cured. The parts are held on to the substrate only through the paste-like behaviour of the adhesive. The consistency of this adhesive needs to be such that the parts do not move as the assembly moves through the various process stages. The ability of the adhesive to prevent parts moving is assessed in electronics assembly through 'sledge' tests – a board with several standard electronic components (of different sizes) slides down an inclined ramp until it hits a stop at the bottom of the ramp; the position of the components is measured to assess the wet strength of the adhesive. The physical properties of the adhesive needed to achieve a good wet strength are the same as those needed for slump resistance and it should be possible to quantify these through rheological measurements.

6. CURE IN ADHESIVES AND RESINS

Being able to monitor the curing process in adhesive and resin materials is important for achieving efficient processing of these types of material. As well as providing a means of optimising efficiency, the monitoring process can help to monitor and prevent errors during the production process.

Adhesives are applied as liquids or soft, deformable solids (e.g. film adhesives) to enable them to wet out adherend surfaces to form intimate contact and provide high interfacial strengths. However, for joints to have useful strength the adhesive must cure or harden. ‘Cure’ is normally described as irreversible and can take place via cross-linking reactions (e.g. epoxies, polyurethanes), polymerisation reactions (e.g. acrylics) or vulcanisation (rubbers). Reversible changes in physical state (e.g. in hot melts) are not strictly covered by the term cure but also provide mechanisms for development of strength in joints. Cure often requires initiation by energetic means (e.g. heat, UV radiation) or chemical species (e.g. hardening agents, condensation reactions, metal catalysts). Cure times can range from seconds to days or weeks depending on adhesive chemistry and the application. Cure time can be a significant portion of the bond manufacture time.

This Section presents some details of the types of chemical and physical processes that occur during the cure of polymeric materials. This is followed by details of the available techniques for cure monitoring, along with an assessment of their suitability as a cure monitoring method. The techniques that have been used to-date by industry are described, and industry’s requirements for the future are outlined.

6.1 DEFINITION OF “CURE”

The key feature of the curing process is that the adhesive or resin material starts as a liquid and during the course of cure it changes to a solid. There are several ways, or mechanisms, by which this change of state from liquid to solid can occur and these mechanisms have their basis in either physical or chemical processes.

Terms describing different points in the cure cycle are given below.

Application Time/Life, Pot Life, Pore Time – synonymous terms for the period from the onset of cure during which the adhesive is still capable of being transferred to the site of cure. There are no formal definitions for these properties and the mode of application will influence the defined time. One suggested definition is the time for the viscosity to double [35-38].

Work Life, Working Time – distinguished from previous terms in that during the work life the adhesive is still capable of being reworked even if it cannot be applied. This point is further into the cure of the material [35-38].

Gel Time – the point at which an infinite molecular network forms and the mix becomes significantly less able to flow under light forces [39]. Can be determined by various standard methods [138-141].

Tack-Free Time, Demould Time – a key point in the development of cure when the material is sufficiently robust to resist damage from contact or handling [142, 143]. Normally at the tack free time the adhesive will be dry to the touch.

Cure Time – the time until completion of the chemical reactions providing cure. Cure time can be determined using thermal methods (e.g. monitoring of exotherms using isothermal DSC) or through the development of a property (e.g. stiffness, strength, hardness).

6.2 PROCESSES OCCURRING DURING CURE

Adhesive and resin materials can achieve cure, or hardening, by three main processes:

- Removal of a solvent or dispersing medium
- Cooling
- Chemical reaction

The basis of these three processes is described briefly in the following sections.

6.2.1 Removal of solvent or dispersing medium

Polymeric materials can be either be dissolved or dispersed in a solvent, which can be organic based or water, to give the liquid form of the adhesive. This liquid is then applied to the substrate and the solvent either evaporates or is absorbed into the substrate, leaving behind the solid polymeric material, which acts as the adhesive between the substrates. In the case of porous substrates like paper and wood, the two substrates to be joined can be brought together whilst the adhesive is still wet and the adhesive left to harden by absorption of the solvent or water. This is the basis if many woodworking and paper glues like PVA (poly(vinyl acetate), casein and starch. With non-porous substrates the solvent must be allowed to evaporate before bringing the two substrates together, and this is the mechanism of many contact adhesives based on polychloroprene. There are many other examples of polymer materials used as the basis for the adhesive component in solvent or dispersion type formulations [8, 144].

6.2.2 Cooling

Adhesives that cure and harden using the cooling method are generally based on thermoplastic polymers. The basis for the process is that thermoplastic materials will soften when heat is applied allowing them to wet the surface of a substrate. On cooling, the thermoplastic will then re-solidify regaining its cohesive strength and thereby join the two materials together. Adhesives that use cooling as their method of cure will initially need heat to be applied, which leads to their general classification as hot-melt adhesives. The main limitation with hot-melt adhesives is that because they are thermoplastic they will necessarily have an upper operating temperature.

There is a wide range of thermoplastic materials that have been used as hot melts, one of the most common being the copolymer of ethylene and vinyl acetate (EVA), used in book-binding. Other polymers that have been used include polyethylenes and polyamides as the main examples, although there are examples of more exotic polymers such as poly(ether ether ketone) (PEEK) being used when higher operating temperatures have been needed.

6.2.3 Chemical reaction

Adhesives can achieve the liquid-to-solid transition by means of chemical reaction whereby the liquid precursor polymer materials, or resins, react in some way, to form a solid, cross-linked network of molecules. There are two main mechanisms by which this cross-linking can occur, either step-growth polymerisation or addition polymerisation. The details of the reactions are beyond the scope of this review, since understanding these reactions essentially forms the basis of the whole subject of organic chemistry [8, 145].

On a practical level, adhesive users will need to know how to make the curing chemical reaction occur and this will depend on whether the adhesive is classified as a one-part or two-part adhesive system. As is suggested by the name, two-part systems consist of two separate components, often called the adhesive and hardener, which are stored separately. The adhesive and hardener are usually supplied in the form of liquids or pastes. Storage can be in separate containers, or in cartridge systems, the latter helping to provide the user with the adhesive and hardener in the correct ratio. When they are then combined, by mixing in some way, a reaction occurs forming a cross-linked network of molecules. Heat is often generated during the curing reaction process and this is known as an exotherm.

One-part adhesives have all of the components necessary to form the final adhesive contained in a single liquid or paste form. One-part adhesives will contain an activator or catalyst chemical component that is triggered, often by heat or some form of radiation like ultra-violet (UV). This means that these one-part adhesives often have to be kept either cold or in sealed containers, and they will have an expiry date, after which they will no longer be active.

There are many different types of one and two-part adhesives and the cross-linking reactions that occur can lead to adhesives that are rubbers, thermoplastics and thermosets. Typical adhesives that cure by chemical reaction include phenolics, epoxies, acrylics, polyurethanes, silicones and polyimides. More information on the range of different types and suppliers/manufacturers of these one and two-part adhesives can be found in various sources [23, 146].

6.3 CURE MONITORING

6.3.1 Available Techniques

There are a large number of processes that have been used to monitor the progress and final state of cure in adhesive and resin systems. A recent literature survey revealed over 20 techniques that have been investigated for use as cure monitoring methods. It is helpful to group these into generic types of technique, and seven general groupings can be identified:

- Chemical
- Electrical
- Mechanical
- Microstructural
- Optical
- Thermal
- Ultrasonic

The various cure monitoring techniques in each of these seven groupings are described in more detail in the following sections.

6.3.2 Chemical Techniques

There are several techniques that can be considered as chemical methods for monitoring the cure of adhesives and resins. The common feature of all the techniques is that they monitor some aspect of the curing process at the atomic or molecular level of the material, where changes are occurring to the atomic or molecular species as the polymer changes from a liquid to a solid material. These chemical techniques are described in the following sections.

Infrared (IR) spectroscopy is a key tool used by chemists to characterise polymeric materials. It makes use of the fact that for polymeric materials the chemical bonds between the atoms in the polymer molecules can vibrate at frequencies in the IR range of the electromagnetic spectrum, i.e. at wave numbers from 100-4000 cm^{-1} . For a molecular motion to be IR active there must be a change in the electric dipole of the molecule. By directing IR light at a polymeric material and measuring the absorption (or transmission) of the various frequencies, it is possible to characterise, or “finger-print”, the polymeric material since it will have specific frequencies at which it is seen to absorb strongly. This “finger-print” of the various frequencies at which the material absorbs is referred to as the IR spectrum. There are various ways of performing IR spectroscopy on a material, and probably the most widely used is known as Fourier transform infra-red or FTIR.

As the cure process for a polymeric material progresses the numbers of a particular chemical bond can either decrease or increase, depending on whether the chemical species is a precursor or final product. By monitoring the IR spectrum of the adhesive as the cure progresses – and chemical species are either consumed or created – the IR absorption intensities relating to these chemical species will change. This change in intensities is the basis of cure monitoring techniques, since it gives direct information about the timescale within which the chemicals involved in the cure reaction have been used and the reaction is complete.

The evolution of the chemical curing process has been successfully followed using IR spectroscopy in laboratory conditions [147], but applying the technique into the factory environment has many potential problems. These include: the method of introducing the IR beam into the sample (see Section 6.3.6 on optical techniques); calibration of the system to give stability and repeatable information; the cost of IR spectrometers and the personnel to use them.

Nuclear Magnetic Resonance (NMR) spectroscopy uses the interaction between a magnetic field and the nuclei of the atoms making up a material to provide characteristic information about the elements and the chemical environment they are in. The NMR technique is only possible with elements that have non-zero nuclear spin. For a detailed description of the theory behind the NMR technique, the reader is referred to more detailed texts [148]. The number of elements with this property of non-zero nuclear spin is somewhat limited and for this reason NMR has mainly been used to study hydrogen and carbon (through the carbon-13 isotope). Both these elements are key constituents in polymeric materials, hence the use of NMR to study them. Like the IR technique described above, particular polymeric materials have unique NMR spectra, or “finger-prints”, that characterise those materials.

NMR can be used to study the evolution of cure by monitoring changes in the NMR spectrum, which indicates that a particular element is changing its chemical environment, i.e. it is undergoing a reaction. The change in the spectra can be monitored in time and the extent of the cure reaction determined. Although chemists have used the NMR technique extensively for the development of new resins and adhesives, and research has investigated its potential for cure monitoring [149, 150], its use in factory production situations has not been attempted. This is due to the cost and the fact that the item being monitored must be placed inside a strong magnetic field. Medical institutions routinely magnetic resonance image (MRI) scan whole people, but this is not at all trivial, and at present an NMR based technique would not be practical in an industrial cure monitoring situation.

Raman spectroscopy is somewhat similar to IR spectroscopy, in that it uses the IR part of the spectrum to interact with the molecules in the adhesive or resin material. The interaction is based on the observation that an incident beam of monochromatic IR light will have a very small amount of light scattered at discrete frequencies just above or below the frequency of the incident light. The phenomenon is similar to that of Rayleigh scattering but the changed frequency light effect is called Raman scattering, with the radiation known as either Stokes' or anti-Stokes' depending on whether its frequency is respectively lower or higher than the incident frequency [148].

The Raman scattering effect depends on whether the molecule being studied has molecular rotations or vibrations that cause some change in a component of the molecular polarisability. The amount of Raman scattered light is very small in comparison with the amount of incident light, and sensitive apparatus is required to detect it. For this reason, Raman spectroscopy has not been studied extensively for use in cure monitoring.

Visible and Ultraviolet techniques rely on resin and adhesive molecules interacting with visible and ultraviolet (UV) radiation, through changes in the electronic structure of the molecules. As the electrons in the molecules change their energy state, they radiate energy in the visible or UV parts of the electromagnetic spectrum. There are three main mechanisms for this process:

- re-emission - where energy is re-radiated at the energy at which it was absorbed, to give an emission spectra;
- fluorescence – whereby some of the energy of the incident radiation is lost, for example through intermolecular collisions and as heat, and the re-radiated energy is therefore at a lower frequency;
- phosphorescence – in which the transition from the electronic excited state is delayed by internal molecular processes and the re-radiation continues, usually at a lower frequency than the incident, for many minutes or even hours after the initial absorption.

These three processes can theoretically be used to monitor the state of cure either through spectroscopic techniques, examining a range of frequencies, or by measuring the intensity of a particular frequency. There have been several studies of these types of techniques, some of which have used fibre optics [151]. Although the techniques can give some information about the cure state, there have been few applications in industry, which may be related to difficulties in applying these techniques when the materials that the resin/adhesives are used with are opaque to visible and UV light.

6.3.3 Electrical Techniques

Dielectric cure monitoring tracks changes in the viscosity and cure state of the resin by monitoring changes in the dielectric properties of the material. Dielectric measurements are made by measuring the voltage and current between a pair of electrodes in order to determine the conductance and capacitance. In cure monitoring of polymers it is the conductance property, or its inverse the resistivity, that is the more useful measure.

The conductance of a material is dependent on the mobility of ions within the material, when they are subjected to an electric field. The ions encounter viscous drag as they move through the medium, and the ions' mobility, which is governed by the viscosity of the medium, determines the conductivity. As a resin material cures, the viscosity of the material changes, which affects the conductivity and hence the dielectric measurement. The ionic conductivity of polymeric materials is non-Ohmic because of the accumulation of ions at the polymer-electrode interface, which leads to polarisation effects. These polarisation effects cause difficulties in trying to model the dielectric aspects of the curing process, which means that it is difficult to define a single parameter that represents the behaviour of the material. The consequence of this difficulty is that in practice the dielectric technique has to be calibrated empirically against the cure cycle of the resin/adhesive system.

In spite of this limitation, the dielectric technique has received wide attention for cure monitoring, mainly because the sensors do not have to be positioned within the curing material [152-154]. Dielectric studies have also been the subject of work by NPL [155] as part of a Performance of Adhesive Joints project, funded by the DTI. The dielectric technique has been used by industry to monitor the cure of resin and adhesive materials and has been shown to be effective, once the initial calibration has been performed.

Electrical resistance of an adhesive can be used as a measure of the state-of-cure, although this is most applicable to conductive adhesives, such as those used in microelectronics that have silver, or other metallic filler particles. The technique works by measuring the current flowing through the adhesive and observing the changes in resistance as the adhesive cures. There is a marked decrease in resistance as the adhesive cures, associated with the formation of the cross-linked network and stabilisation of the filler particle locations, so that current can flow more easily [156, 157]. Since the technique requires a conductive adhesive, it is only applicable in a limited range of industrial applications and is not suitable for development as a general cure-monitoring method.

6.3.4 Mechanical Techniques

Hardness measurement is a simple technique for determining the extent of cure of an adhesive or resin. The hardness of a material is determined by the extent to which the material has cured, and since hardness is also related to the modulus of the material, a hardness value gives an indication of the mechanical properties. Various hardness measurement scales are available and those used for polymeric materials include the Shore A-D scale and the Barcol (Barber-Colman) scale. These can also be related to the Rockwell, Brinell and Vickers hardness scales, although these latter three are more usually used with metals and ceramics than polymers [103].

The procedure for determining the extent of cure would be to measure the hardness value and compare this with a pre-determined value from a sample known to have reached the required state of cure. Several readings of hardness will be required to ensure that a statistically representative area has been tested. The technique has the limitation that it can only be used once the cure process is completed and is not suitable for on-line or real-time monitoring. In spite of this limitation it is very useful as a quick QA/QC method and is widely used by industry.

Quasi-static mechanical testing is a possible method for determining the cure state of an adhesive or resin. Samples of the adhesive would be subjected to the same cure cycle as the item being manufactured, and these samples would then be tested mechanically. The samples could either be made from bulk adhesive or adhesive material bonded to substrates. The mechanical tests could be of many different forms and loading modes, such as tensile, compression, flexure or torsion, depending on the requirements. There are many test standards available for mechanical testing [1-3].

The results of the mechanical test provide information on the properties of the adhesive material and can be compared with the expected properties for a correctly cured adhesive. Any difference in measured and expected properties would be evidence of incorrect cure. The advantage of this test type is that a direct measure of a material property is made, giving some certainty as to its mechanical performance. The disadvantage of mechanical tests is that the test is performed after the adhesive has cured, rather than during the cure process. This means that the tests cannot be used for real-time cure monitoring, and the technique is better suited as a QA type process. An additional disadvantage is that preparation and testing of samples can add time and cost, although this is somewhat dependent on the complexity of the tests chosen.

Dynamic loads can be used to provide information about the state of cure of an adhesive or resin. In many ways the techniques are similar to those for quasi-static tests and have the same advantages and disadvantages. There are variations that use heat combined with dynamic loading and these are considered further in the Section on thermal techniques.

6.3.5 Microstructural Techniques

There are various techniques available to determine the microstructure of materials and it is possible for these techniques to give information on the state-of-cure of adhesives and resins. Techniques that can be used include scanning electron microscopy (SEM), transmission electron microscopy (TEM), standard optical microscopy, and X-ray scattering [144, 149]. Micro-structural analysis can give information on the degree of crystallinity in thermoplastic polymers and also on the distribution of the different phases of a material, such as the rubber toughening particles in epoxy and other adhesives. The techniques can examine the surface of the substrate prior to bonding, to confirm that the appropriate surface treatment has been applied, and can give information about the interface formed between the adhesive and the substrate. SEM and TEM can be used for examining the fracture surfaces of bonded joints after testing or failures in-service, to determine the failure mode.

Most of the techniques require samples to be taken after the cure of the adhesive material, so that the techniques are not readily applicable to on-line cure monitoring. Much of the equipment for performing the analysis techniques is expensive, so that although the

information obtained is useful for chemists, materials scientists and engineers, the cost of the equipment might be difficult to justify solely for cure monitoring.

6.3.6 Optical Techniques

Optical methods can be used to monitor the progress of cure in adhesives and resins. The availability of optical fibres is the main technological driver that has allowed optical techniques to be developed. In many applications the optical fibre is used as a convenient means of introducing the actual measurement technique, such as infrared or Raman spectroscopy [147]. The means by which the fibre optic is connected to and interfaced with both the component and the measuring equipment presents its own technical challenges, but the actual monitoring of the cure is based on the characteristics and capabilities of the technique being introduced through the fibre optic.

Other optical techniques that have also used fibre optics include measuring changes in either the refractive index or strain. The strain measurement method makes use of Bragg gratings that are etched into the optical fibre, the Bragg grating providing a reference point for length changes in the optical fibre. The length change is determined by measuring the wavelength changes to the input light that is reflected from the Bragg grating. The optical fibre is placed into the resin before cure and as the resin cures it bonds to the fibre, inducing strain in the fibre. The strains in the fibre can be correlated with the resin curing process and this has been shown by NPL [158] to be a viable method of determining the extent of cure. This optical fibre strain measurement process is currently a topic of further development work as part of the DTI funded Measurement for Materials Systems (MMS) suite of programmes, MMS10, "Cure Monitoring for Shorter Cycle Times", with NPL as the project lead organisation.

Attempts have been made to use the changes that occur in the refractive index during the cure of a resin to monitor the progress of the cure. These efforts have yielded some advances, but there are difficulties due to the fact that the refractive index does not change very much during the later stages of cure, when the main development of the resin mechanical properties is occurring.

6.3.7 Thermal Techniques

Information about the physical state of a polymeric material can be obtained using thermal analysis methods. In particular the glass transition temperature (T_g) of a polymeric material gives information about its service temperature, state-of-cure and moisture content. The most common thermal analysis techniques are reviewed below.

Dynamic Mechanical Analysis (DMA), also known as **Thermal Mechanical Analysis (TMA)** obtains information about the mechanical properties of a material by applying a sinusoidal load to a specimen and measuring the resultant deformation, whilst the sample is subjected to a controlled temperature programme [64, 124]. The load-deformation response of the sample can be used to provide information about the storage, or elastic, modulus and the loss, or viscous, modulus of the material. The ratio of loss and storage modulus is reported as $\tan \delta$. A plot of a typical DMA trace is shown in Figure 10, which shows how the storage modulus, loss modulus and $\tan \delta$ values would vary with respect to temperature. The applied load can be in various modes such as tension, compression, flexure and torsion, so that a wide range of sample types and materials can be investigated.

Although the DMA technique can be used to obtain information on the modulus of the material, the values calculated are very sensitive to the dimensions of the sample. The main strength of the DMA technique is in determining the glass transition temperature (T_g), since the storage and loss moduli undergo marked changes at the T_g . Various analysis points are used on a DMA plot that can be considered representative of the T_g value. These points are marked on Figure 10 and include the inflection point in the storage modulus and the peak of the loss modulus and $\tan \delta$ curves.

Differential scanning calorimetry (DSC) is a technique that measures the difference between the heat flux into a sample of material under investigation and into a reference sample, as a function of temperature and/or time, while the samples are subjected to a controlled temperature profile [124].

DSC can be used to study a range of properties of polymeric materials including melting and crystallisation behaviour, the glass transition temperature (T_g), specific heat capacity and the curing behaviour. DSC is a well-established technique and is used extensively to characterise polymers. Samples for DSC testing should ideally be flat, to allow good thermal contact between the sample and the pan of the DSC equipment, and of uniform composition.

Advantages of the technique are that a small sample size is required, typically 5-20mg, fast heating rates can be used to obtain data quickly, and there is relatively good reproducibility. The disadvantages of the technique are that because a small sample is used it may not be totally representative of the whole bulk of material. The sample for testing must also be removed from the manufactured item after the cure has occurred, which means that the test can not be performed in real-time or on-line. For some materials it can be hard to assign a T_g value, either because the wrong thermal transition has been assigned as the T_g or because there may be only a small change in heat flux as the T_g is passed through during the temperature ramp.

Rheological Testing: There are several methods by which the rheological properties of a polymer can be determined [49]. Methods include measuring the mass of polymer that flows from a container in a given time or using equipment that measures the torque applied to a sample, which can then be used to determine the shear stress. The properties can be measured as the cure progresses. These methods are well suited to quality control of adhesive/resin materials prior to use, to determine whether they are still within specification. For cure monitoring during production, a separate sample would be required and would need to be subjected to the same cure cycle as the manufactured item. This latter requirement introduces some practical difficulties, which makes the technique less suitable than other possible techniques.

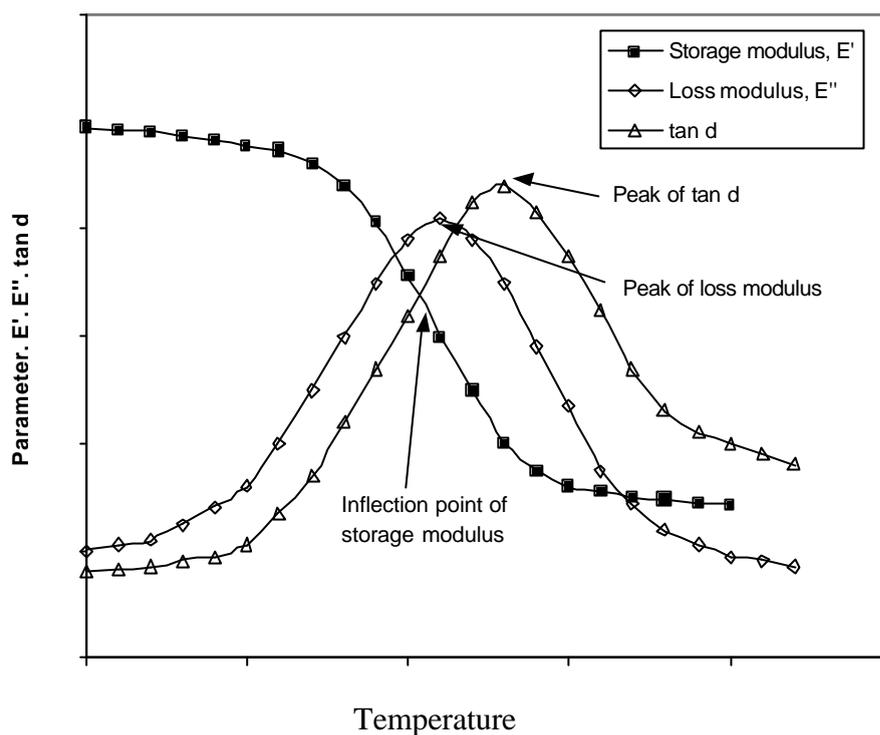


Figure 10: A representative plot of a dynamic mechanical analysis (DMA) trace showing the three potential analysis points

Thermal Gravimetric Analysis (TGA) is a technique that measures the change in mass of a sample as it is exposed to increasing temperature. It provides information on the thermal degradation characteristics of the material. The technique is not particularly sensitive to the changes in adhesives and resins due to different states of cure and this is the main reason it has not been developed further for cure monitoring.

Temperature monitoring: Thermocouples and other temperature sensitive devices can be used to monitor the temperature during the curing process. The monitoring process compares the measured temperature with the specified cure temperature of the material. If the temperature is too low the resin/adhesive will be uncured and if the temperature is too high then the material can be degraded. The specified cure temperature for the material must be known beforehand; otherwise the comparison cannot be made between measured and required temperatures. The technique is simple to implement and use, but it does not make any direct measurement of a physical property of the material, and is therefore reliant on good batch-to-batch consistency of the resin/adhesive.

6.3.8 Ultrasonic Techniques

Standard ultrasonic: It is possible to use the speed of sound in an adhesive material to monitor its state-of-cure. The technique works due to the fact that the velocity of a sound wave is directly related to the modulus of the material, through the relationship:

$$E_l = \rho V_l^2 \quad (4)$$

Where E_l is the longitudinal elastic modulus, ρ is the density and V_l is the longitudinal wave velocity. As a one-part thermoset adhesive material cures its viscosity will initially decrease, due to the applied heat, and then the viscosity will increase as the cross-linking occurs. These changes in viscosity coincide with changes in the modulus, first a decrease followed by an increase, which will similarly change the velocity of sound in the material – a decrease followed by an increase in the velocity. By using probes that emit and detect ultrasound these changes in modulus can be detected, which then provide information on the viscosity and hence state-of-cure of the adhesive. It is also possible to determine information about the visco-elastic properties of the adhesive by monitoring the attenuation of the ultrasound signal. The attenuation of the ultrasound is at a maximum when losses due to viscous effects in the material are at a maximum, and this coincides with the glass transition temperature (T_g).

For the ultrasonic velocity technique to work it is necessary to accurately know the dimensions of the material, so that the velocity can be calculated by measuring the time and dividing by the distance travelled, and this is where the largest potential problems occur. Adhesive materials are usually used in thin layers, which makes the thickness dimension small, so that very accurate time measurement, of the order of nano seconds, is required to detect the change in velocity, which might only change by a factor of two or three. A second problem is that adhesive materials sometimes shrink during cure, which changes the dimensions, so that the time change is now due to both a modulus change and a distance change.

These problems can largely be overcome and ultrasonic probes have been successfully used in the manufacture of wood laminates [159, 160] and for the monitoring of cure in epoxies for concrete repair [155, 161].

Acoustic emission (AE): AE is another possible method for cure monitoring. This technique is based on using ultrasonic emission events, which are created by the curing adhesive, rather than using an ultrasound probe as in the standard ultrasonic technique. The technique requires calibration for different types of adhesive and the AE events that occur have not yet been related to specific physical phenomena arising within the curing adhesive. However, statistical analysis of the AE events has provided evidence for joints with good or poor cure and this suggests that the technique has some potential [162].

6.4. INDUSTRY EXPERIENCES

6.4.1 Cure Monitoring Techniques used in Industry

The cure monitoring techniques currently used by industry are summarised in Table 1. The generic industry sector is given, along with the techniques that the sector is using and any comments about how the technique is applied.

Table 1 Cure monitoring techniques used by various industry sectors.

Industry sector	Cure monitoring techniques used	Comments
Aerospace	temperature (thermocouple) and time FTIR DSC DMA dielectric	Any measurement device that needs placing in the material uses a separate sample from the production part.
Defence	temperature (thermocouple) DSC mechanical tests – stiffness	Mechanical tests samples taken from each production part.
Marine	temperature (thermocouple) hardness (Barcol)	
Transport	temperature (thermocouple)	
General fabricator	temperature (thermocouple or colour change sensor) and time hardness (Barcol) DSC dielectric mechanical tests rheology	Different organisations used different techniques, dependent on the level of sophistication of the final product.

The range of techniques used by industry to monitor cure appears to be quite wide. However, this appearance is somewhat deceptive, since in some of the industry sectors there are only a few organisations operating and not all of them use all of the techniques. The most widely used technique is monitoring of the temperature during cure, with hardness testing, used as a QA check, as the second most common technique.

There is a general trend for high value-added and lower volume industries, such as aerospace, to use more types of, and more sophisticated, cure monitoring techniques. This trend is consistent with the need for greater confidence and evidence that the cure process has been performed correctly on products with higher costs and with more demanding performance requirements.

For industry sectors operating in higher volumes, possibly with lower performance requirements, or perhaps with less serious consequences due to under-performing product, there is the general trend for using less cure monitoring equipment. In some organisations no

cure monitoring instrumentation is used and the assessment of cure relies totally on the experience of the workforce.

6.4.2 Future Cure Monitoring Requirements and Techniques for Industry

At present a gap exists between the theoretical work performed on cure monitoring and what industry is both able to use and able to afford. The techniques that give the most useful information are often not easy for industry to implement and are often too costly. The economics of a particular business or industry sector need to be considered. Adhesives or resins may not be particularly expensive in relation to other parts of the product or costs of the process, so that any cure monitoring technique will need to be cheap enough so that cost savings will be greater than the cost of the equipment.

Some users of adhesives and resins have remarked that it can be hard to find skilled staff able to operate cure monitoring equipment. This is probably a reflection that some of the techniques are very much in the development stage, so that only the researchers who have developed them are able to use the equipment and comprehend the output or results. The techniques need to be further developed to be more robust and with simplified outputs indicating perhaps just “good” or “bad” cure. This will not be a trivial task, since the large range of resin types and curing situations necessarily makes monitoring the cure complicated, and some of the techniques use very sensitive measurements, which are not straightforward to make rugged.

There are many possible techniques, over 20 different ones have been reported, that can be used to monitor the cure of resin and adhesive materials. Many of these techniques have been investigated by researchers, with equipment being developed and reported on, although much of this has been in academic institutions rather than industry. Some of these techniques have been used by industry, but the up-take has generally been limited, with the exception of some high value-added industries such as aerospace.

Cure is recognised as an important part of the production cycle for many polymeric substances, e.g. thermosetting resins and composites. Therefore, cure and cure monitoring is covered in a separate project within the MMS programme (MMS10).

7. SUMMARY

Adhesive bonding is a key manufacturing technology. However, the adhesive industry suffers from a perception within certain industries that its products are a low technology commodity item and, hence, the choice of adhesive for a given application is largely based on cost alone. This is compounded by the lack of measuring techniques available to distinguish performance and processability differences.

In order for adhesive manufacturers to market their products more effectively and for manufacturers to optimise production line performance, the critical application and bonding parameters of both adhesives and substrates need to be quantified. Across many industries considered there is little bonding process monitoring on the production line other than that involving measurement of temperature and pressure. This is perhaps not surprising as these two properties are relatively easy to measure whereas others are more elusive.

There are many different types of processes and materials that can be involved in the manufacture of an adhesive bond. There are many measurement and inspection methods that could be used to improve the bonding process but are either unsuitable or not used for many reasons. The limitations to the wider use of many measurement techniques in general industry are mainly due to three factors:

- cost of the equipment in relation to the value of the product and processing costs;
- ease of implementing the technique in a production environment;
- poor availability of skilled operators to use equipment.

Although many factors influence bonding effectiveness, there are some aspects of the adhesive bonding process that are key to nearly every operation. These are in the areas of flow characteristics, substrate characterisation and inspection, wettability and adsorption on surfaces, initial bond strength and cure. Some of these aspects are interlinked (e.g. flow characteristics and wetting/adsorption).

The key areas needing to be addressed, identified in this project are:

- Techniques for characterising rheology of adhesives for high rate and intermittent dispense processes.
- Quantitative techniques for slump properties and wet strength.
- Inspection of rough and porous surfaces for suitability to bond (e.g. for roughness, porosity, surface layer strength).
- Measurement of substrate wettability, in particular to water-based and hot melt adhesives.
- Measurement of adhesive spread and adsorption on surfaces.
- Determination of tack and setting rates of adhesives with transient properties (e.g. hot melts).

To be useful to industry any measurement techniques developed to meet these needs should be suitable for use on the production line or in small workshops. If this is not possible, then the techniques should be suited to industrial laboratories and depend on robust easy to use equipment. Not least, techniques must be cost effective in order to enable industry to justify their use.

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APPENDIX I: PACKAGING SECTOR NEEDS

Introduction

Adhesives are widely used in many industries for rapid joining, and a key performance requirement is the formation of a reliable bond with sufficient strength and durability.

However, in many industries, including packaging, users tend to operate in relatively low technology environments with low margins, and they are unable to invest in sophisticated analysis equipment. Therefore, simple, quick methods and guidance on good practice for characterising and producing suitable surfaces for bonding are required by industry. Also, greater understanding of adhesive processing characteristics will help reduce scrap rates, cut production costs, enable higher production rates and accelerate the uptake of new materials and processes.

Flexible adhesives, such as hot melts, are widely used. Bonds need to be made rapidly and therefore tack, wetting, cure and high rate rheological properties of the adhesive are critical. The physical characteristics of the materials to be bonded are highly varied; they can be 'hard' or 'soft', 'flexible' or 'rigid', 'porous' or 'non-porous'. Examples include corrugated board, paper, plastic films, rubbers or leather. Simple, quantitative techniques to assess the readiness/receptiveness of these surfaces for bonding rarely exist. Also the coating weight of the adhesive and the proportion absorbed into the substrate can be important factors in achieving the highest bond strength. The quality control techniques that are available are often based on specific industries and processes.

Task 1 of the 'Efficiency Improvements in Rapid Bonding Processes' project is a technical review of process measurements. The specific task of Pira International is to identify industrial measurement needs and existing techniques in the packaging industry by evaluating techniques in the literature and through interviews with companies. This report is a summary of those findings.

Methodology

The adhesive bonding of packaging materials is dominated by polyvinyl acetate (PVA) based emulsion adhesives and ethylene vinyl acetate (EVA) based hot melt adhesives, if the starch and dextrin adhesives used for corrugated cases are excluded (Table 1). It is therefore these two adhesive types that have been studied.

Table 1: UK adhesives production, breakdown by type (%)

Type	1993	1997	2002
Starch and emulsion	14.1	14.2	13.9
Solvent-based	8.3	6.1	3.9
PVA* emulsions	32.1	32.6	31.2
Acrylic	10.2	9.9	9.0
Hot melts	10.9	11.3	12.7
Others	24.4	25.9	29.3

*PVA = polyvinyl acetate

Source: Faraday Technical Review

The measured techniques in academia were found to be largely limited to the determination of surface energies by contact angle.

In order to establish the current measurement practices in the packaging industry a combination of interviews with selected companies and questionnaires were used.

Table 2 below, summarises the number of companies contacted and number of replies received, by sector.

Table 2: Companies contacted by Pira across the packaging supply chain

Sector	Questionnaires/Meetings			Comments
	Sent	Replied	% returned	
Adhesive manufacturers	22	14	64	Majority of UK manufacturers of packaging adhesives
Substrate manufacturers	33	5	14	Selection of paper, cartonboard, film manufacturers
Packer/Fillers	27	10	37	Selection of cereal, tea, pizza, ready meal, biscuit, drinks, healthcare packer/fillers

1.1 Adhesive manufacturers

To ensure batch-to-batch consistency of adhesive production, a few quality control tests are used and these are common to all adhesive manufacturers. These are for hot melt adhesives:

- Brookfield viscosity
- Softening point by ring and ball (occasionally Vicat)

and for PVA (dispersion) adhesives:

- Brookfield viscosity
- Solids content.

Brookfield viscosity

The Brookfield test method for the determination of apparent viscosity is carried out according to BS 2782: Part 7: Method 720C: 1992 (ISO 2555: 1989)⁽¹⁾.

Brookfield viscometers employ the principle of rotational viscometry; they measure viscosity by sensing the torque required to rotate a spindle at constant speed while immersed in the sample fluid – the resin in a liquid state. The torque is proportional to the viscous drag on the immersed spindle and thus to the viscosity of the fluid. Both Newtonian and non-Newtonian fluids can be measured. Most resins are non-Newtonian and the measured viscosity depends on the velocity gradient to which the product is subjected. For these viscometers, the velocity gradient is not the same for every point of the spindle, hence the result is not strictly the ‘true velocity at a known velocity gradient’ and therefore is conventionally called the ‘apparent viscosity’.

However, Brookfield viscometers are easy to use, accurate and flexible – hence their wide use – and measurements can be made on a small quantity of adhesive either quickly for an instantaneous result or over time if required.

Also the viscosity at the temperature of application provides an indication of dripping or ‘stringing’.

Softening point

The softening point of a hot melt adhesive is usually measured by the ring and ball method (BS 2782: Part 1: Method 12A: 1992)⁽²⁾. The temperature at which a steel ball penetrates a pre-formed disc of resin located in a ring is determined by steadily increasing the temperature until penetration occurs.

Less commonly the Vicat softening temperature of the adhesive is determined (ASTM D1525-8)⁽³⁾. In this test procedure, the temperature at which a flat-ended needle of 1mm² cross-section penetrates the resin to a depth of 1mm, under a specified load, is measured under a steadily increasing heating rate.

Softening point is generally used as a second quality control procedure to ensure the right combination of chemicals has been used; comments suggested that, at best, it only provides a very crude indication of heat resistance.

Solids content

The solids content is determined by drying the PVA (dispersion) adhesive to constant weight in an oven.

Less frequently, and often only for product development or problem solving, the following were used:

For hot melts:

- differential scanning calorimetry
- melt flow index
- rheology
- infra-red spectroscopy
- gas liquid chromatography

and for PVA adhesives:

- grit analysis
- infra-red spectroscopy
- pH
- film clarity and wetting.

When developing adhesives for new applications the following performance parameters were most commonly measured for hot melt adhesives:

- thermal stability
- open time
- setting time
- tack
- temperature resistance (high or low depending on application)

- creep resistance (resistance to long term failure under sustained loading) and for PVA (dispersion) adhesives:
- open time
- setting time
- adhesive spread
- tack
- temperature (high or low depending on application)
- creep resistance.

The adhesive joints are generally handmade and therefore the compressive force to manufacture the bond was not measured; the adhesive often being applied to the substrate using a wooden spatula in the preparation of hot melt bonds, or a sheer cube for the preparation of PVA bonds. In the overwhelming majority of cases the acceptability of the adhesive joint was judged by whether fibre tear occurred when the joint was ruptured, and the quality by the depth of fibre tear.

In only a few cases was the wettability/receptivity of the surface investigated. Depending on the application this was by:

- water drop contact angle
- Visking dyne solutions/Sherman pens
- Dennison wax (pick)
- Absorbency (Cobb).

The contact angle that the liquid makes with the surface (wettability) provides a measurement of the adhesion that will occur. It can be measured according to Tappi Method T458cm-94⁽⁴⁾ for papers and Tappi Method T565pm-96⁽⁵⁾ for polymer film surfaces. This technique is not commonly employed as it is perceived as time consuming and requiring a degree of interpretation of the results.

More commonly, the principle of a liquid spreading to determine surface tension is employed, as detailed in ASTM D2578-99a 'Wetting tension of polyethylene and polypropylene films'⁽⁶⁾. This forms the basis of commercially available 'dyne solutions', which determine the suitability of these pre-treated films for ink adhesion (often referred to as Sherman pens). Despite the widespread use of these solutions, the method has notable critics, including W A Zisman⁽⁷⁾.

The Dennison wax test is designed to measure the surface strength of a paper or its resistance to picking (Tappi Method T459om-93 'Surface strength of paper, wax pick test')⁽⁸⁾. Calibrated wax sticks of increasing adhesion are melted and pressed onto the paper surface to be tested. The numerical designation of the wax at which the paper surface breaks, picks or lifts provides a measure of the surface strength of the paper. This is sometimes taken as an indication of the ease of hot melt bonding to the substrate.

Absorbency (Cobb) provides a method of determining the water absorptiveness of sized paper and board under standard conditions (BS EN 20535: 1994)⁽⁹⁾, and hence an indication of the setting time of water based adhesives.

1.2 Substrate Manufacturers

The testing that is undertaken in order to ensure that the surface of the substrate is suitable for adhesive bonding largely replicates that of the adhesive manufacturer:

- fibre tear
- Cobb absorbency
- water drop contact angle
- Dennison wax pick.

These tests are often linked to a customer trial.

At least one substrate manufacturer examines the properties of the boards using an ultrasonic method to determine the rate and depth of liquid penetration relevant to the bonding of PVA adhesives. The equipment is manufactured by 'emco GmbH' in Germany.

1.3 Packer/Fillers

Packer/fillers usually carry out a combination of laboratory assessment and production trial to ensure satisfactory adhesive bonding. The laboratory assessment includes fibre tear and temperature resistance if the pack may be exposed to extremes of temperature. Creep resistance is occasionally checked.

The production trial primarily is to check the runnability of the adhesive, but fibre tear is usually checked, and less frequently application weight and product compatibility.

1.4 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 6mm 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 a microwave detection system for disc wheel gluers, CLNT 100, which monitors the moisture content in the glue flap. It is claimed that it can operate at up to 800m/min, but has the disadvantage of not being suitable for foil board when the microwaves are reflected.

In addition, the company manufactures laser scanners and infrared 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 300m/min.

Most of these on-line glue monitoring systems can be also used to monitor or be 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 cost typically starts at about £15k provided the company already has the glue wheel, code reader and ejection system, although £30-50k is a more typical price. Hence, in the past companies have not fitted such equipment. However, with faster cartoning 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.

Constraints on industry measurement techniques

1.5 Adhesive manufacturers

It is not uncommon for a company to produce 20-40 batches of adhesive per day. Any measurement used for quality control purposes must therefore take minimal time and give unequivocal results. This accounts for the limited range of testing currently undertaken.

MFI, widely used in the plastics industry for batch quality control, has been little used for hot melt adhesives for two reasons:

- A lack of reference data and, to date, a correlation with specific machine performance criteria.
- Hot melt viscosities are typically lower than most polymers at their application temperature and hence are difficult to measure by MFI.

For development purposes the wide variety of substrates often limits the benefit of general viscosity measurements and necessitates the specific substrate to form part of the measurement equation. Hence the current need for time-consuming and costly production line trials.

1.6 Substrate manufacturers

Substrates are usually manufactured against physical and cost specifications – adhesive bonding performance is rarely considered, if at all.

In many instances where the bonding characteristics of the substrate have been compromised, they have been sacrificed for greater aesthetic or barrier requirements.

The onus for satisfactory bonding is placed on the adhesive manufacturer.

1.7 Packer/fillers

Many packaging converting processes operate at high speed e.g. side seam gluing of cartons can reach 90,000 cartons/hour. On-line monitoring systems provide verification of the glue having been applied (often a customer driven requirement), albeit at cost. However, bonding performance is judged universally by the presence or absence of fibre tear. Difficulties arise

when either the substrate is weak and fibre tear strength is below the end use requirements or where the substrate is strong and failure occurs elsewhere in the structure.

The latter may still give a bond of adequate strength.

As in the case of adhesive suppliers, the high speed demands of production necessitate a quick and easily interpreted measurement system. An additional factor is that production resource is often limited and so simple, low cost techniques are needed.

Ideally, packer/fillers would prefer a single adhesive grade for all their on-site applications, thereby avoiding accidental use of the wrong adhesive.

Measurement opportunities

The adhesive industry suffers from a perception within the packaging industry that its products are a low technology commodity item and hence the choice of adhesive for a given application is largely based on cost alone. This is compounded by the lack of measuring techniques available to distinguish performance differences.

In order for adhesive manufacturers to market their products more effectively and for packer/fillers to optimise production line performance, the critical application and bonding parameters of both adhesives and substrates need to be quantified.

Areas needing to be addressed are:

- Quantification of quality of adhesive joint other than by the means of fibre tear alone.
- Adhesive viscosity characteristics need quantifying using techniques appropriate to the application method.
- Measurement of adhesive spread.
- Measurement of substrate wettability to both water-based and hot melt adhesives.

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APPENDIX II: PROCESSES AND PROCESS MEASUREMENTS FOR FOOTWEAR, CLOTHING AND FURNITURE INDUSTRIES

INTRODUCTION

The manufacture of consumer products such as footwear, clothing and furniture requires assembly processes to combine materials of differing characteristics. Adhesives are widely used through their ability to join dissimilar materials, with joints which are durable but at the same time are unobtrusive and do not detract from the aesthetics or handle of the finished product.

Wherever possible rapid bonding processes are preferred, to speed up production and reduce work in progress. Demanding joints may require lengthy multi-step processes - from materials preparation, through adhesive application and drying, to bonding - but even here the bonding step is rapid and may depend on transient phenomena such as tack.

With the nature of the materials and the bonding processes much of the process monitoring is subjective, and there are few numerical measurements other than for temperature and pressure.

This report reviews the bonding processes and current monitoring techniques. It summarises some measurement needs, mostly common to more than one industry or product, which would benefit from cost-effective techniques suitable for use on the production line or in industrial laboratories.

FOOTWEAR: SOLE BONDING

The sole bonding or sole attaching process is the most critical assembly operation in footwear manufacture. The joint is almost always between a fibrous leather or textile upper material and a smooth polymer-based sole material, and has to be relatively strong compared with flexible bonded joints in other products – a peel strength requirement of 5 N/mm is typical.

In order to ensure sufficient joint strength the material surfaces have to be prepared, and to ensure adequate wetting the adhesive must be of low viscosity at application. Solvent borne adhesives are well established, but water-borne adhesives are increasingly used to meet health and safety and environmental regulations, which restrict solvent vapour emissions in the workplace and to the outside atmosphere. Polyurethane adhesives predominate as they can bond a wide range of materials given correct surface pre-treatment, but polychloroprene adhesives continue to be used for bonding leathers and rubbers.

To achieve short bonding times and increase the productivity of the sophisticated presses needed to consolidate the upper-sole joint with its complex curvature, the adhesive is allowed to dry and the dry film activated by heating. It must then have good tack and quick setting properties to provide sufficient initial 'green' strength to prevent the sole from springing away.

Accordingly, the bonding process requires several steps:

- Prepare upper material
- Prepare sole material

- Apply adhesive to upper material
- Apply adhesive to sole material
- Dry adhesive

- Activate adhesive
- Assemble sole and upper
- Press

The following notes outline these steps, the process aspects that are monitored and the current techniques.

Preparation of upper

Leather or coated textile upper materials are prepared by roughing with a rotary wire brush, in manual or automatic machines. The process not only serves to remove weakly bound finishes and coatings, but in the case of leather removes the outer grain layer composed of weak fibres and raises a strong fibre nap for bonding. It may be necessary to remove 25% of the leather thickness. A textured surface that appears to be essentially split leather, which is very rough at the micrometer level, gives poor adhesion. Not only the *surface texture* but also the *roughing depth* must be correct. Both are assessed visually, even in automatic machines.

Preparation of sole

Some types of soles are cleaned with solvent to remove contaminants, for example plasticisers from PVC or mould release agents from polyurethanes. Others are treated with solvent-borne chemical primers that modify the surface, for example the surface chlorination of vulcanised (SBR) and thermoplastic (SBS) rubbers.

Cleaned or primed soles can be checked visually for completeness of *coverage*, aided by use of fluorescent additives and inspection under UV light. Sometimes changes in the material *surface condition* can be detected subjectively, an example is the reduction in friction when thermoplastic rubber is chlorinated. But in general, confirming the effectiveness of the treatment requires wetting tests, contact angle measurements or infrared spectroscopy in the laboratory, or the making of trial bonds.

Adhesive coating of upper and sole

Adhesive *coverage* and *coating thickness* are checked visually. The coating weight can be determined by weighing, and an average per unit area calculated, but this is easier to carry out on test pieces than on shoes on the production line. The degree of adhesive *penetration* into absorbent surfaces is important – if the adhesive soaks in too readily into a porous upper material a change in viscosity or the application of a second coat may be necessary, if it fails to wet the surface properly poor bonds are likely. Short of carrying out scanning electron microscopy (SEM) on cut sections, this can only be assessed visually by experience.

Drying of adhesive

The adhesive must be essentially dry and free from solvent or water at bonding otherwise the green bond strength may be reduced. Residual solvent may also cause damage to thermoplastic materials if it is driven off during heat activation. Judging the *completeness of drying* of an adhesive coat relies on touch, smell or weighing. Routine smelling is not to be encouraged with solvent-based products, for health reasons! Again, weighing is more suited to laboratory trials than production.

One advantage of water-based adhesives is that the degree of drying can be checked very easily using a small conductance probe of the sort used to check dampness in buildings, and these are now used by adhesive technologists in shoe factories.

Activation of adhesive

In this process the adhesive films are decrystallised and made tacky by infrared heating to over 45°C. The film on one surface may be heated to 80-90°C, warming the second cold film when it is brought into contact. Alternatively both surfaces may be heated to about 60°C. Measuring *surface temperature* after heat activation is well established, using either melting crayons or an infrared pyrometer 'gun'. If a pyrometer is used it must be responsive to the correct wavelength range, about 7 -15 micrometres, otherwise misleading results will be obtained.

Assembly

On assembly, assessing manual *alignment* of components is subjective. The adhesive must have sufficient *tack* - known as 'spotting tack', as it allows part of the sole to be 'spotted' or secured locally to the upper while the remainder is aligned. Adhesives usually maintain sufficient tack to allow a misaligned, incorrectly spotted, sole to be detached and the process repeated. The tack also enables the loosely combined assembly to remain intact as it is handled and passed to the press. Tack is measured subjectively, for example by manually spotting heated test pieces, although the SATR/NPL tack tester allows heat activated tack to be measured in the laboratory.

Pressing

The pressing operation conforms the sole to the upper at all points and consolidates the joint for a short period, usually no more than 10-15 seconds, to allow it to start to set and develop green strength. The *overall pressure* in the bonding press can be determined from the total thrust, pneumatic or hydraulic, which is applied. But it is the *pressure distribution* that is critical and this can be checked by making a carbon paper print with the SATRA Pressure Pack or by using SATRAFoil.

The Pressure Pack comprises a sandwich of a pimped rubber sheet, carbon paper and plain paper which is pressed between the upper and sole and the quality and uniformity of the resulting print gives an assessment of the adequacy of the applied pressure and its distribution. SATRAFoil is aluminium foil which has dimples that compress under correct loading to form 'moon craters' and again, the degree and evenness of the effect gives an indication of the effectiveness of the pressing operation.

FOOTWEAR: ANCILLARY ADHESIVE APPLICATIONS

Ancillary adhesive applications in footwear mainly utilise water-borne and hot melt adhesives. They have a less demanding strength requirement than sole attaching, bond strengths of 0.5 – 1.0 N/mm being typical, and retaining the aesthetics and handle of the materials is often important. However such processes often involve rapid adhesive application and bonding, and especially important are the porosity of surfaces, adhesive wetting and penetration, and tack - together with the setting rate for hot melts.

Applications of water-borne adhesives

Natural rubber latex is used for many purposes, giving good wet stick and ‘grab’. Synthetic emulsions or dispersions such as acrylate, polyvinyl acetate, polychloroprene and polyurethane types are used where better adhesion or plasticiser resistance are required, although they have relatively poor wet grab.

Laminating

Natural rubber latex adhesive applied by brush or roller, or by spray to both surfaces, is used to laminate upper components. Bonding is by wet stick or after brief drying. Polyurethanes are used for strong, plasticiser resistant bonds but require heat activation after drying.

Binding, folding, covering

Natural rubber latex is also used to bond edge binding strips to insoles, secure folded strapping materials and attach covers to shoe heels or platform soles. The adhesive is applied by roller coater to bindings and strapping and partly dried before bonding by in-machine rollers. Covers are coated with natural rubber latex or polychloroprene by spray, brush, roller and allowed to dry before bonding to the heel or platform, which is usually precoated with polychloroprene solution.

Bonding stiffeners

Fibreboard heel stiffeners, premoulded to shape, are dipped in adhesive and inserted between the upper and lining. Natural latex adhesives are bonded wet, but PVA is allowed to dry and heat activated after insertion.

Insock insertion

The insock, either full length or confined to the heel, is the component immediately visible inside the shoe. Natural rubber latex is applied by roller, grid applicator or spray gun onto the sock and the bond made by wet stick. Acrylic emulsions are used on difficult materials.

Measurement techniques

The *wetting* of the surface and adhesive *penetration* are assessed visually. Assessment of the *degree of drying* and *tack* is subjective, although the SATRA/NPL tack tester is available for laboratory studies.

Applications of hot melt adhesives

The adhesives used are mainly polyamide, polyester and EVA types.

Laminating

Polyamide hot melt adhesives are used to laminate shoe upper materials and upper components. The adhesive is applied by a heated roller, usually with a gravure surface to produce a discontinuous dot coating, or by a fibre-forming technique to give a fine web. The aim is to produce adequate bonding without significant reduction in the 'breathability' of the materials. The materials are either combined immediately, or in a heated press or roller to reactivate the cooled adhesive.

Folding

The edge of the upper which is top-most in the finished shoe, known as the 'top-line', is chamfered and folded to produce a smooth surface and a neat appearance. The folding machine applies polyamide hot melt adhesive to the edge of the component and the fold is secured by a hammer action.

Bonding stiffeners

Stiffeners are inserted at the heel area of the upper and at the toe ('toe puff') to maintain the shoe shape. The most common stiffener material comprises non-woven fabric impregnated with a thermoplastic resin such as a styrene copolymer, with a surface coating of EVA hot melt adhesive. The stiffener is laminated to the corresponding upper component in a heated press. The completed upper is subsequently reheated and shaped.

Lasting

This is the most critical operation for hot melt adhesives. The shoe upper is stretched around the last (the former on which a shoe is built) and its edge secured to the insole. The insole is usually a board material based on cellulose or non-woven synthetic fibres with a binder.

Sophisticated lasting machines apply hot melt adhesive from a heated nozzle immediately before the upper material is pulled over and flattened onto the insole. The adhesive must have good initial grab and quick setting properties, the bond consolidation taking only 1-2 seconds.

Polyester adhesives are used at the forepart of the shoe as they are quick setting and will hold the complex pleating of the upper material. At the side or waist of the shoe polyamides are preferred, being more flexible and giving better wetting out of the materials. Higher softening point polyamides can also be used at the forepart.

Shank insertion

The shank, a metal or wooden reinforcing strip which stiffens the shoe in the instep region, is often attached to the insole of the lasted shoe with blobs of polyamide or EVA hot melt. This is effectively a temporary attachment as the shank is later sandwiched between the insole and the sole.

Measurement techniques

The *temperature* of adhesive melting chambers and applicators is checked by in-machine thermometers or by infrared pyrometer. Infrared or thermocouple pyrometers can be used to check the temperature of extruded adhesive and heated press platens or rollers.

Assessment of *wetting and penetration* is usually subjective. Adhesive *setting rate* is judged subjectively or empirically in production, but can be checked in the laboratory by making joints with increasing open times.

CLOTHING

Hot melts are the main type of adhesive used in clothing manufacture, for laminating textile components and for bonding 'fusible interlinings' in garments. Interlinings are used to alter the drape and handle of outer fabrics, and to stiffen cuffs and collars. They are bonded to the outer fabric only, with the inner fabric or lining left loose.

The hot melt, usually polyamide, is precoated onto one component of a laminate or onto the interlining material in a scatter dot or random drizzle pattern. Assemblies pass under an infrared heater to a roller press, with possibly a cooling step after pressing. If the adhesive is too hot at pressing it may penetrate excessively or strike through the material, if it is too cold then bonding will be inadequate.

Measurement techniques

The *temperature* reached by adhesive in the bond line is checked using a thermocouple pyrometer. The *pressure* achieved in the bonding press and its uniformity can be measured with a pressure capsule such as SATRA Pressrite. This comprises a sensing element enclosed in a partly inflated bladder. Alternatively pressure mats based on pressure sensitive resistive inks are used. Assessment of adhesive *penetration* is subjective.

FURNITURE

In furniture manufacture wood veneering and structural jointing of wooden components has long been carried out with adhesives. Originally animal glues were used, later supplanted by urea formaldehyde (UF) reactive adhesives and polyvinyl acetate (PVAC) emulsions. The bonding process requires jiggling and clamping and is hardly 'rapid bonding', although it may be accelerated by heat.

UF, water-borne and hot melt adhesives are, however, used for various rapid assembly processes in furniture. Solvent-borne adhesives continue in use for foam bonding.

Applications of liquid adhesives

Paper foil laminating

For attaching decorative foils to medium density fibreboard (MDF) panels two part UF adhesives are used, with the resin and a liquid hardener applied separately to the two surfaces or sequentially to one surface. Adhesive cure on pressing may be accelerated by heat.

PVC foil laminating

Water-borne polyurethane dispersions are used to bond PVC foils as overlays on profiled MDF panels. The adhesive is used with an isocyanate hardener, sprayed on the board surface and allowed to dry. Application of the foil is followed by pressing in a heated membrane press, which causes the foil to flow into machined grooves in the panels and around their edges; the heat also activating the adhesive.

Foam bonding

Solvent-based adhesives continue in use for foam building operations in upholstered furniture, in which cut foam pieces are folded and bonded, bonded to each other or bonded to other surfaces such as wood, in all cases before covering. Polychloroprene adhesives, applied manually, are used in view of their good tack and instant grab.

Applications of hot melt adhesives*Edge banding*

Application of thin decorative edge strips to chipboard panels is carried out in high speed machines using EVA hot melt adhesives. Moisture curing polyurethane hot melts are also used when increased temperature resistance is needed.

Foam bonding

Hot melt adhesive applied from small hand applicators is also used for foam bonding, generally for special applications such as foam to wood bonding where the cost of the equipment can be justified.

Measurement techniques

The *temperature* of presses is measured by in-machine thermometers. Infrared or thermocouple pyrometers are used to check extruded hot melt adhesive and bond lines. Bonding *pressure* is determined from the press thrust, with the effective pressure calculated from the workpiece area. Calibration charts are often used to relate total area to be pressed to required thrust. Adhesive *wetting and penetration, degree of drying and tack* are assessed subjectively.

KEY MEASUREMENT NEEDS

Across the industries considered there is little bonding process monitoring on the production line other than that involving measurement of temperature and pressure. This is perhaps not surprising as these two properties are relatively easy to measure whereas others are more elusive. However, laboratory procedures are sometimes used for assessing surface condition and adhesive properties such as tack.

The process characteristics for which scientific, rather than subjective, measurement techniques are desirable relate to the adherend surface and the adhesive.

For surfaces, means of assessing *texture and roughness, stability, porosity, and wettability* would be generally useful.

For adhesives the *penetration, coverage and film thickness* are key properties. In addition, assessing *tack and setting rate* under quickly changing conditions needs attention, this is especially relevant to hot melts.

To be useful to industry any measurement techniques developed to meet these needs should be suitable for use on the production line or in small workshops. If this is not possible, then the techniques should be suited to industrial laboratories and depend on robust easy to use equipment. Not least, techniques must be cost effective in order to enable industry to justify their use.