Characterisation and surface analysis of polymer interfaces used in dye diffusion thermal transfer printing

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Characterisation and Surface Analysis of Polymer Interfaces used in Dye Diffusion Thermal Transfer Printing

by

Kristian John Sime

Supervisor: Dr. I. Sutherland

A doctoral thesis submitted in partial fulfilment of the requirements for the award of Doctor of Philosophy of Loughborough University

September 1998

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"Characterisation and Surface Analysis of Polymer Interfaces used in Dye Diffusion Thermal Transfer Printing".
Sponsored by the EPSRC and ICI Imagedata.

The research involved determining the processes that occur during dye diffusion thermal transfer printing. Dye diffusion printing is a novel method of printing photo quality graphics from a personal computer. The process involves two polymer films coming into contact, one containing a dye, and the diffusion of the dye from this donor sheet onto the receiving sheet using heating elements to drive the diffusion process. In this high temperature, high pressure, and short time scale regime undesirable adhesion between the two polymer sheets is observed. It is this adhesion and its mechanisms that were investigated.

Several types of homopolymers were used in an attempt to obtain information on the processes involved in the adhesion of the two films during the printing stage. Initially dyes were absent from the polymer films to examine the polymer adhesion alone. It was hoped that the principal factors involved in the unusual joint forming conditions could be explained. The unusual conditions are high heat (250°C) and short time span (10-15 milliseconds). Polystyrene, poly (methyl methacrylate) and poly (vinyl acetate) were chosen to determine the effect of Glass Transition Temperature ($T_g$), surface energies and molecular weight on the polymer adhesion.

Initial results showed that the adhesion was a complex system but it became clear that the $T_g$ of the polymers and the presence of small molecules and contaminants were very important. Work with commercial polymers was undertaken to transfer the knowledge gained from the homopolymers to the more complicated commercial systems using poly (vinyl chloride) and poly (vinyl butyral). To expand the understanding of the results small molecules and dyes were added to these commercial polymers to examine their effects. The surface of the samples were analysed using X-ray Photoelectron Spectroscopy (XPS) and Fourier Transform Infra-red Spectroscopy (FTIR). This was used to determine if there was any migration of the small molecules to the surface of the polymer films. It was also useful in indicating the location of the dyes and how much penetration into the polymers is achieved by them. Atomic Force Microscopy (AFM) was implemented to analyse the surface morphology and gave an insight into the mechanism of the small molecule migration.

The conclusions drawn were that the presence of small molecules had significant affect on the adhesion of the polymers. Compatible small molecules would act as plasticisers and lower the $T_g$ of the polymers giving rise to higher adhesion. Small molecules that were incompatible were found to migrate to the surface in large quantities and would act as weak boundary layers, significantly reducing the adhesion. Work in this area has shown that an autolayering mechanism is occurring that may be useful in producing a release mechanism for the commercial products.
Acknowledgements

I would like to begin by thanking my supervisor Dr. Ian Sutherland for all of his contributions and ideas over the years. I would like to thank my industrial supervisors, Alan Butters, Andrew Slark and Andrew Clifton, whose knowledge and enthusiasm was always inspirational. Acknowledgement must go to the EPSRC and ICI Imagedata for the funding of the project.

A big thank you must go to all of my friends in the polymer laboratory who have made it a joy to work in the section over the years. So in no particular order I would like to thank, Will Taylor, Alex Celik, Wayne Stevens and Matt Irvine - the original four horsemen of polymer research, Matthew Savage, Debbie Hall, David Price, Terry Samios, Helen Jones, Claire Madden, Dave Maton, Jon Houseman and David Neep.

To all of those who helped me from other departments, including Karen from physics, Anne Waddilove and Isla Mathison from ISST, (In fact thanks to everybody at ISST who went on the conference to Hilton Head for an enjoyable week and their subsequent friendships), and Phil Carpenter from ISST, formerly chemistry, Vicky Joss from Liverpool University and Hilton Head, thanks very much.

To all of my friends who have supported me I would like to give thanks, you are too numerous to name, but I would like to mention Chris Martin and Phil Lindsay for their continued friendship through the good and the bad. Neil Tootell because we survived two years in the same house in adverse conditions. Neil Brammall and Scott Baird for their help in me surviving the last few months in Loughborough. Cheers mates.

Finally I would like to thank my family, Dad and Carol who were always there for a chat and advice, and to Mum for her unending faith in me. I would also like to thank Claire Morse, whom I love dearly, for her support, who one day may even read this.
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CHAPTER ONE

INTRODUCTION
1. Introduction

1.1 Current printing methods

There are two commonly used printing methods available for personal computers, ink jet and laser printing\(^1\). A third method has recently appeared on the market. Dye diffusion thermal transfer printing is designed for graphic printing instead of text.

1.1.1 Ink Jet Printing

Ink jet printing uses a spray of fine ink droplets to print onto the substrate. In continuous ink jet printers, mainly found in industry, there are three main components - the control system, the print head and the ink system. The control system is programmed by the PC and holds the information to be printed. The print head then activates. The inks used are water or solvent based. Typical solvents include ethanol and methanol. A jet of ink flows from a nozzle under pressure and is separated into small droplets. These droplets are then electrostatically charged. The character formation is based on a dot matrix system. The stream of electrostatically charged drops is deflected by several plates that are commanded by the control unit and produce the final character or picture.

Drop on demand printers are more commonly found in the office and home environments. These are generally referred to as thermal or bubble jet printers. These work by having a series of channels filled with ink. In each channel is a small resistor and when a drop is required from that channel the resistor is heated. This heating causes the water based solvent to boil
quickly, causing a micro explosion, that forces a drop from the end of the channel or nozzle. Other systems use pulsing Piezo crystals to force drops from the nozzles. The series of nozzles, commonly 32 channels, are arranged in a line and the characters are produced by moving the print head across the substrate.

1.1.2 Laser Printing

In laser printing an electronically stored image or text is transferred to the print unit. Here it controls a laser beam that scans across a photosensitive drum. The pixel elements are created by the laser being turned on and off corresponding to the desired image. Toner powder is attracted to the image areas on the drum, and released onto the positively charged substrate as it passes the drum. The toner is then heated and fixed to the substrate.

1.1.3 Dye Diffusion Printing Techniques

Dye diffusion thermal transfer printing (D2T2) is a novel printing process that is capable of producing a high quality hard copy of an electronically stored image. The process works by the diffusion of a dye from a carrier polymer into a receiver polymer. This transfer is achieved by the application of heat from a thermal printing head. The colour dye ribbon consists of a solid solution of dye in a binder polymer that is then attached to a thin polyethylene terephthalate (PET) base by a subcoat that restricts the backward migration of the dye molecules into the base film. Colour printing is achieved by sequentially over-printing blocks of yellow, magenta and cyan dyes onto the receiver. The receiver sheet usually
consists of clear or white Melinex™ coated with a soluble polyester and a silicone mixture to aid in the release of the dye sheet. The amount of dye transferred is dependent upon the temperature at the dye sheet/receiver interface. Colour tone variation is achieved by controlling the temperature of the thermal print head. The print head is made from a number of resistive elements deposited onto an alumina substrate. They are arranged in a linear array with each pixel being in the order of several microns.

Figure 1.1
Schematic diagram of the workings of the print head as the pairs of polymer sheets are drawn through it.

Interactions between polymer layers will affect the adhesion properties of the system. The aim of this study was to identify the factors affecting adhesion at the short time scale and elevated pressures and temperatures involved in the printing process. At these short time-scales the flow and wetting of one surface by another may be the dominant process affecting
adhesion. Alternatively, providing sufficient compatibility exists between the polymers, then chain entanglement producing interpenetrating polymer networks may be more important.

The short time scales of the printing process can be seen from Figure 1.2. This shows the heating and cooling curves during printing. The graph illustrates the temperatures at the maximum power output. The print power is established using the software drawing package, which gives a range of 0-31 relating to the intensity of the colour on the screen. A setting of 0 gives a black screen and therefore the greatest power while a setting of 31 gives a white screen and thus the lowest print power (no heat is required to print a white sheet as no dye is required to transfer). At lower than the maximum power (heat settings 1 up to 31) the maximum interface temperature decreases linearly although the time scale of the printing remains constant. The pressure the print head exerts on the dye sheet during the printing cycle is also constant over the power range.

The Y-axis is the temperature at the interface and is therefore dependant on the polymers involved and the dye sheet substrate. The figures from the graph are therefore an estimate of the temperatures involved.
Figure 1.2

A graph showing the temperature at the interface of the polymers at a given time in the printing cycle.

How wettability and chain entanglement affect adhesion between two polymers has been the study of experimental work\textsuperscript{10} although no experimental work has been reported in this short time scale regime.

Any polymer films brought together under these conditions of high heat and pressure will have the possibility of adhering. To minimise the risk of adhesion, and therefore poor print quality, the factors affecting the adhesion of the polymer films need to be investigated. This will ultimately lead to a method of choosing suitable polymers and polymer blends to be used in the printing systems that will provide the most robust and highest quality of prints.

1.2 Scheme of Work

Initially a range of homopolymers were selected of varying solubility parameters, surface energies, molecular weight and glass transition temperatures. During the course of the work these polymers were used on both the dye sheets and the receiver sheets. This was to enable information
to be gained about the adhesion between the polymer interfaces after heating in a D2T2 printer. The polymers were tested before and after extraction to understand the effects of any additives and plasticisers.

Once the key parameters affecting adhesion were established work was undertaken to build towards the commercial systems, involving more complex polymers, dyes and additives. Again extraction of additives was undertaken to minimise their effects to allow for a fuller understanding of their role in the adhesion. Work with the addition of additives was completed to develop a possible release mechanism.

Initially these systems were studied before the inclusion of any dye molecules. Once the adhesion systems were understood the role of the dye molecules was investigated. The affect on adhesion of the dyes was observed and the nature of their diffusion through the polymers was examined spectroscopically. Finally the dye molecules were tested in the presence of the additives to determine their compatibility in respect to the final print.
CHAPTER TWO

ADHESION
2. Adhesion

An adhesive can be simply defined as a material that when applied to the surface of materials will join them and resist their separation. Adhesives include cements, glues, primers and pastes. Adhesion is a complex subject involving many factors. Surface chemistry and physics, rheology, polymer chemistry and mechanical properties all need to be understood to fully appreciate adhesion.

Basic requirements for good adhesion are:

- Good contact between the “wetting phase” and the substrate.
- Absence of weak boundary layer.
- Avoidance of stress concentrations which could lead to debonding.

If a region of low strength exists at the interface it is termed a weak boundary layer and it may originate from either the adhesive or adherents. Potential weak boundary layers include dust, grease, metal oxides of relatively low strength and polymer inhomogeneity.

2.1 Mechanisms of Adhesion

There are four principal theories of adhesion\textsuperscript{11,12}.

1. Mechanical Interlocking
2. Diffusion Theory
3. Electronic Theory
4. Adsorption Theory
The mechanical interlocking theory concerns the adhesive interlocking around the irregularities or pores of the substrate. In the diffusion theory the adhesive macromolecules diffuse into the substrate, therefore eliminating the interface altogether. Electronic theory proposes that a double layer of electrical charge can build up at the interface between an adhesive and substrate with different electronic band structure. The adsorption theory states that the adhesive macromolecules are adsorbed onto the substrate and are held there by various forces of attraction, including van der Waals forces, hydrogen bonding and various chemical bonds.

2.1.1 Mechanical Interlocking

A layman's view of adhesion is usually along the lines of mechanical interlocking. The mechanism is usually referred to as "lock and key". The theory states that the adhesive flows and interlocks around the irregularities of the substrate. This occurs at two levels, a macro scale and a micro scale.

2.1.1.1 Macro scale

On a macro scale a simple model can be used to express the theory. This can be seen clearly in figure 2.1.
A liquid resin wets the solid and flows into the porous surface. When this solidifies, due to cooling, curing or solvent evaporation, a mechanically interlocked interface is created. An example of this is the use of roughing the surface of leather. This is of particular importance to the footwear industry\textsuperscript{13}. It has been shown that the surface roughening of the leather raises the fibre ends so that they can become embedded in the adhesive layer, producing a stronger bond.

A further example is the electroless plating of certain plastics with metals\textsuperscript{14}. The base materials are usually either a high impact polystyrene or ABS (acrylonitrile-butadiene-styrene). These polymers share the same structure; a continuous phase of glassy polymer with an elastomer dispersed in it. The first stage involves the etching of the plastic surface with a chromic-sulphuric acid mixture. This oxidises and removes the unsaturated rubbery component leaving a highly porous structure. Silver or palladium is added before the chemical reduction of copper or nickel salt to give the electrical conductivity necessary for the electro-deposition of
copper or nickel and then chromium or the desired finishing metal. To view the interface the plastic is removed by pyrolysis to reveal the copper surface. Photomicrographs of the structure show that the copper can penetrate to a depth of 1\(\mu m\). Extensive study has shown that two mechanisms are simultaneously involved in this adhesion. One - a chemical relationship between plastic and metal; the other is purely a mechanical interlocking mechanism between the metal and the porous substrate which is controlled by the topography of the surface.

2.1.1.2 Micro scale

Packham et al.\textsuperscript{15,16} have changed peoples view of the “Lock and key” macro scale of mechanical interlocking. Their series of experiments demonstrated the importance of topography when molten polyethylene (PE) was adhered to aluminium. Normally the PE melt is contacted with the aluminium and the resulting adhesion is poor. Packham et al. devised a series of experiments to change the surface of the aluminium prior to adhesion.

Anodising the aluminium surface in an acidic electrolyte produces an oxide film consisting of a dense layer next to the metal covered by a more porous layer. The size and number of the pores could be governed by the conditions of the anodising and Packham showed a direct relationship between the size and density of the pores and the adhesive bond strength. The pore sizes varied from 120-300 Å.

When the aluminium substrate was dissolved away the surface of the PE could be examined by Scanning Electron Microscopy. Tufts of diameter
500-2000 Å were seen on the PE surface. Each tuft was made up from a cluster of whiskers that had aggregated together. The individual whiskers had been filling the pores in the aluminium oxide film. Packham showed there was increased adhesion with increased surface topography but he maintains that mechanical keying is not the sole method of adhesion. Further work showed that failure was occurring in the polymer and that PE was present on the aluminium surface after peeling.

Much work has been done to demonstrate the benefits of increasing surface roughness to increase the adhesive joint strength. All of them mention the increased adhesion due to mechanical interlocking but other causes may be involved. Chemical pre-treatment may alter the surface topography but it can also change the chemistry of the surface, often increasing surface oxidation.

Mechanical abrasion of metal surfaces has been linked to increased adhesion. Although it can be seen on micrographs that whilst this abrasion does produce some surface roughening the cavities suitable for mechanical interlocking are not produced. The mechanical abrasion may be increasing the joint strength by removing oil, grease or other release agents; or by moving a weak boundary layer (metal oxide on the surface) and it may even change the surface chemistry. It can also simply increase the surface area to be bonded. The roughening could also be increasing the surface wetting of the adhesives by capillary action thus providing better contact.
2.1.2 Diffusion Theory

The diffusion theory was originally developed by Voyutskii\textsuperscript{17-20}. His original work was concerned with the self adhesion (autohesion) of unvulcanized (not cross-linked) rubber. The theory has now been expanded and encompasses mutual diffusion between different polymers\textsuperscript{21-29}. His basic theory is that the polymer chains at the interface diffuse across said interface and interpenetrate. Eventually the interface will disappear and the two parts will have become one. This interdiffusion requires that the macromolecules or chain segments possess sufficient mobility and are mutually soluble, i.e. have similar solubility parameters. These solubility parameters are an indication as to the compatibility of two components. For interdiffusion to occur the polymers should not have considerable crosslinking and to be above their glass transition temperature.

For autohesion of a polymer to itself the peeling force can be calculated by:

\[
F = 11u\{(d(2+p)/M)^{2/3}K^{1/2}\}rt^{1/4}
\]  

Equation 1

F is the peeling force necessary to separate the two surfaces, \(u\) is the vibrational frequency of a -CH- group, d the density of the polymer, p is the number of chain branches in the molecule, M is the molecular weight, r is the rate of separation of the two surfaces, t the contact time before testing and K a constant, characteristic of the diffusion of the molecule.
Voyutskii argues that the dependence of joint strength on some of these parameters is similar to the expected values for a diffusion process and hence the adhesion is a result of diffusion. His theory predicts that with a diffusion coefficient of $10^{-14} \text{cm}^2\text{s}^{-1}$ it will take approximately a hundred hours for segments of one polybutylene sheet to migrate to a depth of $10\mu\text{m}$ into another sheet. It is also pointed out that much smaller penetration depths can result in high joint strength.

Little direct experimental evidence exists to prove interdiffusion in compatible polymers, but radiotracer studies have shown that macromolecular diffusion does occur. Further work with compatible, non-polar polymers shows that the interphase region may be about $10\mu\text{m}$ deep under favourable conditions. Where the solubility parameters differ between the two polymers no interdiffusion zone could be detected. Methods involving X-ray and neutron reflectometry have seen diffusion over the nanometer range.

Transmittion Electron Microscopy and Energy Dispersive Spectroscopy (TEM/EDS) have been used to observe the interface of a poly (vinyl chloride) and poly (methyl methacrylate) bilayer. It was shown that the interface thickness of the bilayer after 6 hours at 120°C was 1.5 μm. TEM and ellipsometry have been used to observe the interface thickness for PMMA/polystyrene bilayers. After annealing at 140°C the ellipsometry data showed an interfacial thickness of 30Å which was in good agreement with the value obtained by TEM of $50 \pm 30\text{Å}$. By replacing the polystyrene with a poly (styrene-ran-acrylonitrile) containing 38.7% acrylonitrile (SAN-38.7) gave an interface thickness by TEM of $320 \pm 30\text{Å}$ after
annealing at 140°C. The SAN-38.7 has a lower molecular weight than the polystyrene and its miscibility with the PMMA is dependant on the copolymer composition. The measurements were obtained by the selective staining of the polystyrene and San-38.7 with RuO₄.

Several mechanisms have been proposed for the diffusion of polymers across an interface. The Rouse theory\(^{32}\) defines a model where a polymer of N segments is perceived as a string of N+1 beads connected by N springs. These beads are then seen as point sources of friction. The beads can move independently as long as the chain remains unbroken and the springs act as pure elastic forces.

The reptation model was proposed in 1971 by de Gennes\(^{33}\). This model describes the movement of the polymer chains as like that of a snake where the polymer chain follows the path of the lead segment. Any lateral movement is restricted by the presence of neighbouring chains and the polymer is perceived to be moving along a tube created along its length.

In short time scale diffusion where the penetration distances are less than a tube diameter the movement of the chain end is largely unaffected by its environment and the surrounding polymer chains. In this scenario the diffusion is ostensibly Rouse-like in behaviour. As the diffusion distances increase the limiting effects of the tube predominates.

Work has been undertaken to probe the interdiffusion mechanics of polystyrene chains during heat welding\(^{34,35}\). Deuterated polystyrene polymers were used as markers in the investigation and differing molecular weight polymers were investigated to enhance any results. The findings
showed that at high molecular weights the interfaces, probed by Neutron Reflectance and Dynamic Secondary Ion Mass Spectroscopy, had an excess of chain ends that was higher than values predicted by Rouse diffusion but only slightly lower than those predicted by the reptation model. At lower molecular weights the polymers only weakly entangled and observations were obscured by surface roughness effects. Conclusions drawn all indicated the reptation model as the method of diffusion involved in their system.

The criticism for diffusion is that the use of molecular weight and contact time are to be used as parameters in the calculation of joint strength\textsuperscript{36}. It is contended that the effect of these parameters can be explained without referring to diffusion. The effects of molecular weight and contact time can be seen in the effect and the kinetics of wetting and also on the degree of the interfacial contact.

Interdiffusion is the main role of adhesion in plastic welding when the plastics have similar solubility parameters\textsuperscript{37}. By using heat or solvents the polymer chains are given sufficient mobility to interdiffuse. The two surfaces are then held together under pressure until the interface has disappeared.

\textbf{2.1.3 Electronic Theory}

The initial theory for this electronic (or electrostatic) mechanism was proposed by Deryagin\textsuperscript{10,38-40}. He states that if the substrate and adhesive have different electronic band structures then some electron transfer, on contact, at the Fermi levels will take place. The formation of a double layer
of electrical charges will occur at the interface. It is this electrostatic force arising from the contact that contributes significantly to intrinsic adhesion. The controversy surrounding the electronic adhesion theory is:

The electrical double layer could not be identified without the separation of the bond. There is a suggestion that the electrical phenomena observed is caused by the failure event rather than from the adhesion between the materials.

Recently an experiment using an SEM determined that there was a potential distribution at a polymer-metal interface. This showed the existence of a double layer but the extent of the electronic double layer and its effect on adhesion still has to be established.

2.1.4 Adsorption Theory

The adsorption theory is the most accepted theory for adhesion\textsuperscript{41-43}. It states that once intimate contact has been made at the molecular level the materials will adhere because of the interatomic and intermolecular forces which are established between the atoms and molecules of the two surfaces. The name adsorption comes from the phenomenon of adsorption of gases and vapours onto solid materials. In this case the methods of adsorption can be separated into two groups - physical adsorption (or physisorption) and chemical adsorption (or chemisorption). A similar distinction can be made in adhesive bonding. The "physical" forces are generally present and those referred to as "chemical" sometimes augment them.
Table 2.1

Primary and secondary bonds seen in adsorption processes

<table>
<thead>
<tr>
<th>Bond Type</th>
<th>Bond Energy (kJmol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary</td>
<td></td>
</tr>
<tr>
<td>- Ionic</td>
<td>600-1200</td>
</tr>
<tr>
<td>- Covalent</td>
<td>100-800</td>
</tr>
<tr>
<td>Secondary</td>
<td></td>
</tr>
<tr>
<td>- Hydrogen bonding</td>
<td>~40</td>
</tr>
<tr>
<td>- Dipole / Dipole</td>
<td>~20</td>
</tr>
<tr>
<td>- London / dispersion</td>
<td>~10</td>
</tr>
</tbody>
</table>

The dipole / dipole and London / dispersion are also referred to as van der Waals forces. The forces and bonds involved are all of exceedingly short range. London / dispersion forces are particularly important because they are universally present between all atoms or molecules. This is because they arise from and depend solely upon the presence of nuclei and electrons. The other forces are only present when appropriate chemical groupings occur. The short range of the bonds means that the adherents have to achieve the necessary close intimate contact and interaction (wetting and spreading).

Calculations made using only the dispersion forces from the surface free energies yields a result that is considerably higher than experimentally observed. This discrepancy between theory and experiment is put down to air voids, cracks or other defects that cause stress points that initiate joint failure well below theoretical levels.
Secondary forces are thought to be the main mechanism for adhesion with hydrogen bonding being stronger than dispersion forces. Primary bonds have been reported to be formed at some interfaces. Infra-red evidence has been used for the covalent bonds formed between polyurethane adhesive and an epoxy based primer. Ionic bonds have been reported between polymers such as polyacrylic acid and metal oxides.

For many adhesive/substrate systems adsorption seems to be the main mechanism of adhesion. Other methods may be responsible or at least contribute to the overall joint strength. Some advantage may be gained from surface roughing to improve interfacial contact. The chemistry, topography and morphology of the substrates' surface are all important in ensuring intimate contact so that the strong and stable intrinsic adhesion forces can be made across the interface.
CHAPTER THREE

POLYMER INTERFACES
3. Polymer Interfaces

Within the framework of normal adhesion considerations have to be made for contacting polymers and for the interfacial zone\textsuperscript{44}. Polymer interfaces have two features:

1. They are generally hard to characterise.
2. While plausible models of structure are available there is little reliable information at the molecular level.

Often the final structure will be a balance between thermodynamics and kinetics. The diffusion of species towards or away from the interface may be considerably slower than the time-scale of processing (likely to occur in D2T2 printing). A non-equilibrium composition profile may be kinetically trapped as temperature drops or molecular weight increases.

In molecular physics the region between the bulk of a condensed phase and its geometric surface should be termed “the transition layer” while the area of it directly adjacent to this surface is designated “the boundary layer”. This helps to distinguish the zones in the surface region that have different physical properties. In polymers there are substantial differences in the properties of the bulk phase and the boundary and transition layers. Anomalies were detected to distances up to 500nm from the solid surface\textsuperscript{45}. These features are believed to be related to the rigidity of macromolecules and to the intermolecular interactions between them.
3.1 Polymers In Solution

Dissolving polymers in solution is generally a slow process that requires the polymers to be initially swollen by the diffusion of solvent molecules into the polymer. Once the polymers are swollen they can dissolve into solution. If the polymer to be dissolved has strong intermolecular forces, due to hydrogen bonding or crosslinking, then the polymer may not dissolve at all but simply swell. Their solubility of a polymer is therefore determined by several factors. These factors include presence of intermolecular forces, crystallinity, molecular weight, temperature and nature of the solvent.

3.1.1 Solubility Parameter

Solubility occurs when the Gibbs free energy of mixing is negative. The Gibbs free energy is related to the enthalpy and the entropy as show in equation 2.

\[ \Delta G = \Delta H - T \Delta S \]  
\[ \text{Equation 2} \]

Where \( G \) is the Gibbs free energy, \( H \) is the enthalpy and \( S \) is the entropy of the system. For a case where non-polar molecular are used and there is no hydrogen bonding \( \Delta H \) is positive and can be approximated to:

\[ \Delta H = \nu_1 \nu_2 (\delta_1 - \delta_2)^2 \]  
\[ \text{Equation 3} \]

where \( \nu \) is the volume fraction and the subscripts 1 and 2 refer to the solvent and polymer respectively. \( \delta^2 \) is the cohesive energy density and is
derived from the solubility parameters, $\delta$, for the solvent and polymer. A polymer will be expected to dissolve in a solvent if $\delta_1 - \delta_2$ is low generally less than 3.5 - 4.0, i.e. the solubility parameters for the solvent and polymer are close.

3.1.2 Flory - Huggins Theory

In polymer / solvent systems the large difference in molecular size between the solvent and polymer molecules gives rise to a small entropy of mixing. The polymer molecules consist of long, flexible chains. The segments in the chains are limited in their conformations by the segments directly preceding and following it.

Flory and Huggins independently derived a theoretical method of determining polymer compatibility with a solvent. Their methods were based on a statistical interpretation of a lattice system filled with polymer chains and solvent molecules. The number of ways a polymer molecule could be arranged in the solvent filled lattice was calculated and the following expression derived.

$$\Delta G = RT(n_1 \ln v_1 + n_2 \ln v_2 + \chi n_1 v_2)$$  

Equation 4

Where $n_1$ is the moles of a polymer or solvent and $n_2$ the number of moles of a second polymer. $v_1$ and $v_2$ are the volume fractions and $\chi$ is the Flory-Huggins parameter. This parameter is a useful measure of the solvent power. Poor solvent will have a value close to 0.5, as this figure lowers an improvement in solvent power is seen.
The lattice model proposed by Flory-Huggins relies on a uniform, random distribution of polymer molecules in the solution. In dilute systems there will be domains of polymer free solvent. Flory and Krigbaum assumed a system where the polymer rich areas were approximately spherical with a density that is at a maximum at their centre and decreases in an approximate Gaussian function with distance from that centre. Within the volume occupied by one molecule's segments all other molecules are excluded. The long range intramolecular interactions in this exclusion volume can be derived thermodynamically. The molar heat content, entropy and free energy of these interactions are:

All of the models are for polymers in solution although similar conclusions can be draw for polymer / polymer mixtures. The main difference is that the entropy of mixing two polymers is very low due to the fewer conformations available to two large molecular weight polymers.

3.1.3 Polymer Interfaces

As mentioned previously the entropy of mixing of macromolecules is low. The consequence of this is that even a relatively small positive enthalpy of mixing may be enough to prevent the two polymers forming a homogeneous blend. This can also result with similar polymers\textsuperscript{48}, such as polyethylene and polypropylene being immiscible because of their molecular conformation, even though their close solubility parameters suggest their miscibility.

Interfacial energies between polymer melts are also low, typically for two-phase blends they are a few mJ per metre and in the absence of specific
interactions between compounds, increase as the polymers become less similar.

With immiscible polymers the polymer-polymer interface can be seen as two pure homopolymers brought into contact rather than between solutions of one component in another. A certain amount of mixing will still occur at the interface. The existence of the infinitely sharp interface would require all of the polymer molecules to turn back at the interface. This would result in a loss of entropy because the number of conformations available to those molecules at the interface would be considerably limited. Therefore limited segmental diffusion is expected to bring about a favourable change in the free energy since the limited number of unfavourable interactions formed can be offset by the gain in entropy. The more unfavourable the interactions between the polymers gives a higher enthalpy price to be paid for by interdiffusion and the sharper the interface will be.

Various treatments of the polymer-polymer interfaces have been formulated with Helfand and Tagami\textsuperscript{49} applying a self-consistent field theory. The statistics of the polymer chain configurations are determined by a field provided by the concentration profiles. This will in turn, lead to a new concentration profile. To produce this self-consistent interfacial profile the following terms must be balanced.

1. The dependence of free energy on local composition as characterised by the Flory-Huggins interaction parameter $\chi$ (the higher the value of $\chi$ the less favourable is the interaction between the two components).
2. The resistance of the system to fluctuations in density (without this term a low-density interface region would be predicted).

3. Non-local terms, namely the desirability of low composition gradients and the severe loss of entropy associated with sharp interfaces in polymeric systems.

The equation makes several assumptions. Firstly - \( \chi \) is sufficiently small. Secondly, high molecular weights are involved and thirdly, the scale of inhomogeneity is large in molecular terms. The main findings are that the interface thickness is inversely proportional to interfacial tension which is proportional to \( \chi^i \). The method predicts that the interfaces are in the order of nanometres wide and rich in chain ends.

Helfand went on to apply a lattice theory to polymer-polymer interfaces. The results were similar to those produced by his self-consistent field approach for broad interfaces, but they could also be applied to narrow interfaces. The conformational entropy of molecules on a lattice was calculated with a given profile and these used to calculate the equilibrium profile by minimising free energy. The results showed that the same physical picture of a balance between unfavourable interactions and conformational entropy terms leading to a finite interfacial thickness was possible.

Regardless of molecular weight, a minimum amount of energy \( (W_A) \) is required to pull an interface apart. This will generally be higher the lower the interfacial energy is between the phases. When the interface is pulled at a finite rate an additional term is involved, the molecules at the interface
must either disentangle or their covalent bond must break. This effect becomes more significant as the interface becomes broader.

The existence of the chain entanglements means that there will be the additional significance on interfacial tension of kinetic contributions to adhesion\textsuperscript{50-52}. Also some molecular weight effects are to be expected. To test the full contribution from segmental interdiffusion to interfacial joint strength experiments have to be undertaken with the two phases containing polymers with molecular weights exceeding the critical values for entanglement. Therefore the strength can be calculated with no interference from entanglement.

The predictions are that the polymer-polymer interfaces will be rich in chain ends\textsuperscript{53}. Also it is predicted that in a polydispersed system the low molecular weight molecules will migrate to the surface\textsuperscript{54}. This all indicates the importance of molecular weight distribution on the mechanical joint strengths. Chain entanglement can still play an important role in adhesion even with high molecular weight polymer phases.

In polymer-polymer systems the evidence points to the likelihood of an interphase region rather than a sharp interface. This interphase will usually be in the order of nanometres. In simple terms the interphase will have properties intermediate to the two polymers, but this is not universal. The average molecular weights around this interphase will differ from the bulk of the two components. Also impurities and low molecular weight molecules will migrate to this interphase.
3.1.4 Wetting

Wetting is a prerequisite for the formation of a good adhesive joint. Wetting is defined as the extent to which a liquid makes contact with a surface. In polymer interfaces it is characterised as the degree of direct interfacial contact. An adhesive ideally has to be able to spread over the solid substrate displacing any air gaps or other contaminants present at the surface. An adhesive conforming to these conditions must:

1. When liquid have a zero or near zero contact angle on the surface.
2. At some stage during the bonding process have a low viscosity to facilitate wetting.
3. Be brought together with the solid in such a manner as to dispel any trapped air.

Wetting of a polymer surface by a non-viscous liquid is generally quantified via the contact angle of a liquid on a surface at equilibrium\(^{55}\) (figure 3.1).
Young's equation is used to describe the drop in thermodynamic equilibrium with the surface.

\[
\gamma_s = \gamma_{sl} + \gamma_{lv} \cos \theta \\
\text{Equation 5}
\]

where

- \( \gamma_s \): specific surface excess free energy of a solid.
- \( \gamma_{sl} \): interfacial excess free energy of the solid/liquid interface.
- \( \gamma_{lv} \): specific surface excess free energy of a liquid in equilibrium with the vapour.
- \( \theta \): equilibrium contact angle

For low molecular weight liquids a more rigorous treatment replaces \( \gamma_s \) with \( \gamma_{sv} \), the surface energy of the solid on which equilibrium adsorption of vapour from the liquid phase has occurred. \( \gamma_{sv} \) and \( \gamma_{lv} \) both refer to surfaces relative to which the gas phase is at equilibrium vapour pressure. Thus the equation below can be used.
\[ \gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos \theta \]  

Equation 6

Where

\( \gamma_{sv} \) - specific surface excess free energy of a solid in equilibrium with the vapour.

For low surface energy materials, eg. polymers, the amount of vapour adsorption is small and therefore:

\[ \gamma_{sv} \approx \gamma_{s} \]  

Equation 7

For systems where \( \theta = 0 \) it is possible to achieve good wetting over the solid surface. On a rough or heterogeneous surface the equilibrium contact angle\(^{56}\) no longer exists. Figure 3.2 shows how roughness and heterogeneity affects the measured contact angle.
Contact angle variations due to surface roughness and heterogeneity

(a) On a rough surface the receding contact angle ($\theta_{\text{rec}}$) is lower than that obtained from a flat, homogeneous surface. The advancing contact angle ($\theta_{\text{adv}}$) is larger than that obtained from a flat, homogeneous surface.

(b) (---) Low-energy surface, (-----) High-energy surface. When a drop advances across a heterogeneous surface the drop front will tend to stop on a low surface energy area leading to a high value of $\theta_{\text{adv}}$. Subsequently the receding drop front will tend to stop on a high surface energy area so that $\theta_{\text{rec}}$ is lower than $\theta_{\text{adv}}$.

While mechanical interlocking with a rough surface this surface can also weaken bond strength. This is dependant on the adhesive. An adhesive with a low wetting ability or high viscosity not flow into the abrasions thus creating air pockets which not only are areas of non-bonding but also areas
which could produce stress points. Figure 3.3 shows the effect of an adhesive with a low wetting ability.

Figure 3.3
Air pockets created by an adhesive with a high surface energy

If a force is used to increase the wetting of a liquid the most important factor is usually dewetting. This happens when the liquid/liquid interactions are more energetically favourable than solid/liquid interactions. The result is that after the pressure used in the forced wetting is relaxed the liquid retracts across the surface. Again the surface roughness can play a role in dewetting as it does in wetting. The greater the surface roughness the less the dewetting.

Normally for spontaneous wetting to occur the liquid must have a lower surface energy than the substrate. i.e. a liquid with a zero or low contact angle. If the surface of the substrate has a higher energy there will be greater interactions with the liquid.
3.2 Additives

Many different types of small molecules are present in polymers. These include oligomers, surfactants and starting materials left over from the initial polymerisation. Also included are the various additives used in modern polymer production. These include plasticizers, antiplasticizers, compatibilisers, lubricants, heat stabilisers\(^{57}\), UV absorbers\(^{58,59}\), fillers, pigments\(^{60,61}\) and solvent residues. A further set of additives include highly functional organic molecules, notably pharmaceuticals for drug delivery systems and dyes for printing. All of these small molecules can play a part in both the bulk properties and surface characteristics of the polymer.

It has already been mentioned that weak boundary layers can play an important role in adhesion. If these small molecules can migrate to the surface they will contribute greatly to this effect. If they instead remain in the bulk of the polymer then they may, if present in sufficient amount, have a profound effect on the physical properties and subsequently the adhesion.

3.2.1 Bulk Property

Plasticisation\(^{62}\) is the process in which a plasticiser is added to a polymer to affect its bulk properties notably by softening hard and brittle products. The plasticiser works by increasing the free volume in a polymer system thus increasing the mobility of the polymer chains. This effects the polymer's modulus or stiffness, increases elongation and flexibility and lowers the \(T_g\).
It is difficult to characterise the behaviour of a plasticiser in terms of a fundamental property. This is because the behaviour of each plasticiser is different in each polymer.

Antiplasticisers are compounds which when added to a polymer give rise to an increase in tensile modulus and $T_g$. Classes of particularly effective antiplasticizers are chlorinated biphenyls and poly(styrene glycols). It is believed that these compounds work because of their functionality causing bonding between adjacent polymer chains thus giving rise to a cross-linking effect. These compounds have a greater effect on polymers that have a high degree of functionality either on the polymer backbone or side chains.

Several other methods of antiplasticization can be undertaken. The addition of inorganic mineral fillers and glass fibres helps to produce increases in tensile strength. Random fibre orientation is the preferred system which leads to increases in impact strengths and longitudinal strength.

The effects of the addition of dyes to various polymers has been investigated. The effect of interaction of dye molecules in polymer blends giving a $T_g$ decrease is noted and several equations used to express this relationship, notably the Fox equation, see equation 8.

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}}$$  

Equation 8
Where \( T_g \) is the glass transition of the mixture of polymer 1 and diluent 2, \( w_1 \) is the weight fraction of polymer 1 with a glass transition temperature \( T_{g1} \) and \( w_2 \) is the weight fraction of the diluent 2 with a glass transition temperature \( T_{g2} \).

The \( T_g \) of the polymers were sometimes increased and sometimes decreased and this change was attributed to the dye-polymer affinity. Increasing dye-polymer affinity produced stronger interactions leading to a rise in \( T_g \) of the polymer. Excellent correlations were noted between the \( T_g \) change and the dye-polymer solubility parameter match which was used to determine the dye-polymer affinity. The best correlations were obtained when neglecting the dispersion forces in the solubility parameters, indicating that the polar and hydrogen bonding forces controlled the \( T_g \) effects.

### 3.2.2 Migratory Small Molecules and Weak Boundary Layers

Bikerman\(^69\) was the first to introduce the idea that weak boundary layers were a significant part of the adhesive process. Potential weak boundary layers include dust, grease, and metal oxides of relatively low strength. These would be removed prior to the adhesives being applied. The adhesive strength of the bond could then be interpreted using one or more of the four main theories of adhesion, mechanical interlocking, diffusion, electronic and adsorption.

Bikerman believed that weak boundary layers were the main cause of adhesive failure. An example of possible layers is given by Pocius\(^70\).
Figure 3.4 shows the possible layered, rough structure expected on unprepared metals.

Figure 3.4
The layered structure on unprepared metals

Most metals are covered by an oxide layer. Water is generally found as chemisorbed and physisorbed water at the oxide surface. On top of the oxide layer is a layer of adsorbed polar organic molecules. They are normally adsorbed from the atmosphere or they may have been added as a lubricant in the milling process. Further layers include adsorbed non-polar organics and gases. Water is often found present as a liquid. All of these layers can act as a weak boundary layer when an adhesive is brought into contact with the sample.

In most polymer systems the polymer involved is not of uniform molecular weight. Low molecular weight materials often rise to the surface. Here you will also find migratory additives normally used in modern polymers.

Previous studies have shown how PVME can migrate in polyolefins. This has been seen with XPS analysis before and after various washes.
showing a continual migration. Once at the surface it acted as a weak boundary layer and reduced the adhesion.

PVME has also been studied in polystyrene systems where Attenuated Total Reflectance - Fourier Transform Infra-red analysis was used to measure interdiffusion above and below the Tₘ of the polystyrene\textsuperscript{72}. The surface migration of PVME in PVME / Polystyrene blends has been studied by XPS\textsuperscript{73}. It was shown that there was an elevated surface concentration of PVME substantially higher than that found in the bulk.

The role of surfactants used in making latex films has been studied\textsuperscript{74,75}. In the study peel strengths versus concentration curves were established for several surfactants in poly(2-ethyl hexyl methacrylate) bonded to glass. The surfactants included sodium dodecyl sulfate, hexadecyl trimethylammonium bromide, hexadecyl pyridinium chloride and ethoxylated nonyl phenol containing different numbers of ethoxy groups. The results showed a concentration build up of the surfactants at the polymer substrate interface. The concentration curves showed either a maximum or a minimum curve dependant on the surfactant. By reducing the peel rate they were able to reduce the size of the maxima and minima to show that at an extrapolated zero speed the peel strengths are independent of the amount of additives. The maxima and minima are therefore shown to be bulk property affects.

Analysis of the adhesion between PVC and nitrile rubbers\textsuperscript{76,77} show how plasticisation gave an increase in adhesion and the PVC stabilisers have a decreasing effect at high temperatures and long contact time. It is believed
that the stabilisers block the reactive sites at the surface of the PVC reducing the dipolar interaction.

The use of silicone additives in polymers has been investigated\textsuperscript{78}. They are mainly used in the role of surface modification where they are cross-linked at the surface. It has been shown that they have a wide variety of applications including release coatings, lubricants and recently as a flame retardant. It has also been noted\textsuperscript{79} that silicone oils rather than cross linked resins proved to be the better release agents with pressure sensitive adhesive tapes.

Adhesion between polycarbonate (PC) and poly (styrene-co-acrylonitrile) (SAN) has been examined with varying levels of oligomers in the SAN\textsuperscript{80}. It has shown that as the levels of oligomers increases the adhesive strength decreases. The oligomers are believed to migrate to the surface where they dilute any entanglement between the PC and SAN thus reducing interfacial adhesion.

Not all additives that migrate to the surface produce a weak boundary layer. It has been shown\textsuperscript{81} that an aid to adhesion between epoxy resin and poly(isoprene) rubber is to add functionalized rubbers to the poly(isoprene) rubber. The most effective of these was found to be acrylonitrile poly(butadiene carboxylic) copolymer which produced strong interactions with the epoxy resins. The results showed that the increase in adhesive strength was related to the increase in thickness of the interphase region which was seen when there was functionalized rubber enrichment at the surface.
CHAPTER FOUR

PEELING ADHESION
4. **Peeling Adhesion**

The most common way to assess the strength of adhesion is to peel apart the substrates. There are several ways to perform these peel tests as shown in Figure 4.1.\(^{82-84}\)

![Schematic diagrams of several peel test methods](image)

The results of peel tests depend on several variables such as rate of peeling, bond thickness, modulus of the adhesive, orientation and organisation of polymers\(^{85,86}\), temperature, angle of peel and as such it is claimed to be a measure not of pure adhesion, but of adhesion plus the mechanical properties of the adhesive.

Peel tests can be performed in two ways.

1. Place the sample in a test rig and measure the load required to strip the surfaces apart at a given peel rate.
2. Apply a given load and measure the time taken for the bond to peel a measured distance.

It is recognised that the first of these methods gives the more reliable results with less spread\textsuperscript{87}. This is probably due to the complex relationship existing between the load and rate of peeling for the bonds which, due to experimental error, often vary in strength along the length of a test piece.

4.1 Peel Force and Peel Energy

It is straightforward enough to compare the results for a peel in the form of a peel force/width, a second possibility is to derive a term for the peel energy involved from a basic mechanical principle\textsuperscript{88}. To do this the work done by the test machine is equated to the work done on the sample. This will then form the basis for understanding and interpreting peel tests (see figure 4.2).
Consider a strip of length \( x \) being peeled from a substrate by a force \( F \) at an angle \( \omega \) to the substrate. The point of application of the force will have moved a vertical distance \( l \)

\[
l = x(1-\cos\omega) + \Delta x \quad \text{Equation 9}
\]

The first term is the result of freeing a length \( x \) of the strip and subtracting the height difference at the point of peel. The second term \( (\Delta x) \) represents the extension of the free length \( x \) caused by the force \( F \). \( \Delta x \) can be calculated if the tensile properties of the strip material were known otherwise it can be measured experimentally. The work done by the machine, the force used in moving the vertical distance \( l \), can then be written as
\[ F l = F x (\lambda - \cos \omega) \]  

Equation 10

where the expression has an additional term, \( \lambda \), which represents the extension ratio (extended length/original length).

The work done on the sample is then split into two parts. The first is the peel energy \( P \) which is the energy per unit area of peeled substrate surface. This encompasses all of the energy dissipated at the peel front. The second is the work done on stretching the freed strip. This will be the strain energy density \( W_\lambda \) for extension to \( \lambda \). \( W_\lambda \) can again be either calculated from an expression for the tensile stress-strain relationship for the material or it can be evaluated from the work done in an appropriate tensile test. Therefore

\[
\text{work done on the sample} = P b x + W_\lambda b x t \quad \text{Equation 11}
\]

\( W_\lambda \) is expressed per unit volume so it has to be multiplied by the volume of the peeled strip to get the energy stated, \( t \) is the thickness of the strip and \( b \) is its breadth. Equating the work done by the machine with the work done on the sample gives

\[
P = F/b(\lambda - \cos \omega) - W_\lambda t \quad \text{Equation 12}
\]

If the extension of the strip is negligible, this is often with cross-linked polymer substrates, \( \lambda \) is one and \( W_\lambda \) is zero. The experimental conditions may also lead to further simplifications in the equation. With most instruments the peel angles are normally fixed, with 90° and 180° being common values. The equations therefore simplify to
\[ P = \frac{F}{b} \quad \text{at } 90^\circ \quad \text{Equation 13} \]

and

\[ P = 2\frac{F}{b} \quad \text{at } 180^\circ \quad \text{Equation 14} \]

These equations suggest that the peel load at \( 90^\circ \) should be twice the value at \( 180^\circ \).

### 4.2 Peel Energy

The peel energy, \( P \), is the energy (per unit area) dissipated by all the energy-dissipating processes involved in the broad region associated with the peel front. As new surfaces are created at the peel front there will be a thermodynamic term involving work of adhesion \( (W_A) \) or a work of cohesion \( (W_C) \) depending on the locus of failure. Failure within the adhesive layer is cohesive failure and failure at the interface between the substrate and adhesive is interfacial or adhesive failure. If the substrate fails it is a material failure.

To this thermodynamic term several other terms relating to the materials and conditions must be added. These will include terms for plastic deformation of the adhesive close to the fracture surface\(^9\), for viscoelastic dissipation as the peel front advances causing the adhesive to be stressed and then relaxed and for losses in bending the freed strip through the peel angle. Thus \( P \) may be written as the sum of these various terms.
\[ P = W_A (or W_C) + \psi_{\text{plas}} + \psi_{\text{visc}} + \psi_{\text{bend}} + \ldots \quad \text{Equation 15} \]

### 4.3 Factors affecting Peel Tests

#### 4.3.1 Bond Width

The strength of peel is usually expressed as peel strength (grams or pounds) per inch/cm of width. There is also a linear relationship between load and bond width whether the bond fracture is cohesive or adhesive. This is to be expected from the equations derived previously.

#### 4.3.2 Bond Thickness

The thickness of the adhesive will effect the peel strength in several ways. It directly enters into the strain energy density term \((W_{xt})\) and it can also alter some of the dissipation terms by changing the actual angle at the peel front or by altering the volume of polymer in which plastic or viscoelastic dissipation occurs\(^90\).

The results\(^91,92\) show that an increase in adhesive thickness gives a linear relationship with the increase in peel strength. With an adhesive with no energy dissipation the strength was independent of the thickness of the adhesive. It cannot be concluded that the peel strength will increase infinitely with increasing adhesive thickness. The results showed a maximum peel strength in the 100-250 \(\mu\)m range. The highly deformed region around the crack tip will increase as the thickness increases, but this
extension is not always proportional to the increase in thickness. Therefore the highly deformed region will be confined to a relatively small region.

4.3.3 Adhesive Modulus

The best illustration of this type of effect is by considering a polymer adhesive which is becoming more cross-linked with time. This will give rise to increasing stiffness with time. The polymer molecules are free to flow and entangle until sufficient cross-linking has occurred to slow this and finally stop it altogether. The effects are illustrated in figures 4.3 and 4.4.

Figure 4.3
The effect of adhesive modulus on peel strength
With the soft adhesive (low state of cure) there is a large amount of deformation so the area bearing the load is large and the bond strength high. With the hard adhesive (cross-linked) the amount of adhesive deformation is low, therefore the area bearing the load is small and the bond strength low.

4.3.4 Angle of Peel

Most tests are carried out with the peel angles set at 90° or 180°, thus simplifying the previous equations referring to peel strengths. These equations closely follow the observed peel strengths for rubbery adhesives. For other adhesives the angle dependence is different. Polyethylene was peeled from a sulphochromated aluminium at various peel angles. As the
peel angle changes bending losses will vary and the balance between shear and cleavage forces at the peel front will change. This will effect the energy losses at the front. The results can be seen in the graph in figure 4.5.

Figure 4.5
Graph showing the effects of peel angle on adhesion

4.3.5 Peel rate

The rate at which the substrates are separated has a profound effect on the peel strength. With acrylic binders on cellophane substrate\textsuperscript{96}, it was found that at low peel rates the peeling force increased with increasing peel rate and the failure was cohesive. At high peel rates the force was rate independant and the failure was adhesive. At a given peel rate the peeling force increased with thickness. These effects are the result of the rate dependence of deformation in viscoelastic materials. At the slow rates the
effective modulus of the materials is so low that the polymer chains flow apart readily. At higher speeds the material behaves as if it is stiffer and will support higher loads before parting. When the cohesion becomes greater than the adhesive forces then the type of bond failure changes from cohesive to adhesive.
CHAPTER FIVE

EXPERIMENTAL
5. Experimental

5.1 Peel Apparatus Set-up

The peel test apparatus used in the experimental work was an Instron table model 1026 with tension load cell type 2512-107. This gave full scale ranges of 50, 100, 200 and 500 grams. The test apparatus set-up is shown in the schematic diagram in figure 5.1.

Figure 5.1
Schematic diagram of the peel test apparatus

A strip of sample 2.5 cm wide is cut using a scalpel. The thicker receiver sheet is stuck to a metal plate with double sided sticky tape. Both the receiver sheet and the metal plate are clamped in the jaws of the peel test machine. The metal plate is to ensure that the peeling is always at 180°
because of the changes in the peel strength due to any change in peel angle. The dye sheet is then attached to a strip of Melinex that is, in turn, connected to the other jaw of the peel test machine. The rate of peel is set at 100 mm/min. Two samples are used from each printed sheet to gain two peel strengths per sheet.

All recorded peel strengths are measured at 100 mm/min for 30 seconds. The value stated is an average of the peel strength / time curve obtained from this 30 second peel. Two values are measured from separate samples to give some indication of error. Typical random errors were found to be of the order of 10% for samples with moderate peel strengths (10-30 grams/inch). Less strongly bonded samples generally showed a higher percentage error. The smallest possible increment in peel strength measurable using this apparatus was a quarter of a gram.

5.2 Characterisation

5.2.1 Glass Transition Temperatures

The T_g's of the polymers chosen were measure using a Perkin-Elmer DSC-4 differential scanning calorimeter. The polymer sample and an aluminium reference were heated in the calorimeter. A 20 mg sample of each was used and the calorimeter was calibrated using an indium standard. Any difference in thermal behaviour between the sample and reference is recorded, being obtained from the different quantities of electrical energy required to maintain both sample and reference at the same temperature according to the selected rate of temperature change. A graph of heat flow against temperature is produced. From this graph the T_g's of the polymer
samples can be obtained. In the trace a step is observed and this represents a change in specific heat capacity and usually indicates the glass transition temperature.

5.2.2 Molecular Weight

The molecular weights of the polymer samples were measured by size exclusion chromatography. A 60 cm 10 μm PL gel mixed-B column was used with THF as the eluent at a flow rate of 1 ml / minute. Detection was by differential refractive index. A sample concentration of 4 mg in 5 ml was used with a sample loop of 50 μl. The molecular weight and distribution was determined by PL Caliber software using a set of polystyrene standards.

5.2.3 Fourier Transform Infra-red Spectroscopy

The spectra were recorded by using a multiple bounce attenuated total reflectance (ATR) method and a single bounce ATR method. These methods use infra-red transparent prisms with a refractive index typically higher than 2.0. Germanium, sapphire or KRS-5 (an alloy of TlBr and TlI) are normally used. The infra-red radiation enters the prism and is totally internally reflected at the interface between the sample and the crystal. During the reflection some of the radiation penetrates into the sample forming an evanescent wave. This evanescent wave is caused by the interference of the incident and reflected waves and the amplitude decreases exponentially with distance from the interface. A schematic diagram of the multiple bounce ATR attachment can be seen figure 5.2. A schematic of the single bounce ATR attachment can be seen in figure 5.3.
Figure 5.2
Schematic diagram of the multiple bounce ATR attachment

![Diagram of multiple bounce ATR attachment]

Figure 5.3
Schematic of the single bounce ATR attachment

![Diagram of single bounce ATR attachment]

By placing the sample against the prism the evanescent wave can interact with the material and be absorbed at specific wavelengths as in conventional infra-red spectroscopy. The spectrum of the sample is
therefore determined by detecting the infra-red radiation which exits the prism.

The FTIR instrument used was a Nicolet 20 DXC spectrometer set with a resolution of 2 wavenumbers, a mirror velocity of 40 and Happ-Genzel apodisation. The mercury cadmium telluride (MCT) detector was kept at liquid nitrogen temperature for maximum efficiency. The ATR attachment was a SpectraTech Model 300 continuously variable ATR system used with both KRS-5 and Ge crystals. The KRS-5 prism was 50x10x3 mm with a 45° incident face and a reflective index of 2.38. The germanium prism was 25x10x3 mm with a 60° incident face and a reflective index of 4.01. A dry air purge system was used to reduce water vapour interference.

Spectra of the samples were obtained by first taking a background of the crystal without the sample. A water vapour spectra was also measured so that any subtraction could be taken if required. The sample films were then clamped against the crystal faces using rubber pads and a metal clamp. This ensures good optical contact between the sample and crystal. The system's signal to noise ratio was optimised by adjusting the infra-red beam and the mirrors of the ATR attachment. 200-300 scans were used to acquire good spectra.

5.2.4 Ultraviolet / Visible Spectroscopy

If electromagnetic radiation is allowed to impinge upon a transparent medium some of the energy will be reflected, some absorbed and the remained transmitted through the material. The transmitted radiation is
then resolved into its constituent wavelengths by a diffraction grating or prism and an absorption spectrum is produced. The spectrum indicates the wavelengths of the incident beam that have been absorbed by the medium. The Beer-Lambert law is used to express the relationship between the amount of light absorbed and the concentration and path length of the sample:

\[
\log_{10} \frac{I_0}{I} = \varepsilon c l
\]

Equation 16

Where \( I \) is the intensity of the transmitted light, \( I_0 \) is the intensity of the incident beam, \( \varepsilon \) is the molar extinction coefficient (a property of the sample compound at a given wavelength), \( c \) is the concentration of the sample in moles per litre and \( l \) is the path length of the sample cell expressed in centimetres. \( \log_{10}(I_0/I) \) is the value gained from the instrument and generally referred to as the absorbance or optical density.

The instrument used was a Shimadzu UV-VIS Spectrophotometer UV-160 with the absorbance spectra collected between 200 and 1000 nm. The standard method of analysis involves the use of silica solution cells. For the polymer films produced in the experiments a different set was employed. The polymer films including dye were placed in the path of the beam and ran against a background of the corresponding polymer film. This produced an absorbance spectrum of the dye alone allowing for the study of dye concentrations in the films.
5.2.5 Atomic Force Microscopy

In atomic force microscopy a sharp tip attached to a flexible cantilever stylus is raster scanned over the surface of the sample\textsuperscript{99-107}. There are three common techniques used in AFM. They are contact, non-contact and tapping modes.

5.2.5.1 Contact Mode

In contact mode the tip scans the sample in close contact. The force acting between the sample and tip causes minute deflections of the cantilever. These deflections are detected and utilised as feedback signal. By keeping this force constant the tip remains the same height above the sample surface. The deflection of the cantilever to keep this same height is detected by a sensitive differential laser. A diode laser beam is focused onto the back of the cantilever. As the cantilever deflects the reflected beam moves and the difference in intensity between detector quarters is monitored.

5.2.5.2 Non-Contact Mode

Another method of scanning is in a non-contact mode. This is used in situations when the tip contact may alter the sample in some way. The tip hovers between 50 - 150 Angstroms above the surface and attractive van der Waals forces between the tip and sample are detected. Topographical images are again constructed by scanning the tip above the surface.
5.2.5.3 Tapping Mode

Tapping mode is the most recent advance in AFM. Tapping mode overcomes the problem of friction, adhesion and electrostatic forces that can cause problems with conventional scanning techniques. Instead it brings the tip into close contact with the sample to provide the resolution but instead of dragging the tip to the next raster point it lifts the tip from the surface. The raised tip is then cleanly moved to the next sampling point and lowered to get the topographical information.

The AFM used was an ARIS-3300 personal atomic force microscope with a large range ARIS-3075 sample scanning module. A contact mode was used to scan the samples. This provides scan ranges up to 65 μm XY Axes and up to 9 μm Z axes. The magnification possible is up to x200 but with the soft polymer films images at up to only x50 are likely.

5.2.6 X-Ray Photoelectron Spectroscopy (XPS)

XPS uses primary radiation to excite the sample and the electron emission is detected\textsuperscript{108-110}. Soft X-rays are used as the primary radiation and the photoemission is from the core electrons of the atoms in the sample. These electrons are collected and passed through an energy analyser and then to the detector where the kinetic energy is measured. This kinetic energy is related to the binding energy of the core electrons. This results in a very surface specific spectroscopic technique. Quantitative\textsuperscript{111} analysis was achieved by measuring the areas of the peaks after subtracting a Shirley-type background, with appropriate corrections also being made for
photoelectron cross-sections, inelastic mean-free paths\textsuperscript{112}, energy analyser transmission and angular asymmetry in photoemission when required.

The sample is placed in a vacuum chamber with a pressure of less than $10^{-7}$ mbar. The X-rays used to excite the sample are commonly Al K\textalpha{} (1486 eV) and Mg K\textalpha{} (1254 eV). These are produced by high energy electrons (10-15 eV) hitting an appropriate target. A monochromator is not usually required because the characteristic X-ray lines are sufficiently narrow in width. The X-rays irradiate the sample over an area of several square millimetres. The emitted electrons pass through a hemispherical sector energy analyser and then onto an electron multiplier. See figure 5.4 for a schematic of the XPS system.

![Figure 5.4](image)

Schematic of the XPS system

The relationship between the kinetic energy of the electron and the binding energy is shown in the equation below.
Ke = hω - BE - ϕ  

Equation 17

Where $h\omega$ is the energy of the X-ray photon, $BE$ is the binding energy with which the electron was bound to the atom and $ϕ$ is the work function of the spectrometer (this is normally small and is often ignored).

The binding energy of the electron is characteristic of the element from which it was emitted. It is therefore possible to identify the elements present in the surface of the sample from the kinetic energy of the collected core electrons. The core level binding energies of the 1s core electrons increase as a function of atomic number. As a result for heavier elements the X-rays used are not sufficiently energetic to induce emission from the 1s level. Instead emission is observed from less strongly bound electrons in the core (2s and 2p electrons).

Although the binding energy of the core electron depends principally on the charge of the nucleus it is also affected by the chemical bonding of the atom. The changes to the binding energy due to the chemical bonding is small, typically $<10$ eV. These changes are known as a chemical shift and are measurable when a narrow scan is produced.

A VG Escalab spectrometer was used in the experiments. The normal spectrum produced is a broad scan over a wide range of energies. This is possible to detect all elements except for hydrogen and the assignment of the peaks is relatively simple. A narrow scan is over a small range that gives the maximum energy resolution and the chemical shifts are measurable.
Possible errors associated with the XPS results are random errors in measuring the peak areas. These errors are expected to be in the order of 2%.

5.3 Production of Films

The polymer films were made by drawing solutions of the polymers onto the PET substrate using K-bars\textsuperscript{113}. The size of the PET substrate films are 3 inches by 5 inches, the receiver sheets are 125 microns thick and the dye sheets are 6 microns thick. A four micron polymer film is drawn on to the receiver sheets and a one micron film is drawn onto the dye sheets.

K-Bars are produced by winding precision drawn stainless steel wire onto a stainless steel rod which results in a repeating pattern of identically shaped grooves. The diameter of the wound wire precisely controls the wet film thickness. Figure 5.5 shows both a close wound and a spirally wound bar.

A bead of liquid is deposited at the top of the substrate and the bar pulled through the coating liquid. This forms raised lines of coating which, due to their surface tension, immediately flow together to form a flat, uniform film. Close bound bars can produce wet coating thickness' of 4 to 120 \(\mu\text{m}\). Larger thickness' can be achieved using spirally wound bars. Figure 5.6 shows a draw down being undertaken.
Figure 5.5
Close Wound and Spirally Wound K-Bars$^{113}$

Figure 5.6
A K-Bar being used to draw a thin film$^{113}$
Table 5.1
Wet Film Thickness from Close Wound K-Bars

<table>
<thead>
<tr>
<th>Bar Number</th>
<th>Wire Diameter / mm</th>
<th>Wet Film Thickness / μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.05</td>
<td>4</td>
</tr>
<tr>
<td>1</td>
<td>0.08</td>
<td>6</td>
</tr>
<tr>
<td>2</td>
<td>0.15</td>
<td>12</td>
</tr>
<tr>
<td>3</td>
<td>0.31</td>
<td>24</td>
</tr>
<tr>
<td>4</td>
<td>0.51</td>
<td>40</td>
</tr>
<tr>
<td>5</td>
<td>0.64</td>
<td>50</td>
</tr>
<tr>
<td>6</td>
<td>0.76</td>
<td>60</td>
</tr>
<tr>
<td>7</td>
<td>1.00</td>
<td>80</td>
</tr>
<tr>
<td>8</td>
<td>1.27</td>
<td>100</td>
</tr>
<tr>
<td>9</td>
<td>1.50</td>
<td>120</td>
</tr>
</tbody>
</table>

Table 5.2
Wet Film Thickness from a Spirally Wound K-Bar

<table>
<thead>
<tr>
<th>Bar Number</th>
<th>Wire Diameter / mm</th>
<th>Wet Film Thickness / μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>0.25</td>
<td>150</td>
</tr>
<tr>
<td>200</td>
<td>0.36</td>
<td>200</td>
</tr>
<tr>
<td>300</td>
<td>0.51</td>
<td>300</td>
</tr>
<tr>
<td>400</td>
<td>0.76</td>
<td>400</td>
</tr>
<tr>
<td>500</td>
<td>1.00</td>
<td>500</td>
</tr>
</tbody>
</table>

Tables 5.1 and 5.2 show the wet film thickness achievable with the different sized K-Bars. To produce the four micron film on the receiver
sheet a 11.1 % solution in THF was used with a K-bar number 4. This 11.1% solids content with a wet film thickness of 40µm results in a 4.4µm film. The film was drawn and initial solvent evaporation was achieved using a hair dryer. Then the film was placed in an oven at 140° for three minutes. Using several of the polymers the 11.1 % solution proved to be too viscous to be useful. Instead a 5.33 % solution and K-bar number 7 were used. The dye sheet films had to be one micron thick and so a more dilute solution and a smaller K-bar was used. A 4.2 % solution in THF with a K-bar number 3 was used to produce a one micron film. The film was again initially dried using a hair dryer followed by thirty seconds in an oven at 140°.

5.4 Video Printer

A Canon Colour Video Printer RP-420 was used in the experiments. It had been modified so that it no longer accepted a dye sheet cartridge but instead accepted pairs of polymers. The dye sheet was attached to the receiver sheet using adhesive tape. Once fed into the video printer the pair of polymer films were held on a roller and drawn into the printer. The roller drew the sheets past the print head and after printing had been completed would eject the printed sheets.

The software used to run the printer was a TrueArt drawing package. With this software it was possible to change the colour intensity of the screen. If a filled square was drawn it is possible to change the fill colour using the red, blue and green brightness values. A scale of 0-31 was available for this colour change. By varying the colour intensities on the monitor screen the power of the printer could be adjusted. A setting of 0 gives a black
screen and therefore the greatest power while a setting of 31 gives a white screen and thus the lowest print power (no heat is required to print a white sheet as no dye is required to transfer). At lower than the maximum power (heat settings 1 up to 31) the maximum interface temperature decreases linearly although the time scale of the printing remains constant. This means that the setting of the software ranged from the highest temperature at a setting of 0 and the lowest at a setting of 31.
CHAPTER SIX

RESULTS
6. Results

6.1 Starting Polymers

Four polymers were chosen to be used as the dye sheet and receiver sheet polymer coatings. They were chosen for study so that when paired up several questions could be answered about the adhesion mechanisms. In particular the effects of:

1. Surface energy
2. Molecular weight
3. Glass transition temperature (T_g)
4. Temperature in the printer

The aim was to identify the most important factors affecting the peel strength of joints formed between them.

The four polymers chosen were poly (methyl methacrylate) (PMMA) (Aldrich Cat. No. 18,223-0), poly (vinyl acetate) (PVAc) (Aldrich Cat. No. 18,948-0) and a high and low molecular weight polystyrene (PS) (Aldrich Cat. Nos. 18,242-7 and 33,165-1). Their structures can be seen in figure 6.1. Each polymer was used both as dye and receiver sheets and were paired with the three other polymers as well as with themselves. This yielded a four by four matrix of results.
6.1.1 Characterisation

6.1.1.1 Glass Transition Temperature

In general, polymers are either completely amorphous or they have an amorphous phase\textsuperscript{114}. These materials are hard, rigid glasses below a temperature known as the glass transition temperature or $T_g$. Above this temperature amorphous polymers are rubbery - soft and flexible. During the printing process most polymers will pass through this glass transition temperature and this will have a dramatic effect on their properties and hence joint formation. Table 6.1 shows the $T_g$ of the various polymers.

Several physical properties change in the region of the $T_g$. The elastic modulus of a polymer above its $T_g$ can be up to a factor of 1000 lower when compared to its modulus in its glassy state below its $T_g$. The
coefficient of thermal expansion, specific heat capacity, refractive index and mechanical damping all undergo changes at the polymers $T_g$.

6.1.1.2 Molecular Weight

Figures 6.2-6.5 are the results from the molecular weight determinations using GPC. The results showed that the PMMA, high molecular weight PS and the PVAc had single broad distribution, values are polystyrene weight equivalents.

The low weight polystyrene showed a bimodal distribution. The higher molecular weight peak gave a molecular weight of $\sim 120,000$ g mol$^{-1}$ with the lower peak a molecular weight of $\sim 1,000$ g mol$^{-1}$. The molecular weight for the combined peaks was $\sim 55,000$ g mol$^{-1}$. It was decided to replace this sample with another one of a similar molecular weight, Polyscience 50,000 g mol$^{-1}$. This sample too had a bimodal distribution with similar molecular weight peaks.

Figure 6.2

GPC Trace of PVAc
### Molecular Weight Averages

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Mp</td>
<td>147000</td>
</tr>
<tr>
<td>Mn</td>
<td>65000</td>
</tr>
<tr>
<td>Mw</td>
<td>199000</td>
</tr>
<tr>
<td>Mz</td>
<td>435000</td>
</tr>
<tr>
<td>Mz+1</td>
<td>738000</td>
</tr>
<tr>
<td>Mv</td>
<td>173000</td>
</tr>
</tbody>
</table>

Polydispersity (Mw/Mn) 3.06

Area (Response Minutes): 470000

---

**Figure 6.3**

GPC Trace of Polystyrene (280,000 mwt)

![GPC Trace of Polystyrene](image)

### Molecular Weight Averages

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Mp</td>
<td>245000</td>
</tr>
<tr>
<td>Mn</td>
<td>122000</td>
</tr>
<tr>
<td>Mw</td>
<td>278000</td>
</tr>
<tr>
<td>Mz</td>
<td>470000</td>
</tr>
<tr>
<td>Mz+1</td>
<td>679000</td>
</tr>
<tr>
<td>Mv</td>
<td>254000</td>
</tr>
</tbody>
</table>

Polydispersity (Mw/Mn) 2.28

Area (Response Minutes): 424000
Figure 6.4

GPC Trace of PMMA

Molecular Weight Averages

\[
\begin{align*}
\text{M}p & : 74200 \\
\text{M}n & : 42600 \\
\text{M}w & : 95100 \\
\text{M}z & : 188000 \\
\text{M}z+1 & : 329000 \\
\text{M}v & : 85300
\end{align*}
\]

Polydispersity (\(\text{M}w/\text{M}n\))

2.24

Area (Response Minutes):

468000

Figure 6.5

GPC trace of Polystyrene (45,000 mwt)
Molecular Weight Averages

| Mp  | 898  |
| Mn  | 1460 |
| Mw  | 56400 |
| Mz  | 222000 |
| Mz+1 | 344000 |
| Mv  | 38500 |

Polydispersity (Mw/Mn) 38.7
Area (Response Minutes): 795000

Table 6.1 shows the four polymers as well as their physical properties of molecular weight, T_g and surface energies.

**Table 6.1**

Table showing the physical properties of the initial polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Molecular Weight / g mol⁻¹</th>
<th>T_g / °C</th>
<th>Surface Energies mN / m</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>20°C</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>45,000</td>
<td>56.00</td>
<td>40.7</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>280,000</td>
<td>100.00</td>
<td>40.7</td>
</tr>
<tr>
<td>Poly (methyl methacrylate)</td>
<td>120,000</td>
<td>99.75</td>
<td>41.1</td>
</tr>
<tr>
<td>Poly (vinyl acetate)</td>
<td>100,000</td>
<td>41.75</td>
<td>36.5</td>
</tr>
</tbody>
</table>

The surface energies may be split into the dispersion and polar components, using values from the Polymer Handbook¹¹⁵. Table 6.2 shows those values.

**Table 6.2**

Polar and dispersion components to the surface free energy of various polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>γ^d / mJ m⁻²</th>
<th>γ^p / mJ m⁻²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polystyrene</td>
<td>41.4</td>
<td>0.6</td>
</tr>
<tr>
<td>Poly (methyl methacrylate)</td>
<td>35.9</td>
<td>4.3</td>
</tr>
<tr>
<td>Poly (vinyl acetate)</td>
<td>32.3</td>
<td>4.2</td>
</tr>
<tr>
<td>Poly (ethyleneterephthalate)</td>
<td>43.2</td>
<td>4.1</td>
</tr>
</tbody>
</table>
Poly (ethyleneterephthalate) (PET) is the material used as the substrate and so was added to the table so that the work of adhesion between the samples and the substrate could also be calculated. These values were entered into the equation below to calculate the thermodynamic work of adhesion between the various pairs, according to Owens and Wendt\textsuperscript{116}.

\[
W_{1,2} = 2\sqrt{\gamma^d_1 \gamma^d_2} + 2\sqrt{\gamma^p_1 \gamma^p_2}
\]

Equation 18

\(W_{1,2}\) is the thermodynamic work of adhesion between the two surfaces, measured in mJ m\(^{-2}\). \(\gamma^d\) is the dispersion component of the surface excess free energy for the two samples and \(\gamma^p\) is the polar component for the samples. The work of adhesion is defined as the free energy change required to reversibly separate two phases along an interface. It is a hypothetical change that is described and it will not be closely related to experimental measurements. This is because in the context of practical fracture much larger amounts of work are dissipated by other mechanisms, such as the plastic deformation of the polymers around the fracture zone. Table 6.3 shows the works of adhesion for the pairings, all units in mJ m\(^{-2}\).

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|}
\hline
 & PET & PS & PMMA & PVAc \\
\hline
PVAc & 83.0 & 76.3 & 76.6 & 73.0 \\
\hline
PMMA & 87.2 & 80.3 & 80.4 & \\
\hline
PS & 87.7 & 84.0 & & \\
\hline
PET & 94.6 & & & \\
\hline
\end{tabular}
\caption{Work of adhesion for each polymer pairing (mJm\(^{-2}\))}
\end{table}
The table shows that the polymers bonded with the PET substrate should have the greatest work of adhesion, which is beneficial in preventing any substrate / coating failure. The table also suggests that anything bonded with PVAc will yield the lowest work of adhesion. The thermodynamic work of adhesion is dominated by dispersion forces.

6.1.1.3 Fourier Transform Infra-red Spectroscopy

Infra-red spectra were recorded for each sample. These results were then used later as a method of determining the locus of failure of the peeled sheets. The Fourier transform infra-red spectrometer is sensitive enough to determine whether the transfer of a small amount of polymer has occurred.

Figures 6.6 - 6.9 show the ATR spectra recorded for each of the polymer surfaces.

Figure 6.6

FTIR Spectrum of PMMA
Figure 6.7
FTIR Spectrum of PVAc

Figure 6.8
FTIR Spectrum of 45,000 g mol\(^{-1}\) polystyrene
The PMMA spectrum shows the CH$_3$ on the ester group at 2980 cm$^{-1}$, the C=O at 1700 cm$^{-1}$, the O-CH$_3$ deformation at 1490 cm$^{-1}$ and the C-O bond at 1200 cm$^{-1}$. The PVAc spectrum shows the C=O peak at 1740 cm$^{-1}$, the CH$_3$CO deformations at 1400 and 1450 cm$^{-1}$ and the C-O bond at 1240 cm$^{-1}$. Both PS samples show the characteristic aromatic CH stretch at 300-3100 cm$^{-1}$, the aromatic ring stretch at 1600, 1585, 1500 and 1450 cm$^{-1}$ and the CH waggle characteristic of a mono-substituted benzene ring at 700, 750 and the cluster at 1000 - 1150 cm$^{-1}$.

6.1.2 Peel Results

6.1.2.1 ‘Normal’ Dye Sheet

Tables 6.4 and 6.5 show the measured peel strengths of the pairs of polymers at different heat settings. All of the results are expressed in grams/inch.
'Shredded' refers to the fact that the dye sheet substrate ripped during the peeling process. It was therefore decided to dismiss the values gained and to simply note that the polymer/substrate adhesion was equal to or less than the polymer/polymer adhesion strength.
Table 6.4
Peel strengths for the high heat setting (Intensity 5)

<table>
<thead>
<tr>
<th>Receiver Sheet</th>
<th>Polystyrene (280,000 g mol(^{-1}))</th>
<th>Polystyrene (45,000 g mol(^{-1}))</th>
<th>Poly (vinyl acetate)</th>
<th>Poly (methyl methacrylate)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polystyrene (280,000 g mol(^{-1}))</td>
<td>10.75g</td>
<td>13.25g</td>
<td>Shredded</td>
<td>24.50g</td>
</tr>
<tr>
<td></td>
<td>11.00g</td>
<td>15.25g</td>
<td>Shredded</td>
<td>24.50g</td>
</tr>
<tr>
<td>Polystyrene (45,000 g mol(^{-1}))</td>
<td>19.50g</td>
<td>11.00g</td>
<td>Shredded</td>
<td>10.75g</td>
</tr>
<tr>
<td></td>
<td>20.50g</td>
<td>12.00g</td>
<td>Shredded</td>
<td>11.00g</td>
</tr>
<tr>
<td>Poly (vinyl acetate)</td>
<td>21.75g</td>
<td>16.50g</td>
<td>Shredded</td>
<td>Shredded</td>
</tr>
<tr>
<td></td>
<td>19.50g</td>
<td>14.75g</td>
<td>Shredded</td>
<td>Shredded</td>
</tr>
<tr>
<td>Poly (methyl methacrylate)</td>
<td>24.50g</td>
<td>10.75g</td>
<td>Shredded</td>
<td>Shredded</td>
</tr>
<tr>
<td></td>
<td>24.50g</td>
<td>11.00g</td>
<td>Shredded</td>
<td>Shredded</td>
</tr>
</tbody>
</table>

All peel strengths are in grams/inch
Table 6.5

Peel strengths for the low heat setting (Intensity 25)

<table>
<thead>
<tr>
<th>Receiver Sheet</th>
<th>Dye Sheet</th>
<th>Polystyrene (280,000 g mol⁻¹)</th>
<th>Polystyrene (45,000 g mol⁻¹)</th>
<th>Poly (vinyl acetate)</th>
<th>Poly (methyl methacrylate)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polystyrene (280,000 g mol⁻¹)</td>
<td></td>
<td>4.00g</td>
<td>28.75g</td>
<td>17.00g</td>
<td>1.75g</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.50g</td>
<td>24.75g</td>
<td>18.50g</td>
<td>1.50g</td>
</tr>
<tr>
<td>Polystyrene (45,000 g mol⁻¹)</td>
<td></td>
<td>4.75g</td>
<td>6.50g</td>
<td>4.50g</td>
<td>1.00g</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.25g</td>
<td>6.25g</td>
<td>4.50g</td>
<td>1.00g</td>
</tr>
<tr>
<td>Poly (vinyl acetate)</td>
<td></td>
<td>9.50g</td>
<td>Shredded</td>
<td>Shredded</td>
<td>Shredded</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8.00g</td>
<td>Shredded</td>
<td>Shredded</td>
<td>Shredded</td>
</tr>
<tr>
<td>Poly (methyl methacrylate)</td>
<td></td>
<td>0.50g</td>
<td>0.50g</td>
<td>Shredded</td>
<td>0.00g</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.50g</td>
<td>0.50g</td>
<td>Shredded</td>
<td>0.00g</td>
</tr>
</tbody>
</table>

All peel strengths are in grams/inch
6.1.2.2  Locus of Failure

Several methods are used to determine the locus of failure. After the samples have been peeled apart by the peel test apparatus they were viewed under an optical microscope. With magnification x400 it is possible to see the macro scale surface relief. The surface of the polymer sheet before printing appears very flat under the microscope. This is true for all of the polymer samples. After printing several types of relief are visible.

On the dye sheets it is possible to see the "footprints" made by the print heads, using this it is possible to determine the size of the print heads. Unfortunately due to the transparency of the dye sheet very little information about the surface coating of polymer can be determined. This is due to the difficulty in focusing on the transparent micron thick polymer coating on the transparent PET substrate film.

The receiver sheets give interesting results under optical analysis. It is possible to see a bubbling effect on the sheets, this is due to the plastic flow the polymer undergoes under the heat and pressure in the printer. On surfaces that have undergone printing at a high temperature the relief is more predominant than that seen on low heat setting prints. The amount of relief is also dependent on the polymer used in the coating. The poly (methyl methacrylate) and the high molecular weight polystyrene often have less relief than the other polymers. This is probably due to the high $T_g$ of these polymers.
Also on the surface it is possible to see if there has been any transfer of dye sheet polymer onto the receiver sheet. This can be seen as discrete islands on the surface of the polymer. These islands have little relief on them and they stand out clearly from the relief on the receiver sheet polymer. The islands often lie in lines across the polymer, this would indicate that they are caused at the point where the row of print heads makes contact with the dye sheet. The higher temperature at these points causing more flow in the polymer layers leading to stronger adhesion.

The transfer of dye sheet polymers means that there is a mixed mode locus of failure. Failure at the coating / coating interface as well as at the polymer coating / substrate interface. Looking at the receiver sheets showed that there was transfer of the dye sheet polymer onto the receiver sheets. This can be seen in the figures 6.10 and 6.11.

Atomic force microscopy was also used to confirm the locus of failure and it was possible to see a step on the polymer surface of a micron. The thickness of the dye sheet coating is a micron and it is safe to assume that the AFM probe had found the side of an island of transferred material.
Figure 6.10
Photo of polystyrene (280,000 g mol\(^{-1}\)) receiver sheet after printing at heat setting 25 with polystyrene (45,000 g mol\(^{-1}\)) dye sheet at magnification x400.

Figure 6.11
Photo of PMMA receiver after printing at heat setting 25 with polystyrene (45,000 g mol\(^{-1}\)) dye sheet of magnification x 400.

83
It can be seen in table 6.5 that for PMMA dye sheets at the low heat settings, with the exception of the PVAc combination, there was little adhesion between the pairs. Under the optical microscope it was possible to confirm that there was no transfer and that the peel failure must have been at or near the polymer / polymer interface. Apart from these PMMA pairings the rest of the samples showed mixed mode failure under the optical microscope. Although some trends can be identified the presence of mixed failure at the high heat setting limits the interpretation that can be placed on the data.

6.1.2.3 Diafoil Dye Sheet

For further work it was decided to change the PET dye sheet substrate for a Diafoil substrate. This Diafoil sheet is a coated PET film, the coating being an ester which promotes greater adhesion to the polymer coatings. This was done to try and prevent transfer of dye sheet polymer and thus the mixed mode of failure. The results, seen in table 6.6, would then be easier to interpret knowing that all the peeling was along the polymer / polymer interface.
Table 6.6
Peel strengths using the Diafoil dye sheet substrate

Heat Setting - 20

<table>
<thead>
<tr>
<th>Dye Sheet</th>
<th>Receiver</th>
<th>280,000 PS</th>
<th>45,000 PS</th>
<th>PVAc</th>
<th>PMMA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>280,000 PS</td>
<td>0.0</td>
<td>22.0</td>
<td>Shredded</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>45,000 PS</td>
<td>48.5</td>
<td>41.0</td>
<td>Shredded</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>PVAc</td>
<td>35.0</td>
<td>36.0</td>
<td>12.0</td>
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</tr>
<tr>
<td></td>
<td>PMMA</td>
<td>0.0</td>
<td>6.0</td>
<td>Shredded</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Heat Setting - 15

<table>
<thead>
<tr>
<th>Dye Sheet</th>
<th>Receiver</th>
<th>280,000 PS</th>
<th>45,000 PS</th>
<th>PVAc</th>
<th>PMMA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>280,000 PS</td>
<td>Shredded</td>
<td>39.0</td>
<td>Shredded</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>45,000 PS</td>
<td>45.5</td>
<td>Shredded</td>
<td>Shredded</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>PVAc</td>
<td>43.0</td>
<td>Shredded</td>
<td>Shredded</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>PMMA</td>
<td>14.5</td>
<td>10.5</td>
<td>Shredded</td>
<td>0.0</td>
</tr>
</tbody>
</table>

All peel strengths are in grams/mch

The Diafoil dye sheet proved to be very effective at halting the total transfer seen with the normal PET dye sheet. The main difference between these results and those gathered from the normal dye sheets are in the low molecular weight polystyrene samples, using the Diafoil dye sheet with its increased adhesion to the PET, higher peel strengths can be observed. This
could be due to the small molecules present in the samples migrating to the dye sheet / polymer interface in the normal dye sheet. Using the coated Diafoil dye sheet will have reduced their effect at the surface allowing for interfacial failure to occur at the polymer / polymer interface.

The results showed little extra information except that the heat settings are still far from the levels required to produce any interpretable results, that the pairings are either shredding or releasing with no peel strength recorded. The PVAc shredded with everything and the high T_g materials do not bond at all at the lower heat settings, this suggests that the softening of the polymers and contact are the important non equilibrium processes involved.

It was decided to try to obtain measurements over a range of heat settings so that trends could be identified. These results can be seen in table 6.7.
Table 6.7
Peel strengths for polymers (superscript = heat setting)

<table>
<thead>
<tr>
<th>Lowest Heat</th>
<th>Dye Sheet</th>
</tr>
</thead>
<tbody>
<tr>
<td>Receiver Sheet</td>
<td>280,000 PS</td>
</tr>
<tr>
<td>280,000 PS</td>
<td>30.25&lt;sup&gt;13&lt;/sup&gt;</td>
</tr>
<tr>
<td>45,000 PS</td>
<td>51.0&lt;sup&gt;15&lt;/sup&gt;</td>
</tr>
<tr>
<td>PVAc</td>
<td>38.0&lt;sup&gt;13&lt;/sup&gt;</td>
</tr>
<tr>
<td>PMMA</td>
<td>13.25&lt;sup&gt;15&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Low Intermediate</th>
<th>Dye Sheet</th>
</tr>
</thead>
<tbody>
<tr>
<td>Receiver Sheet</td>
<td>280,000 PS</td>
</tr>
<tr>
<td>280,000 PS</td>
<td>37.25&lt;sup&gt;10&lt;/sup&gt;</td>
</tr>
<tr>
<td>45,000 PS</td>
<td>44.0&lt;sup&gt;16&lt;/sup&gt;</td>
</tr>
<tr>
<td>PVAc</td>
<td>48.0&lt;sup&gt;16&lt;/sup&gt;</td>
</tr>
<tr>
<td>PMMA</td>
<td>35.0&lt;sup&gt;16&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>High Intermediate</th>
<th>Dye Sheet</th>
</tr>
</thead>
<tbody>
<tr>
<td>Receiver Sheet</td>
<td>280,000 PS</td>
</tr>
<tr>
<td>280,000 PS</td>
<td>30.25&lt;sup&gt;2&lt;/sup&gt;</td>
</tr>
<tr>
<td>45,000 PS</td>
<td>29.0&lt;sup&gt;2&lt;/sup&gt;</td>
</tr>
<tr>
<td>PVAc</td>
<td>33.25&lt;sup&gt;5&lt;/sup&gt;</td>
</tr>
<tr>
<td>PMMA</td>
<td>64.0&lt;sup&gt;2&lt;/sup&gt;</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>High Heat</th>
<th>Dye Sheet</th>
</tr>
</thead>
<tbody>
<tr>
<td>Receiver Sheet</td>
<td>280,000 PS</td>
</tr>
<tr>
<td>280,000 PS</td>
<td>41.75&lt;sup&gt;2&lt;/sup&gt;</td>
</tr>
<tr>
<td>45,000 PS</td>
<td>25.25&lt;sup&gt;2&lt;/sup&gt;</td>
</tr>
<tr>
<td>PVAc</td>
<td>30.75&lt;sup&gt;2&lt;/sup&gt;</td>
</tr>
<tr>
<td>PMMA</td>
<td>27.5&lt;sup&gt;2&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

Peel strengths are in grams/inch.
Table 6.7 shows the complete set of polymers with each pairing at four heat settings, denoted by the superscript. The majority of these results conform to the usual trend of increasing adhesion with increasing heat. The only anomalies occur when the high molecular weight polystyrene (PS) is used as the dye sheet. A representation of these results can be seen in figure 6.12.

Figure 6.12

Peel strengths of the high molecular weight PS dye sheet against the different polymer receiver sheets

Several trends can be seen in the results. The PVAc and the high molecular weight PS both give reasonably stable results. This could be due to competition between higher heat producing greater adhesion due to the softening of the polymer films providing greater contact and the higher heat producing greater mobility of small molecules in the sample. The low molecular weight PS gives an increase in peel strength with a decrease in heat. This could be due to the migration of the low molecular content of the polystyrene forming a weak boundary layer. This migration will be
enhanced at the higher heats, leading to lower peel strengths. The PMMA results show a peak at heat setting 5 and then a drop in peel strength as the heat decreases. This decrease in peel strength with decreasing heat is as expected but the peak at heat setting 5 rather than at the highest heat is not. At the highest heat it is possible that any small molecules are caused to migrate, this is not happening at lower heats. Therefore at the higher heat there is a weak boundary layer that is not present at lower heats.

The low $T_g$ of the PVAc will mean that it will undergo considerably more flow at all heat setting than the high $T_g$ materials. This suggests that the flow of the samples is an important factor in their adhesion. The low molecular weight polystyrene also has a low $T_g$ but the addition of the oligomer will produce a weak boundary layer that will complicate the interpretation of the results.

At the low heat settings the PMMA and high molecular weight polystyrene will not readily flow, thus limiting contact between the polymers. At the high heat setting the polymers will be more likely to flow, establish contact and chain entangle. The results for PMMA show that at the heat settings used flow has yet to be achieved and thus the peel strengths are low. For the high molecular weight polystyrene the heat settings are at a level where flow has been achieved and the polystyrene is adhering to the other polymers.

The effect of $T_g$ can be seen clearly when attention is drawn to the PVAc on the dye sheet. At the high heat setting it bonds strongly with all other polymers. At the low heat setting it is still bonded strongly with itself and the low molecular weight polystyrene, both of which have low $T_g$, but it
can be peeled apart easily from the PMMA and the high molecular weight polystyrene. From the early calculations on the work of adhesion alone it was predicted that the PVAc pairs would be the easiest to peel apart, the experimental work has now shown that these predictions are not correct. The ability of the polymers to flow and establish good contact is probably more important than energies of interaction and chain entanglement. If chain entanglement was a major factor then the pairings of like polymers would produce the strongest bonds. This is not in agreement the results indicating that other factors have a greater effect.

The effects of molecular weight and $T_g$ can be seen in the polystyrene pairings. This is an important set of results because of the constant factors involved, i.e. surface energies, chemical structure. The only differences between the polystyrene samples is their molecular weights, $T_g$ and possibly surface roughness. At the lower heat settings the pairs with the low molecular weight polystyrene on the receiver sheet have higher peel strengths. This is reasonable because of the limited flow by the high molecular weight polystyrene when on the receiver sheet, thus yielding less contact.

The values gained for the high heat settings show that the peel strengths of the low molecular weight polystyrene on the receiver for the two polystyrenes are now lower than those for the high molecular weight polystyrene. A factor to be taken into account is that the low molecular weight polystyrene contains low molecular weight material that could give a lower peel strength as they migrate to the surface. If chain entanglement is playing a significant role in the adhesion the high molecular weight
polystyrene would be expected to produce a higher peel strength because of the longer chains.

### 6.1.2.4 Weak Boundary Layer

To investigate the possible presence of a weak boundary layer it was decided to extract any small molecules from the polymer samples and to repeat the sets of results. All extractions were twenty four hour Soxhlet extraction with various solvents. PMMA was extracted with methanol, PVAc and the polystyrene samples with diethyl ether. The extracted polymers were then used in a repeat of the earlier experiment keeping the sample heat settings. The solvent used in each extract was analysed using various methods. Firstly, it was allowed to dry enabling a solids content to be determined for each polymer. The results of this can be seen in table 6.8.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Percentage of starting mass removed by extraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extraction Thimble</td>
<td>0.19 %</td>
</tr>
<tr>
<td>PMMA</td>
<td>0.58 %</td>
</tr>
<tr>
<td>PVAc</td>
<td>0.95 %</td>
</tr>
<tr>
<td>280,000 PS</td>
<td>0.02 %</td>
</tr>
<tr>
<td>45,000 PS</td>
<td>11.2 %</td>
</tr>
</tbody>
</table>

Each solid sample was then dissolved in THF and analysed by GPC and FTIR to determine both the molecular weight of the small molecules and the chemical composition of the compounds extracted. Analysis of these fractions using FTIR-ATR was achieved with the sample in THF dried onto a Ge crystal and then analysed. The FTIR spectrum of the extracted
Soxhlet thimble was also analysed and no contaminants from this extraction could be found in the polymer samples.

Figures 6.13 to 6.16 show the FTIR spectra of the extracted small molecules taken from each polymer. These can be compared to figures 6.6 to 6.9 which show the FTIR spectra of the unextracted polymers.

Figure 6.13
FTIR Spectrum of PMMA Extract

![FTIR Spectrum of PMMA Extract](image)

Figure 6.14
FTIR Spectrum of PVAc Extract

![FTIR Spectrum of PVAc Extract](image)
With the exception of PMMA the results show that the small molecules removed in each case were low molecular weight oligomers of the polymer samples only. The PMMA extract showed a double peak at 1700 cm\(^{-1}\), this indicates that there is material present other than PMMA. It could be acid groups from unreacted monomer or contaminants.
Figures 6.17 - 6.21 show the expanded GPC traces of the polymer extracts as well as the extract from the Soxhlet thimble. The GPC results show the extract from the thimble appearing in each of the polymer extracts. In each of the polymer extract it is also possible to see some other low molecular weight fractions.

Figure 6.17

Expanded GPC trace of 280,000 PS Extract

![Expanded GPC trace of 280,000 PS Extract](image)

Figure 6.18

Expanded GPC Trace of 45,000 PS Extract

![Expanded GPC Trace of 45,000 PS Extract](image)
Figure 6.19
Expanded GPC Trace of PMMA Extract

Figure 6.20
Expanded GPC Trace of PVAc Extract

Figure 6.21
Expanded GPC Trace of Thimble Extraction
The extracted polymers were used in the repeat experiments the results of which can be seen in table 6.9.

**Table 6.9**

Peel strengths of initial sets of polymers after extraction (superscript = heat setting)

<table>
<thead>
<tr>
<th>Dye Sheet</th>
<th>280,000 PS</th>
<th>45,000 PS</th>
<th>PVAc</th>
<th>PMMA</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Lowest Heat</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Receiver Sheet</td>
<td>21.5&lt;sup&gt;15&lt;/sup&gt;</td>
<td>15.5&lt;sup&gt;20&lt;/sup&gt;</td>
<td>1.0&lt;sup&gt;10&lt;/sup&gt;</td>
<td>9.0&lt;sup&gt;15&lt;/sup&gt;</td>
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<tr>
<td>280,000 PS</td>
<td>24.0&lt;sup&gt;15&lt;/sup&gt;</td>
<td>13.5&lt;sup&gt;20&lt;/sup&gt;</td>
<td>0.75&lt;sup&gt;30&lt;/sup&gt;</td>
<td>8.5&lt;sup&gt;15&lt;/sup&gt;</td>
</tr>
<tr>
<td>45,000 PS</td>
<td>25.5&lt;sup&gt;15&lt;/sup&gt;</td>
<td>9.25&lt;sup&gt;20&lt;/sup&gt;</td>
<td>2.0&lt;sup&gt;30&lt;/sup&gt;</td>
<td>Shred&lt;sup&gt;13&lt;/sup&gt;</td>
</tr>
<tr>
<td>PVAc</td>
<td>26.5&lt;sup&gt;15&lt;/sup&gt;</td>
<td>11.0&lt;sup&gt;20&lt;/sup&gt;</td>
<td>4.0&lt;sup&gt;40&lt;/sup&gt;</td>
<td>Shred&lt;sup&gt;13&lt;/sup&gt;</td>
</tr>
<tr>
<td>PMMA</td>
<td>23.0&lt;sup&gt;15&lt;/sup&gt;</td>
<td>33.0&lt;sup&gt;25&lt;/sup&gt;</td>
<td>Shred&lt;sup&gt;30&lt;/sup&gt;</td>
<td>44.0&lt;sup&gt;50&lt;/sup&gt;</td>
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<tr>
<td><strong>Intermediate</strong></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Receiver Sheet</td>
<td>27.25&lt;sup&gt;10&lt;/sup&gt;</td>
<td>28.0&lt;sup&gt;15&lt;/sup&gt;</td>
<td>5.75&lt;sup&gt;25&lt;/sup&gt;</td>
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<td>19.25&lt;sup&gt;25&lt;/sup&gt;</td>
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<tr>
<td>PVAc</td>
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<td>29.5&lt;sup&gt;15&lt;/sup&gt;</td>
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</tr>
<tr>
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<td>Shred&lt;sup&gt;20&lt;/sup&gt;</td>
<td>Shred&lt;sup&gt;27&lt;/sup&gt;</td>
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<td></td>
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<tr>
<td>Receiver Sheet</td>
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<td>19.0&lt;sup&gt;5&lt;/sup&gt;</td>
<td>4.5&lt;sup&gt;20&lt;/sup&gt;</td>
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<tr>
<td>280,000 PS</td>
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<td>19.5&lt;sup&gt;5&lt;/sup&gt;</td>
<td>7.5&lt;sup&gt;20&lt;/sup&gt;</td>
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<tr>
<td>45,000 PS</td>
<td>18.5&lt;sup&gt;5&lt;/sup&gt;</td>
<td>15.25&lt;sup&gt;5&lt;/sup&gt;</td>
<td>30.75&lt;sup&gt;20&lt;/sup&gt;</td>
<td>Shred&lt;sup&gt;5&lt;/sup&gt;</td>
</tr>
<tr>
<td>PVAc</td>
<td>17.5&lt;sup&gt;5&lt;/sup&gt;</td>
<td>22.75&lt;sup&gt;5&lt;/sup&gt;</td>
<td>34.25&lt;sup&gt;20&lt;/sup&gt;</td>
<td>Shred&lt;sup&gt;5&lt;/sup&gt;</td>
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<tr>
<td>PMMA</td>
<td>22.0&lt;sup&gt;5&lt;/sup&gt;</td>
<td>10.0&lt;sup&gt;10&lt;/sup&gt;</td>
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<td><strong>Intermediate</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Receiver Sheet</td>
<td>19.5&lt;sup&gt;5&lt;/sup&gt;</td>
<td>10.5&lt;sup&gt;10&lt;/sup&gt;</td>
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<tr>
<td>280,000 PS</td>
<td>27.5&lt;sup&gt;5&lt;/sup&gt;</td>
<td>13.25&lt;sup&gt;5&lt;/sup&gt;</td>
<td>Shred&lt;sup&gt;20&lt;/sup&gt;</td>
<td>8.75&lt;sup&gt;13&lt;/sup&gt;</td>
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<td>Shred&lt;sup&gt;20&lt;/sup&gt;</td>
<td>3.0&lt;sup&gt;15&lt;/sup&gt;</td>
</tr>
</tbody>
</table>
Peel strengths are in grams/inch.

Looking at the polymers against themselves gives the best insight into the role small molecules play on the adhesion. For the high molecular weight PS there is a decrease in peel strength after extraction, this would indicate that the small molecules removed, the low molecular weight oligomers, were acting as a plasticiser. This would give greater adhesion before the extraction as the compatibilised PS would be able to flow and adhere more strongly. The decrease in adhesion is only small which can be linked to the small amount of material actually removed from the PS sample, 0.02% of starting mass.

The low molecular weight PS also has a decrease in adhesion after the extraction, probably for the same reasons. The decrease is larger than that seen for the high molecular weight PS and this reflects the significant increase in the amount of oligomers removed, five hundred times as much from their respective starting masses. The GPC trace for the sample after extraction shows that there are still low molecular weight molecules present in the bimodal mixture so they will still be having an effect on the adhesion.

With the PVAc it is impossible to determine if the extraction had any affect on the adhesion due to the fact that all of the like versus like runs
shredded during the peeling process. This is probably due to the particularly low $T_g$ of the polymer allowing the formation of a good adhesive bond. From the results of the PS samples it is a reasonable assumption to conclude that the low molecular weight oligomers of PVAc were having a plasticisation effect in the polymer before extraction.

The PMMA pairings proved to be the exception of the set. The results show that the peel strengths increase after extraction. This would indicate that the low molecular weight molecules removed were acting as migratory molecules and forming a weak boundary layer in the before extraction pairs. In the PMMA / PMMA system the results show that this small molecule effect does not occur at the lower heat settings but only at the higher heat. This could be due to the energy required to produce migration in the polymer film and the fact that the PMMA is always resistant to adhesion at lower heats because of its high $T_g$. This is consistent with the FTIR results showing impurities extracted.

The results after extraction are consistent with the following interpretation. The PS and PVAc pairings show a decrease after extraction because of the removal of the plasticising small molecules. When pairings include the PMMA there is competition between the plasticisation of one polymer and the migration in the PMMA. In most cases the migration effect in the PMMA is the dominant effect. This clearly shows the importance of the weak boundary layer in adhesion.

When the PMMA is the dye sheet against the other polymer receiver sheets it can be seen that there is a huge increase in peel strength, even at the lower heat settings. There is also an increase in adhesion when the
PMMA is the receiver sheet although the increase in adhesion is not as pronounced. This is probably due to the fact that when the PMMA is the dye sheet it is in closer contact with the heated printing head and so more energy is available to produce migration.

6.1.2.5 Summary

It was hoped that the results from this initial study would answer some fundamental questions governing adhesion in this system. The choice of these starting polymers was made so that various pairings would answer specific questions. The factors expected to produce effects included the molecular weight and $T_g$ of the samples. The surface energies and functionality were thought to play a vital role in the wetting and entanglement, the presence of small molecules was another.

The results show that several factors are present in each case and often compete to produce the adhesion observed. As a result it is impractical to determine a single factor that controls the adhesion but it must be understood that several factors all influence the adhesion.

The mechanical properties of contact and polymer flow are shown to be important in the adhesion due to the increased adhesion between pairings containing low $T_g$ materials. The PMMA and high molecular weight polystyrene tended not to bond at lower heat settings. This indicates that a minimum level of heat is required to soften the polymers before any adhesion can be seen.
The results from the first set of data showed that the low molecular weight PS gave very differing results to that of PVAc, that had a similar molecular weight and T_g, this difference was attributed to the presence of low molecular weight oligomers. The experiments undertaken to explain this effect showed how large a contribution the contaminants and oligomers in the polymer systems had on peel strength. The results from the extracted pairings suggests that small molecules can act as plasticisers giving an increase in adhesion due to a compatibility with the polymer system giving rise to a higher degree of flow and entanglement. It also showed the effect of small molecules as migratory compounds that travel to the surface and form a weak boundary layer that lowers the adhesive strength of the interface.

6.2 Commercial Products

6.2.1 Characterisation

Commercial products used by ICI Imagedata include poly (vinyl chloride) (PVC) (Evipol MP 8085) and poly (vinyl butyral) (PVB) (Sekisui Chemicals LEC B BX-5 grade). The structures of which can be seen in figure 6.22.
In general PVB is used as the dye sheet polymer and PVC the receiver sheet. The Diafoil dye sheet is used in preference to the normal dye sheet as it provided a strong bond with the PVB coating. For the following experiments the polymers will be used as both dye and receiver sheets to provide a more complete picture. One problem encountered was that the 11.1 % solutions of PVB and PVC commonly used to produce the receiver sheet coatings were very viscous, therefore difficult to handle. It was therefore decided to produce the receiver sheets using a more dilute solution and a bigger K-bar (5.33 % solution with K-bar number 7).
The $T_g$ of the two polymers was determined, as before, using DSC and the glass transition temperatures can be seen in table 6.10.

Table 6.10
Glass transition temperatures of the PVC and PVB samples

<table>
<thead>
<tr>
<th>Polymer Sample</th>
<th>Glass Transition Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC</td>
<td>87.5°C</td>
</tr>
<tr>
<td>PVB</td>
<td>90.0°C</td>
</tr>
</tbody>
</table>

The molecular weights were determined from GPC using polystyrene standards, the results can be seen in table 6.11.

Table 6.11
Molecular weights of the PVC and PVB samples

<table>
<thead>
<tr>
<th>Polymer Sample</th>
<th>$M_n$ / g mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC</td>
<td>139,000</td>
</tr>
<tr>
<td>PVB</td>
<td>119,000</td>
</tr>
</tbody>
</table>

From these values it can be clearly seen that the two polymers have both similar molecular weights and $T_g$ but they have differing functionality. FTIR spectra were also collected to provide a fingerprint that would be useful in determining the locus of failure.

Pairings were printed, peeled and then they were analysed by optical microscopy and FTIR to determine the locus of failure. In each case no transfer was observed from one polymer to the other. To remove any
influences from small molecules present in the polymers it was decided to remove them by Soxhlet extraction.
6.3 Extraction and Small Molecules

PVC was extracted for twenty four hours with diethyl ether using the same Soxhlet method as before. PVB was similarly extracted for twenty four hours using hexane as the solvent. In both cases the $T_g$ of the polymers before and after extraction were determined by DSC. With the PVB the solvent used for the extraction was evaporated to dryness and the residue analysed by GPC and FTIR to determine its molecular weight and chemical composition. Two methods were devised to calculate the molecular weight. The first was the direct analysis of the dried extract by dissolving the sample in THF and running it through the standard GPC set up. The second was to run a GPC analysis on the polymer before and after extraction and to subtract the post-extraction trace from the pre-extraction trace to reveal what had been removed. With the PVC sample it was believed that it may contain some aromatic small molecules. Therefore as well as the subtraction method described above an alternative method was used. The GPC system was connected to a dual detection system that contained both refractive index and ultra-violet detectors. In the UV traces it is possible to clearly see these aromatic molecules being removed.

6.3.1 PVB Extraction

The $T_g$ of the PVB before extraction was 90.0°C and after extraction this was raised to 91.0°C. The slight rise would indicate that any small molecules that may have been removed were compatible with the PVB, possibly oligomers, hence had reduced the $T_g$ slightly when present because of a plasticisation effect. The scale of the change of $T_g$ indicates that only a small amount of material was removed. The GPC trace of the
PVB extract showed the expected peak from the thimble extract and also a peak at 1430 polystyrene weight equivalent corresponding to the low molecular weight molecule removed. This GPC trace can be seen in figure 6.23. Figure 6.24 shows the subtracted GPC trace from the polymer before and after extraction.

Figure 6.23

GPC Trace of PVB Extract

![GPC Trace of PVB Extract](image)

Figure 6.24

GPC trace of small molecules in PVB determined by subtraction of the after extraction from the before extraction traces

![GPC Trace of Small Molecules](image)

The peak occurs at approximately 1600 polystyrene weight equivalents. This mirrors the results gained from the direct analysis of the extract.
The FTIR-ATR spectrum of the PVB extract shows that the small molecules removed are simply oligomers of the PVB. The FTIR spectra of PVB before and after extraction and of the extract can be seen in figures 6.25 - 6.27. Table 6.12 shows the vibrations seen in the spectra.

Figure 6.25
FTIR Spectrum of PVB before extraction

Figure 6.26
FTIR Spectrum of PVB after extraction
These can all be seen in the PVB sample before extraction. The carbonyl peak is fairly small due to the small percentage of carbonyl present, 5%. They can also be seen in the extracted PVB although now the carbonyl has been removed. It can be seen that otherwise the extracted PVB is very similar to the unextracted PVB. The extract shows a larger carbonyl which indicates that the oligomers removed included a large proportion of the carbonyl group. There is still a C-O peak in the extract indicating that some of the other functionality was removed as well.
Table 6.12
FTIR vibrations in the PVB spectra

<table>
<thead>
<tr>
<th>Vibration</th>
<th>Wavenumber / cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH Stretching</td>
<td></td>
</tr>
<tr>
<td>CH(_3) asymmetric</td>
<td>2975 - 2950</td>
</tr>
<tr>
<td>CH(_2) asymmetric</td>
<td>2940 - 2915</td>
</tr>
<tr>
<td>CH(_3) symmetric</td>
<td>2885 - 2860</td>
</tr>
<tr>
<td>CH(_2) symmetric</td>
<td>2870 - 2845</td>
</tr>
<tr>
<td>CH</td>
<td>2900 - 2880</td>
</tr>
<tr>
<td>CH(_3)CO</td>
<td>3000 - 2900</td>
</tr>
<tr>
<td>CH Deformation</td>
<td></td>
</tr>
<tr>
<td>CH(_3) asymmetric</td>
<td>1470 - 1435</td>
</tr>
<tr>
<td>CH(_2) asymmetric (scissors)</td>
<td>1480 - 1440</td>
</tr>
<tr>
<td>CH(_3) symmetric</td>
<td>1385 - 1370</td>
</tr>
<tr>
<td>CH</td>
<td>1340</td>
</tr>
<tr>
<td>CH(_3)CO</td>
<td>1360 - 1355</td>
</tr>
<tr>
<td>OH</td>
<td></td>
</tr>
<tr>
<td>Broad polymeric associated OH</td>
<td>3400 - 3200</td>
</tr>
<tr>
<td>C-O stretching - O-H deformation</td>
<td>1150</td>
</tr>
<tr>
<td>C=O</td>
<td></td>
</tr>
<tr>
<td>C=O stretching</td>
<td>1725 - 1705</td>
</tr>
<tr>
<td>Ester C-O</td>
<td></td>
</tr>
<tr>
<td>C-O-C stretching</td>
<td>1150 - 1060</td>
</tr>
</tbody>
</table>
6.3.2 PVC Extraction

The \( T_g \) of the PVC before extraction was 87.5°C and after extraction it had dropped to 86.0°C. This indicates that the small molecules present in the unextracted form were not acting as plasticisers. The small drop in \( T_g \) indicates that the amount of small molecules removed is very small. The PVC was analysed in the same way to gain molecular weight and chemical composition information. It was believed that the PVC could contain some additives with benzene rings present. To better view these compounds it was decided to use the dual detectors available to the GPC system, refractive index (RI) and ultra-violet (UV) detectors. The UV detector should easily pick out the benzene rings to aid in their identification. Figures 6.28 - 6.31 show the GPC traces of the PVC before and after extraction using both detectors. Figures 6.32 and 6.33 show an enlarged look at the small molecules shown in the previous GPC traces. Figure 6.34 shows the subtracted results obtained from the PVC samples before and after extraction. The peak at nineteen minutes is the toluene flow marker peak that is used in the molecular weight calculations. The ultra-violet detector is incapable of detecting the PVC in each sample. The only peaks detected are at the far right end of the trace near to the toluene flow marker, therefore these peaks must contain a chromophore to be detected.
Figure 6.28
GPC trace of PVC before extraction using an RI detector

Figure 6.29
GPC trace of PVC before extraction using a UV detector
Figure 6.30
GPC trace of PVC after extraction using an RI detector

Figure 6.31
GPC trace of PVC after extraction using a UV detector
From these traces it is possible to see the small molecules removed. The RI detector shows two peaks before extraction and only a single peak afterwards. This result is mirrored and considerably clearer indicating that the small molecules removed contain chromophores, multiply bonded units or ring structures, in the trace from the UV detector. There is still a peak present in the after extraction trace indicating that not all of this component has been removed. Using the before extraction PVC with the UV detector it is possible to calculate the molecular weight of the peak.
that is extracted. The extracted peak occurs at a polystyrene equivalent molecular weight of approximately 1000 g mol$^{-1}$.

Figure 6.34
GPC trace of small molecules in PVC

The subtracted trace shows a peak at approximately 700 polystyrene weight equivalents. This is in agreement with the peak seen to be extracted using the UV detector.

Figures 6.35 - 6.37 shows the FTIR spectra of the PVC before and after extraction and the PVC extract. Data received from Evipol concerning the possible additives in the PVC sample indicates at least two compounds may be present. The named two are an alkyl aryl sulphite and an ethoxylated alkyl phenol. Their structures can be seen in figure 6.38.
Figure 6.35
FTIR Spectrum of PVC before extraction

Figure 6.36
FTIR Spectrum of PVC after extraction

Figure 6.37
FTIR Spectrum of PVC Extract

Table 6.13 shows the FTIR vibrations seen in the PVC spectra.
Table 6.13

FTIR vibrations seen in the PVC spectra

<table>
<thead>
<tr>
<th>Vibration</th>
<th>Wavenumber / cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH Stretching</td>
<td></td>
</tr>
<tr>
<td>CH₂ asymmetric</td>
<td>2940 - 2915</td>
</tr>
<tr>
<td>CH₂ symmetric</td>
<td>2870 - 2845</td>
</tr>
<tr>
<td>CH Deformation</td>
<td></td>
</tr>
<tr>
<td>CH₂ symmetric (scissors)</td>
<td>1480 - 1440</td>
</tr>
<tr>
<td>CH₂ rocking</td>
<td>~720</td>
</tr>
<tr>
<td>C-Cl Stretching</td>
<td>750 - 700</td>
</tr>
</tbody>
</table>

The C-H vibrations can clearly be seen in the before and after extraction of the PVC samples. The complexity of the C-Cl region is due to the C-Cl interaction with C-C and other oscillators. The complexity is increased in the polymeric sample. This being the case it is still possible to see several peaks in the 650 - 750 cm⁻¹ region that will correspond to C-Cl and CH₂ rocking. Also visible in the pre-extraction PVC is a small carbonyl peak that can be attributed to additives not identified by Evipol as well as possibly a C-O bond that too can be attributed to some additives.
The aromatic, C-O and sulphite bonds are clearly visible in the extract. These can be seen in figure 6.39, an enlargement of the PVC extract FTIR spectrum. The aromatic C=C stretching at 1600 and 1500 cm\(^{-1}\) are easily seen in the correct proportions. A further C=C stretch is seen at 1450 cm\(^{-1}\) but this is overlapped by CH\(_2\) scissors and CH\(_3\) asymmetric deformations. Coupled C-O stretching and O-H deformation can be seen at 1250 cm\(^{-1}\), which is common in phenols. C-C stretching of the carbon chains can be seen at 1070 cm\(^{-1}\). An S=O bond can be seen at 1170 cm\(^{-1}\) that does not appear in the extracted PVC.
6.3.3 Small molecule Addition

6.3.3.1 PVB

It was decided to deliberately introduce various small molecules into the extracted PVB in an attempt to control the adhesion. The PVB was paired against itself to ensure that no other factors could be influencing the adhesion. The small molecules to be used are listed in table 6.14 along with molecular weights. Figure 6.40 shows the structures of these molecules. Low levels of addition, 1% by weight, are to be used to minimise any plasticisation effects.
Table 6.14
Suppliers and molecular weights of the small molecules

<table>
<thead>
<tr>
<th>Small Molecule</th>
<th>Supplier</th>
<th>Molecular Weight / g mol(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>poly (vinyl methyl ether) PVME</td>
<td>BASF</td>
<td>36,000 by GPC</td>
</tr>
<tr>
<td>nonyl phenol ethoxylate NPE</td>
<td>Croda</td>
<td>2,500 by GPC</td>
</tr>
<tr>
<td>2000 poly (propylene glycol) 2000 PPG</td>
<td>Aldrich</td>
<td>2000 from manufacturer</td>
</tr>
<tr>
<td>425 poly (propylene glycol) 425 PPG</td>
<td>Aldrich</td>
<td>425 from manufacturer</td>
</tr>
<tr>
<td>silicone Tegomer 6440</td>
<td>ICI</td>
<td>6800 from manufacturer</td>
</tr>
<tr>
<td>silicone Tegomer 2311</td>
<td>ICI Imagedata</td>
<td>1500 from manufacturer</td>
</tr>
</tbody>
</table>

Figure 6.40
Structures of the small molecules used

- Tegomer repeat unit
- Poly (propylene glycol) repeat unit
- PVME repeat unit
- Nonyl Phenol Ethoxylate
Additives, to be effective, must be low surface energy so that they:

1. Migrate to the surface.
2. Spread across the surface to produce a weak boundary layer.

PPG is a water soluble polymer with some functionality, ether groups in the polymer backbone. PVME also has ether groups on its side chain. Two different molecular weights of PPG were used. The nonyl phenol ethoxylate is a surfactant with a polar end group on a long fatty chain. It too is a low surface energy molecule. The silicones have been chosen as they are chemically inert and often used as a release agent when crosslinked at the surface. In this instance the Tegomers were not cross linked but instead remained as their low molecular weight discrete molecules. They are again noted for their low surface energies. Two sizes of Tegomers are used to investigate any relation between molecular weight and adhesion.

The molecular weights in most cases are low, relative to the size of the polymer systems used. This should aid migration through the polymer films and lead to increased solubility in the polymer. The exception to this is the PVME with its molecular weight being almost a third of that of the PVB polymer. All the small molecules were added at 1% weight to weight fraction to the receiver sheet polymer.

Table 6.15 shows the results of the small molecule experiments. Included also are the results for the PVB before and after extraction for comparison.
Table 6.15
Peel strengths of PVB with small molecules

All peel strengths are in grams/inch and additives are at the 1% level.

<table>
<thead>
<tr>
<th>Dye Sheet</th>
<th>Heat Settings</th>
<th>7</th>
<th>10</th>
<th>12</th>
<th>15</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVB</td>
<td>Shredded</td>
<td>245.0</td>
<td>106.0</td>
<td>42.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Shredded</td>
<td>252.5</td>
<td>187.5</td>
<td>43.0</td>
<td></td>
</tr>
<tr>
<td>Extracted PVB</td>
<td>Shredded</td>
<td>137.0</td>
<td>170.0</td>
<td>46.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Shredded</td>
<td>72.0</td>
<td>145.0</td>
<td>49.0</td>
<td></td>
</tr>
<tr>
<td>Extracted PVB</td>
<td>Shredded</td>
<td>92.5</td>
<td>33.0</td>
<td>22.5</td>
<td></td>
</tr>
<tr>
<td>+ PVME</td>
<td>Shredded</td>
<td>47.0</td>
<td>32.0</td>
<td>10.25</td>
<td></td>
</tr>
<tr>
<td>Extracted PVB</td>
<td>Shredded</td>
<td>260.0</td>
<td>50.5</td>
<td>13.5</td>
<td></td>
</tr>
<tr>
<td>+ NPE</td>
<td>Shredded</td>
<td>235.0</td>
<td>53.25</td>
<td>15.75</td>
<td></td>
</tr>
<tr>
<td>Extracted PVB</td>
<td>Shredded</td>
<td>230.0</td>
<td>76.0</td>
<td>12.75</td>
<td></td>
</tr>
<tr>
<td>+ 2000 PPG</td>
<td>Shredded</td>
<td>335.0</td>
<td>195.0</td>
<td>22.0</td>
<td></td>
</tr>
<tr>
<td>Extracted PVB</td>
<td>Shredded</td>
<td>167.5</td>
<td>205.0</td>
<td>49.0</td>
<td></td>
</tr>
<tr>
<td>+ 425 PPG</td>
<td>Shredded</td>
<td>210.0</td>
<td>237.5</td>
<td>65.0</td>
<td></td>
</tr>
<tr>
<td>Extracted PVB</td>
<td>6.0</td>
<td>2.5</td>
<td>1.0</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>+ Teg 6440</td>
<td>7.0</td>
<td>2.5</td>
<td>2.0</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>Extracted PVB</td>
<td>54.0</td>
<td>11.5</td>
<td>4.71</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>+ Teg 2311</td>
<td>92.5</td>
<td>12.0</td>
<td>3.5</td>
<td>1.5</td>
<td></td>
</tr>
</tbody>
</table>

The results show that there is not a significant change in peel strength at the lower peel strengths before and after extraction, but there is a decrease in adhesion at the higher heat after extraction. This decrease suggests that the small molecules removed were acting as plasticisers in the unextracted PVB. This fits with the analysis of the extract showing that the small molecules were low molecular weight oligomers of PVB. The increase in adhesion with the unextracted PVB is only noticeable at high heat, this will be due to the high \( T_g \) of the PVB preventing any flow at
lower heats, the effect of the plasticisers only being a contributory factor at high heat.

There is a decrease in adhesion with the addition of the PVME. This suggests that it is not acting as a plasticiser but instead as a migratory molecule forming a weak boundary layer. The NPE gives a slight reduction in adhesion at the lower heat settings but at the higher heat there is a slight increase compared to the extracted PVB producing results similar to that of the unextracted PVB. This suggests that the NPE may be acting as a plasticising agent. The polar group on the chain interacting with the PVB.

The two different molecular weight PPG give varying results, neither gave any significant release, both giving peel strengths similar to the unextracted PVB. The two Tegomers proved to be the best release agents with the higher molecular weight Tegomer 6440 producing the greatest release.

6.3.3.2 PVC

The same small molecules used in the PVB sets were also used in the PVC pairings. The results can be seen in table 6.16.
Table 6.16
Peel strengths of PVC with small molecules

All peel strengths are in grams/inch and additives are at the 1% level.

<table>
<thead>
<tr>
<th>Dye Sheet</th>
<th>Heat Setting</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>7</td>
</tr>
<tr>
<td>PVC</td>
<td>8.5</td>
</tr>
<tr>
<td></td>
<td>7.5</td>
</tr>
<tr>
<td>Extracted PVC</td>
<td>110.0</td>
</tr>
<tr>
<td></td>
<td>51.0</td>
</tr>
<tr>
<td>Extracted PVC + PVME</td>
<td>14.0</td>
</tr>
<tr>
<td>Extracted PVC + NPE</td>
<td>128.0</td>
</tr>
<tr>
<td>Extracted PVC + 2000 PPG</td>
<td>16.0</td>
</tr>
<tr>
<td>Extracted PVC + 425 PPG</td>
<td>195.0</td>
</tr>
<tr>
<td>Extracted PVC + Teg 6440</td>
<td>175.0</td>
</tr>
<tr>
<td>Extracted PVC + Teg 2311</td>
<td>6.5</td>
</tr>
<tr>
<td></td>
<td>6.25</td>
</tr>
<tr>
<td>Extracted PVC + Teg 2311</td>
<td>11.5</td>
</tr>
<tr>
<td></td>
<td>14.5</td>
</tr>
</tbody>
</table>

A comparison with the PVB / PVB pair shows that the PVC has considerably lower peel strengths both before and after extraction. Before extraction this decrease with PVC can be attributed to the presence of the small molecules causing a weak boundary layer. With the extraction of these molecules it might be expected that the two systems have a similar peel strength. The two extracted polymers have similar $T_g$ and molecular weight but different functionality. This functionality is probably the reason for the increase in adhesion in the PVB pairing. Once close contact is made the increased functionality, with the possibility of hydrogen
bonding, will result in better entanglement and secondary bonding of the chains.

The results for the PVC extraction show that there is a significant increase in adhesion between the films after extraction, this will be due to the removal of the small molecules, which form a weak boundary layer. These contaminants are clearly seen in the FTIR analysis of the PVC extract.

The addition of the PVME gives a decrease in adhesion back down to the levels seen for the unextracted PVC. Clearly the PVME is producing a weak boundary layer in this system.

The addition of the NPE gives an increase in adhesion over the unextracted PVC and peel strengths similar to the extracted PVC. From this is can be seen that the NPE has no effect on the extracted PVC. It is possible that either it dissolves in the PVC and remains in the bulk or it failed to spread over the surface.

The addition of the PPG gives varying results depending on the size of the molecules used. The low molecular weight PPG gives results similar to those from the NPE and it is safe to assume that it dissolves in the PVC and remains in the bulk of the polymer. The high molecular weight PPG on the other hand produces a decrease in adhesion, although not back to the levels seen by the unextracted PVC. This shows that the molecule is too large to simply dissolve in the PVC. The Tegomers both gave a reduction in adhesion, with the best release resulting from the Tegomer 6440, the higher molecular weight Tegomer.
6.3.3.3 Coating thickness by XPS

Several peeled joints were chosen for analysis by XPS. The pairings involving the two Tegomers in both polymers and the pairing of PVME in PVC were chosen. PVME in PVB was not analysed due to the inability to easily distinguish between the two polymers, when present in a mixture, both of them having the same constituent atoms (oxygen and carbon).

XPS is a very surface specific method of analysis and by utilising sampling geometry it is possible to produce depth profiling in the top few nanometers. By adjusting the angle of collection of the photoelectrons from normal $90^\circ$ to $30^\circ$ it is possible to change the sampling depth. This technique was used to analyse the surfaces of the polymer pairing before and after printing to produce information on the thickness of the coatings of the small molecules.

Figure 6.41 shows the XPS spectrum of PVB with no additives. The peak areas are measured using a software package and the percentage composition calculated. Figure 6.42 shows the PVB with the addition of Teg 6440 at $90^\circ$ and figure 6.43 shows the PVB with Teg 6440 at $30^\circ$. 
Figure 6.41
XPS spectrum of PVB

Figure 6.42
XPS spectrum of PVB with Teg 6440 at 90°
The increasing size of the Si 2p peak is apparent with the change in sampling angle. The increased peak area with the 30° sampling angle is due to the halving in sampling depth. This indicates that the Tegomer has indeed formed a surface coating.

Figures 6.44 - 6.46 show XPS spectra of the PVC samples with Tegomer 6440. It is possible to see the increase in area of the silicon and oxygen peaks due to the angle change.
Figure 6.44
XPS Spectrum of PVC

Figure 6.45
XPS Spectrum of PVC with Tegomer 6440 at 90°
Tables 6.17 and 6.18 show the results of the XPS data in the form of percentage compositions.

Table 6.17
Percentage surface compositions of PVB and small molecules by XPS

<table>
<thead>
<tr>
<th></th>
<th>C 1s</th>
<th>O 1s</th>
<th>Si 2p</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVB Receiver</td>
<td>79.2%</td>
<td>20.8%</td>
<td>-</td>
</tr>
<tr>
<td>PVB/Teg 6440 dye</td>
<td>77.0%</td>
<td>19.0%</td>
<td>4.1%</td>
</tr>
<tr>
<td>before 90°</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVB/Teg 6440 dye</td>
<td>70.4%</td>
<td>18.5%</td>
<td>11.1%</td>
</tr>
<tr>
<td>before 30°</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVB/Teg 6440 dye</td>
<td>77.3%</td>
<td>20.2%</td>
<td>2.5%</td>
</tr>
<tr>
<td>after 90°</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVB/Teg 6440 dye</td>
<td>75.3%</td>
<td>19.6%</td>
<td>5.0%</td>
</tr>
<tr>
<td>after 30°</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVB/Teg 6440 rec</td>
<td>78.6%</td>
<td>20.0%</td>
<td>1.4%</td>
</tr>
<tr>
<td>after 90°</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVB/Teg 6440 rec</td>
<td>75.9%</td>
<td>20.6%</td>
<td>3.5%</td>
</tr>
<tr>
<td>after 30°</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVB/Teg 2311 dye</td>
<td>77.7%</td>
<td>19.0%</td>
<td>3.3%</td>
</tr>
<tr>
<td>before 90°</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVB/Teg 2311 dye</td>
<td>72.3%</td>
<td>18.6%</td>
<td>9.1%</td>
</tr>
<tr>
<td>before 30°</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVB/Teg 2311 dye</td>
<td>79.6%</td>
<td>19.5%</td>
<td>1.0%</td>
</tr>
<tr>
<td>after 90°</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVB/Teg 2311 dye</td>
<td>78.5%</td>
<td>19.4%</td>
<td>2.1%</td>
</tr>
<tr>
<td>after 30°</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVB/Teg 2311 rec</td>
<td>80.3%</td>
<td>18.9%</td>
<td>0.8%</td>
</tr>
<tr>
<td>after 90°</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVB/Teg 2311 rec</td>
<td>77.8%</td>
<td>19.7%</td>
<td>2.4%</td>
</tr>
<tr>
<td>after 30°</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 6.18

Percentage surface compositions of PVC and small molecules by XPS

<table>
<thead>
<tr>
<th></th>
<th>C 1s</th>
<th>Cl 2p</th>
<th>Si 2p</th>
<th>O 1s</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC Receiver</td>
<td>68.2 %</td>
<td>29.6 %</td>
<td>-</td>
<td>2.2 %</td>
</tr>
<tr>
<td>PVC/Teg6440 dye before 90°</td>
<td>63.5 %</td>
<td>24.2 %</td>
<td>4.9 %</td>
<td>7.4 %</td>
</tr>
<tr>
<td>PVC/Teg6440 dye before 30°</td>
<td>63.8 %</td>
<td>14.7 %</td>
<td>9.4 %</td>
<td>12.2 %</td>
</tr>
<tr>
<td>PVC/Teg6440 dye after 90°</td>
<td>65.1 %</td>
<td>27.5 %</td>
<td>3.4 %</td>
<td>4.0 %</td>
</tr>
<tr>
<td>PVC/Teg6440 dye after 30°</td>
<td>65.1 %</td>
<td>21.1 %</td>
<td>6.1 %</td>
<td>7.7 %</td>
</tr>
<tr>
<td>PVC/Teg6440 rec after 90°</td>
<td>60.5 %</td>
<td>22.1 %</td>
<td>7.9 %</td>
<td>9.5 %</td>
</tr>
<tr>
<td>PVC/Teg6440 rec after 30°</td>
<td>56.6 %</td>
<td>7.1 %</td>
<td>19.0 %</td>
<td>17.3 %</td>
</tr>
<tr>
<td>PVC/Teg2311 dye before 90°</td>
<td>63.7 %</td>
<td>27.3 %</td>
<td>4.3 %</td>
<td>4.7 %</td>
</tr>
<tr>
<td>PVC/Teg2311 dye before 30°</td>
<td>62.3 %</td>
<td>18.1 %</td>
<td>9.7 %</td>
<td>9.8 %</td>
</tr>
<tr>
<td>PVC/Teg2311 dye after 90°</td>
<td>60.6 %</td>
<td>29.0 %</td>
<td>5.0 %</td>
<td>5.4 %</td>
</tr>
<tr>
<td>PVC/Teg2311 dye after 30°</td>
<td>62.5 %</td>
<td>15.4 %</td>
<td>12.2 %</td>
<td>9.8 %</td>
</tr>
<tr>
<td>PVC/Teg2311 rec after 90°</td>
<td>72.5 %</td>
<td>6.7 %</td>
<td>1.2 %</td>
<td>19.6 %</td>
</tr>
<tr>
<td>PVC/Teg2311 rec after 30°</td>
<td>69.6 %</td>
<td>16.8 %</td>
<td>3.2 %</td>
<td>10.4 %</td>
</tr>
<tr>
<td>PVC/PVME dye before 90°</td>
<td>68.8 %</td>
<td>27.8 %</td>
<td>-</td>
<td>3.4 %</td>
</tr>
<tr>
<td>PVC/PVME dye before 30°</td>
<td>77.4 %</td>
<td>16.8 %</td>
<td>-</td>
<td>5.8 %</td>
</tr>
<tr>
<td>PVC/PVME dye after 90°</td>
<td>69.3 %</td>
<td>28.7 %</td>
<td>-</td>
<td>2.0 %</td>
</tr>
<tr>
<td>PVC/PVME dye after 30°</td>
<td>77.3 %</td>
<td>18.1 %</td>
<td>-</td>
<td>4.5 %</td>
</tr>
<tr>
<td>PVC/PVME rec after 90°</td>
<td>71.8 %</td>
<td>22.1 %</td>
<td>-</td>
<td>6.0 %</td>
</tr>
<tr>
<td>PVC/PVME rec after 30°</td>
<td>81.5 %</td>
<td>9.5 %</td>
<td>-</td>
<td>9.0 %</td>
</tr>
</tbody>
</table>

The empirical formula for the PVME is known from its chemical structure. From the XPS information it is possible to determine the compositions of the Tegomers. The empirical formula for the polymers is taken from the analysis of the receiver sheets before printing. Table 6.19 shows the calculated empirical percentages and the empirical formula from the structure.
Table 6.19

Empirical formulae of the polymers and small molecules by XPS

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Structural Formula</th>
<th>XPS Calculated formula</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C %</td>
</tr>
<tr>
<td>PVB</td>
<td>C₈O₂</td>
<td>79.1</td>
</tr>
<tr>
<td>PVC</td>
<td>C₂Cl</td>
<td>68.2</td>
</tr>
<tr>
<td>Tegomer 6440</td>
<td>C₂SiO</td>
<td>52.9</td>
</tr>
<tr>
<td>Tegomer 2311</td>
<td>C₂SiO</td>
<td>56.3</td>
</tr>
<tr>
<td>PVME</td>
<td>C₃O</td>
<td>87.8</td>
</tr>
</tbody>
</table>

Note: Hydrogen is not detected by XPS analysis.

The XPS calculated results seem to mirror the expected values from the structures. The only discrepancy is in the XPS analysis of PVME, these results give a value for the percentage of oxygen lower than expected and a consequent increase in the carbon percentage. This may be due in part to the orientation of the polymer molecule at the surface.

From the percentage compositions at the different angles it is possible to determine the coating thickness of these small molecules using the following equation, which assumes uniform surface coverage:

\[ d = \lambda \left( \ln \frac{I_{90}}{I_{30}} \right) \]  

Equation 19

Where \( d \) is the coating depth, \( \lambda \) is the inelastic mean free path and \( I_{90} \) and \( I_{30} \) are the peak intensities of a chosen atom present in the substrate at 90° and 30°. For the PVC films the chlorine peak is used in the equation and
for the PVB the adjusted carbon peak is used. λ for chlorine is 46.4 Å and for carbon is 45.0 Å\textsuperscript{112}.

Tables 6.20 and 6.21 show the coating depths calculated before and after printing at heat setting 10. Transfer of small molecules from the dye sheet to the receiver sheet is observed.

<table>
<thead>
<tr>
<th>Polymer and Coating</th>
<th>Media</th>
<th>Coating Depth</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC + Teg 2311</td>
<td>Dye Sheet Before Printing</td>
<td>3.1 nm</td>
</tr>
<tr>
<td></td>
<td>Dye Sheet After Printing</td>
<td>1.9 nm</td>
</tr>
<tr>
<td></td>
<td>Receiver Sheet After Printing</td>
<td>2.9 nm</td>
</tr>
<tr>
<td>PVC + Teg 6440</td>
<td>Dye Sheet Before Printing</td>
<td>5.3 nm</td>
</tr>
<tr>
<td></td>
<td>Dye Sheet After Printing</td>
<td>2.3 nm</td>
</tr>
<tr>
<td></td>
<td>Receiver Sheet After Printing</td>
<td>1.2 nm</td>
</tr>
<tr>
<td>PVC + PVME</td>
<td>Dye Sheet Before Printing</td>
<td>3.9 nm</td>
</tr>
<tr>
<td></td>
<td>Dye Sheet After Printing</td>
<td>2.3 nm</td>
</tr>
<tr>
<td></td>
<td>Receiver Sheet After Printing</td>
<td>2.1 nm</td>
</tr>
</tbody>
</table>

The results for the PVME samples show an almost equal split on both the receiver and dye sheet after printing, which would be expected for a cohesive failure in the weak boundary layer of small molecules.

The use of different molecular weight Tegomers allows some deductions to be made about the factors affecting the extent of surface segregation. Two extreme cases are as follows:

If the surface migration was limited by kinetics the lower molecular weight molecules would be expected to move through the substrate and
migrate to the surface to a greater effect than the higher molecular weight molecules. These higher molecular weight molecules would be slower moving in the substrate and hence a lower rate of migration to the surface to have an affect on the adhesion.

If the migration was controlled by a thermodynamic effect this would favour the larger molecules being at the surface as the lower molecular weight molecules would be more soluble in the substrate polymer. The higher molecular weight molecules would have a lower entropy of mixing, therefore be less soluble and tend to phase separate.

In this case it is obvious that the PVME is either migrating to the surface or is present due to a thermodynamically driven equilibrium producing autolayering whilst in solution. A solubility effect is having a greater influence. A solubility argument will state that the smaller molecular weight molecules would have a higher entropy of mixing and therefore remain in the bulk. The larger molecules would have a lower entropy of mixing and therefore would be found at a larger concentration at the surface.

The coating of the higher molecular weight Tegomer is thicker than that for the lower molecular weight Tegomer. This can be attributed to the autolayering effect. This also shows that the thickness of the film may be related to the adhesion as the higher molecular weight Tegomer gave a slightly lower peel strength.

The results for the Tegomers show that the thicknesses of the single layer on the dye sheet does not always correspond to the addition of the two thicknesses on the dye and receiver sheets after printing. The Tegomer
6440 has a larger coating on the initial dye sheet than the addition of the two substrates after peeling. This could be attributed to a migration of Tegomers into either the receiver or dye sheets during the printing process.

Tegomer 2311 shows that all of the original coating on the dye sheet has transferred to the receiver sheet and that more Tegomer has migrated to the surface during the printing and peeling processes. This would seem plausible considering the small size of the molecules.

Table 6.21
Coating depths of small molecules in PVB using XPS

<table>
<thead>
<tr>
<th>Polymer and Coating</th>
<th>Media</th>
<th>Coating Depth</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVB + Teg 2311</td>
<td>Dye Sheet Before Printing</td>
<td>1.5 nm</td>
</tr>
<tr>
<td></td>
<td>Dye Sheet After Printing</td>
<td>0.2 nm</td>
</tr>
<tr>
<td></td>
<td>Receiver Sheet After Printing</td>
<td>0.6 nm</td>
</tr>
<tr>
<td>PVB + Teg 6440</td>
<td>Dye Sheet Before Printing</td>
<td>1.7 nm</td>
</tr>
<tr>
<td></td>
<td>Dye Sheet After Printing</td>
<td>0.5 nm</td>
</tr>
<tr>
<td></td>
<td>Receiver Sheet After Printing</td>
<td>0.5 nm</td>
</tr>
</tbody>
</table>

Table 6.21 shows the similar calculations for the PVB sets. It should be noted that the film thicknesses prior to and after printing are lower than for PVC. Again the higher molecular weight Tegomer has a thicker film before printing although not to the same degree as it had in PVC. Both films in the case of PVB have had some redistribution of coating during printing. This can be seen from the totals of the after printing sheets not adding up to the values for the before printing sheet. This can be explained by an increased solubility of the Tegomer in PVB over PVC or may be due to the formation of droplets of Tegomer on the surface. This would account for there being less Tegomer at the surface prior to
printing, more of the Tegomers dissolved in the bulk of the polymer. During printing the temperature rise would allow more of the Tegomers to migrate back into the bulk from the surface.

By totalling the thicknesses of the films after printing on both the dye and receiver sheets and comparing them to the dye sheet before printing we can see that there is a similar decrease in thickness. 58 % decrease for the Teg 2311 and 55 % decrease for the Teg 6440. This indicates that under the printing conditions there is a similar rate of migration or redistribution away from the surface. Previous results have shown that a solubility factor determines the level of migration prior to printing, with the higher molecular weight Tegomer having a greater film thickness. This indicates that the factors affecting the migration are different during the higher heat of the printing process. The kinetics of autolayering in solution will be different to those seen for the diffusion in the polymer.

6.3.3.4 Summary

It was expected that the lower molecular weight small molecules would migrate to the surface to greater effect than those of higher molecular weight. This has not been the case. In PVC the PVME and Teg 6440 have both been shown to have a higher coating thickness by XPS. In PVB the thicknesses of the two Tegomers are similar with the higher molecular weight sample having a slightly thicker coating. This indicates that factors other than the kinetic factor involving migration is also working. A solubility argument has been proposed that shows that the smaller molecular weight molecules would be more soluble in the concentrated polymer solution and therefore remain in the bulk. The larger molecules
would be less soluble and form an insoluble dispersion in the solution. This is described as an autolayering effect.

Whilst in solution it is possible that a thermodynamic equilibrium is achieved where the dissolved small molecules form a separate layer on top of the dissolved polymer. This autolayered system means that when the films are drawn the small molecules are to be found at the surface as the solvent evaporates. The results of the coating thicknesses after printing does indicate that migration or redistribution does occur but the initial layering is thought to be due to autolayering in solution.

6.3.3.5 Atomic Force Microscopy

6.3.3.5.1 PVC

Figure 6.47 - 6.49 shows the surfaces of PVC with and without the two Tegomers which were acquired by AFM to examine surface morphology. The additives are at the 1 % level.
Figure 6.47
AFM image of PVC

Figure 6.48
AFM image of PVC with Teg 6440
In both cases it is possible to see the ribbons on the surfaces. An enlarged view of the PVC surface with Teg 6440 can be seen in figure 6.50. A cross section and surface analysis of this PVC with Teg 6440 can be seen in figures 6.51 and 6.52.
Figure 6.50
Enlarged view of the PVC with Teg 6440 surface

Figure 6.51
Cross section of PVC sample with Teg 6440
From the cross section it is possible to see the height and shape of the ribbons. An average height of the ribbons is 0.42 microns tall and has a base of 1.2 microns. The surface analysis shows a height histogram of the entire surface in the top graph and below that a histogram of the small white box that can be seen in the top right of the surface view. From this data it is possible to calculate the percentage of material in the raised area. From calculations using the two histograms the coverage of the ribbons is approximately 4%.

The shape of the ribbon is again approximated by a triangle which means the average height is half of the measure height. This value of 0.21 microns is then used along with the percentage coverage of the ribbons determined by the histograms to determine a total Tegomer at the surface.

The XPS data showed a thin film of Tegomer of depth 5.27 nm. Using this value, the height of the rectangle and the percentage cover of the
ribbons from the surface analysis it is possible to determine the total amount of Tegomer that has migrated to the surface.

Average coverage = (% ribbon coverage x (average ribbon height - XPS determined thickness)) + (% area without ribbon x XPS determined thickness)

= (0.04 x 204.73) + (0.96 x 5.27)

= 13 nm

Figures 6.53 and 6.54 show the cross section and surface analysis of the PVC with 1% teg 2311 added.

Figure 6.53
Cross sectional analysis of PVC with Teg 2311
Using the same method as before it is possible to again determine an average thickness of the Tegomer. The cross section shows an average height of 0.095 microns and the histograms of the two areas analysed show the percentage coverage of the ribbons to be 9.8%. The calculations, similar to those before, show that the average coverage is therefore 11 nm.

It is clear that the majority of the Tegomers are at the surface of the polymers. The Teg 6440 produces larger ribbons than the Teg 2311 on the PVC surface. This could be due to the increased viscosity of the Tegomers. Teg 2311 is a viscous liquid whilst Teg 6440 is a waxy solid.
6.3.3.5.2 PVB

AFM images of the surfaces of PVB with and without the Tegomer additives were acquired (Figures 6.55 - 6.57). The additives are at the 1% level.

Figure 6.55
AFM image of PVB surface
Figure 6.56
AFM image of PVB with Teg 6440 surface

Figure 6.57
AFM image of PVB with Teg 2311 surface
Both AFM images of the PVB with additives show different morphology to the plain PVB. PVB with Teg 6440 shows a flatter surface, the image was hard to obtain because of the high level of static from the sample. With the Teg 2311 there can be seen to be a slight coverage by small ribbons. A cross section of this surface can be seen in figure 6.58.

Figure 6.58
Cross section of the AFM image of PVB with Teg 2311

The cross section shows the amount of ribbons on the surface, the base width and the height of the ribbons. The height can be seen to be 0.03 microns and the base width is one micron. On this particular cross section there are fourteen ribbons. Figure 6.59 show further cross section of the surface in an attempt to determine an average coverage.
An average number of ribbons along each cross section is sixteen. Each ribbon has a one micron base so sixteen ribbons of one micron over a fifty micron line gives an 8% coverage of ribbons. The cross sectional area for each ribbon has been calculated as if it were a triangle. This converted to a rectangle of the same base length will give an average height over the width of the ribbon. This height will be half the height of the triangle, i.e. 0.015 microns. The 8% of the surface covered in ribbons is a small amount and therefore the values for the coating thicknesses measured by XPS are not much affected.

Using this value and the amount of coverage it is possible to determine the total amount of Tegomer at the surface using the following approximate relationship.
Average thickness = (% ribbon coverage x (average ribbon height - XPS determined thickness)) + (% area without ribbon x XPS determined thickness)

= (0.08 x (150 - 1.49)) + (0.92 x 1.49)

= 13 nm

If 100% of the Tegomer migrated to the surface the maximum thickness would be 10 nm for a 1% additive in a 1 micron film. The value calculated is only slightly higher than the maximum possible for the amount of Tegomer in the sample and given the approximations involved this shows good agreement. This overestimation can be attributed to the AFM tip artefacts producing ribbon cross sections of a larger base width than actually there. The cross sectional analysis of the sample area is also an estimation and could have contributed to the error.

The value does highlight the fact that it was originally thought that only fifteen percent of the Tegomer was at the surface. This calculation shows that this value is a huge underestimation and that a value nearer eighty or ninety percent is more probable. This shows the efficiency of the autolayering process.

6.3.3.5.3 Continued Heating

The films discussed previously were produced using the standard method, involving a thirty second heating in an oven at 140°. To determine if any further heating would produce any change in topography the films were
subjected to prolonged heating at higher temperatures and then reanalysed by using AFM. The oven was set at $180^\circ$ and the films were kept in for one minute.

Figures 6.60 and 6.61 show PVB with Teg 2311 before the heating and then after prolonged heating.

Figure 6.60
AFM image of PVB with Teg 2311 before prolonged heating
The small ribbons seen on the addition of Teg 2311 can be seen to have disappeared. The surface does show some relief not seen the previous AFM image but the scale is still smaller than the PVB alone.

Figures 6.62 and 6.63 show the PVB with Teg 6440 before and after prolonged heating.
Figure 6.62
AFM image of PVB with Teg 6440 before prolonged heating

Figure 6.63
AFM image of PVB with Teg 6440 after prolonged heating
There are no ribbons on either of the two images but there is slightly more relief in the heated sample. This is possibly due to the heating and flowing of the PVB.

Figures 6.64 and 6.65 show PVC with Teg 2311 before and after prolonged heating.

Figure 6.64
AFM image of PVC with Teg 2311 before prolonged heating
The ribbons observed in the first AFM image have disappeared after prolonged heating and the relief seen is similar to the PVC with no Tegomer. This indicates that the Tegomer has redistributed with the excess heat so as to smooth out the ribbons.

Figures 6.66 and 6.67 show the AFM images of PVC with Teg 6440 before and after prolonged heating.
Figure 6.66
AFM image of PVC with Teg 6440 before prolonged heating

Figure 6.67
AFM image of PVC with Teg 6440 after prolonged heating
Again the ribbons can be seen to disappear with prolonged heating and the relief seen is again similar to the PVC with no additives. This also indicates that the Tegomer has flown under the heat to form a thin film over the PVC surface.

6.3.3.5.4 Summary

The autolayering argument mentioned in the previous summary has now been verified by AFM and also supported by the continual heating results. Figure 6.68 shows schematically the process involved in the evaporation and then prolonged heating of the polymer and small molecule system.

Figure 6.68
Schematic diagram of the autolayering effect

Thermodynamic Equilibrium

Small molecules in solvent

Polymer in solvent

Solvent Evaporation

Polymer

Heat

Polymer
Whilst the solvent is present the small molecules separate into areas of high small molecule concentration in thermal equilibrium with the polymer solution, not necessarily as a separate layer but more possibly as a lace network as the ribbon seen by AFM show. As the solvent evaporates there is a non equilibrium situation and the small molecules are left as a lace network on the surface. They are too viscous to spread and remain in the ribbon structure.

With prolonged heating the raised ribbons are flattened as the small molecules begin to flow and thermal equilibrium is again achieved between the polymer and the small molecules. A simple migration or diffusion mechanism would yield an even layer of small molecules as the small molecules migrate from the bulk after the production of the film. The XPS showed this layer which indicates that some migration does take place. This possible migration is supported by the XPS data after printing which shows that the small molecules have redistributed after printing. Although some migration may take place the ribbon structure confirms that the majority of the small molecules get to the surface of the polymer by an autolayering mechanism as the films are produced.
6.4 Dye Molecules

During printing, a low peel strength is very important. A high level of adhesion can cause the printer to jam or a total transfer of the dye sheet onto the receiver sheet. The addition of the dyes was undertaken to determine whether they act in a similar manner to the small molecules already introduced. The preferred result is that they readily migrate to the surface of the dye sheet during printing causing a decrease in adhesion. Then once in the receiver polymer they migrate into the bulk of the polymer thus inhibiting any surface loss due to mechanical abrasion.

Peel results for the extracted PVC and PVB systems were examined. It was decided to use the extracted polymers to minimise interference from any of the small molecules in the original polymers. FTIR characterisation of the dyes has been undertaken and this analysis is used in determining the depth of penetration of the dyes into the receiving polymer and some degree of dye concentration. The dyes were added in a 1:2 dye : polymer loading by weight.

6.4.1 Yellow Dyes

One yellow dye was used, supplied by ICI Imagedata. The structure of the dye can be seen in figure 6.69.
Table 6.22 shows the peel strengths of the PVB / PVC pairings with the inclusion of the Y2 azopyridone yellow dye.

<table>
<thead>
<tr>
<th>Receiver Sheet</th>
<th>Dye Sheet</th>
<th>Heat Setting (Peel Strength in grams/inch)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>PVB</td>
<td>PVC</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>PVC</td>
<td>-</td>
</tr>
<tr>
<td>PVC</td>
<td>PVB</td>
<td>9.5</td>
</tr>
<tr>
<td></td>
<td>PVB</td>
<td>6.5</td>
</tr>
<tr>
<td>PVB</td>
<td>PVC + Y2</td>
<td>15.0</td>
</tr>
<tr>
<td></td>
<td>PVC + Y2</td>
<td>12.0</td>
</tr>
<tr>
<td>PVC</td>
<td>PVB + Y2</td>
<td>10.0</td>
</tr>
<tr>
<td></td>
<td>PVB + Y2</td>
<td>14.0</td>
</tr>
</tbody>
</table>

The results show that there is an increase in adhesion with the addition of the Y2 dye. This is probably due to the slight solubility of the dye in the
polymers giving a reduction in $T_g$ and thus an increase in softening and adhesion. The dye migration could also be affecting the $T_g$ of the receiver polymer.

6.4.2 Cyan Dyes

Two cyan dyes were used, both supplied by ICI Imagedata. Their structures are given in figure 6.70.

Figure 6.70
Structures of the cyan dyes
Cl Disazothiophene Cyan
Table 6.23 shows the results of the peel test with the cyan dyes. All dye loading was a 1:2 dye / polymer weight fraction.

Table 6.23

Peel strengths for extracted PVC and PVB with C1 and C2 dyes

<table>
<thead>
<tr>
<th>Receiver Sheet</th>
<th>Dye Sheet</th>
<th>Heat Setting (Peel Strength in grams/inch)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>PVB</td>
<td>PVC + C1</td>
<td>5.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.5</td>
</tr>
<tr>
<td>PVC</td>
<td>PVB + C1</td>
<td>7.75</td>
</tr>
<tr>
<td></td>
<td></td>
<td>22.5</td>
</tr>
<tr>
<td>PVB</td>
<td>PVC + C2</td>
<td>7.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8.75</td>
</tr>
<tr>
<td>PVC</td>
<td>PVB + C2</td>
<td>25.75</td>
</tr>
<tr>
<td></td>
<td></td>
<td>36.5</td>
</tr>
</tbody>
</table>

The results show that when PVB is used as the receiver sheet there is only a slight difference in adhesion depending on the dye used. The C2 dye giving slightly higher peel strengths. With PVC as the receiver sheet there is a general increase in adhesion over the PVB receiver and the effect of
the different dyes is more prominent. Possibly with the PVB receiver sheets the effect of the dye was too small to be noticed because of the low peel strengths involved. In the PVC the peel strengths are higher so the effect of the dyes can be seen. The PVC receiver sheet results show that the C2 dye gives greater adhesion. This may be attributed to a $T_g$ effect, the $T_g$ of the PVB dye sheets containing C1 is 88.5°C and containing C2 is 61.6°C as measured by ICI Imagedata.

6.4.3 Magenta Dyes

Two magenta dyes were supplied by ICI Imagedata, their structures can be seen in figure 6.71.

Figure 6.71
Structure of the Magenta dyes
M0 Anthraquinone Magenta
M3 Isothiazole Magenta

Table 6.24 shows the results of the peel tests with the magenta dyes.

Table 6.24
Peel strengths for extracted PVC and PVB with M0 and M3 dyes

<table>
<thead>
<tr>
<th>Receiver Sheet</th>
<th>Dye Sheet</th>
<th>Heat Setting (Peel Strength in grams/inch)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>PVB</td>
<td>PVC + M0</td>
<td>9.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>9.5</td>
</tr>
<tr>
<td>PVC</td>
<td>PVB + M0</td>
<td>21.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>21.0</td>
</tr>
<tr>
<td>PVB</td>
<td>PVC + M3</td>
<td>10.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8.0</td>
</tr>
<tr>
<td>PVC</td>
<td>PVB + M3</td>
<td>32.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>23.5</td>
</tr>
</tbody>
</table>

As with the cyan dyes when PVB is used as the receiver sheet there is little adhesion dependence on the dye used. There is an increase in adhesion when printing into PVC. With the PVC receiver it can be seen
that the dyes do have an effect with M3 giving slightly greater adhesion. The plasticisation effects of the dyes dominate over any weak boundary layers related to the presence of small molecules.

6.4.4 Depth of Penetration of Dyes

The FTIR spectrometer was used to determine the depth of the penetration of the dyes into the two receivers. The attenuated total reflectance (ATR) attachment was used for the analysis and both single and multiple bounce systems were tested. Adjusting the angle of incidence on the multi-bounce attachment changes the depth of penetration into the sample and also by changing the crystal gives a change in depth. With the single bounce attachment there is no angle change available as there is a fixed geometry to the system but a change of crystal is used to give a different depth of penetration. Typical analysis depths are approximately half a micron for the Ge crystal and almost two microns with the ZnSe and KRS-5 crystals.

Using both attachments the depth of penetration of the infra-red beam can be determined using equation 20.

\[
d_p = \frac{\lambda}{2m_i \left[ \sin^2 \phi - \left( \frac{n_2}{n_1} \right)^2 \right]^{1/2}}
\]

Equation 20

Where \( d_p \) is the penetration depth, \( \lambda \) is the wavelength, \( n_1 \) and \( n_2 \) are the refractive indexes of the crystal and polymer respectively and \( \phi \) is the sampling angle. For the single bounce attachment \( \phi \) is considered to be 45°.
due to the permanent geometry of the system. The sampling angle, $\phi$, for the multi-bounce attachment is determined from equation 21.

$$\phi = \phi_{IRA} - \sin^{-1}\left[\frac{\sin(\phi_{IRA} - \phi_{IRF})}{n_1}\right].$$

Equation 21

Where $\phi_{IRA}$ is the angle on the scale on the attachment, $\phi_{IRF}$ is the angle of the prism face and $n_1$ the refractive index of the crystal. The refractive indexes of the various crystals and polymers are given in table 6.25.

Table 6.25
Refractive indexes of the crystals and polymers used in the ATR attachment

<table>
<thead>
<tr>
<th>Sample</th>
<th>Refractive Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge Crystal</td>
<td>4.01</td>
</tr>
<tr>
<td>KRS-5 (TlBe / TIl) Crystal</td>
<td>2.38</td>
</tr>
<tr>
<td>ZnSe Crystal</td>
<td>2.40</td>
</tr>
<tr>
<td>PVB</td>
<td>1.485</td>
</tr>
<tr>
<td>PVC</td>
<td>1.545</td>
</tr>
</tbody>
</table>

The wavelength is determined by the peaks analysed by the FTIR. Peak areas for a polymer and dye peak are determined using the instrument's software. These peaks should ideally not interfere with each other on the spectrum. The wavelength is taken from the average of these two peaks. Table 6.26 shows the peaks used in the Y2 dye experiments.
Table 6.26

Wavenumbers of the peaks used in the determination of the penetration of Y2 dye into the two polymers

<table>
<thead>
<tr>
<th>Sample</th>
<th>Peak / cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y2 dye</td>
<td>1509</td>
</tr>
<tr>
<td>PVB</td>
<td>720</td>
</tr>
<tr>
<td>PVC</td>
<td>872</td>
</tr>
</tbody>
</table>

With the PVC samples it was impossible to find a peak in the PVC that was not obscured by any of the dye peaks. As a result a dye spectrum was subtracted from the dye in PVC prior to the peak area calculation.

Table 6.27 shows the calculated sampling depths for the analysis of the Y2 dye in both PVC and PVB using the fixed geometry single bounce attachment.

Table 6.27

Sampling depths for the Y2 dye in PVC and PVB

<table>
<thead>
<tr>
<th>Crystal and polymer</th>
<th>dp / microns</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge crystal / PVC</td>
<td>0.541</td>
</tr>
<tr>
<td>Ge crystal / PVB</td>
<td>0.457</td>
</tr>
<tr>
<td>ZnSe crystal / PVC</td>
<td>1.832</td>
</tr>
<tr>
<td>ZnSe crystal / PVB</td>
<td>1.343</td>
</tr>
</tbody>
</table>

Samples of the receiver sheet after printing at two heat settings were analysed. PVB versus PVC was studied with both polymers being used as the receiver and dye sheets. The dye sheet prior to printing with the 1:2 w/w dye loading was analysed to give values for a known dye loading.
Equation 19 is used to calculate the depth of penetration of the dye, assuming an exponential decrease in dye concentration with depth, as well as the volume fraction of dye at the surface of the receiver sheet\(^2\).

\[
\frac{A_{\text{pol}}}{A_{\text{dye}}} = \frac{A'_{\text{pol}}}{A'_{\text{dye}}} \left( \frac{d_p}{2V_0k} + \frac{1}{V_0} - 1 \right)
\]  
Equation 22\(^2\)

Where \(A_{\text{pol}}/A_{\text{dye}}\) is the ratio of the polymer and dye peak areas from the FTIR spectra, \(A'_{\text{pol}}/A'_{\text{dye}}\) is the ratio of the polymer and dye peak areas in a 1:1 by weight dye/polymer mix, \(V_0\) is the volume fraction of dye at the surface, \(d_p\) is the penetration depth of the infra-red beam and \(k\) is the penetration of the dye molecules into the substrate.

A plot of \(d_p\) versus \(A_{\text{pol}}/A_{\text{dye}}\) yields the following equations.

\[
\text{Slope} = \frac{A'_{\text{pol}}}{A'_{\text{dye}}} \frac{1}{2V_0k}
\]  
Equation 23\(^2\)

\[
\text{Intercept} = \frac{A'_{\text{pol}}}{A'_{\text{dye}}} \left( \frac{1}{V_0} - 1 \right)
\]  
Equation 24\(^2\)

Table 6.28 shows the \(V_0\) and \(k\) values calculated from these equations for the single bounce method.
The results for the single bounce experiment show a decrease in dye at the surface and penetration depth when going to the lower heat, heat setting 10. The dyes show a similar penetration into both the PVB and PVC although there is more dye at the surface of the PVC, indicating a greater affinity with that polymer. The multiple bounce method showed some physically unreasonable results at the lower heat setting. This was probably due to the low level of dye transferred that the multiple bounce method had difficulty detecting. Printing into PVB showed some similarities between the two methods at high heat settings but there were some discrepancies between the methods when printing into PVC. As a result of this it was decided to continue with the other dyes using only the single bounce method.

Figures 6.72 - 6.79 show the FTIR spectra of the PVB and PVC polymers with the cyan and magenta dyes. In each case the peak areas used in the calculations are shown. In the event of overlap between peaks the dye peak is subtracted from the spectra before the polymer peak area is calculated.
Figure 6.72
FTIR Spectrum of PVB and C1 dye showing the peak areas used in the penetration calculations

Figure 6.73
FTIR Spectrum of PVB and C2 dye showing the peak areas used in the penetration calculations
Figure 6.74
FTIR Spectrum of PVB and M0 dye showing the peak areas used in the penetration calculations

Figure 6.75
FTIR Spectrum of PVB and M3 dye showing the peak areas used in the penetration calculations
Figure 6.76
FTIR Spectrum of PVC and Cl dye showing the peak areas used in the penetration calculations

Figure 6.77
FTIR Spectrum of PVC and C2 dye showing the peak areas used in the penetration calculations
Table 6.29 shows the $V_0$ and $K$ values calculated from the FTIR spectra along with the peel strengths for each pairing.
Table 6.29

$V_0$ and K Values for C1 and C2 Dyes

<table>
<thead>
<tr>
<th></th>
<th>Receiver Sheet</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>PVB</td>
<td>PVC</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>C1</td>
<td>C2</td>
<td>C1</td>
<td>C2</td>
<td></td>
</tr>
<tr>
<td>Heat Setting</td>
<td>V$_0$</td>
<td>0.49</td>
<td>0.27</td>
<td>0.33</td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td>K / $\mu$</td>
<td>0.14</td>
<td>0.17</td>
<td>0.20</td>
<td>0.77</td>
</tr>
<tr>
<td>0</td>
<td>Peel / g/in</td>
<td>4.75</td>
<td>7.88</td>
<td>15.13</td>
<td>31.13</td>
</tr>
<tr>
<td>Heat Setting</td>
<td>V$_0$</td>
<td>-0.24</td>
<td>-0.16</td>
<td>0.65</td>
<td>0.16</td>
</tr>
<tr>
<td>5</td>
<td>K / $\mu$</td>
<td>-0.12</td>
<td>-0.08</td>
<td>0.05</td>
<td>0.46</td>
</tr>
<tr>
<td></td>
<td>Peel / g/in</td>
<td>4.38</td>
<td>6.75</td>
<td>6.75</td>
<td>9.88</td>
</tr>
</tbody>
</table>

The results for the higher heat setting are shown to be more reliable due to the greater transfer of dye and therefore a greater ease of detection by the FTIR. The results for the lower heat setting show that some of the calculations are giving physically unreasonable answers. This is thought to be due to problems encountered with the cyan dyes. At high concentrations, the 50% dye loading, the dye tended to crystallise out. This crystallisation caused surface roughness which impaired the ATR contact and therefore the spectra collected were poor, leading to large percentage errors in measuring small peak areas. These spectra were then used in trying to calculate the $\frac{A_{\text{rel}}}{A_{\text{dye}}}$ values. The poor quality of the spectra at the lower heat setting also complicated the matter in attempting to extrapolate back to find $V_0$. The values for the high heat setting were calculated from better quality spectra and the results gained reflect that.

It can be seen in the higher heat setting that an increase in penetration depth is mirrored by an increase in peel strength. The $V_0$ values show that the dye concentrations at the surface of the receiver sheets are similar to
the concentrations of that found in the dye sheets before printing, i.e. 0.33 dye loading.

Table 6.30 shows the $V_0$ and $K$ values for the magenta dye pairings with the peel strengths.

Table 6.30

<table>
<thead>
<tr>
<th>Heat Setting</th>
<th>PVB</th>
<th>PVC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$V_0$</td>
<td>$K/\mu$</td>
</tr>
<tr>
<td>0 Peel g/in</td>
<td>0.29</td>
<td>0.49</td>
</tr>
<tr>
<td>10 Peel g/in</td>
<td>0.39</td>
<td>0.17</td>
</tr>
</tbody>
</table>

With the exception of M0 in PVC at the lower heat setting all of the values seem reasonable. This result gives a volume fraction greater than one which is impossible. In all cases at the lower heat settings there is less penetration of the dye into the receiver sheets. The M3 dye shows a drop in both $V_0$ and $K$ values at the lower heat setting indicating that less dye is at the surface and any penetration has been to a lower depth. With the M0 dye there has been an increase in $V_0$ and a significant decrease in $K$. This indicates that there is a build up of dye at the surface because very little has diffused away from the interface.
In all cases the presence of dyes affects the adhesion. The peel strengths of the samples increases with the presence of the dyes. This is attributed to the plasticisation effect of the dyes giving rise to a drop in $T_g$ of the polymer, this subsequently results in a softening during printing, greater contact between the sheets and hence better adhesion. The FTIR gave good results at the higher heats but its sensitivity was not good enough at the lower heat to get depth profiles.
6.5 Dye and Small Molecule Combination

6.5.1 Peel results

Tables 6.31 and 6.32 show the peel strength results for the PVB / PVC pairings with both M3 dye and various small molecules. These systems being more representative of the commercial system.

Table 6.31
Peel strengths for the following pairings - PVB Receiver Sheet Versus PVC + M3 Dye + Small Molecules

<table>
<thead>
<tr>
<th>Dye Sheet</th>
<th>Heat Settings</th>
<th>0</th>
<th>2</th>
<th>5</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC + M3</td>
<td></td>
<td>21.0</td>
<td>15.75</td>
<td>25.5</td>
<td>11.5</td>
</tr>
<tr>
<td>PVC + M3 + PVME</td>
<td></td>
<td>15.5</td>
<td>11.5</td>
<td>9.0</td>
<td>7.5</td>
</tr>
<tr>
<td>PVC + M3 + Teg 6440</td>
<td></td>
<td>8.5</td>
<td>9.25</td>
<td>6.0</td>
<td>4.75</td>
</tr>
<tr>
<td>PVC + M3 + Teg 2311</td>
<td></td>
<td>14.75</td>
<td>14.5</td>
<td>11.75</td>
<td>10.5</td>
</tr>
</tbody>
</table>

All peel strengths are in grams/inch and additives are at the 1% level and dye is at the 33% level.

Table 6.32
Peel strengths for the following pairings - PVC Receiver Sheet Versus PVB + M3 Dye + Small Molecules

<table>
<thead>
<tr>
<th>Dye Sheet</th>
<th>Heat Settings</th>
<th>0</th>
<th>2</th>
<th>5</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVB + M3</td>
<td></td>
<td>76.0</td>
<td>64.0</td>
<td>34.0</td>
<td>15.75</td>
</tr>
<tr>
<td>PVB + M3 + PVME</td>
<td></td>
<td>69.0</td>
<td>63.0</td>
<td>26.0</td>
<td>16.5</td>
</tr>
<tr>
<td>PVB + M3 + Teg 6440</td>
<td></td>
<td>73.5</td>
<td>31.75</td>
<td>29.75</td>
<td>10.0</td>
</tr>
<tr>
<td>PVB + M3 + Teg 2311</td>
<td></td>
<td>66.0</td>
<td>70.5</td>
<td>34.0</td>
<td>14.25</td>
</tr>
<tr>
<td></td>
<td></td>
<td>78.0</td>
<td>69.0</td>
<td>33.5</td>
<td>16.0</td>
</tr>
</tbody>
</table>
All peel strengths are in grams/inch and additives are at the 1% level and dye is at the 33% level.

The results in table 6.31 show that the addition of the small molecules to the PVC dye sheet gives a drop in adhesion with PVB. This is consistent with all of the previous findings with these small molecules. The high molecular weight Tegomer gave the greatest drop in peel strength. The PVME and Teg 2311 both gave similar values.

Table 6.32 shows the results with the PVC receiver sheet against the PVB dye sheet. There is little decrease in adhesion with the addition of PVME and Teg 2311. With the inclusion of the Teg 6440 however there is a considerable drop in peel strength.

6.5.2 Characterisation

The receiver sheets were analysed by XPS, FTIR and UV-VIS. The XPS was to determine the coating depth of the small molecules and also to provide a surface volume fraction of dye from the nitrogen in the dye molecules. The FTIR was to determine a penetration depth and also to produce a total dye transfer value. The UV-VIS was to produce optical density data on the total amount of dye transferred.

6.5.2.1 FTIR Spectroscopy and Optical Densities

Table 6.33 shows the weight fraction of dye from optical densities and FTIR data.
Table 6.33
Weight fraction data from both optical densities and FTIR

<table>
<thead>
<tr>
<th>Receiver Sheet</th>
<th>Dye Sheet</th>
<th>Weight Fraction from UV-VIS Data</th>
<th>Weight Fraction from FTIR Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC</td>
<td>PVB + M3</td>
<td>0.10</td>
<td>0.10</td>
</tr>
<tr>
<td>PVC</td>
<td>PVB + M3 + PVME</td>
<td>0.11</td>
<td>0.11</td>
</tr>
<tr>
<td>PVC</td>
<td>PVB + M3 + Teg 6440</td>
<td>0.15</td>
<td>0.07</td>
</tr>
<tr>
<td>PVC</td>
<td>PVB + M3 + Teg 2311</td>
<td>0.12</td>
<td>0.08</td>
</tr>
<tr>
<td>PVB</td>
<td>PVC + M3</td>
<td>0.11</td>
<td>0.09</td>
</tr>
<tr>
<td>PVB</td>
<td>PVC + M3 + PVME</td>
<td>0.12</td>
<td>0.11</td>
</tr>
<tr>
<td>PVB</td>
<td>PVC + M3 + Teg 6440</td>
<td>0.10</td>
<td>0.11</td>
</tr>
<tr>
<td>PVB</td>
<td>PVC + M3 + Teg 2311</td>
<td>0.09</td>
<td>0.09</td>
</tr>
</tbody>
</table>

The UV-VIS and FTIR weight fractions were calculated using a calibration involving a standard film with a known dye content.

The results from the FTIR data were expected to be slightly lower than those from the UV-VIS. This is because the UV-VIS spectroscopy samples through the whole film; thus it includes the total dye transferred. The FTIR data is taken from a sampling depth of under two microns. It is possible that some dye may have travelled further into the polymer system and thus not detected.

In most cases the amount of dye transferred is fairly similar. The lower values for the FTIR data on the PVC are consistent with the findings shown in table 6.30. The K value shows that the M3 dye penetrates further into PVC which means that more of the dye may be beyond the sampling depth of the FTIR. Printing into PVB appears to be more consistent; this is due to the fact that M3 does not penetrate as far into the PVB and so the dye detected by FTIR will be closer to the total amount present.
6.5.2.2 X-Ray Photoelectron Spectroscopy (XPS)

$V_0$ values for the volume fraction of dye at the surface were calculated from the nitrogen peak in the XPS spectra. Firstly the contribution from the small molecule coating were removed from the data. The results were then normalised and the mass contributions of the dye and polymers calculated. These mass contribution were then ratioed to give the volume fraction of dye at the surface. This can be seen in table 6.34 for the PVC dye sheet with Teg 2311 and M3 dye before printing.

Table 6.34
XPS percentages for PVC with M3 dye and Teg 2311 and their subtraction and normalisation

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>O</th>
<th>Cl</th>
<th>Si</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC + M3 + Teg 2311</td>
<td>67.1</td>
<td>7.3</td>
<td>18.7</td>
<td>3.8</td>
<td>2.2</td>
</tr>
<tr>
<td>- Teg 2311</td>
<td>57.76</td>
<td>3.85</td>
<td>18.7</td>
<td>0.0</td>
<td>2.2</td>
</tr>
<tr>
<td>Normalised</td>
<td>70.0</td>
<td>4.6</td>
<td>22.66</td>
<td>0.0</td>
<td>2.67</td>
</tr>
</tbody>
</table>

The values for the starting polymer / dye / Tegomer don't add up to 100% due to the additional sulphur peak from the dye molecule, but this is dismissed in the calculations as it is hard to calculate any peak areas due to the closeness to the Si peak, the nitrogen peak proving to be the more reliable. The Tegomer contributions are removed using the Si values. The empirical formula of the Tegomer is known from the results obtained from the dyes in small molecules and these values are used to ratio the Si peak to determine the carbon and oxygen contributions. With the Tegomer removed the new values are normalised to one hundred percent. The new percentage value for the nitrogen is used to determine amount of
dye present. The new percentage for the chlorine is used to determine the amount of polymer present.

\[ \% N = 2.67 \]

mass of M3 dye molecule = 371 g mol\(^{-1}\)

No. of N atoms in M3 = 5

\[ \% Cl = 22.66 \]

mass of PVC repeat unit = 62.5 g mol\(^{-1}\)

No. of Cl atoms in repeat unit = 1

The fraction of dye at surface is:

\[ V_0 = \frac{V_{\text{Dye}}}{V_{\text{Dye}} + V_{\text{Polymer}}} \quad \text{Equation 25} \]

\[ = \frac{2.67/5 \times 371}{(2.67/5 \times 371) + (22.66/1 \times 62.5)} \]

\[ V_0 = 0.123 \]

Table 6.35 shows the calculation for the \( V_0 \) data from the XPS results.
Table 6.35
V₀ values calculated from the XPS data

<table>
<thead>
<tr>
<th>Receiver Sheet</th>
<th>Dye Sheet</th>
<th>Media Analysed</th>
<th>V₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC</td>
<td>PVC M3</td>
<td>Dye Sheet Before Printing</td>
<td>0.20</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Dye Sheet After Printing</td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Receiver Sheet After Printing</td>
<td>0.19</td>
</tr>
<tr>
<td>PVC</td>
<td>PVC M3 PVME</td>
<td>Dye Sheet Before Printing</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Dye Sheet After Printing</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Receiver Sheet After Printing</td>
<td>0.15</td>
</tr>
<tr>
<td>PVC</td>
<td>PVC M3 Teg 6440</td>
<td>Dye Sheet Before Printing</td>
<td>0.16</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Dye Sheet After Printing</td>
<td>0.09</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Receiver Sheet After Printing</td>
<td>0.10</td>
</tr>
<tr>
<td>PVC</td>
<td>PVC M3 Teg 2311</td>
<td>Dye Sheet Before Printing</td>
<td>0.22</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Dye Sheet After Printing</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Receiver Sheet After Printing</td>
<td>0.14</td>
</tr>
<tr>
<td>PVB</td>
<td>PVC M3</td>
<td>Dye Sheet Before Printing</td>
<td>0.16</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Dye Sheet After Printing</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Receiver Sheet After Printing</td>
<td>0.08</td>
</tr>
<tr>
<td>PVB</td>
<td>PVC M3 PVME</td>
<td>Dye Sheet Before Printing</td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Dye Sheet After Printing</td>
<td>0.16</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Receiver Sheet After Printing</td>
<td>-</td>
</tr>
<tr>
<td>PVB</td>
<td>PVC M3 Teg 6440</td>
<td>Dye Sheet Before Printing</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Dye Sheet After Printing</td>
<td>0.14</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Receiver Sheet After Printing</td>
<td>0.08</td>
</tr>
<tr>
<td>PVB</td>
<td>PVC M3 Teg 2311</td>
<td>Dye Sheet Before Printing</td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Dye Sheet After Printing</td>
<td>0.17</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Receiver Sheet After Printing</td>
<td>0.07</td>
</tr>
</tbody>
</table>

No values can be gained for the PVME in PVB due to the inability to remove the PVME from the calculations because it has a similar elemental composition to the PVB (i.e. only carbon and oxygen molecules).

The values gained from the XPS will be different from those calculated from FTIR. This is because the sampling depth for the XPS is in the order of a few nanometers whilst that for the FTIR is in the order of a micron and the surface data is then gained from extrapolating back. Small variations in the near surface composition will also affect the XPS results. The reorientation of the dye molecules in the outer monolayers could mean that XPS gives a lower value than FTIR; which is not as sensitive to the near surface.
The results show that with the PVC receiver sheet the $V_0$ values for the receiver sheet after printing are consistently higher than those for the PVB receiver sheet.

In each case there is a drop in $V_0$ between the before and after printing in the PVB dye sheets. There is no such drop with the PVC dye sheets and in fact there are some apparent increases in $V_0$. This indicates that the dye is perhaps replenishing itself at the surface when in PVC after printing. There is no such replenishment when the dye has to migrate through PVB.

The values of $V_0$ for the PVB dye sheet against the PVC receiver sheet show that the receiver sheet values and the dye sheet after printing values almost add up to the dye sheet before printing values. This suggests that there is a direct transfer of the dye from the surface of the dye sheet across to the receiver sheet with very little migration of the dye in the bulk of the polymer.

Dye partition values were obtained from ICI Imagedata from partition experiments with PVB versus polystyrene and PVC versus polystyrene at 190°. These values show that for M3 at 190° a value of 0.67 is gained in favour of PVC. Ratioing the values in table 6.35 for the dye and receiver sheets after printing gives similar partition values. Table 6.36 gives these ratios.
Table 6.36
Partition ratios for the M3 dye between the two polymers

<table>
<thead>
<tr>
<th>Receiver Sheet</th>
<th>Dye sheet</th>
<th>Partition ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC</td>
<td>PVB + M3</td>
<td>0.33</td>
</tr>
<tr>
<td>PVC</td>
<td>PVB + M3 + Teg 6440</td>
<td>0.94</td>
</tr>
<tr>
<td>PVC</td>
<td>PVB + M3 + Teg 2311</td>
<td>0.52</td>
</tr>
<tr>
<td>PVB</td>
<td>PVC + M3</td>
<td>0.53</td>
</tr>
<tr>
<td>PVB</td>
<td>PVC + M3 + Teg 6440</td>
<td>0.54</td>
</tr>
<tr>
<td>PVB</td>
<td>PVC + M3 + Teg 2311</td>
<td>0.43</td>
</tr>
</tbody>
</table>

All of the results favour the dye in PVC. The values for the PVB receiver show good consistency. The exceptions being the results for the dye moving from PVB into PVC with no small molecules and with Teg 6440.

It is expected that the dye partition values will rise towards one as the temperature increases and the dye molecules are allowed to move more freely. This does not appear to be the case. The value of 0.67 for the 190° is a higher value than those attained through printing and yet 190° is a minimum temperature achieved during printing. Thus the dyes must be frozen into the polymers at a temperature lower than that during the printing process.

Table 6.37 shows the coating depths of the small molecules in the polymer films by XPS.
Table 6.37
Coating depths calculated from the XPS data

<table>
<thead>
<tr>
<th>Receiver Sheet</th>
<th>Dye Sheet</th>
<th>Media</th>
<th>Coating Depth</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVB</td>
<td>PVC + M3 + PVME</td>
<td>Dye Sheet Before Printing</td>
<td>3.1 nm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Dye Sheet After Printing</td>
<td>1.0 nm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Receiver Sheet After Printing</td>
<td>-</td>
</tr>
<tr>
<td>PVB</td>
<td>PVC + M3 + Teg 6440</td>
<td>Dye Sheet Before Printing</td>
<td>4.1 nm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Dye Sheet After Printing</td>
<td>1.8 nm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Receiver Sheet After Printing</td>
<td>0.3 nm</td>
</tr>
<tr>
<td>PVB</td>
<td>PVC + M3 + Teg 2311</td>
<td>Dye Sheet Before Printing</td>
<td>2.3 nm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Dye Sheet After Printing</td>
<td>0.5 nm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Receiver Sheet After Printing</td>
<td>0.5 nm</td>
</tr>
</tbody>
</table>

These values were again calculated from the following equation.

\[ d = \lambda \left( \ln \frac{I_{90}}{I_{30}} \right) \]  

Equation 26

Where \( d \) is the coating depth, \( \lambda \) is the inelastic mean free path and \( I_{90} \) and \( I_{30} \) are the peak intensities of the atoms at both 90° and 30°.

The results for the PVB receiver sheet show that the coating thickness' on the receiver sheet and dye sheet after printing do not add up to the values obtained from the dye sheet before printing, this shows that some small molecule migration occurs during the printing process. With the PVC
receiver sheets there is again little correlation between the before and after printed sheets indicating that some migration has occurred. The only exception to this is the Teg 2311 in the PVB dye sheet which appears to cohesively fracture leaving the majority on the receiver sheet and no replenishment of the dye sheet occurs. This follows the solubility argument established earlier, that the smaller molecules will be more soluble in the polymers and remain in the bulk.

The thickness of the Teg 6440 films in both cases is considerably thicker than that of the Teg 2311, twice as thick in the PVC and almost four times as thick in the PVB. This increase in thickness can be attributed to the autolayering that occurs during the formation of the films. The higher molecular weight Tegomer will produce a thicker film due to more of the larger sized molecules remaining in a separate layer in the thermal equilibrium established in the solvent. This effect can be linked to the peel strength where the Teg 6440 gives a greater drop in adhesion.
CHAPTER SEVEN

CONCLUSIONS
7. Conclusions

The results have shown that many factors are involved in understanding the adhesion that takes place in dye diffusion thermal transfer printing. The initial experiments were designed to distinguish which factors were important in the adhesion under unusual joint forming conditions of high temperature and short time. Those results showed that there was no simple answer to the problem.

Initial indications were that $T_g$ played an important role. Low $T_g$ materials have been seen to adhere strongly whilst high $T_g$ samples give low adhesion at low power and moderate peel at higher power, where the sample is beginning to flow. The flow is important in achieving a good contact between the samples. It can therefore be seen that this contact is an important factor. Possible mechanical interlocking may occur once flow and wetting have been established. Diffusion of polymers across the interface at these short time scales is unlikely, generally high temperatures and pressures have to be involved for considerably longer periods of time.

The surface energies and thermodynamic works of adhesion do not correlate well with peel strength. This indicates that much more complex interactions are occurring at the interface rather than simple wetting / dewetting. The peel mechanics at the interface during testing would overwhelm the small contributions from adsorption of the polymer films.

The migration of small molecules has been shown to be an important factor. The effects of the small molecules show the importance of weak boundary layers. This would be due to the oligomers and additives in the
sample migrating to the surface to produce a weak boundary layer at the interface and offers the possibility of controlling the adhesion or release properties of various models.

Using a combination of XPS and AFM it has been possible to gain some information about the amount of additives that migrate to the surface. This unique combination of techniques has shown that a considerable percentage of the material is available at the surface to act as a weak boundary layer. This was only possible by combining the compositional and morphological information respectively given by each technique. Either technique alone gives an incomplete description. AFM gives no information on depth profiling and XPS would only give a total coverage of additive, neglecting the small molecules in the ribbons.

The amount of small molecules at the surface has shown that there is probably an autolayering effect occurring during the production of the films. The thicker films for the higher molecular weight tegomers have shown that a simple migration from a solid polymer film is not responsible for the small molecules at the surface. The autolayering argument is supported by the work done on the AFM. The presence of the ribbons is evidence of a solvent evaporation phenomenon. Coupled with the XPS data, showing that there is also a thin coating over the entire film, indicates autolayering has occurred.

The dye work has shown that the dyes have been diffusing into the substrates up to a depth of several microns. These calculations are possible because of the depth profiling obtainable with the FTIR-ATR attachment. The small effect on the peel strengths by the dyes indicates that they are
simply involved in a diffusion process and do not seem to contribute to either a weak boundary layer or to a plasticisation effect. The XPS analysis has been used to show the movement of the dyes across the interface and in determining partition coefficients between the different polymers.

The combination of the small molecules and the dyes has shown that the dye molecules still move across the interface and are unaffected in the whole by the presence of the small molecules. The small molecules are similarly unaffected by the dyes and still produce a weak boundary layer.

The small molecules achieve release without affecting physical properties, i.e. $T_g$. Therefore the incorporation of low levels of autolayering additives in the dye sheet seems to be a viable approach to reducing adhesion during the printing process.
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Lectures Attended

RSC Lectures

“Cascade 1,3-Dipolar Cycloadditions. From Lapworth to Vitamin B₆ to Latent Fingerprints - a colourful Connection.”
Professor R. Grigg · University of Leeds
10th January 1995

“Policing Rivers”
Speaker from the National Rivers Authority
7th February 1995

“Renewable Energy”
Dr. D. Elliot · The Open University
9th May 1995

Departmental Lectures

Autumn Term 1994

Course of postgraduate lectures every Wednesday for ten weeks.

Spring Term 1995

Electrochemistry · Dr. R. J. Mortimer
Spectroscopy · Professor F. Wilkinson
Surface Analysis · Dr. I. Sutherland
Conferences

SPM User Meeting
Burleigh Court - Loughborough University of Technology
31st Jan 1995

Macrogoup
Fifth Family Meeting of the Macro Group
Loughborough University of Technology
19-21st Apr 1995

UK SPM User Group Meeting in association with the Royal Microscopy Society
The University of Nottingham
24-25 Apr 1995

Posters presented at

Twentieth Annual “Anniversary” meeting of the Adhesion Society,
Hilton Head Island, South Carolina, Feb. 23-26 1997

International Conference on Adhesion and Surface Analysis,
Loughborough University, April 16-18 1996.