The Plastics and Rubber Institute

PRI

Adhesive Group
One Day Symposium

PRESSURE SENSITIVE ADHESIVES

Wednesday,
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Bristol University

THE PLASTICS AND RUBBER INSTITUTE

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PRESSURE SENSITIVE ADHESIVES

A one day symposium organised by the PRI Adhesives Group.

Wednesday. November 15th 1989
Bristol University, Bristol, Avon.

Adhesive Group

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OVERVIEW AND INTRODUCTION

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Pressure sensitive adhesives (PSA) have developed considerably since they were first developed in the thirties as replacements for the then standard gummed labels.
Originally these forms of adhesive were constrained to non structural applications and were perhaps the commonest adhesive type used in the home. Gradually such tapes have evolved and are now capable of use in the structural bonding of electronic, automotive and aircraft components. Such forms of adhesive often provide a lower cost better quality bond than other 'wet' adhesives.
PSAs come in many forms perhaps the standard tapes consist of an elastomer treated with tackifiers to make it bond under light pressure on one side and supplied with a lining such as paper of plastic on the other side. Such backing materials often provide the thermal stability of the tape system. These tapes can be further developed by the addition of a second adhesive layer to form a double sided tape. A good example of this is the double sided foam tapes which can accommodate considerable geometric imperfection in the surfaces being bonded. Yet another development is the transfer tape where a PSA is coated upon a backing material. These tapes can then pressed onto a surface and the backing is removed leaving the adhesive evenly spread upon the surface. Two main types of adhesive are used natural or synthetic rubbers and acrylics. The rubbers have the ability to bond to a wide range of surfaces with an high initial bond strength. Acrylics give a lower initial bond strength than rubbers but this gradually increases until often the bond strength exceeds the cohesive strength of the backing material. These acrylic based systems are much more resistant to temperature and UV degradation than the rubber systems. Traditionally acrylics films have been manufactured using hydrocarbon solvents. Now water borne acrylics are emerging and these offer an economic and environmentally

safe alternative where the highest performance is not required

The advantages of using adhesive in film or tape form is quite clear. These include the ease of handling, ease of application with minimal wastage, no drying or curing time and ease of storage. The advantage of using an adhesive which in the end use application does not release solvents into the workplace commends itself to out new green society.

The automotive market is a prime growth area for pressure sensitive adhesives. Many vehicle manufactures make extensive use of these tapes to secure various decorative and protective items. Many of these items such as trims used to be added to the car by drilling the body and then securing a blind rivet onto which the trim was attached. This has the significant disadvantage of creating a possible corrosion point in the cars structure. The advent of double coated foam PSA tapes has obviated such corrosion problems.
The domestic appliance industry has similarly used PSAs to replace many of the mechanical attachment methods such as blind rivets, stud welds and self tapping screws In many applications such as washing machines the ability of PSA's to withstand severe vibrations obviates the need for costly shake proof additions to the standard mechanical fasteners.

In conclusion PSA have developed considerably since their original conception. They are now at the forefront of adhesive technology. The offer considerable advantages to other wet adhesive system and with increasing concern over health and safety means that the use of solvents can be confined to the adhesive manufacturer.

PRESSURE-SENSITIVE TAPES

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Pressure-sensitive tapes

A typical pressure-sensitive tape consists of a backing or support, usually of a polymeric film or paper, which has bonded to it the pressure-sensitive adhesive, a soft, viscoelastic mass. It has the property of forming a bond very rapidly when placed in contact with a surface such as smooth metal or glass. The speed and efficiency of this bond formation are mainly determined by the viscoelastic properties of the adhesive. The science of pressure-sensitive tapes is therefore very much the science of pressure-sensitive adhesive behaviour.

Pressure-sensitive adhesives are unusual materials in the sense that they are somewhere between the viscous and rubber states at room temperature, ie they are viscoelastic. They show sufficient liquid-like behaviour to deform or flow into contact with a smooth surface during the bonding operation, yet they show appreciable resistance to flow during a de-bonding process (which involves a much shorter time-scale), due to molecular entanglements. The bond strength depends on viscoelastic energy dissipation during the de-bonding process, and would be very low if the adhesive showed only elastic behaviour. Thus, the performance of a pressure-sensitive tape depends on obtaining a rather delicate balance of properties in the adhesive polymer.

Viscoelastic properties of pressure-sensitive adhesives

Typical adhesive materials are simple polymers such as polyacrylates or acrylate/vinyl acetate copolymers, or blends of rubbers such as rosin esters, polyterpenes or polymerised petroleum fractions. The viscoelastic properties of these adhesives can be measured in the laboratory using dynamic mechanical measurements and expressed in the form of 'master-curves' of modulus or tan against frequency or rate of deformation. These curves give some idea of the viscoelastic state of the adhesive at deformation rates corresponding to those of the bonding process (which involves a slow deformation) and debonding (which is usually by peeling and involves a fast deformation). Furthermore, these viscoelastic master-curves are well-understood and enable us to predict (at least qualitatively) the effects on viscoelastic behaviour of changing the formulation of the adhesive.

For the purpose of further illustration we will concentrate on the process of de-bonding by peeling.

Peel adhesion behaviour of pressure-sensitive tapes

By considering a 'model' system (Figure 1), it can be seen that the adhesive at the region of separation undergoes a high-speed stress-strain cycle during peeling. Most of the work of peeling is dissipated as viscoelastic hysteresis during this cycle. Thus, the work of peeling is expected to vary with rate and temperature in the same way as tan , the dissipation factor.

From the results of peel tests carried out over a range of rates and temperatures, it is possible to construct a 'master-curve' of peel force against pulling rate covering a very wide range (about 10 decades) of rates. This curve (Figure 2) is analogous to a modulus or tan master-curve, and shows peel adhesion to be changing as the viscoelastic response of the adhesive changes. Thus, different regions of peeling behaviour can be recognised, as the response of the adhesive changes through regions of viscous, rubbery, leathery and glassy behaviour. There are, in fact, three regions of steady peeling (A, B and C) and two regions of oscillatory ('stick-slip') peeling (A-B and B-C), the latter being associated with zones of negative slope in the peel force - rate relationship.

By analogy with the modulus master-curve it is now possible to predict the effects on the peel force master-curve of changing the chemical composition of the adhesive polymer or changing its molecular weight. These effects are seen in a lateral shifting of the whole curve or a change in the width of the 'rubbery' peeling region, respectively. Thus, it can immediately be seen that a slight change in the copolymer composition can have an important influence on the level of peel force at any particular standard rate. Also,

the importance of slight crosslinking in the adhesive can be illustrated. The effects of tackifier resin addition to an adhesive may be rationalised on the basis of a simultaneous change in chemical comp[illegible] molecular weight.

Finally, the introduction of highly polar or hydrogen-bonding groups into an adhesive can cause a large increase in peel force, usually attributed to an increase in interfacial attractive forces. However, such groups usually also affect the viscoelastic behaviour so it is not a simple matter to distinguish between their effects on interfacial attractions and bulk viscoelasticity.

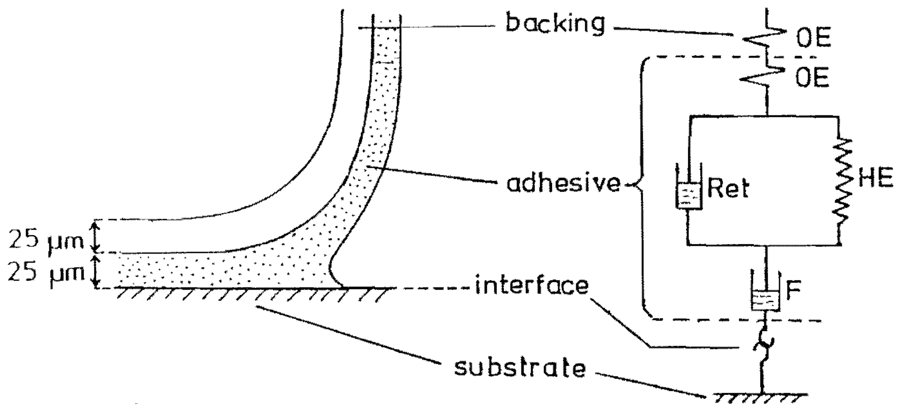

Figure 1 : Peeling joint and assumed mechanical analogue.

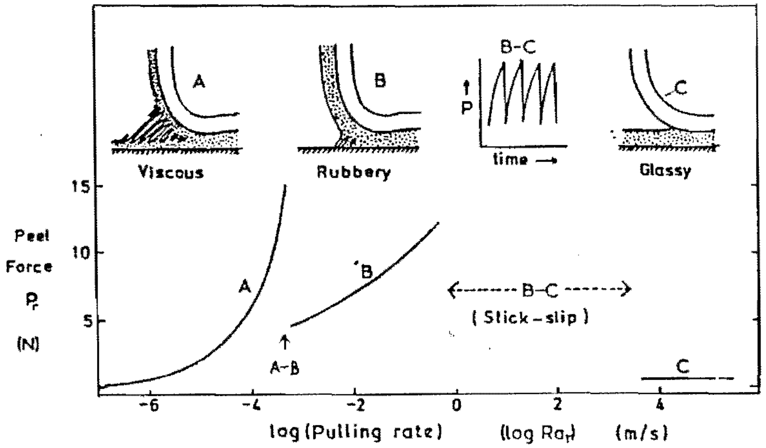

Figure 2 : Dependence of peel force on (log) pulling rate at 296 K for polyester backing/polybutyl acrylate adhesive/glass substrate. Tape is 2.54 cm wide, and other dimensions as shown in figure 1. Drawings illustrate the adhesive behaviour in each region.

PROBLEMS IN LABELLING DANGEROUS GOODS

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The work reported here was done as a result of comments received when a Draft Defence Standard, Labels, Plastic, Self Adhesive, to replace TS 10196 was circulated. On further enquiry it was found that many users had found the self adhesive labels unsatisfactory, they just did not stick well enough. Peel strength measurements showed that few of them met the requirements of the specification, most failed by quite a large margin. Initially there was only an attempt to measure the bond strengths of existing labels but the method called in TS 10196 was shown to give different results to a normal 180 degree peel test (BS 5350 part C11).

Another comment was that a separate MOD specification was not necessary and suggested that BS 4781 should be used instead. This was agreed in principle as it is MOD policy not to issue its own specifications if a suitable British Standard exists. Extra work was required before a decision to adopt the BS because it calls for a different peel test and a different substrate, aluminium instead of the stainless steel of the TS specification. BS 4781 covers both rigid and flexible plastic labels and the peel test procedure is written to cover both types. That procedure was found to be un-necessarily difficult to use on flexible labels and unsuited to the test machine available for the job.

BS 4781 is currently being reviewed and many changes are proposed, these include;

1 An increase in the conditioning time before measurement of the "initial" adhesion from 10-15 minutes to 20 minutes.

2 A reduction in the conditioning time before the measurement of "final" adhesion from 48-72 hours to 24 hours.

3 A change of adhesion test substrate from aluminium to glass.

4 An increase in the minimum "final" peel strength from 12.2 Newtons/25mm width to 15 Newtons/25mm width.

5 Changing to a conventional BS 5350 part C11 peel test for flexible labels.

Attempts were made to obtain sample labels to BS 4781 for the test comparison to be made but none could be found, one supplier did say that he could supply to BS 5609, Printed pressure sensitive, adhesive-coated labels for marine use, including requirements for the label base material.

When sample labels were obtained from one printer they were found to be printed on at least five different base materials, supplied by four different manufacturers. Once the initial shock of receiving such an odd sample was overcome it did prove useful in that it was possible to compare products, other labels including some paper ones were also obtained. The peel results varied greatly for the different materials. The BS 5350 part C11 peel test was used mainly on an aluminium substrate, the same test as is used in BS 5609, a few tests were made on stainless steel for comparison with the original work.

Eventually some label base material was obtained from a manufacturer who supplied two film types, a matt and a glossy vinyl, coated with two different adhesives. Using this material peel testing was done on stainless steel, aluminium and glass substrates.

Exactly what the peel strengths need to be is difficult to ascertain. SI 1244/1984, The Classification, Packaging and Labelling of Dangerous Substances Regulations 1984 states that "Any label required to be carried on a package shall be securely fixed to the package with its entire surface in contact with it..." How many Newtons are there in "securely fixed"!

Recommendations On The Transport of Dangerous Goods, published by the United Nations (the "orange book") and adopted as the basis of SI 1140/1983 states that "All labels should be able to withstand open weather exposure without a substantial reduction in effectiveness". No guidance is given as to what sort of weather nor for how long let alone any hint of how big is substantial.

The Merchant Shipping (Dangerous Goods) Regulations 1981, SI 1747/1981 are more precise. "Where the outer material of the package is such that it will survive at least three months immersion in the sea, then the label shall be similarly durable. If the outer material of the package will not survive, then any inner package which will survive shall be durably labelled..." It is from this clause that the three month sea water immersion test in BS 5609 derives. This is not the sort of test that can be easily done by a user. It cannot be done on every batch of labels so must be regarded as a type approval test.

The limit values in the specifications are usually a result of negotiations between the user and manufacturers representatives on the drafting committees and tend to represent the state of the art values (without too many reject batches) at the time the specification is written.

The Ministry of Defence will most likely require ALL explosives labelling to meet the standards of BS 5609, not just those being transported by or used at sea. For the majority of other applications the revised BS 4781 type 6 will suffice. From a user viewpoint it is currently not possible to know what type of label you are getting, this situation could be rectified if the BS number was printed somewhere on the label. With the situation as it exists, of lots of relatively small printers supplying labels the BS tests can only be done by the label base manufacturer so the only place to print it is on the outside of the release paper.

Most of the results tables include some results obtained using an electrical tape, this is because they were done concurrently with the above work. The reason for the tape work is that the ATMA have indicated an interest in changing the substrate currently called in BS 3924 and the Defence Standards for tapes from stainless steel to glass. This work has shown that the ranking of peel test results on aluminium, glass and stainless steel substrates is not always in the same order hence changes to specification limits could not be made on a "they will all be a bit lower on glass" basis.

VERY HIGH BOND PRESSURE SENSITIVE ADHESIVE TAPES

DR. K.M. FISHER

3M United Kingdom PLC

VHB Joining Systems from 3M represent the most significant advance in adhesive tape technology in recent years. Many people do not believe quite how strong self adhesive tapes can be. To appreciate just how VHB has revolutionised adhesive tape technology, first lets consider conventional double sided tapes and their adhesive systems; rubber or acrylic and the characteristics of those products.

Rubber adhesives provide an excellent bond to a variety of surfaces and can be tailored for permanence or easy removal but they only have moderate temperature stability and ageing characteristics and limited U.V. and solvent resistance. Compare these characteristics with those of acrylate adhesives; these have excellent bonding properties to a variety of surfaces and modified acrylates also adhere to low surface energy plastics. Not only do they have good adhesion they also have good cohesion - high internal strength. Acrylate adhesives have excellent resistance to U.V. light and chemicals and when compared to rubber adhesives have superior ageing characteristics. An adhesive can be 'tailored' and its basic characteristics can be altered to meet specific application requirements. For instance they can be tailored for extreme shear and temperature performance or for high initial tack or high ultimate adhesion. The most obvious effect with this tailoring process is in the firmness of the adhesive and this is how we group or products into families.

Making the first of our Very High Bond foamed acrylic adhesive tapes was the difficult part, it took many years of research and testing before Scotch (TM) Tape No. 4945 in it's present form was finally introduced. Subsequently, it has been relatively easy to produce variations to satisfy a variety of specific application requirements. Since the introduction, in 1984, of Scotch (TM) Tape Number 4945, eight further new acrylic foam products have been added to our joining systems range.

Illustrations are given of the properties which differentiate our products and the applications which

they have been tailored to meet. These include the bonding of thinner materials and the replacement of conventional fixing methods such as rivets. Examples are shown where stresses due to flexing or thermal expansion can be accommodated and dissipated along the whole of the bond line rather than at the point of contact as would be the case with rivets.

VHB acrylic foam tapes are pressure sensitive acrylate adhesives with a viscoelastic core which gives the product all its unique properties. This viscoelasticity is also apparent in the excellent flow characteristics of acrylic foam tapes and leads to very high bonds being made when compared with conventional double coated foam tapes. The initial bond strength or handling strength is almost immediate. There is no need for clamping of materials being joined which would cause manufacturing delays whilst the bond builds up. However, it does take a little time, depending on circumstances up to 72 hours, for a bond to achieve full strength. Even on a range of materials as varied as aluminium, acrylic, ABS, PVC and fibre-glass, acrylic foam tapes have excellent peel adhesions when compared with conventional foam tapes.

In shear, the resilient VHB bond absorbs and dissipates energy. Being viscoelastic, the tape is able to maintain a firm bond in a variety of stress environments. An example of this will be shown comparing the bond made with tape with that of a spot welded assembly.

VHB tapes when compared to mechanical fixing are simple to use, cost effective, there are no holes to drill, no rivets to head no need to use sealants or insulants. Materials with different rates of thermal expansion can be bonded together and thinner surfaces can be used. No point stress cracks, no corrosion and a smoother cleaner appearance of a finished product results. All from a range of VHB tapes each tailored to meet specific application requirements and give long term high strength bonds provided a correct application technique is applied.

This talk includes a cameo of applications in various markets throughout the world, where VHB has been successfully used as a joining and fastening aid in both indoor and outdoor applications.

THE REQUIREMENTS OF PRESSURE SENSITIVE ADHESIVES FOR USE ON SKIN

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Pressure-sensitive adhesives (PSAs) are widely used to adhere medical dressings or devices to human skin. The applications range from wound dressings to ostomy bag mounts and the most common types of PSA used are acrylics, rubber resins and vinyl ethers.

Producing satisfactory adhesion between these PSAs and skin is a complex problem. As an adherent, human skin presents a large number of conditions which tend to oppose bond formation and quickly destroy a bond once it is formed. For example, surface roughness inhibits wetting out, stretching of the skin promotes edge delamination, and the constant turnover of cells and release of water or sebum create weak boundary layers at the interface. These difficulties are compounded by:

i) The skin being very variable between different parts of the body and between different individuals.

ii) The product having to be safe and easy to use (tolerant of abuse).

iii) The adhesive having to meet with other specific requirements which conflict with those for good adhesion, e.g. high shear strength which conflicts with good wetting out, and high water transmission rate which conflicts with good sebum tolerance.

To illustrate how some of these problems may be overcome, three product examples - the polyurethane film wound dressing, the first aid dressing, and the ostomy dressing -are discussed in more detail. These examples show that despite the complexity of skin and the limitations imposed by the requirements of convenience and aesthetics, the principles and techniques used in other areas of PSA technology are increasingly being used to design PSAs for use on skin.

PRESSURE SENSITIVE ADHESIVE SYSTEMS

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Pressure sensitive adhesive systems, or 'tapes' as they are more commonly known, have three basic constructions:-

1) Transfer Tape
2) Double-coated Tape
3) Single-coated Tape

Transfer tape has an unsupported layer of pressure sensitive adhesive on a release liner.

Double-coated tapes are made up of a carrier material coated on both sides with pressure sensitive adhesive and protected by a release liner.

Single coated tape has a face film coated with pressure sensitive adhesive which can be protected by a release liner but not always.

Transfer tapes and double-coated tapes are used for the bonding of two substrates, single-coated tapes on the other hand are used for such diverse uses as masking tapes, insulation TAPES, electrical tapes and in a linered form for decorative and label systems.

The components, which together make-up a pressure sensitive tape, are equally important to each other and complement each other in achieving a successful system, which will perform to requirements at an appropriate cost.

Release liners, whilst not playing a part in the final in-service performance of the tape, play an extremely important part in the overall concept. Paper is the most commonly used material but various filmic types are utilised also. All release liners need to be treated in order to provide a good "release".

Carrier materials range from tearable tissues, non-woven polyesters, films and foams. All carriers are there to provide reinforcement and integrity to the adhesive system.

Tissues and non-woven carriers render a tape usable by hand - they can be torn when cutting would be an inconvenience. Films on the other hand had dimensional stability, an important aspect where die-cut shapes are concerned. Foams are utilised for the gap filling properties when two rigid substrates are bonded together.

Without a doubt the most strategic component is the adhesive employed. There are three basic systems:-

1) Hot-melt
2) Solvent
3) Emulsion

Hot-melt adhesives are thermoplastic being applied hot during the coating process and achieving their pressure sensitive adhesive properties on cooling. The two alternative systems employ adhesives which achieve fluidity for coating by the use of solvents, or water respectively. Both imply the input of energy in order to remove the dispersant, thereby rendering them pressure sensitive.

Pressure sensitive adhesives are based on two concepts using either rubber or acrylic polymers. Rubber adhesives have a multi-compound system incorporating rubber polymers, tackifiers, anti-oxidants and possibly plasticizers. Acrylic adhesives on the other hand are usually a single component system utilising only acrylic polymer. Tackified Acrylics are being developed.

The physical properties of the two systems are very different; rubber systems have high Tack and Peel properties with relatively modest temperature resistance. Acrylics have lower Tack and Peel but higher temperature and shear resistance.

The chemical resistance of the two systems is equally disparate; rubber based adhesives, having very moderate resistance to ultraviolet light, solvents and plasticizer attack, whilst acrylic adhesives are far superior in those aspects.

For some years there has been extensive research into ways of up-rating the modest properties without detriment to the stronger. The research concentrated on the way in which curing of the adhesive occurred.

Conventional curing is a physical process, cross linking of the molecules occurring purely because of proximity to each other being dependent upon dispersion and statistical parameters. By its nature, it is reversible on application of heat or solvents dependent upon the technology employed.

Research has led to radiation curing as a better means of achieving cross-linking. The input of high energy leads to cross-linking of molecules on a chemical rather than a physical level to such an extent that the process is non-reversible.

The degree of cross-linking can be varied by the amount of energy input, hence the amount of chemical cross-linking, thereby enabling an adhesive to be "tailored" to specific requirements.

Of all the possible radiation methods available, Fasson believes Electron Beam Curing provide the greatest flexibility for radiation curing, taking into account all the very many considerations involved in the high speed production process of tape manufacture.

The benefits are plain to see; we can combine the aggressive properties of rubber adhesives with the temperature resistance only previously associated with acrylics. With acrylics we can enhance temperature and shear resistance and increase ultraviolet and solvent resistance to even higher levels.

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