Surface modification of polypropylene to improve its adhesion

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Surface Modification of Polypropylene to Improve Its Adhesion

By

Enshan Sheng, B.Sc.

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

June 1992

Institute of Polymer Technology and Materials Engineering

Collaborating Departments:
Chemistry Department
Institute of Surface Science and Technology

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Dr. R.J. Heath, I.P.T.M.E.

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ABSTRACT

Surface modification of a propylene homopolymer, an ethylene / propylene copolymer, and a rubber-modified polypropylene (PP) has been studied using X-ray photoelectron spectroscopy (XPS), chemical derivatisation, contact angle measurement, scanning electron microscopy (SEM), and an adhesion test. The wettability of PP surfaces was found to have been improved by solvent treatment. Mild adhesion level was obtained using solvent vapour treatment. Chromic acid etching and priming were found effective in improving the adhesion of PP. Flame treatment was found to give excellent adhesion. Optimum air-to-gas ratio and the distance from the inner cone tip of the flame to the polymer surface were found to be ~11:1 and 0.5–1.0 cm respectively. The non-correspondence between oxygen concentration and contact angle at high oxygen concentrations was attributed to sub-surface oxidation and the orientation / migration of oxygen containing functional groups away from the near surface during the flame treatment. This hypothesis was supported by angle resolved XPS results. The use of simple surface composition models has shown that the oxidation depth induced by a mild flame treatment is between 40Å and 60Å, and that oxygen containing functional groups may have orientated or migrated a few angstroms away from the near surface for an intense flame treatment. Trifluoroacetic anhydride (TFAA) has been found to be a good derivatising reagent for hydroxyl groups. About 20% of the oxygen present on the surface of flame treated propylene homopolymer was found to be present as hydroxyl groups, while a slightly higher percentage (~30%) was found for the two copolymers. While hydroxyl groups were found unimportant in the adhesion with an epoxy adhesive, they were found important, but not essential, in the adhesion with a polyurethane paint.
Dedicated to the ones I love,

My parents
My wife
ACKNOWLEDGEMENTS

I would like to thank Dr. I. Sutherland, my supervisor in Chemistry Department, who has devoted many hours and energies to this work. His constant encouragement, constructive criticisms, and effective guidance throughout this project are very much appreciated.

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PART I. INTRODUCTION AND LITERATURE SURVEY

Chapter 1 Introduction ................................................................................................. 1
1.1 Polyolefins and their applications .................................................................. 1
1.2 Aims of the project ............................................................................................ 2

Chapter 2 Some Aspects of Adhesion ...................................................................... 4
2.1 Theories of adhesion ........................................................................................ .4
2.2 Basic requirements for good adhesion ........................................................... 6
2.3 Adhesion test methods and adhesion failure modes ........................................... 7

Chapter 3 Literature Survey on Surface Modification of Polyolefins.............. 10
3.1 Solvent treatment ............................................................................................ 10
3.2 Chemical etching .............................................................................................. 10
3.3 Corona discharge treatment ........................................................................... 13
3.4 Plasma treatment ............................................................................................. 17
3.5 Flame treatment ............................................................................................... 21
3.6 Priming ............................................................................................................ 25
3.7 Summary ............................................................................................................ 26

Chapter 4 Surface Characterisation Techniques ................................................... 27
4.1 Introduction ....................................................................................................... 27
4.2 Contact angle measurement .......................................................................... 27
4.3 Attenuated total reflection infrared spectroscopy .................................... 36
4.4 X-ray photoelectron spectroscopy .................................................................. 39
4.5 Chemical derivatisation..................................................................................... 43
9.3 Effects on diiodomethane contact angles .................................................. 102
9.4 Surface free energy estimated from contact angles ................................. 107
9.5 Effects on surface chemistry ......................................................................... 109
9.6 Adhesion levels with epoxy adhesive and polyurethane paint ........ 113
9.7 Locus of adhesion failure .............................................................................. 115

Chapter 10 Flame treatment .................................................................................... 117
10.1 Flame treatment parameters ...................................................................... 117
10.2 Surface free energy ....................................................................................... 141
10.3 Adhesion level and locus of failure ......................................................... 145
10.4 Correlation between contact angle and oxygen concentration.......... 150
10.5 Correlation between work of acid-base interaction with water ......... 155
   and oxygen concentration
10.6 The non-correspondence between water contact angle and .......... 157
   surface oxygen concentration at high oxygen concentrations
10.7 Correlation between contact angle hysteresis and oxygen .......... 165
   concentration
10.8 Overlayer thickness calculation using simple models ....................... 169
10.9 High energy resolution XPS ....................................................................... 174
10.10 Solvent immersion test ............................................................................ 178
10.11 Effects of ageing ....................................................................................... 180
10.12 Tensile properties ....................................................................................... 182

Chapter 11 Application of Primers ........................................................................ 183
11.1 Surface characterisation .......................................................................... 183
11.2 Adhesion levels ............................................................................................ 185
11.3 Locus of adhesion failure ............................................................................ 186

Chapter 12 Chemical Derivatisation ................................................................ 188
12.1 Derivatisation using model polymers ..................................................... 188
12.2 Dependence of chemical derivatisation on reservoir ......................... 197
   temperature
12.3 Chemical derivatisation of chromic acid etched propylene .......... 198
   polymer surfaces
12.4 Chemical derivatisation of flame treated propylene ..................... 199
   polymer surfaces
12.5 Role of hydroxyl groups on adhesion

PART IV CONCLUSIONS

1. Solvent treatment .............................................................. 203
2. Chromic acid etching .......................................................... 204
3. Flame treatment ................................................................. 204
4. Priming ............................................................................. 205
5. Chemical derivatisation .................................................... 206

REFERENCES ........................................................................... 207

APPENDICES

Appendix A Calibration of Flow Meters ........................................ 214
Appendix B Computer Programme (BASIC) to Calculate Surface Free Energy According to Wu's Harmonic Mean Method
Appendix C Computer Programme (FORTRAN) to Calculate the Oxidation Depth for an Oxygen-rich Surface
Appendix D Computer Programme (FORTRAN) to Calculate the Overlayer Thickness for an Oxygen-depleted Surface
Appendix E Computer Programme (BASIC) to Calculate the Oxygen Concentrations Detected by XPS for a Double Overlayer Model
Appendix F Theoretical Calculations of Elemental Compositions of Chemically Derivatised Surfaces

LIST OF PUBLICATIONS ............................................................. 225
LIST OF FIGURES

2.1 Commonly used adhesion test methods

3.1 Schematic of corona discharge treatment for polyolefin films
3.2 Schematic of plasma treatment
3.3 Schematic of flame treatment

4.1 A sessile drop resting on a solid surface
4.2 Schematic of multiple reflection ATR
4.3 Photoemission process

5.1 Schematic of solvent vapour treatment
5.2 Flame treatment rig
5.3 Double row ribbon burner
5.4 Steel butts for adhesion test
5.5 Composite butt assembly
5.6 Bonding jig
5.7 Tensile test specimen dimensions

6.1 Kruss G40 contact angle measuring system
6.2 Schematic of vacuum frame

7.1 Plots used to estimate surface free energies of untreated PPs
7.2 SEM micrographs of untreated PPs
7.3 ATR-IR spectra of untreated PPs

8.1 SEM micrograph of HPP treated by trichloroethylene vapour for 20sec
8.2 SEM micrograph of BPP treated by trichloroethylene vapour for 10sec
8.3 SEM micrograph of RPP treated by trichloroethylene vapour for 20 sec
8.4 SEM micrograph of HPP treated by trichloroethane vapour for 20 sec
8.5 Effects of trichloroethylene vapour treatment time on the adhesion of HPP to the epoxy adhesive
8.6 Effects of trichloroethylene vapour treatment time on the adhesion of HPP to the PU paint
8.7 SEM micrograph of side A in Table 8.8
8.8 SEM micrograph of side B in Table 8.8

9.1 Chromic acid etching rates at 80°C
9.2 Effects of chromic acid etching time on water contact angle at 22°C
9.3 Effects of chromic acid etching time on water contact angle at 80°C
9.4 Effects of chromic acid etching time on water contact angle hysteresis at 22°C and 80°C
9.5 SEM micrographs of PPs etched with chromic acid for 5 min at 22°C
9.6 SEM micrographs of HPP etched with chromic acid at 80°C
9.7 SEM micrographs of BPP etched with chromic acid at 80°C
9.8 SEM micrographs of RPP etched with chromic acid at 80°C
9.9 Effects of chromic acid etching time on diiodomethane contact angle at 22°C
9.10 Effects of chromic acid etching time on diiodomethane contact angle at 80°C
9.11 Effects of chromic acid etching time on diiodomethane contact angle hysteresis at 22°C and 80°C
9.12 Effects of chromic acid etching time on oxygen concentration of HPP surfaces at 22°C
9.13 Effects of chromic acid etching time on oxygen concentration of HPP surfaces at 80°C
9.14 Deconvolved C1s XPS spectra of untreated HPP and chromic acid etched HPP (5 min at 22°C)
9.15 Effects of etching time on adhesion levels with the epoxy adhesive of HPP etched with chromic acid at 22°C
9.16 Effects of etching time on adhesion levels with the epoxy adhesive of HPP etched with chromic acid at 80°C

10.1 Effects of varying air-to-gas ratio on oxygen concentration and water contact angles for HPP
10.2 Effects of varying air-to-gas ratio on oxygen concentration and water contact angles for BPP
10.3 Effects of varying air-to-gas ratio on oxygen concentration and water contact angles for RPP
10.4 Effects of varying air-to-gas ratio on oxygen concentration and diiodomethane contact angles for HPP
10.5 Effects of varying air-to-gas ratio on oxygen concentration and diiodomethane contact angles for BPP
10.6 Effects of varying air-to-gas ratio on oxygen concentration and diiodomethane contact angles for RPP
10.7 Effects of varying total flow rate on oxygen concentration and water contact angles for HPP
10.8 Effects of varying total flow rate on oxygen concentration and water contact angles for BPP
10.9 Effects of varying total flow rate on oxygen concentration and water contact angles for RPP
10.10 Effects of varying total flow rate on oxygen concentration and diiodomethane contact angles for HPP
10.11 Effects of varying total flow rate on oxygen concentration and diiodomethane contact angles for BPP
10.12 Effects of varying total flow rate on oxygen concentration and diiodomethane contact angles for RPP
10.13 Effects of varying the distance on oxygen concentration and water contact angles for HPP
10.14 Effects of varying the distance on oxygen concentration and water contact angles for BPP
10.15 Effects of varying the distance on oxygen concentration and water contact angles for RPP
10.16 Effects of varying the distance on oxygen concentration and diiodomethane contact angles for HPP
10.17 Effects of varying the distance on oxygen concentration and diiodomethane contact angles for BPP
10.18 Effects of varying the distance on oxygen concentration and diiodomethane contact angles for RPP
10.19 SEM micrographs of dried PU paint before and after wiping with steel wool
10.20 The relationship between water contact angles and surface oxygen concentration for HPP
10.21 The relationship between diiodomethane contact angles and surface oxygen concentration for HPP
10.22 The relationship between water contact angles and surface oxygen concentration for BPP
10.23 The relationship between diiodomethane contact angles and surface oxygen concentration for BPP
10.24 The relationship between water contact angles and surface oxygen concentration for RPP
10.25 The relationship between diiodomethane contact angles and surface oxygen concentration for RPP
10.26 The relationship between surface oxygen concentration and work of acid-base interaction with water for HPP
10.27 The relationship between surface oxygen concentration and work of acid-base interaction with water for BPP
10.28 The relationship between surface oxygen concentration and work of acid-base interaction with water for RPP
10.29 SEM micrographs of HPP treated by flame at various intensities
10.30 SEM micrographs of BPP treated by flame at various intensities
10.31 SEM micrographs of RPP treated by flame at various intensities
10.32 The relationship between surface oxygen concentration and contact angle hystereses of water and diiodomethane for HPP
10.33 The relationship between surface oxygen concentration and contact angle hystereses of water and diiodomethane for BPP
10.34 The relationship between surface oxygen concentration and contact angle hystereses of water and diiodomethane for RPP
10.35 Simple model for an oxygen rich surface
10.36 Simple model for an oxygen depleted surface
10.37 A simple model with double overlayers
10.38 Dependence of oxygen concentration on overlayer thickness and take-off angle according to the simple model in Fig.10.37, O1=15%, O2=5%
10.39 Deconvolved C1s spectra of flame treated HPP
10.40 Deconvolved C1s spectra of flame treated BPP
10.41 Deconvolved C1s spectra of flame treated RPP
10.42 Schematic of the immersion of an interface in a liquid

11.1 SEM micrograph of dried primer M572-170 (~20μm on HPP)
12.1 Theoretical surface oxygen and fluorine concentrations of PVA derivatised with TFAA
12.2 Experimental surface oxygen and fluorine concentrations as a function of reaction time of PVA derivatised with TFAA
12.3 Theoretical surface oxygen and nitrogen concentrations of PVMK derivatised with hydrazine
12.4 Experimental surface oxygen and nitrogen concentrations as a function of reaction time of PVMK with hydrazine
12.5 Surface oxygen and nitrogen concentrations as a function of reaction time of PET with hydrazine
12.6 Correlation between -OH concentration and original oxygen concentration under selected flame conditions for HPP
12.7 Correlation between -OH concentration and original oxygen concentration under selected flame conditions for BPP
12.8 Correlation between -OH concentration and original oxygen concentration under selected flame conditions for RPP
LIST OF TABLES

2.1 Approximate ranges of interaction energies of various types of interaction
2.2 Basic adhesion failure modes

4.1 Critical angles and depths of penetration for PP at 1700 cm\(^{-1}\) with KRS-5 and Ge

5.1 Propylene polymers used
5.2 Model polymers used for vapour-phase derivatisation

6.1 Surface tensions of contact angle liquids
6.2 Measured surface tensions of contact angle liquids

7.1 Surface free energies of untreated PPs estimated according to Owens & Wendt's approach
7.2 Dispersion contribution of surface free energy calculated according to Eq.7.3 for untreated PPs
7.3 Surface free energies of untreated PPs calculated according to Wu's approach
7.4 Contact angle hystereses of water and diiodomethane on untreated PPs
7.5 Adhesion levels of untreated PPs with epoxy adhesive
7.6 Elemental compositions of both surfaces created by adhesion testing of epoxide - HPP (untreated) - epoxide joint
7.7 Assignments of peaks in IR spectra of untreated PPs
7.8 Melting temperature, heat of fusion, and weight-fraction degree of crystallinity of untreated PPs
7.9 Tensile strength of untreated PPs at yield point

8.1 Effects of trichloroethylene wipe on water contact angles of HPP
8.2 Effects of trichloroethylene wipe on adhesion levels of PPs to PU paint
8.3 Elemental compositions of both surfaces created by adhesion testing of epoxide - PU - HPP (wiped with 1:1 by volume heptane + isopropanol) - PU - epoxide joint
8.4 Effects of solvent vapour treatment on water contact angles of PPs
8.5 Effects of solvent vapour treatment on the adhesion levels of PPs to epoxy adhesive
8.6 Effects of solvent vapour treatment on the adhesion levels of PPs to PU paint
8.7 Elemental compositions of both surfaces created by adhesion testing of epoxide - HPP (trichloroethylene vapour 20 sec) - epoxide joint
8.8 Elemental compositions of both surfaces created by adhesion testing of epoxide - PU - HPP (trichloroethylene vapour 20 sec) - PU - epoxide joint

9.1 Surface free energies of HPP etched at 22°C
9.2 Surface free energies of HPP etched at 80°C
9.3 Surface free energies of BPP etched at 22°C
9.4 Angle resolved XPS results of chromic acid etched HPP
9.5 XPS results of PPs etched by chromic acid for 5 min at 22°C
9.6 Adhesion levels with epoxy adhesive and PU paint of PPs etched by chromic acid for 5 min at 22°C
9.7 Elemental compositions of both surfaces created by adhesion testing of epoxide - PU - HPP (chromic acid etched 5 min at 22°C) - PU - epoxide joint

10.1 Surface free energies of HPP treated under selected flame conditions
10.2 Surface free energies of BPP treated under selected flame conditions
10.3 Surface free energies of RPP treated under selected flame conditions
10.4 Adhesion levels of flame treated HPP to epoxy adhesive and PU paint
10.5 Adhesion levels of flame treated BPP to epoxy adhesive and PU paint
10.6 Adhesion levels of flame treated RPP to epoxy adhesive and PU paint
10.7 Comparison of adhesion levels achieved by different surface modifications employed in the study
10.8 Surface oxygen concentrations (atomic%) before and after diethyl ether wash of HPP treated under various flame intensities
10.9 Oxidation depth results according to the simple model in Fig.10.35
10.10 Overlayer thickness results according to the simple model in Fig.10.36
10.11 Work of adhesion of some interfaces upon immersion in some liquids
10.12 Effects of ageing on surface oxygen concentration, water contact angles, and adhesion level with PU paint

10.13 Tensile strengths at yield point of untreated and flame treated PPs

11.1 Surface elemental compositions of dried primers as detected by XPS

11.2 Surface free energy (mJ m$^{-2}$) of dried primer M572-170 as estimated using Owens & Wendt's and Wu's approaches

11.3 Contact angles of water and diiodomethane on dried primer M572-170 and untreated HPP

11.4 Adhesion levels of primed HPP with epoxy adhesive and PU paint

11.5 Adhesion levels of M572-170 primed BPP and RPP with epoxy adhesive and PU paint

11.6 Elemental compositions of both surfaces created by adhesion testing of epoxide - PU - (M572-170) - HPP - (M572-170) - PU - epoxide joint

12.1 Model polymers used in vapour-phase derivatisation

12.2 Elemental compositions of model polymers and untreated HPP derivatised with TFAA for 2 hrs

12.3 Elemental compositions of model polymers and untreated HPP derivatised with hydrazine for 2 hrs

12.4 XPS results of PVA and PVMK derivatised at room temperature for 5 min with TFAA and hydrazine under different reservoir temperatures

12.5 Vapour pressures of TFAA and hydrazine at different temperatures

12.6 Effects of derivatisation with TFAA on contact angle and adhesion for HPP treated with a mild flame
### ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ATR-IR</td>
<td>attenuated total reflection infrared spectroscopy</td>
</tr>
<tr>
<td>BPP</td>
<td>ethylene/propylene copolymer (bumper grade)</td>
</tr>
<tr>
<td>DMF</td>
<td>dimethylformamide</td>
</tr>
<tr>
<td>DMSO</td>
<td>dimethylsulphoxide</td>
</tr>
<tr>
<td>DSC</td>
<td>differential scanning calorimetry</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared spectroscopy</td>
</tr>
<tr>
<td>HDPE</td>
<td>high density polyethylene</td>
</tr>
<tr>
<td>HPP</td>
<td>propylene homopolymer</td>
</tr>
<tr>
<td>IMFP</td>
<td>inelastic mean free path</td>
</tr>
<tr>
<td>LDPE</td>
<td>low density polyethylene</td>
</tr>
<tr>
<td>PAA</td>
<td>poly(acrylic acid)</td>
</tr>
<tr>
<td>PE</td>
<td>polyethylene</td>
</tr>
<tr>
<td>PET</td>
<td>poly(ethylene terephthalate)</td>
</tr>
<tr>
<td>PP</td>
<td>polypropylene</td>
</tr>
<tr>
<td>PU</td>
<td>polyurethane</td>
</tr>
<tr>
<td>PVA</td>
<td>poly(vinyl alcohol)</td>
</tr>
<tr>
<td>PVMK</td>
<td>poly(vinyl methyl ketone)</td>
</tr>
<tr>
<td>RPP</td>
<td>rubber-modified polypropylene</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscopy</td>
</tr>
<tr>
<td>SIMS</td>
<td>secondary ion mass spectrometry</td>
</tr>
<tr>
<td>SSIMS</td>
<td>static secondary ion mass spectrometry</td>
</tr>
<tr>
<td>TEM</td>
<td>transmission electron microscopy</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>WBL</td>
<td>weak boundary layer</td>
</tr>
</tbody>
</table>
PART I  INTRODUCTION AND LITERATURE SURVEY

Chapter 1 Introduction

1.1 Polyolefins and their applications

Pechman \[1\] first reported the formation of a polymer in 1898, which was tentatively identified as polymethylene, from diazomethane in ether (Eq.1.1),

\[ n\text{CH}_2\text{N}_2 \rightarrow \text{CH}_2\rightarrow n + \text{N}_2 \quad \text{Eq.1.1} \]

It is identical in composition with polyethylene (PE). Similarly, polypropylene (PP) and poly(1-butene) were first prepared from their corresponding aliphatic diazo compounds by Buckley and coworkers \[2\]. However, due to the relatively high production costs, these synthetic routes have not aroused any commercial interest.

The polymerisation of olefin monomers became possible after the successful polymerisation of ethylene under high pressure \[3\]. The discovery of Ziegler's catalyst system \[4\], which contains a metal (group I-III) alkyl and a reducible compound of a transition element (group IV-VII), e.g. TiCl\(_4\)-Al(C\(_2\)H\(_5\))\(_3\), marked an important milestone in the development of polyolefins. By using this catalyst, high quality polyethylene can be produced under atmospheric pressure and moderate temperature (50-70°C).

Natta \[5\] discovered that propylene and higher \(\alpha\)-olefin polymers can also be produced by the use of coordination catalysts, e.g. TiCl\(_4\)-Al(C\(_2\)H\(_5\))\(_3\). Natta's discovery led to the development of the PP industry and was the first event in the steric control of a polymerisation process.
There are a wide range of grades of PP to meet the needs of a large variety of applications of PP. Basic types of PP include homopolymer, copolymer, and filled polymer. Owing to their excellent mechanical properties, economy, and chemical resistance, polyolefins have found a wide range of applications. They are widely used in packaging, automotive applications, housewares, appliances, building construction, toys, artificial flowers, electrical uses, etc. [6].

The injection moulding process is employed to produce a high percentage of PP products, with automotive industry being the largest user. Battery cases, interior trim parts, seat backs, supports, child safety seats, etc. are made with impact propylene copolymers. Low modulus propylene copolymers are used for automobile bumpers. Other applications of injection moulding include container closures, medical devices, housewares and furniture. Fibres, packaging, blow moulded bottles are other fields where PP has found wide applications.

Good adhesion is required in a number of applications such as surface painting, printing, heat sealing, adhesive bonding, and metallisation. However, the chemical structure of polyolefins determines their surface properties. With very low surface free energy compared with many other polymers, untreated polyolefins surfaces are not easily wetted by most liquids. In addition, interfacial polar interaction or chemical bonding can not take place due to their chemical inertness. Therefore, in order to achieve good adhesion, some kind of surface modification is necessary. Surface modification methods for polyolefins include solvent treatment, chemical etching, corona discharge treatment, plasma treatment, flame treatment, and priming. They are described in detail in Chapter 3.

1.2 Aims of the project

Aims of this project were to examine the surface effects of a variety of surface treatments for PP, including solvent treatment, chromic acid etching, flame
treatment, and priming. The main study concentrated on flame treatment. The relative effectiveness of such treatments in improving the adhesion of PP was studied and compared.

Modified surfaces were examined using X-ray photoelectron spectroscopy (XPS), XPS in conjunction with chemical derivatisation, contact angle measurement, attenuated total reflection infrared spectroscopy (ATR-IR), and scanning electron microscopy (SEM). In the cases of chromic acid treatment and flame treatment, surface oxygen concentration as detected by XPS was correlated to contact angle results. The reactivity and selectivity of several chemical derivatisation reactions were examined using model polymers with known amount of functional groups.

In an attempt to understand the mechanism of adhesion, locus of adhesion failure was determined using special steel butts, and solvent immersion test was used. The role of hydroxyl groups on adhesion between PP and an epoxy adhesive or a polyurethane paint was studied using chemical derivatisation technique.

Simple surface elemental composition models were also developed and computer programmes written to estimate the oxidation depth or the overlayer thickness.

Functional groups introduced on the surface by chromic acid etching and flame treatment are analysed by XPS in conjunction with chemical derivatisation, and the results are compared with C1s deconvolution results.
Chapter 2 Some Aspects of Adhesion

Adhesion can be defined as the interfacial forces acting across the interface or the strength of these forces between two materials. It is the latter meaning which is normally used. Theories of adhesion, basic requirements for good adhesion, test methods to assess adhesion levels and adhesion failure types are outlined in this chapter.

2.1 Theories of adhesion

Theories of adhesion have been reviewed by many authors [7-9]. They include electrical theory, mechanical theory, diffusion theory, adsorption theory, and weak boundary layer theory.

2.1.1 Electrical theory

This theory was put forward by Deryaguin and coworkers [10-11]. It suggests that at an interface, an electrical double layer is produced, and the consequent coulombic attraction accounts for the adhesion. This theory has been criticised by Voyutskii [12] and Schonhorn [13]. Huntsberger [14] also criticised this theory and concluded that electrostatic attraction may be important in some cases, but its contribution to adhesion is normally small.

2.1.2 Mechanical theory

This theory suggests that adhesion is due to the mechanical interlocking (mechanical keying) around the irregularities or pores of the adherend. However, the formation of voids due to inadequate contact between an adhesive and an adherend with a rough surface may result from high viscosity of the adhesive or low surface free energy of the adherend. This can lead to stress concentrations and hence lower adhesion levels.
2.1.3 Diffusion theory

According to this theory, the adhesion of polymers is due to the interdiffusion of the adherend and the adhesive. Voyutskii [12] is the chief advocate of this theory. The diffusion between two polymers requires the mutual solubility and the mobility of their polymer chains. Otherwise, interdiffusion is thought to be unlikely [7].

2.1.4 Adsorption theory

This is the most popular theory. According to this theory, adhesion is achieved by intermolecular forces at the interface. Intermolecular forces can be Van der Waals' forces, quasi-chemical bonding (e.g. hydrogen bonding), or primary chemical bonding. Van der Waals' forces include London dispersion, Keesom dipole-dipole, and Debye dipole-induced dipole forces. Table 2.1 shows the approximate magnitudes of these interactions.

Table 2.1 Approximate ranges of interaction energies of various types of interaction [17]

<table>
<thead>
<tr>
<th>Type of force</th>
<th>Bond energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Chemical bonds</strong></td>
<td></td>
</tr>
<tr>
<td>Ionic</td>
<td>590 - 1050</td>
</tr>
<tr>
<td>Covalent</td>
<td>63 - 710</td>
</tr>
<tr>
<td>Metallic</td>
<td>113 - 347</td>
</tr>
<tr>
<td><strong>Intermolecular forces</strong></td>
<td></td>
</tr>
<tr>
<td>Dispersion</td>
<td>0.08 - 42</td>
</tr>
<tr>
<td>Dipole-induced dipole</td>
<td>&lt; 2</td>
</tr>
<tr>
<td>Dipole-dipole</td>
<td>&lt; 42</td>
</tr>
<tr>
<td>H-bond (involving F)</td>
<td>&lt; 42</td>
</tr>
<tr>
<td>H-bond (excluding F)</td>
<td>10 - 26</td>
</tr>
</tbody>
</table>

More recently, Fowkes [18-19] proposed the acid-base interfacial bonding...
theory. According to this theory, interfacial interaction can be divided into two parts: London dispersion interaction and acid-base interaction (including hydrogen bonding).

2.1.5 Weak boundary layer (WBL) theory

The presence of a weak boundary layer at the interface is thought to be the cause of adhesion failure. This theory has been the subject of considerable controversy since it was proposed by Bikerman. Possible causes of a WBL include the presence of contaminants (e.g. dust, grease, or low molecular weight materials), and the segregation of low molecular weight materials (e.g. plasticisers, antioxidants, etc.) from the bulk of the polymer.

2.1.6 Combination of the theories

Allen suggested that the real adhesion phenomenon can be explained by a combination of the above theories, rather than suggesting them to be exclusive. Thus,

$$\Psi = a\Psi_E + b\Psi_M + c\Psi_D + d\Psi_A + \ldots$$

Eq.2.1

where $\Psi$ is the overall adhesion, subscripts $E$, $M$, $D$, $A$ represents electrical, mechanical, diffusion, and adsorption contributions to the adhesion respectively. $a$, $b$, $c$, $d$ are their respective constants.

2.2 Basic requirements for good adhesion

To achieve good adhesion, the surface of the adherend must be energetic enough for a mobile phase (e.g. adhesive) to wet it. The wettability of the adherend depends on the surface free energies, the chemistries of both the adherend and the mobile phase, the surface topography of the adherend, the
viscosity of the adhesive and the time the adhesive is in its low viscosity state. Good intimate contact at the interface is essential for good adhesion.

In some cases surface roughness can provide a bigger potential bonding area and a possibility of interlocking of the adhesive around the irregularities or pores of the adherend. However, voids may be produced if the mobile phase can not disperse the air in the asperities in the adherend surface, leading to a decrease in adhesion level due to stress concentrations.

Weak boundary layers can be produced due to improper pretreatment of the adherend. In order to obtain satisfactory adhesion, some kind of surface pretreatment is normally necessary to eliminate the factors contributing to weak boundary layers, e.g. the presence of release agents or other surfactants on the surface.

2.3 Adhesion test methods and adhesion failure modes

Depending on the nature of the sample, various test methods can be used to assess adhesion levels. Fig.2.1 illustrates some methods which are commonly used.
A variety of adhesion failure types can be generated by an adhesion test. Table 2.2 shows some basic failure modes resulting from a tensile adhesion test.
Table 2.2 Basic adhesion failure modes

<table>
<thead>
<tr>
<th>Adhesion failure mode</th>
<th>Schematic diagram</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interfacial failure</td>
<td>![Interfacial failure diagram]</td>
</tr>
<tr>
<td>Cohesive failure</td>
<td>![Cohesive failure diagram]</td>
</tr>
<tr>
<td>Weak boundary layer (WBL) failure</td>
<td>![WBL failure diagram]</td>
</tr>
</tbody>
</table>
Chapter 3 Literature Survey on Surface Modification of Polyolefins

3.1 Solvent treatment

Solvent treatment includes solvent wipe and solvent vapour treatment. In many cases, a solvent wipe can remove a potential weak boundary layer on the substrate surface and hence improve adhesion. For some polymers, such as polystyrene, poly(vinyl chloride), polycarbonate, or polyurethanes, solvent wipe is normally sufficient to obtain a satisfactory adhesion. Unfortunately, this is not the case for polyolefins. Surface roughness is normally not altered by solvent wipe, so limiting mechanical keying. Similarly, polar interaction at the interface with a mobile phase can not be expected. Solvent wipe is normally insufficient to achieve good adhesion for polyolefins.

Solvent vapour treatment has the potential to achieve a better adhesion. Trichloroethylene vapour was used by Garnish and Haskins to pretreat PP\(^{[23]}\). Extensive roughness was shown by SEM. By using double shear test, a six-fold increase in joint strength with an epoxy resin was obtained after 10 seconds exposure to trichloroethylene vapour. The possibility of overtreatment was also observed. The treatment was found to increase the contact angle of water, leading to the view that wettability was not the sole criterion to achieve good adhesion.

3.2 Chemical etching

3.2.1 General

Various strong oxidising reagents have been used for the surface pretreatments of polyolefins. They include chromic acid\(^{[24-31]}\), fuming nitric acid\(^{[32]}\), concentrated sulphuric acid\(^{[29]}\), potassium permanganate\(^{[33]}\), ammonium peroxydisulphate\(^{[34-35]}\), etc. However only chromic acid
treatment is of commercial importance and is reviewed in detail here.

3.2.2 Chromic acid treatment

Several chromic acid formations have been used, e.g.,

1) $\text{K}_2\text{Cr}_2\text{O}_7 / \text{H}_2\text{O} / \text{H}_2\text{SO}_4$ (conc. d=1.84), 5:8:100 by weight \cite{24-30},
2) $\text{Cr}_3\text{O}_7 / \text{H}_2\text{O} / \text{H}_2\text{SO}_4$ (conc. d1.84), 100:145:100 by weight \cite{31}
3) $\text{Cr}_3\text{O}_7 / \text{H}_2\text{O}$, 0.9g $\text{Cr}_3\text{O}_7$ / ml \cite{29}

among which formulation 1 is most extensively studied and commercially used. The treatment can be carried out at room temperature or at an elevated temperature.

All the studies on chromic acid treatment of low density polyethylene (LDPE), high density polyethylene (HDPE), and PP have shown significant increase in adhesion. Treatments at high temperatures (50 - 80°C) are more effective than those at room temperature. Long acid treatment may result in a cohesive failure within the polyolefin, leading to the level-off in adhesion with treatment time \cite{27}. Rates of polyolefin etching by chromic acid at 70°C were determined by Blais et al \cite{27}, with increasing order of etching rate as follows,

$$\text{HDPE} < \text{LDPE} < \text{PP}$$

This phenomenon was interpreted in terms of the relative oxidative resistance of primary, secondary, and tertiary C-H bonds, and the accessibility of chain segments to the etch solution. HDPE undergoes a relatively slow random attack on the secondary -CH$_2$- groups (less reactive than tertiary C-H groups). On the other hand, PP reacts with chromic acid rapidly due to the tertiary C-H sites in the surface layer. LDPE presents an intermediate case due to the presence of some tertiary C-H groups in the polymer.
3.2.3 Effects on surface topography

Severe roughening was observed by transmission electron microscopy (TEM) for both LDPE and HDPE after the chromic acid treatment [27]. This was suggested to be due to the acid penetration and oxidation of highly amorphous regions, resulting in the under cutting of largely unoxidised regions. These in turn are lost mechanically once relatively a few key polymer chains have been cleaved. PP, on the other hand, will be attacked rapidly by the chromic acid because of its dense tertiary C-H sites. Thus scission at relatively close tertiary C-H sites will be frequent, and the resultant products are soluble in the oxidising solution. In this sense, although the reaction is rapid, PP is subject to a relatively uniform attack, resulting in a surface with uniform topographical change.

3.2.4 Effects on surface chemistry

Attenuated total reflection infrared spectroscopy (ATR-IR) has been used to chemically characterise the polymer surface after a chromic acid treatment. Using ATR-IR, Blais et al [27] claimed the identification of -OH (\(-3300 \text{ cm}^{-1}\)), >C=O (\(-1710 \text{ cm}^{-1}\)), -SO₃H (\(-1200 \text{ cm}^{-1}\) and \(1030 \text{ cm}^{-1}\)) on chromic acid treated LDPE surfaces, while no detectable oxidation or sulphonation was observed for chromic acid etched HDPE or PP. Since no gross roughness was introduced on PP surface, the increased adhesion of PP surface was entirely attributed to the possible removal of weakly cohesive layers. Marked ATR-IR spectral changes after treatment of LDPE with CrO₃ / H₂O were also observed by Briggs et al [29]. Carbonyl groups were identified to be present on the surface after the treatment. Ketones were found to be dominant in the early stages, and carboxylic in the later stages of oxidation.

With the introduction of X-ray photoelectron spectroscopy (XPS), more surface specific analysis is now possible. XPS analysis of chromic acid treated PP shows moderate oxidation of the surface [29], contrary to the view of Blais.
et al [27]. The XPS peak intensity ratio O1s : O2s was used to estimate the modification depth of the treatment [29]. It was found that the modification depth for LDPE, HDPE and PP were all within 90Å, with PP having shallower oxidation depth. Thus this treatment only affects a very thin layer on the polyolefin surface, without altering the interior polymer. Tensile strengths of PP were measured both before and after the chromic acid treatment, and no significant difference was found [25].

3.2.5 Mechanism of chromic acid treatment

The reaction of chromic acid oxidation of polyolefins is not fully understood. Initial oxidation of CH\textsubscript{3}, CH\textsubscript{2}, and CH could be as follows,

\[ R\text{CH}_3 + K_2Cr_2O_7 + H_2SO_4 \rightarrow R\text{CH}_2OH \quad \text{Eq.3.1} \]

\[ R_2\text{CH}_2 + K_2Cr_2O_7 + H_2SO_4 \rightarrow R_2\text{CHOH} \quad \text{Eq.3.2} \]

\[ R_3\text{CH} + K_2Cr_2O_7 + H_2SO_4 \rightarrow R_3\text{COH} \quad \text{Eq.3.3} \]

Further oxidation of alcohols may give rise to ketones as in the case of R\textsubscript{2}CHOH, or aldehydes as in the case of RCH\textsubscript{2}OH, and scission products such as ketones, aldehydes, carboxylic acids, etc.

3.3 Corona discharge treatment

3.3.1 General

Corona discharge treatment is an electrical discharge treatment at atmospheric pressure. It is best suited for uniform flat surfaces and is widely used as a surface modification method for polyolefin films, and to a lesser extent for containers. It can be directly integrated into production lines. A
A typical corona discharge treatment for polyolefin films is illustrated in Fig. 3.1.

![Diagram of corona discharge treatment for polyolefin films](image)

Fig. 3.1 Schematic of corona discharge treatment for polyolefin films

The film is passed through an earthed and dielectrically covered base roll, on the top of which a dielectric tube is placed. The gap between the tube surface and the film surface is typically ~1 mm. The film is treated by the ionised gas in the gap created by a high voltage with a high frequency. Multiple dielectric tubes are sometimes used in corona discharge treatment. Important factors affecting the treatment include the power consumed in the discharge, the size of the gap, the film speed, the chemical nature of the gas used for the discharge, and the temperature of operation. High film speed will increase the production rates, but may be at the expense of the effectiveness of treatment. This can be compensated by increasing the power consumed in the discharge, or by the use of multiple dielectric tubes. Effects of some process parameters have been shown by Kruger et al. Various gases can be used in a corona discharge treatment. For example, air, oxygen, nitrogen,
argon, helium, and carbon dioxide have all been applied to the treatment. At a given voltage, it has been shown by Stradal and Goring \cite{37} that the autohesion enhancement of LDPE is only affected by the power consumed in the discharge regardless of the chemical nature of the gas used (O₂, N₂, Ar, He).

3.3.2 Effects on surface topography

Kim and Goring \cite{38} examined the surface morphology of LDPE after corona discharge treatment in various gases. Extensive surface roughness was observed after corona treatment in an oxygen-containing gas (e.g. O₂, air), while treatment in an "inert" gas (e.g. N₂, Ar, He) or H₂ produced a very smooth surface. Surface roughness generated by an oxygen corona was found to increase with time and temperature of the treatment.

3.3.3 Effects on surface chemistry

ATR-IR has been widely used to study the surface chemistry resulted from corona discharge treatment, especially before a much more surface specific technique like XPS was available. By treating LDPE in O₂ corona discharge, Stradal and Goring \cite{37} were unable to detect any oxidation (the presence of >C=O) on the surface using ATR-IR before the bond strength reached its peak, while Blythe et al. \cite{39} detected significant oxidation following a sub-optimal treatment in air corona discharge. Kim and Goring \cite{38} also detected considerable oxidation (>C=O) by ATR-IR on a LDPE surface treated by O₂ corona discharge. The >C=O peak was found to decrease after solvent dipping in CCl₄, suggesting the removal of the degradation products on the surface.

As a more surface specific technique, XPS is able to detect the oxidation within a depth of ~100Å. Briggs and coworkers reported some of the earliest
work in which XPS was used to study polyolefin surfaces treated by corona discharge \[39-41\]. XPS has shown the surface oxidation of LDPE treated by O\(_2\), N\(_2\), Ar, He corona discharge even at low treatment levels, which can not be matched by ATR-IR. Curve fitted XPS spectrum of the treated LDPE has suggested the existence of different oxygen containing functional groups, such as -OH, >C=O, >COO-. To overcome this problem chemical derivatisation technique can be used in order to obtain a detailed picture of the oxidised surface (see section 4.5, Chapter 4). By using gas-phase derivatisation, Gerenser and coworkers \[42\] were able to tag \(~76\%\) of the oxygen incorporated onto corona discharge treated HDPE surfaces, which were identified as -C-O-OH, -OH, isolated >C=O, epoxy and carboxylic acid.

3.3.4 Effects on adhesion

Adhesion of polyolefins can be significantly increased by corona discharge treatment. The increase in adhesion was found to be accompanied by large decrease in contact angle \[43-44\]. There are several theories concerning the increased adhesion generated by corona discharge treatment, including electret formation \[45\], improvement in surface cohesion of the polymer substrate \[46\], and the oxidation of the surface \[47\]. The last theory, due to Owens, was based on the study on the autohesion of LDPE treated by corona discharge. He found that the application of a hydrogen bonding liquid to the adhesive joint completely destroyed the adhesion and that the effects of liquids were reversible. Various chemicals were reacted with the surface to affect the enolisation of ketone groups to a certain extent. Different levels of autohesion were obtained after a reaction, depending on the extent of the influence on the enolisation. The enolisation was completely disabled by the reaction with some reagents (e.g. Br\(_2\)/H\(_2\)O, phenylhydrazine), leading to a total loss of adhesion. He then concluded that the hydrogen bonding between the ketone and enol tautomers of carbonyl groups was responsible for the enhanced adhesion. Briggs and Kendall's work \[40\] also supported this hypothesis.
3.3.5 Mechanism of corona discharge treatment

The most likely mechanism of corona discharge treatment in an oxygen containing gas is a free radical process \[^{[41]}\]. Free radicals can be caused by high energy particles (ions, electrons etc.) produced by corona discharge,

\[
\begin{align*}
R-H & \rightarrow R^* + H^* \\
R-R' & \rightarrow R^* + R'^*
\end{align*}
\]

These chain radicals can react rapidly with $O_2$ to form hydroperoxides from which different functionalities are produced, including -OH, >C=O, carboxylic acid, ester and ether groups, etc.

3.4 Plasma treatment

3.4.1 General

Plasma treatment is an electrical discharge treatment at low pressure, and is also known as glow discharge treatment. Radio frequency plasma using various gases has been extensively studied. Fig.3.2 shows a diagrammatic representation of plasma treatment.

The main part of the plasma treatment is the reaction chamber where the plasma is formed by a high voltage with high frequency between two electrodes, with one of them earthed and the other connected to the high frequency generator. The low pressure necessary for the treatment is obtained by the use of a rotary pump and a diffusion pump. Various gases, including $O_2$, $N_2$, and inert gases can be used for the plasma formation.
3.4.2 Effects on wettability

Surface wettability for polyolefins as with many polymers can be significantly improved within seconds by plasma treatment in a number of gases. Remarkable decrease in contact angle were observed after plasma treatment in oxygen containing gases, e.g. O$_2$ [48-49], CF$_4$ + 5% O$_2$ [48], or in N$_2$ [48], [50-51]. However, plasma treatment of polyolefins (HDPE, PP) in Ar was found ineffective in improving their surface wettability [48]. The wettability of PE was found insensitive to ageing, while a dramatic decrease in wettability occurred with ageing time of PP was found [49]. This was suggested to be due to the migration of oxygen containing groups away from the near surface. In the case of PE, the migration was considered to be reduced by a possible crosslinking.
3.4.3 Effects on surface chemistry

XPS has been increasingly used to examine the chemical modification of a plasma treated surface. Surface oxidation was found to be generated by oxygen plasma treatment of polyolefins (PE, PP) [49]. Plasma treatment of polyolefins in N₂ was accompanied by the incorporation of nitrogen and oxygen onto the surface [50-52]. Substantial oxygen and small amount of nitrogen on the surface of PE treated by Ar plasma were detected. The unexpected incorporation of oxygen by N₂ or Ar plasma treatment, and also the incorporation of nitrogen by Ar plasma treatment, might be caused by the post-plasma radical reaction with atmospheric O₂, water vapour, or N₂ after the removal of the samples from the reactor.

Morra et al [49] studied the effects of ageing on surface oxygen concentration of O₂ plasma treated PE and PP. XPS failed to detect any change in surface oxygen concentration for both PE and PP with ageing time, while static secondary ion mass spectrometry (SSIMS) showed a decrease in oxygen concentration with ageing time for PP. Thus it was concluded that the effect of ageing on O₂ plasma treated PP was due to the migration of oxygen containing groups away from the near surface within the XPS sampling depth.

3.4.4 Effects on adhesion

Good adhesion properties of polyolefins can be obtained by plasma treatment in various gases. Hall et al [53] examined the treatments of a variety of polymers, including PE (HDPE and LDPE) and PP, with O₂ or He plasma. They found that the bond strength increased rapidly initially and then remained nearly constant, perhaps decreased in some cases at long exposure times. PP showed a rapid increase in bond strength with exposure to O₂ plasma. Helium, however, was found ineffective towards this polymer.
under normal conditions, but could produce good bond strength at high
temperatures. Morra et al \cite{49} studied the ageing of both PE and PP treated by
O\textsubscript{2} plasma, and no significant variation in pull strength was found for PE,
while PP showed a clear decrease in pull strength. This was considered to be
due to the motions of oxygen containing groups to the inside of the modified
PP layer. Hansen and coworkers \cite{54} proposed that the reason for the
improved adhesion by plasma treatment was due to the enhancement of
cohesive strength of the weak surface layer by crosslinking. They termed the
treatment as CASING (crosslinking by activated species of inert gases).
However, the effect of ageing on the pull strength of PP \cite{49} can hardly be
explained by this theory. Therefore, the improvement of adhesion by plasma
treatment is thought to be due to the incorporation of oxygen or nitrogen
onto the surface, possibly accompanied by the removal or crosslinking of a
weak surface layer, but the incorporation of oxygen or nitrogen is thought to
be of prime importance.

3.4.5 Mechanism of plasma treatment

A variety of particles exist in a plasma, including electrons, ions, radicals,
atoms, excited atoms and molecules, etc. For example, in oxygen plasma, the
excitation reactions may be represented as follows \cite{119},

\begin{align*}
O\textsubscript{2} + e & \rightarrow O\textsuperscript{-} \quad \text{Eq.3.6a} \\
O\textsubscript{2}\textsuperscript{-} & \rightarrow O + O\textsuperscript{-} \quad \text{Eq.3.6b} \\
O\textsubscript{2} + e & \rightarrow O\textsuperscript{*} + e \quad \text{Eq.3.6c}
\end{align*}

\textit{activated oxygen}
Free radicals may be produced during the plasma treatment of polyolefins.

\[ RH + O_2^* \rightarrow R^* + H^* + O_2 \quad \text{Eq. 3.7} \]

Further reactions of alkyl radical \( R^* \) may be written as

\[ R^* + O_2 \rightarrow ROO^* \quad \text{Eq. 3.8} \]
\[ \text{ROO}^* + H^* \rightarrow \text{ROOH} \quad \text{Eq. 3.9} \]

A variety of functional groups may be generated from hydroperoxides.

3.5 Flame treatment

3.5.1 General

Compared with corona or plasma treatment, flame treatment is a more economical method for the surface modification of polyolefins. Although flame treatment is sometimes used to treat films, it is usually used for thicker articles, particularly for blow moulded plastics bottles. A schematic representation of flame treatment is shown in Fig. 3.3.

In the treatment, a bottle is passed through a ribbon burner which consists of a large amount of closely spaced jets. Single or double row ribbon burners can be used. A mixture of compressed air and a fuel gas is supplied to the burner. Natural gas (predominantly methane), propane, butane, coal gas or any...
mixture of them can be used as a fuel gas.

Fig. 3.3 Schematic of flame treatment

Important parameters for flame treatment include, air-to-gas ratio, total flow rate (i.e. flame intensity), the distance from the flame inner cone tip to the surface to be treated, contact time (the time required for a single point on the surface to pass through the flame), and possibly to a lesser extent, gas type. Hurst and Schanzle [55] studied the flame conditions for the treatment of HDPE by using several primitive wetting or adhesion tests. An optimum air-to-gas ratio, 10.8:1, was found. The gas contained 96% methane and 4% ethane. Optimum distance from flame inner cone tip to the sample surface was found to be 0.6cm, and flame contact time 0.1 sec. It is important that the surface is "flashed treated" without the bulk of the polymer becoming overheated. The increase of contact time may cause dimension change or stress relieving.

3.5.2 Effects on surface chemistry
Unlike corona discharge treatment, flame treatment has received little attention by researchers. Garbassi et al. [56] studied the surface modification of PP using propane-air flame. A constant increase of oxygen concentration on the surface with the increasing number of flame treatments was observed. The oxidation depth was suggested in a later paper [57] to be 100-200Å.

Both oxygen and nitrogen were detected on a flame treated LDPE surface by Briggs et al. [58] using XPS. Curve fitting of the C1s peak suggested the existence of C-O, C=O, and carboxyl functionalities on the LDPE surface. By using XPS in conjunction with derivatisation techniques, a detailed picture of the oxidised surface can be obtained.

### 3.5.3 Effects on adhesion

Flame treatment was found effective in improving the adhesion properties of polyolefins. Briggs et al. [58] found that by using lap shear test, cohesive failure was usually observed for flame treated LDPE bonded to an epoxy resin. Garbassi et al. [56] found virtually no difference in tensile joint strength of flame treated PP with a polyacrylic-polyester or polyurethane paint by varying the iteration of flame treatment after the first treatment.

### 3.5.4 Flame chemistry

In order to understand this mechanism, it is necessary to have a brief look at the flame chemistry. In spite of many investigations, even for the simplest flame, methane flame, the precise chemistry is still not clearly established. The following discussion will concentrate on the combustion of methane [59].

Initiation of the flame reaction presumably occurs either by some surface process yielding radicals or in the gas phase by,

\[
\text{CH}_4 + \text{O}_2 \rightarrow \text{CH}_3 + \text{HO}_2
\]

Eq.3.10
The \( \text{HO}_2^* \) radicals may either attack methane or undergo radical-radical reactions to terminate the reaction chain. At relatively low temperatures, the methyl peroxy radical is formed,

\[
\cdot\text{CH}_3 + \text{O}_2 \rightarrow \cdot\text{CH}_3\text{O}_2^* \quad \text{Eq.3.11}
\]

This will react with other radicals, such as \( \cdot\text{CH}_3^* \), \( \cdot\text{CH}_3\text{O}_2^* \), and \( \text{HO}_2^* \).

\[
\cdot\text{CH}_3\text{O}_2^* + \cdot\text{CH}_3^* \rightarrow 2 \cdot\text{CH}_3\text{O}^* \quad \text{Eq.3.12}
\]

\[
\cdot\text{CH}_3\text{O}_2^* + \cdot\text{CH}_3\text{O}_2^* \rightarrow 2 \cdot\text{CH}_3\text{O}^* + \text{O}_2 \quad \text{Eq.3.13}
\]

\[
\cdot\text{CH}_3\text{O}_2^* + \text{HO}_2^* \rightarrow \cdot\text{CH}_3\text{OOH} + \text{O}_2 \quad \text{Eq.3.14}
\]

\[
\cdot\text{CH}_3\text{O}_2^* + \text{HO}_2^* \rightarrow \cdot\text{CH}_3\text{O}^* + \text{HO}^* + \text{O}_2 \quad \text{Eq.3.15}
\]

Further reaction of methoxy radicals will give methanol and formaldehyde,

\[
\cdot\text{CH}_3\text{O}^* + \text{RH} \rightarrow \cdot\text{CH}_3\text{OH} + \text{R}^* \quad \text{Eq.3.16}
\]

\[
\cdot\text{CH}_3\text{O}^* + \text{M} \rightarrow \text{HCHO} + \text{H}^* + \text{M} \quad \text{Eq.3.17}
\]

\[
\cdot\text{CH}_3\text{O}^* + \text{O}_2 \rightarrow \text{HCHO} + \text{HO}_2^* \quad \text{Eq.3.18}
\]

At higher temperatures, there is some evidence for the reaction,

\[
\cdot\text{CH}_3\text{O}_2 \rightarrow \cdot\text{CH}_2\text{OOH} \rightarrow \text{HCHO} + \text{HO}^* \quad \text{Eq.3.19}
\]

Formaldehyde can be attacked by \( \text{OH}^* \) and \( \text{H}_2\text{O}^* \) radicals,

\[
\text{HO}^* + \text{HCHO} \rightarrow \text{H}_2\text{O} + \cdot\text{CHO} \quad \text{Eq.3.20}
\]
Formyl radicals $^\cdot$CHO can react with oxygen to give carbon monoxide (Eq.3.22) or undergo direct decomposition (Eq.3.23),

$$^\cdot$CHO + $^\cdot$HO$_2$ $\rightarrow$ CO + H$_2$O$_2$$\quad$$\text{Eq.3.22}$$^\cdot$CHO + M $\rightarrow$ CO + H$^\cdot$ + M$$\quad$$\text{Eq.3.23}$$

The flame process is quite complex, and many species are present in a flame. It is probable that the flame treatment of polyolefins follows a free radical process. The process could involve the attack of flame radicals on polyolefin surfaces. Various functionalities, e.g. -OH, >C=O, carboxylic acid, ester, and ether groups can be produced via ROO$^\cdot$ or $^\cdot$ROOH.

3.6 Priming

Primers are sometimes used as an alternative to a surface modification. A primer should have good adhesion not only to the substrate, but also to the top-coating, acting as a bridge between the substrate and the top coating. It can be used as an under-coating, or alternatively as a binder for the top-coating enabling a single process. Chlorinated polyolefins have been developed as primers for polyolefins. Chlorinated PP primers, "Hardlen" developed by Toyo Kasai Kogyo Co. $^{[60]}$ have been found to give substantial improvement in the adhesion to untreated PP. Special primers have also been developed by chlorinating or chlorosulphonating a variety of polymers for different applications. Other examples of primers include CP-343-1, CP-153-2, CP-515-2, and CP-343-3 (Eastman Chemicals) which have been used either as under-coats for polyolefin plastics or as a direct addition for many top-coatings, enabling the one-coat system to be used on unprimed polyolefins $^{[61]}$.
3.7 Summary

Surface pretreatments for polyolefins, including solvent treatment, chemical etching, corona discharge treatment, plasma treatment, flame treatment, and priming, have been reviewed. Each method has its own advantages and disadvantages. Solvent wiping offers the simplest method, but is proved to be inefficient in improving the adhesion of polyolefins. Solvent vapour treatment can give a mild improvement in adhesion for polyolefins, but involves hazardous organic solvent. Satisfactory adhesion can be obtained by chemical etching, which can treat complex sections and can be easily controlled. It is time consuming and involves hazardous chemicals. Corona discharge offers the best way to treat flat sections, especially for films, being limited to simple flat shapes. Plasma treatment can be used for a broad range of substrate geometries and can be easily controlled. However it needs a much higher capital investment, and normally can only be a batch-by-batch process. Flame treatment offers the cheapest treatment and can be incorporated in a production line process. Normally only the thicker sections can be treated by flame due to the high temperature of the flame. Complex shapes are difficult to treat. Priming is an alternative to surface treatment. Complex shapes can be treated. It can also be incorporated in a flow line process. However it requires a separate paint facility.
Chapter 4 Surface Characterisation Techniques

4.1 Introduction

In the study of adhesion science, a wide range of surface characterisation techniques are available for determining both physical and chemical properties. Contact angle measurement has been widely used since last century. It is simple and can be easily set up for low cost. The surface free energy of a polymer can be estimated by contact angle measurement with the aid of an interfacial tension theory. This technique is highly surface specific, since it only characterises the interaction between a liquid and the outmost layer of atoms of the substrate. Attenuated total reflection infrared spectroscopy (ATR-IR) technique has been widely used for surface characterisation, especially before the advent of a more surface specific method. Qualitative and semi-quantitative chemical structural information can be obtained through ATR-IR. However, its surface sensitivity is limited. ATR-IR has a typical sampling depth of ~1μm. X-ray photoelectron spectroscopy (XPS) offers a much more surface specific (~100Å) analysis, and is widely used in the study of adhesion. Other surface analysis techniques, such as Auger electron spectroscopy (AES) and secondary ion mass spectrometry (SIMS), can also be used to study adhesion. All elements except hydrogen can be detected and quantified by XPS. Electron microscopy, including scanning electron microscopy (SEM) and transmission electron microscopy (TEM), can be used to obtain surface topographical information.

In this chapter, contact angle measurement, ATR-IR, XPS and chemical derivatisation are discussed.

4.2 Contact angle measurement

4.2.1 Young's equation
Considering a drop of pure liquid with surface tension $\gamma_{LV}$ resting on a smooth, homogeneous, rigid, isotropic solid surface with surface free energy $\gamma_s$ (Fig. 4.1), there exists the following relationship when the drop is at an equilibrium,

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta$$  \hspace{1cm} \text{Eq. 4.1}

This equation was stated by Young in 1805 [62]. In the equation, $\gamma_{SL}$ is the interfacial free energy between the liquid and the solid, $\theta$ is the contact angle, $\gamma_{SV}$ is the surface free energy of the solid covered with an adsorbed vapour film. $\gamma_s$ and $\gamma_{SV}$ are related through the spreading pressure $\pi_e$ of the adsorbed vapour film,

$$\gamma_{SV} = \gamma_s - \pi_e$$  \hspace{1cm} \text{Eq. 4.2}

It has been suggested that when $\theta > 0$, $\pi_e$ is negligible for low surface free energy surfaces [63-64].

Fig. 4.1 A sessile drop resting on a solid surface

Work of adhesion is defined as,
Combining Eq. 4.1 and Eq. 4.3,

\[ W = \gamma_{LV} (1 + \cos \theta) \]  

Young's equation (Eq. 4.1) ceases to hold if \( \theta = 0 \), and the imbalance of surface free energies is given by the spreading coefficient \( S \) \[^{[65]}\] ,

\[ S_{L/S(V)} = \gamma_S - \gamma_{LV} - \gamma_{SL} \]  

Spontaneous spreading will occur if \( S_{L/S(V)} > 0 \), that is, spreading will be accompanied by a decrease in free energy.

4.2.2 Contact angle hysteresis

Almost all real surfaces are physically or chemically heterogeneous, exhibiting different advancing and receding contact angles. This phenomenon is referred to as contact angle hysteresis. Quantitatively, it is normally defined as the difference between the angle observed after an advance (advancing contact angle \( \theta_{adv} \)) and the angle observed after a retreat (receding contact angle \( \theta_{rec} \)),

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

The common terms, "advancing angle" and "receding angle" are misleading in that they give the impression that measurement is made while advance or retreat is in progress \[^{[66]}\] . In fact, both angles are static.

Young's contact angle
Since contact angle hysteresis is almost universal, the Young's contact angle is not a directly measurable quantity for most surfaces. For a smooth surface, it is popular to use the advancing angle rather than the receding angle as the Young's angle, although the advancing angle can not be used as the Young's angle to estimate the overall solid surface free energy if the hysteresis is appreciable. The lower the hysteresis, the more confidence may be placed in the use of advancing contact angle as a Young's contact angle to estimate the overall surface free energy.

Cassie [67] proposed that the observed contact angle on a patchy, heterogeneous surface should be the area-weighed average,

$$\cos \theta = f_1 \cos \theta_1 + f_1 \cos \theta_2$$  \hspace{1cm} Eq.4.7

where $f_1$ and $f_2$ are the fractional areas of type 1 and type 2, respectively, and $\theta_1$, $\theta_2$ are their respective Young's contact angles. However, model considerations for contact angle hysteresis on a smooth but heterogeneous surface suggest that the resulting contact angle hysteresis is such that the advancing contact angle is representative of the low energy patches, and the receding contact angle of the high energy patches [68]. It therefore means that in this case advancing and receding contact angles are local Young's contact angles, which are representative of low energy and high energy patches, respectively. For patches smaller than 0.1 \( \mu \)m it was further shown that heterogeneity should make a negligible contribution to hysteresis [68].

Some workers report both advancing and receding contact angles, while others only report a single contact angle, either advancing or equilibrium contact angle. For instance, the following technique employed in Zisman's laboratory for applying a drop of liquid to a surface was reviewed by Neumann and Good [69]. A drop of liquid was picked up by a fine platinum
wire (0.05 - 0.1 mm in diameter) which had been cleaned by heating to red with a Bunsen burner. A drop of liquid was formed at the tip of the wire by gently flicking the wire. A sessile drop was formed by bringing the drop slowly to the surface and allowing it flow off the wire. Contact angle was then measured.

Effects of roughness on contact angle

Effects of surface roughness on contact angle have been discussed by many workers [70-75]. It was first suggested by Wenzel [70-71] that for a rough surface with a roughness coefficient \( r \), the ratio of actual area to apparent area, there exists the following relationship,

\[
\cos \theta = r \cos \theta_S \tag{Eq.4.8}
\]

where \( \theta \) is the observed contact angle, and \( \theta_S \) is the Young's contact angle on a smooth surface.

The application of Eq.4.7 to a surface which is sufficiently rough for a liquid to trap air on a solid surface gives Eq.4.9,

\[
\cos \theta = f_s \cos \theta_S - f_a \tag{Eq.4.9}
\]

where \( f_s, f_a \) are the area fractions of liquid-solid and liquid-air interfaces, \( \theta_S \) is the Young's contact angle for a smooth surface.

Effects of surface roughness on contact angle hysteresis has been studied by Johnson and Dettre [73]. It has been shown that surface roughness leads to a large number of metastable configurations. Contact angle hysteresis on rough surfaces can be qualitatively explained by assuming that the advancing and
receding contact angles are determined by a balance between the macroscopic vibrational energy of the drop and the heights of the energy barriers. The heights of energy barriers are approximately proportional to the heights of the asperities. As the energy barriers become smaller (or the vibrational energy becomes greater), hysteresis becomes less.

4.2.3 Methods of measuring contact angle

An excellent review of contact angle measurement techniques has been given by Neumann and Good [69]. Depending on the nature of the sample, different methods can be used. Measurements on flat plate, capillary tube, cylinders, rods, fibres, and powders, etc. were discussed. In the case of flat plate, a variety of techniques are available, including sessile drop or adhering gas bubble method, Wilhelmy gravitational method, capillary rise at a vertical plate method, tilting plate method, and reflection method. Among them, the sessile drop method is the most widely used one owing to the need of only small amount of liquid and small size of sample. The measurement can be carried out by directly measuring the angle from the drop profile or drop dimensions, or by interference microscopy. The accuracy is commonly claimed to be ±2°.

In the measurement of advancing or receding contact angles, if the liquid is added to the drop from a syringe with the needle passing through the upper surface of the drop, the perturbation of the liquid-vapour surface has been worried about needlessly by some researchers. If the drop is not too small, the shape of the drop in the vicinity of the solid surface is completely controlled by the energetics of the three interfaces, not by the shape of the surface far from the three-phase line [69]. In the measurement, it is best to specify some time after stopping the advance or retreat, e.g. 10 sec or 30 sec. Zografi and Johnson [75] measured advancing and receding contact angles in two ways. In the first method, the liquid was added or removed through a syringe needle remained in contact with the drop. In the second method, the liquid was
added or removed from below the sample through a \(-1\mu m\) hole. No significant difference in contact angle was observed between the two methods.

The temperature coefficient is commonly small enough that in routine measurements, thermostating is not necessary \(^{691}\). Contact angle measurement should be made with the drop in an enclosed chamber. As well as protect the drop from atmospheric contaminants, this makes it possible to have the atmosphere around the drop locally saturated with the vapour of the liquid.

4.2.4 Treatment of contact angle data obtained with a series of liquids

**Fox and Zisman's plot and critical surface tension**

By plotting \(\cos \theta \ \text{vs} \ \gamma_{LV}\) for a homologous series of liquids on a solid, Fox and Zisman \(^{76-77}\) found that a straight line could be drawn, i.e.

\[
\cos \theta = 1 + b (\gamma_{LV} - \gamma_{C})
\]

Eq.4.10

where \(\gamma_{C}\) is called the critical surface tension, and \(b\) is a constant. \(\gamma_{C}\) is a quantity characteristic of a given solid, and provides a useful means of summarising wetting behaviour.

**Good and Girifalco's approach**

Good and Girifalco \(^{78-80}\) proposed that

\[
\gamma_{SL} = \gamma_{S} + \gamma_{LV} - 2\Phi (\gamma_{S} \gamma_{LV})^{1/2}
\]

Eq.4.11

where \(\Phi\) is called interaction parameter. \(\Phi\) is a function of the molecular properties of the liquid and the solid, and can be computed from molecular
property data. For common systems, $\Phi$ lies between 0.5 and 1.0.

Fowkes' approach

The theory of surface free energy components was first proposed by Fowkes [63]. He proposed that the surface free energy of a phase could be divided up into several independent components, such as London dispersion contribution ($\gamma^d$) and polar contribution ($\gamma^p$), as represented in Eq.4.12,

$$\gamma = \gamma^d + \gamma^p \tag{Eq.4.12}$$

He then proposed that the interfacial interaction was due to the interaction of like forces, unlike forces were assumed not to interact. The interfacial free energy between a saturated hydrocarbon ($\gamma_{LP} = 0$, $\gamma_L = \gamma_{Ld}$) and a solid can be expressed as,

$$\gamma_{SL} = \gamma_S + \gamma_L - 2 (\gamma_{Sd} \gamma_{Ld})^{1/2} \tag{Eq.4.13}$$

By combining the above equation with the Young's equation (Eq.4.1), $\gamma_{Sd}$ and $\gamma_{Sp}$ can be calculated from contact angle measurement.

Owens and Wendt's approach

Fowkes' equation (Eq.4.13) was extended by Owens and Wendt [83-84],

$$\gamma_{SL} = \gamma_S + \gamma_L - 2 (\gamma_{Sd} \gamma_{Ld})^{1/2} - 2 (\gamma_{Sp} \gamma_{LP})^{1/2} \tag{Eq.4.14}$$

If one of the phases is nonpolar, Eq.4.14 will be the same as Eq.4.13. According to Eq.4.1 and Eq.4.14, the critical surface tension obtained by Fox and Zisman's plot, $\gamma_C$, was shown by Owens and Wendt to be always less than or equal to the total surface free energy [83]. It was also concluded that the use of
nonpolar liquids to determine \( \gamma_C \) leads to a value equal to \( \gamma_s^d \), and that the use of polar liquids to determine \( \gamma_C \) on nonpolar solids leads to a value considerably less than \( \gamma_s \).

**Wu's approach**

A harmonic mean method rather than the geometric mean method when calculating forces acting across the interface was proposed by Wu [85],

\[
\gamma_{SL} = \gamma_S + \gamma_L - \frac{4\gamma_S^d\gamma_L^d}{\gamma_S^d + \gamma_L^d} - \frac{4\gamma_S^p\gamma_L^p}{\gamma_S^p + \gamma_L^p} \quad \text{Eq.4.15}
\]

Eq.4.15 was claimed to give more accurate results on the interfacial free energy between two polymers or between a polymer and an ordinary liquid [85-86]. Water and diiodomethane contact angles were used.

**Equation of state approach**

Basing on thermodynamic arguments, Ward and Neumann [87] first suggested the equation of state,

\[
\gamma_{SL} = f(\gamma_{SV}, \gamma_{LV}) \quad \text{Eq.4.16}
\]

which means that the interfacial free energy is only a function of the total solid and liquid surface free energies. Spelt et al [88] found that the contact angles of two liquids with different polarities on the same solid were identical when their total surface tensions were equal. This finding agreed with the equation of state approach.

**Acid-base interaction**
It has been proposed by Fowkes \cite{16-19} that nearly all intermolecular interactions at interfaces can be reduced to two phenomena: London dispersion interaction and electron donor-acceptor (acid-base) interaction. Hydrogen bonding is regarded as a subset of acid-base interaction, and dipole-dipole interaction is considered negligible. Therefore, work of adhesion can be written as,

\[ W = W^d + W^{ab} \quad \text{Eq.4.17} \]

where \( W^d \) and \( W^{ab} \) are the work of adhesion resulting from dispersion interaction and acid-base interaction respectively. For an interface between a solid and a liquid, the work of acid-base interaction is given by,

\[ W^{ab} = W - W^d = \gamma_L \left( 1 + \cos \theta \right) - 2 \left( \gamma_s^d \gamma_L^d \right)^{1/2} \quad \text{Eq.4.18} \]

where \( \gamma_L \), \( \theta \) can be measured, \( \gamma_L^d \) can be found in literature, \( \gamma_s^d \) can be calculated according to Eq.4.13 by measuring the contact angle of a nonpolar liquid (\( \gamma_L^d = \gamma_L \)), e.g. diiodomethane, on the solid.

4.3 Attenuated total reflection infrared spectroscopy

Newton \cite{90} first discovered that at the interface between two media with different refractive indices, light extends a fraction of a wavelength into the rarer medium beyond the reflecting interface. This phenomenon is employed in attenuated total reflection infrared spectroscopy (ATR-IR) to obtain absorption spectra. Sometimes terms other than ATR are also used, including FTR (frustrated total reflection), FTIT (frustrated total internal reflection), MIR (multiple internal reflection) \cite{91}.

A number of ATR elements are available, e.g. KRS-5, germanium, silver chloride, etc. In the study of polymer surfaces, a multiple reflection ATR
element is normally used. Fig. 4.2 illustrates a single-pass multiple reflection ATR element.

![Diagram of multiple reflection ATR element](image)

**Fig. 4.2 Schematic of multiple reflection ATR**

The angle of incidence, \( \theta \), can be calculated using the following equation \[^91\] ,

\[
\theta = \theta_A - \sin^{-1} \left( \sin \left( \theta_A - \theta_E \right) / n_1 \right) \tag{Eq. 4.19}
\]

where \( \theta_A \) is the angle of incidence of the element position, \( \theta_E \) is the face angle of the ATR element.

In order to obtain total reflection, the angle of incidence, \( \theta \), from the ATR element must not be less than the critical angle, \( \theta_C \) \[^91\]

\[
\theta_C = \sin^{-1} \left( n_2 / n_1 \right) \tag{Eq. 4.20}
\]

where \( n_2 \) and \( n_1 \) are the refractive indices of the rarer medium (sample) and of the denser medium (ATR element), respectively.
Compared with some surface specific techniques, e.g. XPS, ATR-IR is not very surface specific. Its depth of penetration can be calculated as follows\textsuperscript{[92]},

\[ d_p = \frac{\lambda_1}{2\pi \left[ \sin^2 \theta - \left( \frac{n_2}{n_1} \right)^2 \right]^{1/2}} \]

where \( d_p \) is the depth into the rarer medium at which the amplitude of the radiation has reduced to \( e^{-1} \) of its value at the interface, and \( \lambda_1 = \frac{\lambda}{n_1} \) = the wavelength of radiation in the element, \( \lambda \) is the wavelength of the incident light. Table 4.1 gives the critical angles and depths of penetration for PP at 1700 cm\(^{-1}\) with reflection elements KRS-5 and germanium (Ge).

<table>
<thead>
<tr>
<th>Reflection element</th>
<th>( \theta_E )</th>
<th>( \frac{n_2}{n_1} )</th>
<th>( \theta_A )</th>
<th>( \theta )</th>
<th>( \theta_C )</th>
<th>( d_p ) at 1700 cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>KRS-5</td>
<td>45</td>
<td>0.62</td>
<td>45</td>
<td>45</td>
<td>38.4</td>
<td>1.2 ( \mu m )</td>
</tr>
<tr>
<td>KRS-5</td>
<td>45</td>
<td>0.62</td>
<td>55</td>
<td>50.9</td>
<td>38.4</td>
<td>0.84 ( \mu m )</td>
</tr>
<tr>
<td>Ge</td>
<td>60</td>
<td>0.37</td>
<td>45</td>
<td>45</td>
<td>21.9</td>
<td>0.39 ( \mu m )</td>
</tr>
<tr>
<td>Ge</td>
<td>60</td>
<td>0.37</td>
<td>55</td>
<td>56.2</td>
<td>21.9</td>
<td>0.32 ( \mu m )</td>
</tr>
</tbody>
</table>

Note: \( n_2 \) (PP) = 1.49; \( n_1 \) (KRS-5) = 2.4, \( n_1 \) (Ge) = 4.0
4.4 X-ray photoelectron spectroscopy

Also known as electron spectroscopy for chemical analysis (ESCA), X-ray photoelectron spectroscopy (XPS) is one of the most valuable surface analysis techniques now available. Its commercial instruments emerged around 1969-1970 after the pioneering work of Kai Siegbahn (Nobel Prize winner in 1981) and his colleagues. In this section, XPS theory, surface sensitivity and depth profiling, Chemical shift and deconvolution, and quantification are discussed.

4.4.1 Theory

In a basic XPS experiment, a sample is irradiated with a soft X-ray, usually Al Kα (1486.6 eV) or Mg Kα (1253.6 eV), under ultra-high vacuum (UHV). These X-ray photons penetrate into the sample surface of the order of 1-10 μm, resulting in the emission of photoelectrons (Fig. 4.3). Auger electrons are also emitted by the relaxation of an atom with a vacancy in an inner shell.

![Fig. 4.3 Photoemission process](image-url)
The measured kinetic energy \( (E_k) \) of emitted photoelectrons is given by the following equation,

\[
E_k = h\nu - E_b + \phi_s \quad \text{Eq. 4.22}
\]

where \( h\nu \) is the X-ray energy, \( E_b \) is the binding energy of the atomic orbital from which the electron originates, and \( \phi_s \) is the work function of the spectrometer. The photoelectrons emitted are collected and energy analysed by an energy analyser. Each atomic orbital of an element has its unique binding energy. Therefore the presence of an element can be determined by identifying its characteristic photoelectron peaks in an XPS spectrum (distribution of photoelectrons \( N(E) \) vs \( E_b \) or \( E_k \)).

4.4.2 Surface sensitivity and depth-profiling

In contrast to photons which can penetrate into the surface of the order of micrometers, photoelectrons can only travel through the sample surface of the order of tens of angstroms without energy loss. These electrons produce the peaks in the spectrum, while those that undergo energy loss through inelastic scattering form the background above \( E_b \) in the spectrum. Photoelectron inelastic scattering is described by the standard exponential decay law,

\[
I = I_o \exp \left( -\frac{x}{\lambda \sin \theta} \right) \quad \text{Eq. 4.23}
\]

where \( I_o \) is the original electron flux density of electrons with kinetic energy of \( E_k \), \( I \) is the flux density of electrons retaining their initial \( E_k \) after travelling through a material of thickness \( x \), \( \theta \) is the photoelectron emission angle with respect to the sample surface, and \( \lambda \) is the depth at which
photoelectrons have a probability of $1/e$ of escaping without energy loss, and is called inelastic mean free path (IMFP). $\lambda$ is material and kinetic energy dependent. If the electrons are collected normal to the sample surface, i.e. $\theta = 90^\circ$, and assuming $\lambda = 20\AA$, then approximately 63%, 86%, 95% of the XPS signal originate from atoms within the outer 20Å, 40Å, and 60Å respectively. Therefore, XPS is a very surface specific technique.

Composition-depth profiling can be carried out in a number of ways \[94\]. They can be divided into two main categories, non-destructive and destructive methods. Non-destructive methods include the analysis using different core levels of the same element, the analysis using different X-ray sources, and the analysis using different take-off angles. The former two methods use the dependence of $\lambda$ on $K_E$, while the last one uses the dependence of sampling depth on the angle of emission. The sampling depth obtainable using non-destructive methods is limited, being up to $\sim100\AA$. A destructive method has to be employed to probe to a greater depth, with the most popular method being the in-situ inert gas ion etching of the specimen. A major limitation for ion etching is its destructive nature, which may lead to erroneous conclusions if sufficient care is not taken in the interpretation. Ion-induced damage is particularly severe with polymeric systems.

4.4.3 Quantification

Quantitative data can be obtained by measuring the peak intensity (peak area following background removal) which depends on a number of factors. For a sample which is homogeneous within the analysis depth, the intensity of a specific spectral peak, the number of photoelectrons per second ($I$) can be written as $[95]$

$$I = n \cdot \chi \cdot \sigma \cdot \gamma \cdot \lambda \cdot T \cdot D \quad \text{Eq.4.24}$$
where \( n \) is the number of atoms of the element per unit volume. \( \chi \) is the X-ray flux. \( \sigma \) is the photoionisation cross-section. \( \gamma \) is the angular asymmetry factor. It takes account of the fact that the probability of observing photoemission from an orbital possessing angular dependence (i.e. p, d, f, ... orbitals) depends on the angle between the incoming X-ray photon and the ejected photoelectron. \( \lambda \) is the inelastic mean free path (IMFP) of the emitted photoelectrons in the sample. Empirical relationships between \( \lambda \) and the kinetic energy of emitted photoelectrons were proposed by Seah and Dench [96]. \( T \) is the transmission efficiency of the energy analyser. \( D \) is the detector efficiency. Eq.4.23 can be rearranged as follows,

\[
n = \frac{I}{(\chi \cdot \sigma \cdot \gamma \cdot \lambda \cdot T \cdot D)}
\tag{Eq.4.25}
\]

By assigning \( S = \chi \cdot \sigma \cdot \gamma \cdot \lambda \cdot T \cdot D \),

\[
C_A = \frac{n_A}{\sum_i n_i} = \frac{I_A}{S_A} / \sum_i \frac{I_i}{S_i}
\tag{Eq.4.26}
\]

where \( A \) denotes atoms type, \( C_A \) is the fractional atomic concentration. \( S \) is the relative atomic sensitivity factor. \( S \) can be calculated using semi-empirical equations or derived experimentally by recording spectra of standard materials of known concentrations.

4.4.4 Chemical shift and deconvolution

The binding energy of an atomic orbital can be affected by the atom's chemical environment. The binding energy difference caused by the change of chemical environment is termed as the "chemical shift". The ability of XPS to detect this shift (ranging from 0.1 up to 10 eV or more) is important. Some information on surface chemistry can be deduced from the chemical
shift data. For example, the curve fitted C 1s peak in a spectrum of LDPE after a discharge treatment gave three peaks \[39\]. They were ascribed to -CH\(_2\)O- (e.g. alcohol, ether, hydroperoxide) at 286.5 eV, \(\text{C}=\text{O}\) (e.g. aldehyde, ketone) at 288.0 eV, and -C(=O)-O- (e.g. carboxylic acid, ester) at 289.5 eV, with their chemical shifts being 1.5 eV, 3.0 eV, and 4.5 eV respectively with reference to the C 1s binding energy of -CH\(_2\)- (285.0 eV).

The chemically shifted peak can be obscured by peak overlap. A variety of factors contribute to peak width, including the energy resolution of the electron energy analyser and the line width of the photon source used. The removal of this contribution is known as deconvolution. Some improvement in energy resolution can be obtained by using a monochromator or various computational methods.

4.5 Chemical derivatisation

Although XPS is a valuable tool for elucidating chemical structure from the chemical shift, functional groups can not always be conclusively identified. Chemical derivatisation technique can substantially extend the capability of XPS. It uses a chemical reagent which can react specifically with a particular kind of functional group. The derivative has a unique element which can be easily detected and quantified by XPS, thereby indicating surface concentration of functional groups present on the surface. Chemical derivatisation reactions for some functional groups have been summarised by Briggs\[97\].

Derivatisation using a solution reaction has been extensively studied. A comprehensive study by Everhart and coworkers \[98\] used a number of solution reactions to analyse various functional groups on LDPE surfaces introduced by plasma treatment. Briggs and Kendall \[99\] studied corona discharge treated LDPE and related the derivatisation results with adhesion levels. Vapour-phase reaction of sulphur dioxide was also used in their study.
to identify hydroperoxy groups on modified LDPE surfaces.

There exist some possible problems inherent in the use of solution reaction for derivatisation. The solvent used may increase the polymer chain mobility on the surface and therefore result in the reorientation of some functional groups into the bulk. It could also dissolve low molecular weight materials on the surface into the solution, especially for modified surfaces. The reorientation of functional groups could also arise from high temperatures, long reaction times, and prolonged washing after reaction. If ionic derivatives are employed, the washing can be problematical. For example, Everhart et al [98] used alcoholic NaOH to derivatise acid groups, and found that sodium incorporation was not reproducible and was highly dependent on the washing conditions after the reaction.

Considering the above problems associated with solution reactions, vapour-phase derivatisation can be employed. Hammond et al [100-101] first used trifluoroacetic anhydride (TFAA) in vapour-phase to derivatise a hydroxyl model polymer with known amount of hydroxyl groups, a copolymer of methyl methacrylate (MMA) and hydroxypropyl methacrylate (HPMA). The reaction was proved to be successful. They also suggested that there existed a preferential orientation of hydroxyl groups away from the surface and that this orientation was not disturbed by the derivatisation reaction, resulting in the orientation of trifluoromethyl groups introduced by the reaction away from the surface. Vapour-phase derivatisation was also used by Gerenser et al [42] to identify and quantify hydroperoxy, hydroxyl, carbonyl, epoxy, and acid groups on corona discharge treated HDPE surfaces. Some oxygen containing species were thought to have been identified, and accounted for 76% of the oxygen detected. Pochan et al [102] used the same technique to study corona discharged treated poly(ethylene terephthalate). Various oxygen containing groups which accounted for 75% of the oxygen detected were claimed to have been identified.
5.1 Materials and chemicals

5.1.1 Materials

Three propylene polymers, including one homopolymer and two copolymers, were used. Details are given in Tables 5.1 and 5.1a. Model polymers used for vapour-phase derivatisation are listed in Table 5.2.

Table 5.1 Propylene polymers used

<table>
<thead>
<tr>
<th>Type</th>
<th>Abbreviation</th>
<th>Manufacturer</th>
<th>Ref. No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>homopolymer</td>
<td>HPP</td>
<td>Neste</td>
<td>VB8050B</td>
</tr>
<tr>
<td>ethylene/propylene copolymer</td>
<td>BPP</td>
<td>ICI</td>
<td>GWM213</td>
</tr>
<tr>
<td>rubber-filled</td>
<td>RPP</td>
<td>ICI</td>
<td>D1031 5F76</td>
</tr>
</tbody>
</table>

Table 5.2 Model polymers used for vapour-phase derivatisation

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Abbreviation</th>
<th>Molecular weight</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(vinyl alcohol)</td>
<td>PVA</td>
<td>~14,000</td>
<td>Aldrich</td>
</tr>
<tr>
<td>Poly(acrylic acid)</td>
<td>PAA</td>
<td>~250,000</td>
<td>Aldrich</td>
</tr>
<tr>
<td>Poly(vinyl methyl ketone)</td>
<td>PVMK</td>
<td>n/a</td>
<td>Aldrich</td>
</tr>
<tr>
<td>Poly(ethylene terephthalate)</td>
<td>PET</td>
<td>n/a</td>
<td>ICI</td>
</tr>
</tbody>
</table>
### a) Details of propylene polymers used

<table>
<thead>
<tr>
<th>Manufacturer</th>
<th>HPP</th>
<th>BPP</th>
<th>RPP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition</td>
<td>Neste</td>
<td>ICI</td>
<td>ICI</td>
</tr>
<tr>
<td>Melt flow index</td>
<td>isotactric homopolymer</td>
<td>~10% ethylene block copolymer</td>
<td>blend of PP and 20-30% EPDM</td>
</tr>
<tr>
<td>(g/10 min)</td>
<td>3.0</td>
<td>2.0</td>
<td>4.0</td>
</tr>
</tbody>
</table>

### b) Details of other materials used

<table>
<thead>
<tr>
<th>Materials</th>
<th>Manufacturer</th>
<th>Components</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epoxy adhesive</td>
<td>Ciba-Geigy</td>
<td>AV100 (resin): diglycidylether of biphenol A</td>
</tr>
<tr>
<td></td>
<td></td>
<td>HV100 (curing agent): aliphatic amine</td>
</tr>
<tr>
<td>PU paint</td>
<td>ICI</td>
<td>M615-122: polyol</td>
</tr>
<tr>
<td></td>
<td></td>
<td>M210-763: isocynate prepolymer (M.W. 1000~2000)</td>
</tr>
<tr>
<td>Primer M572-170</td>
<td>ICI</td>
<td>Chlorinated polyolefin, thinner (xylene)</td>
</tr>
<tr>
<td>Primer 14-LLB</td>
<td>Toyo Kasei Kogyo</td>
<td>Chlorinated polyolefin, thinner (xylene)</td>
</tr>
</tbody>
</table>
For all polymers, pure films (100µm thick, 50µm in the case of copolymer GWM213) with no additives were kindly produced for this work by Venus Packaging. All films were handled with extreme care using tweezers to avoid contamination. Two primers, Hardlen 14-LLB (ex Toyo Kasei Kogyo) and M572-170 (ex ICI), were used. A two-pack polyurethane (PU) paint, M615-122 and M210-763 (ex ICI, 2.5:1 by volume), was used. The epoxy adhesive for adhesion test was Araldite AV100 + HV100 (ex Ciba-Geigy, 1:1 by weight) (Table 5.1b).

5.1.2 Chemicals

Trichloroethylene, trichloroethane, isopropanol and heptane (analytical grade, ex Fisons) were used for organic solvent treatment. Potassium dichromate (analytical grade) and sulphuric acid (concentrated, specific gravity 1.84), ex Fisons, and ordinary distilled water were used to prepare the chromic acid solution.

Triple distilled water was used for contact angle measurement. Other liquids with high purity (99.9+% for contact angle measurement include ethanediol, dimethylsulphoxide (DMSO), dimethylformamide (DMF), ex Romil Chemicals, and diiodomethane (ex Aldrich).

PET film (100µm) was cleaned with trichloroethylene in an ultrasonic bath. PVA, PAA, and PVMK samples were prepared by solution coating onto a PET film substrate. The coating method involved dipping a clean piece of PET film, first cleaned with trichloroethylene in an ultrasonic bath, into the solutions i.e. 10% PVA aqueous solution, 4% PAA aqueous solution, and 4% PVMK solution in DMF. The films were dried and kept in a desiccator.

Chemical reagents for liquid-phase derivatisation, trifluoroethanol (99.5+% NMR grade), pyridine (anhydrous 99+%), dicyclohexylcarbodiimide (DCC) (99%), di-tert-butylcarbodiimide (DBC 99%), and dichloromethane (anhydrous 99+) were purchased from Aldrich. Diethyl ether (anhydrous),
iso-butyl methyl ketone from Fisons were used as Soxhlet extracting solvents.

Vapour-phase derivatisation reagents, trifluoroacetic anhydride (TFAA 99+%), and hydrazine (anhydrous 98%) were purchased from Aldrich.

5.2 Surface pretreatments

5.2.1 Solvent treatment

Solvent treatment included solvent wipe and solvent vapour treatment. Trichloroethylene, trichloroethane, and isopropanol/heptane (1:1 by volume) were used in this study. Solvent wipe was carried out by wiping the polymer film with a lint-free cloth moistened with one of the above solvents. Similar effects in improving the wetting were obtained by treating the film in an ultrasonic bath with one of the above solvents. Fig.5.1 schematically illustrates the solvent vapour treatment.

Solvent vapour was produced in two beakers by boiling the solvent using an electric heater. More stable vapour was produced in the inner beaker, whereas for the outer beaker condensation occurred due to the surrounding atmosphere. After the beaker had been pervaded with solvent vapour for a couple of minutes, a piece of PP film clamped between two steel frames was put into the vapour in the inner beaker for a designated time.

5.2.2 Chromic acid etching

The chromic acid formation used was $K_2Cr_2O_7 : H_2O : H_2SO_4 (98\%, d=1.84) = 5:8:100$ (by weight). It was prepared as follows, 5 parts of potassium dichromate was put into 8 parts of distilled water. While stirring, 100 parts of concentrated sulphuric acid was slowly added into the mixture of potassium dichromate and water. It was then cooled down to room temperature. A
clear, purple red solution was produced. Chromic acid etching was carried out by dipping a piece of PP film into the chromic acid (either at room temperature or 80°C) followed by rinsing thoroughly in distilled water in four separate beakers. Fresh chromic acid was frequently introduced to replace the old solution. The etched film was then air dried and stored in a desiccator. Etching rates of the three polymers were determined gravimetrically on ~ 6cm x 6cm samples. They were periodically etched, washed, dried, and weighted.

5.2.3 Flame treatment

An internally built flame treatment rig (Fig.5.2) was used to perform the flame treatment.
It compromises a double row ribbon burner (ex WSA Components), a chain conveyor system, and an air/gas mixture supplying system. The burner consists of two rows of closely spaced jets (Fig.5.3).

In order to obtain a more uniform treatment, the burner was inclined $12^\circ$, $\arctan(1.15/5.5)$, during the treatment. The burner was fixed on a base with a toothed pinion, engaged with a non-movable rack under the base. The base with the burner can be moved forwards or backwards, facilitating the variation of the distance from the burner to the polymer film surface. Flame contact time, the time required for a single point on the polymer surface to pass through the flame, can be varied by changing the speed of the conveyor chain through a control box.
A mixture of air (supplied at \(-15\) psi) and natural gas (supplied at \(-0.25\) psi) was fed into the burner. Flow rates of air and gas were monitored by two flow meters calibrated for air at S.T.P. by manufacturers. Further calibration of the flow meters is therefore necessary (Appendix A). Air-to-gas ratio, or flame intensity can be varied by altering the flow rates of air and gas. Flame treatment was carried out by a single pass of a piece of PP film (parallel to the burner face) backed by an aluminium plate through the flame. The film was laid completely flat down on the aluminium plate by the use of adhesive tape at the back of the plate. Edges in contact with adhesive tape were discarded after the treatment.

5.2.4 Application of primers
Primers, Hardlen 14-LLB and the ICI primer M572-170, were supplied ready for use. They were air sprayed using Badger 250 spray gun (ex Badger Air Brush Co.) at a spray pressure of 0.17 MPa (25psi). Compressed air was supplied by an air compressor with water and oil filters (ex Micon Morris & Ingram Ltd.). The primers were allowed to air dry at room temperature for 5 min before the application of the PU paint. Primer thickness after drying was 15 ~ 20μm. Spraying was carried out in a well ventilated fume cupboard.

5.3 Application of surface coating

Two components of the two-pack PU paint, M615-122 and M210-763, were fully mixed together (2.5:1 by volume) to make the PU paint. The paint was then air sprayed at a spray pressure of 0.17MPa (25psi) onto a piece of PP film laid down on a glass plate by adhesive tape at edges which were discarded after curing the paint. The surface coating was air dried for ~10 min and then cured for 30 min in an oven at 90°C. The other side of the film was also coated in the same way. The thickness of dried paint was ~30μm. Surface coating was carried out in a fume cupboard, and an air-fed breathing apparatus was used during the process.

5.4 Adhesion testing

5.4.1 Joint preparation

Mild steel butts of length 50mm and diameter 28mm (Fig.5.4) were skimmed using a lathe, sandblasted, and then degreased with trichloroethylene for 30 sec in an ultrasonic bath.
Fig.5.4 Steel butts for adhesion test. Left: special butt with detachable head suitable for XPS analysis; Right: normal butt.

The butts were then coated with the epoxy adhesive. A specimen was placed between two butts to make a composite butt assembly (Fig.5.5).
These assemblies were then placed in a bonding jig (Fig.5.6) to maintain the vertical alignment. The adhesive was allowed to cure for 16 hours by placing the jig in an oven at 60°C.

5.4.2 Adhesion level testing

Joints after curing were allowed to cool to room temperature. Their tensile strengths were determined by a tensile testing machine (Instron TT) at a cross-head speed of 5 mm/min. For each sample, at least 6 joints were prepared and tested. No interfacial failure between the steel and the adhesive was observed. A joint strength as high as ~44MPa was obtained when two steel butts were bonded directly together with the epoxy adhesive, and a complex failure (interfacial + cohesive) was found. Standard deviation was about 10% of the average bond strength except for solvent vapour treatment.
where a higher percentage (up to ~40%) was found.

Fig. 5.6 Bonding jig

5.4.3 Locus of adhesion failure test

To determine the locus of adhesion failure, special butts with detachable head suitable for XPS spectrometer were used (Fig. 5.4).

The heads after the joint strength test were removed and placed in the XPS spectrometer for surface analysis. In some cases, both surfaces created by adhesion testing of a joint were carefully cut off from normal steel butts using a scalpel, and were analysed using XPS.

5.5 Measurement of tensile properties
Tensile properties of PP films (untreated or treated both sides) were determined by recording their stress-strain curves using a Lloyd tensometer (JJ) at a straining rate of 2 mm/min. Test specimens were prepared with the shape and dimensions illustrated in Fig. 5.7. Six measurements were taken for each sample, and standard deviations were found to be within 1 MPa.

![Fig. 5.7 Tensile test specimen dimensions](image)

5.6 Differential scanning calorimetry (DSC)

DSC traces were recorded using a Du Pont DSC 2910 differential scanning calorimeter. A sample of ~10mg in an aluminium pan was heated from 0°C to 200°C, kept isothermal for 1 min, and then cooled to 0°C. Heating or cooling rate was 10°C/min.
Chapter 6 Surface Characterisation

Contact angle measurement, ATR-IR, and XPS were used to characterise the polymer surfaces both before and after a surface modification. They are described in detail in this chapter.

6.1 Contact angle measurement

6.1.1 Surface tensions of liquids for contact angle measurement

Surface tensions of contact angle liquids are listed in Table 6.1. These values were used to calculate the surface free energies of PP surfaces.

<table>
<thead>
<tr>
<th>Liquid</th>
<th>$\gamma_L$</th>
<th>$\gamma^d_L$</th>
<th>$\gamma_L - \gamma^d_L$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>72.8</td>
<td>21.8</td>
<td>51.0</td>
<td>[63]</td>
</tr>
<tr>
<td>ethane-1,2-diol</td>
<td>48.3</td>
<td>29.3</td>
<td>19.0</td>
<td>[104]</td>
</tr>
<tr>
<td>DMSO</td>
<td>43.54</td>
<td>34.86</td>
<td>8.68</td>
<td>[105]</td>
</tr>
<tr>
<td>DMF</td>
<td>37.3</td>
<td>32.42</td>
<td>4.88</td>
<td>[105]</td>
</tr>
<tr>
<td>diiodomethane</td>
<td>50.8</td>
<td>49.5</td>
<td>1.3</td>
<td>[83]</td>
</tr>
</tbody>
</table>

Contact angle liquids were handled with great care. All containers for them and syringe plungers and barrels were soaked in chromic acid overnight, then washed copiously with distilled water and dried in an oven at ~200°C overnight. Each syringe was used for one liquid only. Syringe needles were washed copiously with distilled water and dried overnight. Before contact angle measurement, syringes and needles were washed using their respective liquids. Diiodomethane was stored in a dark brown bottle and
placed in the dark to avoid decomposition.

Surface tensions of all contact angle liquids at room temperature were measured with Krüss K10T tensiometer using the Du Noüy ring method. The platinum ring was cleaned by heating it to red using a Bunsen burner. At least four measurements were made for each liquid, with an accuracy of within 0.2 mN/m. Results are shown in Table 6.2. Correction factors of Harkins et al.\textsuperscript{[106]} were used.

Table 6.2 Measured surface tensions of contact angle liquids

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Experimental</th>
<th>Correction factor</th>
<th>Corrected values *</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>77.1</td>
<td>0.934</td>
<td>72.8</td>
</tr>
<tr>
<td>ethane-1,2-diol</td>
<td>53.0</td>
<td>0.899</td>
<td>47.6</td>
</tr>
<tr>
<td>DMSO</td>
<td>47.9</td>
<td>0.889</td>
<td>42.6</td>
</tr>
<tr>
<td>DMF</td>
<td>40.4</td>
<td>0.888</td>
<td>35.9</td>
</tr>
<tr>
<td>diiodomethane</td>
<td>61.0</td>
<td>0.825</td>
<td>50.3</td>
</tr>
</tbody>
</table>

* Corrected value = (experimental value) × (correction factor)

Table 6.2 shows a good agreement between measured surface tensions and literature values in Table 6.1.

6.1.2 Contact angle measurement

Contact angles were measured using a Krüss G40 contact angle measuring system (Fig. 6.1) with the drop in an enclosed chamber. A drop of liquid with a diameter of 2 ~ 4 mm was formed at the end of the syringe needle, and brought gently to the polymer surface to allow it flow off the needle. Contact angles of both sides of the drop were measured 30 sec after the its delivery. At least four drops on different specimens were measured for each sample, and
the average was taken. Contact angles obtained this way were designated as "equilibrium contact angles", and subsequently used to calculate the polymer surface free energies. They are thought to be similar to those obtained in Zisman's laboratory, whose measuring procedure was described in [69]. It is recognised that this is not Young's contact angle. Values are consistent and are close to advancing contact angle.

Fig.6.1 Kriiss G40 contact angle measuring system

Advancing or receding contact angles were measured 10 sec after a drop was advanced or receded to cause the movement of the three phase line at a liquid adding/removing speed of about 0.02ml/min. The needle was maintained in the drop throughout the measurement. A drop was advanced twice and receded twice and advancing or receding angles taken. For each sample, at least four drops on different specimens were used and an average taken.
All contact angles were measured at room temperature (22 ± 2°C), with no thermostating procedure. Standard deviation of contact angles measured was found to be within 2° for most of the samples. It was found that contact angle (equilibrium, advancing, or receding) was time dependent, especially for water. Starting from an equilibrium or advancing water drop, contact angles were found to decrease with time to reach the receding contact angle. However, no significant change in contact angle was found during the first minute after the delivery or the advance of the drop. Starting with the drop in a receding mode, contact angle was found remaining unchanged with time. Presaturation of the chamber with the contact angle liquid did not show significant change in contact angle, but was found to hinder the change with time from equilibrium or advancing mode to receding mode. It would therefore appear that it is reasonable to neglect the spreading pressure $\pi_e$ in Eq.4.2.

6.2 Attenuated total reflection infrared spectroscopy (ATR-IR)

An ATR attachment was used on a Nicolet FTIR spectrometer to acquire ATR-IR spectra. The angle of incidence of the element position was 55°, which is equivalent to an angle of incidence of 50.9° and 56.2° (see Eq.4.19) for prisms KRS-5 and Ge, respectively. 500 scans were collected using a MCT (mercury-cadmium-telluride) detector, which operated at liquid nitrogen temperature. Water was subtracted from the spectra.

Single-pass multiple reflection ATR elements, KRS-5 (50mm x 10mm x 3 mm) and Ge (25mm x 10mm x 3mm) (ex Spectra Tech. Inc.) were used. Two pieces of PP film were cut out to fit precisely the surface of the reflection element. To ensure a good contact between the polymer surface and the element surface, two rubber pads were used to back the samples.

6.3 X-ray photoelectron spectroscopy (XPS)
XPS spectra were recorded on a VG ESCALAB MKII spectrometer using Al Kα X-ray source (1486.6 eV) under a vacuum of $10^{-7}$ torr. A specimen of propylene polymer film was cut to a size which could sufficiently cover the surface of a stub and stuck on it with a piece of double-sided adhesive tape. The stub was then mounted on a rotary driven track within the fast entry lock, and transferred to the preparation chamber and finally to the analyser chamber.

All spectra were recorded digitally on a microcomputer using an X-ray source power of 200 watts (10KV - 20mA) in a CAE mode. They were then sent to and stored in a hard disk, and subsequently analysed using an IBM PC. Broad scan spectra were recorded with a pass energy of 80 eV and an aperture of $B_1$ (1mmx4mm). Radiation damage was not found significant under the conditions used. Binding energy of the polymer backbone carbon, taken as 284.6 eV, was used as a reference for charge correction. High energy resolution XPS spectra were recorded at a pass energy of 20 eV and an aperture of $A_4$ (circle with a diameter of 4mm). The scan range was just wide enough to encompass the peak of interest. Deconvolution of high energy resolved XPS spectra were performed by removing the broadening effect of Al Kα line shape using a modified van Cittert deconvolution algorithm.

Quantification was achieved by measurement of peak area following subtraction of a Shirley type background. Correction is made for photoelectron cross section $^{107}$, inelastic mean free path $^{96}$, transmission of the energy analyser $^{108}$ and angular asymmetry in photoemission $^{109}$ (where appropriate).

6.4 Chemical derivatisation

6.4.1 Solution derivatisation
Derivatisation reaction in solution was employed to determine carboxyl groups introduced onto the polymer surfaces. The reaction was carried out as follows. In a solution containing 0.5ml trifluoroethanol (TFE), 1.0ml pyridine, 200mg dicyclohexylcarbodiimide (DCC) in 15ml dichloromethane, a piece of polymer film was reacted for 16 hours. The sample was then washed with anhydrous diethyl ether or isobutyl methyl ketone, and Soxhlet extracted for 12 hours with diethyl ether or isobutyl methyl ketone. Calcium chloride was used as a dessicant during the Soxhlet extraction.

6.4.2 Vapour-phase derivatisation

A vacuum frame was designed and built for vapour-phase derivatisation. It is schematically illustrated in Fig.6.2. A vacuum of ~10⁻⁴ torr in the frame was obtained by the use of a rotary pump, a diffusion pump and two liquid nitrogen traps. There were three sub-frames under the main frame. Each sub-frame was exclusively used for one derivatisation reaction only. To avoid cross contamination, different derivatisation reactions were carried out at a time interval of at least one day. A derivatising reagent was kept in a flask on one side of a sub-frame. Air in the flask was pumped out through the main frame by opening the valve above the flask after the flask had been immersed in liquid nitrogen bath for ~5min. After 10 min, the valve was then closed and the reagent allowed to melt by removing the liquid nitrogen bath. This pumping process was repeated several times in order to expel the impurities in the flask.

A tube containing specimens was put on the other side of the sub-frame and pumped down to a vacuum of ~10⁻⁴ torr by opening the valve above the tube. The reaction was started by closing the valve above the sub-frame and opening the valve above the flask. The flask was kept at ~20°C (room temperature ~25°C) using a water bath during the reaction to avoid the condensation of the reagent on the specimens. After the reaction, a jar
containing liquid nitrogen was used to freeze the reagent, followed by pumping the sub-frame for ~10 min. The reagent was then sealed and the specimen was pumped for ~24 hours. XPS analysis of the specimen was normally performed on the same day.
Fig. 6.2 Schematic of vacuum frame
Chapter 7 Characterisation of Propylene Polymers

Surfaces of untreated propylene polymers were characterised by contact angle measurement, SEM, and XPS. Adhesion levels with epoxy adhesive and locus of failure were determined. Their tensile properties were also measured.

7.1 Contact angle measurement

7.1.1 Surface free energy

Owens and Wendt's method

The following equation was proposed by Owens and Wendt,

\[ \gamma_{SL} = \gamma_S + \gamma_L - 2 (\gamma_S^{d} \gamma_L^{d})^{1/2} - 2 (\gamma_S^{p} \gamma_L^{p})^{1/2} \]  

Eq.4.14

Combining this equation with Young's equation (Eq.4.1) and neglecting the spreading pressure,

\[ (1 + \cos \theta) \gamma_L / (2 (\gamma_L^{d})^{1/2}) = (\gamma_S^{p})^{1/2} (\gamma_L^{p} / \gamma_L^{d})^{1/2} + (\gamma_S^{d})^{1/2} \]  

Eq.7.1

Substituting \( X = (\gamma_L^{p} / \gamma_L^{d})^{1/2} \), \( Y = (1 + \cos \theta) \gamma_L / (2 (\gamma_L^{d})^{1/2}) \),

\[ Y = (\gamma_S^{p})^{1/2} X + (\gamma_S^{d})^{1/2} \]  

Eq.7.2

\( \gamma_L, \gamma_L^{d}, \gamma_L^{p} \) values of water, ethanediol, DMSO, DMF, and diiodomethane are
listed in Table 6.1. A plot of $Y$ vs $X$ is a straight line having a slope of $(\gamma_s^p)^{1/2}$ and an intercept with $Y$ axis of $(\gamma_s^d)^{1/2}$.

Equilibrium contact angles of water, ethanediol, DMSO, DMF, and diiodomethane were measured and used to calculate surface free energies of the three untreated propylene polymers. Fig.7.1 shows the $Y$-$X$ plots of the untreated propylene polymers studied.
Fig. 7.1 Plots used to estimate surface free energies of untreated PPs
(a) HPP, (b) BPP, and (c) RPP
Surface free energies calculated from the slopes and intercepts with Y axis are listed in Table 7.1.

Table 7.1 Surface free energies of untreated PPs estimated according to Owens and Wendt’s approach [(mJ/m²)]

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$\gamma_s^d$</th>
<th>$\gamma_s^p$</th>
<th>$\gamma_s$</th>
<th>$\gamma_s^p/\gamma_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPP</td>
<td>30.3</td>
<td>0.1</td>
<td>30.4</td>
<td>0.003</td>
</tr>
<tr>
<td>BPP</td>
<td>27.7</td>
<td>0.4</td>
<td>28.1</td>
<td>0.014</td>
</tr>
<tr>
<td>RPP</td>
<td>31.4</td>
<td>0.2</td>
<td>31.6</td>
<td>0.006</td>
</tr>
</tbody>
</table>

The total surface free energy of the homopolymer, $\gamma_s = 30.4 \text{ mJ} \cdot \text{m}^{-2}$, agrees quite well with literature value, 30.2 [110]. All three polymers are essentially nonpolar.

Assuming $\gamma_{LP}^d = 0$ for diiodomethane, Fowkes’ equation, Eq.4.13, can be used,

$$\gamma_{SL} = \gamma_s + \gamma_L - 2 (\gamma_s^d \gamma_L^d)^{1/2}$$  \hspace{1cm} \text{Eq.4.13}

Combining with Young’s equation (Eq.4.1), the following equation can be obtained,

$$\gamma_s^d = \gamma_L^2 (1 + \cos \theta)^2 / (4 \gamma_L^d) = \gamma_L (1 + \cos \theta)^2 / 4$$  \hspace{1cm} \text{Eq.7.3}

Eq.7.3 can be used to calculate $\gamma_s^d$. Results are shown in Table 7.2.
Table 7.2 Dispersion contribution of surface free energy calculated according to Eq.7.3 for untreated PPs (mJ/m²)

<table>
<thead>
<tr>
<th>Polymer</th>
<th>( \theta_{D M} )</th>
<th>( \gamma_s^d )</th>
<th>( \gamma_s^d ) in Table 7.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPP</td>
<td>55.6</td>
<td>31.1</td>
<td>30.3</td>
</tr>
<tr>
<td>BPP</td>
<td>55.7</td>
<td>31.0</td>
<td>27.7</td>
</tr>
<tr>
<td>RPP</td>
<td>51.1</td>
<td>33.7</td>
<td>31.4</td>
</tr>
</tbody>
</table>

\( \gamma_s^d \) values obtained using Eq.7.3 are slightly higher than those obtained using plots in Fig.7.1, but they agree reasonably well.

Wu's method

Instead of the geometric mean method, use of a harmonic mean has been proposed by Wu [85] as a means of estimating interactions across an interface, as expressed in Eq.4.15,

\[
\gamma_{SL} = \gamma_s + \gamma_L - \frac{4\gamma_s^d \gamma_L^d}{\gamma_s^d + \gamma_L^d} - \frac{4\gamma_S^p \gamma_L^p}{\gamma_S^p + \gamma_L^p}
\]

Eq.4.15

Combining Eq.4.15 with Young's equation (Eq.4.1), we can get,

\[
\gamma_L (1 + \cos \theta) = \frac{4\gamma_s^d \gamma_L^d}{\gamma_s^d + \gamma_L^d} + \frac{4\gamma_S^p \gamma_L^p}{\gamma_S^p + \gamma_L^p}
\]

Eq.7.4

Two unknowns, \( \gamma_s^d \) and \( \gamma_S^p \) can be solved by measuring contact angles of a pair of liquids. No suitable linear plot exists for the calculation of \( \gamma_s^d \) and \( \gamma_S^p \). A computer programme was written to calculate \( \gamma_s^d \) and \( \gamma_S^p \) (Appendix B).
Although ten pairs can be composed out of the five contact angle liquids, many of them give irrational values of $\gamma_s^d$ and $\gamma_s^p$ considering the nonpolarity of the untreated polymers and the surface free energy of the homopolymer found in literature. Water and diiodomethane (the former is a very polar liquid, while the later is a relatively nonpolar liquid) were used and tested by Wu [85]. In the view of this, they were also used in this work to calculate $\gamma_s^d$ and $\gamma_s^p$, as a comparison to the geometric mean method. Calculated values of $\gamma_s^d$ and $\gamma_s^p$ for untreated propylene polymers are listed in Table 7.3.

Table 7.3 Surface free energies of untreated PPs calculated according to Wu's approach

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$\gamma_s^d$ (mJ m$^{-2}$)</th>
<th>$\gamma_s^p$ (mJ m$^{-2}$)</th>
<th>$\gamma_s$ (mJ m$^{-2}$)</th>
<th>$\gamma_s^d/\gamma_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPP</td>
<td>31.6</td>
<td>1.1</td>
<td>32.7</td>
<td>0.034</td>
</tr>
<tr>
<td>BPP</td>
<td>31.1</td>
<td>1.9</td>
<td>33.0</td>
<td>0.058</td>
</tr>
<tr>
<td>RPP</td>
<td>33.4</td>
<td>1.8</td>
<td>35.2</td>
<td>0.051</td>
</tr>
</tbody>
</table>

$\gamma_s^d$ and $\gamma_s^p$ calculated according to Wu's method are generally higher than those by Owens and Wendt's. Polarities of the these untreated polymers are quite low, and can be regarded as 0. The total surface free energy of the homopolymer is slightly higher than literature value, 30.2 mJ·m$^{-2}$[110].

7.1.2 Contact angle hysteresis

Measurable water and diiodomethane contact angle hystereses $H = \theta_{\text{adv}} - \theta_{\text{rec}}$, were found (Table 7.4) for all three polymers studied.
Table 7.4 Contact angle hystereses of water and diiodomethane on untreated PP surfaces

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Water</th>
<th>Diiodomethane</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>θ_{adv}</td>
<td>θ_{rec}</td>
</tr>
<tr>
<td>HPP</td>
<td>108.4</td>
<td>91.4</td>
</tr>
<tr>
<td>BPP</td>
<td>103.0</td>
<td>88.2</td>
</tr>
<tr>
<td>RPP</td>
<td>105.0</td>
<td>85.8</td>
</tr>
</tbody>
</table>

In order to examine the effects of adsorption and contaminants (if exist), a drop of water or diiodomethane was advanced over the fresh surface of the polymer (θ_{adv,1}), and then retreated (θ_{rec,1}). It was then advanced over the surface which had been previously in contact with the liquid (θ_{adv,2}), and retreated again (θ_{rec,2}). No appreciable difference was found between the two advancing contact angles, θ_{adv,1} and θ_{adv,2}, or the two receding contact angles, θ_{rec,1} and θ_{rec,2}. Contact angle hysteresis, therefore, was unlikely due to adsorption of the liquid by the polymer, or any possible contaminants on the polymer surface. Surface topography was examined using SEM (Cambridge Stereoscan 360) (Fig.7.2).

Results have shown that the surface of HPP is very smooth, while the two copolymers are slightly rough. Thus it is unlikely that the contact angle hysteresis was due to surface roughness. Considering that no other elements except carbon were detected by XPS (see section 7.2), chemical heterogeneity is unlikely to exist on the surface. However, it is possible that physical heterogeneity may exist on the surface, e.g heterogeneous density distribution on the surface, and could contribute to the hysteresis.
(a) HPP

(b) BPP
Fig. 7.2 SEM micrographs of untreated PPs. (a) HPP, (b) BPP, (c) RPP

7.2 X-ray photoelectron spectroscopy (XPS)

XPS was used to examine the surface elemental composition. No other elements except carbon were detected for all untreated propylene polymers studied.

7.3 Adhesion level with epoxy adhesive and locus of adhesion failure

Adhesion levels of untreated propylene polymers with the epoxy adhesive are shown in Table 7.5.

As expected, the adhesion level of the untreated propylene polymer with the epoxy adhesive was very poor. This could be attributed to the low surface free
energy and nonpolarity of the untreated polymer surfaces.

Table 7.5 Adhesion levels of untreated propylene polymers with epoxy adhesive

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Joint strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPP</td>
<td>1.4</td>
</tr>
<tr>
<td>BPP</td>
<td>1.8</td>
</tr>
<tr>
<td>RPP</td>
<td>1.7</td>
</tr>
</tbody>
</table>

Adhesion failures in the adhesive joints were visually interfacial between the polymer and the adhesive. Using special steel butts with detachable head, surfaces created after the adhesion test of a joint were analysed using XPS. Elemental compositions of both sides are shown in Table 7.6.

Table 7.6 Elemental compositions of both surfaces created by adhesion testing of epoxide - HPP (untreated) - epoxide joint

<table>
<thead>
<tr>
<th>Side</th>
<th>Take-off angle</th>
<th>Elemental compositions (atomic%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C</td>
</tr>
<tr>
<td>A</td>
<td>90</td>
<td>100.0</td>
</tr>
<tr>
<td>B</td>
<td>90</td>
<td>87.4</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>90.0</td>
</tr>
</tbody>
</table>

Sides A and B are respectively typical of the untreated HPP (100.0% C) and the epoxy adhesive (83.6% C, 11.4% O, 5.0% N). Therefore the locus of failure was interfacial. The oxygen concentration of side B is less than that of the epoxy adhesive, and angle resolved XPS showed a depletion of oxygen and nitrogen at the near surface. This was possibly due to the orientation of the oxygen containing groups away from the interface.
Without any pretreatment, a propylene polymer was found non-wettable by the PU paint.

7.4 Attenuated total reflection infrared spectroscopy (ATR-IR)

Fig. 7.3 shows the ATR-IR spectra of untreated propylene polymers.

![ATR-IR spectra of untreated PPs](image)

Fig. 7.3 ATR-IR spectra of untreated PPs
Some important peaks are assigned in Table 7.7.

Table 7.7 Assignments of peaks in IR spectra of untreated propylene polymers

<table>
<thead>
<tr>
<th>Band (cm⁻¹)</th>
<th>Group</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>2950.3</td>
<td>-CH₃</td>
<td>asymmetric stretching vibration</td>
</tr>
<tr>
<td>2917.9</td>
<td>-CH₂</td>
<td>asymmetric stretching vibration</td>
</tr>
<tr>
<td>2877.1 / 2867.8</td>
<td>-CH₃</td>
<td>symmetric stretching vibration</td>
</tr>
<tr>
<td>2837.7</td>
<td>-CH₂</td>
<td>symmetric stretching vibration</td>
</tr>
<tr>
<td>1456.3</td>
<td>-CH₃</td>
<td>asymmetric bending</td>
</tr>
<tr>
<td>1376.6</td>
<td>-CH₂</td>
<td>symmetric bending</td>
</tr>
</tbody>
</table>

7.5 Differential scanning calorimetry (DSC)

DSC traces of all three polymers were recorded. Melting temperature $T_p$, the temperature at which the rate of melting is a maximum, and the heat of fusion $\Delta H$ are listed in Table 7.8.

The weight-fraction degree of crystallinity, $W_c$, was estimated from the following equation \[111\],

$$W_c = \frac{\Delta H}{\Delta H^o}$$

Eq.7.5

where $\Delta H^o$ is the heat of fusion of the 100% crystalline polymer, and was taken as 165 J/g \[112\]. Calculated values of $W_c$ according to Eq.7.5 are listed in Table 7.8.
Table 7.8 Melting temperature, heat of fusion, and weight-fraction degree of crystallinity of untreated PP s

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Melting temperature (°C)</th>
<th>Heat of fusion (J/g)</th>
<th>Wc (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPP</td>
<td>167.2</td>
<td>97.9</td>
<td>59.3</td>
</tr>
<tr>
<td>BPP</td>
<td>167.1</td>
<td>84.7</td>
<td>51.3</td>
</tr>
<tr>
<td>RPP</td>
<td>167.7</td>
<td>57.1</td>
<td>34.6</td>
</tr>
</tbody>
</table>

Table 7.8 shows that melting temperatures of the three polymers are virtually the same. The weight-fraction of crystalline PP decreases in the following order,

\[ \text{HPP} > \text{BPP} > \text{RPP}. \]

7.6 Tensile properties

Tensile properties of untreated propylene polymers were measured as described in section 5.5. Table 7.9 shows the tensile strength at yield point. The homopolymer was found to have the highest tensile strength among the three polymers.

Table 7.9 Tensile strength of untreated propylene polymers at yield point

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Tensile strength at yield point (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPP</td>
<td>19.0</td>
</tr>
<tr>
<td>BPP</td>
<td>9.2</td>
</tr>
<tr>
<td>RPP</td>
<td>11.3</td>
</tr>
</tbody>
</table>
8.1 Solvent wipe

8.1.1 Effects on contact angle

Trichloroethylene, trichloroethane, and a mixture of heptane and isopropanol (1:1 by volume) were used in this study, and were found to give similar results. Wiping or rinsing in ultrasonic bath with one of the above solvents was found equally effective in improving the wetting of the PU paint on propylene polymer surfaces, although water advancing contact angle was found to have increased slightly. In the absence of this wipe or rinse, the untreated propylene polymers were non-wettable by the PU paint. Table 8.1 shows the contact angle results before and after trichloroethylene wipe.

Table 8.1 Effects of trichloroethylene wipe on water contact angles of HPP

<table>
<thead>
<tr>
<th></th>
<th>untreated</th>
<th>trichloroethylene wiped</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\theta_{\text{ADV}}$</td>
<td>108.4</td>
<td>112.0</td>
</tr>
<tr>
<td>$\theta_{\text{REC}}$</td>
<td>91.4</td>
<td>92.3</td>
</tr>
<tr>
<td>$H$</td>
<td>17.0</td>
<td>19.7</td>
</tr>
</tbody>
</table>

8.1.2 Effects on adhesion

Compared to other modification methods discussed later on, solvent wipe was found to give the poorest adhesion level with PU paint (Table 8.2). The adhesion was so poor that some joints fell apart before the adhesion testing. Scanning electron microscopy failed to show any change in surface roughness caused by the wipe. No change in chemical composition was
detected by XPS.

Table 8.2 Effects of trichloroethylene wipe on adhesion levels of propylene polymers to PU paint

<table>
<thead>
<tr>
<th></th>
<th>Adhesion level with PU paint (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPP</td>
<td>2.3</td>
</tr>
<tr>
<td>BPP</td>
<td>3.2</td>
</tr>
<tr>
<td>RPP</td>
<td>2.6</td>
</tr>
</tbody>
</table>

8.1.3 Locus of adhesion failure

By using special steel butts with detachable head, locus of failure was examined. Both surfaces created by adhesion testing were analysed by XPS. Table 8.3 gives the locus of failure study results for propylene homopolymer wiped with heptane / isopropanol (1:1 by volume) prior to PU surface coating.

Table 8.3 Elemental compositions of both surfaces created by adhesion testing of epoxide - PU - HPP (wiped with 1:1 by volume heptane + isopropanol) - PU - epoxide joint

<table>
<thead>
<tr>
<th>Side</th>
<th>Elemental compositions (atomic%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>A</td>
<td>96.1</td>
</tr>
<tr>
<td>B</td>
<td>70.7</td>
</tr>
</tbody>
</table>

Side B is typical of the PU paint (72.8% C, 19.8% O, 4.6% N, 2.8% Si), while small amounts of oxygen and silicon were detected on side A, suggesting that

78
complete interfacial failure was unlikely. Weak boundary layer (WBL) could provide a possible explanation, and is thought to have originated from the PU paint rather than from the propylene polymer film. This WBL could be low molecular weight materials with low surface free energy (e.g. silicones) which may have been used as film forming agent in the paint. They might have migrated to the interface from the bulk of the paint, resulting in the decrease of the interfacial free energy.

8.2 Solvent vapour treatment

8.2.1 Effects on surface roughness and contact angle

Organic solvents used for solvent wiping were employed for the solvent vapour treatment. This kind of treatment is a severe physical treatment. A dip of HPP in trichloroethylene vapour gave a dull white finish to the smooth untreated surface. SEM showed a significant surface roughening effect for the homopolymer by the treatment (Fig.8.1) compared to the untreated surface (Fig. 7.2a). Treatment in trichloroethylene vapour caused a slight increase in surface roughness for the two copolymers (Fig.8.2 and 8.3), compared to their untreated surfaces (Fig. 7.2b and c). It is thought that the roughness was produced by the swelling of the polymer surface. A preferential attack on the amorphous or low molecular weight region has been suggested by Ziccarelli [113].

However, treatment in trichloroethane vapour or the mixture of heptane and isopropanol (1:1 by volume) did not show any topographical change to the polymer surface (Fig 8.4).

Prolonged treatment in the solvent vapour could lead to the distortion or even dissolution of the polymer film, especially when trichloroethylene was used. Copolymer BPP, whose film is the thinnest, was subject to an exposure time of 10 sec instead of 20 sec.
Fig. 8.1 SEM micrograph of HPP treated by trichloroethylene vapour for 20 sec

Fig. 8.2 SEM micrograph of BPP treated by trichloroethylene vapour for 10 sec
Fig. 8.3 SEM micrograph of RPP treated by trichloroethylene vapour for 20 sec

Fig. 8.4 SEM micrograph of HPP treated by trichloroethane vapour for 20 sec
Water contact angles of propylene polymers treated by solvent vapour are listed in Table 8.4.

Table 8.4 Effects of solvent vapour treatment on water contact angles of PPs

<table>
<thead>
<tr>
<th>Vapour treatment</th>
<th>$\theta_{\text{adv}}$</th>
<th>$\theta_{\text{rec}}$</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPP untreated</td>
<td>108.4</td>
<td>91.4</td>
<td>17.0</td>
</tr>
<tr>
<td>HPP trichloroethylene vapour 20 esc</td>
<td>148.8</td>
<td>85.0</td>
<td>63.8</td>
</tr>
<tr>
<td>HPP trichloroethane vapour 20 sec</td>
<td>127.5</td>
<td>85.2</td>
<td>42.3</td>
</tr>
<tr>
<td>BPP untreated</td>
<td>103.0</td>
<td>88.2</td>
<td>14.8</td>
</tr>
<tr>
<td>BPP trichloroethylene vapour 10 sec</td>
<td>136.6</td>
<td>80.6</td>
<td>56.0</td>
</tr>
<tr>
<td>RPP untreated</td>
<td>105.0</td>
<td>85.8</td>
<td>19.2</td>
</tr>
<tr>
<td>RPP trichloroethylene vapour 20 sec</td>
<td>120.0</td>
<td>83.1</td>
<td>36.9</td>
</tr>
</tbody>
</table>

Advancing contact angles were significantly increased, while receding contact angles were slightly decreased by solvent vapour treatment. Roughness cannot be the sole reason for this effect here, since trichloroethane also had a similar although less pronounced effect on contact angle without any detectable topographical change on the surface.

Judging from the advancing contact angles, surface wettability had been reduced by solvent vapour treatment. However, the polymer surfaces after the treatment had better wettabilities when the PU paint was applied. This is not surprising considering the practical paint application. The paint is sprayed onto the polymer surface. Initially, the surface is easily wettable because the paint is a xylene solution with an apparent surface tension of 26.4 mN/m as measured by Krüss K10T tensiometer. However, with the evaporation of the solvent, the surface tension will be increased, leading to the shrinking and a tendency to dewet and form drops of the paint. Thus the receding contact angle plays a more important role than advancing angle or static angle does in this process. With a higher receding contact angle,
untreated propylene polymer was less wettable. After the solvent vapour treatment, the receding contact angle was decreased, resulting in a less tendency to dewet of the PU paint on the polymer surface. Better contact between the polymer and the paint, and therefore better adhesion, could be expected. Receding contact angle is also thought to play a more important role than advancing contact angle in the case of the adhesion of propylene polymers to the epoxy adhesive.

8.2.2 Effects on adhesion

Compared to the solvent wipe, solvent vapour treatment was found to give better adhesion. Table 8.5 and 8.6 list some adhesion test results with epoxy adhesive and PU paint after the vapour treatment.

Table 8.5 Effects of solvent vapour treatment on the adhesion levels of PPs to epoxy adhesive

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Treatment</th>
<th>Adhesion level (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPP</td>
<td>untreated</td>
<td>1.4</td>
</tr>
<tr>
<td>HPP</td>
<td>trichloroethylene vapour 20s</td>
<td>5.4</td>
</tr>
<tr>
<td>HPP</td>
<td>trichloroethane vapour 20s</td>
<td>6.1</td>
</tr>
<tr>
<td>BPP</td>
<td>untreated</td>
<td>1.8</td>
</tr>
<tr>
<td>BPP</td>
<td>trichloroethylene vapour 10s</td>
<td>6.0</td>
</tr>
<tr>
<td>RPP</td>
<td>untreated</td>
<td>1.7</td>
</tr>
<tr>
<td>RPP</td>
<td>trichloroethylene vapour 20s</td>
<td>8.7</td>
</tr>
</tbody>
</table>

Solvent vapour treatment slightly improved the adhesion of PP to both epoxy adhesive and PU paint. There are large differences in surface roughness between the treatments of trichloroethylene and trichloroethane. However, no significant difference in adhesion was found. Therefore surface roughness is not the sole reason for the improvement in adhesion level.
Removal of a possible weak boundary layer by the solvent vapour could also account for the improvement, but it does not explain the improved wetting properties.

Table 8.6 Effects of solvent vapour treatment on the adhesion levels of PPs to PU paint

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Treatment</th>
<th>Adhesion level (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPP</td>
<td>trichloroethylene wiped</td>
<td>2.3</td>
</tr>
<tr>
<td>HPP</td>
<td>trichloroethylene vapour 20s</td>
<td>4.0</td>
</tr>
<tr>
<td>HPP</td>
<td>trichloroethane vapour 20s</td>
<td>3.7</td>
</tr>
<tr>
<td>BPP</td>
<td>trichloroethylene wiped</td>
<td>3.2</td>
</tr>
<tr>
<td>BPP</td>
<td>trichloroethylene vapour 10s</td>
<td>2.3</td>
</tr>
<tr>
<td>RPP</td>
<td>trichloroethylene wiped</td>
<td>2.6</td>
</tr>
<tr>
<td>RPP</td>
<td>trichloroethylene vapour 20s</td>
<td>6.4</td>
</tr>
</tbody>
</table>

Slightly better adhesion to epoxy adhesive than to PU paint was obtained. The reason for this is not quite clear. It could result from the reduced roughness of the propylene polymer after bonding with the PU paint (Fig. 8.7) in the case of trichloroethylene vapour treatment. It may also be due to low molecular weight materials, which could well exist in the PU paint, and have migrated to the interface resulting in a weak boundary layer at the interface.

Ziccarelli [113] claimed that excellent bonding adhesion of PP to resin based coating was obtained by trichloroethylene vapour treatment. It should be noted here that adhesion level was assessed by the Scotch tape test method. He also mentioned the limited time (about 48 hours) during which the treatment was effective. This was not observed in the present work.

In order to examine the effects of treatment time on adhesion, HPP was
Fig. 8.5 Effects of trichloroethylene vapour treatment time on the adhesion of HPP to the epoxy adhesive

Fig. 8.6 Effects of trichloroethylene vapour treatment time on the adhesion of HPP to the PU paint
subject to trichloroethylene vapour for different exposure times. Adhesion levels to epoxy adhesive and PU paint are plotted against treatment time in Fig.8.5 and 8.6 respectively.

The results obtained in Fig.8.5 and 8.6 show that the adhesion level increases initially with treatment time, with some evidence for a limiting value at around a treatment time of 20 sec. This does not agree with Garnish and Haskins' [23] view that there exists a time after which overtreatment can occur. They found that a maximum value of adhesion, assessed by double shear test, to an epoxy adhesive was reached when treated for about 10 sec, after which the adhesion dropped rapidly.

8.2.3 Locus of failure

Table 8.7 shows the results of locus of failure study of trichloroethylene vapour treated HPP bonded directly with epoxy adhesive.

<table>
<thead>
<tr>
<th>Side</th>
<th>Take-off angle</th>
<th>Elemental compositions (atomic%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C</td>
</tr>
<tr>
<td>A</td>
<td>90</td>
<td>100.0</td>
</tr>
<tr>
<td>B</td>
<td>90</td>
<td>88.0</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>88.6</td>
</tr>
</tbody>
</table>

Side A is typical of the untreated polymer surface (100.0% C), while side B is typical of the epoxy adhesive (83.6% C, 11.4% O, 5.0% N), suggesting that the failure could have occurred interfacially. The oxygen concentration of side B is less than that of the epoxy adhesive, and angle resolved XPS has shown a
depletion of oxygen at the near surface. This could possibly due to the orientation of oxygen containing groups away from the interface.

Table 8.8 shows the elemental compositions of both surfaces created by adhesion testing of the HPP treated by trichloroethylene vapour for 20 sec prior to PU surface coating.

Table 8.8 Elemental compositions of both surfaces created by adhesion testing of epoxide - PU - HPP (trichloroethylene vapour 20 sec) - PU - epoxide joint

<table>
<thead>
<tr>
<th>Side</th>
<th>Elemental compositions (atomic%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>A</td>
<td>96.6</td>
</tr>
<tr>
<td>B</td>
<td>69.3</td>
</tr>
</tbody>
</table>

Side B is typical of the PU paint (72.8% C, 19.8% O, 4.6% N, 2.8% Si), while side A took small amounts of oxygen and silicon. Like in the solvent wipe treatment, WBL originating from the paint could explain this. Both surfaces were also examined by SEM. They are shown in Fig. 8.7 and 8.8.

Compared to the surface after the treatment (Fig. 8.1), surface roughness of the propylene polymer (Fig. 8.7) had been reduced, which is thought to have been caused by the effect of xylene, the thinner for the PU paint. The solubility parameters of xylene and propylene homopolymer, 18.0 and 18.8 \( (\text{J/cm}^3)^{1/2} \) respectively \([114]\), are very similar, which makes the effect of xylene on the polymer's roughness quite possible according to the "like dissolves like" rule of thumb. On the other hand, the paint side showed a corresponding roughness due to the penetration of the surface coating into the grooves of the rough surface.
Fig. 8.7 SEM micrograph of side A in Table 8.8

Fig. 8.8 SEM micrograph of side B in Table 8.8
8.3 Summary

Solvent treatment has been found to improve the wetting characteristics of the propylene polymers. The reasons for this are not entirely clear. Where significant surface roughness has been observed, the reduction in receding contact angle is explainable. Where significant surface roughness is not detected, it is more difficult to attribute a reason for improved wetting characteristics. It is possible that the solvent vapour has affected the physical properties of the polymer surface in such a way as to improve interaction with the solvent borne paint system.

Poor adhesion levels with PU paint have been observed after a solvent wipe of the propylene polymer surface. Although better adhesion is obtained using solvent vapour treatment, it is still considerably lower than those obtained using other surface pretreatments. A WBL originating from the paint may exist at the interface between PU paint and solvent treated PP.
Propylene polymer surfaces were etched using chromic acid, and characterised by XPS, contact angle measurement, SEM, and ATR-IR. Adhesion levels with epoxy adhesive and PU paint were assessed using a composite butt test.

9.1 Etching rate

Etching rates 80°C in chromic acid of the three polymers studied were determined gravimetrically. Results are shown in Fig.9.1.

Fig.9.1 Chromic acid etching rates at 80°C

Fig.9.1 shows that chromic acid etching rate decreases in the following order,

\[ \text{RPP} > \text{BPP} > \text{HPP} \]
which is the inverse order of the weight-fraction of crystalline PP (Table 7.8).

The copolymer RPP was found to have the highest etching rate among the three polymers studied. This may be caused by the rapid preferential attack of the acid on the amorphous modifying rubber regions in the polymer. The homopolymer, HPP, has the highest crystallinity, and therefore is relatively inert to chromic acid. Indeed, it has the lowest etching rate. The bumper grade copolymer, BPP, presented an intermediate case.

9.2 Effects on water contact angles

Propylene polymers were etched by chromic acid at both room temperature (22°C) and an elevated temperature (80°C). Water contact angles are plotted against etching time in Fig.9.2 and Fig.9.3 for the three propylene polymers at 22°C and 80°C, respectively.
Fig. 9.2 Effects of chromic acid etching time on water contact angles at 22°C
(a) HPP, (b) BPP, and (c) RPP
(a) HPP

(b) BPP

Etching time (sec)

Water advancing contact angle

Water receding contact angle
At 22°C, chromic acid etching was found to significantly decrease water advancing and receding contact angles for all three polymers (Fig.9.2). However, limiting values were obtained in etching times of ~2min and ~10min for water advancing and receding contact angles respectively, after which water contact angles were found virtually unchanged.

Etched at 80°C (Fig.9.3), propylene polymers exhibited similar trends in water receding contact angle as at 22°C. Water receding contact angle decreased rapidly initially. However, advancing contact angle exhibited a minimum at an etching time of ~2sec (a quick dip in the acid solution) for any of the three polymers. An initial rapid decrease in water advancing contact angle was only found for HPP, while only a slight initial decrease was found for BPP or RPP. The initial decrease in water advancing contact angle was followed by a slight increase for HPP and a significant increase for BPP or RPP. Water advancing contact angles which are even higher than the untreated values
were obtained after an etching time of ~10sec for BPP and RPP.

Propylene polymer surfaces etched by chromic acid could well be chemically heterogeneous. For a smooth but chemically heterogeneous surface, advancing contact angle can be representative of the least wettable part on the surface, while receding contact angle can be representative of the most wettable part on the surface [68]. The initial decrease in water receding contact angle, and in water advancing contact angle in the case of treatment at 22°C, was thought to be due to the incorporation of oxygen or sulphur containing functional groups on the surface by the etching of chromic acid.

At 80°C, propylene polymer surface was subject to a severe attack by the acid solution. A gas which could be CO₂ was generated during the etching process. Small gas bubbles could well be formed on the polymer surface, resulting in the under treatment of some patches on the surface. This is also thought to have contribution to the chemical heterogeneity of the etched surface. The patches which had been under-treated were represented by advancing contact angle. The extent of modification of these patches did not depend much on etching time.

At 80°C, water advancing contact angle was found to increase after it attained its minimum for BPP and particularly for RPP. This may be due to the increase in surface roughness caused by long acid etching at a high temperature (Fig.9.7 and Fig.9.8). The extent of this increase in water advancing contact angle corresponds well with etching rate. RPP has the highest etching rate among the three polymers, and has the largest increase in water advancing contact angle after an etching time ~2sec.

Significant water contact angle hysteresis was found (Fig.9.4).
Fig. 9.4 Effects of chromic acid etching time on water contact angle hysteresis. (a) 22°C, and (b) 80°C
High etching temperature generated significantly higher contact angle hysteresis. The extent of contact angle hysteresis was found to increase in the following order,

$$\text{HPP} < \text{BPP} < \text{RPP}$$

which corresponds to the etching rate. At 22°C, SEM did not show significant roughness on etched surfaces of HPP or BPP, while some grooves were found on etched RPP surfaces (Fig.9.5). At 80°C, no significant roughness was observed for HPP (Fig.9.6). However, significant roughness was observed for BPP and RPP, and increased with etching time (Fig.9.7 and Fig.9.8). This was thought to be caused by the preferential attack of the acid on the amorphous regions. Therefore, contact angle hysteresis may be attributed to chemical heterogeneity for those smooth surfaces, while it may be attributed to a combination of surface roughness and surface heterogeneity for BPP and RPP at 80°C.

(a) HPP
Fig. 9.5 SEM micrographs of PPs etched with chromic acid for 5 min at 22°C
(a) HPP, (b) BPP, (c) RPP
Fig. 9.6 SEM micrographs of HPP etched with chromic acid at 80° C.
(a) 2 sec, (b) 30 sec
Fig. 9.7 SEM micrographs of BPP etched with chromic acid at 80° C.
(a) 2 sec, (b) 30 sec
Fig. 9.8 SEM micrographs of RPP etched with chromic acid at 80° C.
(a) 2 sec, (b) 30 sec
9.3 Effects on diiodomethane contact angles

Advancing and receding contact angles of diiodomethane are plotted against etching time in Fig.9.9 and Fig.9.10 for propylene polymers at 22°C and 80°C respectively.

At both temperatures (22°C and 80°C), diiodomethane receding contact angle was found to decrease significantly initially. However, it decreased with a much reduced rate after ~10 min and ~10 sec at 22°C and 80°C respectively. Diiodomethane receding contact angle was found to be 0 on BPP and RPP surfaces after ~10 sec etching at 80°C.

On the other hand, no significant change in diiodomethane advancing contact angle was found on PP surfaces treated at both temperatures except for RPP etched at 80°C. A marked increase with etching time was found after 10 sec of etching for RPP at 80°C.

Only dispersion-dispersion interaction can be expected at the diiodomethane - PP interface according to Fowkes' theory (see section 4.2.4, Chapter 4) since diiodomethane has negligible polarity. Therefore, diiodomethane only characterises the dispersion component of the polymer surface free energy, $\gamma_{sd}$. For smooth surfaces, therefore, it can be concluded that chromic acid etching increased the $\gamma_{sd}$ of the most wettable parts (represented by $\theta_{rec}$) much more significantly than the least wettable parts (represented by $\theta_{adv}$) on the surface. The significant decrease in $\theta_{rec}$ of diiodomethane could be attributed to the incorporation of more polarisable sulphur (possibly present as -SO$_3$H) as detected by XPS.
Fig. 9.9 Effects of chromic acid etching time on diiodomethane contact angles at 22°C. (a) HPP, (b) BPP, and (c) RPP
Fig. 9.10 Effects of chromic acid etching time on diiodomethane contact angles at 80°C. (a) HPP, (b) BPP, and (c) RPP

Diiodomethane contact angle hysteresis (Fig. 9.11) was found to behave the
same way as water contact angle hysteresis (c.f. Fig.9.4).

Fig.9.11 Effects of etching time on diiodomethane contact angle hysteresis at (a) 22°C, and (b) 80°C
9.4 Surface free energy estimated from contact angles

Surface free energies were estimated from contact angles (equilibrium) of water, ethanediol, DMSO, DMF, and diiodomethane. Tables 9.1-9.3 show the results for HPP etched at 22°C and 80°C, and BPP etched at 22°C, respectively. Results according to both Owens & Wendt's (Eq.7.2) and Wu's (Eq.7.4) approaches are presented. If the contribution of surface roughness on contact angle can be neglected, surface free energies obtained can be interpreted with caution to be representative of the least wettable parts on the treated surfaces. For BPP surfaces etched at 80°C and RPP surfaces etched at 22°C and 80°C, surface roughness was generated and negative slopes of Y-X plots (Eq.7.2) (which are irrational) were obtained for some of the samples.

Table 9.1 Surface free energies of HPP etched at 22°C (mJ/m²):

<table>
<thead>
<tr>
<th>Etching time (min)</th>
<th>Owens &amp; Wendt's approach</th>
<th>Wu's approach</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\gamma^p$</td>
<td>$\gamma^d$</td>
</tr>
<tr>
<td>0</td>
<td>0.1</td>
<td>30.3</td>
</tr>
<tr>
<td>2</td>
<td>2.5</td>
<td>32.8</td>
</tr>
<tr>
<td>5</td>
<td>3.9</td>
<td>31.0</td>
</tr>
<tr>
<td>10</td>
<td>2.6</td>
<td>33.1</td>
</tr>
<tr>
<td>20</td>
<td>2.5</td>
<td>33.2</td>
</tr>
<tr>
<td>30</td>
<td>2.4</td>
<td>33.0</td>
</tr>
</tbody>
</table>
Table 9.2 Surface free energies of HPP etched at 80°C (mJ/m²)

<table>
<thead>
<tr>
<th>Etching time (sec)</th>
<th>Owens &amp; Wendt’s approach</th>
<th>Wu’s approach</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\gamma^p$</td>
<td>$\gamma^d$</td>
</tr>
<tr>
<td>0</td>
<td>0.1</td>
<td>30.3</td>
</tr>
<tr>
<td>2</td>
<td>1.2</td>
<td>35.0</td>
</tr>
<tr>
<td>5</td>
<td>0.7</td>
<td>37.7</td>
</tr>
<tr>
<td>10</td>
<td>1.0</td>
<td>36.6</td>
</tr>
<tr>
<td>20</td>
<td>0.5</td>
<td>38.0</td>
</tr>
<tr>
<td>30</td>
<td>0.6</td>
<td>37.8</td>
</tr>
</tbody>
</table>

Table 9.3 Surface free energies of BPP etched at 22°C (mJ/m²)

<table>
<thead>
<tr>
<th>Etching time (min)</th>
<th>Owens &amp; Wendt’s approach</th>
<th>Wu’s approach</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\gamma^p$</td>
<td>$\gamma^d$</td>
</tr>
<tr>
<td>0</td>
<td>0.4</td>
<td>27.7</td>
</tr>
<tr>
<td>2</td>
<td>2.5</td>
<td>31.9</td>
</tr>
<tr>
<td>5</td>
<td>2.4</td>
<td>32.1</td>
</tr>
<tr>
<td>10</td>
<td>2.4</td>
<td>31.9</td>
</tr>
<tr>
<td>20</td>
<td>1.7</td>
<td>34.0</td>
</tr>
<tr>
<td>30</td>
<td>1.3</td>
<td>34.6</td>
</tr>
</tbody>
</table>

It has been shown by Tables 9.1-9.3 that the nonpolarities of the propylene polymers have been altered by chromic acid etching. The etching primarily increases the polar component rather than the dispersion component. Slightly higher $\gamma^d_s$ and significantly higher $\gamma^p_s$ are obtained according to
Wu's approach than according to Owens & Wendt's.

9.5 Effects on surface chemistry

Chromic acid etched polymers were examined using ATR-IR, and were not found to show any oxidation or sulphonation. This is in agreement with the results of Blais et al [27]. However, they observed >C=O (~1710 cm\(^{-1}\)) and -SO\(_3\)H (~1200 cm\(^{-1}\) and 1030 cm\(^{-1}\)) on chromic acid etched LDPE. The inability of ATR-IR to show any oxidation or sulphonation could be due to the dense tertiary C-H sites in the surface layer, enabling a rapid attack of chromic acid on the surface and leaving a very thin modified layer on the surface, which can not be detected by ATR-IR.

As a more surface specific technique, XPS was used to examine the surface atomic compositions of the polymers etched by chromic acid. Moderate oxidation and sulphonation were found. Fig.9.12 and Fig.9.13 illustrate the oxygen concentration as detected by XPS with etching time for HPP etched at 22°C and 80°C, respectively.

Fig.9.12 shows that oxygen concentration initially increases rapidly with etching time at 22°C. It attained its maximum at an etching time of around 5 min. There is a slight decrease in oxygen concentration with etching time after 5 min. The effectiveness of the treatment was increased substantially by increasing the etching temperature. With treatment at 80°C, a similar trend was also found (Fig.9.13), and the maximum oxygen concentration was obtained at an etching time of about 5 sec, a much shorter time than at 22°C. Various sulphur concentrations were found for treatments at both temperatures. On average, a sulphur concentration of ~1.0% was found for treatments at both temperatures.

For treatments at both temperatures, angle resolved XPS showed no variation in oxygen concentration initially with etching time, but an
Fig. 9.12 Effects of chromic acid etching time on oxygen concentration of HPP surfaces at 22°C

Fig. 9.13 Effects of chromic acid etching time on oxygen concentration of HPP surfaces at 80°C
enrichment in oxygen concentration at the near surface for samples treated under long chromic acid etching (Table 9.4). This indicates that mild chromic acid etching generated an oxidised layer on the surface whose thickness is greater than the sampling depth of XPS, \( \sim 100 \text{Å} \), and prolonged acid etching may give a reduced oxidation depth.

ATR-IR did not show any difference between chromic acid etched surface and untreated surface, implying that the modification depth was considerably less than the sampling depth of ATR-IR, \( \sim 1 \mu\text{m} \).

### Table 9.4 Angle resolved XPS results of chromic acid etched HPP

<table>
<thead>
<tr>
<th>Etching temperature</th>
<th>Etching time</th>
<th>Elemental compositions (atomic%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>take-off angle 90°</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C</td>
</tr>
<tr>
<td>22°C</td>
<td>5 min</td>
<td>93.4</td>
</tr>
<tr>
<td></td>
<td>10 min</td>
<td>94.4</td>
</tr>
<tr>
<td></td>
<td>40 min</td>
<td>95.8</td>
</tr>
<tr>
<td>80°C</td>
<td>2 sec</td>
<td>94.2</td>
</tr>
<tr>
<td></td>
<td>1 min</td>
<td>92.4</td>
</tr>
<tr>
<td></td>
<td>5 min</td>
<td>93.5</td>
</tr>
</tbody>
</table>

Both oxidation and sulphonation were also found on chromic acid etched BPP and RPP surfaces. XPS results of all three polymers etched by chromic acid for 5min at room temperature are listed in Table 9.5. Rubber modified polypropylene, RPP, was found to have the highest oxidation.
High energy resolved C1s XPS spectrum of chromic acid etched HPP (5 min at 22°C) failed to show any chemically shifted peaks (Fig.9.14).

Sulphur (0.7%) on the surface could be present as -SO₃H, accounting for 2.1% oxygen present on the surface. The rest of the oxygen (3.8%) on the surface is thought to be below the detection limit of high energy resolved XPS. Liquid-phase derivatisation with trifluoroethanol for 16hrs, followed by Soxhlet extraction with diethyl ether for 8hrs, did show small amount of fluorine (~0.9 atomic%). No fluorine was detected by using isobutyl methyl ketone instead of diethyl ether as an extracting solvent. With a much higher boiling point (114 - 117°C), isobutyl ketone is a much more severe solvent than diethyl ether (boiling point 34.6°C), and may well wash away the derivatised layer.
Fig. 9.14 Deconvolved C1s XPS spectra of (a) untreated HPP, and (b) chromic acid etched HPP (5 min at 22°C)

9.6 Adhesion levels with epoxy adhesive and PU paint

Fig. 9.12 and Fig. 9.13 show the effects of chromic acid etching time on adhesion levels with the epoxy adhesive of the homopolymer (HPP) at 22°C and 80°C, respectively.
Fig. 9.15 Effects of etching time on adhesion levels with the epoxy adhesive of HPP etched with chromic acid at 22°C.

Fig. 9.16 Effects of etching time on adhesion levels with the epoxy adhesive of HPP etched with chromic acid at 80°C.
High adhesion levels of HPP with epoxy adhesive were obtained by chromic acid etching. Limiting adhesion levels were obtained at etching times of 5 min and 10 sec for chromic acid treatment at 22°C and 80°C, respectively.

Chromic acid etching was also found effective in improving the adhesion of BPP and RPP with both epoxy adhesive and PU paint. Table 9.6 shows their adhesion levels, together with those of HPP, after chromic acid etching for 5 min at 22°C.

Table 9.6 Adhesion levels with epoxy adhesive and PU paint of PPs etched by chromic acid for 5 min at 22°C

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Adhesion level (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>with epoxy adhesive</td>
</tr>
<tr>
<td>HPP</td>
<td>25.5</td>
</tr>
<tr>
<td>BPP</td>
<td>16.6</td>
</tr>
<tr>
<td>RPP</td>
<td>11.4</td>
</tr>
</tbody>
</table>

9.7 Locus of adhesion failure

Adhesion levels achieved by chromic acid etching were found so high that complex failures were found in cases of HPP and BPP bonded with epoxy adhesive, or in the cases of BPP painted with PU paint before bonded with epoxy adhesive. These complex failures involved the cohesive failure within the propylene polymer. Complete cohesive failure within the polymer was found in cases where RPP was bonded with epoxy adhesive, or was coated with PU paint before bonded with epoxy adhesive.

Compared with that of HPP bonded directly with epoxy adhesive, the
adhesion level of HPP, painted with PU paint before bonded with epoxy adhesive, was found relatively lower. Its locus of failure was examined using special butts with detachable head for adhesion test. The two surfaces created after the adhesion test were analysed by XPS, and the results are shown in Table 9.7.

Table 9.7 Elemental compositions of both surfaces created by the adhesion testing of epoxide - PU - HPP (chromic acid etched 5 min at 22°C) - PU - epoxide joint

<table>
<thead>
<tr>
<th>Side</th>
<th>Elemental compositions (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>A</td>
<td>87.0</td>
</tr>
<tr>
<td>B</td>
<td>71.5</td>
</tr>
</tbody>
</table>

Side B is typical of the PU paint (C/72.8 O/19.8, N/4.6, Si/2.8), while side A is different from the original acid etched surface (C/93.4, O/5.9, S/0.7). This means that total interfacial failure did not occur. The adhesion failure could be a mixed one involving the interfacial failure between HPP and PU.
Chapter 10 Flame treatment

Propylene polymers were flame treated, then surface characterised by XPS, contact angle measurement, SEM, and ATR-IR. Experimental parameters of flame treatment were examined. They include air-to-gas ratio, flame intensity, the distance between the flame inner cone tip and the polymer surface, and flame contact time. Each of these was studied in turn using XPS and measurement of contact angles (advancing and receding) of water and diiodomethane.

Contact angles of a series of liquids were measured and used to estimate the surface free energies of polymer surfaces treated at various flame conditions. Adhesion level was assessed using the composite butt test. Surface oxygen concentration was correlated to contact angles of water and diiodomethane, and also to contact angle hysteresis. To characterise the treated surface, SEM and ATR-IR were also used. Simple surface composition models were developed to calculate oxygen rich or depleted overlayer thickness. Ageing effects were investigated in terms of oxygen concentration, water contact angles, and the adhesion level with a PU paint. Effects of flame treatment on tensile properties were also studied.

10.1 Flame treatment parameters

10.1.1 Air-to-gas ratio

Effects of varying air-to-gas ratio were examined by varying the air flow rate while keeping the gas flow rate constant at 2.6 l/min and the distance from the inner cone tip to the polymer surface at 1.0cm. Flame contact time, the time required for a single point on the polymer surface to pass through the flame, was kept at 0.04sec. Apart from carbon, only oxygen was detected by XPS on flame treated PP surfaces.
Effects on oxygen concentration and water contact angles

Figs.10.1-10.3 show the oxygen concentration and water contact angles with various air-to-gas ratios for HPP, BPP, and RPP, respectively.

Results obtained in Figs.10.1-10.3 show that the surface oxygen concentration increases with air-to-gas ratio for oxygen deficient flames and reaches a maximum at ~11:1, after which a decrease in oxygen content was found. Water advancing and receding contact angles were found to follow the opposite trend. They decrease with air-to-gas ratio initially, and reach their respective minimum values at ~11:1, followed by the increase of contact angles with air-to-gas ratio. The optimum air-to-gas ratio obtained is slightly higher (~10%) than the stoichiometric ratio, 9.8:1, required for complete combustion of the natural gas (96% CH$_4$ + 4% C$_2$H$_6$, as measured by gas chromatography). This is in line with the result of Hurst et al [55] and Ayres et al [115] both of whom also suggested that an excess of ~10% air was required from the study of flame treatment of PE or PP.

Close correspondence between oxygen concentration and contact angle has been shown by Figs.10.1-3. The number of functional groups (e.g. -OH, C=O, C(=O)O- etc.) introduced onto the surface are thought to be proportional to the oxygen concentration. It can be expected that the higher the oxygen concentration, the greater the interfacial interaction between water and the polymer surface, and therefore the lower the contact angle will be.

Effects on diiodomethane contact angles

Advancing and receding contact angles of diiodomethane were also measured. Results are plotted, together with oxygen concentration, against air-to-gas ratio in Figs.10.4-10.6.
Fig. 10.1 Effects of varying air-to-gas ratio on oxygen concentration and water contact angles for HPP. Gas flow rate was 2.61/min, distance was 1.0 cm
Fig. 10.2 Effects of varying air-to-gas ratio on oxygen concentration and water contact angles for BPP. Gas flow rate was 2.61/min, distance was 1.0 cm
Fig. 10.3 Effects of varying air-to-gas ratio on oxygen concentration and water contact angles for RPP. Gas flow rate was 2.6 l/min, distance was 1.0 cm
Fig. 10.4 Effects of varying air-to-gas ratio on oxygen concentration and diiodomethane contact angles for HPP. Gas flow rate was 2.6 l/min, distance was 1.0 cm
Fig. 10.5 Effects of varying air-to-gas ratio on oxygen concentration and diiodomethane contact angles for BPP. Gas flow rate was 2.6 l/min, distance was 1.0 cm
Fig. 10.6 Effects of varying air-to-gas ratio on oxygen concentration and diiodomethane contact angles for RPP. Gas flow rate was 2.6 l/min, distance was 1.0 cm
As shown by Figs. 10.4-6, diiodomethane advancing contact angles for all three polymers approximately remain constant with various air-to-gas ratios, and are similar to the advancing contact angles of their respective untreated polymers (HPP: 64.1°, BPP: 62.2°, RPP: 64.0°). According to Eq.4.13, and Young’s equation (Eq.4.1), for a nonpolar substrate or a nonpolar liquid,

\[ \gamma_{SL} = \gamma_S + \gamma_L - 2 (\gamma_S^d \gamma_L^d)^{1/2} \]  
\[ \gamma_S = \gamma_{SL} + \gamma_L \cos \theta \]

Combining these two equations, we can get,

\[ \gamma_L (1 + \cos \theta) = 2 (\gamma_S^d \gamma_L^d)^{1/2} \]

where \( \gamma_L^d = \gamma_L \) (i.e. \( \gamma_L^p = 0 \)). Constant \( \theta \) means constant \( \gamma_S^d \), and \( \gamma_S^d \) is approximately equal to that of untreated surface since \( \theta \) approximates the value of untreated surface. Advancing contact angle can represent the least wettable part of the surface, while receding contact angle can represent the most wettable part of the surface \(^{[68]}\). Therefore, the dispersion part of the surface free energy of the least wettable part on the surface remained approximately constant with various air-to-gas ratios.

Diiodomethane receding contact angle varies with air-to-gas ratio less prominently than water receding contact angle. There is some evidence, but not conclusive, that minimum diiodomethane receding contact angle exists at an air-to-gas ratio of around 11:1.

10.1.2 Flame intensity

In the study of flame intensity, the total flow rate was varied while keeping
air-to-gas ratio at 11.8:1, the distance from the inner cone tip to the polymer surface at 1.0cm, and flame contact time at 0.04sec.

**Effects on oxygen concentration and water contact angles**

Fig.10.7-10.9 show the effects of varying flame intensity on oxygen concentration and water advancing and receding contact angles. Much higher surface oxygen concentrations of PP were obtained by Garbassi and coworkers [56] using flame treatment. This could be due to the presence of mineral filler and contaminants on their polymer surfaces.

With more intense flames, the PP film is expected to experience higher temperatures. More radicals will be produced in the flame, resulting the modification, by a radical process, of more segments of the polymer chain on the surface, which will give rise to a higher surface oxygen concentration.

For all three polymers, water receding contact angle initially decreases significantly, while oxygen concentration increases rapidly with total flow rate. Although oxygen concentration further increases steadily with total flow rate, water receding contact angle does not decrease significantly except for RPP. This non-correspondence between oxygen concentration and water contact angle could be explained in terms of sub-surface oxidation [116]. Contact angles are determined by interactions between a contact angle liquid and the outmost layer of atoms on the polymer surface. Therefore, they are expected to be more surface specific then XPS. The oxygen introduced below the outmost layer would be detected by XPS, but have little effect on contact angle.

Water advancing contact angle initially decreases with total flow rate, but then there is some evidence for a minimum. Further increase of total flow rate causes the water advancing contact angle to increase slightly. Therefore, at high flow rates, water advancing contact angle and oxygen concentration
are not in a close correspondence for all three polymers, which is to be discussed in section 10.6.

**Effects on diiodomethane contact angles**

Both advancing and receding contact angles of diiodomethane were measured and plotted, together with oxygen concentration, against total flow rate for all three polymers in Figs.10.10-10.12.

It has been shown by Figs.10.10-10.12 that diiodomethane advancing contact angles for all three polymers approximately remain constant with various total flow rates. These constant values are not too different from their respective untreated polymers (HPP: 64.1°C, BPP: 62.2°, RPP: 64.0°). According to Eq.10.1, $\gamma_s^d$, the dispersion contribution to surface free energy for the least wettable part of the polymer surface, has not been affected significantly by varying flame intensity. It also approximates the $\gamma_s^d$ for its respective untreated polymer surface, since $\theta$ is approximately equal to the value for its untreated polymer.

Diiodomethane receding contact angle decreases slightly with total flow rate. The changes observed are less pronounced than those for water receding contact angle.

10.1.3 Distance

Effects of varying the distance between the flame inner cone tip to the polymer surface were investigated. Air-to-gas ratio was kept at 11.8:1, total flow rate at 33.9 l/min, and flame contact time at 0.04sec.
Fig. 10.7 Effects of varying total flow rate on oxygen concentration and water contact angles for HPP. Air-to-gas ratio was 11.8:1, distance was 1.0 cm
Fig. 10.8 Effects of varying total flow rate on oxygen concentration and water contact angles for BPP. Air-to-gas ratio was 11.8:1, distance was 1.0 cm.
Fig. 10.9 Effects of varying total flow rate on oxygen concentration and water contact angles for RPP. Air-to-gas ratio was 11.8:1, distance was 1.0 cm
Fig. 10.10 Effects of varying total flow rate on oxygen concentration and diiodomethane contact angles for HPP. Air-to-gas ratio was 11.8:1, distance was 1.0 cm
Fig. 10.11 Effects of varying total flow rate on oxygen concentration and diiodomethane contact angles for BPP. Air-to-gas ratio was 11.8:1, distance was 1.0 cm
Fig. 10.12 Effects of varying total flow rate on oxygen concentration and diiodomethane contact angles for RPP. Air-to-gas ratio was 11.8:1, distance was 1.0 cm
Effects on oxygen concentration and water contact angles

Figs. 10.13-10.15 show the effects of varying the distance on oxygen concentration and water contact angles for HPP, BPP, and RPP, respectively.

As the distance increases, the polymer surface becomes further away from the flame reaction zone, which is rich in radicals, the effectiveness of the flame treatment is then expected to be reduced with increasing distance. Figs. 10.13-10.15 have shown that the amount of oxygen present on the surface decreases with the distance, as expected. Water contact angle measurement and perhaps XPS measurement have shown that optimum distance between the flame inner cone tip and the polymer surface is 0.5–1.0 cm. This is in a broad agreement with the result of Ayres et al. [115] who found that the maximum treatment was reached at ~1.0 cm for PP and HDPE.

Effects on diiodomethane contact angles

Effects of varying the distance between the inner cone tip and the polymer surface on both advancing and receding contact angles of diiodomethane are illustrated in Figs. 10.16-10.18.

Like those studied in air-to-gas ratio and flame intensity, diiodomethane advancing contact angles did not vary significantly with the distance for HPP and BPP, and approximately equal to those of their respective untreated polymers. Again it means that the dispersion contribution to the polymer surface free energy (Eq. 10.1), \( \gamma_s^d \), varies little with the distance, and is approximately equal to that of the untreated polymer. However, in the case of RPP, there is some evidence for a slight increase in diiodomethane advancing contact angle with the distance. Diiodomethane receding contact angle behaves in a similar way as water receding contact angle for all three polymers. However, the variation with distance is much less significant than that for water receding contact angle.
Fig. 10.13 Effects of varying the distance on oxygen concentration and water contact angles for HPP. Air-to-gas ratio was 11.8:1, total flow rate was 33.9 l/min
Fig. 10.14 Effects of varying the distance on oxygen concentration and water contact angles for BPP. Air-to-gas ratio was 11.8:1, total flow rate was 33.9 l/min.
Fig. 10.15 Effects of varying the distance on oxygen concentration and water contact angles for RPP. Air-to-gas ratio was 11.8:1, total flow rate was 33.9 l/min
Fig. 10.16 Effects of varying the distance on oxygen concentration and diiodomethane contact angles for HPP. Air-to-gas ratio was 11.8:1, total flow rate was 33.9 l/min
Fig 10.17 Effects of varying the distance on oxygen concentration and diiodomethane contact angles for BPP. Air-to-gas ratio was 11.8:1, total flow rate was 33.9 l/min
Fig. 10.18 Effects of varying the distance on oxygen concentration and diiodomethane contact angles for RPP. Air-to-gas ratio was 11.8:1, total flow rate was 33.9 l/min.
10.1.4 Flame contact time

The time spent by the polymer film in the flame, the width of the flame ribbon (13mm) divided by the conveying speed, was also investigated. It was altered by increasing the conveying speed of the polymer film. Under the experimental conditions used (air-to-gas ratio 11.8:1, total flow rate 33.9 l/min, distance 1.0cm), no significant effects on oxygen concentration or water contact angle were found by varying the flame contact time between 0.02 and 0.07 sec.

10.2 Surface free energy

A series of pure liquids, namely water (triple distilled), ethanediol, DMSO, DMF, and diiodomethane were used for contact angle measurements. Their contact angles (equilibrium) were then used to estimate surface free energies using either Eq.7.2 or Eq.7.4. Propylene polymers treated at selected air-to-gas ratios, total flow rates, and distances were examined. Results, together with the values for untreated polymers, are listed in Tables 10.1-10.3.

It can be seen from Tables 10.1-10.3 that flame treatment primarily affects the polar component, $\gamma_{SP}$, rather than the dispersion component, $\gamma_{Sd}$. The values of $\gamma_{Sd}$ are only slightly higher than those of their respective untreated polymers. In contrast, $\gamma_{SP}$ has been significantly increased.

$\gamma_{Sd}$ is relatively steady, while $\gamma_{SP}$ varies significantly with various air-to-gas ratios, total flow rates, and distances. The relationship, with air-to-gas ratio, total flow rate or the distance, of $\gamma_{SP}$ is in a broad agreement with that of water advancing contact angle. Slightly higher $\gamma_{Sd}$ and significantly higher $\gamma_{SP}$ are obtained using Wu's approach than Owens & Wendt's approach. However, the same trends have been found by using these two methods.
Table 10.1 Surface free energies of HPP treated under selected flame conditions (mJ/m²).

<table>
<thead>
<tr>
<th>Flame conditions</th>
<th>Owens &amp; Wendt's approach</th>
<th>Wu's approach</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\gamma^p_s$</td>
<td>$\gamma^d_s$</td>
</tr>
<tr>
<td>Untreated</td>
<td>0.1</td>
<td>30.3</td>
</tr>
<tr>
<td>Air-to-gas ratio</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.6:1</td>
<td>2.0</td>
<td>31.4</td>
</tr>
<tr>
<td>9.7:1</td>
<td>4.5</td>
<td>30.1</td>
</tr>
<tr>
<td>11.8:1</td>
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Table 10.2 Surface free energies of BPP treated under selected flame conditions (mJ/m²)

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<th>Wu’s approach</th>
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<td>$\gamma_s^d$</td>
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<td>5.1</td>
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<td>4.0</td>
<td>29.0</td>
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<tr>
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<td>28.6</td>
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<td>Total flow rate (l/min)</td>
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<td></td>
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<td>Wu’s approach</td>
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<td>$\gamma_p$ $\gamma_d$ $\gamma_s$ $\gamma_p/\gamma_s$ (%)</td>
<td>$\gamma_p$ $\gamma_d$ $\gamma_s$ $\gamma_p/\gamma_s$ (%)</td>
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<td>Air-to-gas ratio</td>
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<td>8.6:1</td>
<td>2.8 33.6 36.4 7.7</td>
<td>7.0 37.3 44.3 15.8</td>
</tr>
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<td>6.4 35.5 41.9 15.3</td>
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<td>6.8 36.4 43.2 15.7</td>
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<tr>
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<td>8.6 34.9 43.5 19.8</td>
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<tr>
<td>Total flow rate (l/min)</td>
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<td></td>
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<td>4.7 33.5 38.2 12.3</td>
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<td>50.8</td>
<td>3.6 33.0 36.6 9.8</td>
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</tr>
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<td>5.7 36.1 41.8 13.6</td>
</tr>
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<td>Distance (cm)</td>
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<td>3.3 33.6 36.9 8.9</td>
<td>7.7 36.1 43.8 17.6</td>
</tr>
<tr>
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<tr>
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<td>4.6 34.7 39.3 11.7</td>
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10.3 Adhesion level and locus of failure

10.3.1 Adhesion level

Adhesion levels of flame treated propylene polymers with both epoxy adhesive and PU paint were assessed using a composite butt test. Results are listed in Tables 10.4-10.6. Values of untreated polymers are also included.

Tables 10.4-10.6 have shown that flame treatment is very effective in improving adhesion levels of PP to epoxy adhesive or PU paint. Indeed, adhesion levels were so high for most of the samples that locus of failure was cohesive within the PP or complex, involving the cohesive failure of the PP. These compare well with other surface pretreatments (Table 10.7).
Table 10.4 Adhesion levels of flame treated HPP to epoxy adhesive and PU paint

<table>
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<tr>
<th>Flame conditions</th>
<th>Adhesion level (MPa)</th>
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<th></th>
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</thead>
<tbody>
<tr>
<td></td>
<td>with epoxy adhesive</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>with PU paint</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Untreated</td>
<td>1.4 I*</td>
<td>2.3** I</td>
<td></td>
</tr>
<tr>
<td>Air-to-gas ratio</td>
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<td></td>
</tr>
<tr>
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<td>6.2 I</td>
<td>24.7 C</td>
<td></td>
</tr>
<tr>
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<td>20.3 C</td>
<td>25.4 C</td>
<td></td>
</tr>
<tr>
<td>11.8:1</td>
<td>23.9 C</td>
<td>26.4 C</td>
<td></td>
</tr>
<tr>
<td>14.0:1</td>
<td>19.1 C</td>
<td>26.7 C</td>
<td></td>
</tr>
<tr>
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<td>5.1 I</td>
<td>25.8 C</td>
<td></td>
</tr>
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<td></td>
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<tr>
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<td>6.0 I</td>
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</tr>
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<td>22.5 C</td>
<td>25.6 C</td>
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</tr>
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<td>Distance (cm)</td>
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<td>23.6 C</td>
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<td>12.8 C</td>
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<tr>
<td>6.0</td>
<td>3.3 I</td>
<td>4.2 I</td>
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146
Table 10.5 Adhesion levels of flame treated BPP to epoxy adhesive and PU paint

<table>
<thead>
<tr>
<th>Flame conditions</th>
<th>Adhesion level (MPa)</th>
<th>with epoxy adhesive</th>
<th>with PU paint</th>
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<tr>
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<td>3.2 ** I</td>
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<td>Air-to-gas ratio</td>
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<td></td>
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<td>16.9 C</td>
<td></td>
</tr>
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<td>9.7:1</td>
<td>18.9 C</td>
<td>16.0 C</td>
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<td>19.0 C</td>
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<td>15.1:1</td>
<td>19.2 C</td>
<td>3.1 I</td>
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</tr>
<tr>
<td>Total flow rate (l/min)</td>
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<td></td>
</tr>
<tr>
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<td>16.1 C</td>
<td>4.2 I</td>
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</tr>
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<td>18.5 C</td>
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<tr>
<td>6.0</td>
<td>11.8 C</td>
<td>1.6 I</td>
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Table 10.6 Adhesion levels of flame treated RPP to epoxy adhesive and PU paint

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<td>with PU paint</td>
</tr>
<tr>
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<td>2.6 ** I</td>
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</tr>
<tr>
<td>Air-to-gas ratio</td>
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<td>8.9 C</td>
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<td>15.1:1</td>
<td>8.9 C</td>
<td>3.0 I</td>
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<td>Total flow rate (l/min)</td>
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<td>2.2 I</td>
<td>9.1 C</td>
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<tr>
<td>6.0</td>
<td>3.9 I</td>
<td>5.7 I</td>
<td></td>
</tr>
</tbody>
</table>
"I" denotes interfacial failure
"C" denotes complex failure
"M" denotes material failure, i.e. cohesive failure of the PP

**Wiped with trichloroethylene prior to PU surface coating**

Table 10.7 Comparison of adhesion levels of HPP achieved by different surface modifications employed in the study

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Adhesion level (MPa) with epoxy adhesive</th>
<th>Adhesion level (MPa) with PU paint</th>
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</thead>
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<tr>
<td>trichloroethylene vapour 20 sec</td>
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<td>4.0</td>
</tr>
<tr>
<td>Primer M572-170</td>
<td>17.2</td>
<td>18.4</td>
</tr>
<tr>
<td>Chromic acid etching 22°C 5min</td>
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</tr>
<tr>
<td>Flame treatment *</td>
<td>26.4</td>
<td>23.9</td>
</tr>
</tbody>
</table>

| * Air-to-gas ratio 11.8:1, total flow rate 33.9 l/min, the distance 1.0 cm, flame contact time 0.04 sec

Highly oxygen deficient or rich flames, as well as low intensity flames, could result in low adhesion levels. Long distance between the flame inner cone tip and the polymer surface could also have a detrimental effect on adhesion levels.

10.3.2 Locus of failure

Without any treatment of the PU paint prior to the bonding with epoxy adhesive, the adhesion failure was visually interfacial between the cured epoxy adhesive and the PU paint. This is thought to be due to the
detrimental effects of the silicone present on the paint surface (72.8% C, 19.8% O, 4.6% N, Si/2.8%). In order to obtain a joint strength which is meaningful to access the adhesion level between the paint and the polymer surface, this kind of failure should be avoided. Some attempts were made, and a gentle wipe of the PU using fine steel wool was found to be successful. The wipe was sufficient to eliminate its gloss, but gentle enough not to scratch through the paint to the PP film. Isopropanol was used to wipe the paint surface after the wipe with steel wool. SEM has shown that the surface prepared this way was rough and contains deep grooves, while the surface before the wipe was very smooth (Fig.10.19).

The improvement in adhesion level between the epoxy adhesive and the PU paint is thought to be due to the removal of silicon from the paint surface, leading to the exposure of a much more polar paint surface. The roughness caused by the wipe could also, to a lesser extent, account for the improvement in adhesion level by mechanical keying.

The adhesion level between PP and the epoxy adhesive or the PU paint was so high that in most cases, adhesion failure was obviously complex involving the cohesive failure of the PP for HPP and BPP (Tables 10.5 and 10.6), and the complete cohesive failure within the PP for RPP. Interfacial failure only occurred for those treated with flames with highly oxygen deficient or rich, very low intensity, or long distance from the polymer surface, in which cases low adhesion levels were found.

10.4 Correlation between contact angle and oxygen concentration

Water and diiodomethane contact angles (advancing and receding) are plotted against surface oxygen concentration as measured by XPS in Figs. 10.20-10.25.
a) Dried PU paint surface

b) Dried PU paint wiped with steel wool

Fig. 10.19 SEM micrographs of dried PU paint before and after wiping with steel wool
Fig. 10.20 The relationship between water contact angles and surface oxygen concentration for HPP.

Fig. 10.21 The relationship between diiodomethane contact angles and surface oxygen concentration for HPP.
Fig. 10.22 The relationship between water contact angles and surface oxygen concentration for BPP

Fig. 10.23 The relationship between diiodomethane contact angles and surface oxygen concentration for BPP
Fig. 10.24 The relationship between water contact angles and surface oxygen concentration for RPP

Fig. 10.25 The relationship between diiodomethane contact angles and surface oxygen concentration for RPP
It has been shown by Figs.10.20 - 10.25 that diiodomethane advancing contact angle remains approximately constant with various oxygen concentrations for HPP and BPP. In the case of RPP, a slight initial decrease has been found. This implies that the $\gamma_s^d$ of the least wettable parts remains approximately constant with various oxygen concentrations. No significant difference in diiodomethane advancing contact angle was found between untreated and flame treated PP. This means that the $\gamma_s^d$ of the least wettable parts is approximately equal to that of its respective untreated polymer. On the other hand, a slight decrease in diiodomethane receding contact angle with oxygen concentration was found.

Water receding contact angle decreased with oxygen concentration rapidly initially, but no further decrease was found at high oxygen concentrations (>~5 atomic%) (Figs.10.20-10.25). Water advancing contact angle reached a minimum at around 5 atomic% of oxygen. Water contact angles would be expected to decrease as the surface becomes more oxidised. This point is further discussed in section 10.6.

10.5 Correlation between work of acid-base interaction with water and oxygen concentration

The work of acid-base interaction with water, $W_{ab}$, was calculated according to Eq.4.18. The relationship between $W_{ab}$ and surface oxygen concentration is shown in Figs.10.26-28 for HPP, BPP, and RPP. Both $W_{ab}^{adv}$ and $W_{ab}^{rec}$, i.e. works of acid-base interaction with water for the least wettable and most wettable patches on the surface respectively, were calculated according to advancing and receding contact angles of water and diiodomethane. Fig.10.26-28 have shown that $W_{ab}^{rec}$ changes much more significantly than $W_{ab}^{adv}$ with surface oxygen concentration. Both $W_{ab}^{adv}$ and $W_{ab}^{rec}$ increase with surface oxygen concentration rapidly first. However, at high oxygen concentrations (>~5%), they do not further increase with oxygen
Fig. 10.26 The relationship between surface oxygen concentration and work of acid-base interaction with water for HPP

Fig. 10.27 The relationship between surface oxygen concentration and work of acid-base interaction with water for BPP
The relationship between surface oxygen concentration and work of acid-base interaction with water for RPP concentration for all three polymers studied. There is even a slight decrease in the case of $W_{\text{adv}}$ at high oxygen concentrations for HPP and RPP.

10.6 The non-correspondence between water contact angle and surface oxygen concentration at high oxygen concentrations

At high oxygen concentrations, water receding contact angle does not further decrease with oxygen concentration, and water advancing contact angle passes through a minimum as the oxygen concentration continues to increase. It was first thought that this non-correspondence may be due to the presence of low molecular weight materials generated by flame treatment. Thus, specimens of flame treated HPP were washed with diethyl ether in ultrasonic bath for 5 min. Their surface elemental compositions were then examined again using XPS. Results are shown in Table 10.8.
Table 10.8 Surface oxygen concentrations (atomic%) before and after diethyl ether wash of HPP treated under various flame intensities.

Air-to-gas ratio 11.8:1, the distance 1.0cm

<table>
<thead>
<tr>
<th>Total flow rate (l/min)</th>
<th>Unwashed</th>
<th>Washed with diethyl ether</th>
</tr>
</thead>
<tbody>
<tr>
<td>16.9</td>
<td>1.6</td>
<td>1.0</td>
</tr>
<tr>
<td>33.9</td>
<td>6.4</td>
<td>6.7</td>
</tr>
<tr>
<td>67.8</td>
<td>10.7</td>
<td>10.0</td>
</tr>
</tbody>
</table>

Table 10.8 shows little difference in oxygen concentration before and after the wash. Water contact angles were also measured, and no significant difference was found. Therefore, it is unlikely that low molecular weight materials have been generated by the flame treatment.

Surface roughness was then suspected to give rise to this non-correspondence. SEM was used to examine the surfaces after the flame treatment of the three polymers at various flame intensities (Figs.10.29-10.31). Compared with its untreated surface, no significant roughness was generated at various flame intensities for HPP or BPP. Although significant roughness was observed on RPP treated with a mild flame, this roughness did not seem to increase with total flow rate at high flame intensities. Furthermore, if surface roughness caused the non-correspondence, diiodomethane advancing contact angle could be expected to change with oxygen concentration in a similar way as water advancing contact angle. However, diiodomethane advancing contact angle was found approximately constant. Thus, it is unlikely that the non-correspondence between oxygen concentration and water advancing contact angle was caused by surface roughness.
a) HPP treated at total flow rate 16.9 l/min

b) HPP treated at total flow rate 33.9 l/min
c) HPP treated at total flow rate 67.8 l/min

Fig. 10.29 SEM micrographs of HPP treated by flame at various intensities. Flame treatment conditions: air-to-gas ratio 11.8:1, distance 1.0 cm, flame contact time 0.04 sec

a) BPP treated at total flow rate 16.9 l/min
b) BPP treated at total flow rate 33.9 l/min

C) BPP treated at total flow rate 67.8 l/min

Fig.10.30 SEM micrographs of BPP treated by flame at various intensities. Flame treatment conditions: air-to-gas ratio 11.8:1, distance 1.0cm, flame contact time 0.04sec
a) RPP treated at total flow rate 16.9 l/min

b) RPP treated at total flow rate 33.9 l/min
c) RPP treated at total flow rate 67.8l/min

Fig. 10.31 SEM micrographs of RPP treated by flame at various intensities.
Flame treatment conditions: air-to-gas ratio 11.8:1,
distance 1.0cm, flame contact time 0.04sec

If the proportions of functional groups on the surface change with oxygen concentration, a non-correspondence could be expected. If, for example, the concentration of an oxygen containing group which improves the surface wettability does not increase with oxygen concentration at high oxygen concentrations, contact angle would be expected not to decrease with oxygen concentration. However, no significant change in the proportions of oxygen-containing groups with oxygen concentration was observed using deconvolved C1s XPS spectra. The proportion of -OH groups out of the total oxygen concentration was observed approximately constant for a particular PP by using chemical derivatisation with TFAA (see section 12.4).

The non-correspondence between water contact angle and oxygen
concentration at high oxygen concentrations could be explained in terms of sub-surface oxidation and the orientation or migration of oxygen containing groups away from the surface during intense flame treatments. A chemically heterogeneous surface is generated by flame treatment as suggested by high contact angle hysteresis. Advancing contact angle ($\theta_{\text{adv}}$) can be representative of the least wettable part on the surface, while receding contact angle ($\theta_{\text{rec}}$) can be representative of the most wettable part on the surface. With the introduction of oxygen on the surface, both $\theta_{\text{adv}}$ and $\theta_{\text{rec}}$ of water decrease rapidly initially with oxygen concentration. However the oxygen concentration at the near surface may reach its limiting value at an oxygen concentration of $\sim$5% as detected by XPS. Further increase in oxygen concentration below the near surface would not increase the oxygen concentration at the near surface, resulting in the leveling off of water receding contact angle with oxygen concentration. This explains why water receding contact angle does not further decrease with oxygen concentration at high oxygen concentrations.

During the flame treatment, heat is transferred to the polymer surface, which enables the mobility of the polymer chain. The temperature was measured to be $\sim$1100°C at a distance of 1.0cm from the inner cone tip of a flame with a total flow rate of 33.9 l/min, although the contact time was short and the temperature was different from that the polymer surface could reach. Temperatures were even higher at higher flow rates. Functional groups generated by these flames could orientate or migrate away from the surface on some patches, forming the least wettable parts on the surface. Very intense flames could melt the surface layer of the polymer, and hence even partially bury the functional groups. The melting in the surface region of the RPP treated at intensity 67.8 l/min can be clearly seen in Fig.10.31c. The orientation, migration, or even partial "burying" of functional groups on the surface would be expected to increase the water advancing contact angle, but could still enable XPS to detect the increasing extent of oxidation.
10.7 Correlation between contact angle hysteresis and oxygen concentration

Contact angle hystereses of water and diiodomethane are plotted against oxygen concentration in Figs.10.32-10.34.

Overall, contact angle hysteresis of water increases steadily with oxygen concentration. This is thought to be due to the production of a heterogeneous surface. It is thought that hysteresis is unlikely to be due to surface roughness since the diiodomethane contact angle is relatively constant.

The nearly constant diiodomethane contact angle hysteresis implies that the difference in $\gamma_s^d$ between the most and least wettable parts on the surface does not depend much on surface oxygen concentration. Therefore, it can be concluded that the introduction of oxygen on the surface does not have a significant effect on $\gamma_s^d$ of both most and least wettable parts on the surface.
Fig. 10.32 The relationship between oxygen concentration and contact angle hystereses of water and diiodomethane for HPP.
Fig. 10.33 The relationship between oxygen concentration and contact angle hystereses of water and diiodomethane for BPP
Fig. 10.34 The relationship between oxygen concentration and contact angle hystereses of water and diiodomethane for RPP.
10.8 Overlayer thickness calculation using simple models

Simple surface concentration profiles can be employed to estimate the oxidation thickness or the extent of functional groups' orientation / migration. Mild flame treatment may have generated an oxidised layer within the XPS sampling depth. A simple model illustrated in Fig.10.35 can be used.

![Fig.10.35 Simple model for an oxygen rich surface](image)

Assuming that the inelastic mean free paths (IMFP) of C1s ($\lambda_c$) and O1s ($\lambda_o$) are constant within the XPS sampling depth, intensities of C1s ($I_c$) and O1s ($I_o$) photoelectron peaks can be written as:

\[ I_c \propto \chi \sigma_c \gamma_c T D \left[ (1 - O_a) \int_0^d \exp\left(-x/\lambda_c \sin \theta\right) dx + \int_d^\infty \exp\left(-x/\lambda_c \sin \theta\right) dx \right] \]

\[ = (\chi \sigma_c \gamma_c T D \lambda_c) \sin \theta \left[ 1 - O_a + O_a \exp\left(-d/\lambda_c \sin \theta\right) \right] \]

\[ = S_c \sin \theta \left[ 1 - O_a + O_a \exp\left(-d/\lambda_c \sin \theta\right) \right] \quad \text{Eq.10.2} \]

\[ I_o \propto \chi \sigma_o \gamma_o T D \left[ O_a \int_0^d \exp\left(-x/\lambda_o \sin \theta\right) dx \right] \]

\[ = (\chi \sigma_o \gamma_o T D \lambda_o) \sin \theta \left[ O_a \left( 1 - \exp\left(-d/\lambda_o \sin \theta\right) \right) \right] \]
where \( \alpha, \sigma, \gamma, T, \) and \( D \) are defined as in section 4.4.3, chapter 4. \( S_c \) and \( S_o \) are the sensitivity factors of C1s and O1s. \( \theta \) is the take-off angle (with respect to the sample surface). \( \lambda_c \) and \( \lambda_o \) can be calculated according to Seah and Dench's semi-empirical equation for organic compounds [96].

\[
\lambda = \rho \left( \frac{49}{E^2} + 0.11 \ E^{1/2} \right) \text{mg m}^{-2}
\]  

Eq. 10.4

where \( E \) is the electron kinetic energy above Fermi level in eV, \( \rho \) is the specific weight of the polymer, i.e. \( \sim 900 \ \text{Kg/m}^3 \) for PP. Therefore, for PP,

\[
\lambda = \left( \frac{49}{E^2} + 0.11 \ E^{1/2} \right) \times 10/0.9 \ \text{Å}
\]  

Eq. 10.5

Relative oxygen concentration, \([O]\), detected by XPS can be calculated as following,

\[
[O] = \left( \frac{Io}{So} \right) / \left( \frac{Ic}{Sc + Io / So} \right)
\]  

Eq. 10.6

Given the oxygen concentrations detected by XPS at two different take-off angles, e.g. 90° and 30°, the oxidation depth \( d \) and the oxygen concentration in the overlayer can be calculated. A computer programme (FORTRAN) for take-off angles of 90° and 30° was written to do this (Appendix C). Table 10.9 shows angle resolved XPS results for three polymers treated with mild flames. Oxidation depth calculated according to the simple model (Fig.10.35) is also shown in the table.
Table 10.9 Oxidation depth results according to the simple model in Fig.10.35

<table>
<thead>
<tr>
<th>Polymer*</th>
<th>Oxygen concentration (atomic%)</th>
<th>Oxidation thickness (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>90° take-off angle</td>
<td>30° take-off angle</td>
</tr>
<tr>
<td>HPP</td>
<td>5.4</td>
<td>6.7</td>
</tr>
<tr>
<td>BPP</td>
<td>5.5</td>
<td>6.7</td>
</tr>
<tr>
<td>RPP</td>
<td>4.7</td>
<td>6.2</td>
</tr>
</tbody>
</table>

* Polymers were treated with a mild flame: air-to-gas ratio 11.8:1, total flow rate 33.9 l/min, distance 1.0 cm. Oxygen concentration was the average of not less than 8 separate measurements.

Angle resolved XPS results have shown that there is an oxygen enrichment of 20-30% at the near surface, indicating that the oxygen depth is within the XPS sampling depth. Assuming that the simple model in Fig.10.35 can be applied, oxidation thickness was found to be between 40Å and 60Å.

It has been suggested that with severe flame treatments, oxygen containing groups generated can orientate or migrate away from the near surface. A simple model illustrated in Fig.10.36 could be proposed.

Fig.10.36 Simple model for an oxygen depleted surface
Similar to the above discussion, $I_c$ and $I_o$ can be obtained,

\[ I_c \propto S_c \sin \theta \left( 1 - Q_c \exp \left( -\frac{d}{\lambda_c \sin \theta} \right) \right) \]  
\[ I_o \propto S_o \sin \theta \left( Q_o \exp \left( -\frac{d}{\lambda_o \sin \theta} \right) \right) \]  

Eq. 10.7 and 10.8 can also be used to calculate $\lambda_c$, $\lambda_o$, and the oxygen concentration in the substrate. Given the oxygen concentrations detected by XPS at two different take-off angles, e.g. 90° and 30°, the overlayer thickness $d$ and the oxygen concentration below the overlayer can be calculated. A computer programme (FORTRAN) for take-off angles of 90° and 30° was written to perform this (Appendix D). Results for all three polymers are listed in Table 10.10.

### Table 10.10 Overlayer thickness results according to the simple model in Fig. 10.36

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Oxygen concentration (atomic%)</th>
<th>Overlayer thickness (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>90° take-off angle</td>
<td>30° take-off angle</td>
</tr>
<tr>
<td>HPP</td>
<td>8.8</td>
<td>9.5</td>
</tr>
<tr>
<td>BPP</td>
<td>10.5</td>
<td>9.9</td>
</tr>
<tr>
<td>RPP</td>
<td>10.9</td>
<td>9.5</td>
</tr>
</tbody>
</table>

* Polymers were treated with an intense flame: air-to-gas ratio 11.8:1, total flow rate 67.8 l/min, distance 1.0 cm. Oxygen concentration was the average of not less than 8 separate measurements

About 5% and 10% depletion in oxygen at the near surface was found for BPP and RPP respectively. Assuming that the simple model in Fig. 10.36 can be used, the calculated overlayer thicknesses were found to be 2Å and 5Å respectively.
The finding that there was an enrichment in oxygen concentration at the near surface for a mild flame treatment while there was a depletion in oxygen concentration at the near surface for an intense flame treatment supports the hypothesis of functional groups orientation/migration away from the near surface when treated with an intense flame.

Angle resolved XPS does not show any depletion in oxygen at the near surface of HPP treated with an intense flame (Table 10.10). Instead, it seems to have shown a slight enrichment (but much less than that obtained for a mild flame treatment) at the near surface. However, the situation for a real surface may be more complicated. A simple surface composition model illustrated in Fig.10.37 might exist.

Supposing $O_1 = 15\%$, $O_2 = 5\%$, and the specific weight of the polymer is 900 Kg.m$^{-3}$, the dependence of the oxygen concentration detected by XPS on $d_1$, $d_2$, and take-off angles ($90^\circ$ and $30^\circ$) are shown in Fig.10.38. A computer programme (BASIC) was written to perform the calculation (Appendix E).
Fig.10.38 Dependence of oxygen concentration on overlayer thickness and take-off angle according to the simple model in Fig.10.37. O1=15%, O2=5%

It has been shown by Fig.10.38 that given certain thicknesses of d1 and d2, angle resolved XPS could fail to detect the depletion in oxygen concentration at the near surface under certain circumstances. Therefore, even if XPS fails to show any depletion in oxygen concentration at the near surface, it can not rule out the possibility of the orientation / migration of functional groups away from the near surface. Contact angle measurement is the only means available in this study that specifically probes the very near surface.

Simple composition profiles may be a useful starting point for comparison of samples, however, the results must be interpreted with caution. Complex profiles that may be present in some samples can give rise to unexpected results.

10.9 High energy resolution XPS
High energy resolution XPS C1s spectra were obtained and deconvolved to remove the broadening effect due to Al Kα line shape. Results are shown in Figs. 10.39-41.

Fig. 10.39 Deconvolved C1s spectra of HPP. (a) untreated, (b) flame treated with total flow rate 33.9 l/min, and (c) flame treated with total flow rate 67.8 l/min. Air-to-gas ratio 11.8:1, the distance 1.0 cm
Fig. 10.40 Deconvolved Cls spectra of BPP. (a) untreated, (b) flame treated with total flow rate 33.9 l/min, and (c) flame treated with total flow rate 67.8 l/min. Air-to-gas ratio 11.8:1, the distance 1.0cm
Fig. 10.41 Deconvolved C1s spectra of RPP. (a) untreated, (b) flame treated with total flow rate 33.9 l/min, and (c) flame treated with total flow rate 67.8 l/min. Air-to-gas ratio 11.8:1, the distance 1.0 cm
Untreated propylene polymers showed narrow and symmetric C1s peaks. No significant change in C1s spectrum after a mild flame treatment (total flow rate 33.9 l/min) was found. However, intense flame treatment (total flow rate 67.8 l/min) has induced chemically shifted peaks at the higher binding energy side for all three polymers. These peaks can be assigned to C-O, C=O, O=C-O carbons with chemical shifts of \(~1.5\)eV, \(~3.0\)eV, and \(~4.2\)eV respectively. Exact proportion of C-O is difficult to estimate, but is estimated to be in a broad agreement with -OH concentration obtained by derivatisation with TFAA (see section 12.4, Chapter 12).

10.10 Solvent immersion test

Considering the immersion of an interface (A-B) in a liquid (C), as illustrated in Fig.10.42, the expression for the reversible work of adhesion (Eq.4.3) becomes,

\[ W = \gamma_{AC} + \gamma_{BC} - \gamma_{AB} \]  \hspace{1cm} \text{Eq.10.9}

where \(\gamma_{AC}, \gamma_{BC}, \) and \(\gamma_{AB}\) are the interfacial free energies between A and C, B and C, A and B respectively. Given the \(\gamma^d\) and \(\gamma^p\) of these three phases, interfacial free energies and thus work of adhesion, \(W\), can be calculated.
Owens & Wendt's equation (Eq.4.14) is used here.

Spontaneous separation of A and B will occur when W<0. Some work must be done to separate them when W>0, and the separation will not occur spontaneously \[^8^4\]. The immersion of some interfaces in several liquids were carried out. Results, together with their works of adhesion, are shown in Table 10.11. Where separation occurred, it did so in 30 min. Samples which did not show separation were left for one month, and still did not separate.

Table 10.11 Work of adhesion of some interfaces upon immersion in some liquids

<table>
<thead>
<tr>
<th>Interface</th>
<th>Work of adhesion and separation after immersion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Water  Ethandiol  DMSO  DMF  Diiodomethane</td>
</tr>
<tr>
<td>PP (trichloroethylene wiped) - PU</td>
<td>62.0    14.0     2.7    +     -1.1    +     4.7     +</td>
</tr>
<tr>
<td>PP (trichloroethylene vapour 20sec) - PU</td>
<td>n/a*    n/a*     n/a*   -     n/a*    +     n/a*    +</td>
</tr>
<tr>
<td>PP (chromic acid 5min 22°C) - PU</td>
<td>71.2    23.3     12.0   -     8.1     -     13.9    -</td>
</tr>
<tr>
<td>PP (flame treated**) - PU</td>
<td>45.0    7.6      1.7    -     0.6     -     10.6    -</td>
</tr>
<tr>
<td>PP (untreated) - Primer (M572-170)</td>
<td>93.7    31.7     13.0   -     6.5     -     4.1     -</td>
</tr>
</tbody>
</table>

Note:
+: spontaneous separation
-: did not separate
*: Surface free energies of solvent vapour treated polymers not obtainable due to surface roughness
**: Flame treatment conditions: air-to-gas ratio 11.8:1, total flow rate 33.9 l/min, the distance 1.0 cm, and flame contact time 0.04 sec.

Considering the experimental error in obtaining surface free energies, the immersion test results agreed broadly with the work of adhesion results. Spontaneous separation was found for HPP (solvent wiped or vapour
treated) - PU interfaces upon immersion in some of the liquids. Although the work of adhesion of HPP (flame treated) - PU interface upon immersion in DMSO or DMF was found very low, spontaneous separation was not observed. This is thought to be due to the existence of chemical bonding across the interface since the two-pack PU paint is highly reactive and could react with surface functional groups (e.g. -OH groups) introduced by flame treatment.

10.11 Effects of ageing

Propylene polymers treated under identical conditions (air-to-gas ratio 11.8:1, total flow rate 33.9 l/min, the distance from the inner cone tip 1.0 cm, flame contact time 0.04 sec) were kept in sealed glass jars at room temperature for the study of ageing effects. Oxygen concentration, water advancing and receding contact angles and joint strength with the PU paint were measured. Table 10.12 shows the surface oxygen concentration, water contact angles, and adhesion level with PU paint with ageing time.

Considering the experimental errors (standard deviation 1~2°), little change in water advancing or receding contact angles were found for HPP and BPP. For RPP, a notable increase in water receding contact angle, and perhaps a slight increase in water advancing contact angle were observed.

For all three polymers, surface oxygen concentration decreased notably within 22 days of ageing, with little change even after 135 days of ageing. The decrease in oxygen concentration with ageing might be due to the reorientation of the oxygen-containing groups away from the near surface. However, the adhesion level with PU paint was still retained after a long time of ageing.
Table 10.12 Effects of ageing on surface oxygen concentration, water contact angles, and adhesion level with PU paint

<table>
<thead>
<tr>
<th>Ageing time (days)</th>
<th>Oxygen concentration (atomic%)</th>
<th>Water advancing contact angle</th>
<th>Water receding contact angle</th>
<th>Adhesion level with PU paint (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HPP</td>
<td>BPP</td>
<td>RPP</td>
<td>HPP</td>
</tr>
<tr>
<td>0</td>
<td>5.9</td>
<td>5.5</td>
<td>6.2</td>
<td>88.8</td>
</tr>
<tr>
<td>1</td>
<td>5.8</td>
<td>5.5</td>
<td>6.3</td>
<td>88.8</td>
</tr>
<tr>
<td>22</td>
<td>4.4</td>
<td>3.6</td>
<td>5.4</td>
<td>89.7</td>
</tr>
<tr>
<td>43</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>91.9</td>
</tr>
<tr>
<td>135</td>
<td>3.5</td>
<td>3.6</td>
<td>5.6</td>
<td>91.5</td>
</tr>
</tbody>
</table>

* "C" denotes complex adhesion failure
"I" denotes interfacial failure between the PU paint and the propylene polymer
"M" denotes material failure, i.e. cohesive failure within the propylene polymer
Tensile properties of propylene polymers treated with an intense flame were measured. Results are listed in Table 10.13.

Table 10.13: Tensile strengths at yield point of untreated and flame treated PPs

<table>
<thead>
<tr>
<th></th>
<th>Tensile strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HPP (100 µm)</td>
</tr>
<tr>
<td>untreated</td>
<td>19.0</td>
</tr>
<tr>
<td>Flame treated *</td>
<td>26.7</td>
</tr>
</tbody>
</table>

* Flame conditions: air-to-gas ratio 11.8:1, total flow rate 67.8 l/min, the distance 1.0 cm, flame contact time 0.04 sec.

Significant increase in tensile strength was found after flame treatment for HPP and BPP. An increase of ~2 fold in tensile strength was found for BPP after flame treatment, while only a slight increase in tensile strength was observed for RPP by flame treatment. Initially the crosslinking of the polymer chains was suspected to have caused this increase in tensile strength after flame treatment. However, PP film treated by an intense flame was found to dissolve completely in $p$-xylene at 138°C. Therefore, it is unlikely that the increase in tensile strength after flame treatment was due to crosslinking. Meanwhile, a heat treatment of HPP (155°C for 2 min in an oven) gave a similar increase in tensile strength of the polymer. More perfect crystals were observed using optical microscopy under polarised light after an intense flame treatment or heat treatment. DSC showed a slight increase in the heat of fusion. Thus, the increase in tensile strength may be due to the slight increase in crystallinity or to the heat effects of the flame which may have removed the defects in the polymer film.
Chapter 11 Application of Primers

Chlorinated polyolefin primers M572-170 (ex ICI) and Hardlen 14-LLB (ex Toyo Kasei Kogyo) were used instead of a pretreatment to promote the adhesion of untreated PP to epoxy adhesive and PU paint.

11.1 Surface characterisation

Surfaces of dried primers after being air sprayed onto the HPP surface were characterised using XPS, SEM, and contact angle measurement.

XPS has shown that the two primers used have similar surface elemental compositions (Table 11.1). Small amounts of oxygen were also found on their surfaces. They were probably introduced during the chlorination process.

<table>
<thead>
<tr>
<th>Primer</th>
<th>Elemental compositions (atomic%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>M572-170</td>
<td>87.9</td>
</tr>
<tr>
<td>14-LLB</td>
<td>87.2</td>
</tr>
</tbody>
</table>

Surface free energy of dried primer M572-170 was estimated from contact angle results using either Owens & Wendt's (Eq.7.2) or Wu's (Eq.7.4) approach. Results are listed in Table 11.2.

Although its surface free energies are higher, as expected from the introduction of chlorine atoms on the polymer chains, than those of untreated PPs (Table 7.1), it still remains virtually nonpolar. Lower contact
Table 11.2 Surface free energies (mJ·m⁻²) of dried primer M572-170 as estimated using Owens & Wendt's and Wu's approaches

<table>
<thead>
<tr>
<th>Method</th>
<th>$\gamma_s^d$ (mJ·m⁻²)</th>
<th>$\gamma_s^p$ (mJ·m⁻²)</th>
<th>$\gamma_s$ (mJ·m⁻²)</th>
<th>$\gamma_s^d / \gamma_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Owens &amp; Wendt's</td>
<td>36.7</td>
<td>0.2</td>
<td>36.9</td>
<td>0.005</td>
</tr>
<tr>
<td>Wu's</td>
<td>36.0</td>
<td>2.5</td>
<td>38.5</td>
<td>0.065</td>
</tr>
</tbody>
</table>

angles were observed on the primer surface than on the untreated HPP surface. More significant decrease in receding contact angle than in advancing contact angle was found (Table 11.3). Therefore better wettability would be expected in the painting process.

Table 11.3 Contact angles of water and diiodomethane on dried primer M572-170 and untreated HPP

<table>
<thead>
<tr>
<th>Material</th>
<th>Water</th>
<th>Diiodomethane</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\theta_{adv}$</td>
<td>$\theta_{rec}$</td>
</tr>
<tr>
<td>PP (untreated)</td>
<td>108.4</td>
<td>91.4</td>
</tr>
<tr>
<td>PP + M572-170</td>
<td>98.3</td>
<td>74.7</td>
</tr>
</tbody>
</table>

Diiodomethane contact angle hysteresis was found to be much greater on the primer surface than on that of the untreated HPP. Slight roughness was observed using SEM (Fig.11.1) for primer M725-170, and may contribute to the contact angle hysteresis.
11.2 Adhesion levels

Adhesion levels of HPP with both epoxy adhesive and PU paint were significantly increased by priming (Table 11.4). Both chlorinated primers gave similar improvements in adhesion levels.

Table 11.4 Adhesion levels of primed HPP with epoxy adhesive and PU paint

<table>
<thead>
<tr>
<th>Primer</th>
<th>Adhesion level (MPa)</th>
<th>Adhesion level (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>with epoxy adhesive</td>
<td>with PU paint</td>
</tr>
<tr>
<td>PP (untreated)</td>
<td>1.4</td>
<td>2.3 *</td>
</tr>
<tr>
<td>M572-170</td>
<td>17.2</td>
<td>18.3</td>
</tr>
<tr>
<td>14-LLB</td>
<td>17.3</td>
<td>16.7</td>
</tr>
</tbody>
</table>

* Wiped with trichloroethylene prior to PU surface coating
The primer M572-170 was also applied to the two copolymers. Their adhesion levels are listed in Table 11.5. For either of the polymers, similar adhesion levels with epoxy adhesive and PU paint were obtained.

Table 11.5 Adhesion levels of M572-170 primed propylene copolymers with epoxy adhesive and PU paint

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Adhesion level (MPa)</th>
<th>Locus of failure</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>with epoxy adhesive</td>
<td>with PU paint</td>
</tr>
<tr>
<td>BPP</td>
<td>14.2</td>
<td>13.4</td>
</tr>
<tr>
<td>RPP</td>
<td>11.2</td>
<td>11.7</td>
</tr>
</tbody>
</table>

within PP

11.3 Locus of adhesion failure

Special steel butts with detachable head suitable for XPS analysis were used to facilitate the determination of the locus of adhesion failure. Table 11.6 shows the XPS results of both surfaces created by adhesion testing of the HPP primed with M572-170 and subsequently top-coated with PU paint.

Table 11.6 Elemental compositions of both surfaces created by adhesion testing of epoxide - PU - (M572-170) - HPP(untreated) - (M572-170) - PU - epoxide joint

<table>
<thead>
<tr>
<th>Side</th>
<th>Elemental compositions (atomic%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>A</td>
<td>100.0</td>
</tr>
<tr>
<td>B</td>
<td>87.9</td>
</tr>
</tbody>
</table>

Side A is typical of untreated HPP surface, while side B is typical of the
primer M572-170 surface (C/87.9, O/1.7, Cl/10.4 see Table 11.1). This indicates that the locus of adhesion failure was interfacial, between the HPP and the primer.

Both propylene copolymers have lower tensile strengths than the homopolymer. The adhesion failure was found complex for M572-170 primed BPP when bonded directly with epoxy adhesive or coated with PU paint prior to adhesive bonding. This complex failure involved the cohesive failure within the copolymer. A totally cohesive failure within the copolymer was observed for M572-170 primed RPP when bonded directly with epoxy adhesive or coated with PU paint prior to adhesive bonding.
Chapter 12 Chemical Derivatisation

12.1 Derivatisation using model polymers

Model polymers with known amounts of functional groups (Table 12.1) were used to evaluate the vapour-phase derivatisation using a vacuum frame. Their oxygen concentrations determined using XPS are also listed with stoichiometric values in Table 12.1.

Table 12.1 Model polymers used in vapour-phase derivatisation

<table>
<thead>
<tr>
<th>Model polymer</th>
<th>Functional group</th>
<th>Oxygen concentration (atomic%)</th>
<th>stoichiometric</th>
<th>experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(vinyl alcohol) (PVA)</td>
<td>(-C\neq OH)</td>
<td>33.3</td>
<td>28.7</td>
<td></td>
</tr>
<tr>
<td>Poly(acrylic acid) (PAA)</td>
<td>(-C\neq OH)</td>
<td>40.0</td>
<td>33.9</td>
<td></td>
</tr>
<tr>
<td>Poly(vinyl methyl ketone) (PVMK)</td>
<td>(-C\neq )</td>
<td>20.0</td>
<td>17.4</td>
<td></td>
</tr>
<tr>
<td>Poly(ethylene terephthalate) (PET)</td>
<td>(-C\neq O)</td>
<td>28.6</td>
<td>23.6</td>
<td></td>
</tr>
</tbody>
</table>

Oxygen concentrations detected by XPS were found to be approximately \(-15\%\) less than their respective stoichiometric values. This might be due to the orientation of oxygen containing groups away from the near surface.

12.1.1 TFAA derivatisation

Trifluoroacetic anhydride (TFAA) was used to derivatise hydroxyl groups. Its reaction with PVA can be written as,
\[
-C\text{-OH} + CF_3-C=O-C-CF_3 = -C=O-C-CF_3 + CF_3-C\text{-OH}
\]

Eq.12.1

Its reactivity towards PAA, PVMK, and PET was also examined. Assuming that original oxygen atoms and the derivatives are homogeneously distributed in the surface layer, surface atomic concentrations of oxygen (O%) and fluorine (F%) can be derived as following from the conversion factor, \(x\), according to Eq.12.1 (Appendix F),

\[
O\% = \frac{1+x}{6x+1 /[O]_0} \times 100\%
\]

Eq.12.2

\[
F\% = \frac{3x}{6x+1 /[O]_0} \times 100\%
\]

Eq.12.3

where \([O]_0\) is the original surface oxygen concentration, i.e. 0.287, as determined by XPS. O% and F% are plotted against x in Fig.12.1.

Fig.12.1 shows that oxygen concentration decreases rapidly initially, and then slowly as the reaction is driven to completion. Fluorine concentration increases rapidly first, followed by a steady increase afterwards. Fig.12.1 also illustrates that fluorine concentration rather than oxygen concentration should be used to estimate the conversion factor, and that a nonlinear relationship exists between the fluorine concentration and the conversion factor. Chilkoti et al [117] simply equated the ratio, F%/F% at x =1.0), with the conversion factor, implying that the existence of a linear relationship between F% and x.

PVA samples were reacted with TFAA for various times, and fluorine concentrations determined using XPS. Results are plotted in Fig.12.2.
Fig. 12.1 Theoretical surface oxygen and fluorine concentrations of PVA derivatised with TFAA.

Fig. 12.2 Experimental surface oxygen and fluorine concentrations as a function of reaction time of PVA derivatised with TFAA.
TFAA was found to react with PVA rapidly. Limiting fluorine incorporation on the surface was obtained at a reaction time of ~2 hrs. No significant increase in fluorine concentration even after 16 hrs of reaction (corresponding to a conversion factor of ~80%). The incompleteness of the reaction could be due to the difficulty of diffusion of TFAA into the polymer.

The reaction of TFAA with PAA, PVMK, PET, and untreated HPP was found to be minor. Only small amounts of fluorine were detected on these polymers (Table 12.2).

Table 12.2 Elemental compositions of model polymers and untreated HPP derivatised with TFAA for 2 hours

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Elemental compositions (atomic%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>PVA</td>
<td>51.3</td>
</tr>
<tr>
<td>PAA</td>
<td>65.2</td>
</tr>
<tr>
<td>PVMK</td>
<td>78.9</td>
</tr>
<tr>
<td>HPP untreated</td>
<td>97.8</td>
</tr>
</tbody>
</table>

Compared with the reaction of TFAA with PVA, those with PAA, PVMK, or untreated HPP can be normally ignored, suggesting that TFAA is reasonably selective towards hydroxyl groups. The reaction of TFAA with PAA is thought to be via the substitution of acid H atom with a (-C(=O)CF₃) group (Eq.12.4), while the reaction with PVMK could be through the reaction with enol groups (Eq.12.5).
The reaction of TFAA with PVMK was found to be accompanied by a colour change, from clear to purple red.

12.1.2 Hydrazine derivatisation

The reaction of hydrazine with PVMK to form hydrazone can be written as,

\[
\begin{align*}
\text{CH}_2- \text{CH}=\text{CH}_2 + \text{NH}_2\text{NH}_2 & \rightarrow \text{CH}_2- \text{CH}=\text{CH}_2 \text{N}=\text{NH}_2 + H_2O \\
\text{C}=\text{O} & \quad \text{C}=\text{O} \\
\text{CH}_3 & \quad \text{CH}_3
\end{align*}
\]

Eq.12.6

For complete reaction, every single carbonyl group will generate a hydrazone group. For incomplete reaction, the conversion factor, \(x\), can be related to oxygen concentration \(O\%\), and nitrogen concentration \(N\%\), by the following equations (Appendix F),
\[ \text{O\%} = \frac{[O]\circ (1 - x)}{1 + x [O]\circ} \times 100\% \quad \text{Eq.12.7} \]

\[ \text{N\%} = \frac{2 [O]\circ x}{1 + x [O]\circ} \times 100\% \quad \text{Eq.12.8} \]

where \([O]\circ\) is the original oxygen concentration before derivatisation, i.e. 0.174, as detected by XPS. The dependences of \(O\%\) and \(N\%\) on \(x\) are plotted in Fig.12.3.

Fig.12.3 shows that oxygen concentration decreases and nitrogen concentration increases almost linearly with conversion factor. Fig.12.4 illustrates the experimental oxygen and nitrogen concentrations with increasing reaction time.

Initial rapid reaction was found. However, both nitrogen and oxygen concentrations were found to remain constant after 2 hours of reaction, with a conversion factor of about 0.5. Even after 24 hours of reaction, the conversion factor was still only 0.6.

Hydrazine derivatisation was found to be far less selective than TFAA derivatisation. Table 12.3 lists the XPS results of the model polymers and untreated propylene homopolymer derivatised with hydrazine. Although the reaction of hydrazine with PVA can be ignored, the reaction with PAA or PET was found significant, casting doubt on the validity of the use of hydrazine to derivatise ketone groups which was previously reported \(^{[42]}\) \(^{[102]}\).

Hydrazine showed a very high reactivity towards PET. Oxygen and nitrogen concentrations after derivatisation are plotted against reaction time in Fig.12.5.
Fig. 12.3 Theoretical oxygen and nitrogen concentrations of PVMK derivatised with hydrazine

Fig. 12.4 Experimental oxygen and nitrogen concentrations as a function of reaction time of PVMK with hydrazine
Table 12.3 Elemental compositions of model polymers and untreated propylene homopolymer derivatised with hydrazine for 2 hours

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Elemental composition (atomic%)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>O</td>
<td>N</td>
</tr>
<tr>
<td>PVMK</td>
<td>75.0</td>
<td>8.9</td>
<td>16.1</td>
</tr>
<tr>
<td>PVA</td>
<td>70.6</td>
<td>28.5</td>
<td>0.9</td>
</tr>
<tr>
<td>PAA</td>
<td>62.7</td>
<td>27.0</td>
<td>10.3</td>
</tr>
<tr>
<td>PET</td>
<td>61.9</td>
<td>14.1</td>
<td>24.0</td>
</tr>
<tr>
<td>HPP untreated</td>
<td>100.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

White powder like products were observed on the PET film surface after the reaction.
derivatisation reaction with hydrazine. This is thought to be due to the decomposition of the polymer chain by hydrazine. Likely reactions of PET with hydrazine can be expressed by Eq.12.9 and Eq.12.10. Chain scission occurs in Eq.12.9, while a hydrazone is produced in Eq.12.10.

$$\begin{align*}
\text{R-C-OR'} + \text{NH}_2\text{NH}_2 & \rightarrow \text{R-C-NHNH}_2 + \text{R'OH} \\
\text{Eq.12.9}
\end{align*}$$

$$\begin{align*}
\text{R-C-OR'} + \text{NH}_2\text{NH}_2 & \rightarrow \text{R-C-OR'} + \text{H}_2\text{O} \\
\text{Eq.12.10}
\end{align*}$$

Similarly, possible reactions of hydrazine with PAA are illustrated in Eq.12.11 and Eq.12.12.

$$\begin{align*}
\text{\{CH}_2\text{-CH\}_n} + \text{NH}_2\text{NH}_2 & \rightarrow \text{\{CH}_2\text{-CH\}_n} + \text{H}_2\text{O} \\
\text{Eq.12.11}
\end{align*}$$

$$\begin{align*}
\text{\{CH}_2\text{-CH\}_n} + \text{NH}_2\text{NH}_2 & \rightarrow \text{\{CH}_2\text{-CH\}_n} + \text{H}_2\text{O} \\
\text{Eq.12.12}
\end{align*}$$
12.2 Dependence of chemical derivatisation on reservoir temperature

During vapour-phase derivatisation, the reservoir containing the reagent (i.e. TFAA or hydrazine) was maintained in a cool water bath in order to avoid condensation of TFAA or hydrazine on sample surfaces which were kept at room temperature (~22°C). The reservoir temperature was found to have a significant influence on derivatisation reactions. Table 12.4 lists some XPS results of PVA and PVMK derivatised for 5 min under different reservoir temperatures. At a higher temperature, a higher yield of derivatised product was obtained.

<table>
<thead>
<tr>
<th>Derivatization</th>
<th>Reservoir temperature °C</th>
<th>Elemental composition (atomic%)</th>
<th>C</th>
<th>O</th>
<th>N</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVA + TFAA</td>
<td>9</td>
<td></td>
<td>61.7</td>
<td>30.8</td>
<td>7.5</td>
<td></td>
</tr>
<tr>
<td>PVA + TFAA</td>
<td>20</td>
<td></td>
<td>54.0</td>
<td>25.9</td>
<td>20.1</td>
<td></td>
</tr>
<tr>
<td>PVMK + hydrazine</td>
<td>9</td>
<td></td>
<td>83.3</td>
<td>13.3</td>
<td>3.4</td>
<td></td>
</tr>
<tr>
<td>PVMK + hydrazine</td>
<td>20</td>
<td></td>
<td>78.1</td>
<td>11.7</td>
<td>10.2</td>
<td></td>
</tr>
</tbody>
</table>

This phenomenon can be interpreted according to the vapour pressure change at different temperatures. For a phase change, Clapeyron's equation can be written as,

\[
\frac{dP}{dT} = \frac{\Delta S_m}{\Delta V_m} \tag{12.13}
\]

where \( P \) is the vapour pressure, \( T \) is the temperature (in degrees Kelvin), \( \Delta S_m \) is the molar entropy change, and \( \Delta V_m \) is the molar volume change. For
a liquid-vapour boundary, $\Delta S_m \approx 85 \text{ J} \cdot \text{K}^{-1} \text{ mol}^{-1}$ according to Trouton's rule $^{[118]}$. Assuming the vapour behaves ideally, $\Delta V_m = V_m (g) = RT/P$,

$$\ln \left( \frac{P_2}{P_1} \right) \approx \frac{85}{R} \ln \left( \frac{T_2}{T_1} \right)$$  \hspace{1cm} \text{Eq.12.14}

where $P_2, P_1$ are vapour pressures at temperatures $T_2, T_1$ respectively. The conventional boiling point (39.9°C for TFAA and 113.7°C for hydrazine) is the temperature when the vapour pressure is 1 atm. Therefore vapour pressures at other temperatures can be estimated using the above equation. Table 12.5 gives the vapour pressures of TFAA and hydrazine at different temperatures.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Vapour pressure (atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TFAA</td>
</tr>
<tr>
<td>9</td>
<td>0.35</td>
</tr>
<tr>
<td>20</td>
<td>0.51</td>
</tr>
<tr>
<td>30</td>
<td>0.72</td>
</tr>
</tbody>
</table>

Table 12.5 shows a marked increase in vapour pressure with increasing temperature. Vapour pressure is directly proportional to the collision frequency between the vapour molecules and the sample surface. Therefore, the rate of reaction increases with the vapour pressure. This explains why the derivatisation reaction is quicker at a higher reservoir temperature.

12.3 Chemical derivatisation of chromic acid etched propylene polymer surfaces
Propylene homopolymer etched by chromic acid at 22°C for 5 min did not show any incorporation of fluorine after TFAA derivatisation. This is not surprising since alcohol groups would tend to be further oxidised.

\[
\begin{align*}
R-\text{CH} & \text{-OH} & \xrightarrow{\text{K2Cr2O4}} & R-\text{C} = \text{O} \\
| \text{H2SO4} & | \\
R' & & R' & \text{Eq.12.15}
\end{align*}
\]

\[
\begin{align*}
R-\text{CH2-} & \text{-OH} & \xrightarrow{\text{K2Cr2O4}} & R-\text{CH} = \text{O} \\
| \text{H2SO4} & | \\
R' & & R' & \text{Eq.12.16}
\end{align*}
\]

Aldehydes can be further oxidised to give carboxylic acids,

\[
\begin{align*}
R-\text{CH} & \text{= O} & \xrightarrow{\text{K2Cr2O4}} & R-\text{C} - \text{OH} \\
| \text{H2SO4} & | \\
\text{Eq.12.17}
\end{align*}
\]

Therefore, ketones and carboxylic acids could well exist on chromic acid treated surfaces. Positive reaction of treated HPP with hydrazine was observed. 1.4% N was detected by XPS on HPP surface etched for 5 min at 22°C by chromic acid after derivatisation. However, ketones and carboxylic acids can not be distinguished since they both react with hydrazine, as shown by derivatisation results using model polymers. On the other hand, these reactions do not go to completion. Therefore, it is difficult to quantify these functional groups on the surface.

12.4 Chemical derivatisation of flame treated propylene polymer surfaces

Propylene homopolymer and the two copolymers treated under selected flame conditions were derivatised using TFAA. Hydroxyl groups concentration estimated from XPS results are plotted against total oxygen concentration in Figs.12.6-12.8 for HPP, BPP and RPP respectively.
Fig. 12.6 Correlation between \(-\text{OH}\) concentration and original oxygen concentration under selected flame conditions for HPP

Fig. 12.7 Correlation between \(-\text{OH}\) concentration and original oxygen concentration under selected flame conditions for BPP
Overall, an approximately linear relationship between hydroxyl groups concentration and original oxygen concentration has been found for all three polymers. About 20% of the oxygen incorporated onto the homopolymer surface treated under various flame conditions was identified as hydroxyl groups. Slightly higher percentages, ~30%, was found for the two copolymers, BPP and RPP.

12.5 Role of hydroxyl groups on adhesion

The role of hydroxyl groups on adhesion was studied using chemical derivatisation with TFAA. The homopolymer (HPP) was treated with a mild flame, and -OH groups on the surface were derivatised with TFAA. Effects of this derivatisation on water contact angles and adhesion are shown in Table 12.6.
Table 12.6 Effects of derivatisation with TFAA on contact angle and adhesion for HPP treated with a mild flame

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Water contact angle</th>
<th>Adhesion level (MPa)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\theta_{\text{adv}}$</td>
<td>$\theta_{\text{rec}}$</td>
<td>with epoxy adhesive</td>
<td>with PU paint</td>
</tr>
<tr>
<td>HPP</td>
<td>92.7</td>
<td>51.4</td>
<td>23.9±2</td>
<td>26.4±2</td>
</tr>
<tr>
<td>HPP TFAA 2 hrs</td>
<td>95.4</td>
<td>64.4</td>
<td>25.2±2</td>
<td>12.7±2</td>
</tr>
</tbody>
</table>

*: Treated with a mild flame: air-to-gas ratio 11.8:1, total flow rate 33.9 l/min, the distance from the inner cone tip to the polymer surface 1.0 cm.

Table 12.6 shows that the removal of -OH groups on the surface by derivatisation with TFAA slightly decreases the wettability. The adhesion level with the epoxy adhesive remains unchanged, indicating that the presence of -OH groups is not crucial. Although the removal of -OH groups on the surface significantly decreases the adhesion level with PU paint, good adhesion level was still retained. The PU paint is a reactive system, thus the presence of -OH groups on the polymer surface could react with the paint during its cure. Therefore the presence of -OH groups on the surface plays an important role in the adhesion with the PU paint, but is not essential to achieve good adhesion. The removal of -OH groups by the reaction with TFAA increased the receding contact angle (Table 12.6), and therefore increased the tendency of the PU paint to dewet on the surface. This could also adversely affect adhesion.
PART IV CONCLUSIONS

Effects of several surface treatments on surfaces of three propylene polymers (HPP: homopolymer, BPP: bumper grade copolymer, and RPP: rubber-modified) were examined using X-ray photoelectron spectroscopy (XPS), chemical derivatisation, attenuated total reflection infrared spectroscopy (ATR-IR), contact angle measurement, scanning electron microscopy (SEM), and a composite butt adhesion test. Surface treatment methods included solvent treatment, chromic acid etching, flame treatment, and priming. The emphasis was on flame treatment. The aims of this project were to physically and chemically examine the surface effects generated by these treatments, to compare the effectiveness of these treatments, to establish the understanding of the relationship between the results of XPS and contact angle measurement, and to improve the understanding of adhesion mechanism. According to the studies carried out, the following conclusions may be drawn.

1. Solvent treatment

Organic solvent treatment included solvent wipe and solvent vapour treatment. Although solvent wipe slightly improved the wetting of the polyurethane (PU) paint on PP surfaces, the adhesion was poor. Solvent vapour treatment was found to be more effective in improving the adhesion. Gross roughness was observed on HPP surfaces after trichloroethylene vapour treatment, while no significant roughness was found following trichloroethane vapour treatment. However, treatment using either of the solvent vapours was found equally effective in improving the adhesion of HPP. After solvent vapour treatment, water advancing contact angle was increased while the receding contact angle was decreased. XPS did not show any chemical modification on the surface by solvent treatment. Therefore, the improvement in adhesion has been
attributed to the decrease of the tendency of the PU paint to dewet on the surface. Locus of failure studies showed the presence of a layer containing silicon at the interface between solvent treated PP and the PU paint. This may be attributed to the presence of additives (e.g. silicone oil as a film forming aid) in the paint.

2. Chromic acid etching

Chromic acid etching was found to give better adhesion. Etching at an elevated temperature was found more effective than at room temperature. Etching rate was found to increase in the following order, HPP < BPP < RPP. Dramatic decrease in water contact angles, while a less pronounced decrease in diiodomethane contact angles was observed. Receding contact angle was decreased much more significantly than advancing contact angle. Contact angle hysteresis was attributed to surface chemical heterogeneity and possibly also to surface roughness in the cases of BPP and RPP.

3. Flame treatment

Among the treatments studied, flame treatment was found to give the best adhesion. Studies of flame treatment parameters were carried out on three propylene polymers using XPS, contact angle measurement, and an adhesion test. They included air-to-gas ratio, total flow rate, and the distance from the inner cone tip to the polymer surface. Optimum air-to-gas ratio was found to be ~11:1, which is ~10% higher than the stoichiometric ratio required for complete combustion of the fuel gas (natural gas). Optimum distance from the inner cone tip to the polymer surface was found to be 0.5~1.0 cm.

Water contact angles were found to vary more significantly than diiodomethane contact angles under various flame conditions, indicating that flame treatment mainly increased $\gamma_{sP}$ rather than $\gamma_{sd}$ of the surface. Contact angle hysteresis was attributed to surface heterogeneity caused by
flame treatment. Diiodomethane advancing contact angle was found approximately constant with various flame conditions, indicating that the dispersion part of surface free energy for the least wettable part on the surface was relatively constant.

Good correlation between contact angle and oxygen concentration was found at low oxygen concentrations (<~5%). The non-correspondence between contact angle and oxygen concentration at high oxygen concentrations was explained in terms of sub-surface oxidation and the orientation / migration of functional groups away from the near surface during the flame treatment. This hypothesis was supported by angle resolved XPS results.

Simple surface composition models were developed to estimate oxidation depth or overlayer thickness. According to these simple models, mild flame treatment generated an oxidised layer of between 40-60Å, and intense flame treatment generated an oxygen depleted layer of several angstroms.

Ageing of up to 135 days in sealed glass jars at room temperature was found to have little effect on contact angle and adhesion level with PU paint, although a slight decrease in oxygen concentration was found.

Excellent adhesion with both epoxy adhesive and PU paint was obtained with flame treatment. In fact, the adhesion level was so high that in most cases the locus of failure was found to be cohesive within the PP or complex including the cohesive failure of the PP.

4. Priming

Chlorinated polyolefin primers were used to improve the adhesion of PP. Good adhesion levels with both epoxy adhesive and PU paint were obtained by using a primer. Locus of failure was found to be interfacial between PP and the primer.
5. Chemical derivatisation

Model polymers with known amounts of functional groups, i.e. poly(vinyl alcohol) (PVA), poly(acrylic acid) (PAA), poly (vinyl methyl ketone) (PVMK), and poly(ethylene terephthalate) (PET) were used to evaluate the vapour-phase derivatisation reactions. TFAA was proved to be a good derivatising reagent for hydroxyl groups. The reactions of TFAA with acid groups or carbonyl groups were found negligible. However, the reaction of hydrazine with carbonyl groups was found far from completion. The reaction was also not specific. Substantial reaction with acid and ester groups was found.

Vapour-phase derivatisation with TFAA was used to determine the concentration of hydroxyl groups on chromic acid etched and flame treated PP surfaces. No hydroxyl groups were detected on chromic acid etched PP surfaces. This was attributed to the oxidative nature of the acid which can further oxidise hydroxyl groups into carbonyl or acid groups.

About 20% of the oxygen on flame treated HPP surface was found to be present as hydroxyl groups. A slightly higher percentage, ~30%, was found for the two copolymers. The removal of hydroxyl groups on flame treated HPP surfaces by the reaction with TFAA reduced the surface wettability, but had little effect on the adhesion with the epoxy adhesive. Although the adhesion level with PU paint was significantly reduced by the removal of hydroxyl groups, a reduced level of adhesion was retained. Hydroxyl groups on the surface may react with the PU paint, resulting in a very high bond strength and solvent resistance. While hydroxyl groups may play an important role in the adhesion with the PU paint, they are not essential to obtain good adhesion.
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Two flow meters (area type) both of which had been calibrated for air at S.T.P. by manufacturers were used to measure the flow rates of air and natural gas. Air was supplied at an apparent pressure of 15 psi rather than standard pressure, while the specific weight of gas (supplied at an apparent pressure of ~0.25psi) is different from that of air. Therefore, both flow meters should be recalibrated. For an area type flow meter (Fig.A.1),

\[ q_a^2 r_a = q_b^2 r_b \]

**Eq.A.1**
where \( q_a \) is the volume flow rate at specific weight \( r_a \), \( q_b \) is the volume flow rate read from the flow meter, and \( r_b \) is the specific weight of air at S.T.P. (1.29 g/l).

A device illustrated in Fig.A.2 was used to measure the flow rate.

A reagent glass bottle filled with water (2.74 litres) was placed flat in the water tank. The fluid (air or natural gas) from the flow meter, at a constant flow rate, was collected by the bottle through a rubber tube. The water level in the bottle was maintained at the same water level as in the tank. The time spent to displace all the water in the bottle was taken to calculate the flow rate. The accuracy of the time recorded was within 0.5 sec.

The specific weight of air (at an apparent pressure of 15 psi) in the flow meter is,
\[ r_a = 1.29 \times (15 + 14.7) / 14.7 = 2.61 \, (g/l) \]

Where 1.29 \,(g/l) is the specific weight of air at 298K and standard pressure, 1 atm \,(14.7 \,psi). According to Eq.A.1,

\[ q_a = q_b \times (1.29/2.61)^{1/2} = 0.703 \, q_b \]

where \( q_a \) is the volume flow rate at specific weight of \( r_a = 2.61 \, g/l \), thus, the volume flow rate at S.T.P., \( q_a' \), can be calculated according to the following equation,

\[ q_a' = q_a \times r_a' / r_b = q_a \times (2.61/1.29) = 1.42 \, q_b \]

Eq.A.3

Fig.A.3 is the plot of the measured flow rate (using the device in Fig.A.2) and the theoretical flow rate according to Eq.A.3 against the apparent flow rate.

Fig.A.3 Comparison of the measured flow rate and the theoretical flow rate of air
Fig. A.3 shows a good agreement between the measured value and the theoretical value. Air flow rates cited in the flame treatment are all the values calculated according Eq. A.3.

The build-up of the pressure in the flow meter is negligible for natural gas, since the apparent pressure is only 0.25 psi, much less compared to that of the atmospheric pressure, 14.7 psi. Thus the contribution of the pressure to the specific weight change can be neglected. The specific weight of the natural gas (96% CH$_4$ + 4% C$_2$H$_6$) is (96% x 16 + 4% x 30)/22.4 = 0.739 g/l. According to Eq. A.1,

$$q_a = (1.29/0.739)^{1/2} q_b = 1.32 q_b$$  

Eq. A.4

Fig. A.4 shows the plot of measured natural gas flow rate (using the device in Fig. A.2), together with the theoretical value according to Eq. A.4, against the apparent flow rate.

![Graph showing comparison of measured and theoretical flow rates](image)

Fig. A.4 Comparison of the measured flow rate and the theoretical calculated flow rate of natural gas
Again, there exists a good agreement between the measured value and the theoretical value for natural gas. However, the agreement is not as good as that for air. This is thought to be due to the fluctuation of the natural gas flow rate, resulting from the slight difference between the water level in the bottle and that in the tank. A slight water level difference could notably affect the flow rate of natural gas (a pressure of 0.25psi is equivalent to 17.6cm water height). This is not the case for air, since it was supplied at a high apparent pressure of 15 psi. Natural gas flow rates cited in the flame treatment are values calculated according to Eq.A.4.
Appendix B Computer Programme (BASIC) to Calculate Surface Free Energy According to Wu's Harmonic Mean Method

10 REM "CALCULATION ACCORDING TO WU'S HARMONIC MEAN METHOD"
20 INPUT "ENTER DISPERSION COMPONENT OF LIQUID 1";D1
30 INPUT "ENTER POLAR COMPONENT OF LIQUID 1";P1
40 INPUT "ENTER DISPERSION COMPONENT OF LIQUID 2";D2
50 INPUT "ENTER POLAR COMPONENT OF LIQUID 2";P2
60 INPUT "ENTER CONTACT ANGLE OF LIQUID 1";C1
70 INPUT "ENTER CONTACT ANGLE OF LIQUID 2";C2
80 Q1=(1+COS(C1*0.017453))/4*(D1+P1)
90 Q2=(1+COS(C2*0.017453))/4*(D2+P2)
100 S1=D1+P1-Q1
110 S2=D2+P2-Q2
120 R1=P1*(D1-Q1)
130 R2=P2*(D2-Q2)
140 U1=D1*(P1-Q1)
150 U2=D2*(P2-Q2)
160 V1=Q1*D1*P1
170 V2=Q2*D2*P2
180 A=1/S1/S2
190 W=(R1/S1)-(R2/S2)
200 M=(A*(R1*U2-R2*U1)+(V2/S2)-(V1/S1))/W
210 N=A*(U1*V2-U2*V1)/W
220 X1=-M/2+SQR(M*M/4-N)
230 X2=-M/2-SQR(M*M/4-N)
240 Y1=(V1-R1*X1)/(S1*X1+U1)
250 Y2=(V1-R1*X2)/(S1*X2+U1)
260 PRINT "1ST VALUE OF DISPERSION COMPONENT D1 = ";X1
270 PRINT "1ST VALUE OF POLAR COMPONENT P1 = ";Y1
280 PRINT "2ND VALUE OF DISPERSION COMPONENT D2 = ";X2
290 PRINT "2ND VALUE OF POLAR COMPONENT P2 = ";Y2
300 REM "EITHER X1 OR X2 WILL BE RATIONAL. ACCEPT THE Y VALUE FROM THE RATIONAL X VALUE"
310 END
Appendix C  Computer Programme (FORTRAN) to Calculate the Oxidation Depth for an Oxygen-rich Surface (Fig.10.35)

C PROGRAMME TO CALCULATE THE OXIDATION DEPTH OF AN OXYGEN RICH SURFACE
C
C U=ACCURACY, W=MINIMUM THICKNESS, X=MAXIMUM THICKNESS, 
C S=STEP, O1=O% AT 90DEG, O2=O% AT 30 DEG
C
PRINT*, 'PLEASE INPUT U,W,X,S,O1, AND O2'
READ*, U,W,X,S,O1,O2
P=(49.0/(1486.6-284.6)**2.0+0.11*SQRT(1486.6-284.6))*10.0/0.9 
Q=(49.0/(1486.6-530.0)**2.0+0.11*SQRT(1486.6-530.0))*10.0/0.9
PRINT*, 'CALCULATING ... PLEASE WAIT ...
J=-1
10 J=J+1
D=W+S*REAL(J)
IF(D.GT.X) GO TO 60
A1=EXP(-D/P)
A2=EXP(-D/(0.5*P))
B1=EXP(-D/Q)
B2=EXP(-D/(0.5*Q))
E=O1*O2*(A1+B2)+O2*B1+O1
F=O1*O2*(A2+B1)+O1*B2+O2
IF(ABS(E-F)/E).GT.U) GO TO 10
O=1.0/((1.0-B1)/O1-A1+B1)
IF(O.GT.1.0) GO TO 10
O90=(1.0-B1)/(1.0/O+A1-B1)
O30=(1.0-B2)/(1.0/O+A2-B2)
PRINT*
PRINT20,U,W,X,S
PRINT30,O1,O2
PRINT40,D,O,O90,O30
20 FORMAT('U=','F8.4,' W=','F8.4,' X=','F8.4,' S=','F8.4)
30 FORMAT('O1=','F8.4,' O2=','F8.4)
40 FORMAT('D=','F8.4,' O=','F8.4,' O90=','F8.4,' O30=','F8.4)
50 GO TO 70
60 PRINT*, 'NO D AND O FOUND !'
70 PRINT*
END
Appendix D  Computer Programme (FORTRAN) to Calculate the Overlayer Thickness for an Oxygen Depleted Surface (Fig.10.36)

C PROGRAMME TO CALCULATE THE OVERLAYER THICKNESS OF AN OXYGEN DEPLETED SURFACE
C
U=ACCURACY, W=MINIMUM THICKNESS, X=MAXIMUM THICKNESS,
C S=STEP, O1=0% AT 90DEG, O2=0% AT 30 DEG
PRINT*, 'PLEASE INPUT U,W,X,S,O1, AND O2'
READ*, U,W,X,S,O1,O2
P=(49.0/(1486.6-284.6)**2.0+0.11*SQRT(1486.6-284.6))*10.0/0.9
Q=(49.0/(1486.6-530.0)**2.0+0.11*SQRT(1486.6-530.0))*10.0/0.9
PRINT*, 'CALCULATING ... PLEASE WAIT ...'
J=-1
10    J=J+1
     D=W+S*REAL(J)
     IF(D.GT.X) GO TO 60
     A1=EXP(-D/P)
     A2=EXP(-D/(0.5*P))
     B1=EXP(-D/Q)
     B2=EXP(-D/(0.5*Q))
     E=O1*O2*(A1+B2)+O2*B1
     F=O1*O2*(A2+B1)+O1*B2
     IF(ABS(E-F)/E).GT.U) GO TO 10
     D=1.0/(Bl/O1+A1-B1)
     IF(D.GT.1.0) GO TO 10
     O90=Bl/(1.0/O1-A1+B1)
     O30=B2/(1.0/O2-A2+B2)
     PRINT*
     PRINT20,U,W,X,S
     PRINT30,O1,O2
     PRINT40,D,O,O90,O30
20 FORMAT('U=',F8.4,' W=',F8.4,' X=',F8.4,' S=',F8.4)
30 FORMAT('O1=',F8.4,' O2=',F8.4)
40 FORMAT('D=',F8.4,' O=',F8.4,' O90=',F8.4,' O30=',F8.4)
50 GO TO 70
60 PRINT*, 'NO D AND O FOUND !'
70 PRINT*
END
Appendix E Computer Programme (BASIC) to Calculate the Oxygen Concentrations Detected by XPS for a Complex Model (Fig.10.37)

10 INPUT "INPUT THE 1st OVERLAYER THICKNESS = "; D1
20 INPUT "INPUT THE 2nd OVERLAYER THICKNESS = "; D2
30 INPUT "TAKE-OFF ANGLE (IN DEGREES) = "; A
40 A1=SIN(3.14159*A/180)
50 P=(49/(1486.6-284.6))^2+.11*SQR(1486.6-284.6)*10/.9
60 Q=(49/(1486.6-530)^2+.11*SQR(1486.6-530))*10/.9
70 C=A1*(1-.15*EXP(-D1/(P*A1))+.1*EXP(-(D1+D2)/(P*A1)))
80 O=A1*(.15*EXP(-D1/(A1*Q))-.1*EXP(-(D1+D2)/(A1*Q)))
90 PRINT
100 PRINT "OVERLAYER THICKNESS, D = ";D, "TAKE-OFF ANGLE = ";A
110 PRINT "IMFP OF Cls = ";P
120 PRINT "IMFP OF O1s = ";Q
130 PRINT "O% = ";O/(O+C)
140 PRINT
150 STOP
160 END
Appendix F  Theoretical Calculations of Elemental Compositions of Chemically Derivatised Surfaces

F.1 Derivatisation of PVA with TFAA

The derivatisation of poly(vinyl alcohol) (PVA) with trifluoroacetic anhydride (TFAA) can be represented in the following equation,

\[
\begin{align*}
\text{O} & \quad \text{OH} + \text{CF}_3\text{C}=\text{O}-\text{C} \quad \text{CF}_3 \\
\quad & \quad \text{C}=\text{O}-\text{C} \quad \text{CF}_3 + \text{CF}_3\text{C}=\text{OH}
\end{align*}
\]

Eq.12.1

Supposing \( x \) is the conversion factor, and \([\text{O}]_0\) is the oxygen concentration before derivatisation, thus, \( x [\text{O}]_0 \) is the surface oxygen concentration which reacts with TFAA while \((1-x) [\text{O}]_0\) is the surface oxygen concentration which does not react with TFAA. In the reaction with TFAA, every single \( \text{O} \) atom will introduce six more atoms, including \( 3 \text{F} \), \( 2 \text{C} \) and \( 1 \text{O} \). Assuming that all the atoms are homogeneously distributed in the surface region within the XPS sampling depth both before and after the derivatisation. Surface oxygen and fluorine concentrations after derivatisation can be calculated according to Eqs.F.1 and F.2,

\[
\begin{align*}
\text{O}\% &= \frac{[\text{O}]_0 + x [\text{O}]_0}{1 + 6x [\text{O}]_0} \times 100\% = \frac{1 + x}{1/[\text{O}]_0 + 6x} \times 100\%
\end{align*}
\]

Eq.F.1

\[
\begin{align*}
\text{F}\% &= \frac{3x [\text{O}]_0}{1 + 6x [\text{O}]_0} \times 100\% = \frac{3x}{1/[\text{O}]_0 + 6x} \times 100\%
\end{align*}
\]

Eq.F.2

\( \text{O}\% \) and \( \text{F}\% \) are plotted against conversion factor, \( x \), in Fig.12.1.
The derivatisation of poly(vinyl methyl ketone) (PVMK) with hydrazine can be written as,

\[
\text{CH}_2 - \text{CH} = \text{O} + \text{NH}_2\text{NH}_2 = \text{CH}_2 - \text{CH} = \text{NNH}_2 + \text{H}_2\text{O}
\]

Eq.12.6

Supposing \(x\) \([\text{O}]_0\) (\(x\) is the conversion factor) of the oxygen concentration before derivatisation, \([\text{O}]_0\), has been converted into hydrazones, and \((1-x)\) \([\text{O}]_0\) has not been converted. In the reaction with hydrazine, every single \(O\) will be replaced by 2 \(N\) atoms. The reaction does not introduce any other atoms detectable by XPS rather than nitrogen. Assuming that all the atoms are homogeneously distributed in the surface region within the XPS sampling depth both before and after the derivatisation, surface concentrations of \(O\) and \(F\) can be derived as following,

\[
\text{O}\% = \frac{(1-x)[\text{O}]_0}{(1-x)[\text{O}]_0 + 2x[\text{O}]_0} \times 100\% = \frac{(1-x)[\text{O}]_0}{1+x[\text{O}]_0} \times 100\%
\]

Eq.F.3

\[
\text{N}\% = \frac{2x[\text{O}]_0}{(1-x)[\text{O}]_0 + 2x[\text{O}]_0} \times 100\% = \frac{2x[\text{O}]_0}{1+x[\text{O}]_0} \times 100\%
\]

Eq.F.4

\(\text{O}\%\) and \(\text{N}\%\) are plotted against conversion factor in Fig.12.3.
LIST OF PUBLICATIONS

1. E. Sheng, I. Sutherland, D.M. Brewis, R.J. Heath  
   Effects of Flame Treatment on Propylene-ethylene Copolymer Surfaces 
   Presented at ECASIA'91, Budapest, in press by Surface and Interface Analysis

2. I. Sutherland, D.M. Brewis, R.J. Heath, E. Sheng  
   Modification of Polypropylene Surfaces by Flame Treatment 
   Surface and Interface Analysis 17 507 (1991)

3. E. Sheng, R.J. Heath, I. Sutherland, D.M. Brewis  
   Surface Modification of Polypropylene by Flame Treatment - A Study 
   Plastics and Rubber International Aug. 10 (1991)

4. I. Sutherland, E. Sheng, R.J. Heath, D.M. Brewis  
   Flame Treatment and Surface Characterisation of a Rubber-modified Polypropylene, 
   presented at the 2nd International Conference on Adhesion and Surface Analysis, April 1992, to be published by Surface and Interface Analysis

5. I. Sutherland, E. Sheng, D.M. Brewis, R.J. Heath  
   An XPS Study of Flame Treatment of Polypropylene, to be submitted to Journal of Adhesion Science and Technology