Factors affecting adhesion to polyolefins

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Factors Affecting Adhesion

to Polyolefins

by

Denise Katrina Hall

Supervisors: Drs I Sutherland, DM Brewis and RJ Heath

A Doctoral Thesis

Submitted in partial fulfilment of the requirements for the award of Doctor of Philosophy of the Loughborough University of Technology

July 1994

Department of Chemistry

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To Martin and my parents for their love, support and encouragement
Originality

All the work presented in this thesis has been carried out by the author except where acknowledged and has not previously been presented for a degree at this University or any other institution.
Factors affecting the adhesion of paint to polyolefins have been studied. These include solvent pretreatment, types of primer and their method of interaction, flame treatment and the addition of a surface migratory additive to the polyolefin. Surface analysis techniques X-ray photoelectron spectroscopy (XPS), attenuated total reflection infra-red spectroscopy (FTIR-ATR) and contact angle measurements were used along with electron microscopy, diffusion measurements and a lap shear test. Solvent treatments were found to affect the topography of surface, as determined by atomic force microscopy, this causes a reduction in the receding contact angle of water indicating a reduced tendency for the coating to dewet. This gives a greater joint strength. In the case of chlorinated polyolefin primers it has been shown that chain entanglement at the polymer/primer interface is an important factor determining the joint strength and can account for up to 50% of the strength in the systems studied. Chemical interaction between the polyolefin and the paint produced after flame treatment of the polyolefin improves adhesion. Factors determining migration of additives to the polymer surface have been studied. Surface migratory material has been identified but formation of weak boundary layers can lead to little or no improvement in adhesion properties. Further work is needed in this area.
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Conclusions

References
This study concerns the application of paints and primers to polyolefins. The surfaces of polyolefins are unreceptive to surface coatings due to their chemical inertness and lack of functionality. The absence of polarity gives a low surface energy and therefore poor wettability for polar coatings. These difficulties have to be overcome for polyolefins to be more widely used.

Pretreatments of the polyolefin surface are used so that ink and other coatings can be applied. Surface pretreatments alter the chemistry of the surface usually by oxidation, which improves the wettability of the surface. Pretreatments increase the polarity of the surface and the surface energy but must not effect the bulk properties of the polymer. The pretreatments include corona discharge, plasma treatment, flame treatment and chromic acid etching.

Primers offer an alternative means of achieving improved adhesion to polyolefins. A primer is normally a polymeric coating which provides a bridge between the substrate and the coating eg. paint. Primers are generally non-polar/polar in nature. This is to provide compatibility with both the paint, which is usually polar, and the non-polar polyolefin. When using a primer no other method of pretreatment is needed. Unlike other pretreatments, eg. flame treatment, there is no time limit for the application of paint after priming.

Some of the surface treatments such as flame or corona are well established and effective methods but involve an additional process step in manufacture. Incorporation of low levels of migrating additives into the bulk polymer was investigated as a possible way of eliminating this additional step.

In this project various approaches to improving adhesion at polyolefin surfaces have been compared. These include solvent
treatment, surface oxidation, the use of primers and the incorporation of migrating polymer additives.

Adhesion has been measured using a lap shear test. A variety of spectroscopic and microscopic methods have been used to characterise the polymer surfaces and determine the locus of failure. The aim of the work has been to determine the factors affecting adhesion and in particular to evaluate how surface properties may be changed to promote adhesion to polar surface coatings. The changes in surface chemistry have been related to specific interactions of adhesion.
Chapter 2

THEORY
2.1 Adhesion

2.1.1 Theory of Adhesion

2.1.1.1 Introduction

An adhesive may be defined as a material which when applied to the surfaces of materials will join them together so that they resist separation. It should have the ability to join dissimilar materials. Adhesive is a general term and includes cements, glues, primers and pastes. The nature of the forces involved is well understood but the theoretical understanding of their contribution to joint strength lags behind the applied knowledge of the adhesives and primers. The reasons why an adhesive works are complicated by the number of factors involved. Surface chemistry and physics, rheology, polymer chemistry and mechanical properties are all needed to understand adhesion.

2.1.1.2 Interfacial Aspects

It has been accepted for many years that intimate molecular contact is a necessary, though not always sufficient, requirement for developing strong adhesive joints. Intermolecular forces are short range and hence the contact must be at the molecular level. An adhesive ideally needs to be able to spread over the solid surface and displace air and other contaminants that may be present at the surface. An adhesive which conforms to these conditions must:

1) When liquid have a zero or near zero contact angle on the solid.
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 that will dispel any trapped air.

To test the ability of a given adhesive/solid combination to
meet these criteria, it is necessary to consider wetting equilibria, ascertain values of surface energy for both adhesive and solid, examine the kinetics of wetting and consider the details of the bonding operation.

Wetting may be described with reference to a liquid drop resting on a solid surface, see figure 2.1.

![Diagram of a sessile drop](image)

**Figure 2.1.** A Sessile Drop Resting on a Solid Surface.

The energies at the three phase contact point were shown to be related by Young². Young's equation states

\[
\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos \theta
\]

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

\( \gamma_{sl} \) - interfacial free energy of the solid/liquid interface

\( \gamma_{lv} \) - specific surface excess free energy of liquid in equilibrium with the vapour

\( \theta \) - contact angle

\( \gamma_{sv} \) represents the surface free energy of the solid substrate
resulting from the adsorption of the vapour from the liquid. It is usually lower than the surface free energy of the solid in vacuum, $\gamma_s$. This reduction in the surface free energy has been defined by the equilibrium spreading pressure $\Pi_s$ such that

$$\Pi_s = \gamma_s - \gamma_{sv}$$  \hspace{1cm} 2.2
	herefore equation 2.1 may be written as

$$\gamma_s = \gamma_{sl} + \gamma_{lv}\cos\theta + \pi_s$$  \hspace{1cm} 2.3

When $\theta > 90^\circ$ the liquid is non-spreading but when $\theta = 0^\circ$ the liquid wets the solid completely and spontaneously spreads across the surface. Thus for spontaneous spreading to occur

$$\gamma_s \geq \gamma_{sl} + \gamma_{lv} + \pi_s$$  \hspace{1cm} 2.4

For low surface free energy materials $\pi_s$ is usually small and may be neglected therefore

$$\gamma_{sv} \geq \gamma_{sl} + \gamma_{lv}$$  \hspace{1cm} 2.5

It is possible to force a liquid to wet a solid surface completely when $\theta > 0^\circ$ but this requires the application of pressure to spread the liquid. The methods of measurement of the contact angle will be discussed later.

Wenzel$^3$ has shown that surface roughness may change the apparent contact angle, hence the topography of the substrate surface
affects the wetting process. If on a smooth surface $\theta$ is less than $90^\circ$ the result of roughening the surface is to decrease $\theta$ and make the surface more wettable. A liquid can also run along pores and scratches on the surface by capillary action.

When forced application of the liquid is employed it is usually dewetting which is more important. This is the liquid retracting itself back over the surface because liquid/liquid interactions are energetically more favourable than solid/liquid interactions. To obtain information on whether dewetting will occur the receding contact angle can be used. Roughness can also affect the receding angle, the greater the degree of roughness the less the dewetting.

Normally for spontaneous wetting to occur the liquid must have a lower surface energy than the substrate. This will be a liquid with a zero or low contact angle. If the surface of the substrate has a higher energy it will interact more strongly with the liquid.

Air may be entrapped between the substrate and the liquid adhesive. This air may be eliminated if the joint is bonded, for instance, in an autoclave. Air may also be displaced by an adhesive needing a heat cure. If air voids are not eliminated they may produce stress concentrations which reduce the strength of the joint.

2.1.2 Mechanisms of Adhesion

2.1.2.1 Introduction

Once interfacial contact has been obtained intermolecular forces may act across the interface. The nature and magnitude of these forces are extremely important. They must be sufficiently strong and stable to ensure the interface does not act as the weak link in the joint. These intermolecular forces are frequently the main mechanism of adhesion. This is known as the adsorption
theory of adhesion. It is, however, only one of four proposed mechanisms of adhesion which are:

1) Mechanical interlocking
2) Diffusion theory
3) Electronic theory
4) Adsorption theory.

The universal mechanism of adhesion has been sought for many years until recently when it has become accepted that whilst adsorption has the widest applicability each of the other mechanisms may be appropriate in certain circumstances. At times more than one factor may be contributing to adhesion.

2.1.2.2 Mechanical Interlocking

This theory proposes that mechanical interlocking of the adhesive into the irregularities of the substrate surface is the major source of adhesion. One example where mechanical interlocking is important is in the application of polymers to textiles. With textiles the fibre ends are required to interlock with the polymer. If no ends are present, i.e. a continuously wound fibre, the strength is reduced.

The attainment of good adhesion between two smooth surfaces indicates that factors other than mechanical interlocking are involved in adhesion. Tabor et al. studied the adhesion between two perfectly smooth mica surfaces, demonstrated that adhesion may be attained with smooth surfaces.

There is much work in the literature which demonstrates that increasing the surface roughness of the substrate may increase the mechanical strength of the joint. These observations indicate a contribution from mechanical interlocking but other causes may also be involved. Chemical pretreatments have been used when bonding metal to plastics. Some workers have argued that adhesion is due to the surface topography while others have emphasized the role of increased surface oxidation.
It has been observed\textsuperscript{13} that some form of mechanical abrasion will increase the measured joint strength, especially with metals. It can be seen on micrographs though that while roughening does occur cavities suitable for mechanical interlocking are not produced. Mechanical abrasion can ensure that substrates are free from release agents or oil and grease and so remove a weak boundary layer and even change surface chemistry. It has been previously shown that surface roughening may aid the wetting of the adhesive.

To summarise, in certain circumstances mechanical interlocking may contribute to the intrinsic adhesion mechanisms. Often however increases in joint strength are also attributable to other factors such as removal of weak surface layers or improved interfacial contact.

2.1.2.3 Diffusion Theory

Voyutskii\textsuperscript{14,15,16} suggested that adhesion of polymers to themselves and to each other is due to the mutual diffusion of the polymer molecules across the interface. This requires that the macromolecules or chain segments of the polymer possess sufficient mobility and are mutually soluble, i.e. have similar solubility parameters. The solubility parameter is an index of compatibility of two components.

Experimental evidence to support this proposal include the effects of contact time, temperature, polymer type, molecular weight and viscosity on the joint strength. He argues that the type of dependence of joint strength on some of these parameters is similar to that expected for a diffusion process and therefore adhesion is a result of diffusion. Vasenin\textsuperscript{7,18,19} developed qualitative models for the diffusion theory from Fick's laws. Vasenin's theory predicts that with a diffusion coefficient of $10^{-14}\text{cm}^2\text{s}^{-1}$ it takes about 100 hours for segments of one polybutylene sheet to penetrate a depth of 10\textmu m into another sheet. Both Voyutskii and Vasenin point out that a much smaller
penetration can still result in high joint strengths. Jud et al.\textsuperscript{20} have reached similar conclusions and state that an important factor may be to ensure that the degree of interpenetration is sufficient for polymer segments to establish an interpenetrating polymer network. Campion\textsuperscript{21,22} criticised Vasenin's model on the grounds that it does not account for changes in molecular shapes and structures. He states that hole or free volume formation may occur in certain polymer types and this provides a means for more rapid diffusion.

Little direct experimental evidence exists for interdiffusion in compatible polymers. Radiotracer studies\textsuperscript{23} have shown that macromolecular diffusion occurs. Other work\textsuperscript{24} carried out has indicated that with compatible, non-polar polymers the interphase region may be about 10\textmu m deep but where solubility parameters differ no interdiffusion zone could be detected. Stamm and coworkers\textsuperscript{25} have investigated polymer diffusion by X-ray and neutron reflectometry and claim to see diffusion over nanometre levels.

Anand et al.\textsuperscript{26} have criticised the dependence of the measured joint strength on parameters such as contact time and molecular weight. They contend that this dependence may be readily explained by their effect on the kinetics of the wetting and also on the degree of the interfacial contact. Anand also believes that although radiotracer evidence shows that interdiffusion is occurring, the contribution is minimal compared to that from the formation of interfacial secondary bonds.

Interdiffusion plays an important role in plastics welding\textsuperscript{27,28,29} when the plastics have similar solubility parameters. The polymer chains are given sufficient mobility to interdiffuse by either the application of heat or by applying a solvent. The two surfaces are then held together under pressure. The polymers used for this are limited to amorphous thermoplastics because the polymer chain movement cannot be restricted by crosslinks or by a high degree of crystallinity.
2.1.2.4 Electronic Theory

This theory, due to Deryaguin et al.\textsuperscript{30,31}, states that if the adhesive and the substrate have different electronic band structures there is likely to be some electron transfer on contact to balance Fermi levels. This will result in the formation of a double layer of electrical charge at the interface. It is suggested that the electrostatic forces arising from such contact contributes significantly to intrinsic adhesion. This last statement has produced a lot of criticism, as many workers\textsuperscript{32,33} believe that the electric double layer does not affect adhesion. They also suggest that any electrical phenomena observed during fracture arise from the failure event rather than the adhesion between materials.

2.1.2.5 Adsorption Theory

This is generally the most accepted theory for adhesion. It proposes that provided there is sufficient intimate molecular contact achieved at the interface, the materials will adhere because of the interatomic and intermolecular forces which are established between the atoms and molecules in the surface layers of the adhesive and the substrate. There are two types of forces:

1) secondary bonds, most commonly van der Waals' forces but hydrogen bonds may also be included in this category
2) primary bonds, which are chemical bonds across the interface and involve ionic, covalent and metallic bonding.

Huntsberger\textsuperscript{34,35} has calculated the attractive force between two phases due solely to dispersion forces from a knowledge of the surface free energies. He showed that the attractive force would result in a joint strength of approximately 100MPa. This is considerably higher than the experimental strength of most adhesive joints. The discrepancy between theoretical and
experimental joint strength is due to air voids, cracks or other defects which act as stress raisers causing the joint to rupture much below the theoretical value.

Much work\textsuperscript{36,37} has been published to suggest that secondary forces are the mechanism in many joints. Hydrogen bonds may be established at the interface and these are stronger than dispersion forces. Formation of hydrogen bonds across the interface enhances the adhesion, this has been observed by many workers.

In the literature many people have hypothesised that it is possible to correlate the measured strengths of joints with the thermodynamic work of adhesion, $W_A$, where $W_A$ is the reversible work done in the separation of an interface. Similar considerations apply for solid/liquid and liquid/liquid interfaces. Some authors have confirmed\textsuperscript{38,39} a correlation but others have found none\textsuperscript{40,41}. The main cause of disagreement is the test methods commonly employed which yield results that depend on many physical parameters. There is difficulty in separating contributions made by intrinsic adhesion forces from viscoelastic and plastic energy losses in the adhesive and substrate. The correlation proposed would only be possible when the locus of failure is entirely interfacial.

Various types of primary bonds have been reported to be formed at the interface. The type of bond depends upon the chemistry of the interface. Klein et al.\textsuperscript{42} found infra-red evidence of covalent primary bonds between a polyurethane adhesive and an epoxy based primer. Covalent bonds can have some ionic character due to different electronegativity of the atoms involved and this can increase joint strength. Interfacial primary bonds which are ionic in character have been reported\textsuperscript{43,44} between polymers such as polyacrylic acid and metal oxides.

To conclude, evidence in the literature indicates that for many adhesive/substrate interfaces the main mechanism of adhesion is by adsorption. Other methods may be responsible for adhesion or
contribute to adhesion in some cases. There may be some advantages in bonding to a rough surface to improve interfacial contact. The chemistry, topography and morphology of the substrate's surface is important in ensuring intimate interfacial contact is achieved and strong and stable intrinsic adhesion forces are made across the interface.

2.1.3 Adhesion Tests

All tests to determine the strength of a joint are destructive. For butt tests the force needed to pull the sample apart depends on area but for a peel test this is not so. In peel tests the force needed is proportional to the width of the peel strip.

When an adhesion test is carried out the adhesive is usually applied in the form of a fluid or semi-fluid and then allowed to solidify. The adhesives used are generally thermosetting polymers eg. epoxides, polyurethanes or acrylics and hot melts or pressure sensitive systems. The joint is usually cured at elevated temperature and sometimes pressure is applied to the joint. The strength of the joint increases with the length of time under these conditions up to the point of cure. All tests must be carried out under the same conditions if the results are going to be compared or the conditions must be extreme enough not to affect the joint if a small variation in the conditions occurs.

Generally the strength of a joint depends on the testing rate, temperature and joint geometry. In an adhesion test these variables may influence, to a certain extent, the rheological behaviour of the components of the joint, the stress distribution and the interaction forces at an interface. It is important that as well as recording the value of the force required to break a joint, the locus of failure of the joint is known. Whether the joint fails interfacially or in a component may depend on testing variables.
There are various types of test used. The common tests are butt tests, lap shear tests and peel tests (see figure 2.2). The butt and lap shear tests are similar. The butt test is frequently used because of the simplicity and the ease of positioning the matching surfaces. The positioning with a butt test can slip unless locating pins or clamp fixtures are used.

For a lap shear test the accuracy of matching the two sides must be better than that for a butt test or false results can be obtained. Peel tests can be done at a variety of angles. The easiest type is the T-peel, this test must have two flexible components. Other peel tests are those done at an angle to the inflexible component. Occasionally this may cause problems if the flexible component buckles. With a peel test care must be taken that the angle of peel is the same for each test if reproducible results are required.

Figure 2.2. Adhesion Tests in Common Use a) Butt b) Lap shear c) T-peel d) 90° peel.
2.1.4 Primers

Primers are sometimes used as an alternative to surface modification. A primer generally acts as a bridge between the substrate and a top coat and so must have good adhesion to both. Primers can be used for a variety of systems and reasons. They often act as the link between a non-polar substrate and a polar top coat. They can be used to prevent capillary adsorption of an adhesive into highly porous brick or concrete. Primers are also used with metal or wood.

Polyolefins are not amenable to adhesives and surface coatings because of their low surface free energy and unreactivity. Chlorinated polyolefins have been developed for use with polyolefins. Toyo Kasei Kogyo\textsuperscript{45} and Eastman\textsuperscript{46,47} have developed a range of chlorinated polypropylenes and also modified chlorinated polypropylene primers which improve adhesion of polyolefins to other substrates.

Norris and co-workers\textsuperscript{48} studied many different chlorinated polypropylenes on polypropylene by testing them using lap shear tests. He compared their results with other surface treatments. The results were compared by adhesion tests with no surface analysis carried out. However no conclusions were drawn regarding mechanisms for adhesion in this case.
2.2 Contact Angle

2.2.1 Introduction

The surface energy of a polymer cannot normally be directly measured, so indirect methods have been used. In one method an extrapolation is made from the molten polymer and then using the temperature and molecular weight dependence of the surface tension the surface free energy is estimated. This method can give good estimates for pure homopolymers but problems can occur if additives are in the polymer or it has been surface modified. A second method involves using the contact angle of liquids on solid polymer surfaces. A series of equations has been proposed which relate the angle the liquid makes with the polymer to the surface free energy of the solid.

2.2.2 Contact Angle Measurement

When a drop of liquid is placed on a solid surface the extent to which the drop spreads will depend upon the interaction between the solid and the liquid. These interactions are divided into polar and dispersion components. Polar interactions include hydrogen bonds, Keesom forces, which are interactions between two permanent dipoles and Debye forces which arise from interaction between a permanent dipole and an induced dipole moment in a neighbouring molecule. The dispersion interactions are London dispersion forces which arise from fluctuations in electron density in molecules. The contact angle is measured at the three phase boundary, see figure 2.1. is the specific surface excess free energy but is often referred to as surface free energy or surface energy. , the free energy of the liquid/vapour interface, , the free energy of the solid/vapour interface and , the free energy of the solid/liquid interface. Young put forward a relationship for these interactions with the contact angle. His suggestion was written in equation form and applies to flat homogeneous surfaces.
\[ \gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos \theta \]  \hspace{1cm} \text{(2.6)}

\[ \pi = \gamma_s - \gamma_{sv} \]  \hspace{1cm} \text{(2.7)}

\[ \gamma_s \] - the surface free energy of the solid in vacuum

The other basic equation which relates these interactions was suggested by Dupré. He used a quantity called the thermodynamic work of adhesion, \( W_a \), this is the reversible work required to pull apart the liquid/solid interface and create two new surfaces.

\[ W_a = \gamma_{lv} + \gamma_s - \gamma_{sl} \]  \hspace{1cm} \text{(2.8)}

Equations 2.6, 2.7 and 2.8 are combined to give the Young-Dupré equation

\[ W_a = \gamma_{lv}(1 + \cos \theta) + \pi \]  \hspace{1cm} \text{(2.9)}

For low surface energy materials like polymers, \( \pi \) is small and is often neglected, so equations 2.8 and 2.9 become

\[ W_a = \gamma_{lv} + \gamma_{sv} - \gamma_{sl} \]  \hspace{1cm} \text{(2.10)}

and
The contact angle, $\theta$ and $\gamma_{LV}$ can easily be measured. From equation 2.11 $W_A$ can be calculated for any liquid.

Contact angle measurements are highly sensitive to the outermost chemical characteristics of the polymer. A contact angle can be measured to a reproducibility of about $\pm 2^\circ$. There are many different methods for measuring contact angles and these have been reviewed by Neuman and Good. Contact angles can be measured on solids in different forms, e.g. flat pieces and fibres. The flat piece form of polymer is usually measured using a sessile drop and a microscope.

Thermodynamics suggest that on an ideal flat surface there can only be one contact angle, known as the equilibrium angle $\theta_e$, but this is not found to be the case in practice. Young’s equation is for a smooth, homogeneous, rigid, isotropic solid surface. There are generally considered to be three types of contact angle, advancing, 'equilibrium' and receding. The advancing angle is the maximum angle a liquid can make on a solid and the receding angle is the minimum. An angle intermediate between these two and measured after allowing a droplet to fall onto a solid is often mistakenly called the equilibrium value. For most polymer surfaces the equilibrium angle does not exist.

2.2.3 Effect of Roughness

Contact angles can be affected by surface roughness. The effect of surface roughness was studied by Wenzel, he proposed that a roughness factor must be included in the Young equation. The modified Young’s equation becomes

$$W_A = \gamma_{LV} (1 + \cos \theta)$$
where \( r \) - roughness factor
\[ \theta_A \] - apparent equilibrium contact angle

and

\[ r = \frac{\cos \theta_A}{\cos \theta} \]

The roughness will affect the absolute value of contact angle, as \( r \) is always greater than one when \( \theta \) is less than 90°, \( \theta_A \) will be less than \( \theta \). Also when \( \theta \) is greater than 90°, \( \theta_A \) will be greater than \( \theta \).

2.2.4 Contact Angle Hysteresis

The difference between the advancing and the receding angle is known as the contact angle hysteresis.

\[ H = \theta_{adv} - \theta_{rec} \]

Contact angle hysteresis occurs when the conditions for the Young equation are not fulfilled. The two main causes of hysteresis are

1) surface roughness
2) surface heterogeneity.

Johnson and Dettre\textsuperscript{58,59} discussed how roughness affects the hysteresis. A series of energy barriers, caused by the ridges and troughs on the surface, must be overcome for a liquid to spread across the surface. Roughness needs to be in excess of 1\( \mu \)m to begin to affect hysteresis.

Cassie and Baxter\textsuperscript{60} investigated the effect of chemical heterogeneity on the contact angle hysteresis. An increase in heterogeneity usually causes a decrease in the receding angle.
They suggested that the advancing angle was more representative of the least wettable parts of a heterogeneous surface and the receding angle the most wettable.

2.2.5 Interpretation of Contact Angles

Various methods have been proposed for the interpretation of contact angle measurements in relation to the surface free energy and the work of adhesion. These will be briefly reviewed in historical order.

2.2.5.1 Zisman’s Plots

The first theory to emerge was Zisman’s critical surface tension of wetting. The critical surface tension, \( \gamma_c \), is found by plotting a graph of \( \cos \theta \) against \( \gamma_{LV} \) for an homologous series of liquids. \( \gamma_c \) is taken at \( \cos \theta = 1 \). \( \gamma_c \) can only be used as an empirical value for estimating wettability. The values of \( \gamma_c \) are different for different series of liquids, so the values cannot be used as definitive values. \( \gamma_c \) does not equal \( \gamma_{SV} \). At \( \cos \theta = 1 \)

\[
\gamma_c = \gamma_{SV} - \gamma_{SL}
\]

for \( \gamma_c = \gamma_{SV} \), \( \gamma_{SL} \) must be zero but this is not the case as \( \gamma_{SL} \) is positive. Consequently this method cannot be used for calculating surface free energy.

2.2.5.2 Good/Girifalco Approach

Good and Girifalco proposed a geometric mean model for the interaction across an interface. The interaction across a solid/liquid interface is between the liquid molecules and polymer segments. The Young equation becomes
\[ \gamma_{SL} = \gamma_{SV} + \gamma_{LV} - 2 \phi (\gamma_{SL})^{0.5} \]  \hspace{1cm} 2.16

and the work of adhesion becomes

\[ W_a = 2 \phi (\gamma_{SL})^{0.5} \]  \hspace{1cm} 2.17

\( \phi \) is a constant for a given solid/liquid pair. It is an interaction parameter which can be estimated from the molecular properties of both phases or it can be obtained experimentally for each solid/liquid pair.

### 2.2.5.3 Owens/Wendt Approach

Fowkes\(^{54,66,67}\) suggested that a non-polar solid cannot interact with a polar liquid through a permanent dipole. He suggested that the geometric mean term for the molecular interactions could be split into two components for polar and dispersion interactions. Fowkes derived an equation, from the Young equation, in terms of dispersion forces only. Owens and Wendt\(^{68,69}\) expanded the equation to include polar forces.

\[ \gamma_{SL} = \gamma_{SV} + \gamma_{LV} - 2 (\gamma_{SL}^{2P})^{0.5} - 2 (\gamma_{SL}^{3P})^{0.5} \]  \hspace{1cm} 2.18

and the work of adhesion

\[ W_a = 2 (\gamma_{SL}^{2P})^{0.5} + 2 (\gamma_{SL}^{3P})^{0.5} \]  \hspace{1cm} 2.19
2.2.5.4 Acid/Base Interactions

More recent work by Fowkes\textsuperscript{70,71,72} suggested that the dipole-dipole interactions should be replaced by an acid-base term.

\[ W_A = W^{AB} + W^d \]  \hspace{1cm} 2.20

The work of adhesion due to an acid-base pair, \( W^{AB} \), is related to the enthalpy of neutralisation. So equation 2.19 can be written as

\[ W_A = 2 \left( \gamma_L^d \right)^{0.5} f(\Delta H_{\text{neutral}}) \]  \hspace{1cm} 2.21

The measured enthalpies are those which are due to a Lewis acid-base pair. Although the above approach is perhaps more rigorous than that of Owens and Wendt, appropriate values of the energy of acid-base interactions are not always available\textsuperscript{73}. 

2.3 X-ray Photoelectron Spectroscopy (XPS)

2.3.1 Basic Principles

A sample is placed in a vacuum chamber and its surface is excited by primary radiation. The electron emission resulting from this excitation is detected. Soft X-rays are used as the primary radiation. Photoemission is from the core electrons of the atoms present in the sample. The electrons collected are passed through an energy analyser and then to the detector where the kinetic energy is measured. The kinetic energy is related to the binding energy of the core electrons. This enables identification of the atoms present at the surface. Quantitative analysis can be obtained from the relative intensities of the peaks. An important feature of XPS is that it is a comparatively non-destructive technique and can be used to study polymer surfaces.

2.3.2 Instrumentation

The basic set up of an XPS machine is shown in figure 2.3.

![Figure 2.3. XPS Instrumentation.](image)
The analysis is run in a vacuum of less than $10^{-7}$ mbar. The most common X-rays used for XPS are Al Kα (1486 eV) and Mg Kα (1254 eV). These are produced by high energy electrons (10-15 eV) bombarding an appropriate target. The characteristic X-ray lines are sufficiently narrow in width so that a monochromator is not normally necessary. The X-rays irradiate the sample over an area of several square millimetres or more. The electrons emitted from the sample pass through an energy analyser. There are two main types of analyser, the electrostatic cylindrical mirror and the hemispherical sector analyser. The type used in this work was the latter. The electrons then pass to an electron multiplier.

2.3.3 Surface Information

The process of the emission of an electron from an atom is shown in figure 2.4.

![Figure 2.4. XPS Emission Process.](image)

The relationship between kinetic energy and binding energy is shown in the equation.
The binding energy of a core electron is characteristic of the element from which it was emitted. Therefore it is possible to identify the elements present in the sample from the kinetic energy of their core electrons. The core level binding energies of the 1s core electrons increase as a function of atomic number. For heavier atoms the X-rays used are not sufficiently energetic to induce emission from the 1s level. Emission is then observed from the less strongly bound electrons in the core eg. 2s and 2p electrons.

The binding energy of a core level electron depends principally on the charge of the nucleus. The binding energy is also affected by the chemical bonding of the atom. The changes to the binding energy induced by this are small, typically <10eV, but measurable. Changes in binding energy resulting from chemical bonding are known as a chemical shift.

There are two types of spectrum that can be produced, a broad scan and a narrow scan (see figure 2.5). A broad scan is over a wide energy range and will detect all elements except hydrogen. The assignment of peaks from this spectrum is relatively simple. The concentration of elements at the surface can also be determined from this spectrum. A narrow scan is over a small energy range. This type of spectrum is run under conditions that will give maximum energy resolution. The chemistry of an element can be determined from measurement of the chemical shifts in a narrow scan spectrum. This is especially the case with the carbon peak of a polymer as this has been well documented in the literature. In organic compounds
Figure 2.5. Examples of a broad scan XPS Spectrum (top) of SO₂ Flame Treated PP and a narrow scan XPS spectrum (bottom) of Trifluoroethanol derivatised Polyacrylic acid.
a chemical shift of the binding energy is most pronounced when the carbon is bonded to an electronegative element eg. oxygen, nitrogen or a halogen. Chemical shifts arise from the fact that an electron being ejected from an inner atomic shell is affected by the chemical environment as it leaves the molecule. The more highly oxidised a given species the lower electron density in the valence shell and so the greater the energy needed to remove a core electron. Chemical shifts can be described in terms of a simple effective charge model\textsuperscript{74}.

\[ E-E_0 = \Delta E = -\frac{\varepsilon_0^2 q_i q_j}{4\pi^2 r_{i,j}} \sum_{i,j} \frac{q_j e^2}{4\pi^2 r_{i,j}} \]

where
- \( E-E_0 \) - chemical shift of the binding energy
- \( q_i \) - net charge on the atom in question
- \( r \) - atomic radius of the valence shell
- \( q_j \) - net charge on each of the other atoms
- \( r_{i,j} \) - the distance between the given atom and each of the other atoms
- \( e \) - electron charge
- \( \varepsilon_0 \) - permittivity of free space

This equation is only an approximation as it neglects relaxation effects but works reasonably well for most systems.

### 2.3.4 Surface Sensitivity

XPS is a surface sensitive technique because only electrons from the outermost layers have enough energy to escape. Electrons from the bulk lose energy before they manage to escape. Electrons from the bulk have a higher probability of undergoing inelastic collisions with neighbouring bound electrons. A measure of the distance an electron may expect to travel in a solid before losing some kinetic energy is given by the inelastic mean free path, IMFP\textsuperscript{75} or \( \lambda \). The IMFP varies with the kinetic energy of an electron as shown in figure 2.6.
A minimum occurs in the curve for two reasons. The IMFP rises at low kinetic energy because low energy electrons have few processes by which to lose energy. The IMFP rises at higher kinetic energy because the cross section decreases, i.e. the probability of the energy loss processes occurring decreases.

The IMFP\(^7\) can be calculated for organic compounds.

\[ \lambda_d = \frac{49}{E^2} + 0.11E^{0.5} \text{ mg m}^{-2} \] \hspace{1cm} 2.24

and

\[ \lambda_m = \frac{1000\lambda_d}{\rho a} \text{ monolayers} \] \hspace{1cm} 2.25

and

\[ \lambda = \lambda_m a \text{ nm} \] \hspace{1cm} 2.26

\(\lambda\) - Inelastic mean free path
\(E\) - Kinetic energy of electron
\(\rho\) - Density
\(a\) - Monolayer thickness
For C1s electrons excited by Al Kα radiation

\[ E = 1200 \text{ev} \] and \[ \rho = 0.94 \text{gcm}^3 \text{ or } 0.94 \times 10^6 \text{gm}^3 \]
therefore \[ \lambda_A = 3.81 \text{mgm}^2 \text{ or } 3.81 \times 10^6 \text{kgm}^2 \]

so \[ \lambda_A = \frac{1000 \times 3.81 \times 10^6}{0.94 \times 10^6} \]

\[ \therefore \lambda = 4.05 \text{nm} \text{ or } 40\text{Å} \]

\[ 2.3.5 \text{ Quantification} \]

The intensity of photoemission from a homogeneous sample may be written as \(^\text{76}\),

\[ I_A = N_A \sigma_A L_A(\gamma) \lambda_s(E_A) \chi T(E_p, E_A, \omega) D(E_p) \] \quad 2.27

\( I_A \) - Intensity of peak A
\( N_A \) - Number of atoms of type A
\( \sigma_A \) - Photoelectron cross section for a specific orbital
\( L_A(\gamma) \) - Angular asymmetry parameter
\( \lambda_s(E_A) \) - Inelastic mean free path
\( \chi \) - X-ray flux
\( T(E_p, E_A, \omega) \) - Transmission \( E_p \) - Pass energy
\( E_A \) - Kinetic energy of electron
\( \omega \) - Slit width aperture at the front of analyser
\( D(E_p) \) - Detector efficiency

\[ N_A = \frac{I_A}{\sigma_A L_A(\gamma) \lambda_s(E_A) \chi T(E_p, E_A, \omega) D(E_p)} \]

\[ \frac{I_A}{S_A} \] \quad 2.28

where \( S_A \) is known as the relative sensitivity factor

\( S_A \) may be estimated using various semi empirical equations and calculated values for transmission etc. Alternatively \( S_A \) may be
determined by measurements of standard materials. There are advantages and disadvantages to both methods. Using calculated values requires accurate estimation of the parameters involved some of which are instrument specific. Using standards requires availability of well characterised surfaces this is experimentally difficult.

2.3.6 Flame Treatment

XPS has been widely used in adhesion studies. One area of work particularly relevant to this study is flame treatment. It can be used for treating films but is usually used for thicker articles such as plastic bottles. The treatment involves a plastic article passing through a ribbon burner consisting of a large number of closely spaced gas jets. A mixture of compressed air and a fuel gas is supplied to the burner. Important parameters include air:gas ratio, flame intensity which is the total flow rate, the distance from the flame inner core tip to the surface to be treated and contact time.

Sheng 77 studied flame treatment of PP and found optimum air:gas ratio was found to be ~11:1 which is higher than the stoichiometric ratio required for complete combustion of the fuel gas which was natural gas. Optimum distance from the inner core tip to the polymer surface was found to be 0.5-1.0cm.

The precise chemistry of the flame is not clearly established. Initiation of the flame reaction occurs either by radicals produced by a surface process or in the gas phase. These radicals will then react to give other radicals which will give rise to an oxidised surface. The process is complex and many species are present in the flame.

2.3.7 Derivatisation

Chemical derivatisation is used to identity functional groups
at the surface. The technique uses a chemical reagent which reacts specifically with a particular functional group. The derivative has a unique element, such as fluorine, which can be easily detected and quantified by XPS so indicating the surface concentration of functional groups present. Briggs\textsuperscript{78} has summarised chemical derivatisation reactions.

Solution derivatisation has been extensively studied\textsuperscript{79,80} but there are problems involved with the use of a solution. Solvents may increase the polymer chain mobility at the surface with the chance of reorientation of functional groups. Solvents may also dissolve low molecular weight materials present on the surface.

Vapour phase derivatisation can be used to overcome the solvent problems. Hammond et al.\textsuperscript{81,82} successfully used trifluoroacetic anhydride, TFAA, to derivatise model hydroxyl polymers. Using this method Sheng\textsuperscript{76} found that about 25\% of the oxygen on the flame treated PP was present as hydroxyl groups. The removal by tagging of hydroxyl groups reduces the level of adhesion to polyurethane paint. Hydroxyl groups at the surface are thought to react with the PU paint resulting in chemical bonds which account for the high joint strength.
2.4 Fourier Transform Infra-red - Attenuated Total Reflectance Spectroscopy

2.4.1 Principles of FTIR

The use of FTIR is especially applicable to analysing samples that have low transmission or reflection. This is due to FTIR being more sensitive than dispersive spectrometers. The signal to noise ratio is superior, $10^5:1$ typically. An FTIR spectrometer has three components, 1) a source, 2) a Michelson interferometer and 3) a detector, see figure 2.7.

![Figure 2.7. The Components of an FTIR Spectrometer.](image)

Collimated radiation from a broadband infra-red source, A, is directed into the interferometer and impinges on a beam splitter, B. The beam splitter is usually a very thin piece of germanium and splits the beam into two parts of about equal intensity. One beam of the radiation is transmitted through the beam splitter and is directed onto a fixed mirror, C. The other beam of the radiation reflects off the beam splitter and is directed onto a moving mirror, D. The beams reflect off the two mirrors and recombine at the beam splitter. Constructive or destructive interference occurs depending on the position of the
moving mirror relative to the fixed mirror. The resulting beam then passes through the sample and then to the detector.

With an FTIR a "scan" is a mechanical displacement of the moving mirror and not a selection of an individual frequency, as with a dispersive spectrometer. Movement of the mirror changes the path difference between the two beams in the interferometer. When all frequencies are observed at once the detector sees the signed summation of the individual cosine waves. This type of signal is called an interferogram. All the information of a spectrum is contained in the interferogram, as it is all the frequencies added together. A Fourier transform is performed on the interferogram to convert to the frequency domain.

There are a number of advantages of using an FTIR over a dispersive spectrometer.

1. In an FTIR there is only one moving part, the moving mirror. This should, in theory, mean less mechanical wear and a higher reliability.
2. The Felgett advantage is a multiplex advantage and the detector observes all frequencies at once. As a result FTIR is 4000 times faster than a dispersive spectrometer for the same signal to noise ratio.
3. The Jacquinot advantage is the throughput advantage of having no slits or gratings in the spectrometer. Due to this, small samples with low transmission are able to be analysed.
4. Connes advantage arises because the FTIR spectrometer has an internal frequency calibration which is very accurate. A laser measures the mirror movement and this is related directly to frequency. Time is not spent calibrating the spectrometer as with dispersive spectrometers.

2.4.2. Principles of ATR

ATR is a method which involves the internal reflection of
radiation in a medium. A sample is placed in contact with a prism which is optically denser and the radiation is internally reflected in the prism. A standing wave is established in the denser medium, the prism, and there is an evanescent wave in the rarer medium, the sample. The amplitude of the evanescent wave in the rarer medium decays exponentially with the distance from the boundary with the denser medium. If the sample exhibits absorption the wave transmitting in the sample becomes attenuated. The resulting energy loss is referred to as attenuated total reflection, ATR. The loss of energy gives information of the chemical content of the sample. An ATR system is shown in figure 2.8.

![Figure 2.8. Schematic of Multiple Reflection ATR.](image)

An FTIR-ATR spectrum resembles a transmission spectrum. A problem associated with ATR is that the peaks at high wavenumber are less intense than in a transmission spectrum and are also less intense than the peaks at low wavenumber in the same spectrum. As seen from equation 2.29 the sampling depth increases as wavelength increases. Wavenumber is the inverse of λ so as wavenumber decreases the sampling depth increases. Therefore at lower wavenumber more of the sample is probed and so absorptions are more intense than at the high wavenumber end of the spectrum. Also related to this, especially important in
surface analysis, is that the less the depth penetrated by the wave the weaker the signal. A calculation can be made to calculate the sampling depth $d_p$.

$$d_p = \frac{\lambda}{2 \left[ \sin^2 \theta - \left( \frac{n_n}{n_1} \right)^2 \right]^{0.5}}$$

and where $\theta$ the angle of incidence is

$$\theta = \theta_{IRA} - \sin^{-1} \left[ \frac{\sin (\theta_{IRA} - \theta_{IRR})}{n_1} \right]$$

$\lambda$ - wavelength
$n_n$ - Refractive index of the sample
$n_1$ - Refractive index of the prism
$\theta_{IRA}$ - Angle designated on the scale
$\theta_{IRR}$ - Angle of the prism face

**2.4.3 ATR Studies of Surface Structure Changes**

ATR can be used to study changes in the surface orientation or amorphous/crystalline content. Changes in the amorphous/crystalline content have been studied by Hagemann et al. Different sets of bands can be used to study this in PE. In the 1400-1250 cm$^{-1}$ region these bands are associated with the amorphous fraction of a polymer. An increase in intensity of these peaks is a measure of an increase in the amorphous component in a polymer.

The bands at 735-721 cm$^{-1}$ can also be used. In this region two bands are associated with the crystalline fraction, those at 730 and 722 cm$^{-1}$. These bands are narrower than the band which represents the amorphous fraction at 723 cm$^{-1}$. This band overlaps the 722 cm$^{-1}$ band of the crystalline fraction. By monitoring the changes in shape of the peaks, an indication of any change in
the crystalline/amorphous content can be seen.

Another way of investigating any change in the surface structure is to investigate the surface orientation. This may be done using a polariser at various angles. Many people have reported using polarisers, these include Flournoy\textsuperscript{88,89}, Sung\textsuperscript{90} and Mirabella\textsuperscript{91,92}. These papers show ways of obtaining quantitative information about orientation. This involves acquiring data from the polymer along both its long axis and short axis parallel to the beam. To do this properly requires a turning prism mounting.

If one of these is not available data can be collected with only the long axis parallel to the beam, thus making it qualitative only. In this case the ratio between groups of peaks can be measured to obtain the changes in the ratio on altering the polariser angle. This would indicate surface orientation. After treatment the same peaks were measured and ratioed so an indication of change in surface orientation could be observed.
2.5 Compounding

2.5.1 Introduction

Polymer blends are used to fill gaps in performance of existing polymers. Commercial blends can be developed in a shorter time period by blending existing materials rather than develop novel polymers. It is a growing area in the polymer industry. Polymer blends covers several areas of science from chemistry, thermodynamics and interface science to rheology and processing.

A compatible polymer blend is one that is a mechanically processable blend which resists gross phase segregation. The term miscible is used to describe blends which are homogeneous at molecular level. Partially or nearly miscible blends are homogeneous at some temperature regions but phase separate in others.

Polymer blends can be divided into three basic groups:

1) Miscible blends such as polymethylmethacrylate - polyvinylidene fluoride
2) Partially miscible blends such as polystyrene - polyvinyl methyl ether
3) Immiscible blends such as polyethylene - polymethylmethacrylate.

Immiscible polymer pairs outnumber those in the other two groups. Block copolymers have been used as compatibilizers or emulsifiers to try to make blends more miscible.

2.5.2 Study of Miscibility

Polymer/polymer pairs can be investigated for miscibility by optical, morphological, glass transition temperature, $T_g$ and crystalline melting point, $T_m$ behaviour. These properties have been reviewed by several authors\textsuperscript{26-31}. $T_g$ is the most popular and convenient way of investigating the miscibility of polymer
blends.

Optical clarity is usually an indication that two polymers are miscible though it is not sufficient proof. It can be deceptive if the refractive index of the two components of a blend happen to be similar, if the blend has phase separated into two separate layers or if a two phase structure exists with domains smaller than the wavelength of light. Both optical and electron microscopy are also used in the study of blends. The microscopy is based on interference patterns that will occur depending on the phase difference of the components.

The glass transition, \( T_g \), which is the transition of the amorphous region of a polymer from a glassy state to a rubbery state is characteristic for a polymer. \( T_g \) can be measured by dynamic mechanical or dielectric relaxation methods. If the blend is immiscible both \( T_g \)s are seen, whereas if the blend is miscible only one \( T_g \) is seen which is between the two individual \( T_g \)s. This method has its limitations if the \( T_g \)s are close. If there is a small quantity of one polymer in the blend there may be difficulty in resolving the \( T_g \)s.

Differential scanning calorimetry or differential thermal analysis are also used to analyse miscibility. These can be used to measure depressions in the melting points of crystalline polymers in blends. This can be used to calculate the interaction parameter.

All these methods of measurement give different indications of the extent of miscibility because they examine different properties. They use different amounts of blends but if one of the components is in low concentrations it is difficult to resolve any information on the miscibility or otherwise of the blend.
2.6 Diffusion

2.6.1 Introduction

It is important to understand polymer/solvent interactions because solvents are commonly used to deliver surface coatings. Different solvents will affect a polymer to a different extent by swelling and diffusing into the polymer at different rates. Swelling the polymer substrate could effect chain entanglement at the interface, orientation of polymer chains and surface topography. Weight gain can be monitored over time and diffusion coefficients calculated.

2.6.2 Free Volume Theory

The diffusion of small molecules that have very weak thermodynamic interaction with a given polymer may be interpreted in terms of the free volume or "hole" concept. Molecules which are smaller than the average hole size, diffuse through the polymer by local activated jumps of the molecules from one hole to the next unoccupied hole. Simple gases diffuse through polymers by this method. When penetrant molecules are larger than the average hole size fewer holes are available to accommodate the penetrant molecule. Polymer segments must rearrange to allow the penetrant through. Most organic solvents are in this category.

The holes or free volume are formed between adjacent polymer molecules by thermal motion. Polymers with a $T_x$ less than the ambient temperature require little energy for segmental motion to occur. Diffusion in these polymers is a fast process. Polymers with a high $T_x$ require energy for the formation of free volume large enough for diffusing molecules. Diffusion in such systems is a slower process. Peterlin$^97$ pointed out that these holes should not be pictured as permanent voids in the polymer, particularly when the polymer is above $T_x$. 

39
2.6.3 Fick's Laws

Fick produced the governing relations for the diffusion process. Fick's first law of diffusion is based on the hypothesis that the rate of transfer of diffusing substance through unit area of a section is proportional to the concentration gradient measured normal to the section.

\[ F = -D \frac{c}{x} \]

If \( F \) and \( c \) are expressed in the same unit then \( D \) has dimensions \( \text{L}^2/\text{T} \).

The equation is often expressed in the differential form

\[ \frac{dc}{dt} = D \frac{d^2c}{dx^2} \]

Systems whose diffusion characteristics can be described by the above relation are said to follow Fickian diffusion behaviour.

2.6.4 Concentration Dependence of \( D \)

Kwei and Wang have looked at the origin of concentration dependent and independent diffusion. According to them when \( D \) is independent of concentration the average hole size in the polymer is larger than the size of the penetrant molecule. The main diffusion mechanism is one of jumps by the penetrant molecule into pre-existing holes. No major rearrangement of the polymer's free volume is necessary.
When D is concentration dependent the minimum hole size is larger than the average hole size in the polymer. With relatively few pre-existing holes available the free volume of the polymer must be redistributed.

In general the diffusion coefficients of simple gases are concentration independent whereas the diffusion coefficients for larger molecules (organic vapours and liquids) are concentration dependent. In experiments this has generally been found to be the case. The diffusion coefficients for small molecules are larger than those for large molecules.

2.6.5 Diffusion in Polymers

Hopfenburg and Frisch\textsuperscript{101} observed the diffusion of hydrocarbons in a glassy polystyrene system and suggest the behavioural features exhibited would probably occur in most amorphous systems given a sufficient temperature and concentration range. They described three different types of diffusion:

1) Case I or Fickian diffusion in which the rate of diffusion is much smaller than the rate of relaxation in the polymer.

2) Case II diffusion, an extreme case, where diffusion is very rapid when compared with the relaxation process and is controlled by the relaxation of the polymer.

3) Non-Fickian or anomalous diffusion which occurs when the diffusion and relaxation rates are comparable.

2.6.6 Fickian Diffusion

Crank\textsuperscript{99,102} has systematically investigated the mathematics of the diffusion process for both concentration dependent and independent diffusion coefficients. They provide a description of Fickian diffusion. In the early stages of diffusion the amount of penetrant absorbed is directly proportional to the square root of time.
If $M_t$ is mass sorbed at time $t$ and $M_\infty$ is mass sorbed at the equilibrium a plot of $M_t/M_\infty$ versus $t^{0.5}$ produces the general plot as seen in figure 2.9. In some instances the linear part can be observed to exist to beyond 50% of the final equilibrium absorption. Only when the concentration begins to change at the centre of the film does the curve become concave toward the time axis for concentration dependent $D$. This implies that for a purely concentration dependent $D$ system, the absorption vs $\sqrt{t}$ curve is never completely linear.

![Figure 2.9. General Plot of Fickian Diffusion.](image)

$D$ also depends on the temperature, generally increasing with increasing temperature. This fact is consistent with the hole theory of diffusion, since increasing temperature will increase the segmental mobility of the polymer thus allowing more holes to be available.

The structure of the polymer itself also affects the diffusion process. In general, factors which decrease the segmental mobility decrease the diffusion rate. Cross-linking, chain stiffness and crystallisation all tend to reduce the rate of diffusion. Peterlin$^9$ has shown that sorption is proportional to the fractional free volume of the polymer. Since the fractional free volume in crystalline regions is much smaller than in...
amorphous regions then in semi-crystalline polymers practically all the diffusive transport can be considered as taking place in the amorphous region. Crystalline regions act as obstacles to the penetrant molecules.

2.6.7 Case II Diffusion

Case II diffusion is often described as a simple limiting case. The main features of case II diffusion first reported by Alfrey et al.\textsuperscript{103}, involving a glassy polymer, are described:

1) As the sorbent penetrates into the polymer a sharp advancing boundary separates the glassy centre from the outer plasticised surface layer.
2) Behind the advancing front, the swollen gel is essentially in an equilibrium state of swelling.
3) The boundary between the surface layer and the glassy core advances at a constant velocity.
4) The initial gain in mass is directly proportional to time not the square root of time. On a classical plot this appears as a parabola.
5) The kinetics of case II diffusion can be reduced to one parameter - the velocity of the advancing front.
6) The velocity of the advancing front in case II sorption is very sensitive to the thermal history of the glassy polymer.

2.6.8 Non-Fickian or Anomalous Diffusion

Not all diffusion in polymers can be described by Fickian characteristics. Generally in polymers at least 15°C above $T_g$, Fickian diffusion is evident. Anomalies exist below the $T_g$ in many polymers and also above $T_g$ in certain cross-linked and crystalline polymers. Rodgers\textsuperscript{104} summarised the various types of diffusion behaviour using the mass sorption curves and compared these curves with Fickian type diffusion. The plots are shown in figure 2.10.
The term pseudo-fickian describes curves of the same general shape to fickian curves but exhibiting an initial linearity for a much shorter period of time. If a single inflexion, at around 50% $M_e$, is observed this is sigmoid sorption. When a vapour is brought into contact with a polymer sheet a surface sorption equilibrium is attained which involves the swelling and extension of the surface. This surface layer is constrained by the entanglement with molecules in the internal core. At sub $T_g$ temperatures the modulus is large and the surface layer is effectively restrained preventing the establishment of a equilibrium surface concentration until some vapour has penetrated into and has plasticised the internal core. The rate of sorption then speeds up towards its final equilibrium resulting in sigmoid behaviour. A third type is two stage sorption. It is thought that the second stage is brought about with an increase in surface concentration which occurs slowly compared with the diffusion process. The surface concentration determines the overall rate for sorption.
2.6.9 Diffusion in a Plane Sheet.

Assuming Fickian diffusion, if a sheet of polymer is exposed to a liquid capable of sorbing into the polymer the surface is assumed to immediately attain a concentration value equal to the equilibrium concentration value. The mass uptake of the sorbent by the polymer can, when the experiment is carried out at room temperature, be expressed as:

\[
\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_{m=0}^{\infty} \frac{1}{(2m+1)^2} \exp\left[-D(2m+1)^2\pi^2 \frac{t}{l^2}\right]
\]

\(M_t\) - total amount of vapour sorbed at time \(t\)
\(M_\infty\) - equilibrium sorption
\(l\) - thickness of sheet
\(m\) - molar volume

At the early stage of sorption equation 2.33 approximates to

\[
\frac{M_t}{M_\infty} = \frac{4}{\pi^2} \sqrt{\frac{Dt}{l^2}}
\]

It is possible to deduce an average diffusion coefficient from the initial gradient of the sorption curve when plotted against \(t^{0.5}\).

\[
D = \frac{\text{gradient}^2 \pi^4 l^2}{16}
\]
Chapter 3

EXPERIMENTAL
3.1 Materials

Four polymers were used in the work, two homopolymers and two copolymers. They were all supplied in film form. Details are given in table 3.1.

<table>
<thead>
<tr>
<th>POLYMER</th>
<th>POLY-PROPYLENE</th>
<th>POLY-ETHYLENE</th>
<th>ETHYLENE/PROPYLENE COPOLYMER</th>
<th>RUBBER FILLED COPOLYMER</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABBREVIATION</td>
<td>PP</td>
<td>PE</td>
<td>BPP</td>
<td>RPP</td>
</tr>
<tr>
<td>MANUFACTURER</td>
<td>Neste</td>
<td>BP</td>
<td>ICI</td>
<td>ICI</td>
</tr>
<tr>
<td>REFERENCE NUMBER</td>
<td>VB 8050 B</td>
<td>ID 5320 AA</td>
<td>GWM 213</td>
<td>D1025</td>
</tr>
<tr>
<td>THICKNESS (μm)</td>
<td>100</td>
<td>50</td>
<td>50</td>
<td>100</td>
</tr>
<tr>
<td>OTHER INFORMATION</td>
<td>100% Isotactic</td>
<td>Low density</td>
<td>Block copolymer (10% PE)</td>
<td>20-30% EPDM</td>
</tr>
<tr>
<td>MFI (g/10min)</td>
<td>8.0</td>
<td>2.3</td>
<td>2.0</td>
<td>4.5</td>
</tr>
<tr>
<td>Density (kg/m³)</td>
<td>900</td>
<td>921</td>
<td>905</td>
<td></td>
</tr>
</tbody>
</table>

EPDM - ethylene propylene diene terpolymer

Table 3.1. Details of the Polymers Used.

The additives contained in the polymers are listed:-

BPP/GWM 213 - Irganox 1010
Irgaphos 168
Atmer 129
Zinc Stearate
The PE used in the compounding was an Exxon Escorene extrusion grade.

The primers used were Hardlen a chlorinated polypropylene in toluene (14-LLB) from Toyo Kasei Kogyo and the solid version (14-LWP), Tyrin CM730 a chlorinated polyethylene from Dow Chemicals and unplasticised poly(vinyl chloride), uPVC from Aldrich Chemicals. Two pack polyurethane paint (M615-122) and activator (M210-763) supplied by ICI was used. The epoxy adhesive used in the adhesion tests was Araldite AV100 and HV100 supplied by B&K Resins Ltd. a product of Ciba Geigy. The steel for the lap shear tests, supplied by JPL Steel stockholders, was 2.5cm wide bright drawn steel cut into 6cm pieces, shot blasted and cleaned with solvent.

The materials used for compounding are listed in table 3.2.

<table>
<thead>
<tr>
<th>MATERIAL</th>
<th>Abv.</th>
<th>SUPPLIER</th>
<th>OTHER INFORMATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly (vinyl methyl ether)</td>
<td>PVME</td>
<td>BASF Lutanol</td>
<td>supplied 70% (by wt) in toluene</td>
</tr>
<tr>
<td></td>
<td></td>
<td>M40APP</td>
<td></td>
</tr>
<tr>
<td>Poly(propylene - acrylic acid)</td>
<td>P(P-AA)</td>
<td>Polysciences</td>
<td>6% acrylic acid</td>
</tr>
<tr>
<td>Poly(ethylene - vinyl alcohol)</td>
<td>P(E-OH)</td>
<td>Polysciences</td>
<td>14.7% vinyl alcohol</td>
</tr>
</tbody>
</table>

Table 3.2. Details of the Materials compounded with BPP.

The PET used in pressing the compounded pieces was Melinex 23038-59-9 supplied by ICI.
3.2 Chemicals

The liquids used for contact angle measurements were laboratory produced triple distilled water, high purity ethanediol, dimethylsulphoxide (DMSO), dimethylformamide (DMF) all supplied by Romil Chemicals and 99% diiodomethane (DIM) supplied by Aldrich Chemicals.

HPLC grade heptane and propan-2-ol used for the solvent treatment were both supplied by Aldrich Chemicals. The carrier solvents used were toluene (supplied by Careless solvents), dichlorobenzene (BDH Chemicals), cyclohexyl chloride, dichlorobutane (both Aldrich Chemicals) and xylene (Fisons).

Dichloromethane (Careless solvents) was used to remove weak boundary layers from the polymers and also to clean the PET film. Tetrahydrofuran (THF) was the solvent for the gel permeation chromatography (GPC) supplied by Fisons. Methanol used in the compounding section was supplied by Careless solvents.
3.3 Analysis

3.3.1 Surface Energy Measurements

3.3.1.1 Surface Tension of Liquids

All liquids were handled with care to maintain their purity. Syringes and container bottles were all soaked in chromic acid, washed with distilled water and dried overnight in a clean oven before use to remove organic contaminants. Each syringe and container were used for a specific liquid only.

Surface tension of the liquids at room temperature, 20°C ±2°C, were measured with a Kruss Digital Tensiometer K10T using the du Nouy ring method\textsuperscript{105}. At least four measurements were made with an accuracy within ±0.2mNm\textsuperscript{-1}. Results are shown in table 3.3. The correction factors given by Harkins et al.\textsuperscript{105} were used.

<table>
<thead>
<tr>
<th>LIQUID</th>
<th>EXPERIMENTAL VALUE (mJm\textsuperscript{-2})</th>
<th>CORRECTION FACTOR</th>
<th>NEW VALUE (mJm\textsuperscript{-2})</th>
<th>LITERATURE VALUE (mJm\textsuperscript{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>77.1</td>
<td>0.944</td>
<td>72.8</td>
<td>72.8</td>
</tr>
<tr>
<td>Ethanediol</td>
<td>53.0</td>
<td>0.899</td>
<td>47.6</td>
<td>48.3</td>
</tr>
<tr>
<td>DMSO</td>
<td>47.9</td>
<td>0.889</td>
<td>42.6</td>
<td>43.54</td>
</tr>
<tr>
<td>DMF</td>
<td>40.4</td>
<td>0.888</td>
<td>35.9</td>
<td>37.30</td>
</tr>
</tbody>
</table>

Table 3.3. Surface Tensions of the Liquids using the du Nouy Ring Method.

These values are close to the values given in the literature\textsuperscript{106}. The polar and dispersion components of the surface energy were calculated using the "equilibrium" angle on a piece of untreated polyethylene. The PE was assumed\textsuperscript{107} to have a zero polar component and a dispersion component of 33mJm\textsuperscript{-2}. The dispersion
and polar components of the liquids were calculated from

\[ \gamma_L(1+\cos \theta) = 2(\gamma_L^p \gamma_L^d)^{0.5} \quad 3.1 \]

and

\[ \gamma_L = \gamma_L^p + \gamma_L^d \quad 3.2 \]

The calculated values are shown in table 3.4. The values for DIM were taken from the literature\textsuperscript{105}.

<table>
<thead>
<tr>
<th>LIQUID</th>
<th>(\gamma_L) (mJm(^{-2}))</th>
<th>(\gamma_L^p) (mJm(^{-2}))</th>
<th>(\gamma_L^d) (mJm(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>72.8</td>
<td>47.6</td>
<td>25.2</td>
</tr>
<tr>
<td>Ethanol</td>
<td>47.6</td>
<td>13.3</td>
<td>34.4</td>
</tr>
<tr>
<td>DMSO</td>
<td>42.6</td>
<td>9.2</td>
<td>33.4</td>
</tr>
<tr>
<td>DMF</td>
<td>35.9</td>
<td>5.5</td>
<td>30.5</td>
</tr>
<tr>
<td>DIM</td>
<td>50.8</td>
<td>1.3</td>
<td>49.5</td>
</tr>
</tbody>
</table>

Table 3.4. Calculated Polar and Dispersion Contributions to Surface Energy.

These values are also in reasonable agreement with those in the literature.

3.3.1.2 Contact Angle Measurement

Contact angles were measured using a Kruss G40 system. Advancing and receding measurements were taken. A piece of polymer was fixed to a microscope slide using double sided adhesive tape. This was to ensure a flat surface was maintained while measurements were being taken. For advancing angles a 4\(\mu\)l drop of liquid was syringed onto the polymer and allowed to equilibrate for approximately 10 seconds. The drop was advanced
across the polymer surface by adding another 1\(\mu\)l of liquid. The contact angle was then taken as quickly as possible, i.e. within a few seconds. The syringe needle stayed in the drop throughout the procedure.

For receding angles 5\(\mu\)l of liquid was syringed onto the polymer and allowed to equilibrate for 10 seconds with the syringe needle still in the drop. The liquid was then drawn back into the syringe. The receding angle is taken just before the liquid moves back across the surface. For each liquid on each sample an average of 10 drops was taken with a calculated error of \(\pm 2^\circ\).

### 3.3.1.3 Surface Energy Calculations

Using the equation\(^{68}\) which is the Young/Dupré equation and the Owens/Wendt equation combined.

\[
\gamma_L (1+\cos\theta) = 2 (\gamma_s^{\theta_p})^{0.5} + 2 (\gamma_s^{\theta_d})^{0.5}
\]

the values of \(\gamma_s^d\) and \(\gamma_s^p\) can be calculated from the measured or known values of \(\theta, \gamma_L^d, \gamma_L^p\) and \(\gamma_L\). Rearranging the above equation a plot of

\[
x = \sqrt{\frac{\gamma_L^p}{\gamma_L^d}} vs \quad y = \frac{1+\cos\theta}{2} \frac{\gamma_L}{\sqrt{\gamma_L^d}}
\]

should give a straight line.

These values were calculated for the various liquids and a graph plotted. The polar and dispersion components of the solid’s surface energy can be obtained from the gradient and the intercept of the graph.
3.3.2 X-ray Photoelectron Spectroscopy

XPS spectra were recorded on a VG ESCALAB Mark 1 spectrometer using an Al Kα X-ray source (1486.6eV) under a vacuum of $10^{-7}$ mbar. Broad scan spectra were recorded at a pass energy of 85 eV using a B1 aperture (1 cm * 4 mm). A scan width of 1000 eV was used. No evidence of radiation damage was observed.

The carbon 1s peak was used as the reference for charge correction. The binding energy was taken as 284.6 eV. Quantification was achieved by measurement of peak area following subtraction of a Shirley type background. Correction is made for photoelectron cross section\textsuperscript{108}, inelastic mean free path\textsuperscript{109}, transmission of the energy analyser\textsuperscript{110} and angular asymmetry in photoemission\textsuperscript{111} (where appropriate).

3.3.3 Attenuated Total Reflection Spectroscopy

A Nicolet 20DX FTIR spectrometer with a Spectra Tech ATR attachment was used to acquire spectra. The prisms used were a KRS-5 (50 mm * 10 mm * 3 mm) with a face angle of 45° and germanium (25 mm * 10 mm * 3 mm) with a face angle of 60° both from Spectra Tech. Polymer pieces were cut to fit the surface of the prism. A good contact with the element was achieved using two rubber pads at the back of the sample.

300 to 500 scans were collected using a MCT (Mercury - Cadmium - Telluride) detector which operates at liquid nitrogen temperature. Sampling depth of the IR beam was 0.5 μm for the KRS-5 prism and 0.2 μm for the germanium. The polariser used was a ZnSe polariser from Spectra Tech.
3.3.4 Gel Permeation Chromatography

GPC was used to obtain molecular weights and the weight distribution. GPC traces were acquired using a PL mixed gel column with THF as the carrier solvent. An elution rate of 1.0mlmin$^{-1}$ was used.

3.3.5 Differential Scanning Calorimetry

DSC was used to obtain crystallinity information on the polymers. DSC traces were recorded using a Perkin Elmer DSC4 calorimeter. A sample of 2mg in an aluminium pan was heated from 50°C to 250°C at a rate of 20°Cmin$^{-1}$. The instrument was calibrated using an indium standard.

3.3.6 Electron Microscopy

Electron microscopy was used to investigate surface topography. The scanning electron microscope was a Cambridge 360 SEM. The transmission electron microscope was a Jeol JEM 100CX TEM. The replicas were prepared by placing a drop of acetone on the surface and placing onto it a cellulose acetate strip and allowing it to dry. The strip is then taken off and placed onto a microscope slide. This is then carbon coated by evaporation to approximately 10nm thick. Small pieces were then cut out and placed in the viewing grid and the cellulose acetate dissolved away from the carbon replica in acetone.

3.3.7 Atomic Force Microscopy

Further topographical information was obtained using an AFM. The atomic force microscope used was a Topometrix SPM and it was run in contact mode.
3.4 Procedures

3.4.1 Solvent Immersion

The mixed solvent used was heptane : propan-2-ol (1:1 by volume). The polymer was placed in a crystallising dish which contained the solvent and left for the required time. A dish was only used for one type of solvent to prevent cross contamination. After immersion the polymers were air dried.

3.4.2 Priming

The chlorinated polypropylene, Cl-PP, primer was used at a 15% by weight concentration. The solid primer was dissolved in the required solvent and delivered to the polymer by a Badger 250-1 spray gun attached to a BOC compressed gas cylinder at a pressure of 201b/in². The primer was allowed to dry in the air at room temperature then the other side of the polymer was sprayed and dried. The dry thickness of the primer layer was 10 - 15µm.

The chlorinated polyethylene, Cl-PE, primer was dissolved in toluene but as it contained talc, which would affect the experiments, this had to be removed by centrifuging. The PVC was dissolved in THF. The concentration of both was approximately 7% by weight. Both were bar spread using K-bar hand coaters from RK Print-Coat Instruments Ltd.

3.4.3 Painting

The two pack PU paint was mixed to the manufacturer’s directions in a ratio of 2.5:1 paint to activator and was applied using the spray gun to the first side of the polymer. The painted piece was left to dry slightly in a fume cupboard and then cured in an oven at 70°C for 1 hour. The painted piece was allowed to
cool before being turned over for the other side to be painted.

3.4.4 Lap Shear Tests

The polymer specimen (10mm * 25mm) was bonded between two pieces of steel using a 1:1 mixture by weight of hardener to resin. 1% Ballotini by weight (diameter 0.21 mm maximum) was added to the adhesive to give a consistent thickness of glue. The polymer was bonded to the steel accurately to avoid metal/adhesive/metal bond as this would affect the results. A clip was used to hold the bonded pieces together while they were cured in an oven at 50°C for 4 hours.

The bonded test pieces were put into the grips of a Hounsfield Tensometer the same distance apart each time. A cross head speed of 12.7mm.min\(^{-1}\) was used. The readings at the break were taken to the nearest 5kgf. Six readings were taken for each sample and the average taken.

3.4.5 Weak Boundary Layer Removal

A polymer piece was placed in a beaker of boiling dichloromethane for 2 hours. The polymer was then air dried and sprayed immediately.

3.4.6 Diffusion

Diffusion data was acquired using a CI Electronics Mark II vacuum head microbalance in vacuum system. The head unit electromagnetically balanced the torque produced by the sample mass. The balance arm carried a shutter interposed between a lamp and a pair of silicon photocells. A small displacement of this arm caused an imbalance in the light falling on the photocells. Current produced as a result of this imbalance was amplified and passed through the movement coil restoring it to
the original position. The current flowing through the head is in proportion to the applied force.

A schematic view of the microbalance apparatus is shown in figure 3.1.

![Diagram of Diffusion Apparatus]

**KEY**

a - feed line to cold trap and vacuum pump  
b - reservoir  
c - reservoir water jacket  
d - sample  
e - microbalance  
f - copper wire used as counterbalance  
A/B/C - taps

**Figure 3.1. Schematic of Diffusion Apparatus.**

The experiments were operated in a controlled environment, the solvent reservoir being kept 5°C below the rest of the apparatus. This prevented condensation of the solvent onto the polymer or the balance. About 30cm³ of solvent was put into the solvent reservoir.
A sample of polymer (50mm * 9mm) was weighed and then suspended from the left hand side of the balance by a glass thread. Copper wire was placed on the right hand side to counterbalance till near balance was reached. The balance was then electronically zeroed.

The apparatus was evacuated by opening taps A and C. Both were closed and tap B opened to allow dissolved gas out of the solvent. Tap B was closed and tap A opened to let the gas out of the system. This was repeated till all dissolved gas had been released. This ensured the vapour round the polymer was only that of the solvent. After degassing all taps were closed and the zero of the balance checked. Tap C was opened and then simultaneously tap B was opened while setting the recorder running. It was left until the required sorption was reached.

The indicating meter was calibrated for actual weight using copper wire which had been weighed on a four figure balance. The microbalance was zeroed without any weight on the two glass threads. The copper wire was placed on the left hand side and the reading recorded from the meter. Seven different weights of copper were used to produce a calibration graph.

3.4.7 Flame Treatment

The conditions used were an air:gas ratio of 10.3:1 and the total gas flow rate was 30 lmin\(^{-1}\). The flame to polymer distance was 1cm. It was an oxidising flame just above stoichiometric flame conditions.

The PP was derivatised using TFAA in a vacuum rig. The polymer film was exposed for 1.5 hours and then out gassed overnight.

3.4.8 Compounding

The compounding was carried out on a Plastograph Brabender made
by Duisburg. 23g of BPP granules were mixed with the required amount of additive before addition to the Brabender. The Brabender was heated to 190°C and with the mixing rotors at 25rpm the mixed materials were added slowly. Once all the materials were added and had softened they were left to mix for 10 minutes. The mixture was removed and allowed to cool.

PVME was supplied in toluene at 70%, the required amount of solution was calculated for each addition and sprayed onto the BPP granules. The toluene was left to evaporate in a fume cupboard and finally in a vacuum oven. The PVME/BPP granules were introduced into the Brabender as before.

When PE was used instead of BPP the temperature used was 160°C as PE softens at a lower temperature.

Pieces of sample were cut from the compounded polymer for analysis and pressed between PET film on an Apex hydraulic press. The PET film was cleaned in boiling dichloromethane for 1 hour.
Chapter 4

RESULTS and
DISCUSSION
4.1 Characterisation of Polymers

4.1.1 Introduction

The surfaces of the untreated polymer films and the primers were characterised by contact angle measurement, XPS and FTIR-ATR. GPC was used to estimate molecular weights and to identify low molecular components. DSC was used to probe crystallinity and SEM and STEM to identify surface topography. The results from SEM and STEM will be discussed in later sections.

4.1.2 Gel Permeation Chromatography

4.1.2.1 For polymers

GPC of the polymers were recorded by RAPRA Technology Ltd. using ortho dichlorobenzene as the solvent. A polystyrene calibration was used and literature constants of $\alpha=700$ and $k=-3.860$ have been applied in a mathematical procedure to allow for the difference in chemical type between the sample and the calibrants. Table 4.1 shows the results where $M_w$ is the weight average molecular weight and $M_{WD}$ is the molecular weight distribution.

<table>
<thead>
<tr>
<th>Polymers</th>
<th>$M_w$ (gmol$^{-1}$)</th>
<th>$M_{WD}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>233 000</td>
<td>5.2</td>
</tr>
<tr>
<td>PE</td>
<td>106 000</td>
<td>6.4</td>
</tr>
<tr>
<td>BPP</td>
<td>325 000</td>
<td>5.5</td>
</tr>
</tbody>
</table>

Table 4.1. Molecular Weights for Polymers as determined by GPC.

$M_w$ is used as it gave more consistent values for duplicate runs. As each polymer has a low molecular weight part, which is close...
to the reference peak, a small difference in the trace at low weight may have a large effect on calculated Mn (number average molecular mass) values. BPP values are quoted as for polypropylene as this was the major component.

**Figure 4.1.** Graphs Showing the Molecular Weight Distribution of PP and PE.
PE has a lower molecular weight than PP or BPP and a greater amount of low molecular weight material. The molecular weight distributions from GPC for PP and PE are shown in figure 4.1.

4.1.2.2 For Primers

GPC of the chlorinated PP and PE primers was used to see whether the molecular weights of the primers were similar. The molecular weights quoted are from a polystyrene standard calibration and are thus not actual molecular weights but polystyrene equivalents, nevertheless they can still be used for comparison purposes. Table 4.2 shows the results.

<table>
<thead>
<tr>
<th>Primers</th>
<th>Mn (g mol⁻¹)</th>
<th>MWD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl-PP</td>
<td>19 000</td>
<td>2.7</td>
</tr>
<tr>
<td>Cl-PE</td>
<td>33 000</td>
<td>6.6</td>
</tr>
</tbody>
</table>

Table 4.2. Molecular Weights for Chlorinated Primers as determined by GPC.

Although the molecular weights are different the Mn values are of the same order. The major difference is that Cl-PE has a much broader molecular weight distribution.

4.1.3 Contact Angle Measurements

Estimates of dispersion and polar components of surface free energy were calculated using the Owens/Wendt method. An average of ten separate drops was used and the advancing angle was used. The error was ±2°. \( \gamma_L, \gamma_L^d \) and \( \gamma_L^p \) values of the liquids are listed in Table 3.4.

A plot of \( Y \) vs \( X \) gives a straight line with a gradient of \( (\gamma_L^p)^{1/2} \) and a \( Y \) intercept of \( (\gamma_L^d)^{1/2} \).
Figures 4.2 and 4.3 show the plots for the polymer films and figure 4.4 the plots for the primers used.

Figure 4.2. Plots used for the estimation of surface free energy of untreated PP and PE.
Figure 4.3. Plots used for the estimation of surface free energy of the untreated BPP and RPP.

The surface free energies calculated from these plots are given in tables 4.3 and 4.4.

<table>
<thead>
<tr>
<th>Polymers</th>
<th>$\gamma_s^p$ (mJm$^{-2}$)</th>
<th>$\gamma_s^d$ (mJm$^{-2}$)</th>
<th>$\gamma_s$ (mJm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>0.07</td>
<td>27.18</td>
<td>27.25</td>
</tr>
<tr>
<td>PE</td>
<td>0.003</td>
<td>29.46</td>
<td>29.46</td>
</tr>
<tr>
<td>BPP</td>
<td>0.01</td>
<td>27.62</td>
<td>27.63</td>
</tr>
<tr>
<td>RPP</td>
<td>0.008</td>
<td>25.92</td>
<td>25.92</td>
</tr>
</tbody>
</table>

Table 4.3. Surface Free Energy of Untreated Polymers.
Figure 4.4. Plots used for the estimation of surface free energy of chlorinated primers and PVC.

<table>
<thead>
<tr>
<th>Primers</th>
<th>$\gamma_s^p$ (mJm$^{-2}$)</th>
<th>$\gamma_s^d$ (mJm$^{-2}$)</th>
<th>$\gamma_s$ (mJm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl-PP</td>
<td>1.1</td>
<td>27.5</td>
<td>28.6</td>
</tr>
<tr>
<td>Cl-PE</td>
<td>0.6</td>
<td>22.4</td>
<td>23.0</td>
</tr>
<tr>
<td>PVC</td>
<td>0.3</td>
<td>31.5</td>
<td>31.8</td>
</tr>
</tbody>
</table>

Table 4.4. Surface Free Energy of Chlorinated Primers and PVC.

Values are slightly lower than literature values quoted for similar materials, this is due to hysteresis of the contact angle. Advancing angles were used for the calculation since there is no equilibrium value. The advancing angle is a measure of the least wettable part of a heterogeneous polymer surface, ie. the lowest possible value of surface free energy is obtained. Possible sources of hysteresis are roughness or
inhomogeneity of the surface.

All polymers are essentially non-polar surfaces with a low surface energy. The primers have a small polar component and have similar surface free energy to the polymers.

4.1.4 X-Ray Photoelectron Spectroscopy

XPS was used to examine the surface composition of the polymers. No other elements with the exception of carbon were detected on the untreated surface of all the polymers. Detection limits for oxygen under the conditions used were 0.2 atom %.

The elemental composition of the three primers used are listed in table 4.5.

<table>
<thead>
<tr>
<th>Primer</th>
<th>% Carbon</th>
<th>% Chlorine</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl-PP</td>
<td>87.2</td>
<td>12.8</td>
</tr>
<tr>
<td>Cl-PE</td>
<td>86.2</td>
<td>13.8</td>
</tr>
<tr>
<td>PVC</td>
<td>70.4</td>
<td>29.6</td>
</tr>
</tbody>
</table>

Table 4.5. Elemental Compositions of the Surfaces of the Chlorinated Primers and PVC.

Random error in the Cl composition is approximately ±0.5 atom %

4.1.5 Attenuated Total Reflection Spectroscopy

Figure 4.5 shows the spectra of the polymers used in this study. Assignments of the principal peaks$^{12,13}$ are given in the table 4.6, for PP and table 4.7, for PE.
Figure 4.5. FTIR-ATR Spectra of Polyolefins.
The untreated polymer spectra were examined closely at the OH peak wavenumber region for any trace of OH groups on the surface. None was found. Spectra were also recorded using a polariser to investigate the orientation of the polymer films. PE was the only film which showed some molecular orientation at the surface. Spectra of the chlorinated polyolefin primers and PVC were also taken and are shown in figure 4.6.
Figure 4.6. FTIR-ATR Spectra of Primers.
4.1.6 Differential Scanning Calorimetry

DSC of PP and PE were recorded. The crystalline melting point of PP was 161°C and that of PE was 107°C. The degree of crystallinity was, as expected, between 50-70\%\textsuperscript{14}. 
4.2 SOLVENT TREATMENT

4.2.1 Introduction

In industry polymer samples are wiped with solvent when PP automotive parts are examined for defects. Papers have been published which suggest that wiping with a solvent mixture of heptane/propan-2-ol introduces solvent molecules onto the surface which improves the joint strength. Implications are that this would be a cheap and effective means of activating surfaces for adhesion. This approach to adhesion enhancement has not been studied in detail, although in previous work use of a mixed solvent was found more effective than either propanol or heptane in isolation in improving adhesion to chlorinated primers. It was proposed to investigate this claim in more detail using controlled laboratory conditions. Polymer samples were immersed in heptane, propan-2-ol and a 1:1 mixture of the two for varying time periods to see the effects the solvents have on the polymers.

4.2.2 X-ray Photoelectron Spectroscopy

To determine surface composition all polymers were analysed by XPS after immersion and the results shown in table 4.8.
### Table 4.8. XPS Data for Solvent Immersion.

For the two homopolymers uptake of oxygen was always under 0.5 % and usually below the broad scan detection limit of 0.2 %. The copolymer when immersed in the mixed solvent or heptane shows small quantities of oxygen. The rubber filled copolymer showed oxygen after all treatments at levels of ~0.5 - 2.5 %. With both copolymers there was oxygen seen when the copolymers were immersed in HPLC heptane, the oxygen had most probably come to the surface from the bulk. The bulk has additives, stearates, which contain oxygen.

As the XPS was carried out under vacuum any alcohol introduced onto the surface may be removed prior to or during analysis. FTIR-ATR was used to examine the surface to look for introduction of alcohol or migration of additives to the surface. This technique does not use a vacuum but is not as surface specific as XPS. Figure 4.7 shows that no alcohol

<table>
<thead>
<tr>
<th>TREATMENT</th>
<th>% OXYGEN</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PP</td>
</tr>
<tr>
<td>Blank</td>
<td>-</td>
</tr>
<tr>
<td>Mix 15s</td>
<td>0.4</td>
</tr>
<tr>
<td>Mix 5min</td>
<td>0.4</td>
</tr>
<tr>
<td>Mix 10min</td>
<td>-</td>
</tr>
<tr>
<td>Propanol 15s</td>
<td>-</td>
</tr>
<tr>
<td>Propanol 5min</td>
<td>-</td>
</tr>
<tr>
<td>Propanol 10min</td>
<td>-</td>
</tr>
<tr>
<td>Heptane 15s</td>
<td>-</td>
</tr>
<tr>
<td>Heptane 5min</td>
<td>-</td>
</tr>
<tr>
<td>Heptane 10min</td>
<td>-</td>
</tr>
</tbody>
</table>

For the two homopolymers uptake of oxygen was always under 0.5 % and usually below the broad scan detection limit of 0.2 %. The copolymer when immersed in the mixed solvent or heptane shows small quantities of oxygen. The rubber filled copolymer showed oxygen after all treatments at levels of ~0.5 - 2.5 %. With both copolymers there was oxygen seen when the copolymers were immersed in HPLC heptane, the oxygen had most probably come to the surface from the bulk. The bulk has additives, stearates, which contain oxygen.

As the XPS was carried out under vacuum any alcohol introduced onto the surface may be removed prior to or during analysis. FTIR-ATR was used to examine the surface to look for introduction of alcohol or migration of additives to the surface. This technique does not use a vacuum but is not as surface specific as XPS. Figure 4.7 shows that no alcohol
Figure 4.7. Subtracted Spectra to show no Hydroxyl Groups at the Surface.
containing groups were observed at the surface. Also for the two copolymers no carbonyl containing groups were seen. Carbonyl would indicate the presence of migratory additives including stearates.

4.2.3 Contact Angle Measurement

Contact angles were measured to determine the surface free energies of the treated polymers. If there was uptake of alcohol this should be reflected in the changes in the surface free energy. Contact angle measurements are very surface specific due to the short range intermolecular forces involved, the results are shown in table 4.9.

Next page Table 4.9. Contact Angle Results for Solvent Immersion.
<table>
<thead>
<tr>
<th>POLYMER</th>
<th>TREATMENT</th>
<th>SURFACE ENERGY (mJ/m²)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>POLAR</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PP</td>
<td>Blank</td>
<td>0.1</td>
<td>27.2</td>
<td>27.3</td>
</tr>
<tr>
<td></td>
<td>Mix 15s</td>
<td>0.1</td>
<td>28.2</td>
<td>28.3</td>
</tr>
<tr>
<td></td>
<td>Mix 5min</td>
<td>0.3</td>
<td>26.9</td>
<td>27.2</td>
</tr>
<tr>
<td></td>
<td>Mix 10min</td>
<td>0.2</td>
<td>26.4</td>
<td>26.6</td>
</tr>
<tr>
<td></td>
<td>Hept 15s</td>
<td>0.0</td>
<td>29.7</td>
<td>29.7</td>
</tr>
<tr>
<td></td>
<td>Prop 15s</td>
<td>0.0</td>
<td>29.1</td>
<td>29.1</td>
</tr>
<tr>
<td>PE</td>
<td>Blank</td>
<td>0.0</td>
<td>29.5</td>
<td>26.5</td>
</tr>
<tr>
<td></td>
<td>Mix 15s</td>
<td>0.2</td>
<td>28.4</td>
<td>28.6</td>
</tr>
<tr>
<td></td>
<td>Mix 5min</td>
<td>0.1</td>
<td>28.0</td>
<td>28.1</td>
</tr>
<tr>
<td></td>
<td>Mix 10min</td>
<td>0.1</td>
<td>28.3</td>
<td>28.4</td>
</tr>
<tr>
<td></td>
<td>Hept 15s</td>
<td>0.0</td>
<td>29.7</td>
<td>29.7</td>
</tr>
<tr>
<td></td>
<td>Prop 15s</td>
<td>0.0</td>
<td>30.2</td>
<td>30.2</td>
</tr>
<tr>
<td>BPP</td>
<td>Blank</td>
<td>0.0</td>
<td>27.6</td>
<td>27.6</td>
</tr>
<tr>
<td></td>
<td>Mix 15s</td>
<td>0.2</td>
<td>27.2</td>
<td>27.4</td>
</tr>
<tr>
<td></td>
<td>Mix 5min</td>
<td>0.1</td>
<td>26.7</td>
<td>26.8</td>
</tr>
<tr>
<td></td>
<td>Mix 10min</td>
<td>0.0</td>
<td>27.0</td>
<td>27.0</td>
</tr>
<tr>
<td></td>
<td>Hept 15s</td>
<td>0.1</td>
<td>26.6</td>
<td>26.7</td>
</tr>
<tr>
<td></td>
<td>Prop 15s</td>
<td>0.0</td>
<td>28.5</td>
<td>28.5</td>
</tr>
<tr>
<td>RPP</td>
<td>Blank</td>
<td>0.0</td>
<td>25.9</td>
<td>25.9</td>
</tr>
<tr>
<td></td>
<td>Mix 15s</td>
<td>0.3</td>
<td>23.2</td>
<td>23.5</td>
</tr>
<tr>
<td></td>
<td>Mix 5min</td>
<td>0.0</td>
<td>26.6</td>
<td>26.6</td>
</tr>
<tr>
<td></td>
<td>Mix 10min</td>
<td>0.0</td>
<td>26.9</td>
<td>26.9</td>
</tr>
<tr>
<td></td>
<td>Hept 15s</td>
<td>0.1</td>
<td>22.2</td>
<td>22.3</td>
</tr>
<tr>
<td></td>
<td>Prop 15s</td>
<td>0.1</td>
<td>23.4</td>
<td>23.5</td>
</tr>
</tbody>
</table>
As can be seen from the surface energies all the polymers show little change in polar content when treated. This seems to conflict with the XPS data for the copolymers, especially RPP. There is oxygen at the surface according to XPS but this is not reflected in the contact angle result for surface energies. It may be that the oxygen detected by XPS is not present in the outermost atom layer probed by contact angle measurements. Alternatively the oxygen may be present in islands on the surface in which case the advancing contact angle would be typical of the polymer.

4.2.4 Adhesion Tests

Lap shear tests were carried out to determine the effect of the solvent treatment on the joint strengths with a chlorinated PP primed and painted polymer. Results are shown in table 4.10.
<table>
<thead>
<tr>
<th>TREATMENT</th>
<th>JOINT STRENGTHS (N)</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PP</td>
<td>PE</td>
<td>BPP</td>
<td></td>
</tr>
<tr>
<td>Blank</td>
<td>1680 ±125</td>
<td>670 ±94</td>
<td>1760 ±413</td>
<td></td>
</tr>
<tr>
<td>Mix 15s</td>
<td>1600 ±270</td>
<td>650 ±132</td>
<td>2270 ±483</td>
<td></td>
</tr>
<tr>
<td>Mix 5min</td>
<td>2110 ±360</td>
<td>890 ±201</td>
<td>2590 ±278</td>
<td></td>
</tr>
<tr>
<td>Mix 10min</td>
<td>2025 ±277</td>
<td>1060 ±412</td>
<td>2570 ±534</td>
<td></td>
</tr>
<tr>
<td>Heptane 15s</td>
<td>1960 ±390</td>
<td>510 ±233</td>
<td>1970 ±545</td>
<td></td>
</tr>
<tr>
<td>Heptane 5min</td>
<td>1720 ±345</td>
<td>Fell Apart</td>
<td>2150 ±547</td>
<td></td>
</tr>
<tr>
<td>Heptane 10min</td>
<td>1500 ±485</td>
<td>620 ±207</td>
<td>1850 ±395</td>
<td></td>
</tr>
<tr>
<td>Propanol 15s</td>
<td>1490 ±213</td>
<td>725 ±137</td>
<td>1890 ±325</td>
<td></td>
</tr>
<tr>
<td>Propanol 5min</td>
<td>1880 ±121</td>
<td>640 ±196</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Propanol 10min</td>
<td>1180 ±462</td>
<td>690 ±231</td>
<td>2230 ±286</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.10. Joint Strengths with Chlorinated PP Primer as given by Lap Shear Tests for Solvent Immersed Samples.

The standard deviation was calculated for each set of conditions. The error was 25% for PE and 20% for PP and BPP. Treatment with the mixture for 10 minutes appears to have an effect on all 3 polymers. A statistical test was performed to establish whether the results at 10 minutes of the mixture were significantly different from the blank. A t-test was performed on the data and showed that PP and BPP treated with mixed solvent for 10 minutes gave bond strengths significantly above those from untreated polymer at the 99% confidence level. The confidence level for PE was lower at 93%.

Failure surfaces were visually inspected and all appeared to fail at the polymer/primer interface. Some failure surfaces were examined by XPS for confirmation of the type of failure. The polymer side of the failures showed levels of 0 - 0.5 atom % chlorine and the other side had level of chlorine approximately
11 atom %, so failure was principally at the polymer/primer interface.

When the homopolymers were treated with propan-2-ol and heptane separately no increase in joint strength was observed. When they were treated with the mixture for 5 minutes or over the strength of the joint appears to increase this confirms previous results\textsuperscript{115}. It is unclear why this increase in strength should be particularly since no oxygen was detected at the surface using XPS and little or no change in surface energy was measured.

4.2.5 Receding Contact Angle

Although advancing contact angle is not affected by treatment this may not be true for the receding angle. Water was used to obtain the receding angle and the results are shown in table 4.11.

<table>
<thead>
<tr>
<th>TREATMENT</th>
<th>RECEDING CONTACT ANGLE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PP</td>
</tr>
<tr>
<td>Blank</td>
<td>87.5</td>
</tr>
<tr>
<td>Mix 15s</td>
<td>85.2</td>
</tr>
<tr>
<td>Mix 5min</td>
<td>84.4</td>
</tr>
<tr>
<td>Mix 10min</td>
<td>82.2</td>
</tr>
<tr>
<td>Heptane 15s</td>
<td>86.0</td>
</tr>
<tr>
<td>Heptane 5min</td>
<td>82.7</td>
</tr>
<tr>
<td>Heptane 10min</td>
<td>85.3</td>
</tr>
<tr>
<td>Propanol 15s</td>
<td>85.7</td>
</tr>
<tr>
<td>Propanol 5min</td>
<td>85.3</td>
</tr>
<tr>
<td>Propanol 10min</td>
<td>85.7</td>
</tr>
</tbody>
</table>

Table 4.11. Water Receding Contact Angles for Solvent Immersed Samples.
All receding angles were lower after treatment than before. The polymer surfaces have a reduced tendency to dewet. For treatment with the solvent mixture there is a general lowering, across all the polymers, as the time of immersion lengthens the receding angle decreases.

A graph was plotted for the difference in joint strength between the treated sample and the blank versus the difference in hysteresis. This was done for the 5 and 10 minute treated samples with the mixture and is shown in figure 4.8.

The errors involved are ±300N for joint strengths and ±1.5° for hysteresis. There are only three points for each time consequently it is difficult to establish trends. Joint strengths increased from the blank to 5 minutes immersion but the strength remained similar between 5 and 10 minutes, while Δhysteresis continues to increase. This suggests that the
solvent mixture has reached a saturation point for improving joint strength at 5 minutes.

4.2.6 Surface Morphology

To investigate whether a change in roughness is a factor influencing the receding angle and the joint strength some immersed polymers were examined by SEM. The resulting micrographs showed no change in surface roughness after immersion. STEM was also used to obtain information on surface topography. The 10 minute solvent treatment for all polymers are shown in micrographs in figures 4.9-4.11, with the untreated polymer for comparison.

As can be seen the roughness of PP and PE does not change markedly after treatment. The roughness of BPP changes after all treatments. The polymers were also examined at a higher magnification. The micrographs for BPP are shown in figure 4.12. As BPP is a copolymer of PP and PE the swelling will be different for each part and this could effect the structure.

The small circular particles seen on the untreated BPP are most probably from the additive package. Irganox 1010 and Irgaphos 168 are antioxidants but are usually expected to be in the polymer bulk. The particles are more likely to be either Atmer 129, which is glyceryl stearate, or zinc stearate or both. After treatment the additives have been removed or reduced in all cases for BPP. PP shows similar results with additive at the surface being removed by the mixture and propan-2-ol but in this case heptane does not remove additive. PE does not have similar particles at the surface.
DOCUMENTS OF POOR ORIGINAL HARD COPY
Figure 4.9. STEM Micrographs (x5k) of a) PP b) PP Mixture 10mins c) PP Heptane 10mins and d) PP Propanol 10mins.
Figure 4.10. STEM Micrographs (x5k) of a) PE b) PE Mixture 10mins c) PE Heptane 10mins and d) PE Propanol 10mins.
Figure 4.11. STEM Micrographs (x5k) of a) BPP b) BPP Mixture 10mins c) BPP Heptane 10mins and d) BPP Propanol 10mins.
Figure 4.12. STEM Micrographs (x50k) of a) BPP b) BPP Mixture 10mins c) BPP Heptane 10mins and d) BPP Propanol 10mins
To further investigate the topography some AFM was done. The untreated PP and BPP and the 10 minute mixture of PP and BPP were examined. Due to the limited access to AFM it was only possible to study these samples in detail. The PP prints are shown in figure 4.13 and the BPP prints in 4.14.

As can be seen from the print of the PP there appears to be holes on the surface after treatment which are not there on the untreated PP. These holes could explain the receding contact angle results. The holes would fill with water as the drop is being advanced, this would not affect the advancing angle which is representative of the least wettable part of the surface. As the drop was receded over the filled hole the liquid would be attracted to the water in the hole and this would cause the receding angle to decrease. This explains the receding contact angle results. The holes are thought to be formed by the different evaporation rates of the two solvents in the mixture. The holes are not seen on the STEM micrographs although the size of holes is within the capabilities of the STEM. This may be due to problems with the replication procedure. BPP does not show such holes after treatment. The roughening on treatment is severe and this may obscure holes if present. There is a general roughening in agreement with STEM. Both STEM and AFM show that the surface has been modified by solvent treatment which will probably affect contact angle and joint strength.
Figure 4.13. AFM Micrographs of Untreated PP (top) and Mixture 10 minutes treated PP.
Figure 4.14. AFM Micrographs of Untreated BPP (top) and Mixture 10minutes Treated BPP.
4.2.7 Solvent Diffusion

4.2.7.1 With Toluene

Toluene is used as a solvent for the primer delivery. It was thought that possible disruption of the polymer surface by the solvent mixture could aid diffusion of solvent and primer. Diffusion data was recorded after treatment, see figures 4.15-4.17.

Figure 4.15. Diffusion Plot for Immersed PP with Toluene as the Diffusant.
Figure 4.16. Diffusion Plot of Immersed PE with Toluene as the Diffusant.

Figure 4.17. Diffusion Plot for Immersed BPP with Toluene as the Diffusant.
Diffusion rates were calculated assuming Fickian diffusion and are shown in table 4.12.

<table>
<thead>
<tr>
<th>POLYMER</th>
<th>DIFFUSION COEFFICIENT *10^9 (cm^2 s^-1)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BLANK</td>
</tr>
<tr>
<td>PP</td>
<td>10.21</td>
</tr>
<tr>
<td>PE</td>
<td>16.29</td>
</tr>
<tr>
<td>BPP</td>
<td>25.66</td>
</tr>
</tbody>
</table>

Table 4.12. Calculated Diffusion Coefficients for Immersed Polymers with Toluene as the Diffusant.

Maximum uptake of the toluene was also calculated and shown in table 4.13.

<table>
<thead>
<tr>
<th>POLYMER</th>
<th>UPTAKE WEIGHT PER UNIT WEIGHT (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BLANK</td>
</tr>
<tr>
<td>PP</td>
<td>96.5</td>
</tr>
<tr>
<td>PE</td>
<td>84.2</td>
</tr>
<tr>
<td>BPP</td>
<td>151</td>
</tr>
</tbody>
</table>

Table 4.13. Uptake of Toluene into Immersed Polymers.

The diffusion rates are varied but are not reflected in the changes in joint strength. When the mixture was used all the joint strengths increased but when the diffusion data is examined, PP has a higher rate after immersion whereas PE and BPP have a slower rate. For BPP and PE the diffusion into the blank is similar to the diffusion into the mixture treated. Equally there is no evidence that the total uptake is related to joint strength. Overall therefore solvent diffusion would not seem to be an important factor. This is in agreement with the work in section 4.3.5 looking at diffusion of various solvents.
4.2.7.2 With Immersion Solvents

To further investigate such changes the diffusion of the immersion solvents into the polymers were also recorded and shown in figures 4.18-4.20.

![Diffusion Plot for PP with Immersion Solvents as Diffusants.](image)

**Figure 4.18.** Diffusion Plot for PP with Immersion Solvents as Diffusants.
Figure 4.19. Diffusion Plot for PE with Immersion Solvents as Diffusants.

Figure 4.20. Diffusion Plots of BPP with Immersion Solvents as Diffusants.
The diffusion rates were calculated and shown in table 4.14.

<table>
<thead>
<tr>
<th>POLYMER</th>
<th>DIFFUSION COEFFICIENT *10^9 (cm^2s^-1)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MIX</td>
</tr>
<tr>
<td>PP</td>
<td>0.59</td>
</tr>
<tr>
<td>PE</td>
<td>3.29</td>
</tr>
<tr>
<td>BPP</td>
<td>1.03</td>
</tr>
</tbody>
</table>

**Table 4.14.** Calculated Diffusion Coefficients for Polymer with Immersion Solvents as the Diffusant.

Maximum uptake of the solvents was calculated and shown in table 4.15.

<table>
<thead>
<tr>
<th>POLYMER</th>
<th>UPTAKE WEIGHT PER UNIT WEIGHT (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MIX</td>
</tr>
<tr>
<td>PP</td>
<td>110.6</td>
</tr>
<tr>
<td>PE</td>
<td>82</td>
</tr>
<tr>
<td>BPP</td>
<td>149.5</td>
</tr>
</tbody>
</table>

**Table 4.15.** Uptake of Immersion Solvents into the Polymers.

As can be seen from the figures propanol is not taken up by the polymers very quickly or to the same extent as the heptane and the mixture. The mixture appears to be dominated by heptane. In general the diffusion rate for PE is greater than that for PP and BPP. In both PP and PE the rate is greatest for heptane. Neither diffusion coefficient nor total weight gain correlate with the observed changes in bond strength.
4.2.8 Surface Structure

A possible change in the surface structure may be responsible for the increase in the joint strength and the decrease in receding contact angle. A change in the amorphous/crystalline content at the surface can be studied by FTIR - ATR. PE was used to test the theories as this has the simplest spectrum. The peaks between 1400 cm\(^{-1}\) and 1250 cm\(^{-1}\) are due to the amorphous region of the polymer. These peaks are expected to increase in intensity as the amorphous content is increased. As can be seen from figure 4.21 the amorphous peaks did not alter in intensity after treatment.

![Figure 4.21. Amorphous Peak in the PE Spectra Before and after Treatment with Solvent Mixture.](image)
The peaks at 730cm⁻¹ and 722cm⁻¹, in a PE spectra, are sharp and are crystalline bands. There is an amorphous band at 723cm⁻¹ this is a broad band. The peak shapes at this region will change according to the crystalline/amorphous content. This region was again investigated for the PE sample. There was a slight change in crystalline peak shape after treatment as can be seen in figure 4.22. This change is small and is consistent with other results that suggest that the solvent mixture treatment is affecting the surface structure.

![Graph showing crystalline peaks of PE before and after treatment.](image)

**Figure 4.22.** Crystalline Peaks of PE Before and After Treatment.
Another way of changing the surface structure is to alter the surface orientation. This may be analysed using a polariser at various angles. The sample initially used was PE for the reasons stated previously. The doublet of peaks at 1473cm\(^{-1}\) and 1463cm\(^{-1}\) and the doublet at 730cm\(^{-1}\) and 722cm\(^{-1}\) show differences in their ratios within the doublet on changing the polariser angle, see figure 4.23. This shows that the polymer is partially oriented. After 10 minutes solvent immersion in the mixture of solvents the spectra were repeated. Changing the direction of polarisation had the same affect as before, see figure 4.24. The orientation had not been destroyed by the solvent.

![Figure 4.23. Spectra of PE Using a Polariser Before Treatment.](image-url)
Figure 4.24. Spectra of PE Using a Polariser After Solvent Treatment.
The copolymer was then used as this showed more changes in the receding angle. When the polariser angle was altered the spectra remained the same. This implies the surface of BPP is unoriented. With an unoriented surface any affects of immersion would be hard to see. All the peak heights and areas were measured and the doublets of peaks ratioed before and after immersion, there was no change at all after immersion. Subtraction was tried but still failed to resolve clear differences.

4.2.9 Conclusions

The conclusions can be split into two parts, chemical and physical changes. There are two types of chemical change possible at the surface. 1) incorporation of propan-2-ol into the polymer or 2) additive removal at the surface. There is no evidence of incorporation of propanol into the polymers. XPS does not show any evidence of oxygen at the surface but this is a vacuum technique and may remove any incorporated small alcohol molecules. IR does not show any alcohol groups at the surface but this is a less surface specific technique. Incorporation is unlikely as there is no effect on the advancing angle.

There is evidence of some additive removal. This may explain the increase in joint strength but it is difficult to explain the changes in receding angle by this alone. The mixture is more effective than heptane or propanol alone but additives in BPP are removed by both solvents and by propanol for PP.

Physical affects may be changes in crystallinity or in surface morphology. Crystallinity was probed using IR techniques and showed slight change in crystallinity but no orientation change at the surface. Surface morphology, investigated by electron microscopy STEM, showed no change in topography of PP but BPP changed after all solvent treatments. AFM showed changes in topography of PP after treatment with the mixture. The AFM for PP does help explain the receding contact angle results.
The increase in joint strength appears to be explained by removal of additive from the surface and by changes in surface topography. Most probably a combination of both is responsible for the increase in strength. The most severe roughening observed for BPP, which is the material that shows the greater increase in joint strength as a result of solvent treatment.
4.3 Primer Study

4.3.1 Introduction

The factors affecting adhesion at the polymer/primer interface were investigated. The effect of heat, type of solvent used to carry the primer to the polyolefin, possibility of a weak boundary layer at the polyolefin surface and the variation of the type of primer i.e. from a chlorinated PP to a chlorinated PE were studied.

4.3.2 Chlorinated PP Primer

PP, PE, BPP and RPP were all sprayed, with a 15% by weight solution of Cl-PP primer in toluene, painted with a two pack PU paint, cured in an oven at 70°C and the joint strength measured using a lap shear test. The results are shown in table 4.16.

<table>
<thead>
<tr>
<th>POLYMER</th>
<th>JOINT STRENGTHS (N)</th>
<th>STANDARD DEVIATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>1680</td>
<td>125</td>
</tr>
<tr>
<td>PE</td>
<td>670</td>
<td>94</td>
</tr>
<tr>
<td>BPP</td>
<td>1760</td>
<td>413</td>
</tr>
<tr>
<td>RPP</td>
<td>2020</td>
<td>144</td>
</tr>
</tbody>
</table>

Table 4.16. Lap Shear Test Results from Cl-PP Primer.

The failure surfaces were analysed by XPS to obtain the locus of failure, results shown in table 4.17.
### Table 4.17. XPS Results of Failure Surfaces.

<table>
<thead>
<tr>
<th>POLYMER</th>
<th>FAILURE SURFACE</th>
<th>XPS ANALYSIS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>%C</td>
</tr>
<tr>
<td>PP</td>
<td>Side A</td>
<td>99.4</td>
</tr>
<tr>
<td></td>
<td>Side B</td>
<td>88.5</td>
</tr>
<tr>
<td>PE</td>
<td>Side A</td>
<td>99.8</td>
</tr>
<tr>
<td></td>
<td>Side B</td>
<td>90.9</td>
</tr>
<tr>
<td>BPP</td>
<td>Side A</td>
<td>99.9</td>
</tr>
<tr>
<td></td>
<td>Side B</td>
<td>92.0</td>
</tr>
<tr>
<td>RPP</td>
<td>Side A</td>
<td>99.9</td>
</tr>
<tr>
<td></td>
<td>Side B</td>
<td>90</td>
</tr>
</tbody>
</table>

As can be seen from the XPS results there is a small proportion of chlorine remaining on the exposed polyolefin surface. The primer surface has a level of chlorine slightly lower than the standard spectrum of the pure primer. For the polymers the amount of Cl on the polymer side would be 0.35 of a monolayer and so it was concluded that the failure was principally interfacial in all cases. The small amount of chlorine detected on the polyolefin surface is close to the detection limit of the spectrometer. PP has a level of chlorine, residual on the polymer, greater than that observed for the others. The chlorine seen may be due in part to small amounts of low molecular weight material in the primer. The higher chlorine content seen on PP may indicate some entanglement.

From table 4.16 it can be seen that PP, BPP and RPP have similar joint strengths but PE has a much lower joint strength. The copolymer, RPP, has a 20% greater strength than PP homopolymer this probably due to the rubber filler within the copolymer giving the whole primed and painted system better mechanical properties.
properties. Preliminary results recently by Reihs\textsuperscript{16} indicate it may also be due to an interaction between EPDM and Cl-PP. The copolymers are mainly PP in composition, 90\% PP, so it is seen that the PP based polymers have at least a 150\% higher joint strength than PE. Possible reasons for the higher bond strength with PP based systems were examined.

4.3.3 Surface Energies

The polyolefins and the chlorinated PP primer were initially characterised using contact angles to determine their surface free energies, (see tables 4.3 and 4.4). Total surface free energies were in the range 27 - 29 mJm\textsuperscript{2} for the polyolefins and 28.5 mJm\textsuperscript{2} for the primer. These energies can be considered as approximately equal given experimental errors and it is difficult to account for the large differences in joint strength, between PP and PE, on the basis of the surface energetics alone.

4.3.4 Weak Boundary Layer

A possible reason why PP has a better joint strength is that PE may have small molecules at the surface of the polyolefin which will cause a weak boundary layer and so a poor joint. The low molecular weight content of the homopolymers were extracted by placing the polymers in boiling dichloromethane for 2 hours. The polymers were allowed to air dry and then primed and painted. Lap shear tests were carried out to obtain the joint strength and the results shown in table 4.18.
Both polymers have improved strength to the primer after solvent extraction. PP has improved by 11% whereas PE improved by 43%.

Although the joint strength measured for PE has increased PP still has a 95% greater joint strength. So a weak boundary layer is not totally responsible for the difference in joint strength between PP and PE. There could, however, be some effect due to small molecules particularly in the case of PE. Further support for this comes from the GPC traces (figure 4.1) which show that PE has a higher percentage of low molecular weight material compared with PP.

### 4.3.5 Carrier Solvent

The effect of solvent used to carry the primer was investigated to determine if the choice of solvent influenced the joint strength. The choice of solvent could alter joint strength by swelling the polymer substrate and allowing chain entanglement to occur at the interface. Chain entanglement could be extensive, where a significant amount of the primer is entangled with the polymer, or limited where only parts of the primer chain is entangled. A range of 5 solvents, toluene, dichlorobenzene, cyclohexyl chloride, dichlorobutane and xylene, were investigated. They have differing surface tensions, solubility parameters and molecular size but all dissolved the primer completely. Diffusion coefficients of these solvents into the polymer substrates have been measured and compared to the

<table>
<thead>
<tr>
<th>POLYMER</th>
<th>JOINT STRENGTH (N)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BEFORE EXTRACTION</td>
</tr>
<tr>
<td>PP</td>
<td>1680 ±125</td>
</tr>
<tr>
<td>PE</td>
<td>670 ±94</td>
</tr>
</tbody>
</table>

*Table 4.18. Joint Strengths Before and After Solvent Extraction of the Polymers.*
joint strengths for each system.

The diffusion coefficients were obtained using the system described in section 3.4.6. Figures 4.25-4.27 show the diffusion graphs for the various solvent and polymers.
Figure 4.25. Diffusion Plots of Different Carrier Solvents with PP.
Figure 4.26. Diffusion Plots of Different Carrier Solvents with PE.
Figure 4.27. Diffusion Plots of Different Carrier Solvents with BPP.
It can be seen that the solvents have vastly differing diffusion rates, these were calculated assuming Fickian diffusion and are shown in table 4.19.

<table>
<thead>
<tr>
<th>SOLVENT</th>
<th>DIFFUSION COEFFICIENTS *10^9 (cm^2s^1)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PP</td>
</tr>
<tr>
<td>Toluene</td>
<td>5.9</td>
</tr>
<tr>
<td>Dichlorobenzene</td>
<td>0.73</td>
</tr>
<tr>
<td>Cyclohexyl chloride</td>
<td>0.07</td>
</tr>
<tr>
<td>Dichlorobutane</td>
<td>0.62</td>
</tr>
<tr>
<td>Xylene</td>
<td>1.70</td>
</tr>
</tbody>
</table>

**Table 4.19.** Diffusion Coefficients for Carrier Solvents into the Polymers.

The joint strengths were obtained as before and are given in table 4.20.

<table>
<thead>
<tr>
<th>SOLVENT</th>
<th>JOINT STRENGTH (N)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PP</td>
</tr>
<tr>
<td>Toluene</td>
<td>1680 ±125</td>
</tr>
<tr>
<td>Dichlorobenzene</td>
<td>1460 ±258</td>
</tr>
<tr>
<td>Cyclohexyl chloride</td>
<td>1640 ±180</td>
</tr>
<tr>
<td>Dichlorobutane</td>
<td>1900 ±322</td>
</tr>
<tr>
<td>Xylene</td>
<td>1525 ±234</td>
</tr>
</tbody>
</table>

**Table 4.20.** Joint Strength from Use of Different Solvent Carriers for the Primer.
By visual inspection, in all instances, the failure was occurring at or near the polyolefin/primer interface. Some of the exposed surfaces were analysed by XPS to determine the locus of failure. The exposed polyolefin surfaces were found to have a small proportion of chlorine, typically 0.2 - 0.5 atom %. The other failure side had 10-11 atom % of chlorine which is close to that of the pure primer. It was again concluded the failure was largely interfacial between the polyolefin and the primer.

For each homopolymer the joint strength, across the range of solvents, is similar. This seems to indicate that the solvent used to deliver the primer does not have an effect on the joint strength. Although, as can be seen from figures 4.25 & 4.26 and table 4.19, the solvents diffuse into the polymers at a different rate. The total uptake of solvent was also calculated as this would indicate the amount of swelling and the results are shown in table 4.21.

<table>
<thead>
<tr>
<th>SOLVENT</th>
<th>UPTAKE OF SOLVENT PER UNIT WEIGHT (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PP</td>
</tr>
<tr>
<td>Toluene</td>
<td>96</td>
</tr>
<tr>
<td>Dichlorobenzene</td>
<td>57</td>
</tr>
<tr>
<td>Cyclohexyl Chloride</td>
<td>214</td>
</tr>
<tr>
<td>Dichlorobutane</td>
<td>64</td>
</tr>
<tr>
<td>Xylene</td>
<td>142</td>
</tr>
</tbody>
</table>

**Table 4.21.** Total Uptake of Carrier Solvent into the Polymers.

The uptake of solvent differs between the different solvents but again this is not reflected in the joint strengths of the homopolymers.
The copolymer BPP showed a more varied joint strength. The error on the lap shear tests for the copolymer is greater than that for the homopolymers, 15 - 25% compared to 5 - 15%. Even allowing for this greater error the solvent appears to have more of an effect. For BPP there does not appear to be any correlation between the diffusion coefficients for the solvents used and the joint strengths. There is perhaps some correlation with the uptake of solvent and the joint strength for BPP. The two solvents which give the highest joint strength, dichlorobenzene and dichlorobutane, are the two solvents which have the lowest uptake into BPP. Also the solvent with the greatest uptake, cyclohexyl chloride, gives the lowest joint strength.

Why choice of solvent should have an effect with BPP and not with the homopolymers could be due to the two components in BPP swelling at different rates and to different extents. This difference in swelling will cause physical disruption at the surface and this could be responsible for the solvents having greater importance with BPP. This was seen for exposure to heptane and propan-2-ol in section 4.2.

The results obtained for PP and PE were compared to determine whether solvent diffusion could be responsible for the difference in joint strength and whether a change of solvent could promote adhesion to PE. Table 4.20 shows that PE has a lower joint strength than PP no matter what solvent is used. So a change in solvent does not increase adhesion of the primer to PE relative to PP.
Figure 4.28. Comparison of Diffusion of Toluene into PP and PE.

Figure 4.28 shows the difference in the diffusion rates between PP and PE with toluene as the solvent. Table 4.22 shows the results of the diffusion experiments for PP and PE for toluene.

<table>
<thead>
<tr>
<th>POLYMER</th>
<th>DIFFUSION COEFFICIENT $\times 10^9$ (cm$^2$s$^{-1}$)</th>
<th>UPTAKE PER UNIT WEIGHT (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>5.9</td>
<td>96</td>
</tr>
<tr>
<td>PE</td>
<td>17.1</td>
<td>84</td>
</tr>
</tbody>
</table>

Table 4.22. Comparison of Diffusion Data for PP and PE.

If extensive solvent induced chain entanglement between primer and substrate is involved in adhesion, the amount of swelling of the polymer and the uptake of the solvent would have a
significant effect on the joint strength. If the amount of swelling were considered both have a similar uptake per unit weight and so may have similar joint strengths. If diffusion rate was important PE could be expected to have a higher joint strength as toluene diffuses into PE faster than PP in fact the reverse is found to be true. This is further evidence that there is no extensive chain entanglement promoted by the solvent swelling effects.

### 4.3.6 Heat Treatment

As can be seen the solvent carrier does not greatly effect the bond strength for PP or PE. This either means no chain entanglement is promoted or that the heat used to cure the paint and the epoxy for the LST caused rearrangement of the primer molecules, to an equilibrium state, so that the different solvent carriers all give the same joint strength.

To investigate the effect of heat treatment some primed PP pieces were not painted and instead bonded directly to the epoxy for a LST. The system was cured at room temperature for 24 hours so that no extra heat was applied. The LST results were obtained and are shown in table 4.23.

<table>
<thead>
<tr>
<th>SOLVENT</th>
<th>JOINT STRENGTH (N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>1390 ±294</td>
</tr>
<tr>
<td>Dichlorobenzene</td>
<td>1270 ±120</td>
</tr>
<tr>
<td>Cyclohexyl Chloride</td>
<td>1210 ±178</td>
</tr>
<tr>
<td>Dichlorobutane</td>
<td>1290 ±89</td>
</tr>
<tr>
<td>Xylene</td>
<td>1100 ±215</td>
</tr>
</tbody>
</table>

**Table 4.23.** Joint Strengths for Different Solvent Carriers with Room Temperature Cure.
It was not possible to see by visual inspection where the joints had failed so all failure surfaces were analysed by XPS. On analysis all failure surfaces were found to be interfacial between the primer and PP, the exception was the cyclohexyl chloride which failed cohesively in the primer. As can be seen the joint strengths are similar for each solvent, so the solvent does not appear to effect the joint strength.

In the case of PP there was an increase in joint strength, on average, by 30% when the samples were heated to cure after painting and for the epoxy resin bonding. The heat appears to increase the joint strength possibly by promoting chain entanglement. The entanglement seems to be promoted by heat rather than solvent. If heat promotes entanglement then exposure to higher temperature should further increase joint strength. The primed PP was heated in an oven at 100°C for varying times, painted and LST performed. The results can be seen in table 4.24.

<table>
<thead>
<tr>
<th>HEAT TREATMENT (hours)</th>
<th>JOINT STRENGTH (N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1680 ±125</td>
</tr>
<tr>
<td>3</td>
<td>2770 ±236</td>
</tr>
<tr>
<td>9</td>
<td>2280 ±500</td>
</tr>
<tr>
<td>21</td>
<td>2300 ±247</td>
</tr>
<tr>
<td>24</td>
<td>2770 ±166</td>
</tr>
</tbody>
</table>

Table 4.24. Affect of 100°C temperature on Joint Strengths of PP.

Heating at 100°C prior to painting increases the strength by 50%. This was attributed to increased chain entanglement. All the times used produced a similar increase in strength.

A primed piece of PP was heated at 120°C for 3 hours to study the effect of more extreme conditions. The average joint
strength was 3470N which is an additional 37% increase. The progression of the joint strength can be seen in table 4.25.

<table>
<thead>
<tr>
<th>TREATMENT</th>
<th>JOINT STRENGTH (N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Room Temp. cure</td>
<td>1390 ±294</td>
</tr>
<tr>
<td>Cure paint and epoxy</td>
<td>1680 ±125</td>
</tr>
<tr>
<td>100°C</td>
<td>2530 ±300</td>
</tr>
<tr>
<td>120°C</td>
<td>3470 ±104</td>
</tr>
</tbody>
</table>

**Table 4.25. Joint Strength Progression with Increasing Heat Treatment.**

The failure surfaces were analysed to see if there is an increase in chlorine at the polyolefin surface produced by joint failure. If there was an increase in chlorine due to heating, was this related to joint strength? The results are shown in graphical form in figure 4.29.

As can be seen from the graph there appears to be a correlation between joint strength and the amount of chlorine on the PP surface of the failure.

If heating promotes a little chain entanglement with PP could the same occur with PE? Primed PE samples were heated in an oven at 100°C for 3 and 24 hours before painting. LST were carried out and the results shown in table 4.26.

<table>
<thead>
<tr>
<th>HEAT TREATMENT</th>
<th>JOINT STRENGTH (N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>670 ±94</td>
</tr>
<tr>
<td>3 hours</td>
<td>900 ±87</td>
</tr>
<tr>
<td>24 hours</td>
<td>450 ±50</td>
</tr>
</tbody>
</table>

**Table 4.26. Affect of Heat on Joint Strengths of PE.**
No increase in joint strength, comparable to PP, was observed. In fact when heated for 24 hours the primer visibly dewetted on the surface to give small isolated spheres of Cl-PP primer at the surface. Cl-PP and PE are expected to be incompatible and it is thought that it is not possible to generate an interpenetrating polymer network.

4.3.7 Scanning Microscopy

Images, using scanning TEM, were taken of the failure surfaces from replicas. In particular the polymer side of the failure was examined to see if any evidence of chain pull out could be seen. The micrographs of the polymer side are shown in figures 4.30 and 4.31.

It can be seen from the micrographs that PE is not as rough as PP. One part of the PP failure surface showed extensive surface
Figure 4.30. STEM Micrographs (x16k) of PP Side of Failure.
roughness. These micrographs seem to provide evidence consistent with PP having slight chain entanglement whilst PE has none.

4.3.8 Use of a Different Primer

A chlorinated PE primer, Cl-PE, was used instead of a Cl-PP to further examine the effect of polymer/primer compatibility on joint strength. Poly vinyl chloride, PVC, was also used as a primer as this was considered an extreme chlorinated primer. A Cl-PE was used with a molecular weight close to that of Cl-PP and also a similar chlorine content. The Cl-PE and PVC were both bar spread as they proved difficult to spray. Both PP and PE were also primed with Cl-PP by K-bars to ensure compatibility of results. The K-bar specimens gave similar joint strengths to spray deposited primer.

Extraction, by dichloromethane, to remove weak boundaries from PP and PE before priming was also examined. The results of lap shear tests for Cl-PE are shown in table 4.27 and those for PVC in table 4.28.

Figure 4.31. STEM Micrograph (x16k) of PE Side of LST Failure.
Table 4.27. Affect on Joint Strength from Various Treatments with Cl-PE as the Primer.

<table>
<thead>
<tr>
<th>POLYMER</th>
<th>JOINT STRENGTH (N)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BEFORE EXTRACTION</td>
</tr>
<tr>
<td>PP</td>
<td>770 ±200</td>
</tr>
<tr>
<td>PE</td>
<td>730 ±130</td>
</tr>
</tbody>
</table>

Table 4.28. Joint Strength Before and After Extraction When PVC was the Primer.

<table>
<thead>
<tr>
<th>POLYMER</th>
<th>JOINT STRENGTH (N)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BEFORE EXTRACTION</td>
</tr>
<tr>
<td>PP</td>
<td>700 ±240</td>
</tr>
<tr>
<td>PE</td>
<td>580 ±210</td>
</tr>
</tbody>
</table>

XPS was used to examine the failure surfaces. The primer side of the failure gave values of about 11 atom% chlorine which is similar to that for pure Cl-PE. The other failure side showed little chlorine, typically about 0.3 atom % or less. The failure surfaces of PVC showed one side with 23 atom % chlorine and the other side with no chlorine. Each time failure was considered interfacial.

Extraction of the base polymer or heating of the joint once formed did not improve joint strength.

These values were compared to the values obtained with Cl-PP and shown in table 4.29.
Table 4.29. Comparison of Joint Stregths Between PP and PE with Various Primers.

<table>
<thead>
<tr>
<th>PRIMER</th>
<th>JOINT STRENGTH (N)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PP</td>
</tr>
<tr>
<td>Cl-PP</td>
<td>1680 ±125</td>
</tr>
<tr>
<td>Cl-PE</td>
<td>770 ±200</td>
</tr>
<tr>
<td>PVC</td>
<td>700 ±240</td>
</tr>
</tbody>
</table>

When PP is primed with Cl-PE or PVC the joint strength decreased from 1680N to 700N when compared with Cl-PP. This level of 700N is that which PE has when primed with Cl-PP. When PE is primed with Cl-PE or PVC no increase or decrease in joint strength could be detected. It appears that when PP is primed with Cl-PE or PVC chain entanglement does not occur and this is reflected in lower joint strengths. No entanglement is thought to occur with any primer on PE.

4.3.9 Conclusions

For all polymers the failure of the joint was principally interfacial between polymer and primer. Some entanglement was indicated with PP/Cl-PP. Surface energetics cannot explain the differences between PP and PE. Weak boundary layers exist on the surfaces of both PP and PE and joint strength can be improved by their removal. However, weak boundary layers are not the primary factor affecting bond strength in this instance.

The choice of carrier solvent, for the primer, is not an important factor in determining the joint strength of Cl-PP with PP or PE. Choice of solvent affects the joint strength of Cl-PP/BPP more. Dichlorobenzene, dichlorobutane and xylene all increase joint strength compared to toluene, the recommended solvent, whereas cyclohexyl chloride decreases the strength. The
choice of solvent does not improve PE/Cl-PP strength compared with PP/Cl-PP. Extensive chain entanglement caused by solvent swelling is unlikely as the choice of solvent would affect the swelling and so the joint strength.

Heating of the primer/polymer joint increases the strength of the PP/Cl-PP joint but prolonged heating decreases the strength of the PE/Cl-PE joint. The failure surfaces for PP/Cl-PP showed that as the joint strength increased the amount of chlorine seen on the polymer side of the joint increased. Limited chain entanglement is probably occurring and the amount of entanglement is increased as heating temperature is increased.

When the primer was changed to Cl-PE or PVC the joint strength with PP dropped to the level of Cl-PP/PE. The strength of the PE joint with the new primers did not increase and was at the same level as Cl-PP/PE. This implied that when a different primer was used with PP no entanglement occurred. The levels of joint strength can be simplified to:

1) 700N no entanglement, dispersion forces only
2) 1390N limited chain entanglement occurring
3) 1680N limited chain entanglement increased due to the curing cycles of paint and epoxy
4) 2530N increased chain entanglement due to heating at 100°C
5) 3470N further chain entanglement due to excessive heat treatment.

It can be seen that for the Cl-PP/PP joint, 700N may be attributed to dispersion forces and the remaining 980N is due to chain entanglement.

PP should have a higher joint strength with Cl-PP as it is compatible with the primer. PP is incompatible with Cl-PE and PVC and this is the reason why the strength drops. PE with Cl-PP is incompatible but it would be expected that Cl-PE/PE would produce a better joint strength; this was found not to be the case.
4.4 COMPOUNDING and SURFACE CHEMISTRY

4.4.1 Introduction

In the previous section it was demonstrated that strong joints can be produced as a result of chain entanglement at the polymer/primer interface. In this section the effect of modifying the polymer surface to promote adhesion will be investigated. Joint strengths obtained as a result of surface oxidation by flame treatment are compared to those for primed surfaces. The effect of incorporating various additives into the polymer to promote adhesion was also examined.

4.4.2 Flame Treatment

PP was flame treated and XPS spectra recorded of the flamed surface, figure 4.32. The PP was painted directly after flaming with no primer layer. Joint strength was obtained by lap shear test. The failure of the joint was always at the paint/epoxy interface so the strength of the modified polymer/paint interface is greater than the value quoted in table 4.30.

![Figure 4.32. XPS Spectra of Flame Treated PP.](image)
PP was also flamed and derivatised with TFAA, which reacts with the hydroxyl groups produced by flaming. XPS spectra were recorded of the derivatised surface, figure 4.33. The derivatised PP was again painted directly. Joint strength was obtained by a lap shear test and compared with the results from the primer study, see table 4.30. The failure surfaces were analysed by XPS and the failure was shown to be the polymer/paint interface.

![Figure 4.33. XPS Spectra of TFAA Derivatised PP.](image)
Table 4.30. Comparison of Primed PP with Flamed and Derivatised PP.

<table>
<thead>
<tr>
<th>CONDITIONS</th>
<th>JOINT STRENGTH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flamed</td>
<td>&gt;2330 ±180</td>
</tr>
<tr>
<td>Flamed &amp; derivatised</td>
<td>1800 ±416</td>
</tr>
<tr>
<td>Primed Cl-PP</td>
<td>1680 ±125</td>
</tr>
<tr>
<td>Primed Cl-PE</td>
<td>770 ±200</td>
</tr>
</tbody>
</table>

It has been shown that 116 hydroxyl groups are produced by flame treatment and are important in chemical bonding with paint. As can be seen from table 4.30 chemical bonding gives the highest joint strength. The use of TFAA to disable the hydroxyl group gave similar joint strength to that when a Cl-PP primer was used. The TFAA derivatised PP still gave a higher joint strength than when a Cl-PE primer was used, which gives no entanglement. It also gives a higher joint strength than would be expected for untreated PP/PU paint interface ~200N.

In the previous section it was suggested that the joint strength for a non entanglement dispersion only interaction is 700N. As can be seen the derivatised PP gives a joint strength of 1800N. This implies that other types of interaction are acting across the PP/PU paint interface. These could be unreacted hydroxyl groups or other groups introduced by flaming contributing to polar/acid base interactions or chemical bond formation at the interface.

4.4.3 Compounding

4.4.3.1 Introduction

The need for a primer before painting lengthens the manufacturing process. If the primer could be replaced by a
substance within the polymer blend the paint could be applied direct. The added polymer must not affect the bulk properties of the polymer. A surface migratory substance would be ideal as this could be added in small quantities but have a greater affect at the surface. The added polymer must also be compatible with the base polymer and have a sufficiently high molecular weight to provide anchorage by chain entanglement. The condition of compatibility severely limits the choice of materials since not many polymer systems are truly miscible.

4.4.3.2 Polymer Compatibility

The thermodynamics of systems containing polymer molecules was first addressed independently by Flory\textsuperscript{118} and Huggins\textsuperscript{119}. Equations were derived for the free energy of mixing, $\Delta G$, of $n_1$ moles of a polymer or solvent with $n_2$ moles of another polymer\textsuperscript{120}.

$$\Delta G = RT(n_1 \ln \phi_1 + n_2 \ln \phi_2 + \chi n_1 \phi_2)$$ \hspace{1cm} 4.1

where $\phi_1$ and $\phi_2$ are volume fractions

$\chi$ is the Flory-Huggins parameter.

Partial differentiation with respect to $n_2$, $\phi_1$ and $\phi_2$ are both functions of $n_2$, gives the chemical potential, $\mu$.

$$\mu_2 - \mu_2^0 = RT[\ln \phi_2 - (r_2 - 1)(1 - \phi_2) + \chi r_2(1 - \phi_2)^2]$$ \hspace{1cm} 4.2

$r_1$ and $r_2$ are chain segment lengths.

It is a requirement for miscibility across the complete composition range that $\chi \leq 0.5$. In fact $\chi = 0.5$ in the limit of infinite molar mass\textsuperscript{121,122} as $\phi_2 \to 0$. 

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4.4.3.3 Polymer Migration

An interface or surface can be described in thermodynamic terms by the Gibbs Adsorption Isotherm. 

Gibbs - Duhem relation for an interphase under conditions of constant temperature and pressure.

\[-Ad\gamma = \sum_{i} n_{i} d\mu_{i}\]  \hspace{1cm} 4.3

and if we define the surface excess concentration \(\Gamma_{i}\) to be

\[\Gamma_{i} = \frac{n_{i}}{A}\]  \hspace{1cm} 4.4

\(\Gamma_{i}\) is the excess amount of species \(i\) in unit area, \(A\), of the interphase.

then

\[-d\gamma = \sum_{i} \Gamma_{i} d\mu_{i}\]  \hspace{1cm} 4.5

The above equation is the Gibbs Adsorption Isotherm and is for a two component system. The surface excess of one of the components may be defined as zero and equation 4.5 reduces to

\[-d\gamma = \Gamma d\mu\]  \hspace{1cm} 4.6

from this equation if \(\Gamma\) is positive there is surface migration and when \(\Gamma\) is negative there is surface depletion. This can be shown in graphic terms as seen in figure 4.34.

The difference between ABC and BDE gives \(\Gamma\) for the migrating additive. If BDE > ABC \(\Gamma\) is positive and the substance is surface migratory. When BDE < ABC the substance is depleted at the surface.

For a full thermodynamic treatment an expression is needed for
\( \mu \) the chemical potential. Differentiating equation 4.2 with respect to \( \phi_2 \) gives

\[
d\mu = RT \left[ \frac{1}{\phi_2} + (r_2 - 1) - 2x_2(1 - \phi_2) \right] d\phi_2
\]

Substituting into the Gibbs Adsorption Isotherm

\[
-d\gamma = \Gamma d\mu = RT \left[ \frac{1}{\phi_2} + (r_2 - 1) - 2x_2(1 - \phi_2) \right] d\phi_2
\]

In general surface migration is accompanied by a decrease in surface tension (\( d\gamma \) -ve). To promote adhesion an increase in \( \gamma \) is preferred. Since \( \Gamma \) is positive for a migratory species it follows from equation 4.8 that for an increase in \( \gamma \) with increasing concentration of added polymer.

Figure 4.34. Graphical Representation of Surface Migration.
In the limit of infinite molar mass then the requirements for migration with increase in $\gamma$ are $\chi>0.5$. This requirement is clearly inconsistent with the existence of a miscible blend.

Flory-Huggins theory assumes simple lattice model, no volume change on mixing and configurational entropy. More complex theories attempt to allow for these factors\textsuperscript{123}. Nevertheless migration with increase in surface free energy is unlikely.

However there are two ways in which a substance could perhaps be used as a surface migratory compound and still be favourable to paint.

1) Use of a substance which will migrate to decrease surface free energy but could reorientate if exposed to polar solvents or if hydrogen bonding was possible. PVME is one such compound having lower surface free energy than polyolefins but able to undergo specific hydrogen bonding interactions with aqueous systems. Koberstein et al.\textsuperscript{124} have shown that PVME is a surface migratory substance in his work with polystyrene/PVME blends.

2) Use of an additive which is not surface migratory in air but will migrate if heated in contact with a top coat. Again this requires specific interactions between top coat and additive.

Both possibilities have been investigated in this section.

4.4.3.4 Control Copolymer

The copolymer granules were compounded without any surface additives to provide a control. The compounded copolymer was subjected to the same procedures as the compound containing additive.
A freshly cut surface of the material was analysed by XPS 
a) After pressing against PET at 150°C (to give a flat film for use in lap shear test) 
b) After immersion in methanol 
c) After heating at 100°C for 24 hours.

XPS of the control polymer showed no oxygen from the first two treatments but 2 atom % oxygen after heating which came from additive migration. From the control piece it is seen that there is no transfer of small molecules from the PET to the copolymer piece.

The joint strengths of the compounded control copolymer were obtained from a pressed sample piece sprayed directly with polyurethane paint. The average joint strength was 170N.

4.4.3.5 Acrylic Acid

Acrylic acid was used in an attempt to introduce acid groups into the surface. It was commercially available as a copolymer with propylene so it was hoped that there would be some limited compatibility with BPP which would help bind it to the bulk.

The concentrations used were 0.5% and 5.0%. The results from XPS are shown in table 4.31.

<table>
<thead>
<tr>
<th>TYPE OF POLYMER</th>
<th>% OXYGEN</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PRESSED</td>
</tr>
<tr>
<td>BPP/P(P-AA)0.5%</td>
<td>0.7</td>
</tr>
<tr>
<td>BPP/P(P-AA) 5.0%</td>
<td>0.5</td>
</tr>
</tbody>
</table>

**Table 4.31. XPS Results for Acrylic Acid Incorporated BPP.**

The amount of oxygen at the surface after pressing is more than expected, 0.012% and 0.12%. The effect of the treatments were
unexpected in that oxygen is seen after the treatments for 0.5% but not 5.0%. The reasons for this are unclear.

The joint strengths were taken and compared to the control and are shown in table 4.32.

<table>
<thead>
<tr>
<th>TYPE OF POLYMER</th>
<th>JOINT STRENGTHS (N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>170 ±100</td>
</tr>
<tr>
<td>BPP/P(P-AA) 0.5%</td>
<td>225 ±35</td>
</tr>
<tr>
<td>BPP/P(P-AA) 5.0%</td>
<td>67 ±100</td>
</tr>
</tbody>
</table>

Table 4.32. Joint Strengths for Acrylic Acid Incorporated BPP.

It is clear that this compound is not effective in improving joint strength.

4.4.3.6 Vinyl Alcohol

A way of increasing the strength between the polymer and the paint is to introduce a group that will react with the paint. It has been shown that introducing hydroxyl groups onto the surface of a polymer by flame treatment increases the joint strength by a chemical reaction with the paint. If an alcohol containing polymer could be introduced into BPP, encouraged to surface migrate and not phase separate a better bond with the paint would be expected. A suitable commercially available copolymer of PE and vinyl alcohol was found.

Concentrations of 0.5%, 5.0% and 10.0% were used. The XPS results are shown in table 4.33.
After pressing there is no oxygen at the surface so the vinyl alcohol is not a natural migratory substance. The methanol washing encourages a little oxygen to the surface. After heating some oxygen is seen at the surface for all concentrations but this may be from additives in BPP since the levels are similar or less than those found for the BPP itself. The reason why the amount of oxygen is less may be due to the vinyl alcohol interacting with the additives package of BPP preventing its migration to the surface. This is consistent with the results in that when more vinyl alcohol is added the amount of oxygen at the surface is reduced.

The joint strengths are shown in table 4.34.

<table>
<thead>
<tr>
<th>TYPE OF POLYMER</th>
<th>JOINT STRENGTH (N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>170 ±100</td>
</tr>
<tr>
<td>BPP/P(E-OH) 0.5%</td>
<td>200 ±140</td>
</tr>
<tr>
<td>BPP/P(E-OH) 5.0%</td>
<td>240 ±80</td>
</tr>
<tr>
<td>BPP/P(E-OH) 10.0%</td>
<td>290 ±100</td>
</tr>
</tbody>
</table>

Table 4.34. Lap Shear Test Results for Vinyl Alcohol Incorporated BPP.
The vinyl alcohol may aid bonding to the paint by 17 - 70% but it does not increase it to 2330N, the level achieved by flaming the pressed piece and then painting immediately. The lack of increase may be due to non-compatibility between a PE based copolymer and the mainly PP based BPP.

A PE was used instead of BPP to investigate compatibility problems. The levels of P(E-OH) used were the same as for BPP. When the pressed compounded samples were analysed by XPS there was nitrogen at the surface. This probably indicated an antioxidant additive in the PE. The presence of the nitrogen at the surface would affect the results of any lap shear tests so the results would not be comparable to BPP. PE may have more compatibility to P(E-OH) since no discolouring of the compounded sample was seen at 10% concentration. A discolouring of the surface was observed for the BPP/P(E-OH) 10%. Compatibility can not be easily measured at such low levels.

4.4.3.7 Poly(Vinyl Methyl Ether)

PVME was used because it is a known migratory additive in polystyrene, similar behaviour may be expected with polyolefins. It also has the possibility, at the surface, of interacting with hydroxyl containing compounds via hydrogen bonding. PVME was used at concentrations of 0.5% and 5.0%. The results from XPS are shown in table 4.35.

<table>
<thead>
<tr>
<th>TYPE OF POLYMER</th>
<th>% OXYGEN</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PRESSED</td>
</tr>
<tr>
<td>BPP/PVME</td>
<td></td>
</tr>
<tr>
<td>0.5%</td>
<td>0.8</td>
</tr>
<tr>
<td>5.0%</td>
<td>4.5</td>
</tr>
</tbody>
</table>

Table 4.35. XPS Results for PVME Incorporated BPP.
The amount of oxygen at the surface after pressing is greater than that which would be expected, 0.1% and 1.1%. The PVME migrates to the surface readily. After compounding with 5% PVME there was a visible yellowing of the material suggesting phase separation. No such yellowing was observed for other mixtures suggesting some limited compatibility. After methanol washing more PVME comes to the surface, for 0.5% but not 5.0% this may be because the pieces were taken further away from the original compounded surface and so there may be less PVME initially. After severe heat treatment more oxygen was seen at the surface, than the control, some of this will be due to the PVME but some will be additives from the copolymer.

The joint strengths were taken and compared to the control, see table 4.36.

<table>
<thead>
<tr>
<th>TYPE OF POLYMER</th>
<th>JOINT STRENGTH (N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>170 ±100</td>
</tr>
<tr>
<td>BPP/PVME 0.5%</td>
<td>100 ±100</td>
</tr>
<tr>
<td>BPP/PVME 5.0%</td>
<td>33 ±50</td>
</tr>
</tbody>
</table>

Table 4.36. Lap Shear Test Results for PVME Incorporated BPP.

The PVME added polymers have lower joint strengths than the control. The more PVME added the weaker the joint. The assumption from this was the PVME formed a weak boundary layer at the surface. XPS of the failure surfaces were taken but as the paint contains oxygen it was difficult to see if any oxygen was due to the PVME being transferred. The polymer side did not have oxygen on it. To find out whether there was a weak boundary the Cl-PP primer was used so it would be seen if the oxygen appeared on the both sides of the failure surface. The failure surface for the PVME 5.0% are shown in table 4.37.
As can be seen from the results all the oxygen is on the primer side of the failed joint and not on the polymer. The PVME has completely separated from the copolymer. The PVME was a low molecular weight and this may have contributed to the weak boundary. The polymers may also not be compatible with each other. A copolymer of PVME and PP may be successful as an additive for BPP. With this type of system the PVME would be hoped to still be surface migratory but the PP part would bind the PVME to the bulk and therefore avoid the problems of a weak boundary layer.

4.4.3.8 Conclusions

Surface treatment is an effective way of increasing joint strength. Flame treatment of PP produced a joint which was stronger than a primed joint. Derivatisation of hydroxyl groups destroys a substantial amount of the strength introduced by flaming but the level does not drop to 'dispersion forces only' level.

None of the additives are effective as surface treatment. The use of migratory additives as adhesion promoter is difficult due to the limited compatibility of most polymer systems. An added polymer used to promote adhesion must be miscible with the base polymer to avoid formation of a weak boundary layer and also have sufficiently long chain length to allow strength to developed by chain entanglement. These are important requirements not shared by other migratory additives such as processing aids and antistatic agents.
Two special cases in which added polymers could be used to promote adhesion were discussed in this section. Of the systems studied PVME seems the most useful. It surface migrates but causes a weak boundary layer. PVME could be effective if it was in a block copolymer system which would anchor it to the bulk but not hinder the migration to a large extent.
CONCLUSIONS

It has been shown that a solvent mixture of heptane/propan-2-ol can promote adhesion to polyolefins. Results obtained using AFM suggest that the mechanism involves changes in the topography of the surface. The effect on wettability of the surface was measured by contact angle. A reduced tendency of the surface to dewet after treatment is probably responsible for the observed improvements in adhesion.

Studies of chlorinated primers used on polyolefins have shown that chain entanglement between compatible primer/substrate pairs can have a significant effect on joint strength. For the first time it has been possible to attribute the increase in joint strength due to entanglement. Extent of entanglement was measured using XPS of the failed joint surfaces. The most important factor promoting chain entanglement was heating of the formed joints. Less chain entanglement was observed without heating. Choice of solvent used to carry the primer was found to have no appreciable effect on joint strength.

Chemical alteration of the surface by flame treatment produced joint strengths higher than those obtained by using a primer. Derivatisation of a flamed surface with trifluoroacetic anhydride prevents formation of the chemicals bonds between the polymer and the paint and so reduces the joint strength to the level of a primed polymer.

Surface migration in miscible polymer blends has been discussed and a variety of added polymer systems tried in an attempt to improve adhesion of polyolefins to paint. The principal problems in improving adhesion by this mechanism are the compatibility of the blend and the requirement of surface migration. Phase separation and the presence of weak boundary layers have been found to adversely affect the adhesive properties of the systems studied. Of the systems studied PVME appears the most promising. It could be effective if it was in a copolymer system which would anchor it to the bulk but not hinder migration.
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