Functionalisation of Polyolefins and its
Effects on Surface Chemistry and Energetics

by

Rohit Popat

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Department of Chemistry

Supervisors:
I.Sutherland, Department of Chemistry
P.J.Mills, ICI

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Abstract

The surface functionalisation of polyethylene and polypropylene by industrial and laboratory scale corona treatments and by laboratory flame treatment was studied. The surface sensitive techniques of X-ray photoelectron spectroscopy (XPS), attenuated total reflection infra-red spectroscopy (FTIR-ATR), contact angle measurement and electron microscopy (SEM and TEM) were employed. Corona and flame treatments resulted in incorporation of oxygen only into the surfaces of both polyethylene and polypropylene, resulting in improved surface wettabilities. A variety of oxygen functional groups were introduced by the two treatments. The industrial and laboratory scale treatments of both polymers were found to be similar in terms of the oxygen concentrations incorporated and surface wettabilities achieved. The presence of significant amounts of chain scission products were indicated on corona treated surfaces, while only minimal quantities were indicted on flame treated surfaces. This was attributed to their volatilisation during flame treatment. Introduction of sulfur dioxide into the flame and corona regions during treatment resulted in significant improvements in surface wettability. Incorporation of sulfur and nitrogen resulted from the presence of sulfur dioxide. A possible mechanism involving the formation of sulfonic acid groups and ammonium sulfonate groups was suggested. An oxidation depth model developed for use with variable take-off angle XPS showed that significantly deeper oxidation occurred in the presence of sulfur dioxide. Corona treatment was more effective in improving surface wettabilities than flame treatment, this being attributed to heat induced functional group reorientation during flame treatment for polyethylene and to differences in surface chemistry resulting from the two treatments in the case of polypropylene. The surface wettability of polyethylene was more readily improved than the surface wettability of polypropylene after all the treatments investigated. A method for estimating functional group concentrations using chemical derivatisation and contact angle measurement was developed. Functional group estimates for flame treated polyethylene were found to be in good agreement with chemical derivatisation used in conjunction with XPS measurements.

Keywords: polyethylene, polypropylene, XPS, FTIR, SEM; contact angles, surface free energy, corona treatment, flame treatment, derivatisation
Dedicated to
my parents and to Jayne
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PART I INTRODUCTION AND LITERATURE SURVEY

Chapter 1 Introduction

1.1 Polyolefins

Synthetic polymers are now an integral part of modern society. However, the concept of the macromolecule is relatively recent, with the theory of polymeric molecules finding wide acceptance only in the mid-1920's. Today there is a huge diversity in the range of engineering materials available, for example thermoplastics, thermosets and rubbers, with at least one being suitable for almost every application. One of the most widely used groups of synthetic polymers is that of thermoplastic polyolefins. Polyethylene and polypropylene are structurally the simplest and most widely used of the polyolefins, and are available in a multitude of grades, from simple homopolymers to complex copolymers, and from low molecular weights to ultra-high molecular weights. These polymers have found use in a variety of industrial applications, such as the packaging, automotive and construction industries, their wide application stemming from intrinsically good mechanical/fabrication properties, chemical resistance and low cost.

In many applications such as painting, printing and metallisation, good adhesion to the polymer surface is required. However, polyolefins, as a consequence of their non-polar composition, have low surface free energies and thus poor wetting characteristics so that the surfaces of polyolefins are unreceptive to surface decorations. Furthermore, the presence of a weak boundary layer of "small" molecules with low cohesive strength may further reduce adhesion levels. The degree to which these respective factors contribute to the poor adhesion characteristics of polyolefin surfaces is unknown. Therefore, if good adhesion to a polyolefin substrate is required, some form of surface treatment is essential, for example oxidising agent etch, flame or corona treatment. Largely through trial and error, these methods have been found to enhance adhesion to polyolefins, however their modes of activation are only partially understood. Therefore, further investigation of flame and corona discharge methods of surface pretreatment was undertaken.
1.2 Objectives

The aims of this study were to investigate the effects of corona and flame treatments on the surface chemistry of polyolefins surfaces, namely polyethylene and polypropylene, and to compare their relative effectiveness for the pretreatment of these materials. The effects on polyolefin surface properties caused by sulfur dioxide and ammonia gases respectively when introduced into the flame and corona discharge were also studied. These gases were employed in an attempt to introduce acidic and basic functional groups into the treated films, in order to further improve surface properties over conventional treatments, and to open avenues whereby surface properties may be engineered for specific applications. Additionally, in order to discover whether findings from laboratory scale investigations of corona discharge treatment could be applied to industrial scale treatment, the two were compared.

The study of corona discharge treatment consisted of two parts. Firstly, polyolefins corona discharge treated industrially by ICI (Propafilm), Welwyn Garden City were studied. Secondly, films discharge treated, with and without reactive gas atmospheres, on a laboratory scale treater were studied. The effect of corona intensity and concentration of the reactive gas present in the discharge were of main interest.

The effects of flame treatment were studied on films activated using apparatus which allowed, when required, pre-mixing of a reactive gas with the air prior to combustion of the natural gas. Here, the parameters studied were air-to-natural gas ratio, flame intensity and the effects of reactive gases on the polymer surface chemistry under various flame conditions.

Modified surfaces were characterised using several surface sensitive techniques, namely, X-ray photoelectron spectroscopy (XPS), contact angle measurements, attenuated total reflection infra-red spectroscopy (FTIR-ATR), scanning electron microscopy (SEM) and carbon replica transmission electron microscopy (TEM).

Well characterised standard polymers were used to further improve the usefulness of the
vapour phase chemical derivatisation technique for functional group determination. Quantitative oxidation depth models were developed for use with variable take-off angle XPS and for use with O1s/O2s ratios also determined from XPS measurements. Inelastic photoelectron background signals were also inspected to provide further qualitative oxidation depth information. Additionally, the acid/base properties of the treated surfaces were studied by measuring contact angles employing liquids of different pH.
Chapter 2 Literature Survey on Surface Modification of Polyolefins

2.1 Surface Activation

2.1.1 Introduction

A variety of surface pretreatments have been used to improve the adhesion characteristics of polyolefins, for example fluorination, photooxidation and oxidising acid etching including chromic, sulfuric and nitric acids. However through their ease of use and effectiveness, corona and flame treatments have become widely used methods for the pretreatment of polyolefins, the effects of which are further discussed. As plasma treatment/polymerisation using various reactive gases has been studied in the literature and given its similarity to flame and corona treatments, it is also briefly discussed.

2.2 Electrical Discharge Treatment

2.2.1 Aspects of Treatment

Electrical discharge treatment, or corona treatment, is most commonly used in the pretreatment of polyolefin films, although thick walled containers have also been treated in this way. The process is shown schematically in Figure 2.1, which shows that industrial corona treatment can be an “on-line” process, that is the treatment procedure may be incorporated into the film manufacturing process. The film is passed over a dielectric covered base roll at earth potential, 1-2 mm above which is an electrode which is usually made of aluminium. The electrode is connected to a high-frequency generator (~10-20kHz) which provides a sinusoidally varying high voltage causing electrical breakdown of the air gap resulting in the “corona”. The corona consists of high energy, excited species such as ions, radicals, electrons, photons and neutrals.

Corona treatment has been employed industrially for many years to improve the adhesion characteristics of polyolefin films and for this reason it has been the subject of intensive study. The mechanism of activation via corona treatment was in doubt for many years. Carlsson et al applied the ATR-IR technique to study the effects of corona treatment on the surface chemistry of polyolefins, showing that nitrogen coronas resulted
in surface unsaturation as opposed to nitrogen incorporation, while oxygen coronas resulted in surface oxidation in addition to surface unsaturation. Surface oxidation was then implicated in the improved autohesion of polyolefins by Rossmann \textsuperscript{18}, however Stradal \textit{et al} \textsuperscript{19} and Goring \textit{et al} \textsuperscript{20} concluded that although surface oxidation does occur upon corona discharge treatment, the improved autohesion was essentially through electrostatic interactions at the treated surfaces. This conclusion stemmed from work involving inert gas atmospheres such as nitrogen and argon, and the observation that maximum adhesion was achieved before surface oxidation was detected by ATR-IR. However, this interpretation may not necessarily have been correct as ATR-IR analysis, given its relatively large analysis depth, may not have detected very near-surface oxidation which could have improved adhesion levels. Owens \textsuperscript{21} suggested that oxidation of the surface leading to keto-enol groups was primarily responsible for adhesion. He found that on application of a hydrogen bonding liquid to an adhesive joint containing the treated polymer, adhesion was completely destroyed but also found that the effects were reversible. Owens thus found that by disrupting the ability of the carbonyl groups present on the surfaces to undergo keto-enol tautomerism, adhesion was reduced from which it was concluded that hydrogen bonding involving the ketone and enol tautomers was responsible for improved adhesion. However, application of the liquid effectively introduced a weak layer of small molecules and this may have prevented close contact between the adherends producing the reduction in adhesion. With the application of X-ray photoelectron spectroscopy to the problem, Briggs \textit{et al} \textsuperscript{22-25} developed a more detailed picture of the surface chemistry of corona discharge treated polyolefins. They employed
high resolution XPS and chemical derivatisation methods in addition to ATR-IR, identifying the presence of various oxygen functional groups, including -OH, -C=O and -COOH, upon corona treated polyolefins. Thus they confirmed Owens' theory that, even for inert gases, surface oxidation was responsible for improved adhesion of corona treated polyolefins. In addition to surface oxygen, they detected the presence of nitrogen functionality, including -O-NO₂ and -NO₂ groups, although this was probably a result of the high corona intensities used. The importance of surface functionality in promoting adhesion is now widely accepted.

Gerenser et al.²⁶ also employed chemical derivatisation methods in addition to high resolution XPS to investigate corona discharge effects on polyethylene surface chemistry. However, the derivatising agents used here and by Briggs et al.¹³¹ were later found to have poor reproducibility, depending on the reaction conditions used and/or washing regimes employed. Significant oxidation was found upon treatment, and also water washing of the surfaces resulted in a significant loss of oxygen functionality, this being attributed to scission of the polymeric chains. They also found that the surface oxygen concentration decreased with time, reaching a plateau after ~30 days, producing a concomitant increase in the advancing water contact angle. From variable take-off angle XPS, they were able to estimate a depth of oxidation of ~50 Å. Similarly, Lanuaze et al.²⁷ used chemical derivatisation methods although again the agents used in that study have now been shown to be unreliable. Strobel et al.²⁸ also found that removal of chain scission products occurred upon water washing, resulting in significantly reduced surface oxygen concentrations and water wettabilities. Their aging studies of corona treated polypropylene found that the surface oxygen concentration and wettability had no time dependence. More recently, Sutherland et al.³⁰ estimated oxidation depths of ~50-70 Å using simple depth models in conjunction with variable take-off angle XPS. Also, they found significant changes in the oxygen concentration upon aging, while the advancing water contact angles continued to decrease, although their findings were not in agreement with Gerenser et al.²⁶. The disparity in findings between various workers may have resulted from the different polymers employed, for example molecular weights and additive packages may affect the degree of chain scission/surface oxidation.

In addition to the chemical changes induced upon corona treatment, several workers have
investigated the effects of treatment on surface topography. Kim et al.\textsuperscript{20} using both electron and optical microscopy found significant surface roughening upon extended (> 5 minutes) corona treatment of polyethylene. Upon re-examination of the surfaces after solvent washing, much of the surface oxidation and surface structure was removed, from which they concluded that roughening was due to the presence of low molecular weight, oxidised scission products. Similar results were obtained by Strobel \textit{et al.}\textsuperscript{28} and Blais \textit{et al.}\textsuperscript{31}. However, at industrially used levels of energy input, Sutherland \textit{et al.}\textsuperscript{30} did not find any topographical changes using scanning electron microscopy. Thus it is suggested that topographical changes occur only after severe treatment. With the advent of atomic force microscopy (AFM) as a routine analytical technique, Overney \textit{et al.}\textsuperscript{32} examined topographical changes on polypropylene surfaces occurring upon corona treatment. Using this technique they were indeed able to detect surface roughening. However, energy inputs in the range $7.5 \times 10^4 - 1 \times 10^6$ J m$^{-2}$ were employed compared with $10^3$ J m$^{-2}$ for industrial treatments studied by Sutherland \textit{et al.}\textsuperscript{30}, so that this roughening was probably again a result of severe treatment.

Although corona discharges under various atmospheres such as oxygen, nitrogen and argon have been investigated in an attempt to elucidate the mechanism of surface activation, little work has been done on other reactive gas atmospheres to modify surface properties. Work in early US Patents\textsuperscript{33-36} studied the effects on various polymer surfaces of a number of polymerisable and non-polymerisable organic vapours introduced into the corona region via channels in the electrode. Although improved adhesion at treated surfaces was found using certain compounds no spectroscopic characterisation of the surfaces was included, indicating the need for further work on this area.

The quantification of energy input during corona treatment is problematic as it depends upon a number of parameters, including the efficiency of the voltage generation/transmission process. However, the energy input per unit area\textsuperscript{29} may be estimated using equation 2.1 to give an indication of treatment level,

$$E = \frac{P}{Wv}$$ 

\textit{eqn. 2.1}
where $E$ is the power input per unit area in J m$^{-2}$, $P$ is the net power in watts, $W$ is the electrode width in m, $v$ is the film line speed in m s$^{-1}$. This expression incorporates the two primary factors affecting treatment, namely the power input and the film line speed. Clearly, increasing line speed will increase film output, however this may reduce the effectiveness of treatment. Compensation may be made for higher line speed by increasing the voltage used, thereby increasing the energy dissipated in the corona. An additional parameter is the film temperature. Krüger et al.\textsuperscript{37} investigated the effectiveness of treatment at different cooling temperatures on freshly extruded polypropylene film, finding that crystallisation can have a marked effect.

Overall, significant amounts of work on investigating the effects of corona discharge has been performed. However, the work is quite fragmented, being performed on many different polymers with different characteristics in terms of molecular weight, density and additive content. Also, the corona processes employed have been varied in terms of electrode geometry, static or dynamic treatment, electrode gap and the conditions employed such as relative humidity.\textsuperscript{38} Therefore general comparisons on the effects of corona treatment from the literature becomes difficult, so the present study aims to investigate various pretreatments on the same polymer/process systems.

### 2.2.2 Corona Chemistry

A number of workers including Briggs et al.\textsuperscript{22-25} and Gerenser et al.\textsuperscript{26} have provided spectroscopic evidence for the presence of a variety of oxygen containing functional groups on the surface of corona treated polyolefins, for example hydroxyl, carbonyl, carboxyl, and hydroperoxide. The work of Briggs\textsuperscript{24} produced the now the widely accepted theory for oxygen incorporation through a free radical oxidative mechanism via a hydroperoxide intermediate and is summarised in Scheme 2.1. This mechanism shows only oxygen as the reactive species causing incorporation of surface oxygen functionalities, however, other species present in the active corona region can also lead to oxygen incorporation, for example water and ozone. The presence of low molecular weight oxidised material (LMWOM) provides evidence for a free radical type mechanism and also by the observation that polypropylene degrades more quickly under corona treatment than polyethylene. This probably results from radical stabilisation by the pendant methyl.\textsuperscript{39}
Scheme 2.1 The free radical mechanism leading to surface oxidation upon corona discharge treatment

group, so that free radicals on polypropylene are longer lived and may continue with chain degradation whereas free radicals on polyethylene are much shorter lived and therefore cannot undergo as many chain scission reactions.

2.3 Flame Treatment

2.3.1 Aspects of Treatment

In contrast to corona treatment, flame treatment is rarely used for the pretreatment of films, rather it is used for the treatment of thicker articles, particularly blow moulded plastic bottles. Figure 2.2 shows a schematic representation of a plastic bottle undergoing flame treatment. The object is rotated slowly around a central axis so that every point on the surface is passed through the flame which is usually produced by closely spaced jets on a ribbon burner.
Flame treatment leads to surface oxidation, thereby increasing the polarity of the treated surfaces and improving the wetting/adhesion characteristics. The important treatment parameters are the air-to-gas ratio, the total flow rate (indicative of the treatment level), the distance from the flame inner cone tip to the surface of the specimen, and the contact time (the time a point on the specimen spends in the flame), with the exact nature of the fuel gas being unimportant. These parameters were investigated in some detail for the treatment of various polyolefins by Sheng et al. They found that optimum surface oxidation and water wettability was achieved at an air-to-natural gas ratio of ~11:1, this being in agreement with Hurst et al. who studied the flame treatment of polyethylene. Also, increasing the flame intensity increased the level of surface oxidation, although the water wettability did not continue to improve. This was attributed to increased depths of oxidation, which were estimated to be in the range 40-55 Å by variable angle XPS. Additionally, evidence was found to suggest the presence of -C-O, -C=O, -CO₂ functional groups by using high resolution XPS. Free-radical degradation of the polymer surface leading to the presence of low molecular weight oxidised material was also investigated by diethylether washing experiments, however no evidence for any such scission products was provided. Flame treatment of LDPE by Briggs et al. resulted in the incorporation of nitrogen in addition to oxygen, although introduction of the former was probably a consequence of the high flame intensities employed. Oxidation depths were estimated to lie in the range 40-90 Å, with curve fitting of the high resolution C1s peak also suggesting the presence of -C-O, -C=O and -CO₂ functionalities. Evidence for such functionality was also found by Papirer et al. who studied treatment of polypropylene, although in contrast to other studies they found optimum treatment occurred at an air-to-natural gas ratio of 10:1. The presence of scission products was suggested by removal of oxygen functionality upon solvent washing, this resulting in a reduction of surface wettability.

2.3.2 Flame Chemistry

Through environmental concerns on pollution, the combustion of fossil fuels has been extensively researched, resulting in complex reaction mechanisms involving ions, radicals and excited neutrals being deduced. Some of the reactions involved in the combustion of hydrocarbons are given in Scheme 2.2. Clearly the flame chemistry is very complex, involving the production of high energy nitrogen species also. Thus it can be
Scheme 2.2 Some of the reactions involved in the combustion of methane

\[
\begin{align*}
\text{CH}_4 + \text{O}_2 & \rightarrow \text{CH}_3 + \text{HO}_2 \\
\text{CH}_4 + \text{HO}_2 & \rightarrow \text{CH}_3 + \text{H}_2\text{O}_2 \\
\text{CH}_3 + \text{O}_2 & \rightarrow \text{CH}_3\text{O}_2 \\
\text{CH}_3\text{O}_2 + \text{CH}_3 & \rightarrow 2 \text{CH}_3\text{O} \\
\text{CH}_3\text{O}_2 + \text{HO}_2 & \rightarrow \text{CH}_3\text{OOH} + \text{O}_2 \\
\text{CH}_3\text{O} + \text{RH} & \rightarrow \text{CH}_3\text{OH} + \text{R} \\
\text{CH}_2 + \text{OH} & \rightarrow \text{CH}_3 + \text{O} \\
\text{CH}_2 + 2\text{O} & \rightarrow \text{CHO} + \text{OH} \\
\text{CH}_2 + \text{N}_2 & \rightarrow \text{HCN} + \text{NH} \\
\text{CH}_2 + \text{NO} & \rightarrow \text{CH}_2\text{O} + \text{N} \\
\text{N} + \text{OH} & \rightarrow \text{NO} + \text{H} \\
\text{N}_2 + \text{O} & \rightarrow \text{N} + \text{NO} \\
\text{N} + \text{O}_2 & \rightarrow \text{NO} + \text{O}
\end{align*}
\]

Scheme 2.3 Some of the reactions involved in the thermal oxidation of ammonia

\[
\begin{align*}
\text{NH}_3 + \text{H} & \rightarrow \text{NH}_2 + \text{H}_2 \\
\text{NH}_3 + \text{O} & \rightarrow \text{NH}_2 + \text{OH} \\
\text{NH}_2 + \text{O} & \rightarrow \text{NH} + \text{OH} \\
\text{NH} + \text{O}_2 & \rightarrow \text{HNO} + \text{O} \\
\text{NNH} + \text{OH} & \rightarrow \text{N}_2 + \text{H}_2\text{O} \\
\text{HNO} + \text{OH} & \rightarrow \text{NO} + \text{H}_2\text{O} \\
\text{NO} + \text{HO}_2 & \rightarrow \text{NO}_2 + \text{OH} \\
\text{NNH} + \text{NO} & \rightarrow \text{N}_2 + \text{HNO}
\end{align*}
\]
seen how nitrogen could be incorporated into flame treated polymer surfaces, however, high flame intensities would be required as the concentration of the active nitrogen species decays very rapidly with distance from the reaction zone leaving only stable NO\textsubscript{x} combustion products. In this study, it has been attempted to modify the flame treatment of polyolefins by introducing ammonia into the flame, and thus it is important to consider the presence of ammonia on flame chemistry\textsuperscript{51-56}. Some of the steps in the thermal oxidation of ammonia are given in Scheme 2.3. Thus introduction of ammonia further complicates the flame chemistry. However, it has been found that ammonia is rapidly oxidised within the flame to stable products such as NO, so the reactive species such as NH, NH\textsubscript{2}, and CN vanish rapidly with distance from the burner so that nitrogen may not necessarily be incorporated into a surface being flame treated. Sulfur dioxide was also employed in this study, with some of the reactions involved in its thermal oxidation being given in Scheme 2.4\textsuperscript{57,58}. Again a complex flame chemistry has been found\textsuperscript{59-61}. The interesting point to note is the direct interaction of sulfur and nitrogen\textsuperscript{62,63}, this potentially playing an important role in the surface modification of polyolefins. Overall, from the oxidation of methane, ammonia and sulfur dioxide in flames, the probable mechanism of polymer surface activation involves a free radical type mechanism\textsuperscript{64}.
2.4 Plasma Treatment

2.4.1 Aspects of Treatment

The plasmas used for polymer modification are produced in low pressure chambers (usually in the range of 0.05-10 torr) in which the substrate is encased. Their production can be achieved in one of two ways, firstly, by use of a DC or low frequency AC (<1MHz) power source with a direct (resistive) coupling mechanism using electrodes within the low pressure chamber or secondly, by use of an RF or microwave power source with an indirect coupling system (either capacitative or inductive). The coupling mechanisms are summarised in Figure 2.3. The important parameters here are the duration of treatment, the applied voltage and the nature of the discharge gas.

![Capacitative Coupling](image)

![Inductive Coupling](image)

![Direct (Resistive) Coupling](image)

Figure 2.3 Coupling mechanisms for plasma formation

A plasma is essentially an electrical discharge under low pressure, and it too consists of a variety of species which can be chemically active and/or of high energy and may interact with the polymer surface. Various plasma gases including air, oxygen, nitrogen and argon have been employed to increase the hydrophilicity of and to improve the adhesion to the treated polymer surfaces, usually through free radical surface oxidation. Marchant et al. concluded that oxygen incorporation after nitrogen or argon plasma treatment probably occurred through post treatment reaction with atmospheric oxygen or water, although this was in contrast to Gerenser who found no chemical changes upon argon plasma treatment of polyethylene.
Much of the research into plasma modification has centred upon plasma polymerisation on polymeric/metallic substrates. With plasmas, very high energies may be achieved in an enclosed environment so that organic compounds not normally associated with polymerisation reactions can be polymerised, for example acetone and tetrafluoromethane (to increase hydrophobicity). As has been used in the present work, plasmas of ammonia to introduce amine functionality into the polyethylene fibre surfaces have been investigated in the literature. Chappell et al. found that amine groups were indeed introduced by ammonia plasma treatment leading to an improvement in the adhesion to epoxy polyester resin. This improvement was attributed to direct chemical reaction between the epoxy and amine functional groups as well as an increase in the surface wettability of the fibres. Incorporation of amine groups during plasma treatment probably arises through the plasma decomposition of the ammonia molecules, a mechanism for which is given in Scheme 2.5.

\[
\begin{align*}
\text{NH}_3 & \rightarrow \text{NH}_2 + \cdot \text{H} \\
\cdot \text{H} + \text{NH}_3 & \rightarrow \text{NH}_2 + \text{H}_2 \\
\text{H}_2 & \rightarrow 2 \cdot \text{H} \\
2 \cdot \text{NH}_2 & \rightarrow \text{NH} + \text{NH}_3 \\
2 \cdot \text{NH}_2 & \rightarrow \text{N}_2\text{H}_4 \\
2 \cdot \text{NH} & \rightarrow \text{N}_2 + \text{H}_2
\end{align*}
\]

Scheme 2.5 Some of the reactions in the plasma decomposition of ammonia

Other nitrogen containing plasmas which have been investigated include nitric oxide, nitrogen dioxide and acrylonitrile. Clearly, the choice of “monomer” gas or mixture of gases could potentially have significant effects on the surface wetting/adhesion of the substrate and therefore plasma polymerisation has proved to be a popular area of investigation.
Chapter 3 Aspects of Adhesion

3.1 Introduction

Adhesion maybe defined as the strength of forces acting across an interface between two materials. Until recently there were no direct measurements of the strength of interfacial interactions between polymers. Pocius \(^{85}\) used an atomic force balance on several polymer systems, and although finding good agreement with non-polar polymers it was not totally successful in measurements for all types of polymer, giving higher works of adhesion than predicted for polar polymers. Overall, this method has certainly improved understanding of adhesion. No single theory explaining the phenomenon of adhesion exists, rather there is evidence for several discrete theories of adhesion which may all contribute to some degree. Therefore, until it is possible to measure interfacial interactions unambiguously there will continue to be debate over the true nature of adhesion and thus further work in this area is clearly necessitated. The surface and interfacial aspects of adhesion have been briefly reviewed \(^{86,87}\).

3.2 Mechanisms of Adhesion

3.2.1 Electronic Theory

Deryaguin \(^{88-90}\) proposed that two surfaces in intimate contact could be considered as the two plates in an electrostatic capacitor. He suggested that electron transfer would occur on intimate contact between the two adherends resulting in the formation of an electric double layer and adhesion via coulombic interactions. However it was concluded that the contribution of electrostatic interactions to adhesion is minimal \(^{91-93}\).

3.2.2 Mechanical Theory

Here, the major source of adhesion is thought to be the mechanical keying or interlocking of the adherend around irregularities or pores on a textured surface. This explanation was applicable when the materials being bonded were fibrous, for example wood and leather, however when good adhesion of smooth surfaces was achieved this explanation clearly became inadequate. Mechanical interlocking cannot be a universal explanation of
adhesion, but if split into degrees of scale, that is macroscopic and microscopic interlocking, it provides explanation of some observations. An example of the macroscopic interlocking was shown for the adhesion of natural fibre cord into rubber 94, while the work of Packham 95,96 and Venables 97,98 using electron microscopy showed that mechanical interlocking on the microscopic scale was also important.

3.2.3 Diffusion Theory

Voyutskii 91-100 was the main exponent of this theory, which states that, assuming mutual solubility and chain mobility, adhesion between polymers is a direct result of interdiffusion of the polymer chains across the interface. Radiotracer techniques 101 have successfully provided evidence for this mechanism, although if the assumptions are not valid interdiffusion would seem very unlikely, for example polymers where mutual miscibility is not common due to low entropies of mixing. Indeed, evidence showing that appreciable entanglement must occur for adhesion to be affected has been found 102.

3.2.4 Adsorption Theory 103,104

Here, assuming that intimate contact occurs at an interface, adhesive strength is attributed primarily to the action of dispersion forces acting across an interface. In many instances adhesion may be augmented by primary and secondary interactions, for example ionic, covalent, metallic and polar interaction (see Table 3.1 for approximate magnitudes 105,106). This theory is clearly not useful in considering adhesion between smooth and rigid materials where the molecules are essentially fixed and immobile.

3.2.5 Combination of Theories

Rather than being exclusive, it has been suggested that adhesion may be a result of a combination of theories 107, equation 3.1,

\[ \psi = a\psi_E + b\psi_M + c\psi_D + d\psi_A \]

where \( \psi \) is the overall adhesion, E, M, D, A are subscripts representing electrical, mechanical, diffusion and adsorption contributions to adhesion and a, b, c, d are the respective fractional constants
Chapter 3 Aspects of Adhesion

<table>
<thead>
<tr>
<th>TYPE OF FORCE</th>
<th>BOND ENERGY / kJ mol^-1</th>
<th>EQUILIBRIUM LENGTH / nm</th>
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<td>No</td>
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<tr>
<td>Covalent</td>
<td>60-800</td>
<td>0.08-0.3</td>
<td>Yes</td>
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<tr>
<td>Metallic</td>
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<td>0.2-0.6</td>
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<tr>
<td>Intermolecular</td>
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</tr>
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<td>No</td>
</tr>
<tr>
<td>Keesom and Debye</td>
<td>&lt; 20</td>
<td>0.2-0.4</td>
<td>No</td>
</tr>
<tr>
<td>Hydrogen Bonding</td>
<td>&lt; 60</td>
<td>~0.3</td>
<td>Yes</td>
</tr>
</tbody>
</table>

London are dispersion (temporary dipole-temporary dipole) interactions
Keesom are dipole-dipole interactions
Debye are dipole-induced dipole interactions

Table 3.1 Approximate ranges of interaction energies of various types of interaction

3.3 Surface Treatment

Adhesion to polymers may be affected in several ways by the pretreatment of the substrate surface. Introduction of polar functional groups may give rise to increased interfacial interactions at the surface, for example hydrogen bonding, which can lead to improved bond strength. Polar functionalities usually increase the surface energy and can promote better surface wetting. This is especially important in aqueous systems where complete surface wetting is often not achieved. Surface pretreatment can lead to the formation of a weak boundary layer of low molecular weight oxidised material resulting from polymer degradation by chain scission, and can thereby significantly decrease adhesion. Finally, decreased adhesion may result from migration of polar small molecules and additives to the activated surface. The latter two effects may be investigated by extraction, treatment and analysis while the former two effects can be investigated by contact angle and spectroscopic measurement. From this it is clearly evident that surface pretreatment can lead to a degradation in adhesion properties instead of the desired improvement.
4.1 X-Ray Photoelectron Spectroscopy

4.1.1 Introduction

X-ray photoelectron spectroscopy (XPS) is one of a group of ultra-high vacuum (UHV) techniques in which the response of a sample is monitored following initial excitation by some means. This technique, also known as electron spectroscopy for chemical analysis (ESCA) is an extremely valuable analytical technique used to obtain information on the chemical states and compositions of material surfaces. The principles behind the XPS technique are discussed.

4.1.2 Basic Principles

In XPS, primary excitation is achieved using soft X-rays with sufficient energy to induce photoemission of core electrons present in the elements composing the sample. The photoelectrons thus produced are collected and passed to an energy analyser and detector. The photoemission process is shown schematically in Figure 4.1. Therefore, the presence of all atoms containing core electrons can be detected by XPS, that is all the elements of the Periodic Table with the exception of hydrogen and helium.

![Figure 4.1 Schematic representation of the photoemission process](image)
The kinetic energy \( (E_k) \) of a photoelectron emitted from a conducting sample in electrical contact with the spectrometer may be related to its’ binding energy \( (E_b) \) in the orbital of origin by equation 4.1,

\[
E_k = h\nu - E_b - \phi_s \tag{eqn. 4.1}
\]

where \( h\nu \) is the energy of the exciting radiation and \( \phi_s \) is the work function of the spectrometer although this latter term is normally small, being of the order of \(-4\) eV. For an insulating sample, an additional surface potential term should be included to account for surface charging. The binding energy of an electron is characteristic of the atom to which it belongs, so that qualitative identification of surface composition is a straightforward matter with the use of standard tables. Quantification of XPS data is discussed later.

4.1.3 Surface Sensitivity

4.1.3.1 Inelastic Mean Free Path

Although the X-ray photons may penetrate the surface and cause excitation of photoelectrons to a depth of several micrometers, XPS has an analysis depth of only several nanometers. The exact depth depends upon the kinetic energy of the photoelectrons (governed by the X-ray source), the nature of the sample and the angle of the analyser with respect to the sample (the “take-off” angle). This surface sensitivity results from the fact that only the photoelectrons in the outer few nanometers of surface may escape from the sample without energy loss (elastically), and thus possess kinetic energies representative of their original binding energies. Those photoelectrons that undergo energy loss via inelastic collision or scattering form the background electron count and thus do not contribute to the main photoelectron peak. Inelastic scattering is described by an exponential decay law, equation 4.2,

\[
I = I_0 \exp \left( -\frac{x}{\lambda \sin \theta} \right) \tag{eqn. 4.2}
\]
Figure 4.2 Variation of IMFP with photoelectron kinetic energy

where $I_0$ is the original electron flux with kinetic energy $E_k$, $I$ is the electron flux retaining their original kinetic energy, $E_k$, after travelling a distance of $x$ in the material, $\theta$ is the take-off angle with respect to the sample surface and $\lambda$ is the inelastic mean free path of the photoelectron. The variation of inelastic mean free path (IMFP, $\lambda$) as a function of photoelectron kinetic energy is shown in Figure 4.2 and the semi-empirical relationships for estimating IMFP in organic materials are given in equations 4.3, 4.4, 4.5.

$$\lambda_m = \frac{1000}{\rho a} \left( \frac{49}{E^2} + 0.11 \frac{E}{E^{1/2}} \right)$$ \hspace{1cm} \text{eqn. 4.3}

$$\lambda = \lambda_m a$$ \hspace{1cm} \text{eqn. 4.4}

$$a^3 = \frac{10^{24} A}{\rho N n}$$ \hspace{1cm} \text{eqn. 4.5}

where $\lambda_m$ is the inelastic mean free path in monolayers, $\lambda$ is the inelastic mean free path in nm, $\rho$ is the material density in kg m$^{-3}$, $E$ is the photoelectron kinetic energy in eV, $a$ is the monolayer thickness in nm, $N$ is the Avogadro number, $n$ is the number of atoms in the molecule and $A$ is the atomic or molecular weight.
Although XPS is a surface specific technique, it is sometimes not specific enough. For example the work of adhesion is determined primarily by the outer atom layer. Therefore it is desirable to know the variation in elemental concentration within the XPS sampling depth. Non-destructive near-surface depth profiling can be performed in the following ways,

- Analysis using different core-levels from the same element. Most elements have more than one core electron orbital and therefore they may give rise to multiple photoelectron peaks. The electrons in these orbitals will have different binding energies and thus electrons emerging from them will have different inelastic mean free paths and consequently different sampling depths. This may be exemplified by considering oxygen photoelectrons excited using Al Kα X-rays,

\[ \frac{\lambda(02s)}{\lambda(O1s)} = 1.31 \]

where \( E_k \) is the photoelectron kinetic energy and \( \lambda \) is the inelastic mean free path.

- Analysis using different X-ray energies. As equation 4.1 shows, the kinetic energy of the emitted photoelectron depends upon the energy of the X-rays used. Thus by employing the dependence of the IMFP on electron kinetic energy given in equation 4.2, it can be seen that the sampling depth of photoelectrons from a given core level of an element will increase with X-ray energy. Using the example of an O1s peak,

\[ \frac{\lambda_{Al}}{\lambda_{Mg}} = 1.15 \text{ and } \frac{\lambda_{Cr}}{\lambda_{Mg}} = 2.00 \]

Therefore, it is clear that by using different energy X-rays, the analysis depth may
be changed significantly.

- Analysis using different take-off angles. Equation 4.6 gives the angular dependence of electron path length, and is also shown in Figure 4.3,

\[
P = \frac{d}{\sin \theta}
\]

eqn 4.6

where \( P \) is the photoelectron path length, \( d \) is the depth of origin of the photoelectron, and \( \theta \) is the take-off angle with respect to the sample surface. Thus the path length of the photoelectron in the solid is increased at low take-off angles so that only electrons nearer the surface escape elastically, therefore the technique becomes more surface specific. The major requirement for the success of this technique is that the sample must be flat, otherwise shadowing of the incident X-rays and emergent photoelectrons can occur so that shallow angles can become difficult to use.

![Diagram of photoelectron path length](image)

Figure 4.3 Change in path-length with take-off angle

- Analysis of inelastic photoelectron background signals following the main elastic photoelectron peak. This method relies on the fact that the energy distribution of the emitted core photoelectrons depends strongly on their depth of origin as a consequence of elastic and inelastic scattering, this being shown schematically in Figure 4.4. A difference in the decay of the inelastic photoelectron backgrounds with binding energy is clearly observed for the different depth
distributions. For the surface treatment of polymers, the situations shown by Figures 4.4 (a) and (b) are most commonly observed, although situation (c) has been found, for example depletion of oxygen functionality at the surface of flame treated polypropylene at high flow rates\textsuperscript{120}. For a very near surface distribution, the inelastic background decays rapidly to almost the original level prior to the elastic peak. Thus by inspection of the O1s peak inelastic photoelectron backgrounds for polyolefins activated using various oxidising surface treatments, it is possible to obtain information on the relative depths of oxidation.

Figure 4.4 Schematic representation of the XPS lineshapes from an impurity atom distributed at different depths in a polymeric host matrix, (a) narrow surface region, (b) homogenous distribution within the XPS sampling depth, (c) buried layer

4.1.4 Quantification\textsuperscript{121-125}

There are two main methods by which XPS data may be quantified, firstly by chemical standards and secondly by calculation. Chemical standards are used in instrument calibration techniques, however, such methods suffer from the problem that surfaces often differ from the bulk material, thus making it difficult to know exactly the surface composition, that is precisely characterised surfaces are difficult to obtain. For this reason calculation is often preferred.
The intensity of an observed peak may be related to the instrument and sample parameters as in equation 4.7,

\[ I_A = N_A \sigma_A L_A(\gamma) D(E_P) \lambda(E_A) T(E_P, E_A, W) \chi \]  
\text{eqn. 4.7}

where \( I_A \) is the peak intensity from \( A \), \( N_A \) is the number of \( A \) atoms per unit volume, \( \sigma_A \) is the total photoionisation cross-section, \( L_A(\gamma) \) is the angular asymmetry parameter, \( D(E_P) \) is the detector efficiency at the pass energy used, \( \lambda(E_A) \) is the inelastic mean free path, \( T(E_P, E_A, W) \) is the transmission constant with \( E_P \) being the pass energy, \( E_A \) being the photoelectron kinetic energy, \( W \) being the slit width and \( \chi \) is the X-ray flux density. Equation 4.8 may be rearranged as follows,

\[ N_A = \frac{I_A}{\sigma_A L_A(\gamma) D(E_P) \lambda(E_A) T(E_P, E_A, W) \chi} \]  
\text{eqn. 4.8}

By assuming \( S_A = \sigma_A L_A(\gamma) D(E_P) \lambda(E_A) T(E_P, E_A, W) \chi \), the fractional concentration of atom \( A \) is obtained, equation 4.9,

\[ C_A = \frac{N_A}{\Sigma N_i} = \left( \frac{I_A}{\Sigma N_i / S_i} \right) \]  
\text{eqn. 4.9}

where \( C_A \) and \( S_A \) are the fractional atomic concentration and the relative atomic sensitivity factor (rsf) of \( A \) respectively. The relative atomic sensitivity factors may be evaluated using semi-empirical equations.

4.1.5 Chemical Shift

One of the advantages of XPS is that some chemical information may be furnished in the form of “chemical shifts”. The binding energy of an electron in an orbital can be affected by the atoms’ environment, for example oxidation state. A simple charge potential model \(^\text{126}\), where the electronic charge is assumed to reside on the surface of the atom of interest, may be used to understand chemical shifts, equation 4.10,
\[
E_i - E_i^0 = \Delta E = \frac{q_i e^2}{4 \pi \varepsilon_0 r_i} + \sum_{i \neq j} \frac{q_j e^2}{4 \pi \varepsilon_0 d_{ij}}
\]

where \( \Delta E \) is the chemical shift, \( q_i \) is the charge on atom \( i \) ejecting the photoelectron, \( r_i \) atomic radius of atom \( i \), \( q_j \) is the charge on the adjacent atoms, \( d_{ij} \) is the distance between the atom \( i \) and the adjacent atoms \( j \), \( e \) is the charge on the electron and \( \varepsilon_0 \) is the permittivity of free space. The first term gives the coulombic attraction between the photoelectron and the charge on the atom site, while the second term is a summation of the potential interactions at that atom site due to adjacent atoms. Thus if \( r_i \) decreases as a result of removal of valence electron density by, for example, an electronegative element, \( q_i/r_i \) will increase resulting in an increase in binding energy and a chemical shift. Although, the charge potential model has been moderately successful in the interpretation of chemical shift data it does contain some simplifications, for example the electronic charge in a real atom does not reside over the atoms' surface. Also, relaxation effects are ignored, that is the effects of the core-hole resulting from photoemission on the remaining electrons are neglected. However, the practical usefulness of chemical shifts has been shown in the analysis of corona treated LDPE, where curve fitting of the C1s (hydrocarbon \( E_b \) 285.0eV) high resolution spectrum resulted in the synthesis of three peaks at binding energies of 286.5 eV, 288.0 eV, and 289.5 eV. These peaks were assigned to -CH\(_2\)O- (\( \Delta E \sim 1.5 \) eV, alcohol, ether, hydroperoxide), >C=O (\( \Delta E \sim 3.0 \) eV, aldehyde, ketone), and -CO\(_2\)- (\( \Delta E \sim 4.5 \) eV carboxylic acid, ester) respectively.

### 4.1.6 Chemical Derivatisation

It is clear that chemical information can be deduced from chemical shift data, however there is a lack of specificity in binding energies of core levels, with many functional groups inducing similar chemical shifts, for example the N1s binding energies of both MeNO\(_2\) and PhNO\(_2\) are \( \sim 406 \) eV. Additionally, chemically shifted peaks may be obscured in a multifunctional environment by peak overlap and broadening effects caused by such factors as Heisenberg uncertainty broadening of the photoelectron line due to the short lifetime of states, the line width of the X-ray source and shifts due to secondary substituents. For
these reasons, functional groups may not always be identified conclusively by chemical shift measurements. These problems may be overcome by selectively and quantitatively attaching an element not originally present on the surface onto a targeted functional group. Thus the concentration of the functional group may be obtained by determination of the specifically attached "heteroatom". This technique is called "derivatisation", "labelling", or "tagging", and may have the additional advantage of improved sensitivity if the newly attached element has a higher photoionisation cross-section than the atoms originally present. Indeed, chemical derivatisation has also been successfully used in the analysis of surface treated fluoropolymers using infra-red spectroscopy.

The derivatising agent should of course be specific to the functional group of interest, and the reaction should proceed under mild conditions with the solvent being benign. However, harsh reaction conditions are often necessitated for the derivatisation to be quantitative, so that solvent effects such as functional group rearrangement/reorientation through increased chain mobility and/or dissolution of low molecular weight components can be induced. A variety of reagents have been employed for the derivatisation of various functional groups including carbonyl, carboxylic acid, hydroperoxide, hydroxyl, amine groups, however many are not sufficiently selective or reproducible.

In light of the inherent problems of solution phase derivatisation, a move towards vapour or gas phase derivatisation has been made. Here, the sample is simply exposed to the vapour of the derivatising agent, thus removing any solvent associated problems. It is thought that the vapour molecules adsorb onto and diffuse into the sample surface to undergo the specific derivatising reaction. However, finding such specific reactions has proved problematic. Only hydroxyl groups tagged with trifluoroacetic anhydride and carboxylic acid groups tagged with trifluoroethanol have been successfully derivatised in the vapour phase although even these reactions are not completely specific, for example significant reaction between epoxide groups and trifluoroacetic anhydride has been found. The approach to practical derivatisation and surface analysis has been comprehensively reviewed in the literature.
4.2 Fourier Transform Infra-red Spectroscopy

4.2.1 Introduction

Infra-red (IR) spectroscopy is an extremely powerful analytical technique which has been available for many years and is based upon the characteristic absorption of infra-red radiation by a sample through molecular vibrations of functional groups, thus yielding information on sample composition. Application of modern technology has improved infra-red techniques immensely, with microprocessor controlled FT-IR instruments offering greater speed, sensitivity and flexibility than conventional dispersive instruments.

4.2.2 Attenuated Total Reflection

The attenuated total reflection (ATR) method allows the infra-red analysis of material surfaces, and has proved immensely useful in the study of surface oxidation and surface orientation in polymers.

<table>
<thead>
<tr>
<th>MATERIAL</th>
<th>FORMULA</th>
<th>REFRACTIVE INDEX</th>
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<td>Thallous Chloride-Iodide</td>
<td>&quot;KRS-6&quot;</td>
<td>2.19</td>
</tr>
<tr>
<td>Thallous Bromide-Iodide</td>
<td>&quot;KRS-5&quot;</td>
<td>2.38</td>
</tr>
<tr>
<td>Zinc Selenide</td>
<td>ZnSe</td>
<td>2.40</td>
</tr>
<tr>
<td>Silicon</td>
<td>Si</td>
<td>3.40</td>
</tr>
<tr>
<td>Germanium</td>
<td>Ge</td>
<td>4.02</td>
</tr>
</tbody>
</table>

Table 4.1 Materials and refractive indices of commonly used internal reflection elements

In the ATR technique, the sample is placed in optical contact with an optically denser material, which is transparent to infra-red radiation, this being known as an "internal reflection element" (IRE). The IRE may take several forms, for example prisms, hemispheres and trapezoidal reflection plates have been used depending upon whether the
system is single or multiple pass and on the number of reflections required. A number of materials have been successfully employed as IRE's, some of which are detailed in Table 4.1 (148). The infra-red radiation enters the IRE and, at angles of incidence greater than the critical angle, is totally internally reflected so that a standing wave is created normal to the reflecting plane within the IRE. An evanescent wave, whose electric field amplitude decays exponentially with distance is created in the rarer medium, that is the sample. This is shown schematically in Figure 4.5. Interaction between the evanescent wave and the sample may occur, resulting in a measurable attenuation of the propagating infra-red beam within the IRE producing an absorption spectrum resembling a conventional transmission spectrum.

![Figure 4.5 Schematic representation of an ATR IRE](image)

The penetration depth, $d_p$, of the evanescent wave is defined as being the depth at which the intensity is $e^{-1}$ of the original intensity at the reflecting plane, and may be calculated for a non-absorbing medium using the Harrick Equation, equation 4.11,

$$d_p = \frac{\lambda}{2\pi n_1 \left[\sin^2 \theta - \left(\frac{n_2}{n_1}\right)^2\right]^{1/2}} \text{ eqn. 4.11}$$

$$\theta = \theta_{IRA} - \sin^{-1} \left[\sin \left(\theta_{IRA} - \theta_{IRE}\right) / n_1\right] \text{ eqn. 4.12}$$

where $d_p$ is the penetration depth, $\lambda$ is the wavelength of radiation, $n_1$ is the refractive index of the IRE, $n_2$ is the refractive index of the sample (around 1.5 for polymers), $\theta$ is the angle of incidence at the reflecting plane, $\theta_{IRA}$ is the angle designated on the ATR accessory, $\theta_{IRE}$ is the face angle of the IRE. The variation of penetration depth with wavelength of
radiation is shown in Figure 4.6. As equation 4.11 indicates, the penetration depth varies with the wavelength of light, thus at longer wavelengths the ATR spectrum contains chemical information from a greater depth than at shorter wavelengths. Effectively, the longer wavelengths analyse a thicker sample, resulting in this part of the spectrum being relatively more intense. Also, the penetration depth decreases as the angle of incidence increases, and the refractive index of the IRE increases. Thus by appropriate selection of the angle of incidence and the IRE, the analysis depth may be accurately controlled resulting in a depth profiling technique, being successfully applied to the flame treatment of poly(vinyl fluoride)\textsuperscript{149}. Therefore, the ATR technique may be used to probe a depth below the surface varying from a few tenths to several micrometers depending upon the parameters outlined above.

![Figure 4.6 Variation of penetration depth with wavelength of radiation](image)

**Figure 4.6** Variation of penetration depth with wavelength of radiation

**4.3 Surface Free Energy**

**4.3.1 Introduction**

The specific surface excess free energy, often referred to simply as the surface energy, of a
material plays a direct role in interfacial interactions with other materials and is defined as the reversible work done in creating unit area of fresh, flat, free surface. Unfortunately, no direct method for evaluating surface free energy of solids exists, therefore indirect methods have to be used. A commonly used method for the estimation of polymer surface free energies is contact angle measurement, although the correctness of the calculation methods employed is a topic of debate.

4.3.2 Contact Angle Measurement

4.3.2.1 Background

The surface free energy of a solid may be estimated by measuring the contact angle of a liquid drop on a solid surface at the three-phase boundary line, shown schematically in Figure 4.7. Several methods have been devised that allow the measurement of contact angles on solids to an accuracy of 1-2°, some of which are listed below:

- equilibrium sessile drop method
- pendant bubble method
- advancing and receding drop method
- advancing and receding bubble
- drop on a tilted plate

![Figure 4.7 Schematic representation of a liquid drop on a surface](image)

Young first proposed the relationship between the contact angle of a liquid drop on a surface and the surface free energies of the respective liquid and solid, equation 4.13,
Chapter 4 Theory of Techniques

\[ \gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos \theta \]  
\text{eqn. 4.13}

where \( \gamma_{sv} \) is the surface free energy of the solid in equilibrium with the vapour of the contact angle liquid, \( \gamma_{sl} \) is the free energy of the solid-liquid interface, \( \gamma_{lv} \) is the surface free energy of the liquid in equilibrium with its' vapour and \( \theta \) is the contact angle of the liquid drop on the surface. An alternative form of Young’s Equation is equation 4.14,

\[ \gamma_{s} = \gamma_{sl} + \gamma_{l} \cos \theta + \pi \]  
\text{eqn. 4.14}

where \( \gamma_{s} \) is the surface free energy of the solid, \( \gamma_{l} \) is the surface free energy of the liquid and \( \pi \) is the spreading pressure of the vapour over the solid surface. Adsorption of vapour effectively reduces the surface free energy of the solid, however, negligible vapour adsorption occurs on low energy solids, for example polymers, where the contact angle is greater than the generally accepted value of 10° \textsuperscript{152,153}, so that the spreading pressure is usually neglected and thus \( \gamma_{sv} = \gamma_{s} \). Thus when \( \theta > 0^\circ \) (finite contact angle), the liquid is non-spreading on the solid, and when \( \theta = 0^\circ \), spontaneous spreading occurs. The condition for spontaneous spreading may be expressed simply in equation 4.15 or alternatively in equation 4.16,

\[ \gamma_{sv} \geq \gamma_{sl} + \gamma_{lv} \]  
\text{eqn. 4.15}

\[ \gamma_{s} \geq \gamma_{sl} + \gamma_{l} + \pi \]  
\text{eqn. 4.16}

where \( \pi = \gamma_{s} - \gamma_{sv} \). Young’s thermodynamic expression implies that there is only one true contact angle, however, this is not observed experimentally. Young’s relationship assumes that the solid surface is smooth, homogenous, rigid and isotropic, conditions which are rarely fulfilled in real systems, although a few have been found \textsuperscript{153}. This gives rise to three types of contact angle,

- The advancing contact angle, which is made when the liquid drop is advanced across the sample solid surface by the addition of further liquid.
• The receding contact angle, which is made by the liquid drop just before the liquid drop is receded by the removal of liquid

• The equilibrium contact angle

The advancing contact angle is the maximum angle made by the liquid drop, whereas the receding contact angle is the minimum angle made. The difference between the two is known as the contact angle hysteresis. There are two main causes of this hysteresis, surface roughness and surface heterogeneity, so that contact angle measurements may give an indication of the surface roughness or surface heterogeneity of a material.

Dupré suggested that work against intermolecular forces must be done in separating two phases, this quantity being known as the "thermodynamic work of adhesion", and may be expressed as the Dupré Equation, equation 4.17,

\[ W_{ad} = \gamma_s + \gamma_L - \gamma_{SL} \]  

eqn. 4.17

where \( W_{ad} \) is the reversible thermodynamic work of adhesion. By combining equations 4.13 and 4.17, a single expression relating the work of adhesion to known parameters, namely the surface free energy of the liquid and the contact angle, may be obtained. This is known as the Young-Dupré Equation, equation 4.18,

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

eqn. 4.18

Therefore, if liquids of known \( \gamma_{LV} \) are used, a value for \( W_{ad} \) may be arrived at, from which \( \gamma_s \) may be derived.

4.3.2.2 Interpretation of Contact Angles

In an effort to evaluate the surface free energy of solids, Zisman et al. proposed the "critical surface tension of wetting", \( \gamma_C \), calculated from contact angles using a
homologous series of liquids on a solid. An empirical linear relationship was derived, equation 4.19,

$$\cos \theta = 1 + b (\gamma_c + \gamma_{LV})$$  \hspace{1cm} \text{eqn. 4.19}$$

where $b$ is a constant and $\gamma_c$ is the critical surface tension of wetting. Thus by linear extrapolation to $\cos \theta = 1$ of the $\cos \theta$ dependence on $\gamma_{LV}$, a value for $\gamma_c$ may be readily obtained. Unfortunately, different series of homologous liquids result in different values of $\gamma_c$, so that $\gamma_c$ may not be equated to $\gamma_s$, the surface free energy of the solid. However, it may be taken as a threshold value for spontaneous spreading by liquids whose surface tension is below $\gamma_c$, and therefore, as an empirical parameter the critical surface tension of wetting is of some value. Good and Girafalco \textsuperscript{168-170} extended Zisman's work by introducing the interaction parameter $\phi$, with which the interfacial free energy between two phases could be evaluated, equation 4.20,

$$\gamma_{SL} = \gamma_S + \gamma_L - 2\phi_{LV} (\gamma_S \gamma_L)^{1/2}$$  \hspace{1cm} \text{eqn. 4.20}$$

The interaction parameter may be estimated from the molecular properties of both phases \textsuperscript{171-172}, with general values of $\phi$ falling in the range 0.5-1.2. However, cases where $\phi$ is in the range 0.95-1.05 are rare showing that this correction factor is of importance.

Fowkes suggested that interaction between two phases could only occur through like forces, and that interactions between unlike forces were negligible. Thus for a saturated hydrocarbon and a solid surface, where only dispersion forces may operate, the interfacial tension could be given by the following relationship using a geometric mean approximation for dispersion force interactions, equation 4.21,

$$\gamma_{SL} = \gamma_S + \gamma_L - 2(\gamma_S^d \gamma_L^d)^{1/2}$$  \hspace{1cm} \text{eqn. 4.21}$$

For more commonly studied surfaces where polar interactions in addition to dispersion interactions operate, the most popular method for the estimation of surface free energy is
Chapter 4 Theory of Techniques

Based on the theory of fractional polarity also proposed by Fowkes 173-176. He suggested that the surface free energy of a solid could be given by the sum of several independent intermolecular forces, such as dispersion forces and hydrogen bonding, equation 4.22,

$$\gamma_s = \gamma^d + \gamma^p + \gamma^h$$

where $\gamma_s$ is the surface energy of the solid, $\gamma^d$ is the dispersion component of surface energy, $\gamma^p$ is the polar component of surface energy and $\gamma^h$ is the hydrogen bonding component of surface energy. Often the hydrogen bonding component, $\gamma^h$, and polar component, $\gamma^p$, are often encompassed in a single term, $\gamma^p$ or $\gamma^h$. Owens and Wendt 177,178 employed the theory of fractional polarity and suggested that polar interactions, including hydrogen bonds, could also be estimated by a geometric mean, leading to a more comprehensive relationship between the interfacial free energy and its' components, equation 4.23,

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

Thus by measuring the contact angles of two or more liquids of known $\gamma_L^d$ and $\gamma_L^p$, it is possible to evaluate $\gamma_s^d$ and $\gamma_s^p$. However, it has been suggested that the geometric mean could be replaced by the arithmetic, $(\gamma_S^d + \gamma_L^d)/2$, quadratic, $\left\{\left[(\gamma_S^d)^2 + (\gamma_L^d)^2\right]/2\right\}^{1/2}$, anharmonic, $\left[(\gamma_S^d)^2 + (\gamma_L^d)^2\right]/(\gamma_S^d + \gamma_L^d)$, or harmonic, $2\gamma_S^d \gamma_L^d/(\gamma_S^d + \gamma_L^d)$ means 179. Indeed in practice, only the harmonic mean approximation to average interactions across an interface has been used, mainly by Wu 180-182, equation 4.24,

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

Neither approach is ideal, however they are of some use in the comparison of polymers. As stated earlier, all the interfacial polar interactions are often combined into a single term, $\gamma^p$. However, it has been suggested that the primary polar interaction across an interface is
that of an electron donor-acceptor interaction (Lewis acid-base), these principally being hydrogen bonds, and therefore must be considered separately. As a consequence, $W_{ad}$, the work of adhesion may be written in terms of the the work of adhesion due to dispersion interactions, $W^d$, and the work of adhesion due to acid-base interactions, $W^{AB}$, equation 4.25,

$$W_{ad} = W^d + W^{AB}$$

A theory was developed centering on the enthalpy of neutralisation the acidic and basic sites so that $W^{AB}$ may be replaced, equation 4.26,

$$W_{ad} = W^d - nf \Delta H^{AB}$$

where $n$ is the number of acid/base pairs per unit area, $f$ is a factor that converts the enthalpy per unit area to surface free energy and is assumed to have a value equal to unity and $\Delta H^{AB}$ is the enthalpy of neutralisation. The characterisation of different Lewis acids, $A$, and bases, $B$, by two constants $C$ and $E$ was possible by measurement of the enthalpy of neutralisation for those acids and bases in a neutral solvent, $\Delta H^{AB}$, equation 4.27,

$$-\Delta H^{AB} = C_A C_B + E_A E_B$$

Thus, the overall work of adhesion may be evaluated using the appropriate $E$ and $C$ values. However, the usefulness of this method for the practical evaluation of surface free energies/acid-base characteristics is somewhat limited through the lack of $C$ and $E$ values for polymers.

More recently, a method for estimating the surface free energy of a polymer using a group contribution method rather than wetting measurements has been proposed. However, it can clearly not be used for surface modified polymers where the exact number and identity of functional groups is unknown. More comprehensive reviews on wetting and adhesion have appeared in the literature.
5.1 Materials

5.1.1 Polymers

The biaxially drawn (ratio 8:8) films used in this study consisted of coextruded polypropylene cores with polyethylene and polypropylene melt coats (~0.5 μm), the final laminated product having an average thickness of ~25 μm. The polymers contained a total of 0.2% w/w of essential additives only, namely Irganox 1010, Irganox 1330, and Irgafos 168 (see Appendix A), and were manufactured and supplied by ICI(Propafilm), Table 5.1. Polyethylene also contained silica as an anti-blocking agent. The standard polymers used for gas phase derivatisations are detailed in Table 5.2.

<table>
<thead>
<tr>
<th>POLYMERS</th>
<th>REF. NO.</th>
<th>MOL. WT. / g mol⁻¹</th>
<th>DENSITY / kg m⁻³</th>
<th>MFI / dg min⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene Homopolymer *</td>
<td>T4046</td>
<td>N/A</td>
<td>~935</td>
<td>4-5</td>
</tr>
<tr>
<td>Polypropylene Homopolymer</td>
<td>PXC34029</td>
<td>N/A</td>
<td>~906-908</td>
<td>6-9</td>
</tr>
</tbody>
</table>

Table 5.1 Polyolefins used in the programme

<table>
<thead>
<tr>
<th>POLYMERS</th>
<th>ABBREVIATION</th>
<th>MOL. WT. / g mol⁻¹</th>
<th>SUPPLIER</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(vinyl acetate)</td>
<td>PVAc</td>
<td>~500,000</td>
<td>Polysciences Inc.</td>
</tr>
<tr>
<td>Poly(acrylic acid)</td>
<td>PAA</td>
<td>~250,000</td>
<td>Aldrich</td>
</tr>
<tr>
<td>Poly(vinyl alcohol)</td>
<td>PVA</td>
<td>~14,000</td>
<td>Aldrich</td>
</tr>
<tr>
<td>Poly(vinylmethylketone)</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>Aldrich</td>
</tr>
</tbody>
</table>

Table 5.2 Standard polymers used in gas phase derivatisation

The PVA, PAA, PVAc and PVMK were prepared for derivatisation by solution casting onto the PET film. The PET film (100 μm) was first cleaned with trichloroethylene in an
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ultrasonic bath and then dipped into solutions of the standard polymers: 10 % aqueous solution of PVA, 2% solution of PVAc in methanol, 4 % aqueous solution of PAA, 4 % solution of PVMK in N,N-dimethylformamide. The films were dried and stored in a dessicator.

High molecular weight, additive free, polyethylene (A.F. PE) of density ~935 kg m⁻³ was obtained from Polysciences Inc. in the form of pellets. Films suitable for flame treatment were made by sandwiching the pellets in PET film and pressing at 150°C. Prior to use, the PET film had been extracted in dichloromethane for 2 hours in order to remove cyclic trimers and prevent transfer of low molecular weight material from the PET surface to the polyethylene surface.

5.1.2 Chemicals

The liquids used for contact angle measurements were triply distilled water and diiodomethane (99%, Aldrich) stabilised with copper. The derivatising agents were trifluoroacetic anhydride (99+%, Aldrich), 1,1,1-trifluoroethanol (99.5+%, Aldrich), pyridine (99+%, Aldrich), di-α,α,α-trifluoroacetamide (99%, Aldrich) and 3-(trifluoromethyl) phenylhydrazine (96%, Aldrich). Diethylether (99.9+%, Aldrich) was used without drying for solvent washing experiments, and propanone (99.9+%, Aldrich) was used for Soxhlet extraction experiments. Other solvents were dimethylsulphoxide (99.9+%, Romil Chemicals), N,N-dimethylformamide (99.9+%, Romil Chemicals), dichloromethane (99.9+%, Fisons) and methanol which was distilled prior to use. All the other solvents used were of SLR grade.

Sulfur dioxide (99.9%, Air Products–Special Gases Section) and ammonia (99.9%, BOC), both supplied as liquefied gases, were used for reactive gas treatments. An 80% argon / 20% oxygen (BOC) mixture was used to try and minimise the presence of nitrogen in flame experiments.

Standard solutions of different pH used for contact angle titration were made as follows, 0.1M hydrochloric acid was diluted from the concentrated acid (SG 1.16, Fisons), 0.1M sodium hydroxide (AR, Aldrich), sodium chloride (AR, Aldrich).
5.2 Corona Discharge Treatment

5.2.1 Industrial Scale Treatment

Corona treatment was performed directly after film manufacture on an in-line Sherman Treaters (GT140) unit at ICI (Propafilm). An electrode gap of ~2 mm, electrode width of 1 m and a film line speed of 50 m min\(^{-1}\) were used. Films were treated at power levels below, at, and above those used commercially, that is 1, 2 and 3 kW respectively. Untreated films were produced in exactly the same manner except with the electrode system shut off. Samples were stored in the form of “blankets” in a cool, dark environment to reduce the risk of surface contamination.

5.2.2 Laboratory Scale Treatment

Laboratory scale corona treatment was performed on a Tantec Model HV 05-2 Corona Generator using a frequency of 20-30 kHz depending on the load, electrode gap of 2.0 mm, electrode width of 11.5 cm and a film line speed of 10.8 m min\(^{-1}\) throughout. In order to allow comparison between industrial and laboratory scale treatments, energy inputs per unit area were matched as closely as possible using equation 2.1. Therefore power levels of 25, 50 and 74 W respectively were used, with the matched energy inputs being shown in Table 5.3.

<table>
<thead>
<tr>
<th>ENERGY INPUT / J m(^{-2})</th>
<th>INPUT POWER / W</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>INDUSTRIAL</td>
</tr>
<tr>
<td>1200</td>
<td>1000</td>
</tr>
<tr>
<td>2400</td>
<td>2000</td>
</tr>
<tr>
<td>3600</td>
<td>3000</td>
</tr>
</tbody>
</table>

Table 5.3 Matched energy inputs from corona discharge treatment

The reactive gases were introduced directly into the corona region via flow channels in the electrode system. Sulfur dioxide and ammonia were delivered in metered quantities to the corona at apparent pressures of 20 and 5 psi respectively, thus, with the aid of correctly calibrated flow meters the quantities of reactive gas introduced into the corona could be easily controlled (see Appendix B).
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5.3 Flame Treatment

5.3.1 Laboratory Scale Treatment

Polymers were flame treated using apparatus built in-house which employed a 150 mm double row ribbon burner obtained from WSA Components, a chain conveyer system and an air/gas mixture supply system. In order to produce an evenly treated surface, the burner, which comprised of two rows of closely spaced jets, was inclined at an angle of \(-12^\circ\). Figure 5.1. The polyolefin film substrates were mounted onto an aluminium plate and treated by a single pass through a natural gas flame. The flame intensity was varied by altering the total flow rate of air and natural gas while maintaining a constant air-to-natural gas ratio, flame inner cone to polymer distance of 1.0 cm and film speed of 40.5 m min\(^{-1}\) (exposure time of 0.012 seconds) throughout. The burner was fixed on a base and engaged on a non-movable rack under the base, thereby facilitating changes in the burner-to-polymer distance if required.

Air, sulfur dioxide, ammonia and natural gas were delivered in metered quantities to the burner at apparent pressures of 15, 20, 5 and 0.25 psi respectively. Thus, with the aid of correctly calibrated flow meters, the flame intensity, air-to-natural gas ratio, and quantities of reactive gas introduced into the flame could easily be controlled. When required, the ammonia or sulfur dioxide was introduced into the flame by mixing it with the air and natural gas prior to combustion.

Equation 5.1 shows that for the stoichiometric combustion of methane (natural gas consists of \(-96\%\) methane and \(-4\%\) ethane) in oxygen, an oxidant-to-fuel ratio of 2:1 is required, where \(\Delta H_{\text{comb}}^0\) is the enthalpy of combustion,

\[
\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \quad \Delta H_{\text{comb}}^0 = -890.4 \text{ kJ mol}^{-1} \quad \text{eqn. 5.1}
\]

Oxygen constitutes approximately one fifth of the volume of air, therefore, for the stoichiometric combustion of methane in air, an oxidant-to-fuel ratio \(-10:1\) is required. The effects of oxygen deficient and oxygen rich flames were investigated using air-to-natural gas ratios in the range 8-17.5:1. Beyond these limits the resulting flame was very unstable with no or only a poorly defined inner cone such that it was of no use for surface
pretreatment. Here a natural gas flow rate of 2 l min$^{-1}$ was selected with sufficient air being supplied to make up the appropriate ratio.

Figure 5.1 Double row ribbon burner

5.4 X-Ray Photoelectron Spectroscopy

5.4.1 Introduction

Two X-ray photoelectron spectrometers were employed in this study. Routine analysis and some high resolution work was performed on a VG ESCALAB MK I, while most high resolution, all valence band spectra, and elemental mapping images were recorded on a Scienta ESCA 300 based at Daresbury, Cheshire.

5.4.2 Instrumental Parameters

5.4.2.1 VG ESCALAB

A VG ESCALAB MK I spectrometer employing an unmonochromatised Al K$\alpha$ X-ray source (1486.6 eV) at a pressure of $\sim 10^{-7}$ mbar was used for routine analysis. Surface treated samples were analysed by XPS within 48 hours of treatment. Samples were mounted onto metal stubs with the use of double sided tape prior to insertion into the vacuum of the spectrometer.
All spectra were recorded with an X-ray source power of 200 watts (10 kV, 20 mA) and in the constant analyser energy (CAE) mode. Broad scan spectra were obtained at a pass energy of 85 eV with a 10 mm aperture, whereas high resolution spectra were obtained at a pass energy of 20 eV with a 5 mm aperture. All spectra were charge referenced to a C1s binding energy of 284.6 eV. For O1s inelastic photoelectron background analysis, a pass energy of 50 eV and a 10 mm aperture were employed, with all background spectra being calibrated to an O1s binding energy of 530 eV for comparison purposes.

For variable take-off angle XPS, take-off angles of 20°, 90°, 30°, and 45° with respect to the sample surface were used, and were performed in the stated order. This was done in order for the most surface sensitive measurement to be made first and also to reduce systematic errors in the angle setting of the sample stage with respect to the energy analyser. The effects of X-ray beam damage on the treated sample surfaces were also assessed, this being achieved by repeating the experiment on a different area of the same sample and with the take-off angles being used in the reverse order. Thus, beam damage was considered to be minimal if the compositions obtained by both analyses at each respective take-off angle agreed reasonably well.

Deconvolution of high energy resolution spectra was achieved using a modified van Cittert deconvolution algorithm to remove line shape broadening effects of the Al Kα line. Quantification was achieved by measurement of the peak areas after subtraction of a Shirely type background, with appropriate corrections also being made for photoelectron cross-sections 194, inelastic mean free paths 111, energy analyser transmission 121, and angular asymmetry in photoemission 195.

5.4.2.2 Scienta ESCA300

The Scienta ESCA300 employed a monochromated Al Kα X-ray source (1486.6 eV) at a pressure of ~10⁻⁹ mbar. All spectra were obtained within 48 hours of treatment at a 45° take-off angle with respect to the sample surface. Samples were mounted onto metal stubs and were held in place by metal rings which were secured by screws.

All spectra were recorded with an X-ray source power of 2.8 kW (2.8 kV, 100 mA) and in the CAE mode. Broad scan spectra were obtained at a pass energy of 300 eV with a 1.9
mm aperture. High resolution and valence band spectra were obtained at a pass energy of 150 eV with a 0.5 mm aperture. All spectra were charge referenced to the C1s peak at a binding energy of 284.6 eV. All elemental mapping images were obtained in the high spatial resolution lens mode using an acquisition time of 250 s and a 300 eV pass energy. The circular image is that of the electron detector, and has a diameter of 67 mm representing 4 mm on the sample.

5.4.3 Chemical Derivatisation

Gas phase chemical derivatisation was achieved using a glass vacuum frame. Samples were evacuated to a pressure of ~10\(^{-3}\) mbar in a purpose built vacuum frame, Figure 5.2, before being exposed to the derivatising agent. During the reaction period, the derivatising agent was maintained at ~20°C (room temperature ~25°C) to prevent condensation of the reagent onto the specimens. After the prescribed reaction time had elapsed, the reagent containing vessel was immersed in liquid nitrogen, thus quenching the reaction. The samples were maintained at a pressure of at least 10\(^{-3}\) mbar for a further 24 hours after derivatisation to remove physisorbed reagent. Samples were normally analysed by XPS after the degassing process.

![Figure 5.2 Schematic diagram of the vapour phase chemical derivatisation vacuum rig](image-url)
Surface hydroxyl groups were derivatised by reaction with trifluoroacetic anhydride (TFAA) for 1 hour. Two methods were used to study the selective derivatisation of surface carboxyl groups. In the first, the standard polymers PAA, PVA, PET and PVMK were reacted with 1,1,1-trifluoroethanol (TFE) under vacuum, while in the second, the standard polymers were reacted with 1,1,1-trifluoroethanol (0.9 ml), pyridine (0.4 ml), and di-tert-butylcarbodiimide (0.3 ml) under vacuum. Initially, a reaction period of 12 hours was selected, while the kinetics of vacuum procedure employing the TFE, pyridine, and di-tert-butylcarbodiimide were further studied. The standard polymers PAA, PVA, PVMK, PVAc were used to study the selective derivatisation of surface carbonyl groups with 3-(trifluoromethyl)phenylhydrazine using the vacuum frame.

5.5 Fourier Transform Infrared Spectroscopy

5.5.1 Instrumental Parameters

All spectra were recorded on a Nicolet 20-DXC FT-IR spectrometer with a dry air purge, liquid nitrogen cooled MCT (mercury-cadmium-teeluride) detector, and a Spectra-Tech...
Model 300 variable ATR accessory. Spectra were recorded at a resolution of 1.000 cm\(^{-1}\) using 400 scans and a small aperture setting. Water vapour was subtracted from the spectra. The experimental arrangement of the ATR accessory is shown in Figure 5.3. The internal reflection elements used were KRS-5 (thallous bromide-iodide) and germanium prisms. The former was of refractive index 2.38, dimensions 50×10×3 mm, with face angle (\(\theta_{\text{RE}}\)) 45°, and the latter was of refractive index 4.02, dimensions 25×10×3 mm, with face angle (\(\theta_{\text{RE}}\)) 60°.

5.6 Surface Energy Determination

5.6.1 Surface Tension of the Contact Angle Liquids

Syringe barrels and plungers were soaked in chromic acid overnight followed by thorough washing with triply distilled water and drying overnight in a clean oven at ~200°C. Syringe needles were washed in triply distilled water and allowed to dry overnight. Each syringe and needle were used for one liquid only, and were washed with the respective liquid prior to contact angle measurement. Diiodomethane was contained in a dark brown bottle and stored in the dark to minimise decomposition. Contact angle liquids were handled with great care to avoid contamination and subsequent change in surface tension. Literature values for the contact angle liquid surface tensions are listed in Table 5.4.

<table>
<thead>
<tr>
<th>LIQUID</th>
<th>(\gamma_L) / mN m(^{-1})</th>
<th>(\gamma_L^d) / mN m(^{-1})</th>
<th>(\gamma_L^p) / mN m(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>72.8</td>
<td>21.8</td>
<td>51.0</td>
</tr>
<tr>
<td>Diiodomethane</td>
<td>50.8</td>
<td>49.5</td>
<td>1.3</td>
</tr>
</tbody>
</table>

Table 5.4 Literature values of surface tension for contact angle liquids

Surface tensions of all the liquids were measured using the Du Noüy ring method on a Krüss K10T Tensiometer. A minimum of four measurements with an accuracy of 0.2 mN m\(^{-1}\) were recorded for each liquid. Measured surface tensions were subject to correction in order to account for the inner and outer ring radii not being equal and for the liquid that remains on the ring after rupture of the meniscus. Results before and after correction are shown in Table 5.5, showing good agreement with the literature values.
Chapter 5 Materials, Pretreatments and Techniques

<table>
<thead>
<tr>
<th>LIQUID</th>
<th>EXPERIMENTAL $\gamma_L$ / mN m$^{-1}$</th>
<th>CORRECTION FACTOR</th>
<th>CORRECTED $\gamma_L^*$ / mN m$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>77.3</td>
<td>0.933</td>
<td>72.1</td>
</tr>
<tr>
<td>Diiodomethane</td>
<td>59.9</td>
<td>0.833</td>
<td>49.9</td>
</tr>
</tbody>
</table>

* corrected value = experimental value $\times$ correction factor

Table 5.5 Measured surface tensions of contact angle liquids

The acid/base character of the treated surface were briefly studied by contact angle measurement using aqueous acidic, basic and neutral standard solutions. The solutions were hydrochloric acid, sodium hydroxide and sodium chloride all of 0.1M concentration. Their corrected experimental and literature surface tensions are shown in Table 5.6.

<table>
<thead>
<tr>
<th>SOLUTION</th>
<th>pH</th>
<th>CORRECTED $\gamma_L$ / mN m$^{-1}$</th>
<th>LITERATURE$^{197}$ $\gamma_L$ / mN m$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>1</td>
<td>71.0</td>
<td>72.6*</td>
</tr>
<tr>
<td>NaCl</td>
<td>7</td>
<td>72.1</td>
<td>72.9*</td>
</tr>
<tr>
<td>NaOH</td>
<td>14</td>
<td>71.8</td>
<td>74.4*</td>
</tr>
</tbody>
</table>

* 0.5M solution at 20 °C; * 0.1M solution at 20 °C; ° 0.4M solution at 18 °C

Table 5.6 Measured and Literature surface tensions of standard solutions used for pH titration contact angle measurements

5.6.2 Contact Angle Measurement

Contact angles were measured on surfaces within 48 hours of surface treatment in order to minimise aging and contamination effects.

Surface energies were estimated from advancing contact angle measurements performed on a Krüss G40 v1 goniometer. In order to keep the sample flat during measurement, it was mounted onto a microscope slide with double sided tape. The microscope slide was then placed on the sample platform of the instrument and illuminated from behind with a cold light source. A 4 ml droplet of liquid was introduced onto the sample surface via a syringe, with the needle being maintained in the droplet throughout the measurement procedure in order to minimise the vibrational energy of the droplet. The droplet was allowed to equilibrate for ~15 seconds, after which time the three-phase boundary was
advanced over the sample surface by the addition of a further 1 ml of liquid. Advancing and receding contact angles were measured for at least 6 droplets, resulting in average contact angles with standard deviations of not more than 2° in most cases. All measurements were made at room temperature, and it was assumed that drop volume changes and spreading pressure were negligible under the conditions used.

5.7 Electron Microscopy

5.7.1 Scanning Electron Microscopy

Scanning electron microscopy (SEM) was employed for routine topographical analysis. The sample surfaces were sputter coated with 1-2Å of gold prior to insertion into the vacuum of a Cambridge Instruments Stereoscan 360 SEM. An accelerating voltage of 10.0 kV was employed, with samples being observed at a magnification of ×10,000.

5.7.2 Transmission Electron Microscopy

Carbon replicas were made of the samples required for transmission electron microscopy (TEM) analysis. Cellulose acetate softened with acetone was placed on to the sample surface and allowed to mould around any topographical features. The acetone was then allowed to air dry leaving a strong film of cellulose. Once the cellulose was completely dry, it was peeled away from the surface. A carbon film was then deposited onto the cellulose, this laminate then being placed between copper grids ready for insertion into the vacuum of the microscope. The cellulose film was then dissolved away with acetone, leaving the carbon replica which was analysed at magnifications of ×20,000 and ×33,000 using a Jeol 100CX instrument. Samples were observed at an angle of 45° with respect to the sample normal in order to accentuate any topographical features.
6.1 Introduction

The surfaces of the untreated polymer films were characterised by XPS, contact angle measurements, FTIR-ATR and electron microscopy.

6.2 X-Ray Photoelectron Spectroscopy

XPS was used to determine the surface elemental compositions. The presence of carbon only was detected on all the untreated homopolymer polymer surfaces. High resolution Cls and valence band spectra of untreated polypropylene and polyethylene are shown in Figures 6.1 (a)-(b) and 6.2 (a)-(b) respectively. On the additive free polyethylene (A.F. PE) surface, 0.5 %At. of oxygen was detected by XPS, and was attributed to transfer of PET during the film pressing process.

6.3 Contact Angle Measurement

6.3.1 Surface Free Energy

The surface free energies of the untreated polymers, as estimated by advancing water and diiodomethane contact angle measurement are shown in Table 6.1. Spreading pressure was neglected. A comparison between the Owens-Wendt and Wu methods of data analysis is shown.

The Wu method gave a negative value for the surface free energy of untreated polyethylene homopolymer, suggesting that it may not be a totally satisfactory method for estimating surface free energies and is therefore omitted. Although the Wu method estimated small values for polar components, they were of negligible magnitude so that the untreated surfaces were considered to be apolar. The Wu and Owens-Wendt methods agreed reasonably well in their estimates for the surface free energy of polypropylene. These results are in good agreement with literature values for the surface energies of polyethylene $^{178}$ and polypropylene $^{177}$, which are $33.1 \text{ mJ m}^{-2}$ and $30.2 \text{ mJ m}^{-2}$ respectively.
Figure 6.1 Scienta ESCA300 XP spectra of untreated polypropylene (a) high resolution C1s (b) valence band
Figure 6.2 Scienta ESCA300 XP spectra of untreated polyethylene (a) high resolution C1s (b) valence band
Chapter 6 Characterisation of Polymers

<table>
<thead>
<tr>
<th>POLYMER</th>
<th>SURFACE FREE ENERGY / mJ m(^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>OWENS-WENDT METHOD</td>
</tr>
<tr>
<td></td>
<td>(\gamma_s^d)</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>31.9</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>31.6</td>
</tr>
<tr>
<td>A.F. PE</td>
<td>31.5</td>
</tr>
</tbody>
</table>

Table 6.1 The surface energies of the untreated polymers

6.3.2 Contact Angle Hysteresis

For polyethylene, additive free polyethylene and polypropylene, measurable water and diiodomethane contact hysteresis, \(\Delta \theta = \theta_{\text{adv}} - \theta_{\text{rec}}\), were found, Table 6.2,

<table>
<thead>
<tr>
<th>POLYMER</th>
<th>WATER / deg</th>
<th>DIIO DOMETHANE / deg</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\theta_{\text{adv}})</td>
<td>(\theta_{\text{rec}})</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>104.9</td>
<td>83.2</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>106.3</td>
<td>89.3</td>
</tr>
<tr>
<td>A.F. PE</td>
<td>99.6</td>
<td>74.7</td>
</tr>
</tbody>
</table>

Table 6.2 Contact angle hysteresis of water and diiodomethane on untreated surfaces

Analysis by XPS showed that contamination was present only on the additive free polyethylene and not the other untreated surfaces. Thus in the case of the additive free polyethylene, the hysteresis was attributed to chemical heterogeneity, probably arising from some transfer of oxygen functionality during pressing. Also, the slightly lower advancing and receding water contact angles was attributed to the presence of oxygen functionality. The other surfaces were found to be smooth by SEM analysis (section 6.4.1), so that hysteresis could not have been due to roughness. However, physical heterogeneity, that is a heterogeneous distribution of densities from crystalline and amorphous regions could exist on the surface, could contribute to the hysteresis. Another contributory factor could be the adsorption of liquid by the polymer.

6.4 Attenuated Total Reflection Infrared Analysis (ATR)

The ATR method for infrared analysis of surfaces was used, spectra of untreated
Figure 6.3 FTIR-ATR spectrum of untreated polypropylene, upper spectrum KRS-5 crystal $\theta_{\text{IRA}}$ 50°, lower spectrum Ge crystal $\theta_{\text{IRA}}$ 50°

Figure 6.4 FTIR-ATR spectrum of untreated polyethylene, upper spectrum KRS-5 crystal $\theta_{\text{IRA}}$ 50°, lower spectrum Ge crystal $\theta_{\text{IRA}}$ 50°
polypropylene and polyethylene are shown in Figures 6.3 and 6.4 respectively. Spectra acquired with the KRS-5 element showed stronger absorbances than spectra acquired with the germanium element. The KRS-5 element is softer than the germanium crystal and as a result better optical contact between the crystal and sample can be achieved. Also, the germanium element, with its' higher refractive index, is more surface sensitive and effectively analyses less of the sample resulting in weaker absorbances. Peak assignments are shown in Tables 6.3 and 6.4 for polyethylene and polypropylene homopolymers respectively.

6.5 Electron Microscopy

6.5.1 Scanning Electron Microscopy

Scanning electron microscopy at a magnification of ×10,000 showed that the untreated polymer surfaces were very smooth. Figure 6.5 (a) and (b) show scanning electron micrographs of untreated polyethylene and polypropylene respectively.

6.5.2 Transmission Electron Microscopy

Carbon replica TEM of the untreated polymers at a magnification of ×20,000 and ×33,000 found that the surfaces were very smooth. Figure 6.6 (a) and (b) show transmission electron micrographs of untreated polyethylene and polypropylene respectively at ×33,000.
### Chapter 6 Characterisation of Polymers

<table>
<thead>
<tr>
<th>WAVE NUMBER / cm⁻¹</th>
<th>ASSIGNMENT</th>
</tr>
</thead>
<tbody>
<tr>
<td>720, 722</td>
<td>( \text{CH}_2 ) rocking</td>
</tr>
<tr>
<td>730</td>
<td>( \text{CH}_2 ) rocking</td>
</tr>
<tr>
<td>888</td>
<td>( \text{CH}_2 ) rocking</td>
</tr>
<tr>
<td>909</td>
<td>( \text{CH}_2 ) bending in -CH=CH₂</td>
</tr>
<tr>
<td>990</td>
<td>( \text{CH} ) bending in -CH=CH₂</td>
</tr>
<tr>
<td>1050</td>
<td>( \text{CH}_2 ) twisting</td>
</tr>
<tr>
<td>1078</td>
<td>skeletal C-C stretch + some ( \text{CH}_2 ) wag</td>
</tr>
<tr>
<td>1176</td>
<td>( \text{CH}_2 ) wagging</td>
</tr>
<tr>
<td>1303</td>
<td>( \text{CH}_2 ) wagging</td>
</tr>
<tr>
<td>1353</td>
<td>( \text{CH}_2 ) twist</td>
</tr>
<tr>
<td>1368</td>
<td>( \text{CH}_2 ) wagging</td>
</tr>
<tr>
<td>1380</td>
<td>( \text{CH}_2 ) bending , wagging</td>
</tr>
<tr>
<td>1463</td>
<td>( \text{CH}_2 ) bending</td>
</tr>
<tr>
<td>1468</td>
<td>( \text{CH}_2 ) bending</td>
</tr>
<tr>
<td>1473</td>
<td>( \text{CH}_2 ) bending</td>
</tr>
<tr>
<td>1480</td>
<td>( \text{CH}_2 ) bending</td>
</tr>
<tr>
<td>1820</td>
<td>combination of 1100 + 720,730</td>
</tr>
<tr>
<td>1894</td>
<td>combination of 1168 + 720,730</td>
</tr>
<tr>
<td>1903</td>
<td>combination band-unknown origin</td>
</tr>
</tbody>
</table>

Table 6.3 Band assignments for polyethylene homopolymer

<table>
<thead>
<tr>
<th>WAVE NUMBER / cm⁻¹</th>
<th>ASSIGNMENT</th>
</tr>
</thead>
<tbody>
<tr>
<td>809</td>
<td>( \text{CH}_2 ) rock + C-C stretch + C-CH₃ stretch</td>
</tr>
<tr>
<td>841</td>
<td>( \text{CH}_2 ) rock + C-CH₃ stretch</td>
</tr>
<tr>
<td>899</td>
<td>( \text{CH}_3 ) rock + ( \text{CH}_2 ) rock + CH bend</td>
</tr>
<tr>
<td>941</td>
<td>( \text{CH}_3 ) rock + C-C stretch</td>
</tr>
<tr>
<td>973</td>
<td>( \text{CH}_3 ) rock + C-C stretch</td>
</tr>
<tr>
<td>998</td>
<td>( \text{CH}_3 ) rock + ( \text{CH}_2 ) wag + CH bend</td>
</tr>
<tr>
<td>1045</td>
<td>C-C stretch + C-CH₃ stretch + CH bend</td>
</tr>
<tr>
<td>1104</td>
<td>C-C stretch + ( \text{CH}_3 ) rock + ( \text{CH}_2 ) wag</td>
</tr>
<tr>
<td>1168</td>
<td>( \text{CH}_2 ) twist + CH bend + ( \text{CH}_3 ) rock</td>
</tr>
<tr>
<td>1220</td>
<td>( \text{CH}_2 ) twist + CH bend + C-C stretch</td>
</tr>
<tr>
<td>1256</td>
<td>CH bend + ( \text{CH}_2 ) twist + ( \text{CH}_3 ) rock</td>
</tr>
<tr>
<td>1377</td>
<td>( \text{CH}_3 ) symmetric bend + ( \text{CH}_2 ) wag</td>
</tr>
</tbody>
</table>

Table 6.2 Band assignments for polypropylene homopolymer
Figure 6.5 Scanning electron micrographs of untreated (a) polyethylene and (b) polypropylene.
Figure 6.6 Transmission electron micrographs of untreated (a) polyethylene and (b) polypropylene
Chapter 7 Chemical Derivatisation

7.1 Standard Polymers

Vapour phase chemical derivatisation of standard polymers was attempted in order to identify specific labels for carbonyl and carboxylic acid functional groups. The details of the standard polymers are given in Table 7.1.

<table>
<thead>
<tr>
<th>STANDARD POLYMER</th>
<th>FUNCTIONAL GROUP</th>
<th>OXYGEN CONCENTRATION / %At.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVA</td>
<td>hydroxyl</td>
<td>33.3</td>
</tr>
<tr>
<td>PET</td>
<td>aromatic ester</td>
<td>28.6</td>
</tr>
<tr>
<td>PVAc</td>
<td>aliphatic ester</td>
<td>30.0</td>
</tr>
<tr>
<td>PAA</td>
<td>carboxylic acid</td>
<td>40.0</td>
</tr>
<tr>
<td>PVMK</td>
<td>ketone</td>
<td>20.0</td>
</tr>
</tbody>
</table>

Table 7.1 Details of the standard polymers

As the table shows, the oxygen concentrations were determined to be up to 15% below the respective stoichiometric values. This may possibly be due to the orientation of the functional groups away from the near surface, or to small errors in the elemental sensitivity factors employed during quantification. Also, the oxygen peak intensities and consequently the surface stoichiometries of PAA, PVMK and PVAc could be affected by \( \pi \rightarrow \pi^* \) transitions in the C=O group.

7.2 Derivatisation of Carboxylic Acid Functionality

Carboxylic acid groups were derivatised using 1,1,1-trifluoroethanol (TFE). The hypothesised reaction with carboxylic acid groups in PAA is summarised below, equation 7.1,

\[
\left[ \text{CH}_2\text{CH}_2\text{C(O)OH}_x \right ] + \text{HO-CH}_2\text{CF}_3 \rightarrow \left[ \text{CH}_2\text{CH}_2\text{C(O)CF}_3}_x \right ]
\]

eqn. 7.1
For each carboxylic acid group derivatised an overall increase in the number of atoms detectable by XPS of 5 atoms occurs, where 2 carbon and 3 fluorine atoms are added. If it is assumed that the original oxygen atoms, of concentration $[O]_0$ (determined experimentally for PAA to be 0.339), and the derivatives are homogeneously distributed in the surface layer, the surface atomic concentrations of oxygen, $[O]$, and fluorine, $[F]$, can be calculated for a given conversion, $x$, of acid groups to ester groups, equations 7.2 and 7.3 respectively.

\[
[O] = \frac{\text{no. O atoms}}{\text{total no. atoms}} \times 100\% = \frac{[O]_0}{5x[O]_0/2 + 1} \times 100\% = \frac{1}{2.5x + 1/[O]_0} \times 100\% \text{ eqn.7.1}
\]

\[
[F] = \frac{\text{no. F atoms}}{\text{total no. atoms}} \times 100\% = \frac{3\times [O]_0/2}{5\times [O]_0/2 + 1} \times 100\% = \frac{3}{5 + 2/(x[O]_0)} \times 100\% \text{ eqn.7.2}
\]

where $x[O]_0/2$ is the concentration of acid groups reacted. The calculated oxygen and fluorine concentrations as a function of conversion factor are plotted in Figure 7.1,

![Figure 7.1 Theoretical surface oxygen and fluorine concentrations for PAA derivatised with TFE/pyridine/di-t-butylcarbodiimide](image)

\[
\text{Figure 7.1 Theoretical surface oxygen and fluorine concentrations for PAA derivatised with TFE/pyridine/di-t-butylcarbodiimide}
\]
Figure 7.1 shows that oxygen concentration decreases with conversion factor, this being due to the addition of carbon and fluorine in addition to oxygen to the surface. A linear relationship is often mistakenly employed to calculate the acid group concentration, however, equation 7.3 should be used as there is clearly a non-linear relationship between the fluorine concentration and conversion factor.

Standard polymers were used to investigate the selectivity of the carboxylic acid derivatisation reaction using two methods,

1. TFE in a vacuum frame
2. TFE with catalyst system in a vacuum frame

with the samples being maintained at ~-20 °C, and being exposed to the reagent for the appropriate reaction period.

For TFE alone, no fluorine was detected on any samples after a 12 hour reaction time. Table 7.2 indicates that a reaction between the TFE and acid functionality occurred when a catalyst system of di-tert-butylcarbodiimide and pyridine was employed for the derivatisation (12 hour reaction time). The 1,1,1-trifluoroethanol, pyridine and di-tert-butylcarbodiimide mixture was used in the ratio 9:4:3.

<table>
<thead>
<tr>
<th>POLYMER</th>
<th>ELEMENTAL COMPOSITION / %At</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[C]</td>
</tr>
<tr>
<td>PAA</td>
<td>52.9</td>
</tr>
<tr>
<td>PVA</td>
<td>67.7</td>
</tr>
<tr>
<td>PET</td>
<td>74.5</td>
</tr>
<tr>
<td>PVMK</td>
<td>82.7</td>
</tr>
</tbody>
</table>

Table 7.2 Elemental compositions of standard polymers derivatised with TFE/pyridine/di-tert-butylcarbodiimide for 12 hours

From the theoretically calculated elemental compositions, derivatisation of the standard PAA polymer showed that an acid group conversion factor of 75% was readily achieved, indicating that almost all acid groups present were tagged. This almost complete reaction of acid groups was also indicated by the deconvolved high resolution C1s XP spectrum
Figure 7.2 Deconvolved ESACALAB high resolution C1s spectrum of PAA derivatised with TFE/pyridine/di-tert-butylcarbodiimide for 12 hours

<table>
<thead>
<tr>
<th>PEAK</th>
<th>BINDING ENERGY / eV</th>
<th>CHEMICAL SHIFT / eV</th>
<th>CARBON ASSIGNMENT</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>284.6</td>
<td>-</td>
<td>saturated C</td>
</tr>
<tr>
<td>2</td>
<td>286.8</td>
<td>2.2</td>
<td>-CH2O-</td>
</tr>
<tr>
<td>3</td>
<td>288.6</td>
<td>4.0</td>
<td>-CO2-</td>
</tr>
<tr>
<td>4</td>
<td>292.2</td>
<td>7.6</td>
<td>-CF3</td>
</tr>
</tbody>
</table>

Table 7.3 Peak assignments for Figure 7.2

which showed an almost 2:1:1:1 ratio between C:OCH2:CO2:CF3, Figure 7.2. Negligible amounts of surface fluorine were detected on the other standard polymers indicating that minimal reaction between the hydroxyl, ketone and aromatic ester groups had occurred. Therefore the selectivity of this gas phase derivatisation reaction towards acid groups was found to be reasonably good. The vacuum frame method worked very well and is therefore preferable to the bench method proposed by Ratner as it is a "cleaner" method, that is, there is less chance of surface contamination and also the handling of toxic chemicals is less extensive.
The catalysed acid tagging reaction between PAA and TFE for various exposure times was also investigated by XPS, Figure 7.3. The catalysed esterification reaction proceeded reasonably rapidly with limiting fluorine incorporation occurring after a reaction time of ~5 hours, resulting in an acid group conversion factor of ~75%.

Esterification reactions are usually acid catalysed, probably explaining why TFE alone was not successful as a derivatising agent. However, acid catalysis is not possible for gas phase reactions. Esterification reactions can also be catalysed by dehydrating agents such as dicyclohexylcarbodiimide which is commonly used. Unfortunately dicyclohexylcarbodiimide is a solid at room temperature and is therefore not suitable as a gas phase catalyst. However, di-t-butylcarbodiimide is a liquid at room temperature with a vapour pressure suitable for gas phase reactions. Equation 7.4 shows the mechanism of esterification with di-t-butylcarbodiimide, explaining why this method was successful as a derivatisation route.

Although a high conversion of acid groups was achieved not all groups were tagged. This
may have been caused by slow diffusion of the three reagents required for reaction into the 
sub-surface. If the reaction was diffusion controlled, the number of reacted acid groups 
would fall with depth into the polymer surface. Thus, the depth distribution of the 
fluorinated ester in the surface was investigated. This was achieved by utilising the greater 
sampling depth of the photoelectrons originating in the F2s (KE ~ 1453.5 eV, λ ~ 46.6 Å) 
orbitals compared to those from the F1s (KE ~ 798.5 eV, λ ~ 34.5 Å) orbitals. Therefore, 
if the extent of reaction was limited by diffusion, the F1s/F2s ratio would decrease with 
reaction time. To a 95% confidence level \(^{210}\), the F1s/F2s ratio was found to be invariant 
with increasing reaction time, Figure 7.4, showing that the limiting factor was not 
diffusion. Thus, the limiting factor was probably related to changes in the reactivity of the 
acid groups, the rate probably being slowed with increasing conversion of functional 
groups. The reactivity of the remaining underivatised groups was probably reduced by the 
presence of the electron withdrawing fluorine derivatives so that no further esterification 
reactions could proceed. Although quantitative depth distribution information on the 
fluorine atoms may be obtained by examination of inelastic photoelectron background 
signals, the method was used only qualitatively. Figure 7.5 shows the F1s inelastic 
photoelectron background signals for PAA derivatised with
Figure 7.4 F1s/F2s ratios with reaction time for PAA derivatised with TFE/pyridine/di-t-butylcarbodiimide

Figure 7.5 The F1s inelastic photoelectron background signals for PAA derivatised with TFE/pyridine/di-t-butylcarbodiimide for various reaction times
Figure 7.6 F1s/F2s ratios with reaction time for PVA derivatised with TFAA

Figure 7.7 The F1s inelastic photoelectron background signals for PVA derivatised with TFAA for various reaction times
Chapter 7 Chemical Derivatisation

TFE/pyridine/di-t-butylcarbodiimide at various reaction times. After 16 hours of reaction time, the inelastic photoelectron background remained horizontal, indicating that the concentration of fluorine atoms was constant with depth. Also, the background signals were very similar to each other at all the reaction times investigated, indicating that fluorine concentrations were constant with depth at all reaction times and confirming the results from F1s/F2s ratio measurements.

7.3 Derivatisation of Hydroxyl Functionality

Hydroxyl functional groups have been successfully derivatised in the gas phase using trifluoroacetic anhydride, TF AA. It was found that the limiting conversion of the hydroxyl groups was ~80% which occurred after a reaction period of approximately two hours. The inability to reach 100% conversion was attributed to the difficulty in diffusion of TF AA through the polymer surface. Therefore, the depth distribution of the fluorine containing ester was investigated using the F1s/F2s ratios and F1s inelastic photoelectron background signals as in section 7.2.

Again, if the extent of reaction was limited by diffusion, the F1s/F2s ratio would decrease with reaction time. To a 95% confidence limit, the F1s/F2s ratio was found to be invariant with reaction time for PVA derivatised with trifluoroacetic anhydride, indicating that the reaction was not diffusion controlled, Figure 7.6. As for the carboxylic acid group derivatisation, the rate of reaction this reaction was probably slowed at high conversions due to the electron withdrawing effect of the fluorine derivatives on the remaining unreacted hydroxyl groups. Figure 7.7 shows the F1s inelastic photoelectron background signals for PVA derivatised with TF AA at various reaction times. After 0.08 hours and 2 hours reaction time, the background signals decreased with binding energy, while for longer reaction times the backgrounds remained horizontal with binding energy. Although almost complete conversion of hydroxyl groups had occurred at all the reaction times studied, the difference in inelastic photoelectron background signals suggested that some difference in the concentration of fluorine incorporated with depth existed at short reaction times. This was in contrast to the analysis of the F1s/F2s ratios from the same spectra which suggested no time dependence on the depth distribution of fluorine atoms with time. The reason for the difference was attributed to the different sampling depths of the two
methods. Elastic photoelectrons have a maximum sampling depth of \( \sim 3 \lambda \), therefore the elastic F2s photoelectrons, which sample more deeply than the F1s photoelectrons and thus govern the maximum sampling depth of the method, originate from a maximum depth of \( \sim 100-150 \AA \) (\( \sim 10-15 \) nm). However, the inelastic photoelectron backgrounds from the F1s orbitals used for the Tougaard analysis may potentially originate from several thousand angstroms into the surface. For these reasons, the latter method probes much deeper into the sample surface than the former method. Thus, over the much greater sampling depth of the inelastic photoelectron background method, the incorporation of fluorine with depth may indeed be affected by reaction time. However, for the practical purpose of hydroxyl functional group determination by derivatisation, incorporation of fluorine is indeed homogeneous with photoelectron sampling depth for the reaction times employed.

### 7.4 Derivatisation of Carbonyl Functionality

Previous attempts have been made to selectively derivatise carbonyl groups in the gas phase using hydrazine \(^{26,211}\). However these proved to be unreliable \(^{193}\), with hydrazine reacting significantly with ester and acid functionalities. Therefore, a derivative of hydrazine, 3-(trifluoromethyl) phenylhydrazine, was investigated for the derivatisation of carbonyl functionality. The delocalisation effect of the phenyl ring in combination with the strong electron withdrawing effect of the trifluoromethyl group present on the phenyl ring would be expected to reduce the availability for reaction of the lone pair of electrons on the \(-\text{NH}_2\) group. Therefore the nucleophilicity of the compound would probably be reduced and could thus reduce the possibility of reaction with other functional groups. Thus the selectivity towards carbonyl groups should be improved.

The hypothesised reaction with PVMK is summarised in equation 7.5. Assuming that the original oxygen atoms present before derivatisation is \([O]_o\) (determined experimentally for PVMK to be 0.175) and the number of oxygen atoms converted into the hydrazone derivative are \(x[O]_o\) (where \(x\) is the conversion factor), the number of oxygen atoms not converted to the hydrazone derivative are \((1-x)[O]_o\). For each carbonyl group reacted an overall increase in the number of atoms detectable by XPS of 11 occurs, where 1 oxygen atom is removed, 7 carbon, 2 nitrogen and 3 fluorine atoms are added. If the derivatives
are homogeneously distributed in the surface layer, the surface atomic concentrations of oxygen, $[O]$, nitrogen, $[N]$, and fluorine, $[F]$, can be calculated for a given conversion of carbonyl groups, equations 7.6, 7.7 and 7.8 respectively. The predictions for elemental composition as a function of conversion factor are shown in Figure 7.8. Again, the relationships between elemental concentrations and conversion factor are non-linear.

\[
[O] = \frac{\text{no. O atoms}}{\text{total no. atoms}} \times 100\% = \frac{(1-x)[O]_0}{1+11x[O]_0} \times 100\% \quad \text{eqn. 7.6}
\]

\[
[N] = \frac{\text{no. N atoms}}{\text{total no. atoms}} \times 100\% = \frac{2x[O]_0}{1+11x[O]_0} \times 100\% \quad \text{eqn. 7.7}
\]

\[
[F] = \frac{\text{no. F atoms}}{\text{total no. atoms}} \times 100\% = \frac{3x[O]_0}{1+11x[O]_0} \times 100\% \quad \text{eqn. 7.8}
\]

Derivatisation using 3-(trifluoromethyl)phenylhydrazine was found not to be very selective towards carbonyl groups. Table 7.4 shows elemental compositions of the standard polymers after they were derivatised for 18 hours with 3-(trifluoromethyl)phenylhydrazine. Although reaction with the carbonyl containing standard polymer occurred, only a low conversion factor of $\sim 20\%$ was achieved (18.2% from the measured nitrogen concentration - eqn. 7.7, and 20.2% from the measured fluorine concentration - eqn. 7.8). More importantly than low carbonyl conversion were the significant reactions occurring with acid and hydroxyl functionalities, although this reagent was less reactive towards ester groups compared to hydrazine. Further work on the variation in conversion factor with reaction time was not undertaken as it was evident that this reaction was not suitable as a selective derivatising method. Also, only a small conversion was achieved after 18 hours reaction so that extended reaction periods would probably be required for higher conversions, this clearly being impractical for use as a tagging method.
Chapter 7 Chemical Derivatisation

Figure 7.8 Theoretical surface oxygen, nitrogen and fluorine concentrations for PVMK derivatised with 3-(trifluoromethyl)phenylhydrazine

<table>
<thead>
<tr>
<th>POLYMER</th>
<th>ELEMENTAL COMPOSITION / %At</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[C]</td>
</tr>
<tr>
<td>PVMK</td>
<td>74.8</td>
</tr>
<tr>
<td>PVAc</td>
<td>68.8</td>
</tr>
<tr>
<td>PVA</td>
<td>66.3</td>
</tr>
<tr>
<td>PAA</td>
<td>64.0</td>
</tr>
</tbody>
</table>

Table 7.4 Elemental compositions of standard polymers derivatised with 3-(trifluoromethyl)phenylhydrazine for 18 hours

Equation 7.9 shows a possible reaction of PVA with 3-(trifluoromethyl)phenylhydrazine,

\[
\begin{align*}
\text{CH}_2\text{CH}_2\text{OH}_x + \text{NH}_2\text{NH} & \rightarrow \text{CH}_2\text{CH}_2\text{NH}_2\text{NH} \\
& \text{eqn. 7.9}
\end{align*}
\]
Possible reactions with PAA are shown in equation 7.10,

\[
\begin{align*}
\text{CH}_2\text{CH-CH-} & + \text{NH}_2\text{NH} \\
\text{C=O} & \quad \text{OH} \\
x & \quad \text{CF}_3
\end{align*}
\Rightarrow
\begin{align*}
\text{CH}_2\text{CH-CH-} & \\
\text{C=NH} & \quad \text{OH} \\
\text{CF}_3 & \quad \text{CF}_3
\end{align*}
\]

\[\text{eqn. 7.10}\]

7.5 Summary

Vapour phase chemical derivatisation for the quantification of functional groups in a complex chemical environment is clearly extremely useful. However, the technique is not straightforward, with the existence of non-linear relationships between labelling atoms and functional group concentrations. The derivatisation of carbonyl groups has proved to be the most problematic, with reliable estimates of hydroxyl and carboxylic acid concentrations being readily obtainable. Depth distributions of the labelling atoms were also investigated. The TFE reaction with PAA was reasonably complete within the XPS sampling as was the reaction of TFAA with PVA.
8.1 Introduction

Polyethylene and polypropylene were treated on an industrial scale corona discharge apparatus at ICI(Propafilm) immediately after the films were manufactured. The surfaces were characterised by XPS, FTIR-ATR, electron microscopy and advancing contact angle measurement. The effects of corona intensity were studied.

8.2 Surface Topography

No visual roughening was observed on any sample after treatment. Routine analysis by SEM using a magnification of \( \times10,000 \) showed no effect of treatment on surface topography, Figures 8.1 (a) and (b) showing scanning electron micrographs of polyethylene and polypropylene respectively treated at a 2 kW corona intensity. Diethylether washing experiments had shown the presence of significant quantities of low molecular weight material. Such material could form a layer on the surface and thus obscure any surface roughening that may have resulted from corona treatment. Therefore treated samples were washed in diethylether and analysed by SEM. However, no roughening was revealed.

8.3 Effects on Surface Composition and Contact Angle

Analysis by XPS one day after film treatment showed that surface modification by the incorporation of oxygen only had occurred for both polyethylene and polypropylene. Figures 8.2-8.3 (a) and (b) show the effects of corona intensity on the surface oxygen concentration and the advancing water and diiodomethane contact angles for polyethylene and polypropylene respectively. These figures showed that the oxygen concentrations increased with corona intensity for both polymers, with more oxygen being consistently incorporated into polyethylene surfaces. As a result of surface oxidation, significant improvements in the water wettabilities of both polymers occurred, with the advancing water contact angles decreasing with corona intensity. The lowest advancing water contact angles measured were 61.8° and 67.3° for polyethylene and polypropylene respectively, evidencing excellent improvements in the surface water wettabilities over the
Figure 8.1 Scanning electron micrographs of (a) polyethylene and (b) polypropylene corona discharge treated at an intensity of 2 kW
Figure 8.2 Effect of varying corona intensity on surface oxygen and advancing (a) water (b) diiodomethane contact angles for polyethylene
Figure 8.3 Effect of varying corona intensity on surface oxygen and advancing (a) water (b) diiodomethane contact angles for polypropylene
untreated homopolymers. These results indicated that increasing the corona intensity further could result in greater improvement in the surface wettability. The higher oxygen concentrations and lower water contact angles for polyethylene at each corona intensity indicated its' relative ease of activation.

The advancing diiodomethane contact angles for both polyethylene and polypropylene appeared not to vary with corona intensity. However, the advancing diiodomethane contact angles were \(\sim 8^\circ\) lower than on the respective untreated surfaces. This was attributed to increased interfacial interactions through the formation dipole-induced dipole interactions between polar surface functional groups and the polarisable diiodomethane and also possible interactions with surface unsaturation.

8.4 Correlation Between Oxygen Concentration and Work of Adhesion

Figures 8.4 (a) and (b) show the correlation between oxygen concentration and works of adhesion calculated from advancing water and diiodomethane angles respectively for polyethylene and polypropylene combined. Works of adhesion were calculated from the Young-Dupré Equation.

Figure 8.4 (a) showed that the work of adhesion with water changed less rapidly at high oxygen concentrations. This could have been due to increased sub-surface oxidation. Attempts were made to identify the depth of oxidation for both polymers using variable angle XPS. It was assumed that an oxygen enriched layer was produced, and also that the incorporated oxygen was distributed homogeneously through the layer.\(^{193}\) Thus, by using oxygen concentrations obtained at take-off angles of \(30^\circ\) and \(90^\circ\), an estimate for the thickness of the oxidised layer was obtained. From these measurements, layer thickness' of 50-70 Å were obtained for both polyethylene and polypropylene, suggesting that both polymers were oxidised to similar depths. Given this similarity in oxidation depths, the modified layer of polyethylene was probably more oxidised than of polypropylene. Care should be taken when comparing oxidation depth information from XPS and contact angle measurements as the latter measurements are more surface specific and so may result in slightly different interpretations of the obtained data. Given the assumptions made in the oxygen depth model, the absolute values of depth must be regarded as approximate.
Figure 8.4 The relationship between oxygen concentration and work of adhesion from advancing (a) water and (b) diiodomethane angles for polyethylene and polypropylene at all corona intensities.
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Statistical analysis showed that the work of adhesion with diiodomethane did not increase significantly with corona intensity.

8.5 Low Molecular Weight Oxidised Material

Low molecular weight oxidised material can be produced as a result of polymer chain scission during surface modification via a free radical type mechanism. This scission material would be present at the surface and would be of low cohesive strength. Contact angle data could be affected by the presence of such material, for example by dissolution into contact angle liquid with subsequent reduction of the liquids' surface tension, thus providing misleading data on the surface wettability. Also such a layer of material could form a weak boundary layer and adversely affect adhesion, although this would depend upon the quantity of the low molecular weight material and compatibility with the adhesive or printing ink used. In order to check for the presence of such material, the corona treated samples were washed in diethylether and then reanalysed by XPS and water contact angle measurement.

Table 8.1 shows the surface oxygen concentrations and advancing water contact angle data for industrially corona discharge treated polyethylene before and after washing in diethylether. Significant decreases in the oxygen concentration were found after washing at all corona intensities. A decrease of almost 20% in the surface oxygen was observed at the lowest corona intensity, with ~25% and ~45% reductions at intensities of 2 kW and 3 kW respectively. From these observations it was evident that a significant proportion of the incorporated surface oxygen was in the form of low molecular weight oxidised fragments. At corona intensities of 2 kW and 3 kW, removal of the oxygen containing low molecular weight fragments produced reductions in the surface wettabilities, at least an 8° increase in the advancing water contact angles. However, the advancing water contact angles indicated that the diethylether washed surfaced had retained some water wettability. Indeed, the advancing water contact angles were reasonably similar for all samples after diethylether washing, suggesting that the washing procedure may have had an ‘equalising’ effect on the surface. This equalisation of wettability was probably caused by reorientation of functional groups remaining at the surface.
Table 8.1 Surface oxygen and advancing water contact angle data for corona discharge treated polyethylene before and after washing with diethylether

<table>
<thead>
<tr>
<th>CORONA INTENSITY / kW</th>
<th>UNWASHED [O] / %At.</th>
<th>[H_2O]_{adv} / deg</th>
<th>DIETHYLETHER WASHED [O] / %At.</th>
<th>[H_2O]_{adv} / deg</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.3</td>
<td>83.0</td>
<td>1.9</td>
<td>80.9</td>
</tr>
<tr>
<td>2</td>
<td>6.5</td>
<td>70.5</td>
<td>4.9</td>
<td>78.8</td>
</tr>
<tr>
<td>3</td>
<td>9.3</td>
<td>61.8</td>
<td>5.0</td>
<td>77.6</td>
</tr>
</tbody>
</table>

Table 8.2 Surface oxygen and advancing water contact angle data for corona discharge treated polypropylene before and after washing with diethylether

<table>
<thead>
<tr>
<th>CORONA INTENSITY / kW</th>
<th>UNWASHED [O] / %At.</th>
<th>[H_2O]_{adv} / deg</th>
<th>DIETHYLETHER WASHED [O] / %At.</th>
<th>[H_2O]_{adv} / deg</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.8</td>
<td>89.0</td>
<td>1.6</td>
<td>105.2</td>
</tr>
<tr>
<td>2</td>
<td>3.4</td>
<td>74.4</td>
<td>1.4</td>
<td>102.3</td>
</tr>
<tr>
<td>3</td>
<td>6.1</td>
<td>67.3</td>
<td>2.4</td>
<td>97.3</td>
</tr>
</tbody>
</table>

Table 8.2 shows the surface oxygen concentrations and advancing water contact angle data for industrially corona discharge treated polypropylene before and after washing in diethylether. At low corona intensity, little of the surface oxygen was removed by diethylether washing, however, ~60% of the surface oxygen was removed at the higher corona intensities. A large increase in the advancing water contact angle was found as a result of solvent washing, showing that the wettability of the surface had been dramatically reduced. Indeed, the wettabilities of the treated polypropylene surfaces after diethylether washing approached that of the untreated homopolymer in spite of the presence of some oxygen functionality. This was attributed to reorientation of polar functional groups away from the outer monolayers and into the sub-surface, an area to which contact angle measurements are not sensitive. It was clearly evident that for polypropylene over half of the oxygen functionality introduced by corona treatment at the commercially used intensity of 2 kW was contained in low molecular weight fragments. Thus greater amounts of scission fragments were generally found on treated polypropylene surfaces than on treated polyethylene surfaces indicating a greater susceptibility to free-radical degradation. This
Figure 8.5 Variation in hydroxyl concentration with corona intensity for polyethylene and polypropylene

Figure 8.6 Percent of incorporated surface oxygen present as hydroxyl functionality
Figure 8.7 Deconvolved ESCALAB C1s high resolution XP spectra of polyethylene and polypropylene corona treated at corona intensities of 2 kW.

<table>
<thead>
<tr>
<th>PEAK</th>
<th>BINDING ENERGY / eV</th>
<th>CHEMICAL SHIFT / eV</th>
<th>GROUP</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PE</td>
<td>PP</td>
<td>PE</td>
</tr>
<tr>
<td>-</td>
<td>284.6</td>
<td>284.6</td>
<td>-</td>
</tr>
<tr>
<td>1</td>
<td>285.9</td>
<td>286.0</td>
<td>1.3</td>
</tr>
<tr>
<td>2</td>
<td>287.5</td>
<td>287.5</td>
<td>2.9</td>
</tr>
<tr>
<td>3</td>
<td>288.7</td>
<td>288.7</td>
<td>4.0</td>
</tr>
</tbody>
</table>

Table 8.3 Peak assignments for Figure 8.6

was attributed to the presence of the free-radical stabilising pendant methyl group on polypropylene. Overall, care should be taken in interpreting XPS and contact angle data when making judgements on levels of surface modification, especially when the presence of low molecular weight material is suspected.

8.6 Chemical Derivatisation

The TFE method for the determination of carboxylic acid groups was not available at this stage and therefore data on this functional group is not available. The hydroxyl group
Figure 8.8 FTIR-ATR spectra of industrially corona treated polyethylene, KRS-5 crystal, $\theta_{IRA} 45^\circ$

Figure 8.9 FTIR-ATR spectra of industrially corona treated polypropylene, KRS-5 crystal, $\theta_{IRA} 45^\circ$
concentration was estimated from chemical derivatisation with TFMA assuming 80% \( (x = 0.8) \) conversion of hydroxyl groups, equation 8.1,

\[
\text{hydroxyl concentration} = \frac{1}{3x/[F] + 6x} \times 100% \quad \text{eqn. 8.1}
\]

Figure 8.5 indicated that the hydroxyl concentrations for both polyethylene and polypropylene did not change with corona intensity, with estimates for polyethylene being consistently higher than for polypropylene. However, Figure 8.6 showed that although the absolute hydroxyl group concentration did not vary, the hydroxyl group concentration expressed as a percentage of the incorporated surface oxygen decreased with corona intensity. This indicated that more of the other types of functional groups must have been incorporated into the polyethylene surfaces, for example carboxylic acid, carbonyl groups. The presence of more highly oxidised functionality after severe treatment was not surprising. Indeed, polyethylene and polypropylene were very similar in this respect. High resolution XPS of the C1s peak of polyethylene and polypropylene treated at 2 kW corona intensity confirmed the presence of such groups, showing that complex oxygen functional group environments existed on both polymer surfaces, Figure 8.7. From chemical shift data, the presence of C-O (hydroxyl, ether) at \( \Delta \varepsilon \sim 1.5 \) eV, C=O (aldehyde, ketone) at \( \Delta \varepsilon \sim 3.0 \) eV and CO\(_2\)- (carboxylic acid, ester) at \( \Delta \varepsilon \sim 4.2 \) eV were revealed. Analysis by FTIR-ATR confirmed the presence of C=O groups on the surfaces of both polyethylene and polypropylene, Figures 8.8 and 8.9 respectively. For polyethylene, the absorbance peak occurred at \( \sim 1720 \) cm\(^{-1}\) and was assigned to ketones (range \( 1725-1705 \) cm\(^{-1}\)) possibly being due to oxidation of the polymer backbone. For polypropylene on the other hand, the absorbance main peak occurred at \( \sim 1730 \) cm\(^{-1}\) and was assigned to aldehydes (range \( 1740-1720 \) cm\(^{-1}\)) possibly being due to oxidation of pendant methyl groups. The absorbances from this group increased with corona intensity for both polymers, and was particularly noticeable for polypropylene where the absorbance increased by over 200% from 1 kW to 3 kW corona intensity. This indicated that the C=O group concentrations increased with corona intensity, confirming the reduction in the percent of oxygen present as hydroxyl at the higher intensities. However in absolute terms this should be interpreted with care as absorbances are strongly affected by the optical contact between sample and internal reflection element.
8.7 Surface Free Energy

Advancing water and diiodomethane contact angles were used to estimate surface free energies according to the method of Owens-Wendt. The effects of industrial corona treatment on the surface free energies of polyethylene and polypropylene are shown in Tables 8.4 and 8.5 respectively.

The introduction of oxygen functionality into polyethylene surfaces by corona treatment produced an increase in the surface polarity and consequently the total surface free energy. The polar component, $\gamma_S^p$, increased with corona intensity while the dispersion component, $\gamma_S^d$, remained unchanged. These estimates suggested that the total surface energy, $\gamma_S^{\text{tot}}$, could continue to increase with corona intensity, however, the increased presence of low molecular weight fragments should also be considered.

Corona treatment of polypropylene also resulted in an increase in the polar component of surface free energy leading to the total surface free energy increasing with corona intensity. Not surprisingly from the lower oxygen concentrations and water contact angles for a given corona intensity, lower polar components were estimated for polypropylene than polyethylene. An apparent decrease in the dispersion component was observed, and as a consequence the total surface free energy did not increase as much as would have been expected from the increases found for the polar component. The harmonic mean method of Wu to estimate surface free energies was also employed. Slightly higher polar components were estimated in most cases for both polymers, but the general trends found were in agreement with those found using Owens-Wendt method.

The low molecular weight fragments present on the treated surfaces contained much of the introduced oxygen, so that care should be taken in the interpretation of the contact angle measurements made on these surfaces and therefore of the surface energy estimates given. Thus, the values shown in Table 8.4 and 8.5 give an indication of surface energies in the presence of small molecules. It has been suggested that contact angles, and therefore surface free energies of surfaces washed with polar solvents should be taken as being representative of the level of surface activation achieved. However, reorientation effects induced as well as removal of oxygen functionality by washing should be taken into account.
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### Table 8.4 The effects of corona intensity on the surface free energy of polyethylene

<table>
<thead>
<tr>
<th>CORONA INTENSITY / kW</th>
<th>$\gamma_s^p$ / mJ m$^{-2}$</th>
<th>$\gamma_s^d$ / mJ m$^{-2}$</th>
<th>$\gamma_s^\text{tot}$ / mJ m$^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>untreated</td>
<td>0</td>
<td>31.9</td>
<td>31.9</td>
</tr>
<tr>
<td>1</td>
<td>5.2</td>
<td>31.5</td>
<td>36.7</td>
</tr>
<tr>
<td>2</td>
<td>12.8</td>
<td>30.0</td>
<td>42.8</td>
</tr>
<tr>
<td>3</td>
<td>20.2</td>
<td>28.1</td>
<td>48.3</td>
</tr>
</tbody>
</table>

### Table 8.5 The effects of corona intensity on the surface free energy of polypropylene

<table>
<thead>
<tr>
<th>CORONA INTENSITY / kW</th>
<th>$\gamma_s^p$ / mJ m$^{-2}$</th>
<th>$\gamma_s^d$ / mJ m$^{-2}$</th>
<th>$\gamma_s^\text{tot}$ / mJ m$^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>untreated</td>
<td>0</td>
<td>31.6</td>
<td>31.6</td>
</tr>
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<td>1</td>
<td>3.2</td>
<td>29.8</td>
<td>33.0</td>
</tr>
<tr>
<td>2</td>
<td>11.2</td>
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<tr>
<td>3</td>
<td>18.4</td>
<td>24.9</td>
<td>43.3</td>
</tr>
</tbody>
</table>

Account. As a result there is no simple solution to estimating a single, reliable surface energy for surface treated polymers in the presence of low molecular weight scission products.

### 8.8 Aging Effects

The effects of aging on the surface compositions and water wettabilities of corona treated samples were followed over a period of ~7 months. The treated polymer films used for aging studies were stored as “blankets” under dark, dry conditions at room temperature in order to avoid surface contamination. As a consequence of this storage method, no evidence was found to indicate contamination of sample surfaces.

The aging behaviour of polyethylene and polypropylene surfaces corona treated at various intensities as indicated by oxygen concentration is shown in Figures 8.10 and 8.11 respectively. These figures show that both polymers aged significantly. Also, Table 8.6 shows the effect of aging on the surface oxygen concentration and work of adhesion.
Table 8.6 Effects of aging on oxygen concentration and water work of adhesion for polyethylene and polypropylene treated at a 2 kW corona intensity

calculated from the advancing water contact angle for polyethylene and polypropylene after treatment at a 2 kW corona intensity. The surface oxygen concentration increased with time at first but then started to decrease once more while the water wettability continued to decrease with aging. The most marked changes occurred at low corona intensity for both polymers where maxima in the oxygen concentrations were indicated after ~65 days of aging. Maxima in the oxygen concentrations for both polymers at this time were also indicated at 2 kW corona intensity, while only slight increases were found at 3 kW corona intensity.

The decrease in work of adhesion without a corresponding reduction in surface oxygen in the initial stages of the aging process was unexpected, and was in contrast to another study which reported no change in oxygen concentration or wettability over a period of 30 days. However, the period of study here was much greater, allowing changes over a longer time scale to be detected. The reduction in the surface interactions was attributed to reorientation/migration of oxygen containing functional groups within the modified surface layer. Movement of functional groups away from the near surface would reduce the surface free energy of the polymers and have a large effect on the work of adhesion. Since XPS measurements have a sampling depth of several nanometres, they would be less affected by functional group migration in the very near surface region. The enhanced oxygen concentration on aging was also thought to be due to an increased sub-surface concentration of functional groups produced by reorientation/migration in the modified region. While polar functional groups reorientate away from the air-polymer interface in order to minimise the surface free energy, it was hypothesised that polar functional groups...
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Figure 8.10 Effect of aging on the surface oxygen concentration for polyethylene

Figure 8.11 Effect of aging on the surface oxygen concentration for polypropylene
in the sub-surface slightly beyond the XPS sampling depth actually migrate towards the surface. The near surface would have a greater polarity than the bulk and would therefore be an energetically more stable environment for polar groups to occupy. Thus oxygen functionality would migrate towards the surface leading to the increased oxygen concentration observed. This could also explain why the smallest changes in the oxygen concentration were observed at the highest corona intensities. It would be reasonable to expect that the depths of oxidation at these higher intensities would be greater than at lower corona intensities, and also to expect a less rapid decay in oxygen concentration over the XPS sampling depth and slightly beyond. Thus energetically, there would be no great benefit produced by the migration of polar groups to the surface, resulting in the relatively unchanged oxygen concentrations over the aging period. However, at low intensities, the oxygen concentration would be expected to decay much more rapidly. Thus, migration of polar groups towards the surface would be much more energetically favourable, resulting in the large oxygen concentration changes observed with aging.
9.1 Introduction

Laboratory scale corona discharge apparatus was used to modify polyethylene and polypropylene surfaces which were subsequently characterised by XPS, FTIR-ATR, electron microscopy and contact angle measurement. The effects of corona intensity were studied. The effects of varying the corona intensity on polyethylene and polypropylene surfaces using a laboratory scale corona discharge treater were studied in order to allow a comparison to be made with industrial scale corona treatment, and also to form a basis for the evaluation of reactive gas corona treatment. The energy inputs per unit area used here were matched as closely as possible to those used in the industrial treatment in order to allow sensible comparisons to be made.

9.2 Surface Topography

Routine analysis by scanning electron microscopy using a magnification of ×10,000 did not show any evidence of surface roughening at any corona intensity. Scanning electron micrographs at a magnification of ×10,000 of polyethylene and polypropylene after treatment using a 50 W corona intensity are shown in Figures 9.1 (a) and (b) respectively. Treated samples after washing in diethylether were also analysed by SEM, but these also did not reveal any hidden topographical features. Carbon replica transmission electron microscopy was also used to look for surface topographical changes. A higher resolution may be achieved using this method compared to SEM, and therefore would be more able to reveal topographical changes upon treatment. At a magnification of ×33,000, this method also did not reveal any changes in surface topography for polyethylene and polypropylene corona treated at a 50 W intensity, Figures 9.2 (a) and (b) respectively. As surface roughening on the micrometer scale is required for contact angle hysteresis, then the observed hysteresis could not have been due to roughness of samples.

9.3 Effects on Surface Composition and Contact Angles

For both polyethylene and polypropylene, surface modification by incorporation of oxygen only was found. Figures 9.3-9.4 (a) and (b) show the effects of corona intensity on the
Figure 9.1 Scanning electron micrographs of (a) polyethylene and (b) polypropylene corona treated at a 50 W intensity
Figure 9.2 Transmission electron micrographs of (a) polyethylene and (b) polypropylene corona treated at a 50 W intensity
surface oxygen concentration and advancing water and diiodomethane contact angles for polyethylene and polypropylene respectively. The surfaces of both polymers showed steady increases in surface oxygen concentration with corona intensity, with more oxygen being incorporated into polyethylene surfaces than polypropylene surfaces at each respective intensity. Thus the relative difficulty in the treatment of polypropylene was exemplified, this being in agreement with earlier studies. There was some indication that the oxygen concentration for polypropylene had begun to tail-off with corona intensity, so that further increase in the corona intensity may not have produced significant increases in the incorporation of oxygen into the surface. This may have been due to the production and volatilisation of low molecular weight oxidised fragments during the corona treatment. Polypropylene is thought to be more prone to chain scission due to the radical stabilising effect of the pendant methyl group, leading to the greater production of small molecules at high intensity and resulting in an overall loss of oxygen functionality after volatilisation. This may also provide an explanation for the relative difficulty in its' pretreatment.

As expected for polyethylene, the advancing and receding water contact angles followed the opposite trend to the oxygen concentration and decreased steadily with corona intensity. Typically the water contact angle hysteresis was ~25°, probably being due to chemical heterogeneity resulting from a slight patchiness in treatment. Thus incorporation of oxygen led to a major improvement in the water wettability of polyethylene, the lowest advancing water contact angle of 60.2° being found at an intensity of 74 W. The lowest contact angle from industrial corona treatment was 61.8° and although this compared well, industrially treated samples were generally slightly less wettable than their laboratory treated counterparts.

The advancing and receding water contact angles followed the opposite trend to the oxygen concentration for polypropylene also. Both advancing and receding angles decreased less rapidly at higher corona intensities in good correspondence with the oxygen concentration, indicating that increased corona intensity may not have produced any further improvement in the surface wettability. The water contact angle hysteresis was ~20°, again probably due to a slight chemical heterogeneity. The lowest advancing water contact angle on polypropylene of 70.5° was achieved at an intensity of 74 W, representing an excellent improvement in the water wettability over the untreated polymer surface.
Figure 9.3 Effect of varying corona intensity on surface oxygen concentration and advancing water (a) and diiodomethane (b) contact angles for polyethylene
Figure 9.4 Effect of varying corona intensity on surface oxygen concentration and advancing water (a) and diiodomethane (b) contact angles for polypropylene
This also compared well with industrial treatment where the lowest contact angle was 67.3°, although the indication from this treatment was that the water contact angles could continue to decrease with corona intensity. Overall, the oxygen concentrations incorporated into the surfaces of both polymers were higher after laboratory scale treatment, although the levels of water wettability were only slightly better after this type of treatment. This could have been due to laboratory treatment producing slightly greater depths of oxidation. Oxidation depths are further discussed in Chapter 13.

The advancing and receding diiodomethane contact angles on both polymers appeared not to vary with corona intensity, however, with only three data points statistical analysis was not possible. However, for both polymers the advancing contact angles were ~8° lower than on the untreated surfaces and the receding contact angles were ~20° lower. This was probably due to the introduction of polar oxygen functionality onto the treated surfaces. Groups such as carbonyls could induce dipoles in the polarisable diiodomethane, thereby increasing the level of interfacial interactions and lowering the contact angles. Such behaviour would be especially noticeable in the receding contact angles where the dipole-induced dipole interactions would have to be broken before the liquid could dewet.

9.4 Correlation Between Oxygen Concentration and Work of Adhesion

Figures 9.5 (a) and (b) show the correlation between oxygen concentration and works of adhesion calculated from advancing water and diiodomethane angles respectively for polyethylene and polypropylene combined. Works of adhesion were calculated from the Young-Dupré Equation.

Although the advancing water contact angles continued to decrease with increasing oxygen concentration, the work of adhesion with water began to tail-off at these higher oxygen concentrations. Increased sub-surface oxidation was indicated by the less rapid increase in the water work of adhesion at high oxygen concentrations, this being in agreement with results obtained for industrial corona treatment. Statistical analysis to 95% confidence levels showed that the work of adhesion with diiodomethane did not increase significantly with corona intensity.
Chapter 9 Laboratory Scale Corona Treatment

Figure 9.5 Correlation between oxygen concentration and work of adhesion from advancing (a) water (b) diiodomethane contact angles combined for polyethylene and polypropylene.
Chapter 9 Laboratory Scale Corona Treatment

9.5 Low Molecular Weight Oxidised Material

In order to check for the presence of low molecular weight oxidised material, the corona treated samples were washed in diethylether and then reanalysed by XPS and water contact angle measurement.

Table 9.1 shows the surface oxygen concentrations and water contact angle data for corona discharge treated polyethylene before and after washing in diethylether. At low corona intensity, analysis by XPS showed that only a minor reduction in the surface oxygen concentration had resulted from diethylether washing. However, upon increases to corona intensities of 50W and 74W, almost a quarter of the surface oxygen concentration was washed away in each case. Clearly, a significant proportion of the oxygen incorporated into the polyethylene surface had been present as low molecular weight oxidised fragments. Removal of these scission products equalised the advancing and receding water contact angles over the range of corona intensities studied at average values of 71.3° and 30.7° respectively. The average advancing water contact angle from the washed surfaces was similar to that found at low corona intensity, this being reasonable given the observed oxygen concentrations and reorientation effects induced by diethylether washing. Indeed, the observed water contact angles upon diethylether washing still represented a good level of water wettability in comparison to the untreated polyethylene surface.

Table 9.2 shows the surface oxygen concentrations and water contact angle data for corona discharge treated polypropylene before and after washing in diethylether. A large effect was produced by diethylether washing of treated polypropylene. Reductions in the oxygen concentration after diethylether washing of 40%, 65% and 70% at corona intensities of 25W, 50W and 74W respectively were found. Thus for polypropylene, most of the oxygen introduced to the surface was in the form of small molecules, again indicating the relative ease in its' free radical degradation. The decrease in surface oxygen concentration produced the expected reduction in the advancing and receding water contact angles. The advancing angle was equalised over the range of corona intensities to an average of 97.2°, representing a major decrease in the water wettability of the surface to almost the level of the untreated polymer.
Table 9.1 Surface oxygen and water contact angle data for polyethylene corona discharge treated before and after washing with diethylether

<table>
<thead>
<tr>
<th>CORONA INTENSITY / W</th>
<th>[O] / %At.</th>
<th>θ H₂O_adv / deg</th>
<th>θ H₂O_rec / deg</th>
<th>DIETHYLEThER WASHED</th>
<th>[O] / %At.</th>
<th>θ H₂O_adv / deg</th>
<th>θ H₂O_rec / deg</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>7.9</td>
<td>70.9</td>
<td>39.3</td>
<td>7.6</td>
<td>71.3</td>
<td>32.4</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>8.7</td>
<td>62.8</td>
<td>28.8</td>
<td>6.7</td>
<td>69.3</td>
<td>30.9</td>
<td></td>
</tr>
<tr>
<td>74</td>
<td>13.2</td>
<td>60.2</td>
<td>19.0</td>
<td>10.1</td>
<td>73.2</td>
<td>28.8</td>
<td></td>
</tr>
</tbody>
</table>

Table 9.2 Surface oxygen and water contact angle data for polypropylene corona discharge treated before and after washing with diethylether

<table>
<thead>
<tr>
<th>CORONA INTENSITY / W</th>
<th>[O] / %At.</th>
<th>θ H₂O_adv / deg</th>
<th>θ H₂O_rec / deg</th>
<th>DIETHYLEThER WASHED</th>
<th>[O] / %At.</th>
<th>θ H₂O_adv / deg</th>
<th>θ H₂O_rec / deg</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>2.5</td>
<td>82.0</td>
<td>60.9</td>
<td>1.5</td>
<td>98.7</td>
<td>68.5</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>6.3</td>
<td>72.2</td>
<td>49.9</td>
<td>2.2</td>
<td>96.5</td>
<td>61.9</td>
<td></td>
</tr>
<tr>
<td>74</td>
<td>7.4</td>
<td>70.5</td>
<td>48.2</td>
<td>2.2</td>
<td>96.4</td>
<td>60.4</td>
<td></td>
</tr>
</tbody>
</table>

Thus, the presence of more scission products was suggested on the treated polypropylene surfaces than treated polyethylene surfaces. This was in agreement with industrial treatment, where ~45% and ~60% of the oxygen incorporated into polyethylene and polypropylene surfaces respectively was removed upon diethylether washing. This was attributed to the comparatively easy free-radical degradation of polypropylene. Corona discharge treatment was also found to be different from flame treatment (Chapter 11) where minimal amounts of low molecular weight fragments were suggested. This was attributed to volatilisation of the scission fragments by “hot” flame treatment, while relatively large amounts of fragments are retained during “cold” corona treatment.

9.6 Chemical Derivatisation

Figures 9.6 (a) and (b) show the hydroxyl and carboxylic acid functional group concentrations for corona treated polyethylene and polypropylene respectively. Functional group concentrations were estimated from equations 9.1 and 9.2. using the measured
fluorine concentrations from derivatization experiments and assuming 80% (x = 0.8) and 75% (x = 0.75) conversion of hydroxyl and carboxylic acid groups respectively.

\[
\text{hydroxyl concentration} = \frac{1}{3x/[F] + 6x} \times 100\% \quad \text{eqn 9.1}
\]

\[
\text{carboxylic acid concentration} = \frac{2x}{3/[F] - 5} \times 100\% \quad \text{eqn. 9.2}
\]

Over the range of corona intensities investigated, the hydroxyl and carboxylic acid concentrations appeared to remain unchanged with intensity for polyethylene. There was some variation in the percentage of oxygen present as hydroxyl and carboxylic acid groups, however no definite trend was identifiable. The hydroxyl concentration exceeded the carboxylic acid concentration at all corona intensities. This would be expected as volatilisation of oxygen containing small molecules would result in the loss of carboxylic acid groups. There was an excess of oxygen after accounting for hydroxyl and carboxylic acid functionalities, these in total accounted for ~7 %At. of the oxygen detected. This suggested that other oxygen functionalities, for example carbonyl groups, were produced in significant proportions by corona discharge treatment. For polypropylene, the hydroxyl and carboxylic acid group concentrations were also apparently unchanged with corona intensity, again with the hydroxyl concentration generally exceeding the carboxylic acid concentration. The percentage of oxygen introduced as hydroxyl and carboxylic acid groups decreased with corona intensity from ~32% to ~24% and ~32% to ~13% respectively. The latter finding was slightly surprising, as more carboxylic acid groups would have been expected under the greater oxidising power at high corona intensities so that greater amounts of low molecular weight oxidised fragments and chain ends would be anticipated. However, the volatilisation of some small molecules probably reduced the overall percentage of carboxylic acid groups. Also, the complex mechanisms at work could allow chain scission to occur in such a way that other oxygen functional groups are produced at chain ends. Again, there was an excess of oxygen after accounting for hydroxyl and carboxylic acid functional groups, suggesting the presence of other types of functional groups, for example carboxyls, especially at higher corona intensities. However, FTIR-ATR analysis did not detect the presence of carbonyl functional groups on the surfaces of either polymer. This was in contrast to industrial corona treatment.
Figure 9.6 Variation in hydroxyl and carboxylic acid concentrations with corona intensity for (a) polyethylene and (b) polypropylene.
where the presence of carbonyl groups was detected. This may have been due to the industrial treatment being slightly more oxidising than the laboratory treatment, producing greater quantities of carbonyl groups and fewer hydroxyl groups. Thus the lower concentration of carbonyls may not have been detected on the laboratory treated samples.

High resolution XPS using the Scienta ESCA300 was then employed in order to further elucidate the nature of the functional groups introduced by laboratory scale corona treatment. The chemical shift induced by polar oxygen functionality was observed in the high resolution Cls spectra for both polyethylene and polypropylene corona treated at an intensity of 50W, Figure 9.7. The Cls photoelectrons appeared to be chemically shifted by up to 4.5 eV, suggesting the presence of -C-O (hydroxyl, ether, $\Delta E \sim 1.5$ eV), -C=O (ketone, aldehyde, $\Delta E \sim 3.0$ eV) and -CO$_2$ (carboxylic acid, ester, $\Delta E \sim 4.2$ eV) on the treated surfaces. Although the chemical shifting was clearer than on the flame treated polymers, definitive assignment of the chemically shifted peaks was still not possible due to their very low intensity. Although small compared to primary shifts, chemical shifting from secondary substituents (they may be up to $\sim 0.7$ eV), could have caused peak
Table 9.4 Percent of oxygen present as hydroxyl after laboratory and industrial corona treatment for polyethylene and polypropylene

<table>
<thead>
<tr>
<th>ENERGY INPUT /J m⁻²</th>
<th>PERCENTAGE OF OXYGEN INCORPORATED AS -OH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>POLYETHYLENE</td>
</tr>
<tr>
<td></td>
<td>laboratory</td>
</tr>
<tr>
<td>1200</td>
<td>34.2</td>
</tr>
<tr>
<td>2400</td>
<td>36.8</td>
</tr>
<tr>
<td>3600</td>
<td>25.0</td>
</tr>
</tbody>
</table>

broadening thereby lowering resolution and thus further complicating functional group assignments. Therefore, as suggested in section 4.1.6, high resolution XPS is not always preferable to chemical derivatisation methods for functional group determination.

High resolution XPS showed that laboratory and industrial scale corona treatments were reasonably similar in terms of the types of functional groups incorporated, that is -C-O, -C=O and -CO₂ type groups were incorporated by both treatments. However, chemical derivatisation showed that a greater concentration of hydroxyl groups was incorporated by laboratory treatment, although this effect was less evident at the corona higher intensities studied, Table 9.4. Given the slightly higher oxygen content of laboratory treated surfaces, it is suspected that more carbonyls, carboxylic acid groups etc. were present on these treated surfaces.

9.7 Surface Free Energy

Advancing water and diiodomethane contact angles were used to estimate surface free energies according to the method of Owens-Wendt. The effects of corona intensity on the surface free energies of the two polymers are shown in Tables 9.5 and 9.6.

Thus, introduction of oxygen functionality into the polyethylene surfaces by corona treatment led to large increases in the polar components, although the dispersion components remained constant just below the level of untreated polymer surface. The overall effect was to increase the total surface energy. The surface energy began to level-off at high corona intensities, suggesting that the maximum surface energy had nearly been achieved so that increased corona intensity would probably not have improved them
further. Indeed, in light of diethylether washing experiments, increased corona intensity may not necessarily have improved the polymer adhesion characteristics as the formation of a layer of small molecules with low cohesive strength could occur. The polar components were significantly increased through the introduction of oxygen functionality into the polypropylene surfaces. As for polyethylene, the tailing-off in surface energy at high corona intensities suggested that further improvement was unlikely. The estimated dispersion component appeared to be slightly reduced upon treatment, this probably being due to the geometric mean model employed.

<table>
<thead>
<tr>
<th>CORONA INTENSITY / kW</th>
<th>SURFACE FREE ENERGY / mJ m⁻²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\gamma_s^P$</td>
</tr>
<tr>
<td>untreated</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>12.7</td>
</tr>
<tr>
<td>2</td>
<td>18.2</td>
</tr>
<tr>
<td>3</td>
<td>20.7</td>
</tr>
</tbody>
</table>

Table 9.5 The effects of corona intensity on the surface free energy of polyethylene

<table>
<thead>
<tr>
<th>CORONA INTENSITY / kW</th>
<th>SURFACE FREE ENERGY / mJ m⁻²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\gamma_s^P$</td>
</tr>
<tr>
<td>untreated</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>7.5</td>
</tr>
<tr>
<td>2</td>
<td>13.7</td>
</tr>
<tr>
<td>3</td>
<td>14.9</td>
</tr>
</tbody>
</table>

Table 9.6 The effects of corona intensity on the surface free energy of polypropylene

The surface energy estimates for polypropylene after both laboratory and industrial scale treatments were in good agreement, while the estimates after laboratory treated polyethylene were slightly higher than for industrially treated surfaces, this probably arising through their slightly higher oxygen concentrations and better water wettabilities. The slightly higher estimates at the lower intensities after laboratory treatment could have arisen through differences in electrode geometry. Care must be taken in the interpretation
of these contact angle measurements and therefore of these surface energy estimates, as the small molecules present on the treated surfaces contained much of the introduced oxygen. Thus, the values shown in Table 9.6 and at higher corona intensities in Table 9.5, give an indication of surface energies biased by the presence of small molecules. Overall, the laboratory and industrial treatments were found to produce similar levels of surface modification for both polymers. Therefore the laboratory treatment procedure could be confidently used to model the industrial treatment procedure in studies to improve the corona discharge method.
Chapter 10 Reactive Gas Corona Treatment

10.1 Introduction

Control over the acid/base characteristics of a polyolefin surface could allow it to be tailored to the requirements of a specific coating, for example epoxy adhesives could benefit from the presence of surface amine groups, thereby offering great advantages to the coatings industry. Thus, the laboratory scale corona discharge treater described previously was used to investigate the introduction of sulfur dioxide and ammonia gases into the corona discharge region. It was hypothesised that introduction of ammonia into the corona discharge region could lead to the incorporation of basic amine groups into the polyolefin surfaces, while sulfur dioxide could lead to the incorporation of sulfonic acid groups. The effects of varying the reactive gas concentration at constant corona intensity on the polyethylene and polypropylene surfaces were studied using XPS, FTIR-ATR, electron microscopy and contact angle measurement.

10.2 Sulfur Dioxide Treatment

Sulfur dioxide gas was bled into the corona discharge through evenly spaced channels in the treating electrode. Sulfur dioxide flow rates in the range 20-70 ml min$^{-1}$ were used. Beyond a flow rate of 70 ml min$^{-1}$ a stable corona could not be maintained and therefore greater flow rates were not investigated. A constant corona intensity of 50 W which had been determined previously to produce good surface activation was employed throughout.

10.2.1 Effects on Surface Composition and Contact Angles

Figures 10.1 (a) and (b) show the effects of varying the sulfur dioxide flow rate on the surface compositions of polyethylene and polypropylene respectively treated at a 50 W intensity. Analysis by XPS showed that the surfaces of both polymers had been modified by the incorporation of oxygen, sulfur and nitrogen. Thus the aim of incorporating sulfur into the polyolefin surfaces had been achieved, although the presence of nitrogen was unexpected. The surface chemistry of the sulfur dioxide corona treated surfaces is discussed further in section 10.2.2. For polyethylene statistical analysis showed, to 95 % confidence limits, that all the elemental concentrations were invariant with sulfur dioxide
Figure 10.1 Effects of varying the SO₂ flow rate on surface compositions for (a) polyethylene (b) polypropylene treated at a 50 W corona intensity
Figure 10.2 Effects of varying the SO₂ flow rate on advancing (a) water (b) diiodomethane contact angles for polyethylene and polypropylene treated at a 50 W corona intensity
flow rate. For polypropylene, concentrations of the newly introduced elements were found to increase with sulfur dioxide flow rate. For both polymers, the elemental concentrations followed the order oxygen > sulfur > nitrogen. To date, XPS had shown that all the other flame and corona treatments had produced greatest surface oxidation/modification of polyethylene surfaces. However, for sulfur dioxide corona treatment the converse was found, indeed, over double the concentration for each element was observed on the polypropylene surfaces than the polyethylene surfaces at a given sulfur dioxide flow rate. Previously it was suggested that extensive degradation polypropylene chain occurred via relatively long lived free radicals. However upon introduction of sulfur dioxide, reaction of the radicals on the polypropylene surface with the active sulfur species present could reduce chain scission and lead to the retention of surface functionality. The presence of low molecular weight material is discussed further in section 10.2.4. Functional group retention could also result in increased oxidation depths (Chapter 13).

Figure 10.2 (a) shows the advancing water contact angles while Figure 10.2 (b) shows the advancing diiodomethane contact angles for polyethylene and polypropylene after sulfur dioxide corona treatment at various sulfur dioxide flow rates and constant 50 W corona intensity. To 95% confidence limits, the advancing water contact angles remained invariant with sulfur dioxide flow rates for both polyethylene and polypropylene, remaining at average values of 37.4° and 59.8° respectively. Thus, the best improvements in surface wettability were achieved at the lowest sulfur dioxide flow rate, this clearly being advantageous for potential industrial application. The wettability of polypropylene was clearly improved by this treatment, possessing wettabilities more often associated with well treated polyethylene surfaces. Conventional laboratory corona treatment at the same intensity resulted in advancing water contact angles of 62.8° and 72.2° for polyethylene and polypropylene respectively, clearly exemplifying the excellent improvements achieved in the water wettabilities of both polymer surfaces upon introduction of sulfur dioxide into the corona region. The improvements were attributed to the introduction of polar oxygen/sulfur/nitrogen functional groups into the surfaces of both polymers, allowing the development of strong interfacial interactions to occur between the polar surfaces and the polar water molecules.
For polyethylene, receding water contact angles of $< 10^\circ$ were measured at all flow rates, while for polypropylene receding angles of $\sim33^\circ$ were measured. Thus, strong interfacial interactions were indicated in the receding water contact angles also, with the water being unable to dewet from the treated polyethylene surfaces, with the values of receding water contact angles for polypropylene again being more often associated with polyethylene. The invariance in the water contact angles was expected for polyethylene where the compositions of the treated surfaces were the same at all sulfur dioxide flow rates. For polypropylene, much higher levels of surface modification than on polyethylene were detected by XPS, however, this was not translated into better surface wettabilities. The extra functionality could have been introduced into the sub-surface leading to a greater depth of oxidation, and indeed there was some evidence for polypropylene being oxidised to a slightly greater depth than polyethylene (Chapter 13).

Advancing and receding diiodomethane contact angles were unaffected by sulfur dioxide flow rate, remaining unchanged to 95% confidence levels at average values of 51.3° and 25.6° respectively for polyethylene and 54.0° and 24.7° respectively for polypropylene. The advancing diiodomethane contact angles were $\sim4\text{.}7^\circ$ lower on the treated surfaces than on the untreated surfaces. A greater reduction of $\sim20^\circ$ in the receding diiodomethane contact angles on treatment was also measured. As on previous occasions, this was attributed to the formation of strong dipole-induced dipole interactions between the polar surfaces and the polarisable diiodomethane molecules.

Overall, sulfur dioxide corona treatment produced excellent improvements in the wettability of both polymers, with reductions of $\sim25^\circ$ and $\sim10^\circ$ in the advancing water contact angles over conventional corona treatment for polyethylene and polypropylene respectively. With significant reductions in the receding contact angles also being found, sulfur dioxide corona treatment showed great potential for industrial application.

10.2.2 Surface Chemistry

The methods of FTIR-ATR and XPS were employed to explain the complex polymer surface chemistries resulting from sulfur dioxide corona treatment.
Figure 10.3 FTIR-ATR spectrum of (a) polyethylene (b) polypropylene corona treated at 50 W and 40 ml min⁻¹ SO₂ after subtraction of the untreated polymer spectrum; Ge crystal, θ_{IRA} 50°
A) Infra-red Spectroscopy

Figures 10.3 (a) and (b) show FTIR-ATR spectra of sulfur dioxide corona treated polyethylene and polypropylene after subtraction of the untreated film spectra. Although noisy, new absorbances at ~1100 cm\(^{-1}\) and ~1420 cm\(^{-1}\) were found for polyethylene and at slightly shifted frequencies of ~1115 cm\(^{-1}\) and ~1430 cm\(^{-1}\) for polypropylene. For both polymers, the new absorbances were consistent with the presence of S=O functionality.

B) X-Ray Photoelectron Spectroscopy

Figure 10.4 (a) shows ESCALAB survey scan spectra while Figures 10.4 (b)-(e) show Scienta ESCA300 C1s, O1s, S2p and N1s high resolution XP spectra respectively of polyethylene and polypropylene corona treated at an intensity of 50 W and sulfur dioxide flow rate of 40 ml min\(^{-1}\). Slight asymmetry on the high binding energy side of the C1s photoelectron peaks provided some evidence for multifunctional group environments on the surfaces of both polymers, although definitive assignments were still not possible. However, significant intensities from C-O shifted carbon atoms would be expected given that oxygen concentrations of ~20 %At. were consistently found for polypropylene. Therefore, the low intensities of the shifted peaks suggested that minimal amounts of the incorporated oxygen was bound to carbon. The S2p peak is slightly broader than those for S-O compounds measured by Beamson\(^{23}\). The difference was not due to sample charging and thus may reflect the presence of of more than one form of sulfur VI or secondary shifts. However, the chemical shifts were too small to curve fit with confidence. Only a single N1s peak with a full width at half maximum (FWHM) of ~1.7 eV was detected. The O1s peak showed clear evidence for at least two components, the most intense at 532.0 eV and a less intense component at higher binding energy.

After correction to a hydrocarbon C1s binding energy of 284.6 eV, the measured O1s, S2p and N1s binding energies for the two polymers are shown in Table 10.1. The binding energies suggested that the surface chemistries on the two polymers were similar. Appendix C contains selected binding energies for oxygen, sulfur and nitrogen used to assign the measured binding energies. The sulfur binding energy indicated that it was in the hexavalent state and bonded to oxygen, for example as -OSO\(^3\) (E\(_b\) ~169 eV) or as -SO\(^3\) (E\(_b\) ~168 eV). This would be consistent with the majority of oxygen being bonded to sulfur instead of to carbon as indicated by the high resolution C1s XP spectra in Figure...
Chapter 10 Reactive Gas Corona Treatment

(a)

(b)
Figure 10.40 Polyethylene and polypropylene corona treated at an intensity of 50 W, SO₂ flow rate 40 ml min⁻¹ (a) ESCALAB survey scan and Scienta ESCA300 high resolution (b) Cls (c) O1s (d) S2p (e) N1s spectra

Figure 10.5 Oxygen concentration with sulfur and nitrogen concentrations for laboratory corona treated polyethylene and polypropylene at all sulfur dioxide flow rates
Chapter 10 Reactive Gas Corona Treatment

10.5. The nitrogen binding energy was suggestive of several possibilities, firstly -NR\textsuperscript{+} (E\textsubscript{b} \sim 402 eV) including NH\textsubscript{4}\textsuperscript{+}, secondly -NO (E\textsubscript{b} \sim 402 eV) although not in the form of -NO\textsubscript{2} or -NO\textsubscript{3} as the binding energies would be too high (E\textsubscript{b} \sim 404 eV and \sim 406-407 eV respectively) and thirdly nitrogen bonded to electron withdrawing groups such as -C=O or -CO\textsubscript{2} (E\textsubscript{b} \sim 400 eV). The second and third possibilities were discounted as the majority of incorporated oxygen would have to be bound directly to the sulfur in order to produce its' measured binding energy, thus only minimal amounts could be bound directly to nitrogen or carbon. Indeed, only minimal amounts of -C-O species were indicated by high resolution XPS, in addition to which there were no peaks assignable to strongly absorbing C=O group (1700-1770 cm\textsuperscript{-1}) in the infra-red spectrum, further discounting the third possibility. Therefore, in light of the sulfur binding energy and minimal amounts of NO/CO species, the nitrogen was thought most likely to be present as NH\textsubscript{4}\textsuperscript{+}. Although the NH\textsubscript{4}\textsuperscript{+} ion absorbs reasonably strongly in the infra-red (~3300-3030 cm\textsuperscript{-1}), it may not have been detected given the much reduced sampling depth at this wavelength (section 4.2.2). An alternative assignment consistent with the data could have been a sulfonamide (-RSO\textsubscript{2}NH\textsubscript{2}). However, this was thought to be less likely as an absorption at \sim 1640 cm\textsuperscript{-1} attributable to N-H bending in the amide was not found, this being a section of the IR spectrum in which ATR has good sensitivity. Extensive reaction with the derivatisation agents was also found, suggesting that sulfur functional groups of the type -OSO\textsubscript{3}H and -SO\textsubscript{3}H \textsubscript{2} were also present. Although no O-H stretching absorption (1530-3500 cm\textsuperscript{-1}) was observed in the infra-red spectrum, this absorption is very broad and weak for sulfonic acids and therefore may not be detected.

<table>
<thead>
<tr>
<th>POLYMER / TREATMENT</th>
<th>O1s</th>
<th>S2p</th>
<th>N1s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene SO\textsubscript{2}</td>
<td>532.1</td>
<td>168.8</td>
<td>402.0</td>
</tr>
<tr>
<td>Polypropylene SO\textsubscript{2}</td>
<td>532.0</td>
<td>168.8</td>
<td>401.8</td>
</tr>
</tbody>
</table>

Table 10.1 Corrected O1s, S2p and N1s binding energies measured on the Scienta ESCA300 for sulfur dioxide corona treated polyethylene and polypropylene; corona intensity 50 W, SO\textsubscript{2} flow rate 40 ml min\textsuperscript{-1}

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As stated previously, consistently more sulfur than nitrogen was detected on both polymer surfaces. Figure 10.5 shows a straight line correlation between oxygen concentration and the sulfur and nitrogen concentrations. The correlation showed [S]/[O] and [N]/[O] ratios of 0.31 and 0.22 respectively, suggesting a stoichiometry of N₂S₃O₉.

C) Additional Information

Sulfur dioxide flame treatment of additive free polyethylene showed that the nitrogen contained within the additives was not responsible for the concentrations detected upon treatment, for example resulting from their migration towards the polar surface. Thus it was concluded that nitrogen incorporation occurred via reactions during the treatment process. In order to investigate this, the presence of nitrogen during sulfur dioxide flame treatment was minimised by using an Ar/O₂ oxidant supply. However, nitrogen concentrations similar to those incorporated when using the usual air oxidant supply were nonetheless detected. This suggested that nitrogen incorporation did not involve the direct combination of the polymer chains with the activated nitrogen species, that is the nitrogen was probably not bonded directly to the polymer chain. Rather, nitrogen incorporation probably arose through reaction with an activated sulfur species on the polymer surface. Indeed, this suggested two possibilities in the case of flame treatment. Firstly, that the activated sulfur was very reactive towards nitrogen, combining rapidly with the small quantities which may have diffused into the flame from the surroundings during Ar/O₂/SO₂ flame treatments in order to produce the measured nitrogen concentrations. Secondly, the activated sulfur species could have been long lived, combining with nitrogen via post-treatment reactions. Also, contact angle measurement with liquids of different pH had indicated that the sulfur dioxide treated surfaces had some acidic character, even in the absence of -C-O groups such carboxylic acids.

D) Mechanism of Functionalisation

The complexity of the data obtained quite clearly indicates the complex nature of the surface chemistries produced. However, the data may be summarised as below,

- minimal amounts of oxygen bonded directly to carbon
- high sulfur binding energy ⇒ in hexavalent state bound to oxygen, -OSO₃⁻ -SO₃⁻
- absorptions assignable to S=O stretching in the infra-red spectrum
Figure 10.6 Possible mechanism for surface functionalisation for sulfur dioxide flame and corona treated polyolefins

- acidic surface character, not attributable to carboxylic acids through lack of CO
- high nitrogen binding energy \( \Rightarrow -\text{CO}_2 - \text{NH}_2 - \text{N=O} \text{ NH}_4^+ \)
- no \( \text{N=O} \) \( \text{N-H} \) \( \text{C=O} \) absorption in infra-red spectrum \( \Rightarrow \) not \( -\text{CO}_2 - \text{NH}_2 \) \( \text{N=O} \)

From this data it is suggested that free radicals are initially formed on the polymer surfaces in the conventional manner, with introduction of sulfur occurring as a consequence of this. The surface free radicals could then combine with the activated sulfur species present, which then proceed to react with the nitrogen species present to form an ammonium salt. Alternatively, the surface free radicals could form peroxy free radicals in the conventional manner, followed by reaction with the activated sulfur species which could then continue in the formation of an ammonium salt. The mechanism for ammonium ion incorporation \textit{via} either route is unclear, although it could involve \( \text{N}^+ \) radicals which are certainly known to be present in flames\textsuperscript{215}. An alternative to ammonium salt formation could be for the activated sulfur species to abstract a proton from the polymer, thereby forming the sulfonic acid. This would increase the acidic character of the surface, and is consistent with "pH titration" contact angle measurements (section 10.5). This possible mechanism for surface
Figure 10.7 Elemental mapping images of (a) C1s (b) O1s (c) S2p and (d) N1s for polyethylene sulfur dioxide doped corona treated at an intensity of 50 W and SO₂ of flow rate 40 ml min⁻¹
Figure 10.8 Elemental mapping images of (a) C1s (b) O1s (c) S2p and (d) N1s for polypropylene sulfur dioxide doped corona treated at an intensity of 50 W and \( \text{SO}_2 \) of flow rate 40 ml min\(^{-1} \).
Chapter 10 Reactive Gas Corona Treatment

functionalisation is summarised in Figure 10.6.

The figure indicates that chain degradation and the production of CHO products, for example hydroxyl, carbonyl, carboxylic groups, could also be formed. However, from the minimal quantities of carbon-oxygen species and the reduced extent of chain scission (section 10.2.4), it is believed that these routes are less favoured than those leading to sulfur/nitrogen incorporation. Such a mechanism could thus retard the progression of chain scission reactions by reacting with peroxy radicals, leading to the retention of surface functionality and an increase in the depth of oxidation. It could also go some way towards satisfying the oxygen/sulfur/nitrogen stoichiometry suggested by Figure 10.4.

E) Elemental Surface Distributions

Elemental distributions over the treated polymer surfaces were studied by obtaining their respective elemental mapping images using the Scienta ESCA300 instrument. Figures 10.7 (a)-(d) show elemental mapping images for C1s, O1s, S2p and N1s respectively from polyethylene sulfur dioxide corona treated under the same conditions as employed for high resolution XPS analysis. Except for a slight lowering towards the left hand side, the photoelectron intensities were reasonably uniform over the scan lengths for all the elemental maps. The correspondence in the lowered intensity regions for all the maps suggested that the lowering was due to topographical effects rather than a heterogeneous distribution of functional groups. Figures 10.8 (a)-(d) show elemental mapping images for C1s, O1s, S2p and N1s respectively from polypropylene sulfur dioxide corona treated under the above conditions also. As for polyethylene, the photoelectron intensities were reasonably uniform over the scan lengths for all the elemental maps. Thus, no heterogeneity was detected on sulfur dioxide corona treated surfaces at the spectrometer resolution (~25µm).

10.2.3 Correlation Between Oxygen Concentration and Work of Adhesion

Figures 10.9 (a) and (b) show the correlation between oxygen concentration and works of adhesion calculated from advancing water and diiodomethane angles respectively for polyethylene and polypropylene combined.

No correlation was found between surface oxygen concentration and work of adhesion with water. This was attributed to a difference in the depths of oxidation for the two polymers. A slightly lower concentration of polar functionality at the near surface of polypropylene could have resulted from increased sub-surface oxidation (section 13.2), leading to a lower wettability in spite of the higher elemental compositions. The presence of sulfur and nitrogen also complicates the relationship. Statistical analysis showed that the work of adhesion with diiodomethane did not vary significantly with SO2 flow rate.

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![Graph](image)

Figure 10.9 The relationship between oxygen concentration and work of adhesion from advancing (a) water (b) diiodomethane contact angles for polyethylene and polypropylene at all SO$_2$ flow rates, corona intensity 50W
10.2.4 Low Molecular Weight Oxidised Material

Sulfur dioxide corona discharge treated samples were washed with diethylether and reanalysed by XPS and water contact angle measurement in order to check for the presence of low molecular weight material. Tables 10.2 and 10.3 show the elemental concentrations and water contact angle data for corona treated polyethylene and polypropylene respectively at various sulfur dioxide flow rates before and after washing.

For polyethylene, reductions of ~15% in the oxygen concentrations were found upon washing, although the sulfur and nitrogen concentrations were largely unchanged. Indeed, the sulfur-to-nitrogen ratio remained at ~2:1 before and after washing. Loss of polar functionality through washing produced an increase in the advancing water contact angle of ~8-10°, although the receding angle was unaffected and remained <10°. Thus even after washing, an average advancing water contact angle of 43.9° and receding water contact angles below 10° were measured, indicating that strong interfacial interactions were still being developed. Indeed, the advancing water contact angles after diethylether washing were still lower than those measured on conventionally flame and corona treated surfaces prior to washing. The extent of chain scission was clearly lower than upon conventional corona treatment of polyethylene where ~25 % of the incorporated oxygen was removed on washing. This was attributed to the active sulfur species in the corona region combining with the majority of surface free radicals thereby retarding the progression of chain scission reactions.

Reductions of ~30-70% in the oxygen concentrations, ~30-75% in the sulfur concentrations were found upon diethylether washing of the treated polypropylene surfaces, while the nitrogen concentrations were less affected. This suggested that a significant proportion of the incorporated sulfur was present in soluble material. The amount of each element removed generally decreased with increasing sulfur dioxide flow rate. Thus, the presence of low molecular weight, soluble material was indicated even though in section 10.2.1 it was suggested that the presence of sulfur dioxide could reduce the extent of chain scission and aid the retention of functionality. However, it is believed that instead of the volatilisation of small, oxidised fragments after extensive chain degradation, reduced chain scission resulting in relatively large, non-volatile fragments
Table 10.2 Elemental concentrations and advancing water contact angle data for polyethylene treated using a 50 W corona intensity at various sulfur dioxide flow rates before and after washing with diethylether

<table>
<thead>
<tr>
<th>SO₂ FLOW (ml min⁻¹)</th>
<th>UNWASHED</th>
<th>DIETHYLETHE R WASHED</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[O] / %At</td>
<td>[S] / %At</td>
</tr>
<tr>
<td>20</td>
<td>9.1</td>
<td>2.7</td>
</tr>
<tr>
<td>30</td>
<td>8.5</td>
<td>2.7</td>
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<tr>
<td>40</td>
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</tr>
<tr>
<td>70</td>
<td>15.8</td>
<td>4.5</td>
</tr>
</tbody>
</table>

Table 10.3 Elemental concentrations and advancing water contact angle data for polypropylene treated using a 50 W corona intensity at various sulfur dioxide flow rates before and after washing with diethylether

<table>
<thead>
<tr>
<th>SO₂ FLOW (ml min⁻¹)</th>
<th>UNWASHED</th>
<th>DIETHYLETHE R WASHED</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[O] / %At</td>
<td>[S] / %At</td>
</tr>
<tr>
<td>20</td>
<td>18.5</td>
<td>4.6</td>
</tr>
<tr>
<td>30</td>
<td>18.9</td>
<td>5.7</td>
</tr>
<tr>
<td>40</td>
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<td>6.4</td>
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<tr>
<td>55</td>
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<td>6.0</td>
</tr>
<tr>
<td>70</td>
<td>25.5</td>
<td>8.3</td>
</tr>
</tbody>
</table>

Table 10.2 and Table 10.3 show that the elemental concentrations and advancing water contact angles change significantly after washing with diethylether. The removal of polar functionality had the greatest effect on the water contact angles at the lower two sulfur dioxide flow rates, resulting in increases of between 10-30°.
in the advancing and ~10° in the receding contact angles. At the other flow rates, only small changes in the advancing and receding contact angles were found. Thus, these observations were consistent with a competition between two reaction paths for the surface free radicals, the first being production of low molecular weight material through chain scission and the second being reaction with the activated sulfur species retarding chain scission. At increasing sulfur dioxide flow rates, the latter reaction path was thought to be more favoured, resulting in the presence of fewer scission fragments and only minimal changes in surface compositions upon solvent washing.

10.2.5 Surface Free Energy

Advancing water and diiodomethane contact angles were used to estimate surface free energies according to the method of Owens-Wendt. The effects of sulfur dioxide corona discharge treatment on the surface free energies of polyethylene and polypropylene are shown in Tables 10.4 and 10.5 respectively.

Introduction of the polar oxygen/sulfur/nitrogen functional groups into the treated polyethylene surfaces produced dramatic increases in the estimated polar components. As with the advancing water contact angles, the estimated polar components were invariant with sulfur dioxide flow rate, remaining at an average value of 44.8 mJ m⁻². Clearly the estimated polar components were in excess of the estimated dispersion components, this observation not being commonly observed in the flame and corona treatment of polyolefins. The dispersion components were also unaffected by sulfur dioxide flow rate, resulting in total surface energies of over 70 mJ m⁻² being estimated.

The introduction of these elements into the polypropylene surfaces also increased the polar components, which remained at an average value of 24.4 mJ m⁻² from which total surface energies of over 50 mJ m⁻² were estimated. Again, excellent improvements in the total surface energies were estimated, showing the potential of introducing sulfur dioxide into the corona region for the successful surface modification of polypropylene which is usually difficult to activate.
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<table>
<thead>
<tr>
<th>SO₂ FLOW RATE / ml min⁻¹</th>
<th>SURFACE FREE ENERGY / mJ m⁻²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\gamma_s^p$</td>
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<tr>
<td>untreated</td>
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</tr>
<tr>
<td>70</td>
<td>45.0</td>
</tr>
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</table>

Table 10.4 The effects of varying sulfur dioxide flow rate on the surface free energy of polyethylene treated at a 50 W corona intensity

<table>
<thead>
<tr>
<th>SO₂ FLOW RATE / ml min⁻¹</th>
<th>SURFACE FREE ENERGY / mJ m⁻²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\gamma_s^p$</td>
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<td>untreated</td>
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<td>28.0</td>
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<tr>
<td>70</td>
<td>21.0</td>
</tr>
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</table>

Table 10.5 The effects of varying sulfur dioxide flow rate on the surface free energy of polyethylene treated at a 50 W corona intensity

The Wu method agreed reasonably well with Owens-Wendt method in the trends predicted. The polar components estimated using the former method, and consequently the total surface free energies estimated, were consistently higher than those using the Owens-Wendt method. Overall, the estimated polar components and the total surface energies were much higher than those obtained from conventionally corona treated polyolefins, and indeed double those obtained from sulfur dioxide flame treatment. Therefore, sulfur dioxide corona treatment has been shown to produce significantly better surface activation of polyolefins than the conventional treatments currently used.
10.3 Ammonia Treatment

Ammonia gas was introduced into the corona region through evenly spaced channels in the treating electrode. Flow rates in the range 30-200 ml min\(^{-1}\) were used. Below 30 ml min\(^{-1}\), a stable corona could not be formed and so was unsuitable for pretreatment. Beyond a flow rate of 200 ml min\(^{-1}\) it was envisaged that industrial application would be limited due to the problems associated with environmental pollution. A constant corona intensity of 50 W was employed throughout.

10.3.1 Effects on Surface Composition and Contact Angles

As for conventional corona discharge treatment, analysis by XPS showed that the surface compositions of both polymers had been modified by the introduction of oxygen only. Figures 10.10 (a) and (b) show the effects of ammonia flow rate on the surface oxygen concentration and advancing water contact angles for polyethylene and polypropylene respectively.

For polyethylene, the surface oxygen concentration went through a maximum at an ammonia flow rate of \(-55\) ml min\(^{-1}\). Although a maximum in oxygen concentration was found, to 95% confidence limits, the advancing and receding water contact angles on the treated surfaces were invariant with ammonia flow rate, remaining at average values of 63.4° and 30.8° respectively. Thus the surface wettability of ammonia corona discharge treated polyethylene did not depend critically on the surface composition. For polypropylene treated under the same conditions, the oxygen concentration did not vary with ammonia flow rate to 95% confidence limits. A lowering in the advancing and receding water contact angles resulted from surface oxidation, with the water contact angles also being invariant with ammonia flow rate. As for conventional corona treatment, polyethylene was more readily treated than polypropylene, with higher oxygen concentrations being incorporated and better surface wettabilities.

To 95% confidence limits the advancing and receding diiodomethane contact angles were found to be invariant with ammonia flow rate for both polymers. However, for both polymers the advancing contact angles were \(-9°\) lower than on the untreated surfaces and the receding contact angles were \(-20°\) lower. This lowering of the diiodomethane contact
Figure 10.10 Effect of varying NH₃ flow rate on oxygen concentration and advancing water contact angles for (a) polyethylene (b) polypropylene, corona intensity 50W
angles was attributed to dipoles induced by the polar oxygen functionality introduced upon treatment.

Comparisons showed that slightly higher oxygen concentrations were detected upon ammonia corona treatment than conventional treatment on polyethylene surfaces, while similar oxygen concentrations were detected using both types of treatment for polypropylene surfaces. However, for both polymers no additional improvements were obtained by ammonia over conventional corona discharge treatment in terms of surface wettability. Through this similarity with conventional corona treatment, it is suggested that the surface chemistries resulting from ammonia and conventional treatments are also similar. The lack of nitrogen functionality can be explained by comparing flame and corona treatments, both being high energy density treatments with similar mechanisms of surface activation. It is suggested that the ammonia molecules were probably rapidly oxidised to the stable products HCN, N$_2$ and NO (see section 12.3.1.1) in the corona, thereby preventing the activated nitrogen species from reacting with surface free radicals. Overall, the initial aim of introducing basic functional groups into the polyolefin surfaces was not achieved.

10.3.2 Correlation Between Oxygen Concentration and Work of Adhesion

Figures 10.11 (a) and (b) show the correlation between oxygen concentration and works of adhesion calculated from advancing water and diiodomethane angles respectively for polyethylene and polypropylene combined.

The work of adhesion with water appeared to tail-off at high oxygen concentrations, however the spread of oxygen concentrations on the treated polymer surfaces was not very wide so that this trend was only tentatively assigned. The trend was in agreement with conventional laboratory corona treatment suggesting that it is correct, although in light of the invariant advancing water contact angles no firm conclusions for or against this dependence could be drawn. Statistical analysis showed that the work of adhesion with diiodomethane did not change significantly with ammonia flow rate. This was again not entirely surprising given the invariance in the advancing diiodomethane contact angles.
Figure 10.11 The relationship between oxygen concentration and work of adhesion from advancing (a) water and (b) diiodomethane contact angles for polyethylene and polypropylene at all corona intensities.
10.3.3 Low Molecular Weight Oxidised Material

In order to check for the presence of low molecular weight material, the ammonia corona treated polymers were washed with diethylether and reanalysed by XPS and water contact angle measurement.

At all ammonia flow rates, ~35% of the oxygen incorporated into the polyethylene surfaces was removed by washing, compared to ~25% for conventional corona treatment at the same intensity. Loss of functionality resulted in increases of up to 10° for both advancing and receding water contact angles, thus the treated polyethylene surfaces retained reasonable water wettability even after diethylether washing. Although similar water wettabilities were observed after washing of ammonia and conventionally corona treated surfaces, slightly greater amounts of scission fragments were apparently present. Solvent washing also had a large effect on the surface compositions of ammonia corona treated polypropylene, with reductions of >66% in the oxygen concentrations at all ammonia flow rates. With the removal of oxygen, increases of ~20° and ~10° in the advancing and receding water contact angles respectively were found. Similar reductions in the surface oxygen concentrations and water wettabilities were found for ordinary corona discharge treatment. Overall, comparisons showed that for the treatment of polypropylene, there were no significant differences in the surface compositions, water wettabilities or levels of chain scission produced by ammonia over ordinary air corona discharge treatment. As for conventional corona treatment, greater amounts of scission fragments were indicated on polypropylene than polyethylene for a given treatment.

10.3.4 Surface Free Energy

Advancing water and diiodomethane contact angles were used to estimate surface free energies according to the method of Owens-Wendt. The effects of ammonia corona discharge treatment on the surface free energies of polyethylene and polypropylene are shown in Tables 10.6 and 10.7 respectively.

The polar component of surface free energy for polyethylene increased significantly upon
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### Table 10.6 The effects of ammonia corona discharge treatment on the surface free energy of polyethylene

<table>
<thead>
<tr>
<th>NH$_3$ FLOW RATE / ml min$^{-1}$</th>
<th>SURFACE FREE ENERGY / mJ m$^{-2}$</th>
<th>$\gamma_s^p$</th>
<th>$\gamma_s^d$</th>
<th>$\gamma_s^{tot}$</th>
</tr>
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<tbody>
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<td>19.4</td>
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</tr>
<tr>
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<td></td>
<td>19.8</td>
<td>28.2</td>
<td>47.0</td>
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### Table 10.7 The effects of ammonia corona discharge treatment on the surface free energy of polypropylene

<table>
<thead>
<tr>
<th>NH$_3$ FLOW RATE / ml min$^{-1}$</th>
<th>SURFACE FREE ENERGY / mJ m$^{-2}$</th>
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<th>$\gamma_s^{tot}$</th>
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</table>

incorporation of oxygen by ammonia corona discharge treatment. The dispersion component remained constant at a level just below that of the untreated polymer surface. The surface energies estimated here were very similar to those estimated after conventional corona treatment at an intensity of 50 W. This was not surprising given that similar water and diiodomethane contact angles were measured after the two treatments.

Treatment of polypropylene increased the estimated surface free energy. The primary effect was to increase the polar component, although a slight apparent decrease in the dispersion component was also found. Surface energies estimated here were slightly lower
than for polypropylene surfaces after conventional corona at a 50 W intensity. Given the higher oxygen concentrations and lower water contact angles, the higher total surface energies for treated polyethylene surfaces than for treated polypropylene surfaces were expected. Trends from the harmonic mean method were in agreement with the geometric mean method for both polymers.

10.4 Surface Topography

No visual effects were seen on any sample upon treatment. Routine analysis by SEM using a magnification of ×10,000 also showed no effect on surface topography at any sulfur dioxide or ammonia flow rate before or after diethylether washing. Carbon replica TEM was also used to detect topographical changes, however, a magnification of ×33,000 did not reveal roughening on either polymer treated using a sulfur dioxide/ammonia flow rate of 40 ml min⁻¹ and 50W corona intensity before or after diethylether washing.

10.5 Acid-Base Character

The aim of surface pretreatment was to improve the surface wettability of the substrate. The types of functional groups present on the surfaces could have a significant effect on the achievable surface wettability. Clearly, it would be preferable to maximise the concentration of the types of functional groups that improve the surface wettability most effectively. The presence of acidic or basic functional groups could be an important factor in this improvement. Ionisation of such functional groups under appropriate conditions could increase interfacial interactions between the surface and contacting liquid, thereby improving wettability. Thus, interfacial acid-base interactions were probed by measuring advancing and receding contact angles using liquids of different pH. The technique of “pH titration” where the advancing contact angle was plotted as a function of pH was found to give some information on the acidity of polyethylene functionalised with chromic acid/sulfuric acid ²¹⁶ and on monolayer films containing acidic and basic functionalities ²¹⁷. In this previous work, buffered solutions were used, however, the effect of these buffers on the surface tensions of liquids was not considered. In this study, the differences in the surface tensions of the liquids used were <5 % (section 5.6.1), but they were nonetheless accounted for by using works of adhesion calculated from the Young-Dupré Equation.
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<table>
<thead>
<tr>
<th>POLYMER / TREATMENT</th>
<th>SURFACE COMPOSITION / % At.</th>
<th>θ_{adv} / deg</th>
<th>θ_{rec} / deg</th>
</tr>
</thead>
<tbody>
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<td>37.9</td>
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<td>Polypropylene air</td>
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</tr>
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</table>

Table 10.8 Surface compositions and water contact angle data for the corona treated polymers used to study interfacial acid-base interactions, corona intensity 50 W, SO₂/NH₃ flow rate 40 ml min⁻¹

The interfacial acid-base interactions occurring at surfaces treated with and without reactive gases were investigated. A corona intensity of 50 W was used, with a sulfur dioxide or ammonia flow rate of 40 ml min⁻¹ when required. Table 10.8 gives the surface compositions and the average water contact angle data for the polymers treated under the above conditions. Thus the compositions and wettabilities were confirmed to be typical of the levels previously attained, so the interfacial acid-base interactions probed were representative of the surfaces previously examined.

Figures 10.12 (a) and (b) show the variation in the work of adhesion calculated from advancing and receding contact angles respectively as a function of pH for corona treated polyethylene and polypropylene. It was hypothesised that acidic functional groups could ionise at high pH while basic functional groups could ionise at low pH and thereby increasing interfacial interactions and the work of adhesion. From advancing contact angles, the only instance where the work of adhesion increased with pH was on polyethylene after sulfur dioxide corona treatment, indicating that ionisation of this surface had occurred at high pH. Overall from advancing contact angles, there was a general lack of dependence of work of adhesion on pH for both polymers, suggesting that little ionisation had occurred after the other treatments studied. However, in all instances except one the works of adhesion calculated from receding contact angles were found to increase with pH. This indicated that ionisation had indeed occurred, and that all the surfaces possessed some acidic character. The exception was polyethylene after sulfur...
Figure 10.12 Work of adhesion from (a) advancing (b) receding contact angles as a function of pH for corona treated polyethylene and polypropylene under various conditions, corona intensity 50W, SO₂/NH₃ flow rate 40 ml min⁻¹.
dioxide treatment, where the receding contact angles were <10° at all levels of pH. In order to allow comparison with the other treatments, a contact angle of 10° was assumed for this surface resulting in a work of adhesion of 140.9 mJ m⁻², this being shown by the dashed line on Figure 10.12 (b). This represents a minimum value in the work of adhesion for this surface. The different behaviour found between the works of adhesion calculated from advancing and receding contact angles respectively exemplified the importance of the dewetting process in the analysis of acid-base behaviour at surfaces. Ionisation at the surface-liquid interface increases interfacial interactions, and therefore these interactions must first be broken if the liquid is to dewet. The receding contact angle is a dewetting measurement and is therefore more sensitive to the effects of functional group ionisation than the advancing contact angle.

The works of adhesion for both polymers were generally found to be higher at all pH levels when corona treated in the order SO₂ > air > NH₃, providing confirmation on the effectiveness of the sulfur dioxide treatment method. The “pH titration” method appeared to indicate that all the corona treated surfaces possessed some acidic character. However, the extraction of polar, low molecular weight scission products from the corona treated surfaces should be considered. These scission products could contain acidic functionality which could be ionised at high pH, leading to their dissolution. Consequently the surface tension of the contact angle liquid could be affected, thereby inducing errors in estimated works of adhesion.
Chapter 11 Laboratory Scale Flame Treatment

11.1 Introduction

Polyethylene and polypropylene were flame treated using laboratory scale apparatus and
the resulting surfaces characterised by XPS, FTIR-ATR, electron microscopy and contact
angle measurement. The experimental parameters investigated were the air-to-natural gas
ratio and the flame intensity at various flame stoichiometries.

11.2 Flame Treatment Parameters

11.2.1 Surface Topography

No visual effects were seen after any of the flame treatments investigated, with routine
analysis by SEM before and after diethylether washing using a magnification of \times10,000
also showing no effects on surface topography. Carbon replica TEM was also employed,
however, neither polymer treated at a total flow of 30.5 \text{l min}^{-1} and an air-to-natural gas
ratio of 11.8:1 showed any evidence of surface roughening at a magnification of \times33,000.

11.2.2 Air-to-natural Gas Ratio

The effects of varying the air-to-natural gas ratio were studied by maintaining a constant
natural gas flow rate of 2 \text{l min}^{-1} while supplying sufficient air to make up the appropriate
ratio.

11.2.2.1 Effects on Surface Composition and Contact Angles

Analysis of the treated samples by XPS showed that the surface composition had been
modified by the introduction of oxygen only. Figures 11.1-11.4 (a) and (b) show the
variation of surface oxygen alongside advancing/receding water or diiodomethane contact
angles with air-to-natural gas ratio for both polyethylene and polypropylene.

A) Polyethylene

For polyethylene, the surface oxygen concentration increased rapidly with air-to-natural
gas ratio, until a maximum was reached at a ratio of \sim11:1 after which the oxygen
Figure 11.1 Effects of air-to-natural gas ratio on oxygen concentration and (a) advancing (b) receding water contact angles for polyethylene
Figure 11.2 Effects of air-to-natural gas ratio on oxygen concentration and (a) advancing (b) receding diiodomethane contact angles for polyethylene
Figure 11.3 Effects of air-to-natural gas ratio on oxygen concentration and (a) advancing (b) receding water contact angles for polypropylene
Figure 11.4 Effects of air-to-natural gas ratio on oxygen concentration and (a) advancing (b) receding diiodomethane contact angles for polypropylene
concentration decreased rapidly. Surface oxygen had a significant effect on the water contact angles, with the advancing angle reaching a minimum at an air-to-natural gas ratio of ~11:1. The receding water contact angle followed a similar trend to that of the advancing angle. There was an overall maximum in the water contact angle hysteresis at this ratio. These findings showed the existence of an optimum air-to-natural gas treatment ratio at a slightly higher than stoichiometric ratio, this being in agreement with previous studies on non-oriented films. A good correspondence between the oxygen concentration and water contact angle was clearly evident. The observed reduction in water contact angles was attributed to the increased interfacial interactions between polar oxygen functionality on the polymer surface and polar water molecules.

The advancing diiodomethane contact angle was largely unchanged by variations in air-to-natural gas remaining just below the level of the untreated surface at ~50°. The receding diiodomethane contact angle, on the other hand, went through a minimum at the optimum ratio, resulting in a maximum in the diiodomethane hysteresis at this ratio, but the changes were smaller than the changes in the receding water contact angles.

Contact angle hysteresis can be caused by surface roughness or by a heterogeneous surface consisting of most wettable and least wettable parts. However, roughness was not observed by SEM or TEM, and so contact angle hysteresis was probably a result of the heterogeneous surface. Here, the receding contact angles would be representative of the most wettable parts of the surface and the advancing contact angles would be representative of the least wettable parts of the surface. Introduction of polar functionality to an essentially non-polar surface would allow polar interactions, in addition to dispersion interactions, to occur at the polymer-water interface thus affecting the water contact angles. However, these groups would not have such a noticeable effect on the diiodomethane contact angles as this liquid interacts with the polymer surface essentially via dispersion forces only. A slight increase in the dispersion component of surface free energy for the most oxidised domains, for example by the presence of polarisable unsaturated oxygen functionality, could account for the minimum in the receding diiodomethane contact angle. Another contributory factor to this behaviour could be the formation of induced dipoles in the very polarisable diiodomethane by the polar functionality on the polymer surface.
B) Polypropylene
There was some evidence for a maximum in the oxygen concentration at an air-to-natural gas ratio of \(~11:1\) for polypropylene also, however, with the oxygen concentrations varying between only 2 \%At. and 3.3 \%At. the evidence was not conclusive. The advancing and receding water contact angles remained largely unaffected by changes in air-to-natural gas ratio, averaging \(94.5^\circ\) and \(68.8^\circ\) respectively. Advancing and receding diiodomethane contact angles also did not vary significantly, remaining at similar levels to those of the untreated surfaces. Overall, XPS and contact angle measurements suggested that treatment of polypropylene was mostly independent of exact flame composition, which should result in the same effective level of treatment being achieved under most air-to-natural gas ratios. The extent of oxidation was found to be less than that of polyethylene. To 95 \% confidence levels, the advancing and receding diiodomethane contact angles were invariant with air-to-natural gas ratio.

11.2.3 Flame Intensity
The flame intensity was varied by altering the total flow rates of air and natural gas while maintaining the appropriate air-to-natural gas ratio. Total flow rates in the range 20-55 l min\(^{-1}\) were studied. Above 55 l min\(^{-1}\), relaxation of the oriented polymer films made reliable contact angle measurement impractical. Air-to-natural gas ratios of 8:1, 10.3:1 and 11.8:1 were investigated. For the oxygen rich flame conditions, the surface chemistry of treated samples was studied via vapour phase chemical derivatisation, and the effect of diethylether washing on treated samples was investigated.

11.2.3.1 Effects on Surface Composition and Contact Angles
For both polymer types, XPS analysis showed that surfaces were modified by oxygen incorporation only.

A) Polyethylene
Figures 11.5-11.7 (a) and (b) show the effects of flame intensity on the surface oxygen concentration alongside the advancing water and diiodomethane contact angles for polyethylene treated at air-to-natural gas ratios of 8:1, 10.3:1 and 11.8:1 respectively.
A-1) Oxygen Deficient Flame Conditions (Figure 11.5)
At an air-to-natural gas ratio of 8:1 the surface oxygen concentration increased rapidly with intensity reaching a plateau of ~13 %At. at a total flow rate of ~30 l min\(^{-1}\). This increase in oxygen concentration would be expected as more fuel is present at higher flow rates, probably resulting in higher concentrations of excited species in the flame and therefore allowing more polymer segments to be modified. Both advancing and receding water contact angles showed a strong dependence on flow rate, following the opposite trend to the surface oxygen concentration by decreasing rapidly at first then reaching plateau levels of ~65° and ~25° respectively at a flow rate of ~30 l min\(^{-1}\).

A-2) Stoichiometric Flame Conditions (Figure 11.6)
Increased flame intensity under stoichiometric flame conditions caused a slight increase in the oxygen content of the surfaces only, with no strong dependence on flame intensity being indicated. The oxygen concentrations introduced were slightly lower than those introduced by treatment under oxygen deficient flame conditions. This could have been due to the more efficient combustion of the fuel, so that fewer excited species were present in the flame to cause surface functionalisation. Oxygen incorporation improved the water wettability, but to 95% confidence levels, the advancing and receding water contact angles were unaffected by flame intensity variations, remaining at average values of ~74.1° and ~26.1° respectively. These water contact angles were slightly higher than those measured at the 8:1 air-to-natural gas ratio, and were attributed to the slightly lower oxygen concentrations.

A-3) Oxygen Rich Flame Conditions (Figure 11.7)
The surface oxygen concentration increased gradually with flame intensity after treatment under oxygen rich flame conditions. The oxygen concentrations were similar to those incorporated under stoichiometric conditions, probably also as a consequence of efficient fuel combustion. The advancing water contact angles were found to decrease with flame intensity, suggesting that further enhancement in surface wettability could be affected at higher intensities. However, the relaxation of the oriented films occurred at intensities higher than those used here was so significant that such treatment would clearly be impractical. The receding water contact angles did not correspond very well with the surface oxygen concentration and remained reasonably constant with flame intensity.
Figure 11.5 Effect of varying flame intensity at an air-to-natural gas ratio of 8:1 on surface oxygen concentration and (a) water and (b) diiodomethane contact angles for polyethylene.
Figure 11.6 Effect of varying flame intensity at an air-to-natural gas ratio of 10.3:1 on surface oxygen concentration and (a) water and (b) diiodomethane contact angles for polyethylene
Figure 11.7 Effect of varying flame intensity at an air-to-natural gas ratio of 11.8:1 on surface oxygen concentration and (a) water and (b) diiodomethane contact angles for polyethylene
To 95% confidence limits, the advancing and receding diiodomethane contact angles were unchanged by variations in the flame intensity at any air-to-natural gas ratio. However, the advancing and receding diiodomethane contact angles on the treated polyethylene surfaces were up to 9° and 12° below those respective contact angles on the untreated surfaces. This was attributed to polar surface functional groups inducing dipoles in the polarisable diiodomethane molecules and thereby increasing the levels of interfacial interactions.

These figures showed that the most effective surface treatment was obtained using oxygen deficient flame conditions, where advancing water contact angles of ~64° at oxygen concentrations of ~14 %At. were detected. Under such conditions, incomplete combustion of the natural gas probably resulted in more effective introduction of excited species onto the surface, causing greater surface oxidation and improved wettability. Similar oxygen concentrations were produced under the other flame conditions investigated, although surface wettabilities were different. The difference in wettabilities could have been due to different extents of molecular reorientation away from the near surface caused by the heat of treatment. Under oxygen rich conditions, more diluent (nitrogen etc.) would be present and could act to reduce the heat transferred to the polymer, thereby reducing the extent of functional group reorientation.

B) Polypropylene
Figures 11.8-11.10 (a) and (b) show the effects of flame intensity on the surface composition alongside the advancing water and diiodomethane contact angles for polypropylene treated at air-to-natural gas ratios of 8:1, 10.3:1 and 11.8:1 respectively.

B-1) Oxygen Deficient Flame Conditions (Figure 11.8)
Under oxygen deficient flame conditions, the oxygen concentration at first increased with flame intensity, levelling off to ~7 %At. at a flow rate of ~32 l min⁻¹. The advancing and receding water contact angles showed some scatter indicating no clear trend.

B-2) Stoichiometric Flame Conditions (Figure 11.9)
Under stoichiometric conditions, the oxygen concentration increased linearly with flame intensity, with the advancing and receding water contact angles following the opposite trend and decreasing rapidly. Less oxygen was introduced than under reducing flame
Figure 11.8 Effect of varying flame intensity at an air-to-natural gas ratio of 8:1 on surface oxygen concentration and (a) water and (b) diiodomethane contact angles for polypropylene
Figure 11.9 Effect of varying flame intensity at an air-to-natural gas ratio of 10.3:1 on surface oxygen concentration and advancing (a) water and (b) diiodomethane contact angles for polypropylene
Figure 11.10 Effect of varying flame intensity at an air-to-natural gas ratio of 11.8:1 on surface oxygen concentration and advancing (a) water and (b) diiodomethane contact angles for polypropylene
conditions, this probably being due to the presence of more excited species in the flame through incomplete combustion of the fuel under such conditions.

**B-3) Oxygen Rich Flame Conditions (Figure 11.10)**

Good correspondence between oxygen concentration and water contact angles was found for the treatment of polypropylene by an oxygen rich flame. The oxygen concentration increased almost linearly with flame intensity, with an accompanying decrease in both advancing and receding water contact angles. As for the treatment of polyethylene, treatment of polypropylene under stoichiometric and oxygen rich flame conditions produced similar surfaces in terms of composition and wettability. This was again attributed to the more efficient combustion of the fuel.

To 95% confidence levels, the advancing and receding diiodomethane contact angles on treated polypropylene surfaces were unchanged by variations in flame intensity at all the stoichiometries studied, remaining similar to those on the untreated surface.

Although flame treatment under reducing conditions resulted in slightly more oxygen being incorporated into the polypropylene surfaces than under the other conditions studied, the exact flame composition did not make any great differences in the water wettabilities found. This was in contrast to polyethylene, where oxygen deficient conditions were the most effective in improving surface wettability. The lower oxygen concentrations on the treated polypropylene surfaces and its general difficulty in treatment was attributed to its degradation into low molecular weight fragments, these then being rapidly volatilised under all the flame conditions investigated.

Generally, similar oxygen concentrations and water contact angles were found after flame and laboratory corona treatments of polyethylene. However, the different flame conditions employed resulted in different wettabilities for a given surface composition, and therefore comparisons between the two treatments should be made with great caution. Corona treatment of polypropylene resulted in higher oxygen concentrations and lower water contact angles than flame treatment. The difference probably arose through the more rapid volatilisation of scission fragments by "hot" flame treatment compared to "cold" corona treatment, with some contribution from heat induced functional group reorientation away.
from the near surface. Volatilisation could, at least in part, account for the different surface chemistries produced by the two treatments (section 11.2.3.3).

### 11.2.3.2 Low Molecular Weight Oxidised Material

In order to check for the presence of low molecular weight oxidised material, the samples treated under oxygen rich flame conditions were subject to washing in diethylether and reanalysis by XPS and water contact angle measurement.

Table 11.1 shows the surface oxygen concentrations and water contact angle data for flame treated polyethylene before and after washing in diethylether. Analysis by XPS showed a small decrease in the surface oxygen concentration of between 10-16 % upon washing, suggesting the presence of some low molecular weight material. Washing of the surfaces with diethylether had the effect of equalising the advancing water contact angles over the range of flame intensities investigated. This was attributed to the slight decrease in surface oxygen for heavily oxidised samples, with some possible contribution from diethylether induced reorientation of functional groups towards the bulk also. In spite of the removal and reorientation of the oxygen functional groups, the diethylether washed polyethylene surfaces still retained some water wettability. Indeed, advancing and receding water contact angles were similar to those attained with a medium flame intensity.

Polypropylene was also flame treated and washed with diethylether, Table 11.2 shows the surface oxygen and water contact angle data. A very small decrease in the surface oxygen concentration was found after washing, indicating that very little low molecular weight oxidised material was present on the treated surfaces. This was consistent with polypropylene being very susceptible to free radical chain degradation. The polymer chains could break down rapidly into small molecules which are then rapidly volatilised from the surface by the heat of the treatment, while the small molecules remain on the surface after corona treatment. The small increase in both advancing and receding water contact angles was attributed to the reorientation of functional groups away from the near surface. More scission fragments were indicated on polyethylene than on polypropylene surfaces for a given treatment level, this being the opposite of that observed for corona treatment.
Chapter 11 Laboratory Scale Flame Treatment

<table>
<thead>
<tr>
<th>FLOW RATE /1 min⁻¹</th>
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<th>DIETHYLETHER WASHED</th>
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Table 11.1 Surface oxygen concentrations and water contact angle data for polyethylene flame treated using an air-to-natural gas ratio of 11.8:1 before and after washing with diethylether

<table>
<thead>
<tr>
<th>FLOW RATE /1 min⁻¹</th>
<th>UNWASHED</th>
<th>DIETHYLETHER WASHED</th>
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</thead>
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<td></td>
<td>[O] / %At.</td>
<td>θ H₂O_adv / deg</td>
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<tr>
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<tr>
<td>52.3</td>
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<td>90.8</td>
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Table 11.2 Surface oxygen concentrations and water contact angle data for polypropylene flame treated using an air-to-natural gas ratio of 11.8:1 before and after washing with diethylether

This was attributed to polypropylene chains being more easily degraded into small fragments than polyethylene chains, allowing greater loss of functionality through volatilisation. Thus, the presence of only minimal quantities of low molecular weight oxidised material was indicated, with less than 20% of the oxygen introduced into flame treated polyethylene and polypropylene being removed by diethylether washing. For laboratory scale corona treatment, on the other hand, up to 25% and 70% of the oxygen concentration was removed upon washing of the treated polyethylene and polypropylene surfaces respectively. Clearly, there was a significant difference in the amount of scission
products remaining on the polymer surfaces after flame and corona treatments. The relative lack of scission fragments on flame treated surfaces was attributed to their volatilisation by the heat of the process. Less volatilisation would be expected from corona treatment due to its "cold" nature. The presence of scission fragments could potentially degrade adhesion to the treated surface, consequently their presence is undesirable. Thus, the absence of such material on flame treated surfaces provides an advantage for flame treatment over corona treatment.

11.2.3.3 Chemical Derivatisation

Hydroxyl and carboxylic acid functional group concentrations were determined for polyethylene and polypropylene surfaces flame treated under oxygen rich conditions. This was achieved via the use of vapour phase chemical derivatisation in conjunction with XPS using the previously given methods (section 9.6).

Figure 11.11 shows the hydroxyl and carboxylic acid group concentrations respectively for polyethylene. To 95% confidence limits, the hydroxyl and carboxylic acid group concentrations were unchanged with increasing flame intensities remaining at average values of 3.2 %At. and 1.6 %At respectively. This corresponded to ~32% of the total incorporated oxygen being present as hydroxyl and ~16% being present as carboxylic acid. When compared to ~3.0 %At. and ~2.2 %At. estimated for hydroxyl and carboxylic acid group concentrations respectively for corona treated polyethylene, both flame and corona treatments appeared to produce similar types of surface chemistry on this polymer, however this comparison could not be confirmed. The hydroxyl concentration consistently exceeded the carboxylic acid concentration and this probably was due in part to the volatilisation of scission fragments.

For polypropylene, no carboxylic acid functionality was observed at any flame intensity. In this case, the carboxylic acid groups were probably at the ends of scission products, so in the light of diethylether washing studies their absence would be expected. Figure 11.12 shows that the hydroxyl concentrations increased with flame intensity, although the percentage of oxygen present as hydroxyl went through a maximum of ~32% at a total flow rate of ~41 l min⁻¹. This compared to a decrease in the percentage of oxygen present
Figure 11.11 Variation in hydroxyl and carboxylic acid concentrations with total flow rate for polyethylene, air-to-natural gas ratio 11.8:1

Figure 11.12 Variation in hydroxyl concentration with total flow rate for polypropylene, air-to-natural gas ratio 11.8:1
as hydroxyl from 32.0% to 24.3% after corona treatment of this polymer. This, in conjunction with the presence of carboxylic acid groups after corona treatment showed that these two treatments produced quite different surface chemistries upon treatment of polypropylene, and goes some way in explaining the difference in water wettabilities and estimated surface energies resulting from these two treatments.

For flame treated polyethylene, the hydroxyl and carboxylic acid group concentrations accounted for ~6 %At. (~3 %At. each respectively) of the total surface oxygen at all intensities. This constituted between 75%-45% of the incorporated oxygen, so that other functional groups, for example carbonyls, must have been responsible for making up the balance. Similarly for polypropylene, the hydroxyl functional group concentration represented between 11%-25% of the oxygen incorporated, with of course carboxylic acid groups making no contribution. However, FTIR-ATR analysis did not detect the presence of C=O groups on the surfaces of either polymer. Therefore in order to allow further identification of the functional groups on the flame treated polyethylene and polypropylene surfaces, high resolution XPS using the Scienta ESCA300 was performed. Figure 11.13
shows high resolution C1s XP spectra for the polymers treated at a total flow rate of 30.5 l min⁻¹ at an air-to-natural gas ratio of 11.8:1. There appeared to be some suggestion of a chemical shift due to various polar oxygen functional groups on the high binding energy side of the C1s peak, however, definite assignments to specific functional groups were not possible. Although curve fitting techniques can be useful in systems which have reasonably well known surface structures, in the case of flame treated polymers where the surface chemistry is unknown these techniques are not necessarily that useful. The fitting procedure can often be arbitrary in terms of the number and widths of peaks used, with the best fitting envelopes sometimes giving chemically unreasonable results. Also, the weak shifted peaks were superimposed on an inelastic background, for which no suitable methods for removal exist, making their observation more difficult.

11.2.3.4 Determination of Functional Group Concentrations from Works of Adhesion

An attempt was made to investigate the effect of the various functional groups on the surface wettability. After derivatisation of hydroxyl and carboxylic acid functional groups, advancing water contact angles were measured. Derivatisation of a functional group "blocks" its ability to interact with a liquid at the surface, therefore by selectively "blocking" functional groups and then measuring water contact angles an indication of their relative importance at the surface may be obtained. Figures 11.14 (a) and (b) show the effects of functional group derivatisation on the works of adhesion with water after flame treatment at various intensities for polyethylene and polypropylene respectively. XPS analysis of derivatised samples soaked in water for two minutes showed only minor changes in fluorine concentration, indicating that hydrolysis of the hydroxyl and carboxylic acid ester derivatives was not significant. Thus a true reflection on the wettability of the derivatised surfaces was thought to be given by contact angle measurement.

For polyethylene, the overall effect of functional group "blocking" was indeed to reduce the work of adhesion. The ability of hydroxyl and carboxylic acid groups to undergo hydrogen bonding was stopped by derivatisation, and so a reduction in water wettability would clearly be expected. Although derivatisation of carboxylic acid groups produced a decrease in work of adhesion, the most significant effect was observed upon derivatisation
Figure 11.14 Variation in the work of adhesion with flame treatment before and after derivatisation for (a) polyethylene (b) polypropylene
of hydroxyl functional groups, probably stemming from their greater initial concentration. For polypropylene, no carboxylic acid groups had been detected, and therefore an unchanging work of adhesion after derivatisation was expected. Derivatisation of hydroxyl groups with TFMA did not produce a change in the work of adhesion either, this probably being due to the low number of hydroxyl groups present on the surfaces in the first instance.

Using the advancing water contact angles measured on PVA and PAA standard polymers before and after derivatisation, the change in work of adhesion per functional group upon derivatisation was estimated for hydroxyl and carboxylic acid functional groups. Assuming that the standard polymer surfaces consist of cubes of volume \( V \), containing single repeat units of the standard polymer, the volume \( V \) may be simply calculated using equation 11.1,

\[
V = \frac{M}{\rho N_A}
\]  

eqn. 11.1

where \( M \) is the molar mass of the repeat unit (kg mol\(^{-1}\)) and \( \rho \) is the polymer density (kg m\(^{-3}\)), \( N_A \) is the Avagadro constant. Thus, the area occupied by one repeat unit, \( A \), is given by equation 11.2,

\[
A = V^{2/3} = \left(\frac{M}{\rho N_A}\right)^{2/3}
\]  

eqn. 11.2

The product of the change in the work of adhesion upon derivatisation of the standard polymer, \( \Delta W_{\text{ad standard}} \) (J m\(^{-2}\)), and the area occupied per OH/COOH group (given by \( A \)) then gives the change in the work of adhesion per functional group on derivatisation, equation 11.3,

\[
W_{\text{ad per functional group}} = A \Delta W_{\text{ad standard}} = \Delta W_{\text{ad standard}} \left(\frac{M}{\rho N_A}\right)^{2/3}
\]  

eqn. 11.3
where $\Delta W^\text{standard}_{\text{ad}} = W^\text{standard}_{\text{ad}} - W^\text{standard+deriv}_{\text{ad}}$. For PVA, $\rho$ is 1270 kg m$^{-3}$ and the molar mass of the repeat unit is $44 \times 10^3$ kg mol$^{-1}$, while for PAA, $\rho$ is $\sim$1200 kg m$^{-3}$ and the molar mass of the repeat unit is $72 \times 10^3$ kg mol$^{-1}$. Table 11.3 shows surface compositions, advancing water contact angle data, and the work of adhesion per functional group, calculated from equation 11.3, for the two standard polymers before and after derivatisation.

<table>
<thead>
<tr>
<th>POLYMER</th>
<th>SURFACE COMPOSITION/%At</th>
<th>$\theta_{\text{adv}}$ / deg</th>
<th>$W_{\text{ad}}$ per group / J</th>
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<td>105.8</td>
</tr>
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</table>

Table 11.3 Surface compositions, water contact angle data and work of adhesion per functional group for the standard polymers PVA and PAA

Therefore, knowledge of the change in work of adhesion per functional group on derivatisation allows the number of hydroxyl and carboxylic acid groups per unit area for the flame treated polymers to be estimated, equations 11.4 and 11.5 respectively,

\[ \text{no. OH groups per unit area} = \frac{\Delta W^\text{flame}_{\text{ad}}}{\Delta W_{\text{ad}} \text{ per OH group}} \quad \text{eqn. 11.4} \]

\[ \text{no. COOH groups per unit area} = \frac{\Delta W^\text{flame}_{\text{ad}}}{\Delta W_{\text{ad}} \text{ per COOH group}} \quad \text{eqn. 11.5} \]

where $\Delta W^\text{flame}_{\text{ad}} = W^\text{flame}_{\text{ad}} - W^\text{flame+deriv}_{\text{ad}}$. For treated polyethylene, typical values of $1.5 \times 10^{18}$ and $7.5 \times 10^{17}$ hydroxyl and carboxylic acid groups per square meter respectively were obtained. To allow comparison with functional group concentrations estimated by XPS, the near surface functional group concentrations were estimated using equation 11.6,

\[ [\text{GROUP}]_{\text{exp \%At.}} = [\text{GROUP}]_{\text{theo}} \times \frac{\text{no. groups per unit area for flamed polymer}}{\text{no. groups per unit area for standard polymer}} \quad \text{eqn. 11.6} \]
where \([\text{GROUP}]_{\text{theo}}\) is the theoretical functional group concentration obtained from the standard polymers (PVA = 33.3 %At. and PAA = 40.0 %At.) and the number of groups per unit area for the standard polymer is equal to \(1/\text{A}\) obtained from equation 11.2. Figures 11.15 (a) and (b) show the hydroxyl and carboxylic acid group concentrations for polyethylene and polypropylene respectively flame treated at various total flow rates and at an air-to-natural gas ratio of 11.8:1. For polyethylene, neither the hydroxyl group nor carboxylic acid group concentrations increased significantly with total flow rate, this being in agreement with the derivatisation/XPS methods employed. However, the estimated concentrations for the respective functional groups obtained from this method were approximately double those estimates obtained from derivatisation/XPS. This was probably because contact angle measurement and works of adhesion are determined by the outer atom layer, whereas the XPS analysis depth is \(-5\) nm. From oxidation depth models, the oxygen concentration at the outer surface was estimated by extrapolation of variable take-off angle XPS to be approximately twice that detected by XPS over the whole sampling depth and thus the apparent discrepancy can be explained in terms of the variation in the composition as a function of depth. Oxidation depths are discussed further in Chapter 13.

This method did not yield useful estimates for the hydroxyl and carboxylic acid group concentrations for flame treated polypropylene. This was attributed to the presence of only low concentrations of these groups, resulting in only small changes in the work of adhesion upon derivatisation. Overall, this method provided functional group concentration estimates that were in good agreement with chemical derivatisation methods. Therefore, in the future this technique could be employed to provide reliable functional group concentration estimates without the use of XPS analysis and more importantly their concentration at the near surface.

11.3 Correlation Between Oxygen Concentration and Work of Adhesion

For polyethylene and polypropylene flame treated at all the air-to-natural gas ratios and flame intensities investigated, the correlation between surface oxygen and the works of adhesion water and diiodomethane contact angles are shown in Figures 11.16 (a) and (b) respectively. Figure 11.16(a) also shows data from conventional corona treatment.
A linear correspondence was found between the surface oxygen concentrations and the works of adhesion with water, this suggesting near surface oxidation. This was in contrast to corona treatment where the work of adhesion with water began to tail-off at higher oxygen concentrations, this being attributed to sub-surface oxidation. Clearly, for a given oxygen concentration corona treatment resulted in a higher work of adhesion with water than flame treatment. The lower work of adhesion from flame treatment could have arisen through differences in the surface chemistries produced by it and corona treatment. Although chemical derivatistion had shown that this could have been true for polypropylene, the surface chemistry of polyethylene after the respective treatments were thought to be reasonably similar. Thus, a difference in surface chemistries was not thought to be the case. Alternatively, the lower works of adhesion could have arisen through reorientation of the functional groups away from the near surface, this being induced by increased chain mobility at the high temperatures of flame treatment.

Statistical analysis showed that the work of adhesion with diiodomethane increased slightly with increasing oxygen concentration, although the effect was much smaller than the increase in the work of adhesion with water. Although the advancing diiodomethane contact angles on both polymers were invariant with flame intensity at all the stoichiometries investigated, they were approximately $10^\circ$ lower on treated polyethylene surfaces than treated polypropylene surfaces. The higher oxygen concentration on the polyethylene surfaces could have resulted in the formation of more dipole-induced dipole interactions between polar surface functional groups, such as C=O, and the polarisable diiodomethane molecules, thereby decreasing the contact angle and increasing the work of adhesion. Thus the slight increase in the work of adhesion with water was probably a consequence of the higher oxygen concentrations present on the polyethylene surfaces.

11.4 Surface Free Energy

Advancing water and diiodomethane contact angles were used to estimate surface energies according to the method of Owens-Wendt. The effects of air-to-natural gas ratio on the surface energies of polyethylene and polypropylene respectively are shown in Tables 11.4, while the effects of flame intensity are shown in Tables 11.5 for the respective polymers.
Figure 11.15 Variation in hydroxyl and carboxylic acid group concentrations for (a) polyethylene and (b) polypropylene calculated from works of adhesion with water.
Figure 11.16 The relationship between oxygen concentration and work of adhesion from advancing (a) water and (b) diiodomethane contact angles for polyethylene and polypropylene treated at all the air-to-natural gas ratios and flame intensities investigated.
11.4.1 Air-to-natural Gas Ratio

In the flame treatment of polyethylene, the primary effect of varying the air-to-natural gas ratio on the surface energy was to increase the polar components, with the dispersion components remaining largely constant. The polar component reached a maximum at approximately the stoichiometric flame conditions, which resulted in a maximum for the total surface energy at this point also. This was in reasonable correspondence with the observed minimum in advancing water contact angles. Flame treatment of polypropylene also showed a small increase in the polar component of surface energy, although it did not really change with variations in air-to-natural gas ratio. However, there was a small decrease in the dispersion component, so that the overall effect was to maintain a constant total surface free energy slightly below that of the untreated polymer. This was a surprising result as the introduction of oxygen functional groups would be expected to result in an increased surface free energy. This suggested that the Owens-Wendt method of estimating the surface free energy of a treated polymer may not be completely reliable.

11.4.2 Flame Intensity

After treatment under oxidising and reducing flame conditions, the polar components of polyethylene increased steadily with flame intensity, while after treatment under stoichiometric flame conditions the polar components did not change with flame intensity. The dispersion components remained largely unchanged with flame intensity at all the air-to-natural gas ratios investigated. Thus, the total surface energies with flame intensity increased only after treatment under oxidising and reducing conditions. The greatest improvement in surface energy occurred under the oxygen deficient flame conditions, with a polar component of 18.2 mJ m⁻² being produced at the highest flow rate. The oxygen concentration at this point was 13.8 %At., and although similar oxygen concentrations were produced while using other flame stoichiometries, comparable surface energies were not found.

Change in the flame intensity at an air-to-natural gas ratio of 8:1 produced some suggestion of a maximum in the polar component in the surface free energy of polypropylene, mirroring the advancing water contact angle behaviour. However, the
Chapter 11 Laboratory Scale Flame Treatment

<table>
<thead>
<tr>
<th>AIR:GAS RATIO</th>
<th>POLYETHYLENE</th>
<th>POLYPROPYLENE</th>
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</thead>
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<td>$\gamma_s^p$</td>
<td>$\gamma_s^d$</td>
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<td>31.6</td>
</tr>
<tr>
<td>17.4:1</td>
<td>3.9</td>
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</table>

Table 11.4 The effect of air-to-natural gas ratio on the surface free energy of polyethylene and polypropylene

evidence was not conclusive as the range of surface energy values was small. Under stoichiometric and oxygen rich flame conditions, the polar component increased gradually with flame intensity. The dispersion components were unchanged with flame intensity after treatment under all the flame stoichiometries studied, although in most cases they remained at values (of up to 6 mJ m$^{-2}$) below that of the untreated polymer. This resulted in total surface energies slightly below that of the untreated polymer. As a consequence of their higher oxygen concentrations and lower water contact angles, the treated polyethylene had higher surface energies than similarly treated polypropylene surfaces under all the conditions studied.

For the flame treatment of polyethylene, the greatest increase in estimated polar component and total surface energy occurred under reducing flame conditions, these being 18.2 mJ m$^{-2}$ and 47.0 mJ m$^{-2}$ respectively. The greatest polar component and total surface energy for polyethylene after laboratory corona treated were 20.7 mJ m$^{-2}$ and 50.0 mJ m$^{-2}$ respectively suggesting that the two treatments produced similar improvements for this polymer. However given the variety of flame treatment parameters investigated, comparison with corona treatment should be approached with caution. For a given
Chapter 11 Laboratory Scale Flame Treatment

<table>
<thead>
<tr>
<th>TOTAL FLOW / 1 min⁻¹</th>
<th>SURFACE FREE ENERGY / mJ m⁻²</th>
<th>POLYETHYLENE</th>
<th>POLYPROPYLENE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \gamma_s^p )</td>
<td>( \gamma_s^d )</td>
<td>( \gamma_s^{\text{tot}} )</td>
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<tr>
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Table 11.5 The effects of flame intensity at various air-to-natural gas ratios on the surface free energy of polyethylene and polypropylene

flame intensity, there was no great variation in the polar components and total surface energies of polypropylene treated at the three flame stoichiometries investigated, so that they remained at \(~2.5\ \text{mJ m}^{-2}\) and \(29.4\ \text{mJ m}^{-2}\) respectively. After laboratory corona treatment of polypropylene, maximum polar components and total surface energies of \(14.9\ \text{mJ m}^{-2}\) and \(40.8\ \text{mJ m}^{-2}\) were estimated, indicating that corona treatment was significantly more successful than flame treatment in the activation of this polymer. A noticeable effect
on flame treated polypropylene surfaces was the slight apparent decrease in the estimated
dispersion components after treatment, despite the indication from unchanged
diiodomethane contact angles that the surface dispersion interactions had been unaffected.
From this it was concluded that the observed decrease in dispersion component was a
result of shortcomings in the calculation methods used.

The harmonic mean method of Wu was also employed, estimating slightly higher
dispersion components and in most instances significantly greater polar components than
the Owens-Wendt method. Overall the Wu method estimated greater total surface
energies than the Owens-Wendt method, although similar trends were indicated by each
method. However, surface free energy estimates can be misleading as the apparent
decrease in the dispersion component for polypropylene, and the unphysical surface energy
estimate for the untreated polyethylene homopolymer obtained from the Wu method
indicated. These anomalous estimates were attributed to the inherent assumptions of the
calculations, these methods being valid only for ideal surfaces which are smooth and
homogeneous. Also, real interactions at surfaces do not exactly follow either the
geometric or the harmonic mean models employed in these calculations and for these
reasons the validity of surface energy estimates is somewhat doubtful. Therefore,
interpretation of raw advancing and receding contact angle data probably provides the
most reliable measure of surface wettabilities, as well as providing information on surface
roughness and heterogeneity.
Chapter 12 Reactive Gas Flame Treatment

12.1 Introduction

The laboratory scale flame treatment apparatus described previously was used to investigate the effects of introducing sulphur dioxide and ammonia gases into the flame. As for reactive gas corona treatment, it was hypothesised that use of these gases could lead to the incorporation of sulfonic acid and basic amine groups respectively into the polyolefin surfaces. The presence of the reactive gases at various concentrations, flame intensities and air-to-natural gas ratios were studied. The resulting treated surfaces were characterised with XPS, FTIR-ATR, electron microscopy and contact angle measurement.

12.2 Sulfur Dioxide Treatment

Sulfur dioxide gas was bled into the flame by mixing it with the air and natural gas prior to combustion. Flow rates in the range 20-200 ml min\(^{-1}\) were used. Beyond 200 ml min\(^{-1}\) of sulfur dioxide, industrial applications could be limited due to environmental problems. The effects of using a constant flame intensity while varying the sulfur dioxide flow rate at air-to-natural gas ratios of 11.8:1 and 8:1 respectively were studied. A total flow rate of 30.5 l min\(^{-1}\) which had previously been determined to produce good surface activation was employed. Also, the effects of varying the flame intensity under stoichiometric flame conditions at a constant sulfur dioxide flow rate of 40 ml min\(^{-1}\) were studied.

12.2.1 Sulfur Dioxide Flow Rate

12.2.1.1 Effects of Surface Composition and Contact Angles

A) Oxygen Deficient Flame Conditions

Figures 12.1 (a) and (b) show the effect of sulfur dioxide flow rate during flame treatment under reducing conditions on the surface compositions of polyethylene and polypropylene respectively. Analysis by XPS showed that as for sulfur dioxide corona treatment, the surfaces had been modified by the incorporation of oxygen, sulfur and nitrogen functionality. The oxygen concentrations for both polymers reached plateau levels at \(-40\) ml min\(^{-1}\) of sulfur dioxide, while the sulfur and nitrogen concentrations remained invariant with sulfur dioxide flow rate. At all the sulfur dioxide flow rates, in
Figure 12.1 Effect of varying the SO$_2$ flow rate on the surface compositions for (a) polyethylene (b) polypropylene at constant flame intensity of 30.5 l min$^{-1}$ and at an air-to-natural gas ratio of 8:1
Figure 12.2 Effect of varying the SO$_2$ flow rate on the advancing water and diiodomethane
contact angles for (a) polyethylene (b) polypropylene at constant flame intensity of 30.5 l 
min$^{-1}$ and at an air-to-natural gas ratio of 8:1
agreement with sulfur dioxide corona treatment, the concentrations of the newly incorporated elements were in the order oxygen > sulfur > nitrogen. More oxygen was detected on polyethylene surfaces than polypropylene surfaces, although the surface compositions of the two polymers had some resemblance with generally similar sulfur and nitrogen concentrations being detected. Thus polyethylene was again more readily treated than polypropylene on reactive gas treatment. This was in contrast to sulfur dioxide corona treatment where almost double the concentrations of each new element were found on polypropylene than on polyethylene. Although the presence of sulfur dioxide was thought to reduce the extent of chain scission, some scission is still believed to occur during flame treatment, so the difference between the corona and flame treatments could simply have been a result of volatilisation of the resulting scission fragments.

Figures 12.2 (a) and (b) show the effects of sulfur dioxide flow rate during flame treatment at an air-to-natural gas ratio of 8:1 on the advancing water and diiodomethane contact angles respectively for polyethylene and polypropylene. To 95 % confidence levels, the advancing and receding water contact angles for polyethylene were invariant with sulfur dioxide flow rate. The advancing angle remained at an average value of 62.3°. For polypropylene, the advancing water contact angles reached a plateau value of ~76° at a sulfur dioxide flow rate of ~40 ml min⁻¹, suggesting the existence of a minimum reactive gas flow rate which allows the achievement of optimum surface wettability. The receding angle also followed the same trend. These advancing water contact angles compare to angles of 67.8° and 91.0° for polyethylene and polypropylene respectively after conventional flame treatment at the same intensity and flame stoichiometry. Thus, improved water wettabilities were measured on both polymers upon introduction of sulfur dioxide, especially for polypropylene. This improvement was attributed to the development of strong interfacial interactions between the sulfur/nitrogen/oxygen functional groups and the polar water molecules. However, the improvement was not as good as that seen upon sulfur dioxide corona treatment, where average advancing water contact angles of 37.4° and 59.8° were measured at all sulfur dioxide flow rates on polyethylene and polypropylene respectively. For sulfur dioxide flame treated polyethylene, where the elemental concentrations were slightly higher than for similarly corona treated polyethylene, the lower water wettability may have resulted from heat induced
reorientation of functional groups away from the near surface. The lower wettability of
doped flame treated polypropylene was probably simply due to the lower elemental
concentrations, with functional group reorientation making some contribution. To 95 %
confidence limits, the advancing and receding diiodomethane contact angles on both
polymer types were independent of sulfur dioxide flow rate. The receding diiodomethane
contact angles were reduced by ~10° upon treatment compared to the untreated surfaces,
probably resulting from dipole-induced dipole interactions formed between the polar
surface and the polarisable diiodomethane molecules.

B) Oxygen Rich Flame Conditions

Figures 12.3 (a) and (b) show the effect of sulfur dioxide flow rate during flame treatment
at an air-to-natural gas ratio of 11.8:1 on the surface composition of polyethylene and
polypropylene respectively. As with the reducing flame conditions, oxygen, sulfur and
nitrogen were detected by XPS analysis. The sulfur and nitrogen concentrations were
invariant with sulfur dioxide flow rate for polyethylene, while there was a small increase in
the oxygen concentration. For polypropylene, concentrations of the newly introduced
elements were invariant with sulfur dioxide flow rate.

Figure 12.4 (a) and (b) show the advancing water and diiodomethane contact angles
respectively for polyethylene and polypropylene at various sulfur dioxide flow rates after
flame treatment under oxidising flame conditions. From the minimal changes in surface
compositions with sulfur dioxide flow rate, it was not surprising to find that to 95 %
confidence limits, the advancing and receding water contact angles on both polymers were
invariant with sulfur dioxide flow rate. The advancing water contact angles remained at
average values of 60.4° and 87.8° for polyethylene and polypropylene respectively. These
angles compared to 75.8° and 93.8° after conventional flame treatment at the same air-to-
natural gas ratio but at the slightly higher flame intensity of 34.8 l min⁻¹. Thus further
improvements in the surface wettabilities of both polymers were achieved by use of sulfur
dioxide.

The advancing and receding diiodomethane contact angles on both polymers were also
invariant with sulfur dioxide flow rate. The receding contact angles were 15-20° degrees
lower than on the untreated polymers. This again attributed to the formation of dipole-
Figure 12.3 Effect of varying the SO₂ flow rate on the surface compositions for (a) polyethylene (b) polypropylene at constant flame intensity of 30.5 l min⁻¹ and at an air-to-natural gas ratio of 11.8:1
Figure 12.4 Effect of varying the SO₂ flow rate on the advancing water and diiodomethane contact angles for (a) polyethylene (b) polypropylene at constant flame intensity of 30.5 l min⁻¹ and at an air-to-natural gas ratio of 11.8:1.
induced dipole interactions between the treated polymer surfaces and the polarisable diiodomethane molecules.

Overall, for a given sulfur dioxide flow rate slightly more of each new element was incorporated under oxygen deficient conditions than under oxygen rich conditions. This may have resulted from more efficient/rapid oxidation of the fuel/sulfur dioxide mixture to stable products under the oxygen rich conditions so that fewer activated species may have been present for reaction with the polymer surfaces. Also, more effective volatilisation of the scission products produced through the extra heat evolved by the efficient fuel combustion could have resulted in loss of functionality. Optimum activation of both polymers was achieved at the reasonably low sulfur dioxide flow rate of 40 ml min$^{-1}$ under oxidising and reducing flame conditions.

12.2.1.2 Correlation Between Oxygen Concentration and Work of Adhesion

Figures 12.5 (a) and (b) show the correlation between oxygen concentration and works of adhesion with water and diiodomethane for polyethylene and polypropylene respectively. In Figure 12.5 (a), two trend lines labelled polyethylene (PE) and polypropylene (PP) have been indicated. The behaviours of the two polymers were significantly different, with the work of adhesion being independent of surface oxygen concentration for polyethylene but increasing linearly with surface oxygen concentration for polypropylene. The difference may have involved competition between chain scission and sulfur incorporation. For polypropylene, the surface free radicals could combine with the active sulfur species present more rapidly than undergoing chain scission, thereby reducing the extent of chain scission. Through these reduced levels of chain scission, the resulting fragments would be larger and would not be as volatile, resulting in functional group retention. At higher sulfur dioxide flow rates, more polar groups could be retained thus promoting strong interfacial interactions as indicated by the work of adhesion with water. The relative surface compositions would not be affected as carbon in addition to oxygen/sulfur/nitrogen would be retained. For polyethylene where free radical degradation is less efficient than on polypropylene, the presence of sulfur dioxide would make less impact on the extent of scission. To 95% confidence levels, the work of adhesion with diiodomethane was invariant with sulfur dioxide flow rate.
Figure 12.5 The relationship between oxygen concentration and work of adhesion from advancing (a) water (b) diiodomethane contact angles for polyethylene and polypropylene at all SO$_2$ flow rates; total flow rate 30.5 l min$^{-1}$, air-to-natural gas ratios 8:1, 11.8:1
12.2.2 Flame Intensity

12.2.2.1 Effects of Surface Composition and Contact Angles

The effects of varying the flame intensity at an air-to-natural gas ratio of 10.3:1 and a constant sulfur dioxide flow rate of 40 ml min\(^{-1}\) on the surface compositions of polyethylene and polypropylene are shown in Figures 12.6 (a) and (b) respectively. The treated polyolefin surfaces were modified by the incorporation of oxygen, sulfur and nitrogen, their concentrations increasing with flame intensity for both polymers and following the general order of oxygen > sulfur > nitrogen. Polyethylene was found to be more readily treated than polypropylene for a given flame intensity, this being in agreement with previous treatment methods except sulfur dioxide corona treatment. For both polymers, there was some indication for a levelling-off in the oxygen concentration with flame intensity, although the sulfur and nitrogen concentrations continued to increase almost linearly.

The variations in the advancing water and diiodomethane contact angles with flame intensity are shown in Figures 12.7 (a) and (b) respectively. The advancing and receding water contact angles for both polymers decreased rapidly with flame intensity and, as expected, reached a plateau level at a total flow rate of \(\sim 30 \text{ l min}^{-1}\). The plateau in the advancing water contact angles corresponded reasonably well to the oxygen concentrations on both polymers, suggesting that the greatest surface activation could be achieved at an intermediate flame intensity. As in section 12.2.1.1, the improvement in surface wettability was attributed to incorporation of oxygen, sulfur and nitrogen.

To 95% confidence limits, the advancing and receding diiodomethane contact angles on polypropylene were independent of sulfur dioxide flow rate with only a small decrease with flow rate being measured on polyethylene. The advancing diiodomethane contact angles on the treated surfaces of both polymers were similar to those measured on the untreated surfaces, although the receding contact angles were \(\sim 10^\circ-20^\circ\) lower. This lowering was again attributed to the formation of interfacial dipole-induced dipole interactions between the polar surface and the polarisable diiodomethane molecules.
Figure 12.6 Effect of varying the flame intensity on the surface compositions for (a) polyethylene (b) polypropylene at constant of \( \text{SO}_2 \) flow rate 40 ml min\(^{-1} \) and at an air-to-natural gas ratio of 10.3:1
Figure 12.7 Effect of varying the flame intensity on the advancing water and diiodomethane contact angles for (a) polyethylene (b) polypropylene at constant SO$_2$ flow rate of 40 ml min$^{-1}$ and at an air-to-natural gas ratio of 10.3:1.
12.2.3 Surface Chemistry

A) Effect of Additives

The incorporation of nitrogen into the treated surfaces could have resulted from interactions between active sulfur species present in the flame and additive molecules already present in the polymers. Therefore, the effects of the polymer processing/stabilising additives on the polyolefin surface chemistry upon treatment were investigated. Two routes were taken, firstly, the films used throughout this study were extracted in an organic solvent to remove the additives, and secondly, additive free polyethylene was purchased (section 5.1.1). The first route had the advantage of the films being the same as those used throughout this study, although complete extraction of the additives could never be guaranteed. The second method did not suffer from the uncertain presence of additives, although the different molecular weight and density of the additive free polyethylene could add uncertainty to the effects of treatment. Thus, through the use of these methods in combination, it was believed that it would be possible to identify whether incorporation of sulfur/nitrogen was additive or process related.

<table>
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<th>POLYMER / TREATMENT</th>
<th>SURFACE COMPOSITION / %At</th>
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<th>$\theta_{DIM_{adv}}$ / deg</th>
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Table 12.1 Surface compositions and average contact angle data on solvent extracted polyethylene (X.PE) and additive free (A.F.PE) before and after flame treatment; total flow rate of $30.5 \text{ l min}^{-1}$, air-to-natural gas ratio of 11.8:1, SO$_2$ flow rate of $40 \text{ ml min}^{-1}$

The solubilities of the additives and their structures are given in Appendix A. All the additives showed good solubility in propanone, so the films were Soxhlet extracted in propanone for 36 hours. Propanone allowed easy air drying of the film after extraction and also film integrity was unaffected so that easy treatment of the films was still possible. Table 12.1 shows the surface compositions and average contact angle data of additive free...
and solvent extracted polyethylene before and after flame treatment using a total flow rate of 30.5 \text{ l min}^{-1} at an air-to-natural gas ratio of 11.8:1 and a sulfur dioxide flow rate of 40 \text{ ml min}^{-1} when required.

The small surface oxygen concentration on the solvent extracted polyethylene was attributed to the presence of additives. The oxygen present on the additive free polyethylene was attributed to transfer of low molecular weight material from the PET films used to press the films (section 6.2). Slight differences in the oxygen concentrations and contact angle data between the solvent extracted, additive free and the unextracted polyethylene treated under these conditions were observed. However, nitrogen and sulfur were still incorporated in significant quantities and therefore their incorporation could not have been a direct consequence of the polymer additives present. Oxygen, sulfur and nitrogen incorporation upon treatment of solvent extracted polypropylene also supported this conclusion. Thus, the incorporation of nitrogen must indeed have been a result of processes in the flame or post-flame regions and not as a consequence of the polymer additives.

B) Oxidant Supply

The presence surface nitrogen was shown not to be attributable to the polymer additives present. Alternatively, it could have originated via reactions with nitrogen species in the flame combustion region or the post-flame region. To investigate this, the presence of nitrogen in the flame was minimised by using a mixture of Ar/O\textsubscript{2} (4:1) as the oxidant instead of the usual compressed air. However, upon use of this oxidant during sulfur dioxide flame treatment, similar surface compositions and water contact angles to those obtained when using the compressed air oxidant were found. Therefore, incorporation of the nitrogen species was thought to probably occur via reactions in the post-flame region, possibly with long lived sulfur species present on the treated surfaces.

C)\textit{X-Ray Photoelectron Spectroscopy}

High resolution XPS was also employed to aid assignment of the various functional groups introduced during treatment. Figure 12.8 shows the high resolution C\textsubscript{1}s XP spectra for polyethylene and polypropylene flame treated using a total flow rate of 30.5 \text{ l min}^{-1} at an air-to-natural gas ratio of 11.8:1 and a sulfur dioxide flow rate of 40 \text{ ml min}^{-1}. Compared
Figure 12.8 Scienta ESCA300 high resolution C1s spectra of polyethylene and polypropylene flame treated at a total flow rate of 30.5 l min\(^{-1}\), air-to-natural gas ratio of 11.8:1, SO\(_2\) flow rate of 40 ml min\(^{-1}\) to conventional flame treatment, only slight asymmetry on the high binding energy side of the C1s photoelectron peaks was observed. This suggested that only relatively few carbon-oxygen bonds had been formed, that is only a small amount of the total oxygen incorporated into the surfaces of both polymers was directly bonded to carbon. Definitive assignment of the possible oxygen containing functional groups was again not possible due to the low intensities of the chemically shifted peaks.

<table>
<thead>
<tr>
<th>POLYMER / TREATMENT</th>
<th>BINDING ENERGY / eV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O1s</td>
</tr>
<tr>
<td>Polyethylene SO(_2)</td>
<td>532.0</td>
</tr>
<tr>
<td>Polypropylene SO(_2)</td>
<td>532.0</td>
</tr>
</tbody>
</table>

Table 12.2 Corrected O1s, S2p and N1s binding energies measured on the Scienta ESCA300 for sulfur dioxide doped flame treated polyethylene and polypropylene: total flow rate 30.5 l min\(^{-1}\), air-to-natural gas ratio 11.8:1, SO\(_2\) of flow rate 40 ml min\(^{-1}\)
After correction to the saturated C1s binding energy of 284.6 eV, the O1s, S2p and N1s binding energies measured on the Scienta ESCA300 for polyethylene and polypropylene flame treated using the above conditions are shown in Table 12.2. The binding energies for all the elements were very similar to those measured after sulfur dioxide corona treatment, indicating that surface chemistries produced by the two treatments were very similar.

D) Additional Information
As for conventional flame treatment, determination of hydroxyl and carboxylic acid groups by chemical derivatisation was attempted. However, fluorine concentrations >12 %At. were consistently found upon derivatisation. Given the minimal concentration of C-O species, the high fluorine concentrations were attributed to reaction between the sulfur/oxygen functional groups and the TFAA/TFE derivatisation agents, indicating the presence of reactive functional groups on the treated surfaces. For this reason further derivatisation work was not performed on sulfur dioxide treatments.

E) Elemental Surface Distributions
The distribution of the various elements/functional groups over the treated surfaces could have important effects in terms of surface wetting and adhesion characteristics. Therefore their distribution was investigated by obtaining elemental mapping using the Scienta ESCA300. Figures 12.9 (a)-(d) show Scienta ESCA300 elemental mapping images for C1s, O1s, S2p and N1s respectively from polyethylene sulfur dioxide flame treated under the same conditions as employed for high resolution XPS analysis. On the left hand side of the C1s map there appeared to be a high photoelectron intensity, whereas on the left hand side of the O1s, S2p and N1s maps there were low photoelectron intensities. This suggested that there was a slight depletion of the oxygen/sulfur/nitrogen functional groups on this side of the treated surface, that is there was some suggestion of a heterogeneous distribution of functional groups across the surface. Figures 12.10 (a)-(d) show Scienta ESCA300 C1s, O1s, S2p and N1s elemental mapping images respectively from polypropylene sulfur dioxide flame treated under the above conditions also. On the right hand sides of the O1s, S2p and N1s maps there were low photoelectron intensities while the intensity remained high for the C1s map, again suggesting that there was some depletion of functional groups. Thus, for flame treatment there was some suggestion for
Figure 12.9 Elemental mapping images of (a) C1s (b) O1s (c) S2p and (d) N1s for polyethylene flame treated at a total flow rate 30.5 l min\(^{-1}\) an air-to-natural gas ratio 11.8:1 and SO\(_2\) of flow rate 40 ml min\(^{-1}\)
Figure 12.10 Elemental mapping images of (a) C1s (b) O1s (c) S2p and (d) N1s for polypropylene flame treated at a total flow rate 30.5 l min\(^{-1}\) an air-to-natural gas ratio 11.8:1 and SO\(_2\) of flow rate 40 ml min\(^{-1}\)
heterogeneous distribution of functional groups across the surfaces of both polymers, this being in contrast to the homogeneous distributions found after sulfur dioxide corona treatment. This heterogeneity could have resulted from reorientation of functional groups during the heat of flame treatment, however, no firm conclusions could be drawn on this given the limited number of elemental mapping images.

Given the incorporation of oxygen, sulfur and nitrogen and their similar binding energies, the surface chemistries produced on sulfur dioxide flame and corona treated surfaces were thought to be similar. This suggested that the mechanisms of functionalisation were also very similar. This would not be surprising given the similarities in the mechanisms of functionalisation of the two respective conventional treatments.

12.2.4 Low Molecular Weight Oxidised Material

It was suggested in section 12.2.1.2 that use of sulfur dioxide during treatment could have had a significant effect on chain degradation. Thus, in order to check for the presence/lack of scission products, the sulfur dioxide flame treated surfaces were washed with diethylether and then reanalysed by XPS and water contact angle measurement.

A) Oxygen Deficient Flame Conditions

Tables 12.3 and 12.4 show the surface elemental compositions and advancing water contact angle data before and after diethylether washing for polyethylene and polypropylene respectively, flame treated at various sulfur dioxide flow rates using a total flow rate of 30.5 l min\(^{-1}\) at an air-to-natural gas ratio of 8:1. For polyethylene, consistent reductions of at least 40% in the oxygen, sulfur and nitrogen concentrations were detected upon diethylether washing. This loss of functionality lowered the water wettabilities, with the advancing water contact angle increasing by \(\sim 10^\circ\) upon washing in most cases. Thus the presence of scission products was indicated, their presence being in contrast to conventional flame treatment at an air-to-natural gas ratio of 11.8:1, where minimal changes in surface compositions and wettabilities were found upon washing. Significant removal of oxygen, sulfur and nitrogen was found upon diethylether washing of sulfur dioxide flame treated polypropylene surfaces also, with at least 30-40% of each non-carbon element being removed in most cases. Increases of \(\sim 10^\circ\) in the advancing water
# Chapter 12 Reactive Gas Flame Treatment

## Table 12.3 Elemental concentrations and advancing water contact angle data for polyethylene flame treated using various sulfur dioxide flow rates and a total flow rate of 30.5 l min\(^{-1}\) at an air-to-natural gas ratio of 8:1 before and after washing with diethylether

<table>
<thead>
<tr>
<th>SO(_2) FLOW /ml min(^{-1})</th>
<th>UNWASHED</th>
<th>DIETHYLETHER WASHED</th>
<th>(\theta_{\text{H}_2\text{O}}) / deg</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>8.4</td>
<td>2.2</td>
<td>1.0</td>
</tr>
<tr>
<td>30</td>
<td>13.4</td>
<td>2.3</td>
<td>2.0</td>
</tr>
<tr>
<td>40</td>
<td>15.7</td>
<td>3.3</td>
<td>1.8</td>
</tr>
<tr>
<td>55</td>
<td>15.8</td>
<td>3.0</td>
<td>1.7</td>
</tr>
<tr>
<td>70</td>
<td>16.0</td>
<td>2.7</td>
<td>1.9</td>
</tr>
<tr>
<td>200</td>
<td>14.6</td>
<td>2.9</td>
<td>2.5</td>
</tr>
</tbody>
</table>

## Table 12.4 Elemental concentrations and advancing water contact angle data for polypropylene flame treated using various sulfur dioxide flow rates and a total flow rate of 30.5 l min\(^{-1}\) at an air-to-natural gas ratio of 8:1 before and after washing with diethylether

<table>
<thead>
<tr>
<th>SO(_2) FLOW /ml min(^{-1})</th>
<th>UNWASHED</th>
<th>DIETHYLETHER WASHED</th>
<th>(\theta_{\text{H}_2\text{O}}) / deg</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
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<tr>
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<td>2.5</td>
<td>1.5</td>
</tr>
<tr>
<td>200</td>
<td>8.8</td>
<td>3.1</td>
<td>1.7</td>
</tr>
</tbody>
</table>

The removal of surface functionality was again in contrast to conventional flame treatment. Similar reductions in surface elemental compositions and water wettabilities for both polyethylene and polypropylene were found. Previous observations had indicated that polypropylene was more readily degraded than polyethylene on surface pretreatment, suggesting that the presence of sulfur dioxide in the flame did indeed have an effect on chain scission mechanisms. In section 12.2.1.2 it was suggested that introduction of sulfur dioxide into
Table 12.5 Elemental concentrations and advancing water contact angle data for polyethylene flame treated using various sulfur dioxide flow rates and a total flow rate of 30.5 l min⁻¹ at an air-to-natural gas ratio of 11.8:1 before and after washing with diethylether

<table>
<thead>
<tr>
<th></th>
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Table 12.6 Elemental concentrations and advancing water contact angle data for polypropylene flame treated using various sulfur dioxide flow rates and a total flow rate of 30.5 l min⁻¹ at an air-to-natural gas ratio of 11.8:1 before and after washing with diethylether

<table>
<thead>
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<td>92.4</td>
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<td>89.9</td>
<td>5.7</td>
<td>1.4</td>
<td>1.4</td>
<td>94.4</td>
</tr>
</tbody>
</table>

the flame could reduce the extent of chain degradation and this is indeed believed to be the case. Instead of volatilisation of small, oxidised fragments after extensive chain degradation, reduced chain scission resulting in relatively large, non-volatile fragments is thought to occur. Through their large size, these fragments would lack volatility and thus be retained on the surface during the treatment process and leading to a greater depth of
oxidation (Chapter 13). However, as they would contain many polar functional groups, these large fragments would still be soluble in solvent, and therefore a change in surface composition would be expected upon polar solvent washing. Thus, the removal of polar functionality suggested that chain scission did occur upon sulfur dioxide flame treatment, however the levels of chain scission were thought to be much reduced.

B) Oxygen Rich Flame Conditions

Tables 12.5 and 12.6 show the surface elemental compositions and advancing water contact angle data before and after diethylether washing for polyethylene and polypropylene respectively flame treated at various sulfur dioxide flow rates using a total flow rate of 30.5 l min\(^{-1}\) at an air-to-natural gas ratio of 11.8:1. In contrast to the reducing flame conditions, minimal differences in the surface compositions were found upon washing of both polymers, suggesting that oxidised scission products were not present. The reduced presence of activated species through efficient oxidation of the fuel/sulfur dioxide mixture could have been responsible for the lack of scission fragments.

12.2.5 Surface Free Energy

Advancing water and diiodomethane contact angles were used to estimate the surface energies according to the method of Owens-Wendt.

The effects of flame intensity at a constant sulfur dioxide flow rate of 40 ml min\(^{-1}\) and air-to-natural gas ratio of 10.3:1 on the surface energy of both polymers are shown in Table 12.7. Introduction of oxygen, sulfur and nitrogen functional groups into the surfaces of both polyethylene and polypropylene increased interfacial polar interactions and consequently the estimated polar components of surface free energy. The estimated polar components of both polymer surfaces rapidly reached constant values at total flow rates where the advancing water contact angles reached plateau values. As has been seen on previous occasions, the higher polar group concentrations resulted in better water wettabilities and estimated polar components for polyethylene which were higher, and in some instances double, than those for polypropylene. The estimated dispersion components were unaffected by variations in flame intensity. As a result, total surface energies of ~50 mJ m\(^{-2}\) for polyethylene and ~40 mJ m\(^{-2}\) for polypropylene were readily
### Table 12.7 The effects of total flow rate on the surface energy of polyethylene and polypropylene after sulfur dioxide flame treatment; air-to-natural gas ratio 10.3:1, sulfur dioxide flow rate 40 ml min⁻¹

<table>
<thead>
<tr>
<th>TOTAL FLOW / l min⁻¹</th>
<th>SURFACE FREE ENERGY / mJ m⁻²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>POLYETHYLENE</td>
</tr>
<tr>
<td></td>
<td>(\gamma_s^p)</td>
</tr>
<tr>
<td>untreated</td>
<td>0</td>
</tr>
<tr>
<td>20</td>
<td>3.5</td>
</tr>
<tr>
<td>25</td>
<td>20.0</td>
</tr>
<tr>
<td>30</td>
<td>23.3</td>
</tr>
<tr>
<td>35</td>
<td>25.7</td>
</tr>
<tr>
<td>45</td>
<td>24.8</td>
</tr>
<tr>
<td>55</td>
<td>24.5</td>
</tr>
</tbody>
</table>

### Table 12.8 The effects of sulfur dioxide flow rate on the surface energy of polyethylene and polypropylene; total flow rate 30.5 l min⁻¹, air-to-natural gas ratio 8:1 and 11.8:1

<table>
<thead>
<tr>
<th>SO₂ FLOW / ml min⁻¹</th>
<th>SURFACE FREE ENERGY / mJ m⁻²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>POLYETHYLENE</td>
</tr>
<tr>
<td></td>
<td>(\gamma_s^p)</td>
</tr>
<tr>
<td>untreated</td>
<td>0</td>
</tr>
<tr>
<td>air:gas 8:1</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>40</td>
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<td>70</td>
</tr>
<tr>
<td></td>
<td>200</td>
</tr>
<tr>
<td>air:gas 11.8:1</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>30</td>
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<td></td>
<td>40</td>
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<tr>
<td></td>
<td>70</td>
</tr>
<tr>
<td></td>
<td>200</td>
</tr>
</tbody>
</table>
achieved, these being $\sim 10 \text{ mJ m}^{-2}$ greater than those obtained after conventional flame treatment under the same flame intensities and stoichiometry.

Table 12.8 shows the effects of sulfur dioxide flow rate on the surface energy of both polymers flame treated at a total flow rate of 30.5 l min$^{-1}$ using air-to-natural gas ratios of 8:1 and 11.8:1. Although there were slight differences in the surface compositions after treatment of polyethylene at the two air-to-natural gas ratios, the advancing water and diiodomethane contact angles were similar suggesting similar surface energies. Again, total surface energies of $\sim 50 \text{ mJ m}^{-2}$ were readily achieved under both sets of flame conditions. Although the surface energies of polyethylene were significantly improved by introduction of sulfur dioxide, they did not match those obtained by sulfur corona treatment where total surface energies of $\sim 70 \text{ mJ m}^{-2}$ were estimated.

Introduction of functionality into the polypropylene surfaces also resulted increased interfacial polar interactions, increasing the estimated polar components. The polar component rapidly reached a plateau level at which the advancing water contact angle also reached a plateau after treatment at the 8:1 air-to-natural gas ratio. This produced total surface energies of $\sim 40 \text{ mJ m}^{-2}$. After treatment under oxidising flame conditions, the polar components were not as high as those estimated after treatment under reducing flame conditions producing total surface energies of just below $40 \text{ mJ m}^{-2}$. The estimated dispersion components after treatment under both sets of flame conditions were reasonably constant with sulfur dioxide flow rate. This compared to $>50 \text{ mJ m}^{-2}$ after sulfur dioxide corona treatment.

Thus, for the sulfur dioxide flame treatment of both polyethylene and polypropylene, the greatest improvements in surface activation were produced using a total flow rate of $\sim 35 \text{ l min}^{-1}$ under reducing flame conditions and at a sulfur dioxide flow rate of $\sim 40 \text{ ml min}^{-1}$. However, for the purposes of practical adhesion, chain scission under reducing flame conditions should be considered. Higher surface energies were estimated for both polymers after sulfur dioxide corona treatment, although scission fragments should again be seriously considered. The Owens-Wendt and Wu methods both agreed reasonably well in the trends indicated for polar components, dispersion components and total surface energies for both polymers under all the conditions investigated.
Chapter 13 Oxidation Depth Profiling

13.1 Introduction

The surface sensitivity of the XPS technique can be changed by varying the angle at which electrons are collected from the sample surface, known as the take-off angle, $\theta$. This technique is called variable take-off angle XPS and was used to obtain information on the depth distribution oxygen atoms in the flame and corona treated polymer surfaces. The ratio of the O1s/O2s photoelectron peaks was also used to study the depth of oxidation, this data being obtained from high resolution O1s and O2s photoelectron spectra using the Scienta ESCA300 instrument. In both cases, models assuming an exponential decay in the oxygen concentration were developed. Information on the depth distribution of oxygen atoms may also be deduced from the O1s inelastic background, this method being used to qualitatively confirm oxidation depth estimates obtained from variable take-off angle XPS measurements.

13.2 Depths of Oxidation Using Variable Take-off Angle XPS

Surface treatment produces an oxidised surface layer. Assuming that the inelastic mean free paths $^{111}$ (IMFP, $\lambda$) of the C1s ($\lambda_c = 40.5\text{Å}$) and the O1s ($\lambda_o = 35.7\text{Å}$) photoelectrons are constant within the XPS sampling depth, a simple exponential model can be used to estimate the thickness of the oxidised layer, shown schematically in Figure 13.1.

Thus, the intensity ($I_0$) of the O1s photoelectron peak, given an exponential decay in concentration with depth, can be written as follows, equation 13.1,

$$I_0 \propto \sigma_0 L T D \chi \int_0^\infty C_o \exp \left(-k x\right) \exp \left(-\frac{x}{\lambda_o \sin \theta}\right) \, dx \quad \text{eqn. 13.1}$$

Combining the exponential factors, equation 13.2 is obtained,

$$I_0 \propto \sigma_0 L T D \chi C_o \int_0^\infty \exp \left(-\frac{k \lambda_o \sin \theta + 1}{\lambda_o \sin \theta}\right) x \, dx \quad \text{eqn. 13.2}$$

Integrating equation 13.2 over depth $x = 0$ to depth $x = \infty$ gives equation 13.3,
Figure 13.1 Schematic diagram of a simple exponential decay model for oxygen concentration with depth

\[
I_0 \approx \sigma_0 L T D \chi C_0 \left[ \left( \frac{\lambda_0 \sin \theta}{k \lambda_0 \sin \theta + 1} \right) \exp \left( \frac{k \lambda_0 \sin \theta + 1}{\lambda_0 \sin \theta} \right) \right]_0 \quad \text{eqn. 13.3}
\]

By defining \( S_0 = \sigma_0 L T D \chi \lambda_0 \) and by evaluating the integral \( 13.3 \) gives equation \( 13.4 \),

\[
I_0 \approx \frac{S_0}{\lambda_0} C_0 \left( \frac{\lambda_0 \sin \theta}{k \lambda_0 \sin \theta + 1} \right) \quad \text{eqn. 13.4}
\]

where \( L, T, D \) and \( \chi \) were defined in section 4.1.4, \( \lambda_0 \), \( \sigma_0 \) and \( S_0 \) are the inelastic mean free path, the photoemission cross-section and the relative sensitivity factor for the O1s photoelectrons respectively, \( x \) is the depth into the polymer surface, \( \theta \) is the take-off angle with respect to the sample surface and \( C_0 \) is the oxygen concentration at the outer monolayer. Here, \( k \) is a pre-exponential factor whose inverse gives the depth at which the oxygen concentration falls to \( e^{-1} \) of the value at the surface, that is \( C_0 e^{-1} \). Therefore, comparing values of \( 1/k \) for different samples provides the depth distribution information. Contact angle measurements are most sensitive to the outer monolayer of surface,
therefore estimation of $C_O$ may allow a correlation with work of adhesion to be found.

As for the O1s photoelectrons, the peak intensity for the C1s ($I_C$) photoelectrons can be written as follows, equation 13.5,

$$I_C \propto \sigma_C \lambda T D \chi \int_0^\infty C_c \exp \left( -\frac{x}{\lambda_c \sin \theta} \right) dx$$  eqn. 13.5

where $C_C$ is the carbon concentration at the outer monolayer. Now, if the oxygen concentration is $C_O$ and assuming an exponential decay in its concentration with depth, $x$, the carbon concentration, $C_C$, may be calculated using equation 13.6,

$$C_C = 100 - f C_O \exp(-k x)$$  eqn. 13.6

The factor, $f$, takes into account non-carbon and non-oxygen atoms detected on the surfaces, this being a requirement for sulfur dioxide corona and flame treatments. Thus $f$ is given by equation 13.7,

$$f = \frac{\sum[\text{non-C}] \text{atoms}}{[O] \text{atoms}}$$  eqn. 13.7

Clearly $f = 1$ when carbon and oxygen only are present on the surface. Assuming that the sulfur and nitrogen atoms have the same depth distribution as the oxygen atoms, surface compositions from sulfur dioxide treatments resulted in average values of $f=1.40$ and $f=1.60$ for polyethylene and polypropylene respectively. Substitution of equation 13.6 into equation 13.5 produces equation 13.8,

$$I_C \propto \sigma_C \lambda T D \chi \int_0^\infty (100 - f C_O \exp(-k x)) \exp \left( -\frac{x}{\lambda_c \sin \theta} \right) dx$$  eqn. 13.8

Defining $S_C = \sigma_C \lambda T D \chi \lambda_C$, followed by simplifying the exponential factors and integrating between depth $x = 0$ and depth $x = \infty$, equation 13.9 is produced,

$$I_C \propto \frac{S_C}{\lambda_c} \left( 100 \lambda_c \sin \theta - f C_O \left( \frac{\lambda_c \sin \theta}{k \lambda_c \sin \theta + 1} \right) \right)$$  eqn. 13.9
where $\lambda_C$ and $S_C$ are the inelastic mean free path and the relative sensitivity factor for the C1s photoelectrons respectively. Now, the relative carbon and oxygen concentrations may be calculated using equation 13.10,

$$[C] = \frac{I_C/S_C}{\Sigma I_i/S_i} \quad [O] = \frac{I_O/S_O}{\Sigma I_i/S_i} \quad \text{eqn. 13.10}$$

Thus if an average value of $\lambda = (\lambda_C + \lambda_O)/2 = 39.7$ Å is taken for the inelastic mean free paths of the O1s and C1s photoelectrons, then a relationship between the $[C]/[O]$ ratio and $\sin \theta$ may be found from the equations shown above, equation 13.11,

$$\frac{[C]}{[O]} = 100 \frac{k \lambda \sin \theta}{C_O} + \frac{100}{C_O} - f \quad \text{eqn. 13.11}$$

Therefore if the assumed exponential decay model approximates to the true oxygen depth profile, the $[C]/[O]$ ratios obtained from XPS measurements when plotted against $\sin \theta$ should produce straight lines with,

$$\text{intercept} = \frac{100}{C_O} - f \quad \text{gradient} = \frac{100 k \lambda}{C_O}$$

from which the values of $C_O$ and $1/k$ may be found.

Variable take-off angle XPS was used to study the oxygen depth profiles produced in polyethylene and polypropylene by flame and corona treatment with and without reactive gases. For flame treatment, a total flow rate of 30.5 l min$^{-1}$ and an air-to-natural gas ratio of 11.8:1 (8:1 for ammonia flame treatment of polypropylene, see section 11.3) were used, while for corona treatment an intensity of 50 W was employed. For reactive gas treatments, an $\text{SO}_2/\text{NH}_3$ flow rate of 40 ml min$^{-1}$ was used. Surface compositions were obtained at take-off angles, $\theta$, of 20°, 30°, 45° and 90° with respect to the sample surface, thus the lowest take-off angle provided the most surface sensitive measurement. The surface composition measurements were repeated and average values taken in order to calculate the $[C]/[O]$. Errors in the gradients and y-intercepts were calculated $^{221}$, and the upper and lower limits were used to estimate the errors in $1/k$ and $C_O$. 

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The typical behaviour of [C]/[O] ratios with sin θ are shown in Figures 13.2 (a) and (b), these being for polyethylene and polypropylene respectively corona treated at a 50W intensity. A sulfur dioxide flow rate of 40 ml min⁻¹ was used when required during both treatments. A slight increase in the [C]/[O] ratio was found in the repeat surface composition measurements for some of the treated samples, this being attributed to X-ray beam damage. The conventionally flame and corona treated surfaces appeared to be most affected by X-ray beam damage, especially flame treated polypropylene. In this instance only the initial set of surface composition measurements were employed. Those surfaces treated using an ammonia corona or flame were apparently less affected by such damage, while only minimal changes in the [C]/[O] were measured on repeat analysis for sulfur dioxide treatments of both polymers. Generally, treated polypropylene surfaces were more prone to X-ray degradation than similarly treated polyethylene surfaces.

Table 13.1 gives the estimated depths of oxidation, 1/k, the estimated oxygen concentrations at the very outer surface, C₀, and their approximate errors for treated polyethylene and polypropylene respectively. Within the estimated errors, the calculations showed that polyethylene and polypropylene were generally oxidised to similar depths. However, polypropylene was oxidised to a greater depth than polyethylene after sulfur dioxide corona treatment where almost double the oxygen concentration was incorporated into the polypropylene surfaces than into the polyethylene surfaces. Given this difference in oxygen concentration, a higher oxidation depth for polypropylene was therefore not unreasonable. Depths of oxidation were significantly greater after sulfur dioxide treatments than conventional air or ammonia treatments and may have been due to a reduction in the extent of chain scission upon using sulfur dioxide, resulting in the retention of functionality. Rather than oxygen functional groups being incorporated into low molecular weight material and consequently being lost through volatilisation, they could instead be retained on the surface. Washing with diethylether suggested that this could have been generally true for both corona and flame treatments. Although ammonia treatments produced surfaces similar to those produced by conventional treatment, they appeared to be oxidised to a greater depth. This may also have been through retention of scission fragments at the treated surfaces. The depths of oxidation resulting from both corona and flame treatments appeared to be similar within the estimated errors, following
Figure 13.2 [C]/[O] ratio versus the sine of the take-off angle from ARXPS measurements on (a) polyethylene (b) polypropylene treated at a of 50W corona intensity and sulfur dioxide flow rate of 40 ml min\(^{-1}\) when required
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<table>
<thead>
<tr>
<th>TREATMENT POLYMER</th>
<th>Co / %At.</th>
<th>± error / %At.</th>
<th>1/k / Å</th>
<th>± error / Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE air flame</td>
<td>21.8</td>
<td>2.1</td>
<td>24.1</td>
<td>2.6</td>
</tr>
<tr>
<td>PP air flame</td>
<td>17.3</td>
<td>2.1</td>
<td>18.2</td>
<td>7.2</td>
</tr>
<tr>
<td>PE NH3 flame</td>
<td>18.0</td>
<td>5.0</td>
<td>39.9</td>
<td>3.0</td>
</tr>
<tr>
<td>PP NH3 flame</td>
<td>9.8</td>
<td>3.0</td>
<td>26.5</td>
<td>3.1</td>
</tr>
<tr>
<td>PE SO2 flame</td>
<td>21.6</td>
<td>1.0</td>
<td>118.4</td>
<td>20.4</td>
</tr>
<tr>
<td>PP SO2 flame</td>
<td>19.2</td>
<td>3.1</td>
<td>113.4</td>
<td>25.4</td>
</tr>
<tr>
<td>PE air corona</td>
<td>25.8</td>
<td>9.1</td>
<td>17.1</td>
<td>6.3</td>
</tr>
<tr>
<td>PP air corona</td>
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<td>10.0</td>
<td>20.4</td>
<td>8.2</td>
</tr>
<tr>
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<td>57.4</td>
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<td>3.1</td>
<td>50.8</td>
<td>9.4</td>
</tr>
<tr>
<td>PE SO2 corona</td>
<td>21.6</td>
<td>3.2</td>
<td>90.0</td>
<td>22.4</td>
</tr>
<tr>
<td>PP SO2 corona</td>
<td>17.3</td>
<td>5.0</td>
<td>117.4</td>
<td>26.4</td>
</tr>
</tbody>
</table>

Table 13.1 Depth information obtained from variable take-off angle XPS measurements for polyethylene and polypropylene flame and corona treated under various conditions

The general trend,

SO2 treatment > NH3 treatment > conventional treatment

Flame and corona treatment both with and without reactive gas produced surfaces with similar Co values of ~20 %At. The exceptions were polypropylene surfaces after ammonia treatment, which had Co values of ~10 %At., half the values estimated for the other treatments. This was surprising as the water wettabilities of the ammonia treated surfaces were similar to those resulting from conventional air flame and corona treatments. The reasons for this were unclear, however the presence of ammonia may have affected the chemistry of the treatment processes in some way. Given the higher oxygen concentrations introduced by the sulfur dioxide treatments, Co values similar to the other treatments was unexpected. However, these lower than expected estimates probably
resulted from the much greater depths of oxidation so that the oxygen functional groups were distributed over whole of this depth, resulting in less oxygen functionality at the outer monolayer.

Generally for a given treatment level, more oxygen was consistently detected on polyethylene surfaces over the whole XPS sampling depth than on polypropylene surfaces. This difference in oxygen concentrations usually resulted in at least a 20 mJ m\(^{-2}\) difference in the work of adhesion (calculated from advancing water contact angles) between the two polymers. However, the estimated \(C_0\) values were only slightly lower for polypropylene than for polyethylene indicating that only a small difference in the oxygen concentration at the outer monolayer makes a great difference in the achievable level of surface wettability. Good surface wettability is often equated with high surface oxygen concentrations obtained from XPS measurements. However, polar functional groups at a depth of several nanometers within the surface, which are detected by XPS, do not contribute to the wetting properties of that surface so that the above assumption is clearly incorrect. The presently employed mathematical depth model exemplified this point and also provided an estimate for the amount of oxygen required at the outer monolayer which is required to improve the surface wetting characteristics from reasonable to good.

Thus, the model developed for use with variable take-off angle XPS was reasonably successful in providing information on the oxidation depths of corona and flame treated polyolefins. A general trend on the relative depths of oxidation produced from the reactive gas treatments was revealed. The estimated oxygen concentration at the outer monolayer, \(C_0\), provided an explanation on the better surface wettabilities of polyethylene compared to polypropylene. The requirement for a high oxygen concentration or strong interfacial interactions at the outer monolayer of surface in order to promote good wetting was also indicated. However, the absolute values of 1/\(k\) and \(C_0\) can only be regarded as approximate given the assumptions made in the derivations, for example the value of inelastic mean free paths for the O1s and C1s photoelectrons.

13.3 Depths of Oxidation Using O1s/O2s Photoelectron Peak Ratios

Most atoms have more than one core electron orbital, and consequently many atoms give
rise to multiple photoelectron peaks. Electrons in different core orbitals have different binding energies, therefore the photoelectrons emerging from them will have different inelastic mean free paths and consequently different sampling depths.

Information on the depth distribution of oxygen was obtained from O1s and O2s peak intensities from XP spectra collected using the Scienta ESCA300. As in section 13.2, an exponential decay in oxygen concentration as a function of depth was assumed. Thus an expression for the intensity of the O1s photoelectron peak can be written, equation 13.12,

\[ I_{O1s} \propto \sigma_{O1s} T_{O1s} L D \chi \int_{0}^{\infty} C_{O} \exp(-kx) \exp \left( -\frac{x}{\lambda_{O1s} \sin \theta} \right) dx \]  

where \( \theta \), \( L \), \( D \), \( \chi \), \( x \), and \( k \) are as defined previously, \( \sigma_{O1s} \), \( T_{O1s} \) and \( \lambda_{O1s} \) are the photoemission cross-section, transmission factor and inelastic mean free path for the O1s photoelectrons respectively. Thus,

\[ I_{O1s} \propto \sigma_{O1s} T_{O1s} L D \chi C_{O} \int_{0}^{\infty} \exp \left( -\frac{k \lambda_{O1s} \sin \theta + 1}{\lambda_{O1s} \sin \theta} \right) x \, dx \]  

integration of equation 13.13 between depth \( x = 0 \) and depth \( x = \infty \) gives equation 13.14,

\[ I_{O1s} \propto \sigma_{O1s} T_{O1s} L D \chi C_{O} \left( \frac{\lambda_{O1s} \sin \theta}{k \lambda_{O1s} \sin \theta + 1} \right) \]  

An expression for the intensity of the O2s photoelectron peak, \( I_{O2s} \), may also be written in an analogous manner, equation 13.15,

\[ I_{O2s} \propto \sigma_{O2s} T_{O2s} L D \chi C_{O} \left( \frac{\lambda_{O2s} \sin \theta}{k \lambda_{O2s} \sin \theta + 1} \right) \]  

where \( \sigma_{O2s} \), \( T_{O2s} \) and \( \lambda_{O2s} \) are the photoemission cross-section, transmission factor and inelastic mean free path for the O2s photoelectrons respectively. Thus, a relationship between the \( I_{O1s}/I_{O2s} \) ratio and \( 1/k \) may be obtained by division of equation 13.14 by equation 13.15, resulting in equation 13.16,

\[ \frac{I_{O1s}}{I_{O2s}} = \frac{\sigma_{O1s} T_{O1s} \lambda_{O1s} (k \lambda_{O2s} \sin \theta + 1)}{\sigma_{O1s} T_{O1s} \lambda_{O2s} (k \lambda_{O1s} \sin \theta + 1)} \]
The $\chi$ terms cancel as it is the same for both the $O_{1s}$ and $O_{2s}$ orbitals; the $D$ terms cancel as the photoelectrons are retarded to the same constant kinetic energy prior to entering the energy analyser, so the detector efficiency is the same for both $O_{1s}$ and $O_{2s}$ photoelectrons; and there is no angular asymmetry in photoemission for $s$-orbitals. Therefore, by defining $P_1 = \sigma_{O_{1s}} T_{O_{1s}} \lambda_{O_{1s}}$ and $P_2 = \sigma_{O_{2s}} T_{O_{2s}} \lambda_{O_{2s}}$ and by rearranging equation 13.16, $1/k$ may be evaluated using equation 13.17,

$$\frac{1}{k} = \frac{I_{O_{1s}}\lambda_{O_{1s}}\sin \theta - I_{O_{2s}}\lambda_{O_{2s}}\sin \theta}{I_{O_{2s}}\lambda_{O_{1s}} - I_{O_{1s}}\lambda_{O_{2s}}}$$

From the literature, $\sigma_{O_{1s}} = 2.93$, $\sigma_{O_{2s}} = 0.1405$, $T_{O_{1s}} = 1.1$, $T_{O_{2s}} = 0.8$, $\lambda_{O_{1s}} = 35.7$ Å, $\lambda_{O_{2s}} = 46.8$ Å; with $\theta = 45^\circ$, $I_{O_{1s}}$ and $I_{O_{2s}}$ being measured.

Thus, this method was used to study the oxygen depth profiles produced in polyethylene and polypropylene by flame and corona treatment with and without reactive gases. For flame treatment a total flow rate of 30.5 l min$^{-1}$ and an air-to-natural gas ratio of 11.8:1 (8:1 for ammonia, see section 11.3) were used, while for corona treatment an intensity of 50 W was employed. A sulfur dioxide flow rate of 40 ml min$^{-1}$ was used when required. Figures 13.4 (a) and (b) show typical valence band spectra for polyethylene and polypropylene respectively after conventional and sulfur dioxide corona treatment at an intensity of 50 W, from which $O_{2s}$ peak intensities were measured. Upon air corona treatment the $O_{2s}$ photoelectron peaks were readily apparent in the valence band spectra for both polymers, although much of the original band structure was retained - this being in agreement with valence band studies on plasma treated polyethylene and polypropylene. However, upon sulfur dioxide corona treatment the valence band spectra were significantly changed, this change probably being due to the chemical bonding between sulfur/nitrogen and the carbon/oxygen at the treated polymer surfaces.

The $O_{1s}$ and $O_{2s}$ spectra were obtained consecutively under the same instrument conditions. Counts per sweep were computed and these values used to obtain the depth information. Instrument time did not allow analysis of ammonia flame and corona treated surfaces. Table 13.2 shows the intensities of the $O_{1s}$ and $O_{2s}$ photoelectron peaks and their ratio. The model developed for estimating oxidation depths from $O_{1s}/O_{2s}$ peak intensity ratios was unsuccessful, yielding unphysical results. In order to overcome this
Figure 13.4 Valence band spectra for corona treated (a) polyethylene and (b) polypropylene, corona intensity 50 W, SO$_2$ flow rate of 40 ml min$^{-1}$
Chapter 13 Oxidation Depth Profiling

<table>
<thead>
<tr>
<th>TREATMENT / POLYMER</th>
<th>I_{O1s} / counts</th>
<th>I_{O2s} / counts</th>
<th>I_{O1s} / I_{O2s}</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE air flame</td>
<td>52,334.3</td>
<td>558.2</td>
<td>93.8</td>
</tr>
<tr>
<td>PP air flame</td>
<td>15,618.3</td>
<td>163.7</td>
<td>95.4</td>
</tr>
<tr>
<td>PE SO2 flame</td>
<td>204,285.3</td>
<td>4,117.6</td>
<td>49.6</td>
</tr>
<tr>
<td>PP SO2 flame</td>
<td>248,794.7</td>
<td>5,578.6</td>
<td>44.6</td>
</tr>
<tr>
<td>PE air corona</td>
<td>161,734.3</td>
<td>1,752.2</td>
<td>93.7</td>
</tr>
<tr>
<td>PP air corona</td>
<td>44,513.2</td>
<td>492.0</td>
<td>90.5</td>
</tr>
<tr>
<td>PE SO2 corona</td>
<td>303,539.4</td>
<td>7,403.4</td>
<td>41.0</td>
</tr>
<tr>
<td>PP SO2 corona</td>
<td>248,794.7</td>
<td>5,578.6</td>
<td>44.6</td>
</tr>
</tbody>
</table>

Table 13.2 Peak intensities, their ratios and depth estimates from the O1s and O2s photoelectrons

problem with this mathematical model, experimentally determined relative sensitivity factors for the O1s and O2s photoelectrons respectively could be used. However, instrument time did not allow their determination. Additionally, more accurate estimates for the respective photoelectron transmission constants could improve this method.

The ratio of intensities still provided some information on the depths of oxidation. The O2s photoelectrons emanate from ~30 % deeper than the O1s photoelectrons (section 4.1.4.2), therefore a low O1s/O2s ratio indicates deep oxidation while a high O1s/O2s ratio indicates shallow oxidation. These results confirmed that sulfur dioxide treatment produced surfaces which were oxidised more deeply than conventional treatments. The depths of oxidation resulting from flame and corona treatments were found to be similar. The similar O1s/O2s ratios for both polyethylene and polypropylene suggested that they were oxidised to similar depths also. These observations were in agreement with variable take-off angle XPS.

13.4 Depths of Oxidation Using the O1s Inelastic Photoelectron Background Signal

Depth information may be obtained by examining the inelastic photoelectron background
signal towards the high binding energy side of a photoelectron peak. In the present study, this method for probing elemental depth distributions was used qualitatively to confirm the depths of oxidation estimated from variable take-off angle XPS.

Polyethylene and polypropylene surfaces were corona treated using an intensity of 50 W with an \( \text{SO}_2/\text{NH}_3 \) flow rate of 40 ml min\(^{-1} \) when required. The preceding chapters have shown that treatment under these respective conditions produce surfaces with different surface oxygen concentrations. Therefore, to enable comparisons of the inelastic photoelectron background signals to be made, the peak heights were normalised to the full scale on the y-axis. Figures 13.4 (a) and (b) show the normalised O1s inelastic photoelectron background signals for appropriately corona treated polyethylene and polypropylene respectively. For the respective polymers surface treated with a conventional air or ammonia corona, the inelastic photoelectron background signals on the high binding energy side of the O1s photoelectron peak returned to almost the background level prior to the peak. Also, the background profiles produced by both types of treatment were similar. These observations indicated that the depths of oxidation produced upon air and ammonia corona treatment were relatively shallow and of similar absolute magnitudes. In contrast, the inelastic photoelectron backgrounds for the polymers treated with a sulfur dioxide corona increased after the peak and then reached a plateau level. These observations suggested that sulfur dioxide corona treatment produced more deeply oxidised surfaces.

The photoelectron peak heights from the flame treated polymers were normalised in the same way as for the peak heights from the corona treated polymers. Figures 13.5 (a) and (b) show the normalised O1s inelastic photoelectron background signals for polyethylene and polypropylene respectively flame treated with and without reactive gases. A total flow rate of 30.5\( \text{ l min}^{-1} \) at an air-to-natural gas ratio of 11.8:1 (8:1 for ammonia, see section 11.3) were used with an \( \text{SO}_2/\text{NH}_3 \) flow rate of 40 ml min\(^{-1} \) when required. For the conventional air and ammonia flame treatments, the low signal-to-noise ratio resulting from slightly lower oxygen concentrations made interpretation of the inelastic photoelectron background difficult. Although less convincing than for similar corona treatments, the depths of oxidation appeared to be reasonably shallow and of similar magnitudes for the two treatments. Again the depths of oxidation appeared to be greater
Figure 13.4 The normalised O1s inelastic photoelectron background signals for (a) polyethylene and (b) polypropylene corona treated under various conditions; corona intensity 50 W, $\text{SO}_2/\text{NH}_3$ flow rate 40 ml min$^{-1}$.
Figure 13.5 The normalised O1s inelastic photoelectron background signals for (a) polyethylene and (b) polypropylene flame treated under various conditions; total flow rate 30.5 l min\(^{-1}\), air-to-natural gas ratio 11.8:1 (8:1 NH\(_3\)), SO\(_2\)/NH\(_3\) flow rate 40 ml min\(^{-1}\).
for sulfur dioxide treatments. These results were in broad agreement with variable take-off angle XPS. Thus, this method of inspecting the inelastic photoelectron background signals indicated that the depths of oxidation followed the general trend,

$$\text{SO}_2 \text{ treatment} > \text{NH}_3 \text{ treatment} = \text{conventional treatment}$$

Although no measure of the absolute depths could be made from this method, given its approximate nature the overall trends observed for the various flame and corona treatments were in reasonable agreement with variable take-off angle XPS measurements. Unfortunately, the background signals did not allow meaningful comparison between the relative oxidation depths for the two polymer types to be made, and so no conclusions could be drawn on this matter.
PART IV SUMMARY

Chapter 14 Comparison Between Treatments

14.1 Comparison of Industrial Scale and Laboratory Scale Corona Treatments

The effects of corona intensity using an industrial treatment procedure and a laboratory treatment procedure were investigated. The surfaces of both polymers were modified by the incorporation of oxygen only after both industrial and laboratory scale corona treatment. After both treatments, the oxygen concentration increased with corona intensity. Results were similar for both methods with the possible exception of the low energy inputs where laboratory scale treatment resulted in slightly better surface wettabilities for both polymers. Otherwise for a given energy input by each treatment, similar water contact angles were found on both polymers. For both types of treatment, the work of adhesion with water showed signs of reaching a plateau with oxygen concentration, suggesting that for both treatments more sub-surface oxidation was occurring at higher corona intensities.

The presence of significant quantities of scission fragments was indicated after both laboratory and industrial treatments, with the industrially treated surfaces generally showing the greatest percentage change in surface oxygen concentration after diethylether washing. After solvent washing, the water contact angles on laboratory and industrially treated polypropylene approached those of the untreated film, while polyethylene retained more water wettability after laboratory treatment than industrial treatment.

High resolution XPS showed that similar functional groups were incorporated into the treated polymer surfaces by both treatments. Chemical derivatisation showed that for polypropylene, the hydroxyl group concentrations were similar after both treatments while for polyethylene approximately double the hydroxyl group concentration was found after laboratory treatment than after industrial treatment.

Although polyethylene was oxidised to a greater extent, the laboratory scale treatment produced surfaces which had similar characteristics in terms of wettability to those
produced by industrial treatment. Therefore this similarity allowed confident employment of the laboratory treatment procedure to model an industrial treatment procedure for the development enhanced corona methods for future industrial use.

### 14.2 Comparison of Laboratory Scale Flame and Corona Treatments

The effects and relative efficiencies of flame intensity under oxidising conditions and corona intensity for the surface treatment of the two polymers are briefly compared.

Both treatments resulted in the incorporation of oxygen only into the surfaces of all the polymers. Indeed, similar oxygen concentrations were introduced into both polymers by the two treatments. A model for estimating oxygen depth distributions for use with variable take-off angle was developed. This model estimated that both flame and corona treatments resulted in oxidation depths in the range 15-25Å for both polymers. Surface oxidation also resulted in increased interfacial interactions as measured by water contact angles, although the water wettability was generally better for a given oxygen concentration after corona treatment. Accordingly, significantly higher polar components and total surface energies were estimated for both polymers upon corona treatment. Thus, corona treatment was found to more efficiently incorporate polar oxygen groups and also more successfully improve surface wettability than flame treatment.

The better water wettabilities of corona treated surfaces could have resulted from a different surface chemistry to that produced by flame treatment, thus high resolution XPS and chemical derivatisation techniques were employed to investigate any differences. High resolution XPS confirmed the presence of various carbon-oxygen functional groups on the surfaces of corona and flame treated surfaces, however quantification was not possible. Chemical derivatisation showed that on polyethylene the hydroxyl group concentration remained constant with treatment intensity at average values of ~3.6 %At. and ~3.0 %At. after flame and corona treatments respectively. The carboxylic acid group concentrations also remained constant with treatment intensity at average values of ~1.9 %At. and ~2.2 %At. after the two respective treatments. A novel method the techniques of chemical derivatisation and contact angle measurement developed for the estimation of functional group concentrations confirmed the hydroxyl and carboxylic acid group concentrations
estimated using chemical derivatisation/XPS for polyethylene. Thus, the surface chemistry for polyethylene after the two treatments was indicated to be very similar, however this could not be confirmed by comparing the percentage of the total incorporated oxygen present as each respective functional group. This suggested that the lower wettability of flame treated polyethylene probably was a consequence of heat induced functional group reorientation. For corona treated polypropylene, the hydroxyl and carboxylic acid functional groups remained constant at average values of \(-1.4\) %At. and \(1.0\) %At. respectively. However, upon flame treatment no carboxylic acid groups were indicated while their concentration remained at average values of \(-1.0\) %At. Therefore, it is suggested that the lower wettability of flame treated polypropylene was in part due to the lack of carboxylic acid groups with some contribution from heat induced functional group reorientation.

After flame treatment of both polymers, minimal changes in the oxygen concentrations were detected upon solvent washing indicating the presence of only minimal quantities of soluble scission products. However, after corona treatment significant removal of oxygen functionality from the surfaces of both polymers occurred upon solvent washing. There was clearly a difference in the levels of scission fragments remaining at the polymer surfaces after the two treatments, the difference being readily explained by the heat evolved during flame treatment. Minimal heat is produced by corona treatment thus allowing the retention of scission products, while these scission products are readily volatilised by “hot” flame treatment.

Overall, corona treatment was found to improve the surface wettability more than flame treatment. However, this desirable improvement should be viewed with caution given the potential problems associated with low molecular weight material.

14.3 Comparison of Conventional and Sulfur Dioxide Corona Treatments

Sulfur dioxide was introduced into the corona region during treatment with the aim of improving the surface wettabilities of polyethylene and polypropylene by the incorporation of surface sulfonic acid groups. Thus, the effects of corona treatment with and without the presence of sulfur dioxide were investigated in detail for the first time using several surface
sensitive techniques. Here, the results from conventional and sulfur dioxide treatments are briefly compared.

For both polymers, introduction of sulfur dioxide into the corona resulted in the incorporation of sulfur and nitrogen in addition to the oxygen found for conventional corona treatment. Less oxygen was incorporated into both polymers in the absence of sulfur dioxide. Surprisingly, more of each newly introduced atom was detected on polypropylene than polyethylene upon sulfur dioxide treatment, although polyethylene still retained superior wettability (see section 10.2.1 for explanation). This was in contrast to conventional corona treatment, and indeed all the other treatments investigated, where the converse was found.

At a sulfur dioxide flow rate of 40 ml min⁻¹ and corona intensity of 50 W, advancing and receding water contact angles of 37.5° and <10° respectively were measured for polyethylene, while for polypropylene they were 57.8° and 31.5° respectively. The water contact angles measured on conventionally treated polyethylene at the same intensity were 62.8° and 28.8° respectively, while for polypropylene they were 72.2° and 49.9° respectively. Comparison of these contact angles clearly showed that use of sulfur dioxide returned major improvements in the surface water wettability of both polymers. Indeed, the wettability of sulfur dioxide treated polypropylene resembled that of conventionally treated polyethylene. Although the estimated oxygen concentration at the outer surface by the exponential surface composition model was slightly lower after sulfur dioxide treatment, the better water wettabilities probably resulted from strong dipole-dipole interactions between the polar sulfur-oxygen groups and the polar water molecules. As a result of these strong interfacial polar interactions, polar components almost double those estimated for conventionally treated surfaces were found for sulfur dioxide treated surfaces. The sulfur dioxide treated surfaces were also found to possess some acidic character which the conventionally treated surfaces did not.

High resolution C1s XP spectra of both polymers indicated that minimal amounts of oxygen were directly bonded to carbon, this being consistent with the sulfur being present in a highly oxidised state as indicated by the high resolution S2p spectra. This was in contrast to conventional treatment where all the oxygen was necessarily bound to carbon,
being present in a variety of functional groups as indicated by high resolution XPS and chemical derivatisation. The presence of sulfur dioxide also resulted in significantly increased oxidation depths for both polymers, increasing by four to six times over conventional treatment. This was attributed to a reduction in the extent of chain scission as a consequence of the surface free radicals combining with the activated sulfur species present instead of undergoing degradation reactions. Indeed, this was indicated by a lower percentage of the incorporated oxygen being removed upon sulfur dioxide treatment than upon conventional treatment.

Overall, the surface wettabilities of both polymers after sulfur dioxide treatment were markedly better than after conventional treatment, indicating the potential of sulfur dioxide treatment for use in industrial applications.

14.4 Comparison of Conventional and Sulfur Dioxide Flame Treatments

The effects of introducing sulfur dioxide into the flame during treatment on polyolefin surfaces was investigated in detail for the first time using the surface sensitive techniques of XPS, FTIR-ATR, contact angle measurements and electron microscopy. Sulfur dioxide was introduced under various flame conditions with the aim of improving upon the surface properties achievable by conventional flame treatment. Here, the effects of flame intensity under stoichiometric conditions with and without sulfur dioxide are briefly compared.

In addition to the oxygen that was introduced into the surfaces of both polymers after conventional treatment, introduction of sulfur dioxide resulted in the incorporation of sulfur and nitrogen also. With increasing severity of conventional flame treatment, the oxygen concentrations increased gradually between 8.1-12.5 %At. for polyethylene and steadily between 1.6-6.6 %At. for polypropylene. Introduction of sulfur dioxide into the flame had a marked effect on oxygen incorporation for both polymers, its’ concentration levelling-off at a total flow rate of ~30 l min⁻¹. Oxygen concentrations of ~13 %At. and ~10 %At. were observed for polyethylene and polypropylene respectively. Clearly more oxygen was incorporated into both polymers upon introduction of sulfur dioxide at a medium flame intensity than was incorporated at the highest flame intensity studied in the absence of sulfur dioxide.
The presence of sulfur dioxide also significantly improved the surface wettability of both polymers, with advancing water contact angles of \( \sim 60^\circ \) being measured on polyethylene and \( \sim 78^\circ \) on polypropylene after treatment at a total flow rate of \( \sim 30 \, \text{l min}^{-1} \). The lowest water contact angles measured upon conventional treatment occurred at the highest flame intensity of \( 55 \, \text{l min}^{-1} \) and were \( 74.1^\circ \) and \( 85.8^\circ \) on polyethylene and polypropylene respectively. Indeed, the best wettability for polyethylene after conventional treatment was at the highest flame intensity under reducing conditions resulted, this being a contact angle \( \sim 63^\circ \). Clearly the sulfur dioxide treated polyolefin surfaces possessed better surface wettabilities than their conventionally treated counterparts, indeed the polar components for both polymers after sulfur dioxide treatment were at least double those after conventional treatment.

High resolution C1s XP spectra of both polymers after sulfur dioxide treatment indicated that minimal amounts of the oxygen were bonded directly to carbon. This correlating well with the high resolution S2p XP spectra which indicated that the sulfur was present in a highly oxidised form, that is significant amounts of oxygen were bound to it. This was in contrast to conventional treatment where all the oxygen was necessarily bound to carbon, being present in a variety of functional groups as indicated by high resolution XPS and chemical derivatisation. The presence of sulfur dioxide also resulted in increased oxidation depths for both polymers, increasing by at least a factor of four over conventional treatment.

The treatment of polyethylene appeared to be easier than the treatment of polypropylene for both treatments, with polyethylene also possessing some acidic character. Overall, the surface wettabilities of both polymers after sulfur dioxide treatment were better than after conventional treatment.

### 14.5 Overview

Table 14.1 shows the maximum and minimum oxygen, advancing and receding water contact angles for the two polymers after the various treatments investigated. The table includes data from flame treatment at an air-to-natural gas ratio of 11.8:1. Care should be taken in using this table as data was obtained from treatment under a variety of conditions,
Table 14.1 Summary of the minimum and maximum oxygen concentrations and water contact angles prior to diethylether washing for the polymers after the various treatments investigated for example flame intensity and reactive gas flow rate. However in terms of surface wettabilities, the data provided confirmation for a general order in the effectiveness of flame and corona treatment,

\[ \text{SO}_2 \text{ treatment} > \text{NH}_3 \text{ treatment} = \text{conventional treatment} \]

The table also showed that corona treatment more effectively improved surface wettability than flame treatment, with polyethylene being more effectively treated than polypropylene.

<table>
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<tr>
<th>TREATMENT / POLYMER</th>
<th>[O] (max) / %At.</th>
<th>[O] (min) / %At.</th>
<th>$\theta_{\text{adv}}$(max) / deg</th>
<th>$\theta_{\text{adv}}$(min) / deg</th>
<th>$\theta_{\text{rec}}$(max) / deg</th>
<th>$\theta_{\text{rec}}$(min) / deg</th>
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<tr>
<td>PE air flame</td>
<td>13.1</td>
<td>8.3</td>
<td>81.5</td>
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<td>90.8</td>
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<td>58.3</td>
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<td>92.3</td>
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<td>71.2</td>
<td>65.2</td>
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<td>7.3</td>
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<td>71.7</td>
<td>34.3</td>
<td>27.8</td>
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<td>PP NH$_3$ flame</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PE industrial corona</td>
<td>9.3</td>
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<td>-</td>
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<td>-</td>
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<td>PP air corona</td>
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<td>70.5</td>
<td>60.9</td>
<td>48.2</td>
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<tr>
<td>PE SO$_2$ corona</td>
<td>15.4</td>
<td>8.9</td>
<td>37.8</td>
<td>36.8</td>
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<td>&lt;10</td>
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<td>PP SO$_2$ corona</td>
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<tr>
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<td>77.2</td>
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Chapter 15 Conclusions

15.1 Chemical Derivatisation

Carboxylic acid groups were selectively derivatised to ~75% conversion using a mixture of 1,1,1-trifluoroethanol, pyridine and di-t-butylcarbodiimide. Selective derivatisation of carbonyl groups using 3-(trifluoromethyl)phenylhydrazine was unsuccessful, with significant reactions occurring with hydroxyl and carboxylic acid groups. This work clearly shows that there are problems with using hydrazine and its derivatives for selective derivatisation methods.

15.2 Conventional Industrial Corona Treatment

Both polymers were modified by oxygen incorporation only, leading to increased interfacial polar interactions with water. The greater oxygen concentrations and better water wettabilities showed that polyethylene was more easily activated than polypropylene. High resolution XPS indicated the presence of -C-O, -C=O and -COO species on both polymers, the presence of hydroxyl and carbonyl groups being confirmed by chemical derivatisation and FTIR-ATR respectively. Significant quantities of scission fragments were indicated, polypropylene apparently being more susceptible to chain degradation than polyethylene. This is clearly important as the presence of a layer of low cohesive strength could potentially reduce levels of adhesion. Maxima in the oxygen concentrations of both polymers after ~65 days of aging were found but wettability of both polymers decreased steadily with aging, this behaviour being attributed to the reorientation of functional groups within the modified layer.

15.3 Conventional Laboratory Corona Treatment

Surface modification of both polymers occurred through oxygen incorporation, surface functionalisation resulting in increased interfacial polar interactions with water. Industrial and laboratory corona treatments were found to be similar in the levels of activation produced on both polymers. High resolution XPS indicated the presence of multifunctional group environments on both polymer surfaces, the presence of -OH and -COOH groups also being confirmed by chemical derivatisation. Greater oxygen
concentrations and better water wettabilities showed that polyethylene was more easily activated than polypropylene. Significant quantities of scission fragments were indicated on both polymer surfaces although polypropylene was apparently more susceptible to chain degradation. Oxidation depths in the range 17-20 Å were estimated for both polymers. Both polymer surfaces were shown to possess some acidic character by “pH titration” measurements, this being attributed to the presence of carboxylic acid groups.

15.4 Sulfur Dioxide Corona Treatment

Sulfur and nitrogen in addition to oxygen were incorporated into the surfaces of both polymers resulting in significantly increased interfacial polar interactions with water. Higher concentrations of each element were introduced into polypropylene than polyethylene for a given SO2 flow rate, this being attributed to the inhibition of chain degradation reactions. However, polyethylene still maintained superior surface wettability. A possible mechanism for surface functionalisation leading to the formation of acid group and ammonium salt formation was identified. The presence of such groups probably resulted in the surface acidic character of both polyethylene and polypropylene. Imaging XPS indicated homogeneous elemental distributions over both polymer surfaces were. Oxidation depths of ~90Å and 120Å were estimated for polyethylene and polypropylene respectively, the increased depths being thought to result from retention of functional groups through reduced levels of chain degradation. Overall, introduction of SO2 produced significant improvements in the surface wettability of both polymers over conventional corona treatment.

15.5 Ammonia Corona Treatment

No nitrogen was detected on either polymer at any NH3 flow rate, with surface modification occurring by the incorporation of oxygen only. The lack of nitrogen was attributed to the rapid oxidation of ammonia into stable by-products. Interfacial interactions increased upon surface oxidation, the surface wettability of polyethylene being more easily improved than polypropylene. Both polymer surfaces possessed some acidic character as measured by receding contact angle “pH titration”. Oxidation depths of ~50-60Å were estimated for both polymers. Overall introduction of NH3 provided no
additional improvement in surface wettability over conventional corona treatment

15.6 Conventional Flame Treatment

Both polymers were modified by oxygen incorporation only, resulting in increased interfacial polar interactions with water. The greater oxygen concentrations and better water wettabilities under all the flame conditions studied showed that polyethylene was more easily activated than polypropylene. An optimum air-to-natural gas ratio of ~11:1 was found for the treatment of polyethylene, with the suggestion for a similar optimum for polypropylene. However, flame intensity variations at an air-to-natural gas ratio of 8:1 generally produced the best water wettabilities, this possibly resulting from the presence of more excited species through incomplete combustion of the fuel. High resolution XPS indicated the presence of various oxygen functional groups on the surfaces of both polymers, chemical derivatisation confirming the presence of -OH and -COOH groups on polyethylene and -OH groups on polypropylene. A new method for estimating -OH and -COOH group concentrations at the near surface using the techniques of chemical derivatisation and contact angle measurements was developed. The obtained estimates were in good agreement with those obtained from chemical derivatisation/XPS measurements for polyethylene. Conventional flame and corona treatments resulted in similar chemistries on polyethylene, although the wettabilities were better after the latter treatment. This lower water wettability was attributed to heat induced reorientation of functional groups. The two treatments resulted in significantly different surface wettabilities and chemistries on polypropylene. Thus the lower wettabilities were attributed to both surface chemistry and heat induced reorientation of functional groups. Minimal quantities of scission fragments were indicated on the surfaces either polymer, this being due to their volatilisation by the heat of the treatment. Similar oxidation depths of ~18-25Å were estimated for both polymers.

15.7 Sulfur Dioxide Flame Treatment

Sulfur and nitrogen in addition to oxygen were incorporated into the surfaces of both polymers, resulting in significantly increased interfacial polar interactions. Polyethylene was more readily activated than polypropylene. A similar surface chemistry to that
produced by SO₂ corona treatment was indicated. Imaging XPS suggested that a heterogeneous elemental distributions over both polymer surfaces, this being thought to occur through reorientation/migration of functional groups through the heat of the treatment. Polyethylene appeared to posses strong acidic surface character, while polypropylene showed no indication of possessing any surface acid/base characteristics. Similar oxidation depths of ~113-118 Å were estimated for both polymers, the increase over conventional treatment being attributed to a decrease in the extent of chain scission resulting from introduction of SO₂. Significant improvements in the wettabilities of both polymers over conventional flame treatment were produced by the presence of SO₂, although it was not as successful in improving the surface wettabilities of either polymer as SO₂ corona treatment. This was also thought to be due to reorientation of functional groups induced by the heat of the flame treatment.

15.8 Ammonia Flame Treatment

Surface modification of both polymers occurred by the incorporation of oxygen only, with no surface nitrogen being detected at any NH₃ flow rate. This lack of nitrogen was attributed rapid oxidation of the NH₃. Interfacial polar interactions increased as a consequence of surface functionalisation, the surface wettability of polyethylene being more readily improved than polypropylene. Similar oxidation depths of ~25-40Å were indicated for both polymers, with neither polymer showed any indication of possessing acidic/basic surface character. No further improvement in surface wettability over conventional flame treatment was achieved by introduction of NH₃.

15.9 Oxidation Depth Profiling

An exponential oxidation depth model for use with variable take-off angle XPS was successfully developed, providing the general trend for the oxidation depths produced by the various treatment of SO₂ > NH₃ > conventional. Analysis of O1s/O2s peak intensity ratios confirmed the oxidation depth trends provided by variable take-off angle XPS with inspection of O1s inelastic photoelectron background signals providing further confirmation of this trend. The contact angle method developed for the determination of -OH and -COOH group concentrations provided estimates for polyethylene that were in good agreement with variable take-off angle XPS measurements.
Recommendations for Further Work

1. Adhesion or ink testing of SO$_2$ flame/corona treated surfaces
2. Further investigation of sulfur dioxide treatment chemistry, for example by water washing to check for ammonium salt hydrolysis
3. Possible analysis of chain scission fragments by SSIMS, GCMS
4. Topographical analysis of the surfaces using AFM
5. Introduction of amine groups into the polymer surfaces, for example by introducing a layer of triethylamine in solution over the polymer surfaces immediately prior to treatment
6. Determination of relative sensitivity factors for the O1s and O2s photoelectrons for use with the oxidation depth model developed
References

<table>
<thead>
<tr>
<th>Reference</th>
<th>Author(s)</th>
<th>Journal/Patent No.</th>
<th>Date/Volume</th>
<th>Year</th>
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<tr>
<td>44.</td>
<td>C.W.Hurst, R.E.Schanzle</td>
<td>Modern Packaging 40 163</td>
<td>(1966)</td>
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Appendix A Solubilities and Structures of Additives

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<th>IRGANOX 1010</th>
<th>IRGANOX 1330</th>
<th>IRGAFO 168</th>
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<td>Propanone</td>
<td>47</td>
<td>18</td>
<td>10</td>
</tr>
<tr>
<td>Benzene</td>
<td>56</td>
<td>34</td>
<td>34</td>
</tr>
<tr>
<td>Trichloromethane</td>
<td>71</td>
<td>28</td>
<td>36</td>
</tr>
<tr>
<td>Ethylacetate</td>
<td>46</td>
<td>27</td>
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<tr>
<td>n-Hexane</td>
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<td>10</td>
<td>11</td>
</tr>
<tr>
<td>Methanol</td>
<td>1.0</td>
<td>3.0</td>
<td>&lt;0.01</td>
</tr>
</tbody>
</table>

Table A1 Solubilities of the additives used in the studied polymers, %w/w *

IRGANOX 1010

pentaerythritetetrakis-(3,5-diteriarybutyl-4-hydroxyphenylpropionate)

---

238
IRGAFOS 168
tris-(2,4-ditertiarybutylphenyl)phosphite

IRGANOX 1330
1,3,5-tris-(3'S'-ditertiarybutyl-4'-hydroxybenzyl)isocyanurate

where tBu represents the tertiarybutyl group:

Footnotes

* Technical Data, Ciba-Geigy
Appendix B Calibration of Flow Meters

Gas flow rates were measured with the use of area type flow meters, all of which had been calibrated for air at STP (273K, 1Atm) by the manufacturers. Pressurised cylinders delivered air, sulphur dioxide, and ammonia at 15, 20 and 5 psi apparent pressures respectively, while the natural gas was delivered at ~0.25 psi. Thus, under the experimental conditions employed, the specific weights of the gases used were different to those at which the flow meters had been calibrated by the manufacturers, thereby necessitating recalibration.

The meters were calibrated simply by measuring the time taken for the fluid being used, at the appropriate operating conditions, to displace a known quantity of water contained within a reagent bottle. The time taken to displace the water could easily be measured to an accuracy of 0.5 sec, thus making it simple to calculate the actual flow rate.

Neglecting fluid friction on the float surface, changes in fluid specific weight may be compensated for, equation A1

\[ q_a^2 r_a = q_b^2 r_b. \]  
\text{eqn. A1}

where \( r_a \) and \( r_b \) are the specific weights of the fluids and \( q_a \) and \( q_b \) are the true volumetric flow rates at the same scale reading under two different operating conditions, a and b respectively.

If a volumetric flow rate of \( q_o \) is required at STP (pressure \( P_o \), temperature \( T_o \)), the true volumetric flow rate is \( q_b \) at the operating conditions (pressure \( P_b \), temperature \( T_b \)) used. Thus, the flow rate \( q_b \) delivers an equivalent number of moles of fluid at a flow rate of \( q_o \) at STP. Assuming the ideal gas law, equations A2 and A3,

\[ q_b = \frac{n_b R T_b}{P_b t} \quad q_o = \frac{n_o R T_o}{P_o t} \quad \text{eqns. A2 and A3} \]

where \( R \) is the universal gas constant, and \( t \) is the flow time. Therefore, by equating moles of fluid flowing per unit time that is \( n_b/t=n_o/t \), an expression for \( q_b \) in terms \( q_o \) of may be derived, equation A4,

\[ q_b = \left( \frac{P_o T_b}{P_b T_o} \right) q_o \]  
\text{eqn. A4}
Equation A1 may now be used to calculate the true flow rate, $q_a$, at the manufacturers calibration conditions (air at STP), that would give the same meter reading when used under the experimental conditions (volumetric flow rate $q_b$, pressure $P_b$, temperature $T_b$). Substituting in equation A1 for $q_b$ results in equation A5,

$$q_a = \left( \frac{P_o T_b}{P_b T_o} \right) \sqrt{ \frac{T_b}{T_o} } q_o$$  \hspace{1cm} \text{eqn A5}

From manufacturers calibration charts, it is then possible to find the meter reading corresponding to $q_a$, and therefore to $q_b$.

Clearly, the measured flow rates must be corrected for the temperature (291K) and pressure (764 mm Hg) at the time of measurement such that they correspond to STP flow rates. Further correction must be made in order to account for the accumulation of water vapour, being proportional to its saturated vapour pressure (17 mm Hg), within the reagent bottle during the actual calibration procedure. This would result in a higher calculated flow rate. The calibration graphs for air and natural gas flow meters after application of the above corrections, figures A1 and A2, show excellent agreement with theoretical predictions indicating that flow rates calculated using the above procedures are reliable.

![Figure A1 Comparison of the measured and theoretical flow rates of air.](image)
Figure A2 Comparison of the measured and theoretical flow rates of natural gas.

Clearly, meters could not be calibrated for sulphur dioxide and ammonia due to their solubility in water. However, it was concluded that after successful calibration of the natural gas flow meter the mathematical corrections used were equally applicable to the reactive gases used.

Footnotes

Appendix C Selected Binding Energies of Oxygen, Sulfur and Nitrogen

Table C1 gives selected average binding energies for oxygen, sulfur and nitrogen. Table C2 gives the names and acronyms of the polymers used in Table C1.

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<th>COMPOUND / POLYMER</th>
<th>BINDING ENERGY / eV</th>
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<tr>
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<tr>
<td>N₂H₄SO₄</td>
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<tr>
<td>Na₂SO₄²⁻</td>
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</tr>
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<td>BzMeSO₂</td>
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<td>KAP⁺/ULTEM C(=O)NC(=O)</td>
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<td>PAAHC -NH₃⁺</td>
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<td>PVBTMAC -N(CH₃)₃⁺</td>
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<td>CTN C-O-C / C-O*-NO**2</td>
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* referenced to aromatic CH at C1s=284.70 eV

Table C1 Selected average binding energies for oxygen, sulfur and nitrogen

243
### Appendix C Selected Binding Energies of Oxygen, Sulfur and Nitrogen

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<th>ACRONYM</th>
<th>POLYMER NAME</th>
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<td>KAP</td>
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<td>PAAHC</td>
<td>poly(allylamine hydrochloride)</td>
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<td>PVBTMAC</td>
<td>poly(vinylbenzyltrimethylammonium chloride)</td>
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<td>PNS</td>
<td>poly(4-nitrostyrene)</td>
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<td>poly(hexamethylene sulfone)</td>
</tr>
<tr>
<td>PES</td>
<td>poly(ether sulfone)</td>
</tr>
<tr>
<td>PSS</td>
<td>poly(sodium 4-styrenesulfonate)</td>
</tr>
</tbody>
</table>

Table C2 Polymer names and acronyms

Footnotes


b *Handbook of X-Ray Photoelectron Spectroscopy*, Perkin-Elmer
List of Refereed Publications

“Corona Discharge Treatment of Polyolefins”
Presented at the 16th Annual Meeting of the Adhesion Society, Williamsburg 1993

“Vapour-phase Chemical Derivatisation of Surface Functional Groups by X-Ray Photoelectron Spectroscopy”

“Depth Profile Studies on Corona Discharge Treated Polyolefins Using X-Ray Photoelectron Spectroscopy”
R. P. Popat, I. Sutherland, in preparation

“Enhanced Corona Discharge Treatment of Polyolefins”
R. P. Popat, I. Sutherland, in preparation

List of Conference Proceedings

“Corona Discharge Treatment of Polyolefins”
I. Sutherland, R. P. Popat, D. M. Brewis, P. J. Mills, R. Calder
Proceedings of the 16th Annual Meeting of the Adhesion Society, Williamsburg 1993