

Degradation of polypropylene filtration membranes.

Author:

Olney, Katherine

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Degradation of Polypropylene Filtration Membranes

by
Katherine Olney

A thesis submitted in fulfillment of the requirements for the
degree of
Doctor of Philosophy

School of Chemical Engineering and Industrial Chemistry
University of New South Wales
Sydney, Australia

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Abstract

The general mechanism of oxidation of polypropylene has been widely discussed in the literature based on oxidation with gaseous oxygen. However, the oxidation behaviour of high surface area polypropylene by aqueous solutions has not been fully documented. Polypropylene hollow fibre membranes, extruded from Ziegler-Natta polypropylene, degrade during their service life by reactions with the components of aqueous feedstreams, the most aggressive and common being dissolved chlorine. This project investigates the mechanism of oxidative degradation of polypropylene membranes using hypochlorous acid (HOCl), a common disinfectant used in drinking water. The effect of HOCl concentration and temperature on the oxidation of the Ziegler-Natta polypropylene membranes was evaluated.

Additional polypropylene fibre membranes were extruded from metallocene polypropylene. The metallocene polymer was expected to contain significantly lower levels of impurities and oxidation products formed during polymerisation and processing, and have a narrower molecular weight distribution due to a highly controlled polymerisation process. The oxidation of these fibres by aqueous hypochlorous acid was also investigated.

Detection of changes in polypropylene fibres caused by oxidative degradation is difficult as small oxidation conversions may have significant effect on the fibre characteristics. Physical degradation was detected in the polypropylene fibre membranes by loss of mechanical strength. Characterisation of chemical degradation was carried out by differential scanning calorimetry for crystallinity and melting temperature; FT-IR for carbonyl, hydroperoxide and unsaturation content; gel permeation chromatography for molecular weight analysis and x-ray photoelectron spectroscopy for surface elemental analysis.

The presence of catalyst and metallic residues in commercial polypropylene has been suggested in the literature to influence polypropylene oxidation. The effect of several transition metal salts on the oxidation of polypropylene fibres in hypochlorous acid was investigated.

The commonly accepted theory of polypropylene oxidation involves generation of a tertiary radical by abstraction of the tertiary hydrogen atom on the polymer backbone by an existing free radical. A low molecular weight organic compound, 2,4-dimethylpentane, was used as a model for pure polypropylene to test the applicability of this theory for polypropylene fibre oxidation using hypochlorous acid. Analysis of the reacted organic compound was carried out by GC-MS.

Commercial polypropylene contains, among other impurities, a significant amount of unsaturated terminal carbon-carbon bonds which may preferentially oxidise. A low molecular weight organic compound, 2-methylbut-1-ene, was used as a model for the terminal unsaturated groups in polypropylene to determine whether or not oxidation of these groups occurs by hypochlorous acid.

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Chapter 1 Introduction

1.1 General Introduction

USF Filtration, formerly Memtec Ltd., polypropylene hollow fibre membranes are used for continuous microfiltration of aqueous systems in a variety of industrial and domestic applications. The polypropylene fibres undergo degradation during their service life after exposure to particular contents of certain feed streams, of which the most aggressive is dissolved chlorine. Degradation results in a loss of mechanical strength of the fibres. In industrial applications, degradation of the fibres is detected by loss of integrity of the membrane allowing passage of otherwise retained material into the filtrate. The degradation of USF Filtration polypropylene fibre membranes by dissolved chlorine causes accelerated loss of integrity of the filtration modules, usually inside the warranty period. This poses a significant economic problem as the degraded modules require replacement at the expense of USF Filtration. In this respect, an understanding of the degradation mechanism of PP fibre membranes by dissolved chlorine is necessary in order to minimise the rate of this reaction.

Degradation of polypropylene during its service life is caused by reactions of the polymer with oxygen. The mechanism of polypropylene degradation has been a subject of many publications^{1,2,3,4,5,6}. Generally these mechanisms are based on an auto-oxidative model proposed by Bolland and Gee^{7,8}. During oxidative degradation polypropylene undergoes chain scission, forming hydroperoxides by reaction with oxygen. These hydroperoxides decompose generating radicals which may then initiate oxidation at additional sites.

The mechanisms of oxidation of polypropylene oxidation have been proposed based on studies of bulk PP oxidised using gaseous oxygen^{1,2,3,4,5,6}. Very little work has been carried out using very high surface area polypropylene fibres,

however it has been observed that the increased surface area of PP powder increases the rate of oxidation compared to PP film⁹. Polypropylene oxidation in an aqueous environment has not been widely studied. Polypropylene fibres, commonly used as suture material in: dental applications; contact lens implantation and internal surgery^{10,11,12,13,14}, undergo oxidation when in contact with blood, enzymes, human tissue or incident UV light such as in the eye.

Detection of changes in polypropylene caused by oxidative degradation is difficult as small oxidation conversions may have significant effects on the polymer properties. Physical degradation is detected in polypropylene by loss of mechanical strength of the fibre^{15,16}. Chemical changes in the polymer may be detected by : differential scanning calorimetry (DSC) measuring changes in crystallinity and melting temperature¹⁷; infrared spectrometry (FT-IR) measuring carbonyl, hydroperoxide and unsaturation content^{18,19,20,21,22} ; gel permeation chromatography (GPC) for molecular weight analysis; and x-ray photoelectron spectroscopy (XPS) for surface elemental analysis ²³.

The mechanism of oxidative degradation of polypropylene depends on the presence of metallic residues from the polymerisation catalyst or from processing equipment^{24,25,26,27,28} , the presence of 'tie molecules' ^{29,30,31,32} and the amount of unsaturation^{33,34,35}. The rate of oxidation depends on temperature and concentration of oxidant, generally oxygen. Photochemically initiated oxidation depends on the presence of chromophoric groups which absorb UV radiation^{36,37,38,39,43, 40}.

Inhibition of polypropylene oxidation may achieved by using an appropriate antioxidant system. Much has been written in the literature about the stabilisation of polypropylene degraded thermally^{41,42}, mechanically⁴² and chemically⁴³.

Anti-oxidants may be classified as either primary or secondary, depending on the mechanism of stabilisation⁴⁴. Primary antioxidants are free radical scavengers which terminate chain reactions during oxidation. Secondary antioxidants destroy hydroperoxides which are the source of free radicals.

Traditional Ziegler-Natta catalyst technology for the production of polypropylene produces polymer with a broad molecular weight distribution containing metallic catalyst residues and oxidised polymer chain end-groups. In a process named viscosity breaking or 'vis-breaking', organic peroxides are used to modify the polymer molecular weight by cleavage of the high molecular weight chains. As a result, the high molecular weight tail is removed and a narrowing of the molecular weight distribution occurs⁴⁵. The resulting polymer may contain impurities due to unwanted oxidation of the polypropylene, terminal unsaturated carbon-carbon bonds at sites where chain cleavage occurred, and organic peroxide residues.

A new generation of catalysts for polyolefin polymerisation, metallocenes, remove the necessity for polymer visbreaking by their ability to engineer polymers to the desired molecular weight distribution. Like traditional Ziegler-Natta catalysts, metallocenes contain a metal atom, usually titanium or zirconium, which is linked to two rings of five carbon atoms and to two other groups⁴⁶. It is expected that metallocene catalysed polypropylene will contain less impurities and be more resistant to oxidation than Ziegler-Natta polypropylene.

1.2 Aim of the Thesis.

Aqueous chlorine degradation reduces the lifetime of USF Filtration polypropylene hollow fibre filtration membranes. The aim of this work is to:

- i) Clarify the nature of the oxidation products formed on the PP fibres.
- ii) Propose a mechanism by which oxidation of the PP fibres occurs.

iii) Determine the effect of temperature and oxidant concentration on the oxidation.

iv) Evaluate the oxidation resistance of fibres from metallocene PP compared to Ziegler-Natta PP.

1.3 Survey of the Thesis

Chapter 2 consists of an overview of the literature concerning the oxidative degradation of PP and the chemistry of chlorine in water. Chapter 3 deals with the modelling of PP oxidation using low molecular weight organic compounds. Chapter 4 deals with the determination of the oxidation products of PP fibres by aqueous chlorine and the effect of temperature and oxidant concentration on the oxidation. Chapter 5 deals with the effect of metallic impurities on the oxidation rate. The effect of stabilisers on the aqueous oxidation of PP is investigated in Chapter 6. In Chapter 7 the resistance of metallocene PP fibres to aqueous chlorine degradation is compared with fibres from Ziegler-Natta PP.

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Chapter 2 Literature review

2.1 Definition of Degradation

The term polymer degradation is used to denote the changes in physical properties caused by chemical reactions with the polymer. In previous studies^{1,2,3,4} it has been assumed that the chemical reactions for degradation occur directly with the polymer backbone. However, for this work the term degradation is used to denote any chemical reaction (either with the polymer backbone, or any impurity in the polymer) that causes a change in the physical properties of the polymer. This amendment takes into account the effect of catalyst or other impurities which, even in low concentrations, may have a significant effect in very high surface area polypropylene. Studies carried out and reported in Chapter 5 show that this is the case.

2.2 Polypropylene

Polypropylene (PP) is a crystalline thermoplastic resin. Polypropylene was first polymerised by Natta *et al*⁵ with a Ziegler catalyst, resulting in polypropylene with three possible structures. Of the three stereoregular forms of PP available, isotactic and syndiotactic are highly ordered and are able to form crystalline PP. The atactic form, being highly disordered, is unable to crystallise⁶. Isotactic PP is an essentially linear, highly crystalline polymer. The high crystallinity imparts to it high tensile strength, stiffness and hardness. Isotactic PP consists of a helical arrangement of the polymer chains due to the steric requirements of the pendant methyl groups. In the helical conformation alternate chain bonds take trans and gauche positions, thus relieving the steric hindrance. The PP helix has 3 (CH₂) units per turn⁷. Four possible spiral configurations of isotactic PP are possible, resulting in polymer chains that can readily align and interlock forming a crystal⁸.

Polypropylene produced with heterogeneous Ziegler-Natta catalysts have weight average molecular weights in the range of 3×10^5 to 7×10^5 ⁹. The MWD of PP resin is primarily a function of catalyst type with a polydispersity range of 5-20 for heterogeneous and 2-4 for homogeneous catalysts¹⁰. The broad MWD is due to the broad distribution of active sites on the heterogeneous catalysts.

The susceptibility to oxidation of PP is influenced by the polymer structure. Hydrogens bonded to tertiary carbons are more readily removed by radical reactions than those on secondary atoms^{11,12}. Hence, polypropylene oxidises more readily than linear polyethylene.

2.2.1 General Polypropylene Morphology

Semicrystalline polymers are essentially two phase systems consisting of clusters of crystals embedded in the bulk amorphous polymer. The amorphous fraction consists of chain segments that are not part of the crystal structure. In the amorphous state, the position of one chain segment relative to another is relatively disordered. The polymer chains making up amorphous state form random coils which are highly entangled with one another¹³.

Isotactic polypropylene displays three common crystalline structures: monoclinic (α form), hexagonal (β form) and triclinic (γ form)¹⁴. The most common form, monoclinic, is the most stable and compact of the three. The crystalline fraction comprises isotactic polypropylene molecules which chain-fold to form lamellae; some of these molecules are long enough to be part of more than one lamellae and are called 'tie molecules'. The structure of semi-crystalline polymers is explained by three possible models^{13,15} :

1. The Fringed Micelle Model. In this model the disordered regions separating the crystallites (crystalline regions) are amorphous. Inside the crystallites the polymer chains are precisely aligned. The polymer chains are sufficiently long that they pass in and out of the amorphous and crystalline regions, binding them

together. The 'fringes' represent transition material between the crystalline and amorphous phases.

2. Polymer Single Crystals/ The Folded Chain Model. The crystalline regions are isolated from the amorphous polymer. Polymer molecules in the crystals are folded back on themselves, allowing re-entry into the crystal. The polymer chains are aligned perpendicular to the crystallite surface.

3. The Switchboard Model. Chains re-enter the crystal randomly rather than by regular chain folding as described in Model 2. This results in non-ideal chain folding.

Crystalline polypropylene may occur in two different morphological forms¹⁶ :

1. Crystallisation from dilute solutions leads to the formation of lamellar single crystals. The single crystals are composed of thin, flat lamellae about 100 angstroms thick. Lamellae thickness is dependent on crystallisation temperature. Polymer chains are oriented normally to the surface of the lamellae and undergo chain folding.

2. Crystallisation from the melt leads to the formation of spherulites. Bulk crystallisation from the melt occurs readily in isotactic polypropylene due to its flexible chain backbone. Semi-crystalline polypropylene, formed by melt crystallisation, most probably follows the proposed model 3, which describes random re-entry into the crystallite as opposed to adjacent re-entry¹⁷. On crystallisation from the melt, nucleation occurs at a single nucleus (or nuclei) and from this nucleation point lamellae grow outward. The point of initiation may be a foreign particle (heterogeneous nucleation) or may arise spontaneously in the melt (homogeneous nucleation). Some crystallising molecules can have both ends in growing lamellae with the remainder in the amorphous region. The formation of the lamellae from a single nucleus results in the formation of a spherical network of crystallites. This growth pattern is named spherulitic crystal growth and the lamellar network spherulites which are composed of individual lamellar

crystalline plates^{18,19}. The individual lamellae in the spherulites are bonded together by tie molecules which lie partly in more than one crystallite. The existence of tie molecules between both lamellae and spherulites was shown by Keith *et al*^{20,21,22}. Tie molecules contain a high percentage of strained bonds compared to the bulk polymer and support a disproportionate share of the load in the amorphous region²³. Hence, during oxidation tie molecules are more likely to break, and their loss will have a large impact on the deterioration of the polymer. Scission of tie molecules at interspherulitic boundaries is particularly detrimental.

Isotactic PP consists of 4 different types of spherulites, which have been well described in previous work^{24,25}. In between the lamellar structures lies amorphous material which is rich in low molecular weight material as well as any impurities. Spherulites are generally polyhedral in shape and range in size from 1 to 100 μm .

2.3 Membranes

A membrane is an interphase that separates two phases and restricts the transport of species from one phase to another²⁶. Microporous membranes consist of a solid matrix with defined pores with a range of pore sizes. Separation of the various chemical components is achieved by sieving with the pore diameters and the particle sizes being the determining factor. Membranes may be either asymmetric or symmetric:

1. An asymmetric membrane consists of a very thin polymer layer (usually 0.1 to 0.01 μm) on a highly porous 100 to 200 μm thick substrate²⁶. The skin represents the actual membrane, while the substrate serves only as a support and has little or no effect on the separation characteristics of the membrane.
2. Symmetric membranes differ from asymmetric membranes in that the structure is uniform throughout, ie no support is necessary. The entire bulk of the membrane determines its separation characteristics. Hollow fibre membranes prepared from polypropylene are symmetric.

2.3.1 Preparation of Polypropylene Hollow Fibre Membranes by Solvent Extraction

Polypropylene hollow fibre membranes are extruded by USF Filtration using a patented solvent extraction process. This process involves the conversion of a homogeneous polymer/solvent solution into a two phase system with a solid, polymer rich phase forming the membrane structure and a liquid, polymer poor phase forming the membrane pores²⁷. Phase separation is achieved by cooling the homogeneous solution to a temperature at which the two phases are no longer homogeneous. Microporous membranes made in this way have a large variety of pore sizes.

2.4 Practical Evidence of the Degradation of Polypropylene Fibres

2.4.1 USF Filtration Hollow Fibres

USF Filtration polypropylene hollow fibre membranes are used for microfiltration of aqueous systems in a variety of industrial and domestic applications. The polypropylene membranes allow passage of the feed water from the outside of the fibre to the inside, resulting in retention of larger impurities, such as sewage, dirt and other organic material, on the fibre surface. A gas backwash is used to remove the solid impurities accumulated on the fibre surface. Applications of USF Filtration Continuous Microfiltration (CMF) include: domestic water supplies, secondary and tertiary sewage, well water, river and sea water, consumable liquids (such as cider, orange juice, wine, vinegar and fermented broth) and industrial waste streams (such as caustic, silicon waste water and lead containing water).

In practical industrial applications, the polypropylene membranes undergo degradation after exposure to particular contents of certain feed streams. In industrial applications, degradation of the fibres is detected by loss of integrity of the membrane allowing passage of otherwise retained material into the filtrate.

The contents of aqueous feed streams suspected to cause degradation of the PP fibres include: dissolved oxygen, ozone, peroxides, cationic solutions, caustic solutions, sodium metabisulfite, inorganic dirt, organic material, oils, fats, non-ionic surfactants and chlorine solutions. Of these chlorine causes the most immediate and significant damage to the fibres. This is partially due to its presence in most municipal water feed streams as a disinfectant.

The degradation of USF Filtration polypropylene fibre membranes by dissolved chlorine causes accelerated loss of integrity of the filtration modules, usually inside the warranty period. This poses a significant economic problem as the degraded modules require replacement at the expense of USF Filtration. In this respect, an understanding of the degradation mechanism of PP fibre membranes by dissolved chlorine is necessary in order to minimise the rate of this reaction so that degradation occurs outside the warranty period.

2.4.2 Surgical Sutures

Polypropylene is widely used in contact lens implantation both as loop material and as an internal suture²⁸. As well as in the eye, PP sutures are used in other parts of the body, including as dental sutures. PP sutures are preferable to nylon and PET which react with human tissue²⁸.

PP suture material, used in contact lens implantation, have been observed to degrade in vivo ^{28,29,30,31} as have sutures used in dental applications³². Analysis of the degraded sutures showed the formation of carbonyl groups, suggesting that oxidation occurred²⁸. Drews³³ observed that PP sutures underwent only slight degradation in the iris, however sutures embedded in actively metabolising tissue degrade much more rapidly. This effect of ocular sutures was supported by Jongebloed *et al* ³⁰ who found that the part of the suture not in contact with tissue did not undergo degradation. Jongebloed *et al*³¹

showed that the presence of enzymes is the primary cause of degradation of PP sutures.

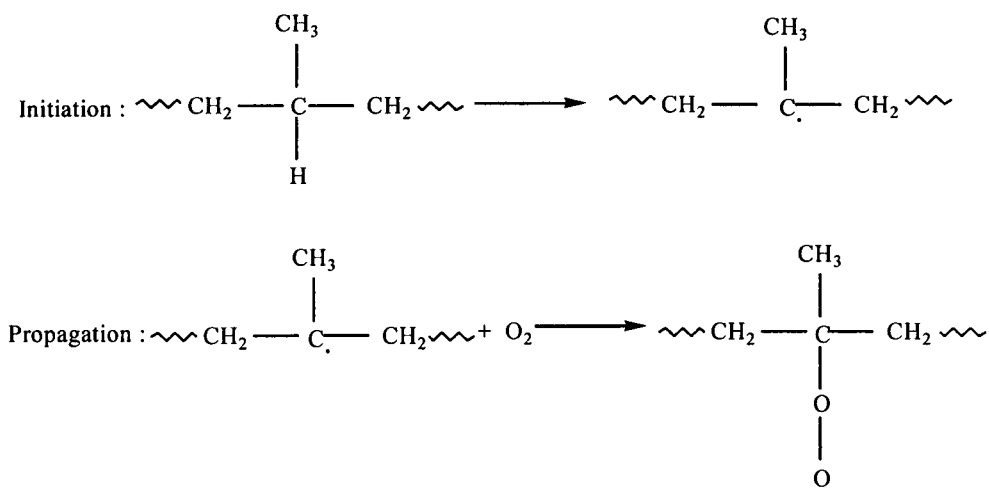
The degradation of PP sutures may be catalysed by metallic ions, such as iron in blood, or enzymes by accelerating hydroperoxide decomposition²⁸. The degradation of intraocularly placed PP is most probably initiated by UV radiation due to exposure to direct sunlight. However, the effect of irradiation of the eye is limited by the absorption spectrum of the cornea which passes only UV light with wavelengths longer than 300nm. The wavelength of terrestrial sunlight is generally longer than 290nm and the chromophoric activity of the carbonyl group is at a maximum around 300nm⁶¹. Jongebloed *et al*³⁰ proposed that the sterilisation of the PP sutures may cause initiation of degradation prior to implantation in human tissue.

2.5 The Degradation Mechanism

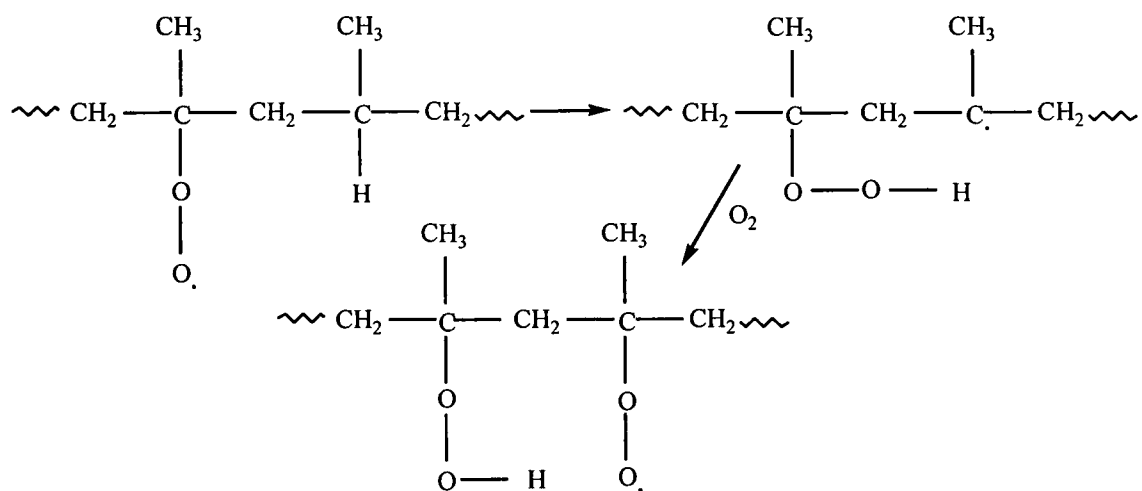
2.5.1 Overview

Most studies into the oxidative degradation of polypropylene use oxygen as the oxidant. Since the solubility of oxygen in polypropylene is only a little lower than in a hydrocarbon liquid, oxygen is always present in polypropylene samples that have been exposed to air³⁴. During the oxidation process the typical oxygen absorption profile for a polymer is characterised by an auto-accelerating period which is followed by a rapid almost linear rate of oxygen absorption. The addition of an initiator removes the slow auto-accelerating induction time and stabilisers extend it. During the initial stages of oxidation the hydroperoxide concentration in the polymer increases, indicating that they are the primary products of auto-oxidation. However, these hydroperoxides are unstable and break down to give carbonyl compounds, which are readily detected by FT-IR measurements. It has been found that there is a correlation between the carbonyl index of oxidised polymers and their physical degradation³⁵.

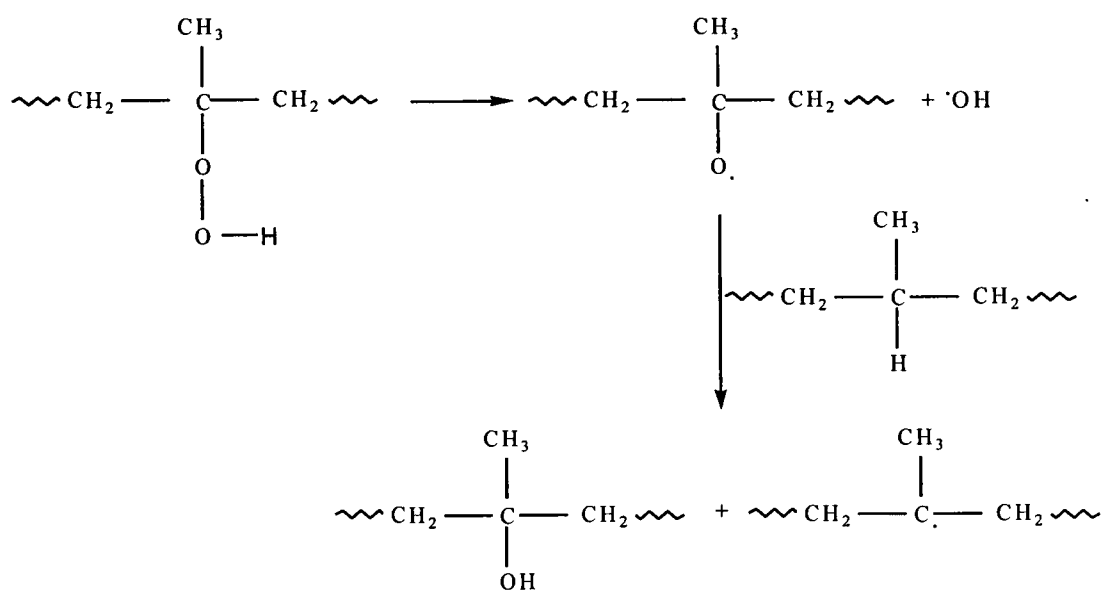
Bolland and Gee^{37,1} proposed a basic oxidation mechanism for polypropylene in which peroxides play the key role as shown in Scheme 1:


$$\begin{array}{c} \text{CH}_3 \\ | \\ \sim \text{CH}_2 - \text{C} - \text{CH}_2 \sim \\ | \\ \text{O} \\ | \\ \text{O} \cdot \end{array} + \begin{array}{c} \text{CH}_3 \\ | \\ \sim \text{CH}_2 - \text{C} - \text{CH}_2 \sim \\ | \\ \text{H} \end{array} \longrightarrow \begin{array}{c} \text{CH}_3 \\ | \\ \sim \text{CH}_2 - \text{C} \cdot - \text{CH}_2 \sim \\ + \\ \begin{array}{c} \text{CH}_3 \\ | \\ \sim \text{CH}_2 - \text{C} - \text{CH}_2 \sim \\ | \\ \text{O} \\ | \\ \text{O} - \text{H} \end{array} \end{array}$$

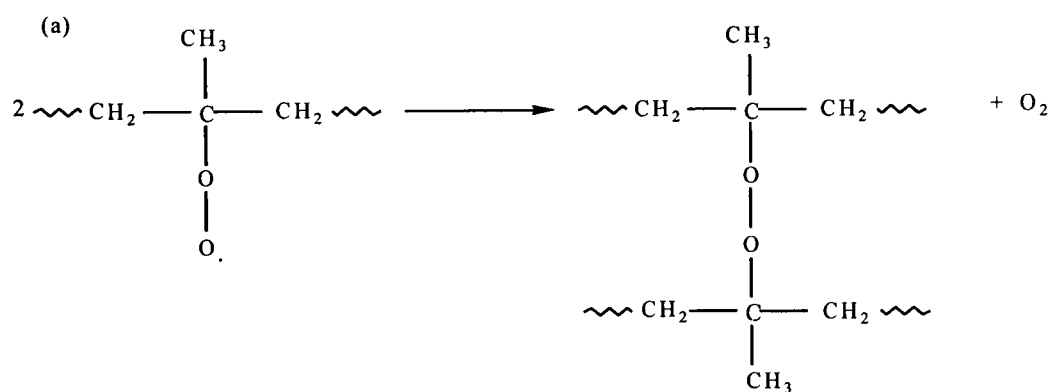
(b) Intramolecular

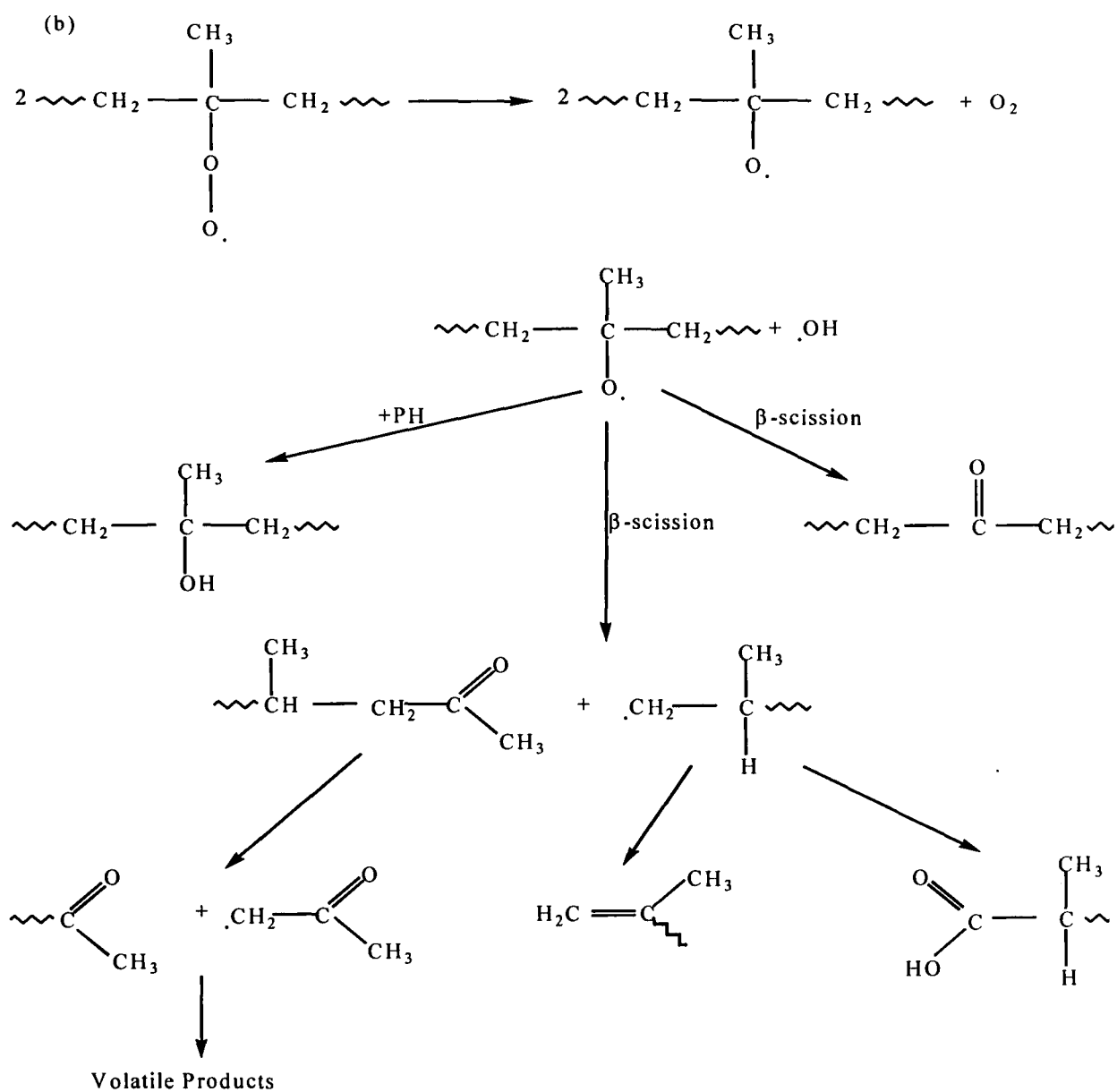


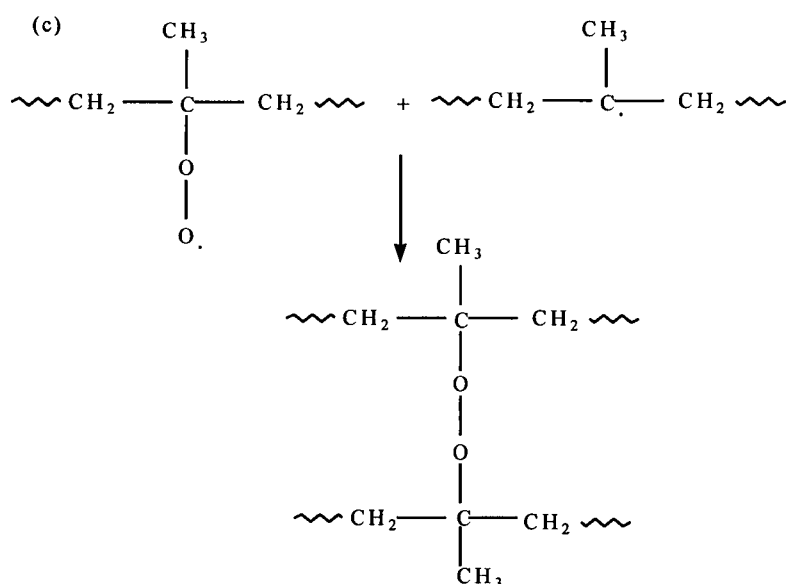
Chain Branching :



Termination :







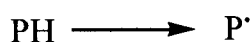
Scheme 1 : Polypropylene Oxidation.

The net result of this mechanism is an increase in the concentration of alcohols and peroxides and a decrease in molecular weight.

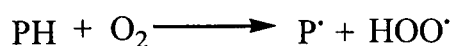
2.5.2 Modes of Initiation of Degradation

The experimental work carried out in this thesis concerns the aqueous chemical degradation of polypropylene. However, in order to fully understand the mechanism of chemical degradation a complete study of degradation by other pathways is necessary. In terms of initiation of polypropylene degradation there are a number of schools of thought³⁸ :

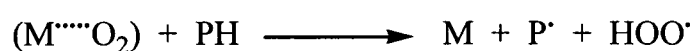
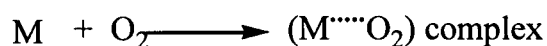
- Polymer thermolysis



- Polymer-oxygen interaction



- Metallic impurities (M)



These processes initiating polypropylene degradation occur by one of several modes of initiation³⁹: thermal, chemical, mechanical, photochemical, radiation or biological. In most practical applications initiation occurs by a combination of these processes¹². Chemical degradation refers to processes which are induced under the influence of chemicals (eg acids, bases, gases etc.). Thermal degradation occurs when a polymer, at elevated temperatures, undergoes chemical changes without the involvement of a second compound. Biological degradation occurs by the reaction of enzymes, produced by microorganisms, with the polymer. Mechanically initiated degradation occurs under the influence of high shear forces. Photochemically initiated degradation occurs when chromophoric groups in the polymer absorb incident radiation. Regardless of which mode of initiation occurs, the resulting short chain radicals ensure that the propagation and termination reactions are identical.

2.5.2.1 Thermally Initiated Degradation

All polymers degrade at high temperatures in the absence of an oxidant. Scission of C-C, C-H or C-O bonds at ambient temperatures is unlikely due to the high energy required to reach the bond dissociation energies, (respectively 260-400, 320-420 and 330kJ/mol)³⁹. The absorption of sufficient energy to achieve the dissociation occurs above 400°C. Chain scission in polypropylene occurs at sites in the chain containing weak links due to impurities such as C=C and C-O-C as well as tertiary C-H bonds.

Thermal initiation occurs either by main chain scission, side group scission or rupture of weak bonds. The result of this initiation are free radicals which are unstable and highly reactive, producing hydroperoxides by reaction with oxygen or forming unsaturated chain ends as shown in Chapter 5 Scheme 3. The free radicals also abstract hydrogen atoms from neighbouring polymer chains. The rate of hydrogen abstraction increases significantly with temperature.

2.5.2.2 Mechanically Initiated Degradation

Mechanical degradation occurs when sufficient energy, from externally applied forces, is concentrated in a particular segment of the polymer as a result of the non-uniform distribution of internal stress³⁹. As a result of this highly concentrated energy, bond scission occurs forming short chain radicals. Mechanical degradation of polypropylene produces predominantly the radicals:

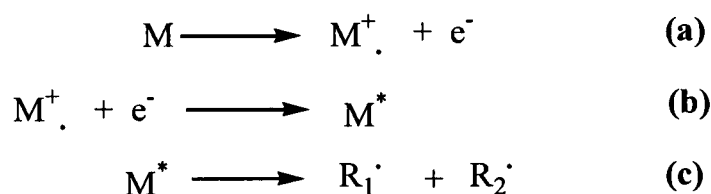


These radicals behave as described in Section 2.5.2.1.

Stress, applied to a semi-crystalline polymer, causes main-chain scission in tie molecules connecting the crystalline and amorphous regions³⁹. A steadily increasing strain produces an increasing concentration of free radicals. This is because initially the shortest tie molecules are ruptured, but as strain increases additional longer tie molecules are broken, increasing the overall radical concentration. Compared to the amorphous region, significantly higher mechanical forces are required to produce free radicals in crystalline polypropylene³⁹.

2.5.2.3 Radiation Induced Degradation

Ionising radiation incident on polypropylene generates ions, radicals and electronically excited molecules, all of which are unstable. Free radicals are generated as shown in Scheme 2³⁹:



Scheme 2

Reaction (a) shows the primary radiolytic step generating a radical cation, which then captures a thermalised electron producing an excited molecule as shown in Reaction (b). This excited molecule subsequently decomposes forming 2 radicals. In the presence of oxygen these radicals form peroxides which decompose as described in Section 2.5.1.

After initiation by radiation, polypropylene undergoes oxidation^{40,41}. The resistance of polypropylene to radiation oxidation is strongly dependent on PP morphology. Nishimoto *et al*⁴² found that the radiation resistance of polypropylene increases with decreasing spherulite size.

2.5.2.4 Photodegradation and Photooxidation

Pure saturated polypropylene should be resistant to photo-degradation and photooxidation, however it is the presence of impurities in commercial polypropylene, formed during polymerisation and processing, that act as initiation sites for degradation^{43,44}. Photodegradation is defined as photo-initiation followed by degradation occurring in the absence of oxygen. Photooxidation is defined as photoinitiation followed by oxidation occurring with oxygen⁴⁵.

The wavelength of UV and visible radiation from the sun is sufficient to break C-C, C-O and C-H chemical bonds. These bonds absorb light with a wavelength of <200nm. Carbonyl groups and conjugated C=C have an absorbance maxima between 200 and 290nm³⁹. In terms of photochemically initiated degradation the light absorbing (chromophoric) impurities are^{45,43, 46}: saturated and unsaturated carbonyls, aromatics, metallic impurities, oxygen-polymer charge transfer complexes and saturated and unsaturated hydroperoxides. Of these, it is believed that the carbonyls and hydroperoxides are the major contributors to photochemical initiation⁴⁷. This radiation is first absorbed by the chromophoric groups present in the polymer which then transfer the energy to the bonds to be

broken. Because the absorption of radiation is the first step in photo-degradation, reaction is concentrated in the surface layers of the polymer and results in a skinning effect³⁵.

Carbonyl Groups

The degradation process utilising carbonyl groups follows that suggested by Norrish⁴⁸ outlined by Allen and McKellar^{43, 49} as shown in Figure 1. The Norrish type 1 process leads to the formation of short chain free radicals in the presence of UV light.

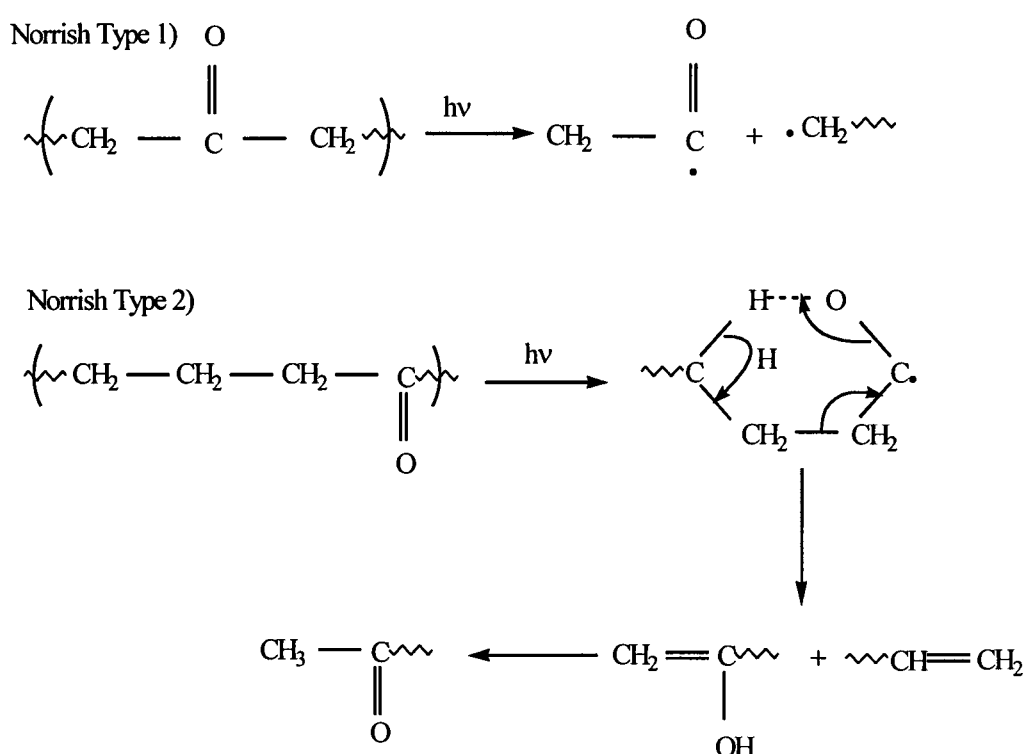


Figure 1 : Decomposition of carbonyl groups according to the Norrish mechanism.

The Norrish type 2 process occurs via a 6 membered cyclic intermediate. The resulting products contain one olefinic group and one enolic group.

The decomposition of carbonyls by the Norrish reactions proceed in the absence of oxygen. In the presence of oxygen, ie in photooxidation, macroradicals formed by Norrish decomposition undergo further reactions with oxygen, generating

peroxyl radicals instead of the otherwise generated species⁴⁵. These peroxyl radicals produce more chromophoric species, creating an auto-oxidative effect.

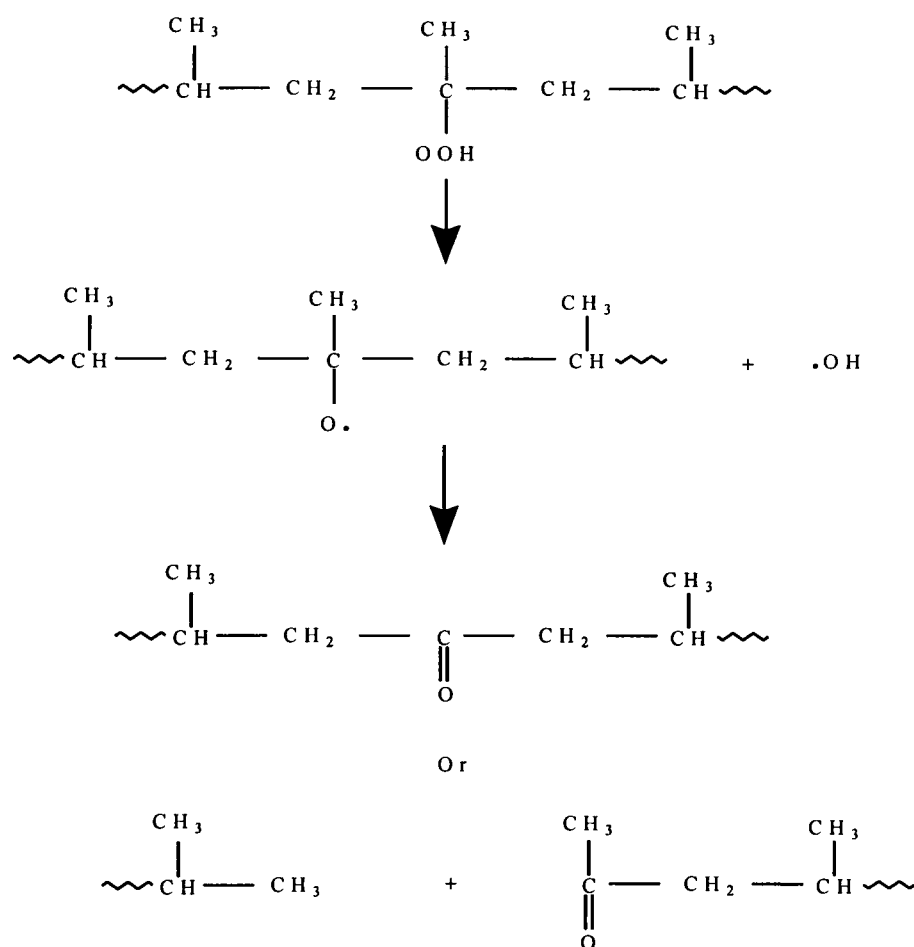


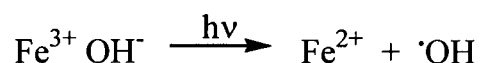
Figure 2 : Photochemical decomposition of hydroperoxides.

Hydroperoxide Groups

Photodegradation utilising hydroperoxide groups follows that outlined by Carlsson and Wiles⁶¹ as shown in Figure 2. Photolysis of all chromophores with oxygen produce hydroperoxide as a primary product⁵⁰. Efficient protection of polypropylene from photo-initiated degradation is obtained by preventing photolysis of polypropylene hydroperoxide by either destroying any hydroperoxide groups present or deactivating those that are photo-activated⁶¹. These kinds of stabiliser systems are discussed in detail in Chapter 6.

Metallic Impurities

Metallic impurities, such as Ti and Fe, present in the polymer are believed to sensitise the photooxidation of polypropylene due to their UV absorption upto ~350nm⁴⁵. Aluminium, present as a residual Ziegler-Natta catalyst, absorbs only at <300nm, and is probably an unimportant photoinitiator⁵⁰. The metallic impurities, usually present in the form of oxides, absorb UV radiation producing free radicals by an electron transfer process as shown in :



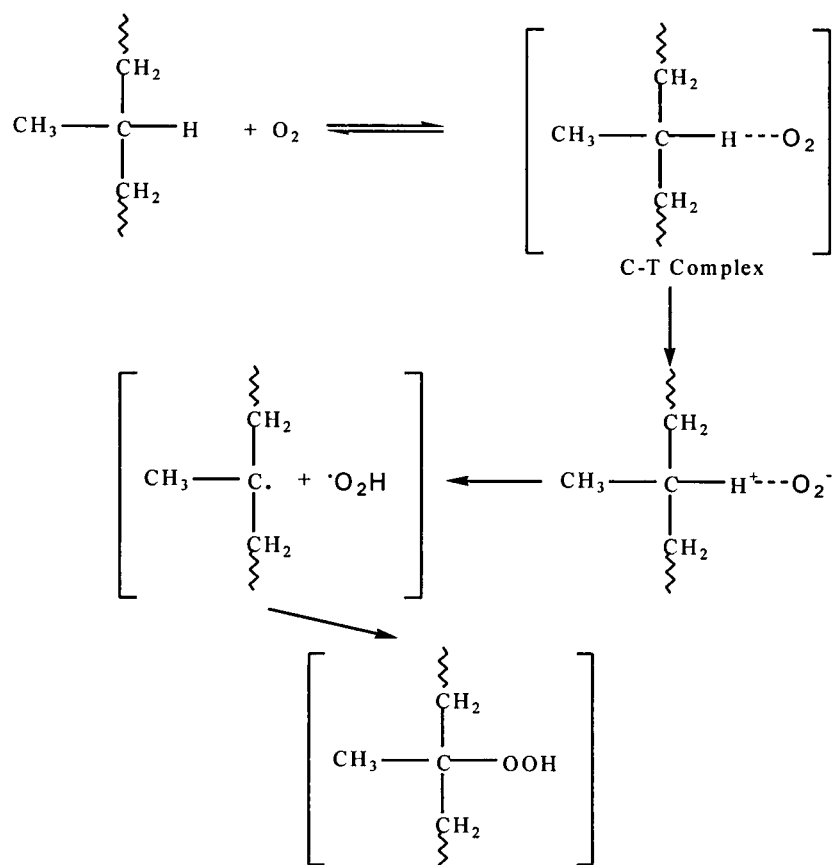
Scheme 3

These radicals may then react with the polymer.

Charge Transfer Complex

It has been reported that formation of a charge transfer (C-T) complex may occur on collision between oxygen and a polymer molecule⁵⁰. UV absorption of this C-T complex, a source of instability of the polymer, has been reported to result in hydroperoxide formation as shown in Scheme 4⁵⁰.

The UV absorption of the PP-O₂ complex has been found to be extremely low and is unlikely to be a primary photo-initiator due to the low concentration of radicals produced⁵⁰. Olefin-O₂ complexes have much more intense UV absorptions, approximately 400 times that for PP-O₂ complexes, and so are better photoinitiators.



Scheme 4 : Formation of a charge-transfer complex from polypropylene.

2.5.3 Peroxide Formation and Decomposition in Polypropylene Degradation.

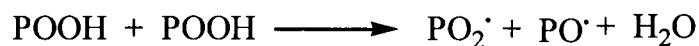
Hydroperoxides are known to be the crucial products of the free radical degradation of polypropylene being successively formed and decomposed during the degradation process^{51,52}. Hydroperoxides are present in polypropylene as impurities generated by oxidation during processing and storage. Polypropylene hydroperoxides consist of two types either hydrogen bonded, detected using infra-red absorption at 3400cm^{-1} , or free, detected at 3550cm^{-1} ⁵³.

Hydroperoxides decompose efficiently, generating free radicals which begin new oxidative chain reactions. Tertiary hydroperoxide is known to be the main product of oxidation of isotactic PP by all modes of initiation⁵⁴. The

decomposition of hydroperoxides present occurs either by a unimolecular mechanism⁵⁵:

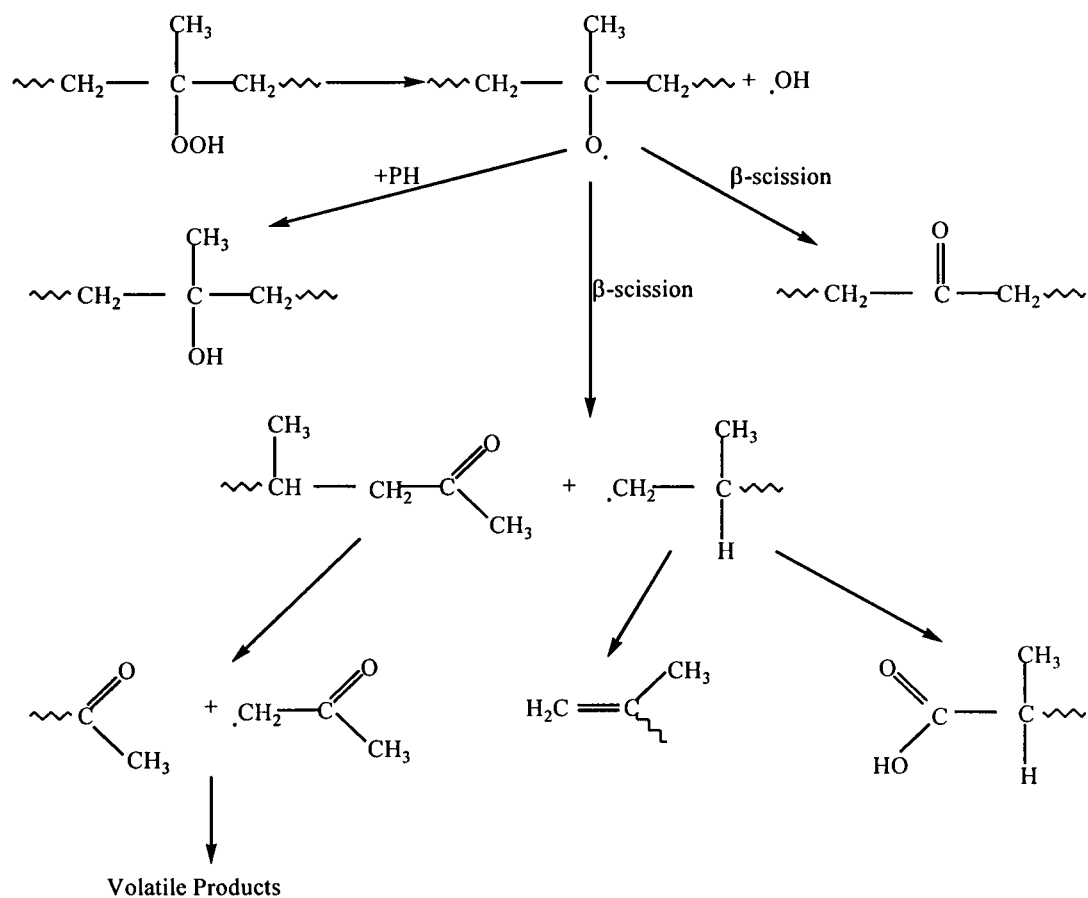


or by a bimolecular mechanism ⁵⁶



As the concentration of peroxides increases throughout the degradation, the above processes may become the main source of radicals. Zolotova and Denisov⁵⁷ reported that the bimolecular decomposition of hydroperoxides is ten times as fast as the unimolecular decomposition.

The generation of hydroperoxides during PP degradation was outlined in Scheme 1 and described by Allen and McKellar^{43,58}. Decomposition of the hydroperoxides occurs as shown in Scheme 5⁵⁹.



Scheme 5 : Hydroperoxide Decomposition

Significant experimental evidence supports this mechanism. According to Norrish⁴⁸, chain β -scission occurs resulting in an observed drop in molecular weight of the polymer. Severini *et al*⁶⁰ showed that β -scission is the main chain scission process with a linear correlation between carbonyl absorbance and molecular weight. In the presence of hydroperoxides, β -scission is most likely the major source of backbone scission since approximately 15% of the photolysed hydroperoxide groups undergo this reaction⁶¹. A major product of the decomposition reaction is observed to be tertiary alcohol⁶². As a by-product of the degradation process it is reasonable to expect that short chain volatile matter be produced. Carlsson and Wiles⁶³ showed that the major volatiles formed were carbon monoxide, water and acetone.

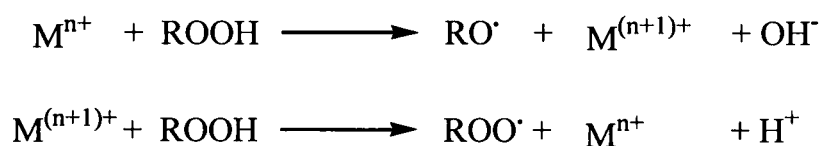
It is agreed in the literature that in the initial stages of degradation of polypropylene the concentration of peroxides in the polymer increases with reaction time^{64,1}. George *et al*⁶⁵ believe that these hydroperoxides are formed by the rapid oxidation of the polypropylene in localised zones of high instability. The time it takes for the formation of these peroxides is recognised as the induction period, their decomposition being responsible for the oxidation of polypropylene⁴. In the case of polypropylene degradation the hydroperoxides formed are predominantly tertiary (~90%) with the remainder being secondary⁵¹. The decomposition of these tertiary hydroperoxides leads to backbone scission, giving a complex mixture of low molecular weight compounds.

Bolland and Gee¹ proposed a mechanism for the unimolecular decomposition of polypropylene hydroperoxides into hydroxy and alkoxy radicals. However, due to the high activation energy, this reaction is unlikely to occur at low temperatures (ie below 50°C). It is generally agreed in the literature that the peroxides formed on degradation of polypropylene contain a fast and slow decomposing fraction at temperatures above 50°C^{66,67,68} and also at temperatures below 50°C⁶⁴.

Gijsman *et al*⁶⁹ showed that the low temperature (50-90°C) degradation mechanism for polypropylene deviates from the mechanism provided by Bolland and Gee^{1,37}. They also showed that the peroxides formed during degradation consist of two fractions, one fast decomposing, consisting of peracids or peresters, and one slow decomposing, consisting of tertiary hydroperoxides. As well, during the induction period of degradation only slowly decomposing peroxides are formed. Their conclusions were that the low temperature oxidation takes place in two stages. In the first stage (induction period) the degradation is controlled by the decomposition of hydroperoxides which is catalysed by metal impurities. During this period oxidation products are formed which are preferentially oxidised forming peracids or peresters. The second stage results in an increase in the degradation due to the decomposition of the peracids present. This is contrary to the classical mechanism proposed by Bolland and Gee.

Gijsman *et al*⁸⁸ found that the degradation mechanism of polypropylene is dependent on the reaction temperature. They found that at low temperatures (50-90°C) the decomposition of peroxides is accelerated by the catalyst residues, while at high temperatures (>90°C) the decomposition is thermal and only slightly dependent of catalyst concentration.

Gijsman *et al*⁶⁹ showed that at low temperatures the residual titanium catalyst influences the induction period of degradation and the amount of peroxide present. The polymerisation catalyst residues catalysed the decomposition of hydroperoxides, resulting in a shorter induction period. The effect of the transition metal ions is to reduce the activation energy for hydroperoxide decomposition³⁵. They suggested that the acceleration of peroxide decomposition by catalyst residues occurs as described by the Haber-Weiss mechanism. Catalyst residue is denoted by M:



Scheme 6 : Haber-Weiss Mechanism for hydroperoxide decomposition.

2.5.4 The Induction Period.

The existence of an induction period in the degradation of polypropylene is commonly acknowledged in the literature⁷⁰. Some argue that during this period no formation of oxidised products, such as carbonyl compounds, are detectable yet small variations in mechanical properties and molecular weight are observed⁷⁰. This absence of significant carbonyl formation during the early stages of degradation suggest that hydroperoxides play an important role in the induction process⁷¹.

On the other hand Celina *et al*⁷² used FT-IR emission spectroscopy to conclude that all oxidation products of polypropylene were formed immediately from the onset of oxidation. Also George *et al*⁶⁵ have shown by measurements of mechanical properties and molecular weight that extensive degradation occurs in the induction period. Gugumus⁷³ also showed that in the early stages of oxidation carbonyl groups and associated hydroperoxides are formed, while free hydroperoxides and carbonyl groups increase in the latter stages of oxidation. Using chemiluminescence Lacey and Dudler⁹² observed that at high degrees of oxidation, the primary oxidation products may be further oxidised forming, among other things, di-ketone species.

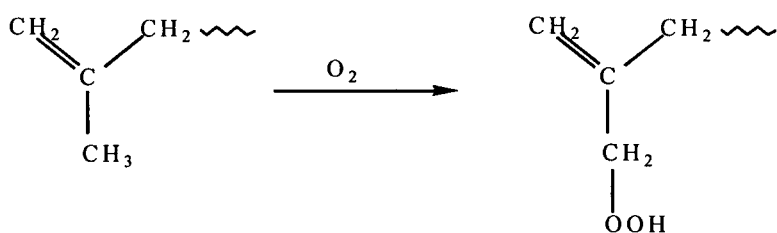
Boss and Chien⁷⁴ observed an increase in induction period with increasing sample thickness for PP samples less than 15mm. The induction period for PP samples thicker than 25mm was independent of thickness.

2.5.5 Reaction of C-C Double Bonds

A significant amount of residual unsaturated carbon-carbon bonds is commonly observed in Ziegler-Natta polypropylene. Molecular weight control of polypropylene after polymerisation is achieved by chain breaking using organic peroxides. As a result, unsaturated carbon-carbon bonds are formed at the sites of chain scission at chain ends. (Further information dealing with the mechanism of C=C formation is given in Chapter 5.)

2.5.5.1 Oxygen Attack

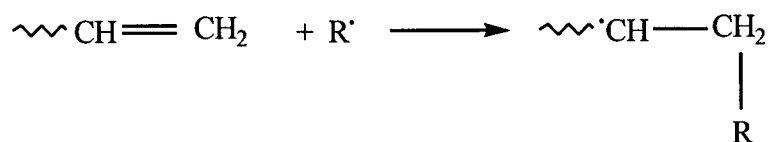
The introduction of an olefinic bond into polypropylene renders it much less resistant to oxygen attack. Oxygen attacks across the carbon-carbon double bonds at polymer chain ends producing hydroperoxides^{75,76} as shown in Scheme 7. O₂ reacts more rapidly with C-C unsaturation than O₃ to form a hydroperoxide⁵⁰.



Scheme 7

2.5.5.2 Free Radical Attack

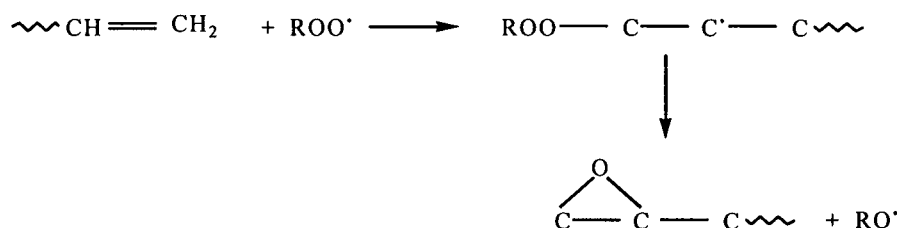
Free radicals, produced during polypropylene oxidative degradation, readily react with C=C bonds present in polypropylene generating macroradicals as shown in Scheme 8⁷⁷.



Scheme 8 : Formation of macroradicals.

Free radicals present in polypropylene may be alkyl or alkoxy radicals from polymer chain scission, chloride radicals formed from the HOCl solution (Section 2.6) or hydroxy radicals formed by hydroperoxide decomposition.

Carbon-Carbon double bonds can also react with hydroperoxy radicals present, forming epoxides as shown in Scheme 9⁷⁷. This reaction is energetically favoured due to the formation of a σ -bond as opposed to a π -bond.



Scheme 9

The rate and selectivity of this reaction is determined by steric factors. It is for this reason that the methyl substituted $\text{CH}_2=\text{C}(\text{CH}_3)-$ bond, shown in Scheme 7, which is formed in PP visbreaking does not participate in free radical addition reactions⁷⁷. The steric environment allows only a radical addition to a $-\text{CH}=\text{CH}_2$ bond. Any further substitution of the bond prevents radical addition.

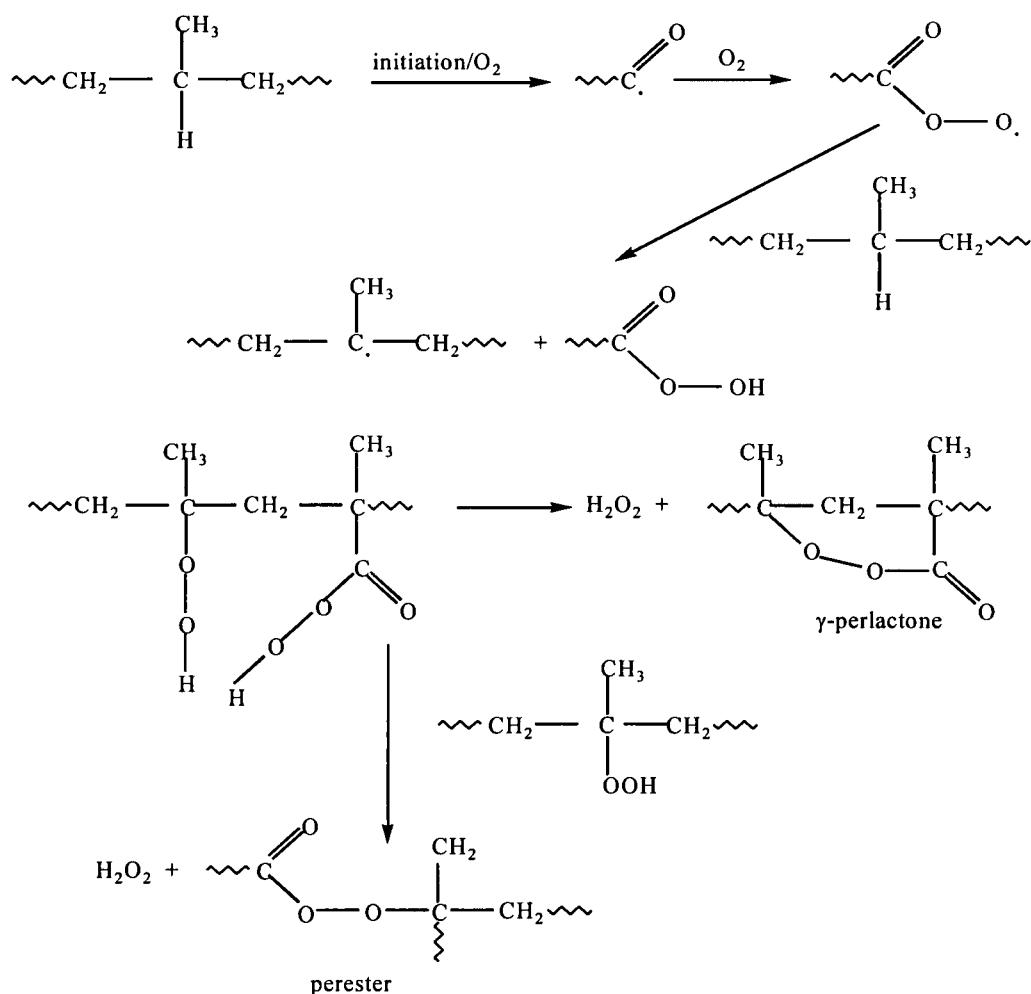
Carbon-carbon unsaturation on the polymer backbone influences the degradation during the induction period, but its effect becomes negligible once sufficient oxidation products are formed⁷⁸. During the degradation process the formation of C-C double bonds is thought to occur only in oxygen deficient conditions⁹². In oxygen rich environments the amount of C-C double bonds is observed to decrease as degradation progresses⁴⁷.

2.5.6 Localised Degradation

It has been recognised that commercial polypropylene will have macroscopic variations in physical properties and structure resulting from non-homogeneous mixing during processing, variations in local stress due to non-uniform cooling

and hence localised differences in crystal morphology^{79,80}. The formation of low molecular weight species by chain scission may result in a plasticising of the polymer chains in this region, and hence a higher local rate of degradation. More detail regarding the nature of these variations is given in the introduction to Chapter 5. These sites present in polypropylene, containing impurities and high local stress will be degraded preferentially to the bulk polymer in the presence of an oxidant.

It has been suggested in the literature that the oxidative degradation of polypropylene occurs to a large extent in small zones in the polymer^{81,82}. Using chemiluminescence studies George *et al*⁶⁵ found evidence of zones of high reactivity in the polymer as did Dudler *et al*⁸³. In another study George *et al*⁸⁴ observed the formation of γ -lactones from the onset of degradation, indicating that oxidation is occurring in localised zones with high reactivities.



Scheme 10 : Formation of peresters and γ -perlactones.

Lacoste *et al*⁵⁴ observed the formation of peresters and γ -perlactones which may be formed in small zones at high oxidation conversions. They proposed that the formation of peresters is favoured in zones of the polymer where hydroperoxides surround the other oxidation products. The formation of peresters and γ -perlactones is shown in Scheme 10.

When a semicrystalline polymer undergoes chemical attack it generally degrades more quickly in the non-crystalline phase than in the crystalline phase^{85,86}. The reason for this is the oxygen required for degradation can diffuse relatively freely through the non-crystalline region but not readily into the crystalline. Degradation may also readily occur at the phase boundary between the crystalline and non-crystalline regions, thus weakening the network which holds the

crystalline regions together. Any defects or impurities in the polymer they will be present in the non-crystalline phase, and so degradation will occur preferentially at these sites. These impurities may be due to catalyst residue, residual oxidation products from extrusion or processing or molecules under high stress due to non-uniform quenching. Hence degradation of polypropylene is heterogeneous on a macroscopic and microscopic scale due to the impermeability of the crystalline phase to oxygen⁸⁷, presence of localised catalytic and other impurities⁸⁸ and low mobility of radicals⁸⁹.

The localised oxidative degradation of polypropylene, being a heterogeneous process, should produce in the degraded samples either a bi-modal molecular weight distribution or a broadening of the distribution as given by the polydispersity index⁹⁰. Oxidative degradation occurring homogeneously throughout the polymer should produce a narrowing of the molecular weight distribution and a decrease in the overall molecular weight. Girois *et al*⁹⁰ in their work observed a decrease in polydispersity with degradation of polypropylene film. This evidence contradicts the hypothesis of a heterogeneous degradation which would result in either a bi-modal molecular weight distribution or a broadening of the same.

How does degradation of the bulk polymer propagate from these reactive sites? Gugumus⁹¹ proposed a possible scenario. With high levels of localised oxidation taking place in the amorphous regions, large amounts of products with low molecular weight will be formed as well as large amounts of free peroxides. These products diffuse to adjacent amorphous regions, with low or negligible oxidation products, and initiate oxidation. Hence, the number of amorphous regions oxidised will increase. Dudler *et al*⁹² observed this phenomenon in the chemiluminescence studies of degradation of polypropylene films. They surmised

that volatile products, presumably containing peroxides, contaminated adjacent undegraded sites and accelerated their rate of degradation.

Much has been written in the literature supporting the theory of PP degradation at localised sites. Celina and George⁹³ interpreted the oxidation of polypropylene powder as occurring in localised zones with high extents of oxidation producing volatiles (H_2O and CO_2) as well as secondary oxidation products. Using chemiluminescence microscopy Lacey and Dudler⁹⁴ showed that the oxidation of polypropylene films is heterogeneous, predominating in the less crystalline regions at the boundaries of the spherulites. Richters⁹⁵ analysed degraded polypropylene films and observed via SEM severe oxidation in isolated areas of the polymer. Further elemental analysis showed the oxidised areas to be extraordinarily high in metal content (particularly iron which was a residual from processing and extruding equipment). Gugumus⁹⁶ observed that the degradation, at temperatures as low as 40 and 60°C occurs as a heterogeneous process due to the restriction of the oxidation to the polymer surface.

2.6 Aqueous Chlorine Chemistry.

2.6.1 Introduction

Chlorine is commonly used in water treatment due to its toxicological characteristics and its oxidative capacity as well as its effectiveness, low cost and ease of application. Practical applications of chlorine include:

- i) The control of fouling of heat exchange surfaces with biological material in freshwater, and the control of fouling by marine organisms in seawater^{97,98}.
- ii) As a strong disinfectant in waste treatment, potable and surface water applications⁹⁹.

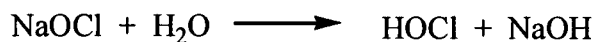
iv) Chemical and physical alteration of waste streams in industrial waste treatment.

For these applications the streams are either dosed with aqueous sodium hypochlorite or bubbled with chlorine gas. The former is more common for health and safety reasons, however both methods produce hypochlorous acid which is the active species in disinfection.

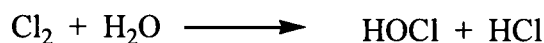
USF Filtration applications involve the downstream microfiltration of some chlorinated solutions using polypropylene hollow fibre polypropylene membranes. The presence of chlorine, in particular hypochlorous acid, in these waste streams detrimentally effects the stability of the polypropylene membranes.

2.6.2 Hypochlorous Acid

Liquid bleach, sodium hypochlorite (NaOCl), has been used as a household disinfectant since the 1930's. In water it rapidly disperses to form hypochlorous acid (HOCl):



HOCl may also be produced by the hydrolysis of chlorine gas:



Complete hydrolysis of the chlorine gas occurs in less than 1 second at room temperature¹⁰¹. Hypochlorous acid is a weak acid meaning that it undergoes partial dissolution as follows¹⁰⁰ :



In this equation the equilibrium between HOCl and OCl⁻ is maintained even if the HOCl is being consumed. In solutions with pH between 6.5 and 8.5 both HOCl and the hypochlorite ion (OCl⁻) are present to some degree. At pH values above 9 only the hypochlorite ion exists. Table 1 shows the percentage of undissociated HOCl to OCl⁻ at several temperatures and pH values.

pH	Percent HOCl		
	0°C	20°C	30°C
5	99.9	99.7	99.7
6	98.5	97.5	96.9
7	87.0	79.3	75.9
8	40.2	32.5	24.0
9	6.3	3.7	3.1
10	0.7	0.4	0.3
11	0.1	0	0

Table 1 : Percentage of undissociated HOCl for various pH values and temperatures¹⁰¹.

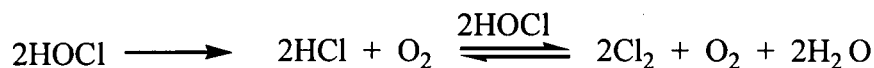
The germicidal efficiency of HOCl is a function of its pH, which determines the amount of HOCl and OCl⁻ present. Hypochlorous acid (HOCl) is an effective disinfectant for killing bacteria, cysts and spores¹⁰¹. HOCl is similar in structure to water. The germicidal efficiency of HOCl is due to the relative ease with which it can penetrate cell walls. This penetration is similar to that of water and can be attributed to both its low molecular weight and its electrical neutrality. After penetration of the cell walls, the HOCl reacts with the cytoplasm to produce stable nitrogen-chlorine bonds with the cell proteins. The chlorine then attacks the coenzymes present essential to respiration, resulting in death of the organism . The hypochlorite ion, on the other hand, is a poor disinfectant because of its inability to diffuse through the cell wall. The obstacle to this passage is the negative electrical charge.

2.6.3 Decomposition of Sodium Hypochlorite (NaOCl), Hypochlorous Acid (HOCl) and Hypochlorite Ion (OCl⁻).

HOCl is produced by dispersing NaOCl in water. The stability of NaOCl is in the order of 10 times higher than the stability of HOCl¹⁰³. NaOCl undergoes slow decomposition to NaCl and oxygen according to:

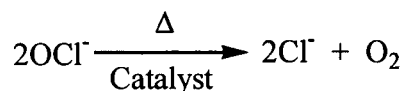


Allmand *et al*¹⁰² observed that HOCl decomposes to form HCl and oxygen in the presence of heat or light. Hypochlorous acid solutions are stable if kept at low temperatures in the dark. At 0°C the decomposition rate of a 1M HOCl solution is 0.3%/day, while at 20°C the decomposition rate is 3%/day¹⁰³. The decomposition of hypochlorous acid occurs as:



The rate of this reaction is increased by heat and light. The presence of heavy metal cations such as iron, copper, nickel and cobalt catalyse the decomposition with iron being the most effective of these¹⁰¹. The decomposition is also concentration dependent, a high HOCl concentration solution decomposes faster than solutions containing low HOCl concentration. So, hypochlorous acid is a source of oxygen while it undergoes decomposition.

The hypochlorite ion decomposes with heat and a low concentration of metallic ions to chloride and oxygen as is shown in⁹⁷:



The hypochlorite ion may undergo reduction in the presence of a suitable reductant to form a chloride ion as shown:

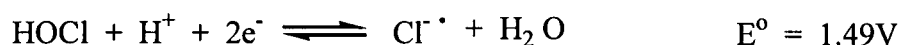


2.6.4 Radical Formation from HOCl Solutions.

Dissolved chlorine in the form of hypochlorous acid significantly oxidises PP fibre membranes, most probably using a free radical mechanism. Initially, these radicals may be generated by HOCl in the presence of metallic impurities or hydroxy radicals produced in hydroperoxide decomposition.

Metallic Impurities

Chlorine, in the form of HOCl, has a valence of +1. HOCl is a strong oxidising agent. When a substance is oxidised by HOCl the Cl^+ species gains two electrons from the reducing agent forming Cl^- , a chloride radical with a -1 valence¹⁰¹. The HOCl reduction proceeds as^{104,105}:



Scheme 11

This reaction occurs in the presence of a reducing agent such as aluminium, iron, titanium. It is commonly observed in the literature that commercial polypropylene contains small amounts of metallic impurities typically aluminium and titanium due to residual Ziegler-Natta catalysts, and copper and iron due to metallic processing equipment¹⁰⁶. HOCl in direct contact with active sites due to metallic impurities in PP fibres undergoes a redox reaction with the metal present, producing a chloride radical. Electrode potential reactions for some of these reducing agents are shown in Figure 3¹⁰⁴.

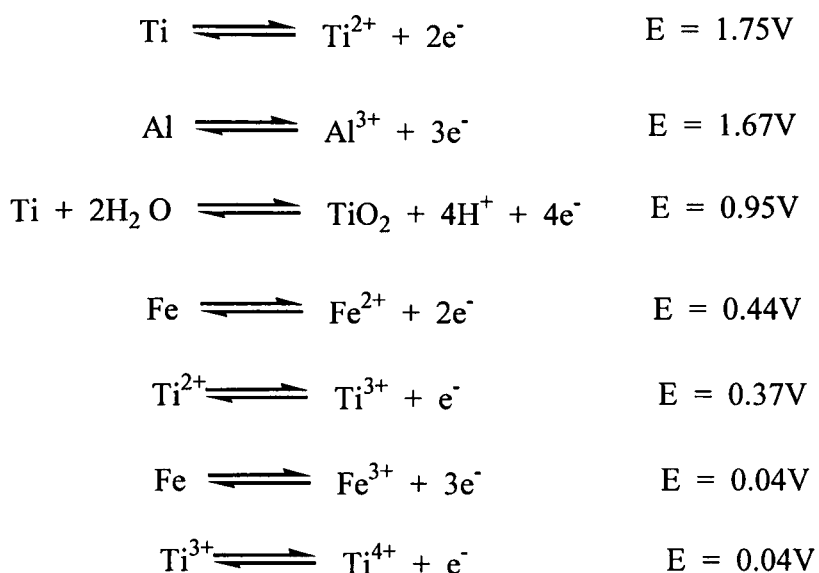
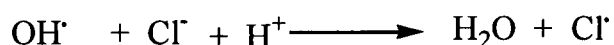


Figure 3 : Electrode potentials for common transition metals.

Hydroxy Radicals

Polypropylene oxidation produces as an intermediate product tertiary hydroperoxide as shown in Scheme 1. Commercial polypropylene is known to contain significant oxidation products which includes alkyl hydroperoxides which are formed during extrusion and processing. Alkyl hydroperoxides readily undergo decomposition to form a macroalkoxy radical and a hydroxy radical as shown in Scheme 5. Hypochlorous acid in contact with active sites in the PP fibres containing decomposed hydroperoxides generate chloride radicals by reaction with the hydroxy radicals¹⁰¹:



Scheme 12

In summary, chloride radicals may be formed from hypochlorous acid by two possible mechanisms:

i) Redox reaction of HOCl with metallic impurities present in PP fibre active sites as shown in Scheme 11.

ii) Reaction of chloride ions with hydroxy radicals present as a by-product of hydroperoxide decomposition at active sites in PP fibres as shown in Scheme 12.

Both scenarios require contact of the HOCl solution with an active site in the polypropylene. For this reason pure polypropylene, ie containing no impurities from processing, in contact with HOCl would not generate any active radicals and so no oxidation can occur. This is discussed in detail in Chapter 3.

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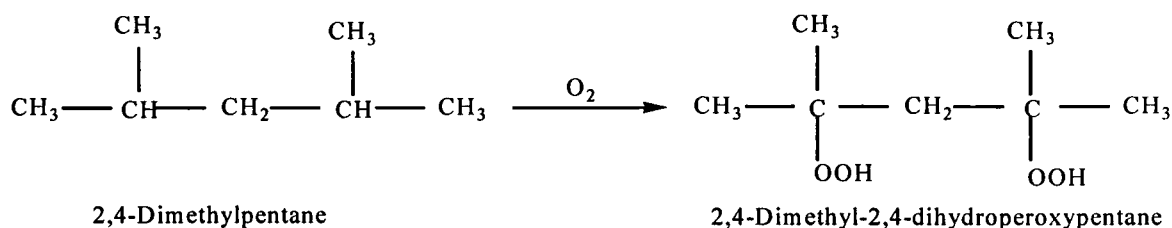
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Chapter 3 Chemical Modelling of Polypropylene.

3.1 Introduction

Commercial polypropylene contains a variety of impurities such as residual metals from Ziegler-Natta catalysts and metal processing equipment, unsaturated carbon-carbon groups from chain scission during visbreaking, hydroperoxides and other oxygenated species from oxidation during processing, storage or extrusion. These species all contribute to (or interfere with) PP oxidation.

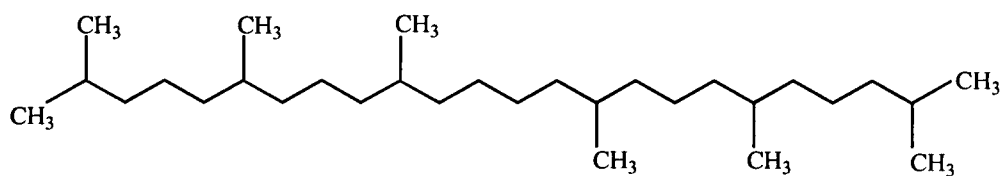
In order to understand the mechanism of pure polyolefin reactions, short chain organic compounds are commonly used in the literature to model the behaviour of these polymers under different conditions. Rust¹ used 2,4-dimethylpentane, Scheme 1, as a model compound for the air oxidation of polypropylene and found that the predominant product was 2,4-dimethyl-2,4-dihydroperoxypentane.



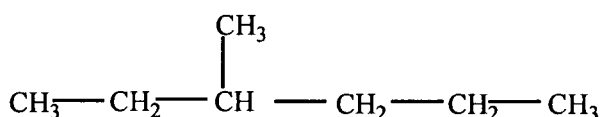
Scheme 1 : Air oxidation of 2,4-dimethylpentane.

Jois *et al*² used squalane, 3-methylhexane and nonane, Figure 1, as model compounds for an ethylene-propylene copolymer in the examination of free radical graft reactions. The model compounds were chosen to compare the reactivity of primary vs secondary vs tertiary carbons towards bromination. Bromination of squalane occurred primarily at the tertiary carbon, however secondary carbon bromination occurred to a small degree. Some formation of unsaturated molecules were observed due to debromination. Bromination of 3-methylhexane occurred predominantly at the tertiary carbon, and to a small

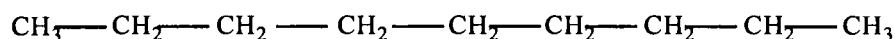
degree at secondary carbons. Bromination of nonane occurred at secondary carbon atoms.



Squalane : $C_{30}H_{67}$



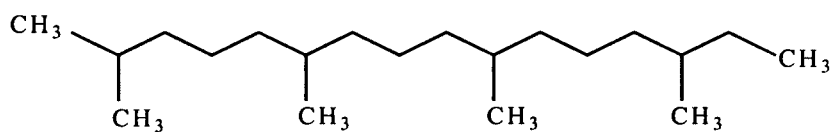
3-Methylhexane



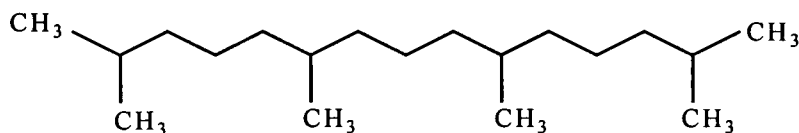
nonane

Figure 1 : Chemical structures of squalane, 3-methylhexane and nonane.

Squalane, Phytane, and pristane, Figure 2, have also been used as model polypropylene compounds³. Squalane, phytane and pristane were subjected to thermocracking at 250°C and analysed by high resolution capillary gas chromatography. The tertiary protons in the middle of the molecule were found to generate a larger radical population than those at the chain ends.



Phytane : $C_{20}H_{42}$



Pristane : $C_{19}H_{40}$

Figure 2 : Chemical structures of Phytane and Pristane.

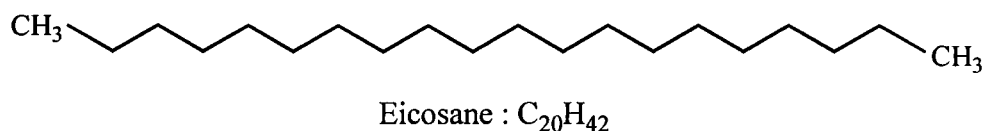


Figure 3 : Chemical structure of eicosane.

Russell⁴ used squalane and eicosane, Figure 3, as low molecular weight models for polymers containing secondary and tertiary hydrogen atoms in the grafting of maleic anhydride. It was shown that using squalane and eicosane the grafts consisted almost exclusively of single succinic anhydride units.

In terms of polypropylene degradation the classical mechanism assumes a pure polymer sample where initiation of oxidation occurs by abstraction of a tertiary hydrogen atom by a radical. It is only more recent work^{5,6,7,8} that takes into account the possibility of impurities in the polymer taking part in the degradation process. Carbon-carbon unsaturation on the polymer may also influence the degradation process^{9,10}.

Commercial polypropylene contains residual unsaturated C-C bonds formed during visbreaking as a result of chain scission. The C=C groups are formed at sites of chain scission and so exist primarily at chain ends of the newly scissioned molecules. Oxygen readily reacts across C=C groups, generating hydroperoxides as shown in Section 2.5.5.

3.2 Objectives

This study concerns the oxidation behaviour of polypropylene in hypochlorous acid. Two low molecular weight organic compounds are used in this work to model PP oxidation. The model compound 2,4-dimethylpentane, Scheme 1, is used in Part (1) to simulate tertiary hydrogen abstraction, and the low molecular

weight compound 2-methylbut-1-ene, Figure 4, is used in Part (2) to model the reaction of terminal unsaturated C-C bonds with oxygen.

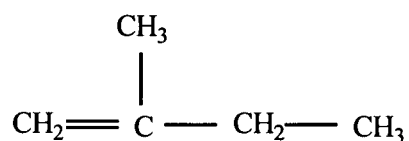


Figure 4 : Chemical Structure of 2-methylbut-1-ene.

Part 1

Polypropylene fibres undergo significant oxidation in the presence of hypochlorous acid. The classical mechanism of PP oxidation supposes that initiation of oxidation of polypropylene occurs by direct abstraction of the tertiary hydrogen atom from the polymer backbone by radicals, followed by reaction with oxygen. The objective of this work was to determine whether or not pure polypropylene undergoes oxidation by abstraction of tertiary hydrogen atoms using HOCl as the oxidising agent. A low molecular weight compound, 2,4-dimethylpentane (Scheme 1), was used as a model to simulate the behaviour of pure polypropylene under HOCl oxidising conditions.

Part 2

The objective of Part (2) was to determine whether or not oxidation occurs across terminal carbon-carbon double bonds on the polypropylene backbone using hypochlorous acid. A low molecular weight compound, 2-methylbut-1-ene, Figure 4, was used to simulate the terminal C=C groups which are present in commercial polypropylene due to chain scission during visbreaking.

3.3 Experimental

Materials and procedure

Degradation experiments were carried out using sodium hypochlorite, obtained from Ajax Chemicals at a concentration of 700ppm, 2,4-Dimethylpentane (2,4-

DMP) density 0.673g/cm^3 , and 2-methylbut-1-ene (2-MB) were obtained from Sigma-Aldrich and used without further purification.

For the oxidation reactions, 20mL of sodium hypochlorite and 10mL of the respective model compounds were placed in a sealed reactor. For the 2,4-DMP experiments, (Part 1), the resulting concentration of sodium hypochlorite in the reactor was 466ppm with the neat 2,4-DMP. For the 2-MB experiments, (Part 2), two sodium hypochlorite concentrations were used 10ppm and 466ppm with the neat 2-MB. Solutions were stirred constantly, using a magnetic stirrer, throughout the oxidation to ensure contact between the oxidant and the model compound. The oxidation reactors for both model compounds were kept at 20 and 50°C. The reactors were placed in a dark box and were kept sealed for the duration of the degradation.

Samples of the model compound were taken after 200 hours, a time chosen since under these conditions PP fibres are significantly degraded, and analysed via GC-MS. For the 2,4-dimethylpentane experiments, samples were analysed using a column temperature 35-220°C heated at a rate of 3°C/minute. For the 2-methylbut-1-ene experiments, samples were analysed using a (50%-Phenyl)-methylpolysiloxane column at a temperature of 30°C. The split ratio for the injector system used was 15:1, and an acetone solvent was used. The detector was started after 2.5 minutes as the retention time of the solvent in the column was 2 minutes. Before analysis of the samples, the column was flushed several times with HPLC grade acetone to remove any contaminants. This was necessary due to the expected low MS signal due to the probable low concentration of oxidised products in the organic solution. Prior to injection into the column organic samples were diluted to 10% with HPLC grade acetone. Determination of products was carried out by comparing mass spectra obtained with the online database.

3.4 Results and Discussion

3.4.1 Part 1 : 2,4-Dimethylpentane studies

Prior to analysis of the reacted samples, an unoxidised sample of 2,4-dimethylpentane was analysed by GC-MS. The resulting spectra showed small impurities due to tetrahydrofuran, at a retention time of 53 seconds. A signal for this compound was also observed in the reacted samples, and so did not effect oxidation. The DMP model compound after oxidation at 20 and 50°C was analysed via GC-MS. The overall GC spectra for the sample reacted at 20°C is shown in Figure 5. The GC spectra for the sample oxidised at 50°C shows signals at the same retention times, hence the products formed during both reactions appear to be identical. The content of the products in the total sample is measured by the intensity of the base peak (taken as 15 seconds) compared to the standard carrier signal. Using both the spectra for the oxidised DMP samples reacted at 20 and 50°C the signal of the base peak was calculated to be less than 0.1% of the standard carrier signal, indicating that the oxidised products represent at most 0.1wt% of the DMP model compound sample. So, >99.9% of the DMP model compound did not oxidise. However, oxidation products formed from the 0.1% of DMP that did undergo oxidation were able to be identified.

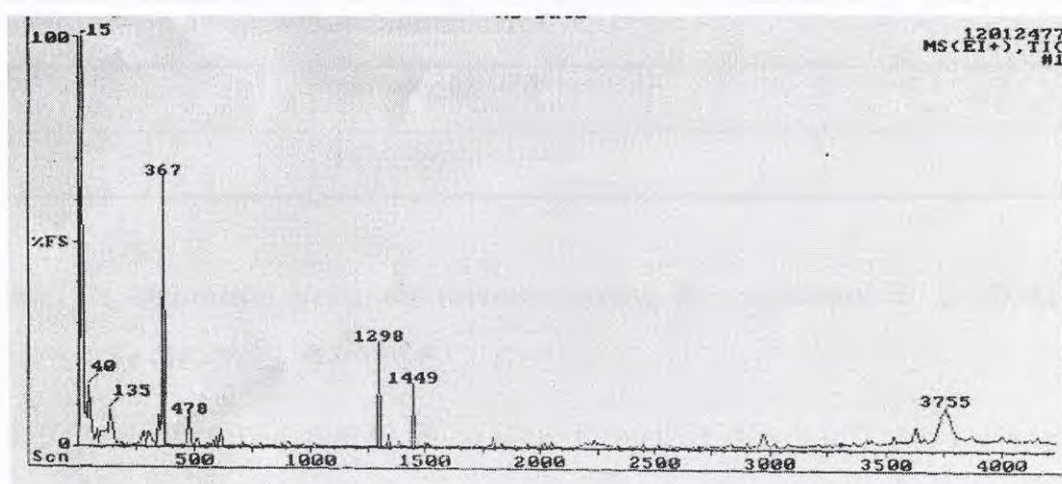


Figure 5 : Gas chromatogram for 2,4-DMP treated with HOCl.

Compounds contained in the oxidised sample were identified using the mass spectra and in this work will be referred to by their retention time through the GC. A summary of the oxidised compounds identified in the reacted samples, together with their retention times are shown in Table 1.

Retention Time (sec)	Compound
40 54	Low molecular weight fragments of 2,4-DMP
77	4-methyloctane
135	4-methylpent-2-enol.
273	1-ethenyloxypentane
367	x-chloro-2,4-dimethylpentene
478	3-chloro-2,4-dimethylpenta-1,4-diene or 1-chloro-2,4-dimethylpenta-1,3-diene
561 580 597	dimethyl alkene
614	3-hydroxy-3,5-dimethylhexan-2-one or 3,3-dimethylbutanoic acid.
1298	1-chloro-2,3-dimethylbutan-1-ol
1449	dichloroalkenol
1797	carboxylic acid
3755	dimethyl alkanone

Table 1 : Oxidation products formed during the oxidation of 2,4-DMP as detected by GC-MS.

A wide variety of oxidation products were formed as shown in Table 1. Based on signal intensity of the GC chromatogram, Figure 5, the major products of oxidation of DMP with HOCl are:

- i) chlorinated dimethylpentene, observed after 367 seconds.
- ii) 1-chloro-2,3-dimethylbutan-1-ol, observed after 1298 seconds.

Low molecular weight DMP fragments observed after 40 and 54 seconds and alkene groups observed after 561, 580 and 597 seconds suggest the occurrence of DMP chain scission, in small amounts.

From the data in Table 1 a range of oxygen containing groups were produced as shown by the formation of alcohols observed after 135 and 1298 seconds, carboxylic acids observed after 614 seconds, alkoxy groups observed after 273 seconds, and alkanones observed after 614 and 3755 seconds. However, no hydroperoxides were detected. So, oxidation of the DMP model compound producing oxygen containing species occurred to a small extent.

Several chlorinated products were also observed after 367, 478, 1298 and 1449 seconds. These products are not observed in the degradation of polypropylene fibres most probably because their concentration in degraded polypropylene fibres is so low that it is undetectable by XPS analysis. Alternatively, they may be formed in PP degradation as intermediates which continue reacting, and as a result are undetectable.

The concentration in the reactors of both the HOCl and the 2,4-DMP was extremely high compared to the level required to degrade polypropylene under the same conditions. After 4 days in 20ppm HOCl at 20°C the degradation of polypropylene fibre membranes results in a 20% increase in the oxygen content of the polymer. At this point the elongation at break of the fibres is zero and degradation is virtually complete. Using a HOCl concentration of 466ppm, extensive degradation should be observed after 8 days. As the total percentage of oxidation products for the reaction of 2,4-DMP at 20 and 50°C is less than 0.1%, we can assume that the sodium hypochlorite attack on the polymer backbone of

polypropylene is not the major cause of degradation. So, the main pathway of degradation of polypropylene using sodium hypochlorite does not proceed by radical attack on the polymer chain (abstracting the tertiary hydrogen atom). However it is possible that a very small percentage (less than 0.1%) of the oxidation products formed may be due to attack on the polymer chain. This process would not effect the overall degradation rate, or the products formed as a result of degradation.

In summary, oxidation of DMP results in oxidation of less than 0.1% of the model compound. So, it is concluded from this work that oxidation of polypropylene by HOCl does not occur to an appreciable degree by hydrogen abstraction of the HOCl solution or by any species present in the pure HOCl solution.

3.4.2 Part 2 : 2-Methylbut-1-ene studies

Prior to the analysis of the reacted 2-MB samples, both the neat sodium hypochlorite (NaOCl) solution and the 2 methylbutane (2-MB) solution were analysed by GC-MS. The neat NaOCl contained 2 low level impurities (triethylene glycol and 4-methylpentan-2-one-4-ol). The retention time of both these species is below that of the mobile phase, acetone, so their effect on the GC-MS analysis can be ignored. The 2-MB sample contained a significant amount of butylated hydroxy toluene (BHT) which is a commonly used anti-oxidant.

The mass spectra for the oxidised 2-MB solution showed signals for a range of products as well as that for BHT. Identification of products was carried out using the mass spectra of the sample compared to an online database. The resulting products along with their GC retention times are shown for the two HOCl concentrations in Table 2.

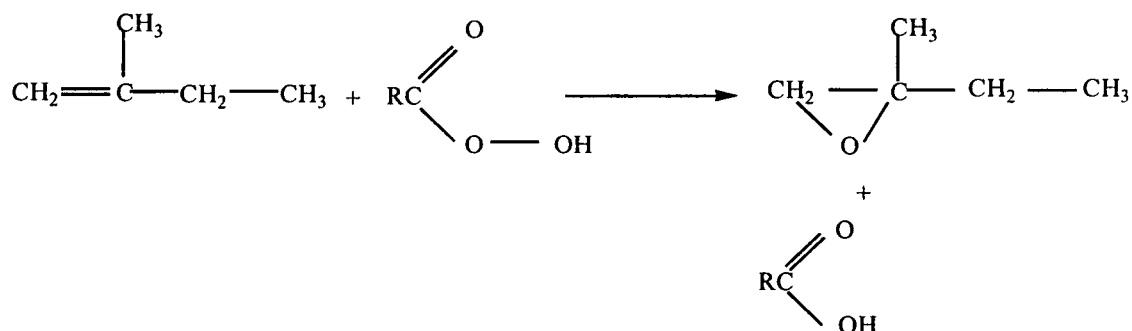
Retention time (min)	Compound ([HOCl] = 466ppm)	Compound ([HOCl] = 10ppm)
2.65	chloroform	
3.03	2-methylbutylene oxide	2-methylbutylene oxide
3.71	2-methylbut-1-en-1-ol (C ₅ H ₁₀ O)	
4.67	1-chloro-2-methylbut-2-ene	
6.3	2-ethyl-3-methylpent-1-en-4-one	2-ethyl-3-methylpent-1-en-4-one
7.31	hept-3-en-2-one	hept-3-en-2-one
7.96	3-ethyl-4-methylpent-2-ene	3-ethyl-4-methylpent-2-ene

Table 2 : Oxidation products formed during the oxidation of 2-MB using 466ppm and 10ppm HOCl as detected by GC-MS.

The oxidation of 2-MB using HOCl produces several oxidation products containing alkanones, alcohols, epoxides as well as more unsaturated carbon groups. The formation of these products are summarised below:

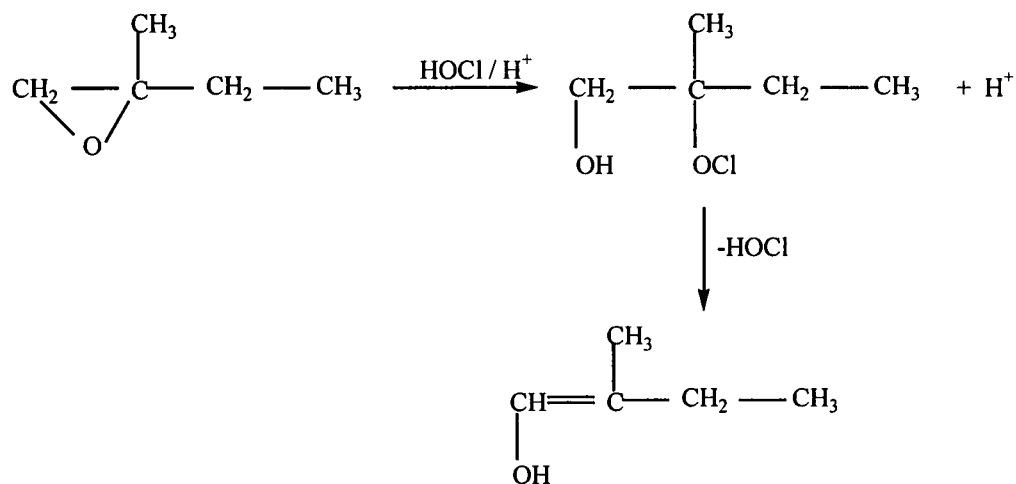
1. Chloroform, observed after 2.65 minutes, is formed by the chlorination of a methyl group after scission from the 2MB molecule. Chloroform is produced only at high degrees of oxidation.
2. The epoxide, 2-methylbutylene oxide, is an expected product, formed by the addition of oxygen from –OOH groups in peracids across terminal carbon-carbon double bonds in 2MB, as shown in Scheme 2¹¹¹². As discussed in Section 2.5.5, oxidation of unsaturated carbon-carbon bonds generally produces hydroperoxides (-OOH groups) as the major product. However, GC-MS analysis of the oxidised 2MB showed no evidence of –OOH formation either as hydroperoxides or peracids. This lack of -OOH content is most probably due to their complete

reaction with unoxidised 2MB molecules, generating carboxylic acids as shown in Scheme 2.



Scheme 2 : The reaction of unsaturated carbon groups with hydroperoxides forming epoxides.

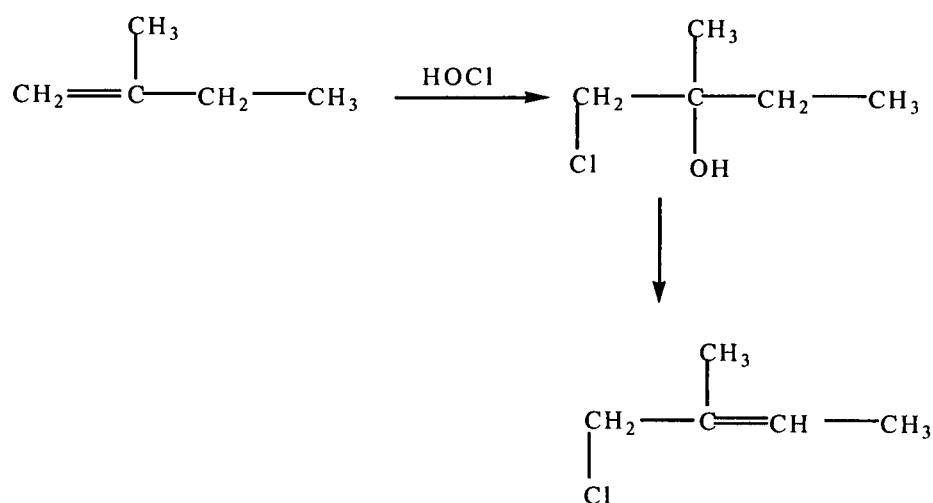
3. The epoxides, formed in Scheme 2, react readily with water undergoing acid-catalysed cleavage to form alcohols. The formation of 2-methylbut-1-en-1-ol may occur in this way as shown in Scheme 3 ¹¹.



Scheme 3 : The formation of 2-methylbut-1-en-1-ol by epoxide cleavage.

4. Hydrochlorination of C=C bonds occurs by Markovnikov addition of HCl, forming a saturated hydrochloride. Hydration of C=C bonds occurs by addition of water across the C=C group, producing a saturated alcohol¹³. Chemically, HOCl behaves similarly to water. The formation of 1-chloro-2-methylbut-2-ene,

observed after 4.67 minutes, may occur by addition of HOCl across the C=C, followed by loss of H₂O as shown in Scheme 4.



Scheme 4 : Formation of 1-chloro-2-methylbut-2-ene from 2MB.

5. The products 2-ethyl-3-methylpent-1-en-4-one, observed after 6.3 minutes and 3-ethyl-4-methylpent-2-ene, observed after 7.96 minutes, are most probably formed by reaction of 2MB molecules.

From the data in Table 2 it is evident that oxidation of the model compound 2-MB with HOCl has occurred. There are several implications of this. The formation of oxidised products by the reaction of HOCl with terminal unsaturated groups in the 2MB model compound suggests that terminal carbon-carbon double bonds present in polypropylene will react with HOCl in a similar manner. So, during PP oxidation with HOCl the formation of carboxylic acids and the consumption of hydroperoxides, Scheme 2, and the formation of alcohols, Scheme 3, would be expected as a result of C=C oxidation.

Of the products formed from the oxidation of 2-MB at high HOCl concentration two contain chlorine : 1-chloro-2-methylbut-2-ene and chloroform, neither of which are formed in the low concentration degradation. This is either due to:

1) A too low HOCl concentration to encourage addition of chlorine across the carbon-carbon double bonds, or

2) The chlorinated products may be only formed at sufficiently high degrees of oxidation.

XPS analysis of PP fibres degraded by varying degrees with HOCl showed no sign of chlorine addition to the polymer (this is discussed in Section 3.4.3.4). So, it is most likely that the formation of chlorinated products occurs only at high HOCl concentrations. At low HOCl concentrations the oxidation mechanism takes precedence.

In summary, oxidation of 2MB, a model compound for terminal C=C groups, with HOCl produced a variety of oxidation products particularly: carboxylic acids, alcohols, ketones, alkenes and chlorinated alkenes. Several mechanisms have been proposed for product formation. It appears that HOCl significantly oxidised 2MB, and hence HOCl may oxidise terminal C=C groups present in PP hollow fibres.

3.5 Conclusions

This study was carried out i) To determine whether or not oxidation of polypropylene occurs by hydrogen abstraction by a pure HOCl solution and ii) To determine whether terminal C=C bonds, present in commercial PP, undergo oxidation by a HOCl solution. Part i) was carried out using a low molecular weight compound, 2,4-dimethylpentane (DMP), as a model for tertiary carbon atoms present in polypropylene. This model was to simulate the oxidation behaviour of pure PP, without any residual impurities from processing or storage. Part ii) was carried out using low molecular weight compound, 2-methylbut-1-ene (2MB), as a model for terminal C=C groups present in commercial PP.

Reaction of the PP model compound DMP with HOCl resulted in oxidation of less than 0.1% of the model compound. So, it is concluded from this work that

oxidation of polypropylene by HOCl does not occur to an appreciable degree due to hydrogen abstraction by the HOCl solution or by any species present in the pure HOCl solution. So, oxidation of commercial PP using HOCl must proceed by generating active species in either the HOCl or on the polymer to initiate oxidation.

Reaction of the terminal C=C model compound 2MB with HOCl produced a wide variety of oxidation products in significant amounts. The oxidation products consisted particularly of : carboxylic acids, alcohols, ketones, alkenes and chlorinated alkenes. Mechanisms for the formation of these products were proposed. So, it appears that HOCl significantly oxidises terminal C=C groups in the 2MB model compound. It would be expected then that HOCl would react in a similar manner with terminal C=C groups in commercial PP.

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Chapter 4 Oxidative Degradation of High Surface Area Polypropylene by Aqueous Hypochlorous Acid.

4.1 Introduction

Oxidative degradation of polypropylene has been studied extensively for bulk polymer, film, powder and pellets. Relatively few investigations have been made in the oxidation of PP fibres¹. High surface area polypropylene fibre membranes are more vulnerable to oxidative degradation than bulk polypropylene for several reasons:

1. Their large surface area to volume ratio. Oxidative degradation of PP fibres with aqueous hypochlorous acid (HOCl) depends on contact area between the oxidant (HOCl) and the polymer. For a fixed volume of PP, samples with a large surface area would be expected to oxidise more readily than samples with a smaller surface.
2. The large surface area of PP fibres results in a higher percentage of the polymer in direct contact with the oxidant, and hence a higher concentration of impurities in the amorphous region in direct contact with the oxidant. i) This reduces the need for the oxidising chloride and oxygen to diffuse through the polymer to the active sites, thus increasing the overall oxidation rate. ii) This increases the ease with which chlorine radicals are formed by reaction with the hydroxy radicals formed as a result of hydroperoxide decomposition at the active sites. An increase in the rate of formation of chlorine radicals will result in an increase in the rate of PP oxidation as compared to low surface area PP.
3. High surface area PP fibres do not undergo a 'skinning' effect. Polypropylene hollow fibre membranes consist of fine polymer strands, approximately 0.02 μ m in width, surrounded by pores. Dissolved oxygen and chloride ions readily diffuse through the less than 0.02 μ m of polymer, completely penetrating the polymer at all

depths from the surface. Removing the dependence of diffusion of species through the polymer increases the rate of oxidation compared to thicker samples.

4. During the thermal extrusion process, some oxidation of the polypropylene may occur generating hydroperoxides and other oxidation products which increase the susceptibility of the material to degradation. Stabilisers may be added to the polymer melt prior to extrusion to prevent this occurrence.

Another limitation with research reported in the literature is the lack of data on the non-gas phase oxidation of PP. Numerous studies of PP have involved PP oxidation by oxygen in the gas phase, usually at elevated temperatures. Some researchers, however, have analysed PP oxidation with gaseous oxygen at ambient temperatures as discussed in Section 2.5.3 dealing with Peroxide Formation and Decomposition in Polypropylene Degradation. No previous work has investigated the aqueous oxidative degradation of polypropylene by hypochlorous acid or by dissolved oxygen.

4.2 Determining the Extent of Degradation

Several initiation processes are usually involved in most practical applications of PP degradation usually either thermal, photochemical or mechanical². In this work the oxidative degradation will undergo chemical and to a certain extent thermal initiation. The oxidation is monitored by means of i) The change in carbonyl index, changes in hydroperoxide content and unsaturated carbon-carbon content as measured from FT-IR analysis ii) Changes in crystallinity and molecular weight determined from DSC, FT-IR and GPC measurements and iii) Changes in oxygen content measured by XPS. These results are correlated with the mechanical properties of the degraded polymer.

4.2.1 Elongation at Break

Elongation at break is commonly used in the literature to determine the extent of degradation of semi-crystalline polymers³. The strength of semi-crystalline polymers results from the entanglement of the individual polymer chains and the presence of crystalline regions which add stability to the amorphous regions as, well as the presence of tie molecules. The existence of tie molecules between both lamellae and spherulites was shown by Keith *et al*^{4,5,6}. Tie molecules are generally long enough to exist in both the amorphous and crystalline regions, binding the two regions together. Tie molecules contain a high percentage of strained bonds compared to the bulk polymer and support a disproportionate share of the load in the amorphous region⁷. Hence, during oxidation tie molecules are more likely to break, and their loss will have a large impact on the deterioration of the polymer. Scission of tie molecules at interspherulitic boundaries is particularly detrimental. Hence, if the polymer molecular weight is reduced by chain scission then the polymer strength will decrease.

Data supporting the action of tie molecules have been found in the literature. Flood *et al*⁸ proposed that the improved tensile properties for polypropylene with a broad molecular weight distribution is due to an increase in the number of tie molecules present as compared to those in polypropylene with a smaller molecular weight distribution. Tzoganakis *et al*⁹ observed that the number of tie molecules and tie molecule entanglements decreased with molecular weight.

When monitoring the degradation of polypropylene fibres, some decrease in elongation at break will be observed before the oxidation products reach infrared detectable limits¹⁰. This is because small amounts of chain scission detrimentally effect the tensile strength of the fibres. The PP fibre is only as strong as its weakest

point. This means that when measuring the elongation at break of PP fibres by stretching a 10cm sample of the fibre, degradation at one point in the polymer may cause loss of integrity of the fibre.

According to Bamford¹¹, chain (β)-scission occurs resulting in an observed drop in molecular weight of the polymer. Severini *et al*³ showed that β -scission is the main chain scission process with a linear correlation between carbonyl absorbance and molecular weight. In the presence of hydroperoxides, β -scission is most likely the major source of backbone scission since approximately 15% of the photolysed hydroperoxide groups undergo this reaction¹².

4.2.2 FT-IR Spectroscopy

FT-IR spectroscopic methods are commonly used in the literature to monitor the extent of degradation of polypropylene^{13,14}. Oxidation of polypropylene generates a variety of final products, most of which absorb IR signals in the carbonyl region. For this reason it is sometimes difficult to identify the exact nature of products formed using only FT-IR techniques. Hydroperoxides, intermediate products formed during oxidation, and unsaturated C-C groups however are readily identified using FT-IR spectroscopy.

The major products formed during PP oxidation can be readily monitored using FT-IR spectroscopic techniques typically in the region 1620-1800cm⁻¹¹⁵. This signal is a composite of absorbances from the formation of many carbonyl products including aldehydes 1735cm⁻¹, ketones 1690cm⁻¹, terminal carbonyls at 1716cm⁻¹ and carboxylic acids at 1720cm⁻¹. Hydroperoxide content can also be detected at 3550 cm⁻¹ for free hydroperoxides and 3400cm⁻¹ for hydrogen bonded hydroperoxides^{16,17}, as can vinyl groups at 1633 and 3100cm⁻¹³.

4.2.3 Surface analysis - X-ray Photoelectron Spectroscopy (XPS)

Surface analysis by X-ray photoelectron spectroscopy (XPS) is accomplished by irradiating the sample with monoenergetic x-rays and analysing the electrons emitted. The x-rays interact with atoms on the surface of the sample, approximately the first few nm, by a photoelectric effect, causing the inelastic scattering of photoelectrons. The emitted electrons have kinetic energy given by

$$KE = h\nu - BE - \phi_s$$

where $h\nu$ is the energy of the incident photon, BE is the binding energy of the atomic orbital from which the electron originates, and ϕ_s is the spectrometer work function.

The XPS spectrum obtained is a plot of number of emitted electrons per energy interval versus their kinetic energy. Each element has a unique elemental spectrum and the identity of the elements present can be obtained using curve fitting and functional group derivatisation followed by comparison with a database.

One of the dominant oxidation products from polypropylene degradation, the hydroperoxide group, is readily destroyed by X-rays. Lacoste *et al* ¹⁸ observed that the oxygen atom percentage, as detected via XPS, decreased with X-ray exposure time by as much as 40%. This problem was overcome by measuring oxygen content over a period of exposure times and extrapolating back to zero time.

4.2.4 Differential Scanning Calorimetry

The measurement of crystallinity and transitions in polypropylene can be carried out using dilatometry or thermal methods, such as DSC¹⁹. DSC yields peaks relating to endothermic and exothermic transitions, shows changes in heat capacity and gives quantitative information relating to enthalpic changes in the polymer.

Degree of crystallinity may be calculated from the heat of fusion of a semicrystalline sample. At the crystalline melting temperature excess heat is pumped into the sample to effect the transition from crystalline solid to melt. The amount of heat required for this process is the heat of fusion (ΔH_f) and is proportional to the fraction of crystal present and the mass of sample analysed²⁰. Crystallinity is calculated using this heat relative to the heat of fusion for a pure crystalline sample²¹:

$$X (\%) = \Delta H_f (\text{per g of sample}) / \Delta H_f (\text{per g of crystal}) * 100$$

Where ΔH_f is the latent heat for isotactic polypropylene, 165J/g²¹.

Determination of the heat of fusion for a semicrystalline sample requires the selection of a start and end point for the melt peak. A baseline for the melt transition is then determined internally by the software. Selection of the start and end peaks by the user introduces a small degree of uncertainty. Individual crystallinity values used in this work were obtained as an average of 3 calculations from the same data. In all cases the error was small, less than 2%.

Polypropylene membranes used in this experimental work are extruded from semicrystalline isotactic PP pellets. The resulting membranes have a crystallinity of approximately 33.1%. Changes in the polymer crystallinity occur during degradation due to chain scission and subsequent crystalline rearrangement.

4.3 Objectives

The objectives of work carried out in this chapter are:

1. To determine the effect of hypochlorous acid (HOCl) concentration and temperature on the aqueous oxidative degradation of PP hollow fibre membranes.

The extent of degradation of the fibres will be determined using tensile strength measurements, FT-IR, DSC, GPC and XPS techniques.

2. To derive a proposed mechanism of oxidation of PP fibres in aqueous HOCl.

3. To compare the products and mechanism of the aqueous oxidation of PP fibres with the products observed in the literature for gaseous oxidation of bulk PP.

4.4 Experimental

4.4.1 Materials

Polypropylene was studied in the form of hollow fibre membranes. The membranes were extruded by USF Filtration from polypropylene pellets. Generally, prior to extrusion a hindered phenolic stabiliser is added to the polymer to prevent degradation during processing. The fibres used in this work contain no stabilisers added for the extrusion process, however they will contain small amounts of residual stabilisers from the supplier's polymerisation and storage processes.

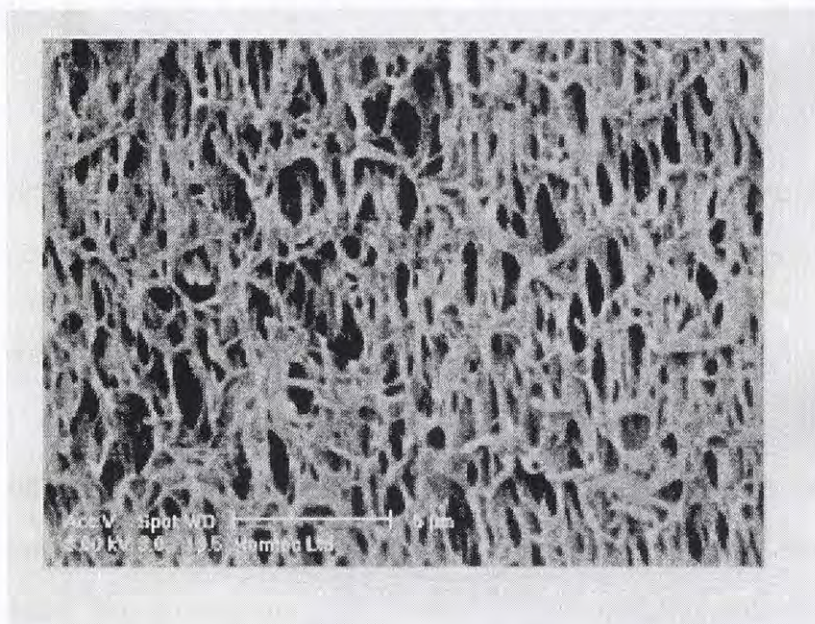


Figure 1 : Scanning Electron Micrograph of cross-section of polypropylene fibre wall.

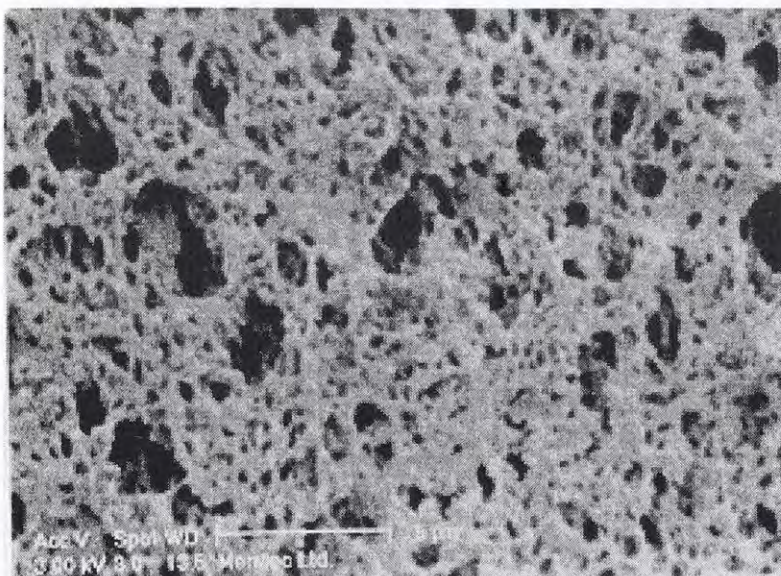


Figure 2 : Scanning Electron Micrograph of polypropylene inside wall.

The membranes produced are hollow fibres with an inner diameter of 250-290 μm and outer diameter of 650 μm . The membranes have a nominal pore size of 0.2 μm , strand thickness of 0.02 μm , density of 0.088g/cm³ and a specific mass of 0.046 m²/g, Figure 1 and Figure 2. The polypropylene is 81-94% isotactic and 30% crystalline.

Degradation experiments were carried out using chlorine in the form of aqueous sodium hypochlorite (Ajax Chemicals), 125g/l dissolved in reverse osmosis water.

4.4.2 Method of Degradation

For this experimental work polypropylene degradations were carried out using either controlled or sealed reactors. Both utilised an aqueous system, however, the former was carried out in the absence of oxygen with constant free chlorine levels, while the latter was carried out with limited oxygen and free chlorine present.

Controlled degradation experiments were carried out in a continuously stirred closed reactor, which was placed in a water bath at temperatures of 20, 40 and 60°C. A schematic is shown in Figure 3. The water bath was kept at constant temperature using a Braun controlled recirculating heater. Oxygen was removed from the solution by regassing with high purity argon for 30 minutes prior to the degradation experiments and after each sample was removed from the reactor.

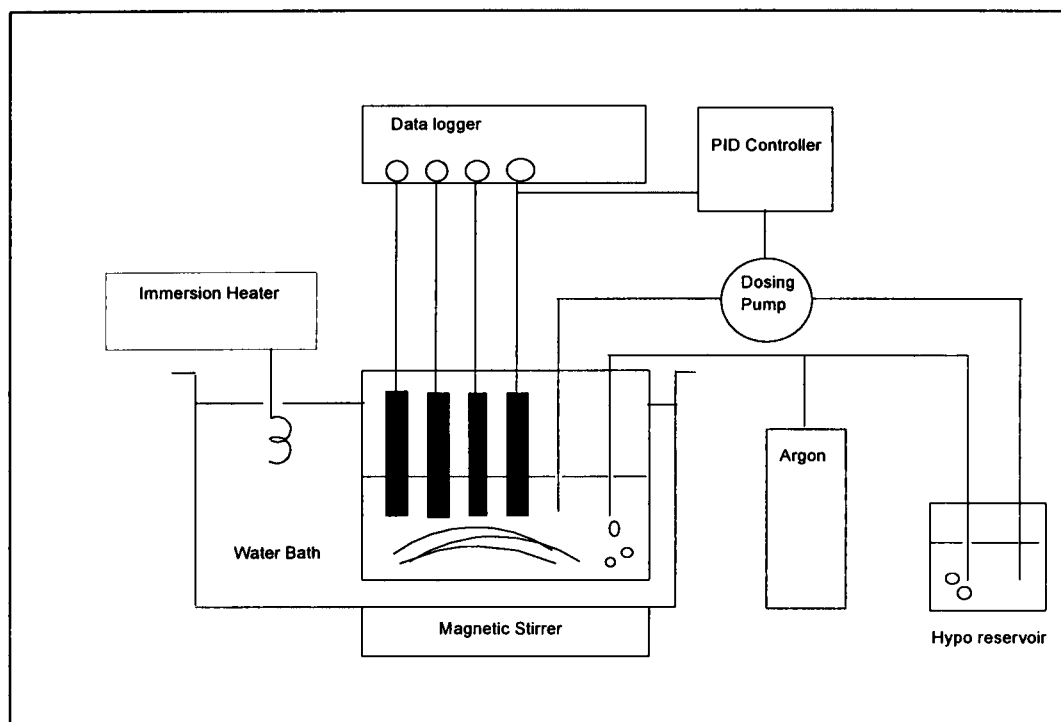


Figure 3 : Schematic illustrating the controlled degradation system.

Polypropylene membranes were degraded in a continuously stirred sodium hypochlorite solution with a hypochlorous acid concentration varying from 0 to 20ppm. Membrane fibre samples were placed in a teflon sample holder inside the reactor. Probes suspended inside the reactor monitored conductivity, pH, hypochlorous acid concentration and oxygen redox potential (ORP) of the reactant solution. This data was logged periodically by an 8 channel Datalogger-DT100 datalogger. A constant hypochlorous acid concentration was maintained by controlled dosing with a high concentration sodium hypochlorite solution. The

measuring probe for chlorine control was a Prominent Dulcotest CLE 2.2 which measures only HOCl. The reaction assembly, (including reactor, probes and water bath and recirculating heater), was housed in a dark box for the duration of the oxidation.

Sealed system degradation experiments were carried out in sealed reactors with constant volume at temperatures of 20 and 50°C. Oxygen was not removed from the solution prior to degradation experiments. As the system for each degradation was sealed, the oxygen content of the water was at most 40ppm as calculated from the saturated solubility of oxygen in water at standard lab conditions²².

Polypropylene membranes used in this study are hydrophobic. For this reason all samples are wetted out prior to all chlorine degradation studies in an appropriate solvent (such as ethanol) for 10 minutes to ensure completely wetted samples. The samples were then rinsed in reverse osmosis (RO) water.

Fibre samples were removed from the reactor vessel routinely after specified amounts of time, washed with distilled water and allowed to dry. Samples were then placed separately in sealable bags.

4.4.3 Method of Fibre Analysis

4.4.3.1 Elongation at Break

The elongation at break of the membrane fibres was measured using an Instron 4301 tensometer with a static load cell of 10N and a crosshead speed of 100mm/min. The elongation at break of the degraded membranes is expressed as a percentage of the elongation at break of a group of undegraded control membranes (in notation referred to as %BE as %Control). Note: A group of test fibres is considered

degraded for industrial purposes if %BE as %Control is less than 50%. At this point the fibre has insufficient integrity to function as a filtration membrane.

4.4.3.2 FT-IR Spectroscopy

FT-IR analysis was carried out on the polypropylene fibres which were cold pressed between polished steel discs into a transparent thin film on an hydraulic press. A similar method was used by George *et al*²³ and was found to have no effect on the oxidative stability of the polymer. FT-IR spectra were recorded using a Shimadzu FT-IR-8210PC. The IR absorptions were expressed as the difference between the peak absorption and the absorption at a base line.

4.4.3.3 Surface analysis - X-ray Photoelectron Spectroscopy (XPS)

Fibre membranes were analysed as a transparent thin film prepared using an hydraulic press at 15 tonne at room temperature. Samples were mounted on an osenetic stainless steel die and analysed using a Kratos XSAM 800 BCI.

4.4.3.4 Differential Scanning Calorimetry (DSC)

DSC measurements were carried out using a Shimadzu DSC-50 with a TA-50WS thermal analyser. Approximately 4mg of membrane fibre samples were placed in hermetically sealed pans and heated from -100 to 190°C at 20°C/min. Samples were prepared by finely chopping the fibre samples into lengths of about 2-3mm. The DSC system was constantly flushed with nitrogen during the analysis. Each sample was scanned only once, but for reproducibility 3 separate DSC analysis were carried out per sample.

4.4.3.5 Gel Permeation Chromatography (GPC)

GPC measurements were carried out on the polypropylene fibre membranes using a PL GPC-210 with a PLgel 2 * mixed bed-B column. The solvent used was 1,2-

dichlorobenzene and samples were analysed at approximately 140°C. The GPC system was calibrated using polystyrene narrow molecular weight standards.

4.4.3.6 Scanning electron microscopy

SEM analysis was performed using a Philips XL-20 electron microscope. Membrane fibres were freeze fractured using liquid nitrogen, mounted and gold coated using a Biorad SEM coating system. Membrane fibres were mounted so that any of 3 analyses could be carried out: fibre outer surface, fibre inside surface of fibre wall structure.

4.5 Results and Discussion

4.5.1 Identification of Oxidation Products using FT-IR Spectroscopy

FT-IR spectroscopy is a useful tool to analyse the products of degradation of polypropylene as has been discussed in the literature^{24,25,26,27,28}. It gives a detailed analysis of the functional groups formed on the polymer due to degradation.

As mentioned in Section 4.5.2.2 the undegraded polypropylene contains some impurities from the polymerisation and visbreaking processes such as metallic impurities and oxidation products eg hydroperoxides, carbonyl compounds, unsaturated C-C groups. These species are important as they may act as initiation sites for the degradation process.

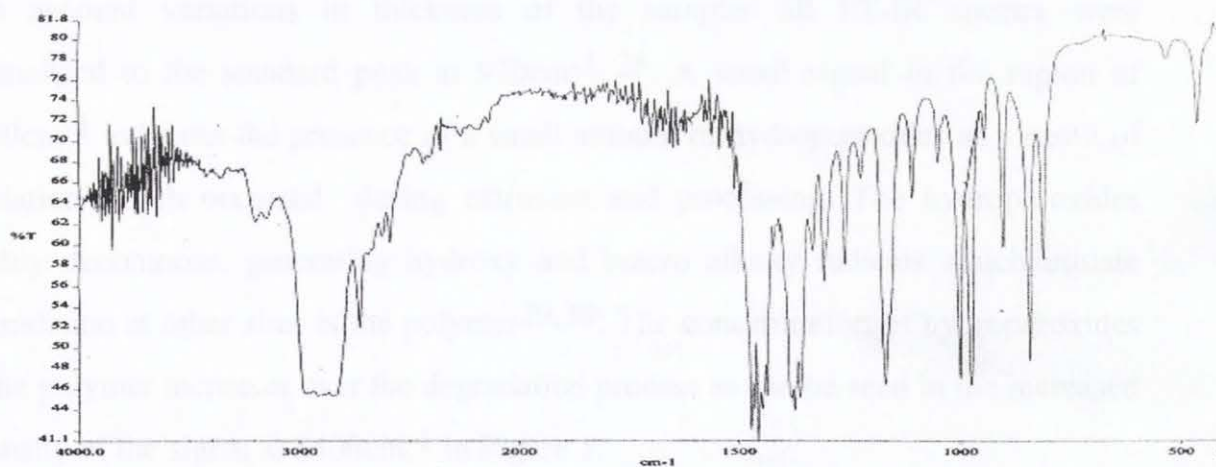


Figure 4 : FT-IR spectra for a thin film pressed from undegraded polypropylene fibres.

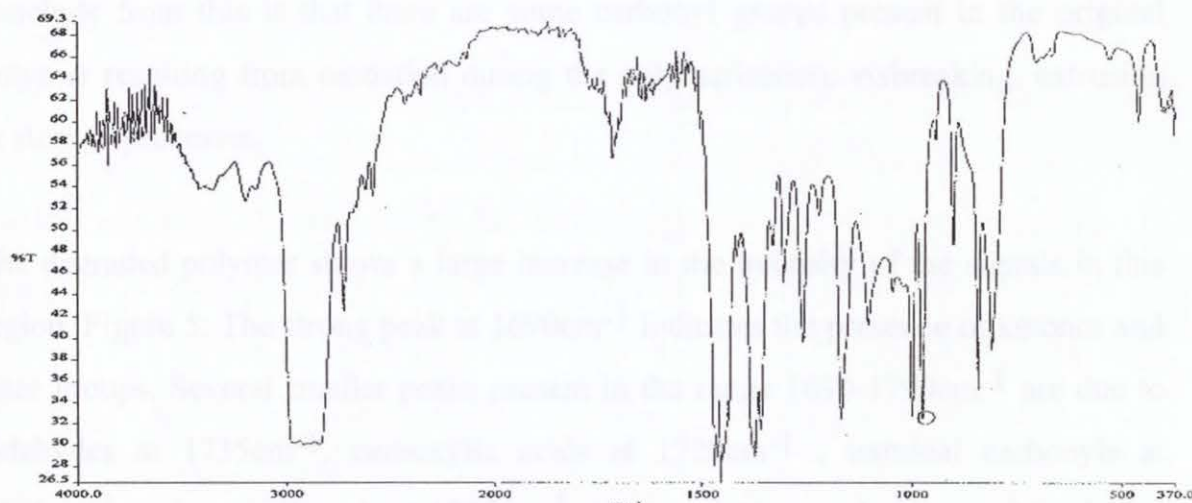


Figure 5 : FT-IR spectra for a thin film pressed from degraded polypropylene fibres (%BE as % of control=0).

Figure 4 shows a sample spectra for the ‘undegraded’ polypropylene fibres. To take into account variations in thickness of the samples all FT-IR spectra were normalised to the standard peak at 970cm^{-1} ²⁵. A small signal in the region of 3400cm^{-1} indicates the presence of a small amount of hydroperoxides as a result of oxidation which occurred during extrusion and processing. The hydroperoxides readily decompose, generating hydroxy and macro alkoxy radicals which initiate degradation at other sites in the polymer^{29,30}. The concentration of hydroperoxides in the polymer increases over the degradation process as can be seen in the increased intensity of the signal at 3400cm^{-1} in Figure 5.

Carbonyl compounds, observed at $1620\text{-}1800\text{cm}^{-1}$, are a commonly accepted by-product of oxidation. The low intensity signal in this region for undegraded polypropylene, Figure 4, indicates that some carbonyl groups are present, however it is difficult to resolve the individual peaks and distinguish their exact nature. If the polymer were free of impurities we would expect no signal in this area, so all we can conclude from this is that there are some carbonyl groups present in the original polymer resulting from oxidation during the polymerisation, visbreaking, extrusion or storage processes.

The degraded polymer shows a large increase in the intensity of the signals in this region, Figure 5. The strong peak at 1690cm^{-1} indicates the presence of ketones and ester groups. Several smaller peaks present in the range $1690\text{-}1790\text{cm}^{-1}$ are due to aldehydes at 1735cm^{-1} , carboxylic acids at 1720cm^{-1} , terminal carbonyls at 1716cm^{-1} and a small peak at 1780cm^{-1} due to γ -lactones. Analysis of the broad shoulder in the region $1500\text{-}1650\text{cm}^{-1}$ showed the presence of vinyl ethers at 1618cm^{-1} , ketones at 1605cm^{-1} and a secondary peak due to vinyl alkene at 1598cm^{-1} .

In summary, undegraded PP contains a small amount of hydroperoxides, low levels of carbonyl compounds and significant amounts of carbon-carbon unsaturation. These impurities are all due to oxidation which occurred during extrusion and processing. Significantly degraded PP contains an increased concentration of hydroperoxides, as well as a large range of identifiable compounds, particularly ketones and esters.

4.5.2 The Induction Period

The mechanisms proposed in the literature discuss evidence of an induction period in the degradation process³¹. The induction period may be defined as the length of time at the start of degradation when no observable changes due to oxidation occur in the polymer. The duration of the induction period for the oxidation of PP fibres with HOCl will be determined using data obtained from tensile strength, FT-IR, XPS and DSC analysis of degraded fibres.

4.5.2.1 Mechanical Strength

The elongation at break is a good indication of the mechanical strength of the membrane fibres and is commonly used to represent the degree of degradation of membrane fibres. However, when the membranes become extremely degraded the elongation at break is measured as zero and at this point the technique is meaningless. In this case, an alternative measurement of degree of degradation is required. Figure 6 illustrates the change in elongation at break for degradations using 10ppm hypochlorous acid.

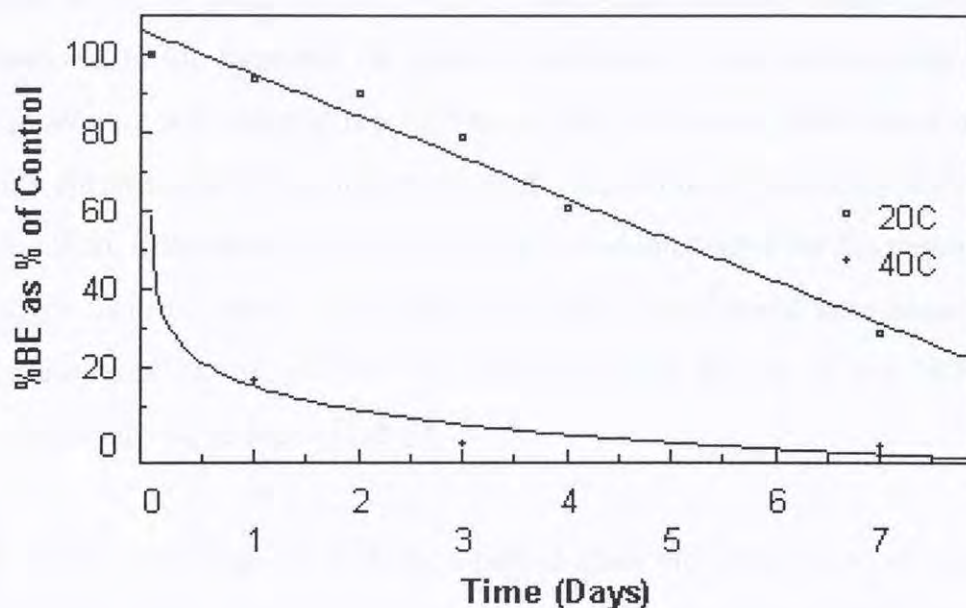


Figure 6 : Degradation time profile for fibres in 10ppm HOCl at 20 and 40°C

It is evident that even at low temperature the physical effect of degradation is evident almost immediately. From the data in Figure 6 it appears that the degradation at 20°C exhibits an initial slow degradation period of 0-2 days, during which time only a 10% loss in elongation at break occurs as compared to 90% for the degradation at 40°C over the same period.

The information offered from Figure 6 therefore relates to the induction period in two ways:

- 1) The loss of mechanical strength observed early in the degradation may occur within the induction period (as observed by George *et al*³²). If this is the case we should then observe a further acceleration of the degradation process later on. From just the mechanical strength data shown it is impossible to determine whether or not this occurs due to the 'limit of measurement' of the tensile technique.

2) The induction period of degradation may be so short that after the first sample has been taken, at both 20 and 40°C, it may have already ended. Induction periods observed in the literature for gaseous oxidation of low surface area PP at elevated temperature are typically reported to be 200-1000 hours (8-40 days) in duration. For high surface area PP the induction period should be significantly lower. If this is the case then, from the data in Figure 6, the induction period for the degradation at 20°C ranges from 0-2 days. The situation is more complicated here because of the high surface area of the polymer which allows easy access of the HOCl (present in solution) to the surface of the PP.

In order to examine the induction period more closely a series of degradation were conducted over a 48 hour period using 0, 10 and 20ppm HOCl as the oxidant at ambient temperatures. The results are shown in close up in Figure 7 and as an overview in Figure 8.

Figure 7 and Figure 8 illustrate the existence of a short time, approximately 2-3 hours, at the beginning of the degradation where a slight increase in tensile strength of the fibres occurs. The length of this period is dependent on chlorine concentration. The short period of inactivity may be explained in two ways. i) it may be the induction period that is frequently discussed in the literature. If so, then the brevity of this period is most probably due to the ease of access of the HOCl solution to the fibre as well as its high surface area, or ii) it may just be evidence of a lag time to allow for diffusion of chloride and hydroxy radicals and oxygen to the surface of the fibres and their subsequent reaction producing chain scission and a decrease in the mechanical strength of the fibres. More chemical and analytical information will be presented to distinguish between these two scenarios.

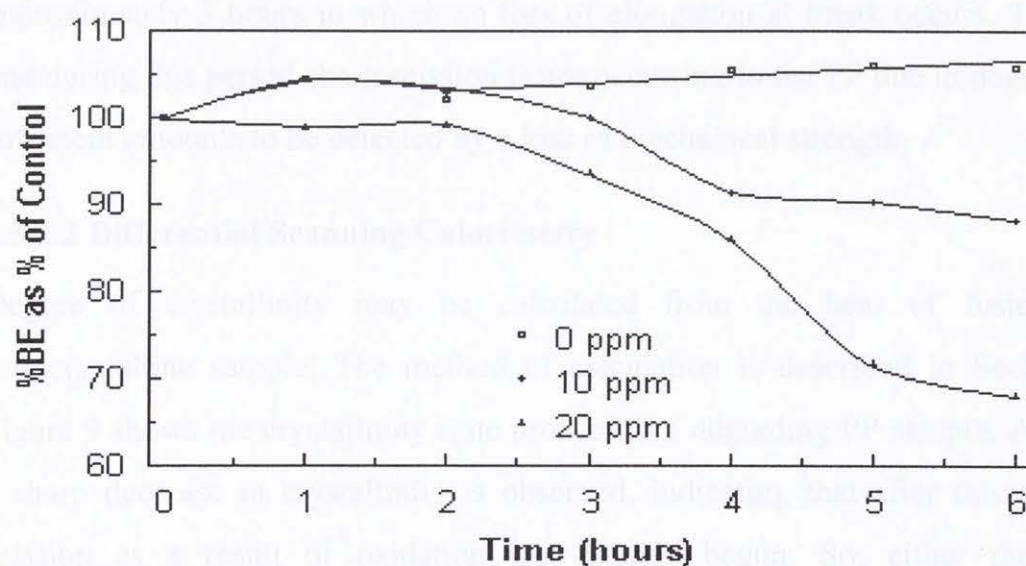


Figure 7 : Degradation time profile for samples at 20°C in three different concentrations of HOCl.

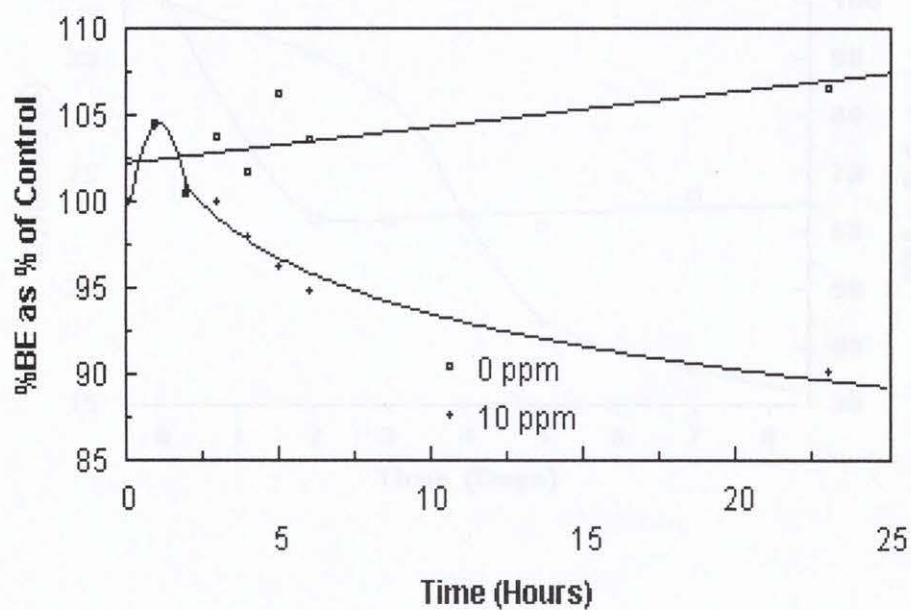


Figure 8 : Extended degradation time profile for samples at 20°C in HOCl

In summary, based on mechanical strength data an induction period occurs lasting approximately 3 hours in which no loss of elongation at break occurs. This means that during this period chain scission is not occurring in the PP due to degradation in sufficient amounts to be detected by a loss of mechanical strength.

4.5.2.2 Differential Scanning Calorimetry

Degree of crystallinity may be calculated from the heat of fusion of a semicrystalline sample. The method of calculation is described in Section 4.2.4. Figure 9 shows the crystallinity time profile for a degrading PP sample. After 1 day a sharp decrease in crystallinity is observed, indicating that after this time chain scission as a result of oxidation has already begun. So, either the polymer crystallinity does not exhibit an induction period, or the induction period is much less than 1 day in duration.

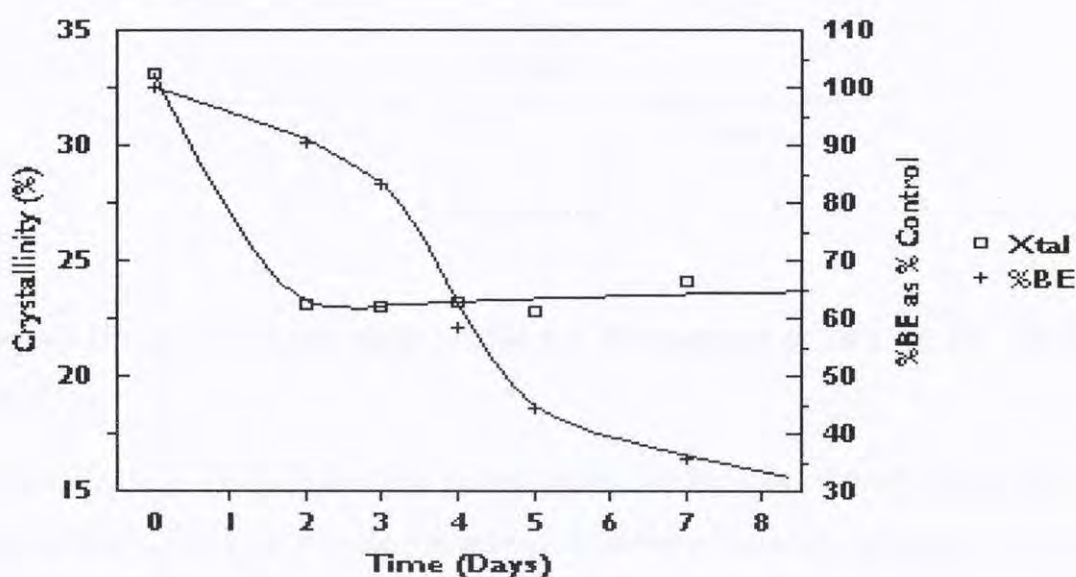


Figure 9 : Changes in crystallinity with time for polypropylene fibre degrading in 10ppm HOCl at 20°C.

In order to examine the induction period more closely a series of degradation were conducted over a 23 hour period using 10 and 20ppm HOCl as the oxidant at ambient temperatures. Figure 10 shows the existence of an induction period of approximately 1 hour, followed by a decrease in crystallinity. This short induction period allows for the generation of chloride and hydroxy radicals by reaction with metallic impurities in active sites of the polymer. These radicals may then attack tie molecules, abstracting hydrogen atoms and resulting in chain scission and loss of crystallinity.

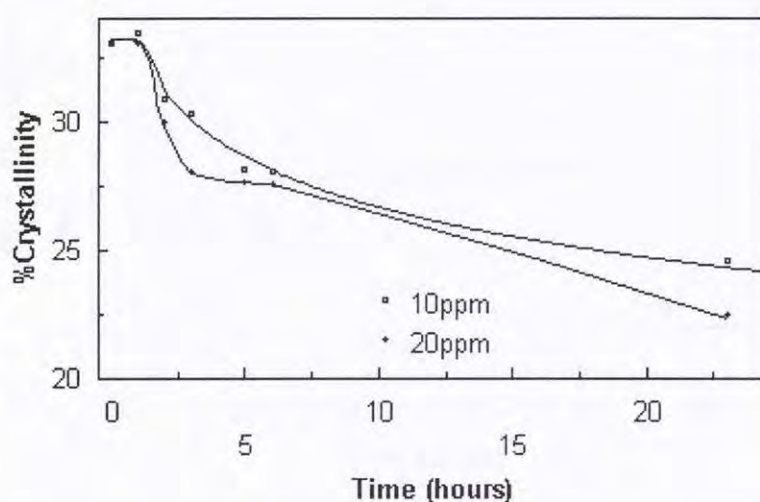


Figure 10 : Crystallinity time profile for PP samples at 20°C in 10 and 20ppm HOCl.

In summary, a 1 hour induction period exists for the loss of crystallinity due to PP degradation. The 1 hour induction period, in terms of loss of crystallinity, is the time taken for the first hydroxy and chloride radicals to form, diffuse to active sites (possibly containing tie molecules) and oxidise the species at these sites (probably tie molecules). With a net result of chain scission and loss of crystallinity.

4.5.2.3 FT-IR Spectroscopy

Undegraded polypropylene contains small amount of hydroperoxides and carbonyl compounds, and significant amounts of unsaturated carbon-carbon bonds as shown in Figure 11. The existence of an induction period for oxidation product formation is evident.

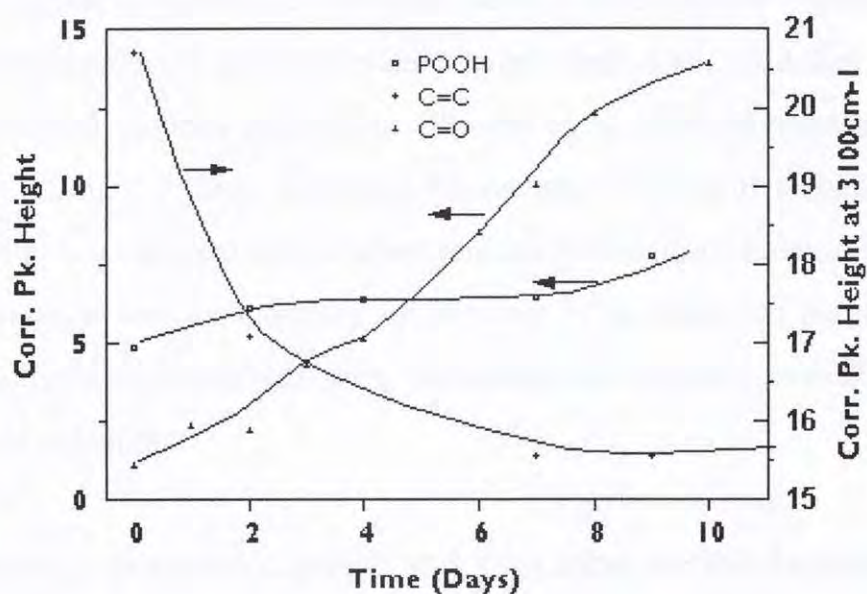


Figure 11 : Degradation time profile of oxidation product content: hydroperoxides (corrected peak height at 3400cm^{-1})(plotted on y-axis); carbonyl groups (corrected peak area at $1620\text{-}1800\text{cm}^{-1}$) (plotted on y-axis); C=C bonds (corrected peak height at 3100cm^{-1}) (plotted on 2y-axis). Fibres are degraded in 10ppm HOCl at 20°C .

During the initial period of 0-2 days a significant, approximately 20%, decrease in C=C concentration is observed. This is due to the reaction of unsaturated groups, generated during visbreaking, with dissolved oxygen present in the HOCl solution. A large amount of hydroperoxides are formed by oxidation of these residual unsaturated bonds, but only a slight increase in hydroperoxide content is observed

over the same period. This is due to rapid decomposition of the hydroperoxides formed as well as residual hydroperoxides from extrusion and processing, producing carbonyl compounds. Formation of hydroperoxides by hydrogen abstraction followed by oxidation may occur during this period, but the effect is small in comparison to the hydroperoxides formed from C=C oxidation.

The formation of carbonyl compounds shows a rapid increase between 0-1 days due to decomposition of hydroperoxides formed from C=C oxidation and processing residuals. This sudden increase is followed by a slow increase in total carbonyl content during 1-2 days, indicating the presence of a short induction period. This appears to be consistent with a heterogeneous model of oxidation. The early stage of low oxidation activity indicates the presence of an induction period during which oxidation occurs at isolated sites, accounting for the slow overall increase in the extent of oxidation.

In summary, an induction period of 2 days exists for the formation of oxidation products in PP oxidation. During this time, oxidation of existing unsaturated groups by dissolved oxygen occurs generating hydroperoxides. Decomposition of some of these hydroperoxides formed as well as residual hydroperoxides from processing occurs generating a small amount of carbonyl compounds.

4.5.2.4 X-ray Photoelectron Spectroscopy

XPS analysis was used as an alternative method to determine the oxygen content of the PP fibres. The resulting data appears in the form of %oxygen atoms relative to carbon atoms. XPS studies of degrading PP fibres showed the presence of a short induction period from 0-2 days, during which time a slight increase in oxygen content occurs on the fibre surface as observed in Figure 12. This slight increase in oxygen content is most probably due to either i) reaction of unsaturated C-C bonds,

present as a by-product of visbreaking, with dissolved oxygen, or ii) isolated oxidation of tertiary radicals generating hydroperoxides in low concentrations, or most probably iii) a combination of i) and ii). The end of the induction period corresponds with a large drop in mechanical strength, indicating chain scission due to the generation of sufficient tertiary radicals and carbonyl groups.

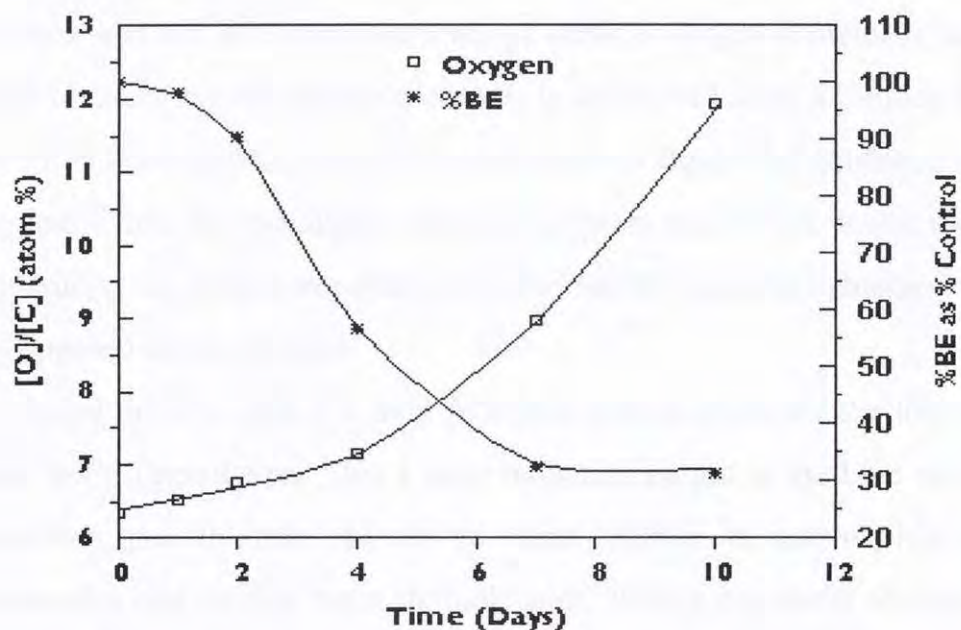


Figure 12 : XPS Oxygen content time profile for degrading polypropylene fibres in 10ppm HOCl at 20°C.

In summary, XPS analysis of the oxygen content of degrading PP shows a 0-2 day induction period. During this period a slight increase in oxygen content is observed, most probably due to reaction of C=C groups with dissolved oxygen, as well as low level oxidation of tertiary radicals.

4.5.2.5 Conclusions

This section of work has evaluated the oxidative degradation of PP hollow fibre membranes during the early stages to isolate the existence of an induction period.

Several conclusions can be drawn regarding the length, nature and detection of the induction period for the oxidative degradation of PP hollow fibres using hypochlorous acid. All induction times discussed here are in terms of PP hollow fibre degradation using 10ppm HOCl at 20°C. Analysis of degraded fibres was determined using 4 methods: i) elongation at break, ii) DSC measurements of crystallinity, iii) FT-IR measurements of hydroperoxide, carbonyl and unsaturation content and iv) XPS measurements of surface oxygen content. A summary of the data obtained for the induction periods is shown in Figure 13. Since the degradation of PP is heterogeneous then it is reasonable to expect the existence of an induction period. From the techniques trialed, it appears that FT-IR is the most reliable for measuring the induction period as it monitors the chemical changes of the polymer, as opposed to the physical.

1. Based on DSC data a 1 hour induction period exists for the loss of crystallinity due to PP degradation. This 1 hour induction period is the time taken for the first hydroxy and chloride radicals to form, diffuse to active sites containing tie molecules and oxidise these tie molecules. With a net result of chain scission and loss of crystallinity.
2. Based on mechanical strength data an induction period occurs lasting approximately 3 hours in which no loss of elongation at break occurs. This means that during this period chain scission is not occurring in the PP due to degradation in sufficient amounts to be detected by a loss of mechanical strength. After this 3 hour period, significant loss of mechanical strength occurs.
3. Based on FT-IR data an induction period of 1-2 days exists for the formation of oxidation products in PP oxidation. During this time, oxidation of existing unsaturated groups by dissolved oxygen occurs generating hydroperoxides. Decomposition of some of these hydroperoxides formed as well as residual

hydroperoxides from processing occurs generating a small amount of carbonyl compounds.

4. XPS analysis of the oxygen content of degrading PP shows a 2 day induction period. During this period a slight increase in oxygen content is observed, due to reaction of C=C groups with dissolved oxygen, as well as low level oxidation of tertiary radicals. This period is followed by a significant increase in surface oxygen content.

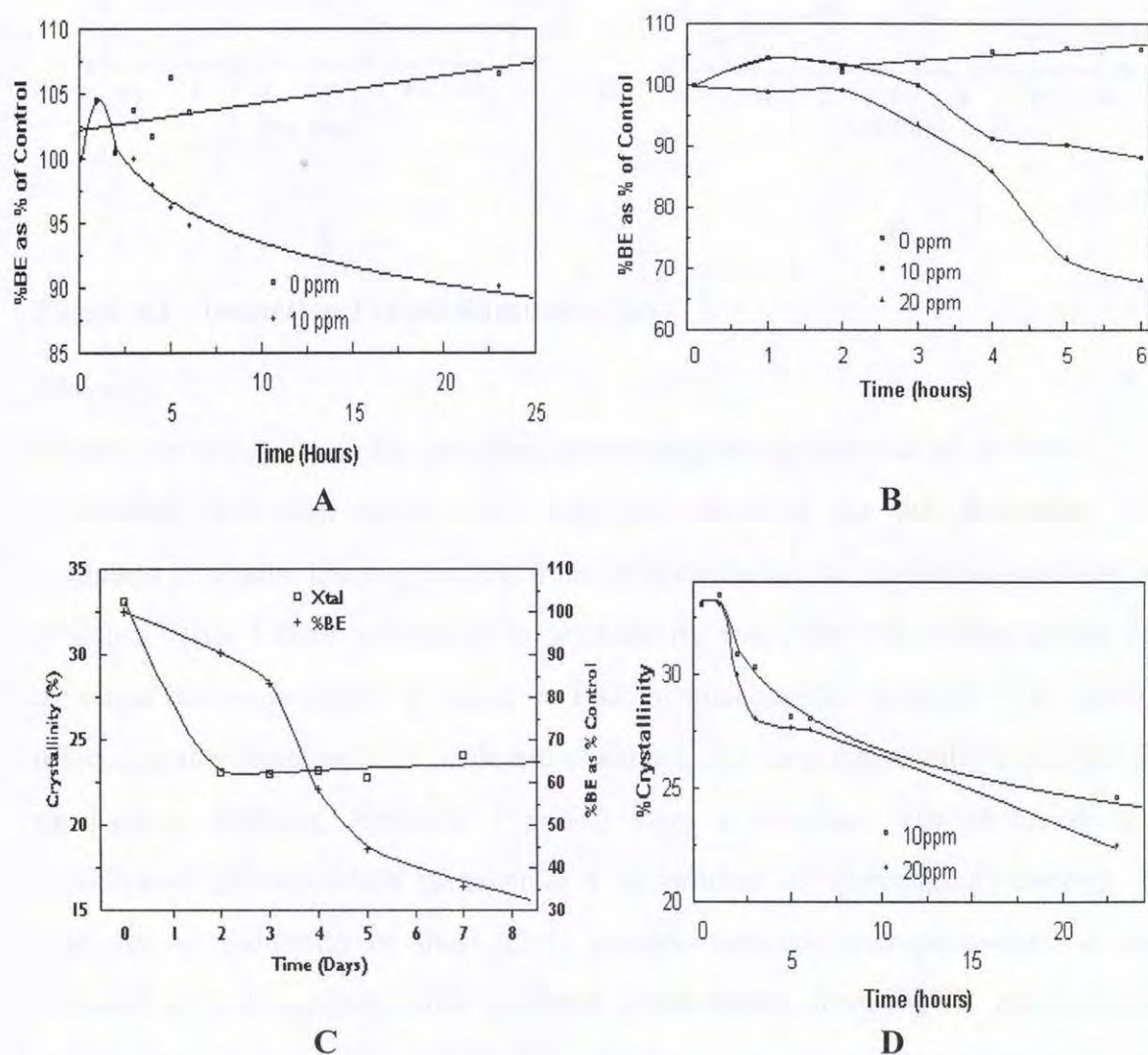
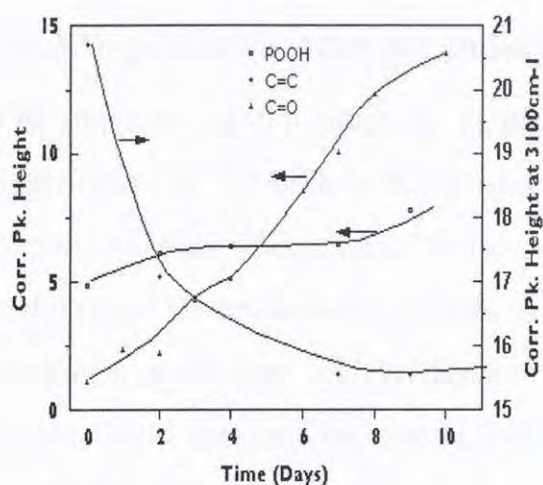
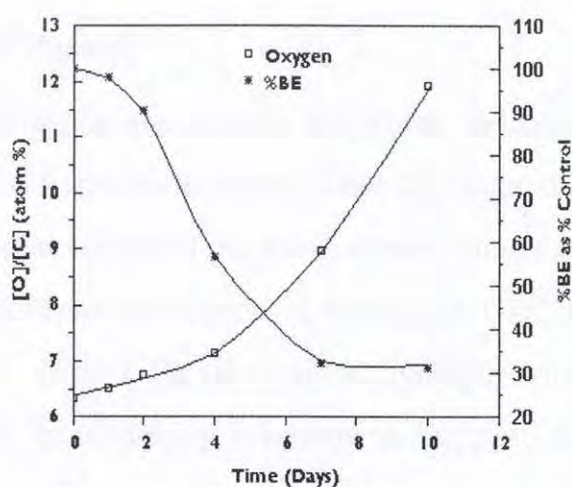


Figure 13 : Induction Period Summary Data



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Figure 13 : Induction Period Summary Data

Summary

Events occurring during the induction period may be summarised as follows:

An overall induction period of 2 days was observed for the generation of all oxidation products. During the first hour of degradation, no oxidation products were detected. After 1 hour a decrease in crystallinity was observed, indicating the onset of chain scission. After 4 hours a loss of mechanical strength was observed indicating the occurrence of sufficient chain scission to detrimentally effect the fibre mechanical strength. Between 1 and 2 days a decrease was observed in the unsaturated carbon-carbon (present as a by-product of visbreaking) content. This was due to oxidation of these C=C groups, forming hydroperoxides. A slight increase in hydroperoxide and carbonyl composition, from FT-IR measurements, and surface oxygen content, from XPS measurements, was observed during this time as a result of the C=C oxidation. After 2 days, a significant increase in carbonyl and

hydroperoxide content, from FT-IR measurements, and total oxygen content, from XPS measurements, was observed indicating the onset of oxidation.

4.5.3 Degradation After the Induction Period

The objective of this study is to determine the mechanism by which oxidative degradation of PP hollow fibres occurs in hypochlorous acid after the induction period. Analysis of degraded PP fibre samples is carried out using several analytical techniques: i) mechanical strength to determine elongation at break, ii) GPC to determine molecular weight distributions, iii) FT-IR to monitor hydroperoxide, carbonyl and unsaturation content, iv) XPS for total oxygen content and v) DSC for crystallinity measurements.

4.5.3.1 Mechanical Strength

The elongation at break is indicative of the amount of chain scission occurring during PP degradation. Figure 14 illustrates the change in elongation at break of PP fibres for degradations using 10ppm hypochlorous acid at 20°C.

From the data in Figure 14 it appears that between 2 and 7 days the fibres lose approximately 40% of their tensile strength. This rapid increase in the rate of loss of tensile strength may indicate the presence of an auto-accelerating effect. The maximum rate of loss of mechanical strength occurs after 5 days. As the elongation at break approaches zero, the tensile testing technique becomes inaccurate in determining the extent of degradation and alternative analytical methods must be used.

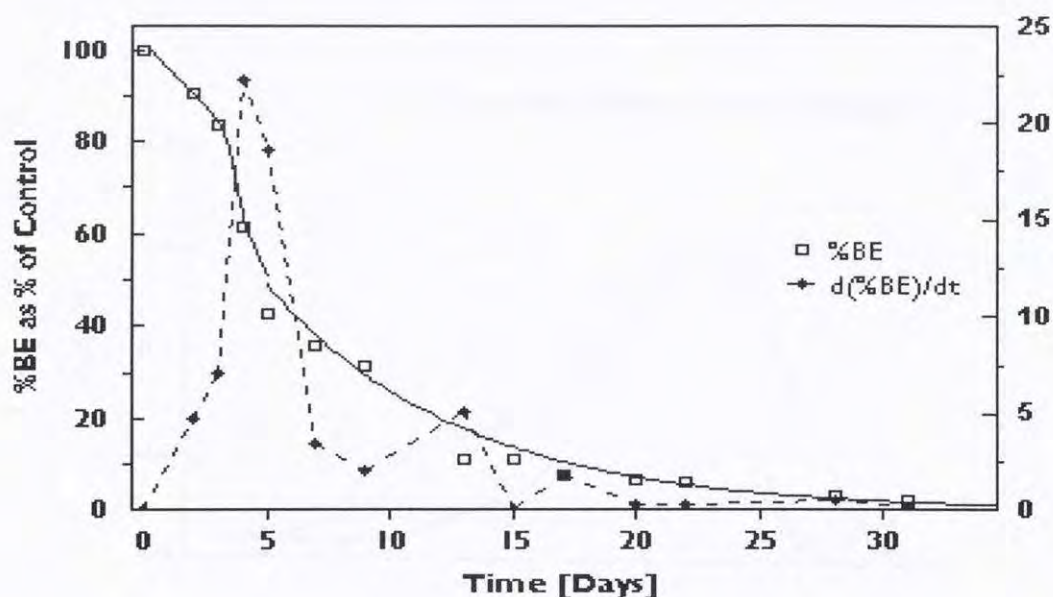


Figure 14 : Degradation time profile for PP fibres in 10ppm HOCl at 20°C.

In summary, after an 'induction period' the elongation at break for PP fibres undergoes a rapid decrease. This is due to a rapid increase in the rate of chain scission of the PP fibres. The 'accelerating' effect occurs because each chain scission produces additional radicals which initiate oxidation at additional sites.

4.5.3.2 Molecular Weight Changes During Degradation

Measurements of molecular weight were carried out on polypropylene fibres degraded to differing degrees. The molecular mass distribution for five degraded samples analysed sequentially under the same conditions is shown in Figure 15.

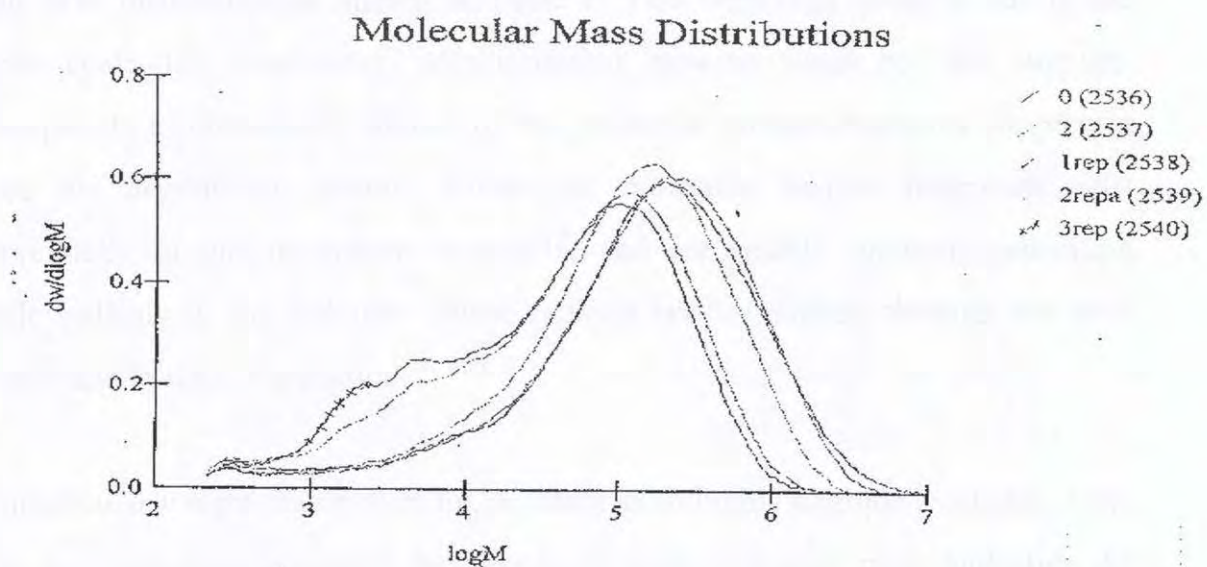


Figure 15 : Molecular mass distribution for 5 degraded polypropylene fibre samples.

Sample	%BE as % of Control	M_w	M_n	Polydispersity
0	100	378950	13450	28.2
2	58.3	350450	12500	28
1rep	11.5	234250	13200	17.7
2repa	0.8	128250	7100	18.1
3rep	0	104750	5700	18.4

Table 1: Polydispersity and elongation at break data for samples analysed via GPC.

The undegraded polymer, sample 0 with a polydispersity of 28, had an extremely broad MW distribution as shown in Table 1. This very high value is due to the poorly controlled continuous polymerisation process used by the supplier. Consequently a considerable amount of low molecular weight fragments are present before the degradation begins. These low molecular weight fragments exist preferentially in the amorphous regions³³, and are readily oxidised generating mobile radicals in the polymer. These radicals readily diffuse through the bulk polymer and initiate degradation.

The molecular weight distribution for the three most highly degraded samples, 1rep, 2repa and 3rep, show a gradual decrease in the peak molecular mass indicating the occurrence of bulk chain scission due to the degradation process. A summary of the properties of the samples 0, 2, 1rep, 2repa and 3rep is shown in Table 1.

As shown in Figure 15 the molecular weight distribution for the two most highly degraded samples, 2repa and 3rep, shows the appearance of a secondary peak resulting in a bimodal distribution. The appearance of this bimodal MWD indicates that chain scission, and hence degradation, is occurring at localised sites resulting in an overall heterogeneous oxidation as predicted in the literature³⁴. An overall lowering of molecular weight is observed for the three most highly degraded samples, 1rep, 2repa and 3rep. This overall decrease indicates that chain scission is occurring elsewhere in the polymer as well as in the isolated sites, however at a slower rate. Chain scission of PP in the active sites generates free radicals which are able to diffuse through the PP and initiate degradation in the bulk polymer. Consequently, it is expected that some degradation will occur outside the active sites

due to initiation by these free radicals. However, the rate of oxidation in the bulk PP will be low compared to the active sites.

Sample 2 with a %BE of 58.3% showed a slight lowering of molecular weight but showed no evidence of a bimodal distribution. This suggests that during the induction period and the early stages of degradation the rate of chain scission at the isolated sites is low.

Over the course of the degradation the observed drop in polydispersity indicates that bulk chain scission has occurred forming low molecular weight fragments. The narrowing of the molecular weight distribution can be explained by the scission of a large amount of high molecular mass (or long chain) fragments, resulting in a large number of shorter chain fragments. High molecular weight chains exist either preferentially in the crystalline region, or as tie molecules connecting several crystalline regions and passing through the amorphous phase. Since oxidation occurs preferentially in the amorphous region due to oxygen diffusion limitations, the high molecular weight chain scission occurs as tie molecule chain scission. These tie molecules, under high levels of stress, have been observed to act as active sites for degradation³⁵. Hence, the introduction of the shorter chain fragments formed from the tie molecules acts to narrow the distribution - not broaden it as is predicted by the literature heterogeneous model.

Melting temperature of a polymer is also a good indicator of molecular weight changes during degradation. Melting temperatures were obtained via DSC using approximately 4mg polymer fibre samples. The limitation with relying solely on this technique is the relatively small changes which occur with T_m as shown in Table 2

resulting in a large relative error. Also, the T_m gives only an indication of the trends in molecular weight occurring during degradation, not their absolute values.

Sample	T_m ($^{\circ}\text{C}$)	M_w	M_n
0	154.0	378950	13450
1rep	152.3	234250	13200
2	152.1	350450	12500
2repa	151.5	128250	7100
3rep	149.8	104750	5700

Table 2 : Changes in melting temperature compared to molecular weight for degrading polypropylene.

The heterogeneous model for polypropylene degradation predicts either the development of a bi-modal molecular weight distribution or a broadening of the same. From the data observed in this work it is probable that the degradation of polypropylene fibres occurs in an heterogeneous manner, meaning preferentially at certain sites in the polymer.

The changes in molecular weight distribution during degradation can be summarised as follows:

1. The average molecular weight decreases during degradation due to chain scission.
2. The appearance of a bimodal MWD indicates that chain scission, and hence degradation, is occurring at localised sites resulting in a high local but low total rate of degradation.
3. The lack of appearance of a bi-modal MWD in less degraded samples suggests that during the early stages of degradation the rate of chain scission at the isolated sites is low. Alternatively, SEC may not be sufficiently sensitive at low conversions to detect the low molecular weight degradation products.

4. A narrowing of the molecular weight distribution during degradation occurs due to the scission of a large amount of high molecular weight (or long chain) fragments, resulting in a large number of shorter chain fragments. It is possible that a large percentage of these long chains undergoing scission are tie molecules.

4.5.3.3 FT-IR Spectroscopy

Section 4.5.1 shows a sample spectra for the ‘undegraded’ polypropylene fibres. To take into account variations in thickness of the samples all FT-IR spectra were normalised to the standard peak at 970cm^{-1} ²⁴. A small signal in the region of 3400cm^{-1} indicates the presence of a small amount of hydroperoxides as a result of oxidation which occurred during extrusion and processing. The hydroperoxides readily decompose, generating hydroxy and macro alkoxy radicals which initiate degradation at other sites in the polymer^{34,37}. The concentration of hydroperoxides in the polymer increases over the degradation process as can be seen in the increased intensity of the signal at 3400cm^{-1} in the spectra shown in Section 4.5.1. Based on the intensity of the signal at 3400cm^{-1} , the concentration of hydroperoxides in the polymer was determined for a range of samples degrading in HOCl as shown in Figure 16. Over a 32 day period the hydroperoxide content increased to over 2 times its level in the undegraded sample. After this time the hydroperoxide concentration in the polymer was still increasing. This suggests 3 properties of PP oxidation in HOCl:

1. Hydroperoxides do not necessarily decompose instantaneously to form free radicals. They may have a ‘residence time’ in the polymer which contributes to the observed increase in POOH concentration during degradation.
2. Hydroperoxides may decompose to form more than 1 active radical, each of which are then able to initiate oxidation at additional sites generating hydroperoxides. So decomposition of one hydroperoxide group effectively

generates at least 2 additional hydroperoxide groups. This contributes to the increase observed in POOH concentration in Figure 16.

3. After 32 days the PP contains sufficient active sites for oxidation to be continuing. This suggests that free radicals formed by hydroperoxide decomposition attack PP not only at active sites containing catalyst residue and other impurities, although these sites are preferentially oxidised, but abstract hydrogen atoms from tertiary bonded carbons throughout the amorphous polymer.

This observation supports the commonly accepted view of polypropylene oxidation which involves the formation of hydroperoxides, followed by their decomposition to form radicals and other oxidised species, predominantly carbonyl compounds.

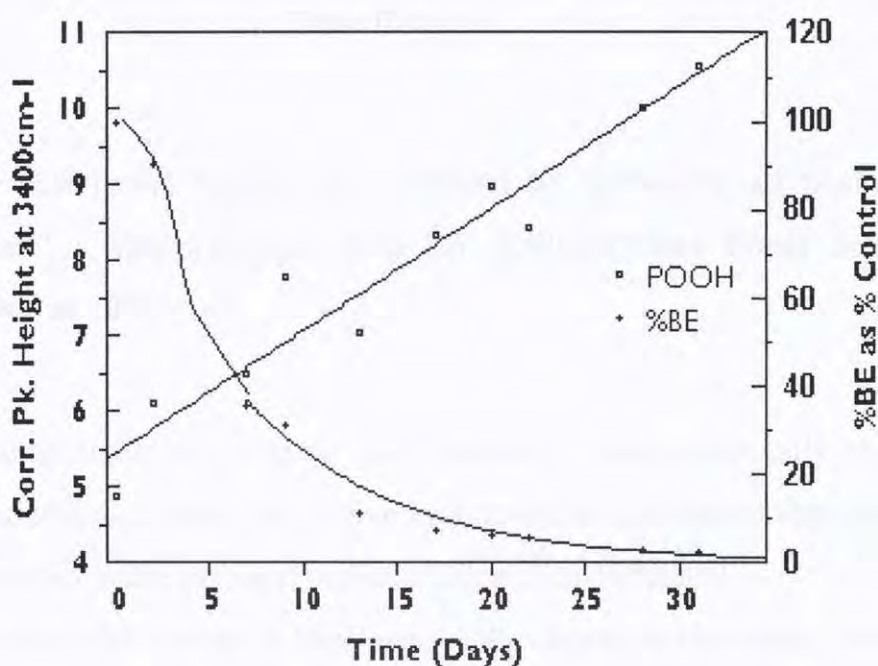


Figure 16 : Hydroperoxide content (as indicated by the corrected peak height at 3400cm^{-1}) over time for polypropylene fibres degrading in 10ppm HOCl at 20°C .

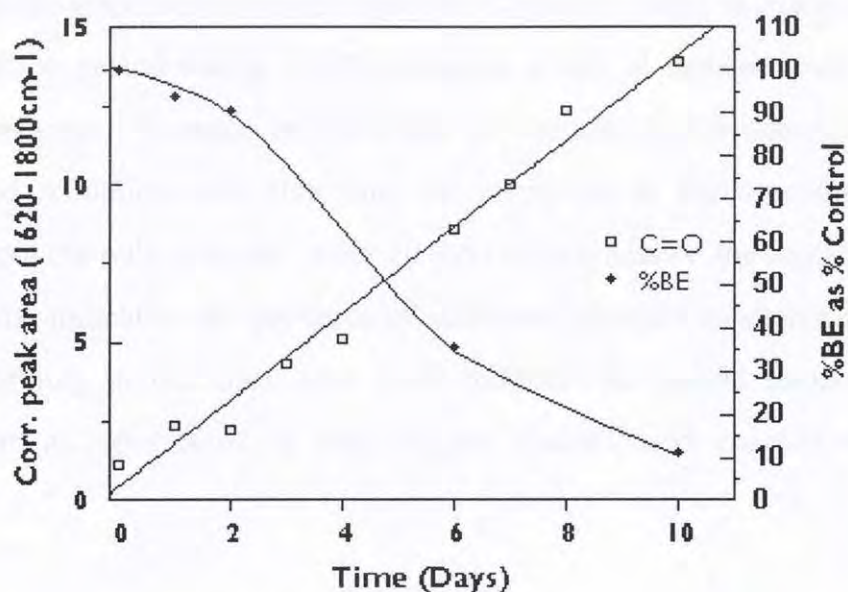


Figure 17 : Carbonyl content (as indicated by the corrected peak height at $1620\text{-}1800\text{cm}^{-1}$) with oxidation time for polypropylene fibres degrading in 10ppm HOCl at 20°C .

Carbonyl compounds, observed at $1620\text{-}1800\text{cm}^{-1}$, are a commonly accepted by-product of oxidation. During the course of degradation the largest change in the FT-IR spectra occurs in the carbonyl region 1620cm^{-1} to 1800cm^{-1} .

Figure 17 shows the change in total area of the signals in this region for a sample degraded at 20°C in 10ppm HOCl. Alternatively, a plot of change in peak height of signals in this region with time would show the same trend, as observed by George *et al*³⁶ in their work. They also noticed an exponential increase in the extent of oxidation with time. This was interpreted, according to the heterogeneous model, as an increased fraction of the polymer which had been oxidised. The present data

shows a similar trend, a slow increase in total oxidation lasting 1-2 days, followed by a steady increase in extent of oxidation with time. This appears to be consistent with a heterogeneous model of oxidation. The early stage indicates the presence of an induction period during which oxidation occurs at isolated sites, accounting for the slow overall increase in the extent of oxidation. The subsequent increase in extent of oxidation with time may be attributed to the spreading of oxidation throughout the bulk polymer. After 10 days of degradation the oxygen content is still increasing, indicating the presence of additional sites for oxidative attack. Once all the remaining active sites have been oxidised we would expect the extent of oxidation, as represented by total oxygen content, with time to reach a limiting value.

The major by-product of the vis-breaking process is the formation of unsaturated chain ends at every site of chain cleavage for molecular weight control. These C=C bonds readily react with oxygen or other oxidants in the polymer. During the degradation process the formation of C=C bonds is thought to occur only in oxygen deficient conditions³⁷. In oxygen rich environments the amount of C=C bonds is observed to decrease as degradation progresses³⁸. Based on the intensity of the signal at $3000-3200\text{cm}^{-1}$, for vinyl alkenes, the concentration of C=C bonds decreased over the degradation process by 30% from the original level in the undegraded sample as shown in Figure 18. The degradation process, in this work, is carried out in the presence of dissolved oxygen formed by the decomposition of the hypochlorous acid. So we can assume that only a small amount of compounds containing C=C bonds are being produced during degradation. This means that more than 30% of the initial concentration of C=C groups are consumed in the degradation process.

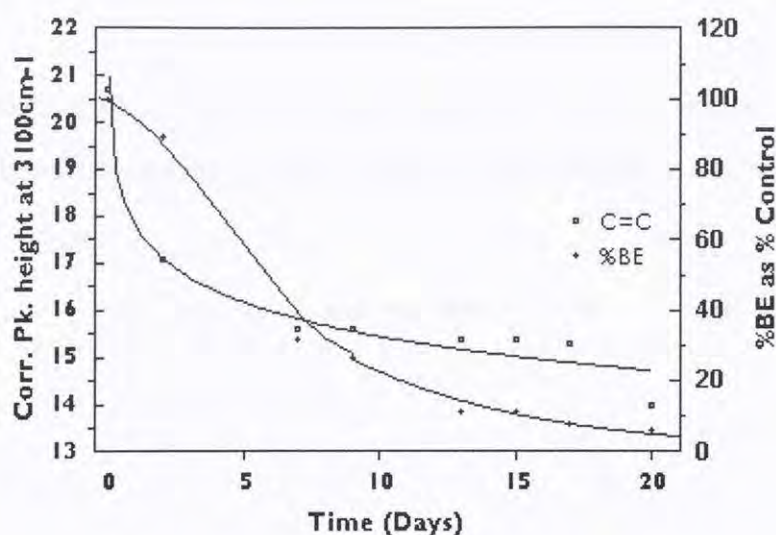


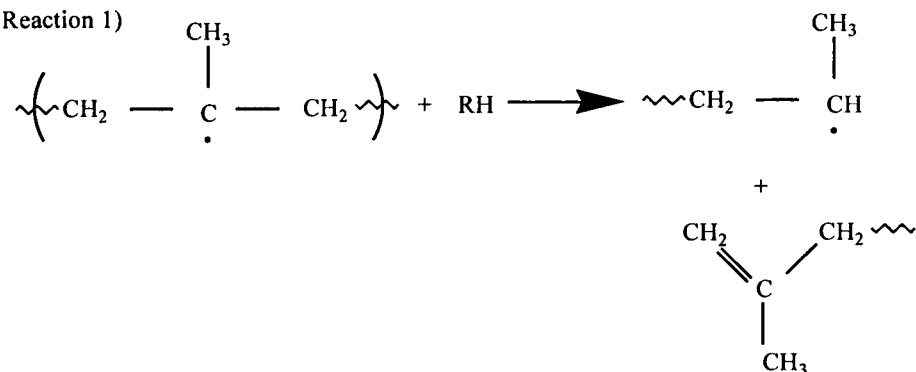
Figure 18 : C=C content (as indicated by the corrected peak height at 3100cm⁻¹) with time for polypropylene fibres degrading in 10ppm HOCl at 20°C.

The observed decrease in carbon-carbon unsaturation during degradation suggests that competing oxidative reactions are occurring due to the presence of dissolved oxygen. Carbon-Carbon double bonds are formed during the degradation process by β -scission of peroxides, long chain radicals or carbonyl compounds^{39,40} as shown in Scheme 1. In the presence of oxygen the tertiary radical in Reaction 1 would readily oxidise forming a tertiary hydroperoxide as shown in Scheme 2. In the presence of oxygen the unsaturated carbon-carbon bonds formed in Scheme 1 in both Reaction 1 and 2 would readily react forming unsaturated hydroperoxides. So, the competing reactions are: Scheme 1 forming unsaturated groups, Scheme 2 acting to prevent their formation by forming tertiary hydroperoxides and Scheme 3 generating unsaturated hydroperoxides.

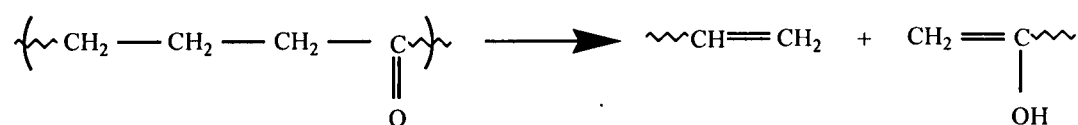
It would appear then that the unsaturated carbon-carbon bonds present in the polymer initially undergo oxidation with dissolved oxygen producing unsaturated hydroperoxides. The formation of unsaturated groups by i) carbonyl scission during oxidation is limited, and ii) by tertiary radical scission is hindered by the occurrence

of Scheme 2. Hence, Scheme 2 and Scheme 3 are the major oxidation reactions, while Scheme 1 Reaction 2 may occur to a small degree in the presence of light.

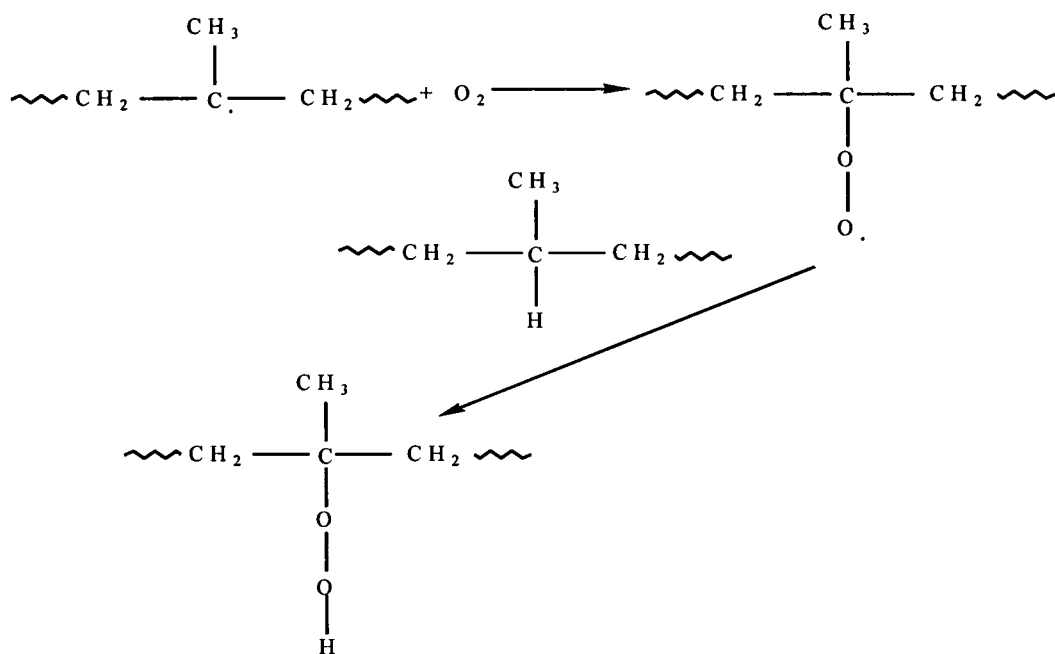
Reaction 1)



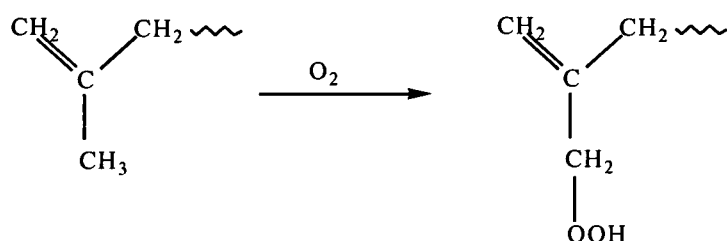
Reaction 2)



Scheme 1 : The formation of C=C bonds via beta-scission.



Scheme 2 : Formation of tertiary hydroperoxides by the reaction of tertiary radicals with dissolved oxygen.



Scheme 3 : Formation of hydroperoxides by oxidation of unsaturated C-C bonds.

Summarising the degradation after the induction period in terms of FT-IR spectroscopy:

1. a) The concentration of hydroperoxides increases linearly during oxidation. This increase in POOH concentration is due to hydroperoxide decomposition generating more than 1 active radical, each of which are then able to initiate oxidation at additional sites generating additional hydroperoxides. b) Radicals derived from hydroperoxide decomposition initiate oxidation at all sites throughout the polymer, not just at active sites containing impurities, as is observed by the constant increase in POOH concentration. If initiation took place only at active sites a constant or zero POOH level would eventually be reached.
2. The carbonyl content increases steadily, almost linearly, during degradation, without experiencing any observed decreases in the rate of C=O formation. This suggests that carbonyl compounds are the major oxygenated product. These carbonyl compounds form as a result of POOH decomposition.
3. The concentration of unsaturated carbon=carbon bonds decreases significantly during degradation. The presence of dissolved oxygen causes competing reactions: a) C=C generation by β -scission of tertiary radicals or by the reaction of 2 free radicals resulting in termination, b) to a small degree C=C generation by β -scission of carbonyl compounds in the presence of light, c) The reaction of tertiary radicals

with dissolved oxygen producing hydroperoxides and d) The reaction of unsaturated carbon-carbon bonds with dissolved oxygen. Reaction c) and d) predominate with reaction b) occurring to a small extent only in the presence of light.

4.5.3.4 X-ray Photoelectron Spectroscopy

Trends in oxygen content of polypropylene membranes can be observed from FT-IR spectra by integrating the signal peak area in the carbonyl region, from 1620-1800 cm^{-1} . Alternatively, X-ray photoelectron spectroscopy (XPS) spectra may also be used to calculate oxygen content by measuring the intensity of the oxygen (O 1s) signal.

X-ray excitation generates electrons from atoms below the surface of the sample, however only those electrons close to the surface escape and are detected by the XPS spectrometer. As XPS is a surface technique, the oxygen content calculated from XPS data will be considerably higher than FT-IR data which measures the bulk oxygen content. Concentrations are expressed as oxygen atom to carbon atom percentages.

Lacoste *et al*⁴¹ observed that although XPS should be able to resolve the spectra into distinct peaks due to specific oxygen containing groups, it was not possible due to effects such as instability of some byproducts to X-rays and peak broadening. However, the overall oxygen content of the samples was able to be determined.

One of the dominant products of oxidation, the hydroperoxide group, is readily destroyed by radiation. Lacoste *et al*⁴¹ noticed a large decrease (~40%) in the oxygen content with radiation exposure and their data corrected accordingly. Using the Kratos XSAM system the total exposure time of the sample to X-rays is approximately 15 minutes. To investigate this time radiation effect samples were

analysed for oxygen content after known lengths of exposure time. The resulting differences were small (approximately a decrease of 2%), however all data was adjusted back to zero time to compensate for these slight discrepancies. This value is much lower than the value observed by Lacoste *et al*⁴¹. This is most probably due to differences in the operating system, differences in the X-ray dose and data analysis as well as the nature of the samples being analysed.

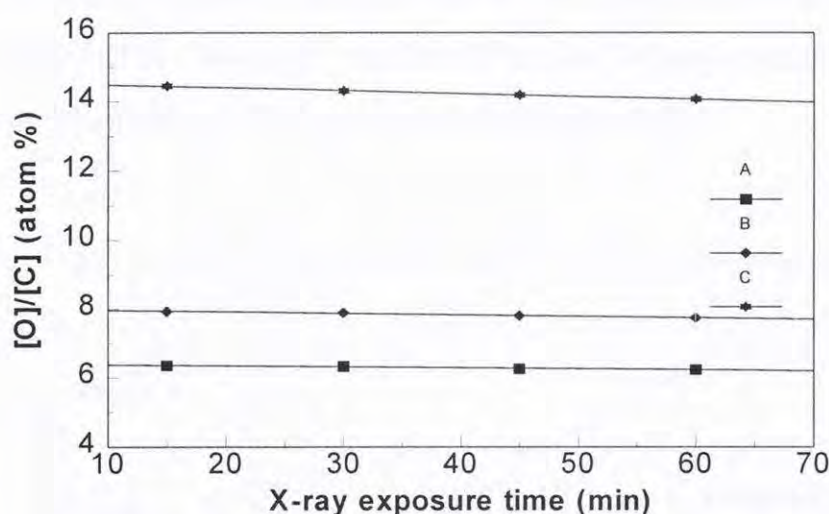


Figure 19 : Changes in oxygen content with X-ray exposure time for 3 polypropylene samples with %BE as %Control of A:100%, B:17%, C:0.5%.

FT-IR analysis of degraded fibres in Section 4.5.1 showed that undegraded fibres contain a small amount of hydroperoxides and carbonyl groups and a significant amount of unsaturated carbon-carbon bonds. XPS analysis also show a high level of oxygen in the undegraded polymer (6.35% corrected to zero time of X-ray exposure). This oxygen content represents carbonyl, alcohol and peroxide content of the polymer.

As XPS is a surface analysis technique, oxygen data represents surface oxygen content only. XPS shows a high surface area oxygen content as compared to the

values for the bulk polymer obtained by FT-IR studies. FT-IR studies were carried out by transmission spectroscopy which averages the carbonyl absorbance through the thickness of the film.

XPS studies of degraded polypropylene fibres showed a marked increase in the oxygen content over the course of the degradation as shown in Figure 20. A maximum oxygen content of 23.8% was measured for a highly degraded sample, %BE: 0.5%. This high value would not be indicative of the oxygen content for the entire polymer as XPS is a surface technique only.

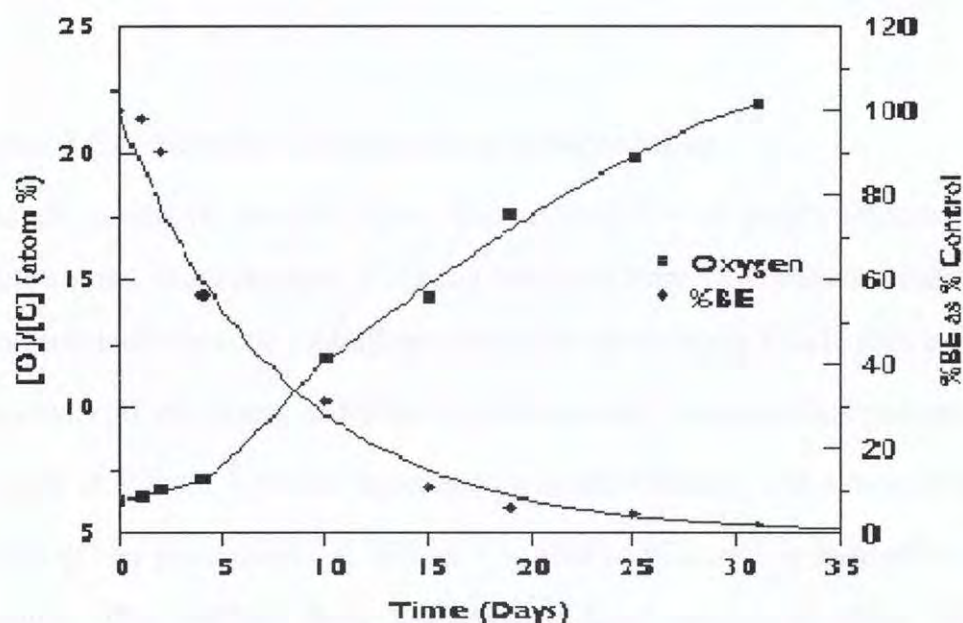


Figure 20 : XPS Oxygen content time profile for degrading polypropylene fibres in 10ppm HOCl at 20°C.

As shown in Figure 20 after the 2 day induction period, discussed in Section 4.5.2, the oxygen uptake onto the polymer undergoes an acceleration, followed by a slight

‘tailing off’ effect. This acceleration is due to oxidation of tertiary radicals and unsaturated carbon-carbon groups formed during the induction period or generated during processing. The tailing off effect is caused by a slight decrease in concentration of oxidising sites in the polymer. For a completely oxidised polymer the oxygen content would reach a constant values with a zero rate of oxygen uptake due to zero available oxidation sites.

XPS studies of oxygen content during PP degradation show an accelerating effect due to rapid oxidation of tertiary radicals and C=C groups, followed by a deceleration due to a decrease in the concentration of available oxidation sites.

4.5.3.5 Crystallinity Changes During Degradation

As discussed in Section 4.2.4, the crystallinity of polypropylene fibres may be determined using the heat of fusion obtained from DSC measurements. In this work another indication of crystallinity was also made using FT-IR data by comparing the intensity of the signal at 998cm^{-1} , present only in crystalline polypropylene, to the signal at 970cm^{-1} which appears in atactic, isotactic and syndiotactic PP ⁴². The ratio of the peak height at 998cm^{-1} to that at 970cm^{-1} is indicative of crystallinity trends. This method does not give a direct numerical value for crystallinity. However, a regression was carried out correlating this FT-IR peak height data with DSC crystallinity using samples with a known crystallinity.

$$\% \text{Crystallinity} = 19.1 * (\text{H}_{998} / \text{H}_{970}) + 8.5$$

The R^2 for this relationship was 0.39. Using this relationship it was then possible to equate the value of the crystalline peak height with crystallinity. Peak height data, and crystallinity data calculated in this manner are compared to crystallinity data calculated from DSC heat of fusion in Figure 21. The data plotted in Figure 21 was

obtained from polypropylene fibres degrading in approximately 10ppm free chlorine at room temperature. The free chlorine concentration in the degrading solution was not monitored or controlled, rather the solution was refreshed daily to 10ppm.

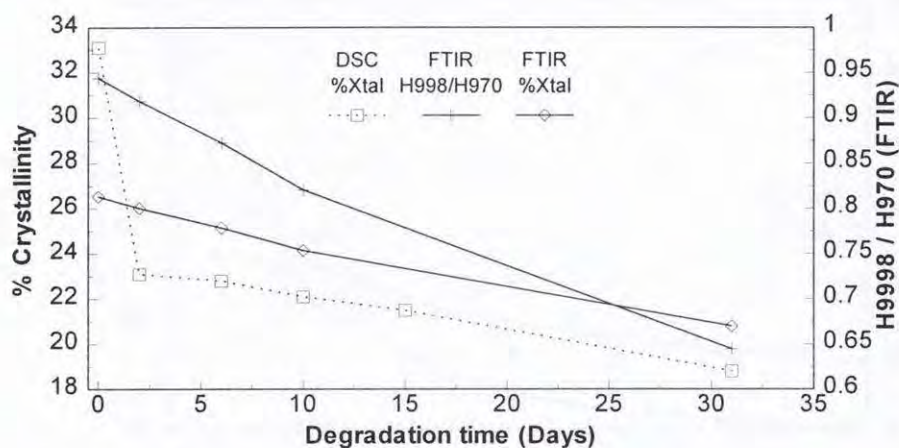


Figure 21 : Comparison of DSC crystallinity data with that calculated from FT-IR spectra for a sample degrading over time.

Using FT-IR data the peak at 998cm^{-1} undergoes only a relatively small change in height with degradation as observed with data obtained in this study. Also, FT-IR peak intensity is dependent on film thickness, and slight variations will produce erroneous data. This is particularly detrimental measuring trends in crystallinity where degradation results in small changes in peak height. As a result the crystallinity data calculated from FT-IR spectra differs from the actual DSC values as shown in Figure 21. Also, the low R^2 value for the regression model indicates a poor correlation between DSC crystallinity data and FT-IR peak height data. So, for determining the crystallinity of degrading polypropylene fibres, DSC will be used in the rest of this study. The reasons for this are as mentioned above and: i) Degrading PP undergoes significant changes in heat of fusion, reducing the error involved in

measurement, and ii) The DSC technique produces numerical values for crystallinity directly, rather than by a correlation.

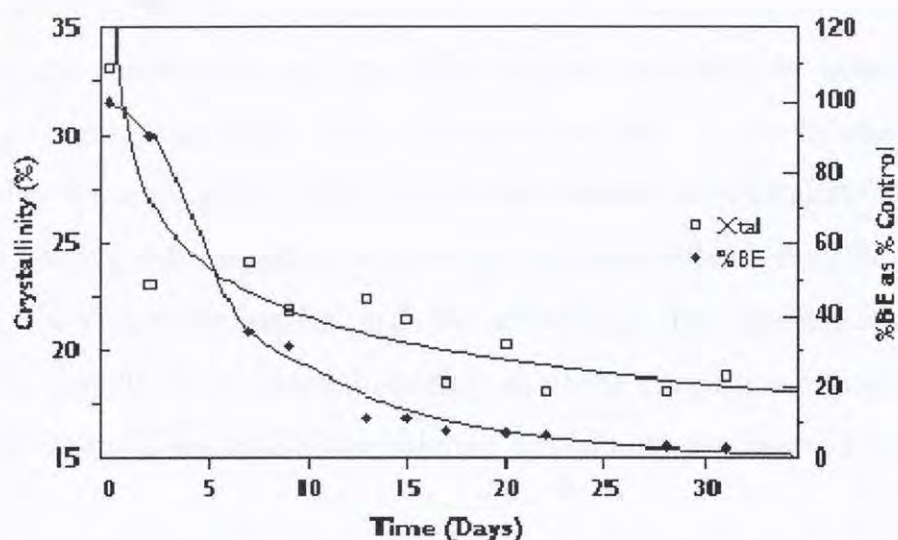


Figure 22 : Changes in crystallinity with time for polypropylene fibre degrading in 10ppm HOCl at 20°C.

As can be observed in

Figure 22, crystallinity decreases with time of degradation of polypropylene samples. After the 2 day induction period, the PP crystallinity undergoes a deceleration in its rate of decrease. The trend in decrease of crystallinity mirrors that for elongation at break, indicating that both these techniques indirectly measure chain scission. As the degradation time increases, the amount of chains undergoing scission decreases. Hence, a decrease in the rate of oxidation is observed. After complete oxidative degradation the crystallinity would reach a constant value.

Why does the crystallinity decrease with degradation? In a semi-crystalline polymer degradation occurs preferentially in the amorphous region due to the permeability of

scission producing a large amount of low molecular weight components. If this degradation is restricted only to the amorphous region, then the formation of these low molecular weight fragments will have no effect on the polymer crystallinity as the crystalline regions will remain intact. Hence, for a decrease in the crystallinity to be observed, some of the degradation reactions must occur at phase boundaries between the amorphous and crystalline regions resulting in scission of highly stressed, highly entangled, high molecular weight 'tie molecules'. These 'tie molecules' are sufficiently long that they exist in both the crystalline and amorphous regions binding them together. Portions of the tie molecules exist in the crystalline regions, the remainder pass through the amorphous. The scission of these sorts of molecules would cause a partial opening up of the crystalline regions due to chain end motions and a decrease in the polymer crystallinity, as observed in this study.

From Figure 22, it is evident that scission of tie molecules occurs in bulk during the first 10 days of degradation. As these molecules are highly stressed they degrade preferentially⁴⁵. The result of this is a sudden early decrease in crystallinity and an opening up of the crystalline regions.

In summary, crystallinity of PP fibres decrease with degradation due to oxidation resulting in chain scission particularly of tie molecules. During the course of the degradation the crystallinity decrease undergoes a deceleration due to a decrease in rate of oxidation. This is mirrored by the elongation at break.

4.5.3.6 Conclusions

The objective of this study was to determine the mechanism of oxidation of PP hollow fibre membranes using hypochlorous acid. Degraded PP fibres were analysed for:

1. Elongation at break as measured by mechanical strength.

2. Molecular weight distribution by GPC.
3. Oxidation product content by FT-IR.
4. Total oxygen content by XPS.
5. Crystallinity by DSC.

Section 4.5.2 dealt with the induction period, this work deals primarily with the degradation after the induction period. Several conclusions were drawn and these are summarised below:

1. After the induction period, the elongation at break for PP fibres undergoes a rapid decrease. This is due to a rapid increase in the rate of chain scission of the PP fibres. The 'accelerating' effect occurs because each chain scission produces additional radicals which initiate oxidation at additional sites. So, oxidation of PP fibres results in chain scission and radical generation.

2. The average molecular weight decreases during degradation due to chain scission. The appearance of a bimodal MWD in highly degraded samples indicates that chain scission is occurring at localised sites resulting in a high local but low total rate of degradation. This is consistent with the heterogeneous model of degradation. The lack of appearance of a bi-modal MWD in less degraded samples suggests that during the early stages of degradation the rate of chain scission at the isolated sites is low. The molecular weight distribution narrows during degradation due to the scission of high molecular weight (long chain) molecules. It is probable that a large percentage of these long chains undergoing scission are tie molecules.

3. FT-IR studies of degraded PP fibres may be summarised as:

a. i) Hydroperoxide concentration increases linearly during oxidation. This increase in POOH concentration is due to hydroperoxide decomposition generating more than

1 active radical, each of which are then able to initiate oxidation at additional sites generating additional hydroperoxides. ii) Radicals derived from hydroperoxide decomposition initiate oxidation at all sites throughout the polymer, not just at active sites, resulting in a constant increase in POOH concentration.

3b. Carbonyl content increases linearly during degradation after the induction period. This suggests that carbonyl compounds, formed as a result of POOH decomposition, are a major oxidation product.

3c. Unsaturation content decreases significantly during degradation. C=C groups are generated by i) β -scission of tertiary radicals and ii) β -scission of carbonyl compounds. The presence of dissolved oxygen causes two extra competing reactions: iii) The reaction of tertiary radicals with dissolved oxygen producing hydroperoxides and iv) The reaction of unsaturated carbon-carbon bonds with dissolved oxygen. In PP hollow fibre oxidation with aqueous HOCl reactions iii) and iv) predominate with reaction ii) occurring to a small extent.

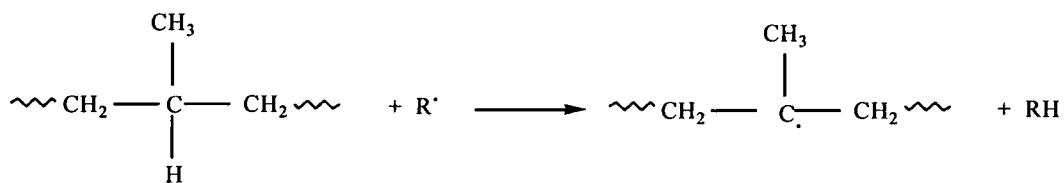
4. XPS studies of oxygen content during PP degradation show an accelerating effect due to rapid oxidation of tertiary radicals and C=C groups, followed by a deceleration due to a decrease in the concentration of available oxidation sites.

5. Crystallinity of PP fibres decrease with degradation due to oxidation resulting in chain scission particularly of tie molecules. During degradation the crystallinity decrease undergoes a deceleration due to a decrease in rate of chain scission.

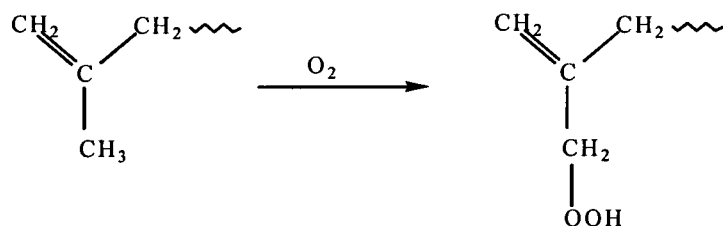
Using this information a basic oxidation mechanism is proposed:

1. Formation of chloride and hydroxy radicals by reaction with metallic impurities at active sites. This mechanism is shown in Section 2.6.

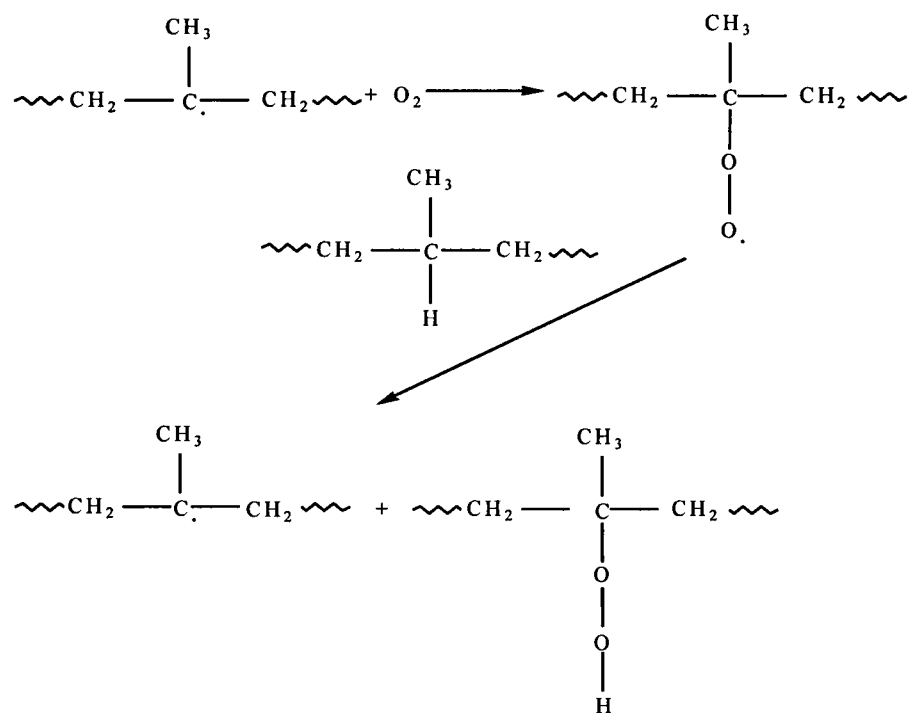
2. Formation of tertiary radicals by hydrogen abstraction by chloride or hydroxy radicals.



3a. Formation of hydroperoxides by reaction of unsaturated groups with dissolved oxygen.



3b. Formation of tertiary hydroperoxides by reaction with dissolved oxygen.



4. Hydroperoxide decomposition generating carbonyl compounds and short chain radicals.

and physical changes caused in polypropylene fibres during degradation. Degradation during and after the induction period under consistent reaction conditions was discussed in Section 4.5.2 and 4.5.3. This Section will focus on the external system conditions causing the degradation and their effect on the rate and products of the reaction during and after the induction period.

4.5.4.1 Temperature effects

Degradation of polypropylene fibres at low temperatures results in: chain scission causing a drop in polydispersity and molecular weight, formation of oxidation products on the polymer, decrease in crystallinity and a loss of tensile strength. The rate of the degradation reaction can be expressed as the rate of change of the above mentioned properties. In this work both the formation of oxidation products and the loss of tensile strength will be used to monitor the process, as will changes in crystallinity to a certain extent.

The rate of reaction for the degradation of polypropylene fibres by sodium hypochlorite is dependent on: HOCl concentration, reaction temperature and active site concentration. The active sites consist of either: catalyst and metallic residue, tie molecules or residual processing impurities such as C=C, hydroperoxides and carbonyl compounds. At any given temperature the rate of degradation can be expressed as:

$$\text{rate} \propto [\text{HOCl}]^{\alpha} [\text{Active sites}]^{\beta}$$

Using the experimental set-up the hypochlorous acid concentration is monitored constantly. As the degradation occurs by a heterogeneous mechanism the active site concentration will vary. The concentration of unsaturated groups in the degrading polymer can be measured using FT-IR spectroscopy as discussed in Section 4.5.2.3, however the concentration of catalyst residue and ‘tie’ molecules cannot. The rate of

reaction will subsequently be monitored by the effects of these reactants on the polymer structure.

The Induction Period

The rate of formation of carbonyl products, as measured from FT-IR spectra, with degradation time is a good indication of the reaction rate. Figure 23 shows the increase in carbonyl content as well as the trend for rate of formation of carbonyl groups for degradations carried out at 20°C and 40°C. It appears that at the elevated temperature a marked drop in induction period occurs, from 2 days to less than 1 day at a HOCl concentration of 10ppm. This is observed also in crystallinity trends in Figure 26. Increasing the reaction temperature from 20 to 40°C results in a drop in induction period, with respect to crystallinity, from 1-2 days to less than 1 day at a HOCl concentration of 10ppm. The induction period in terms of hydroperoxide content is decreased from 1-2 days to less than 1 day with an increase in temperature from 20 to 40°C as shown in Figure 24. Figure 25 shows a decrease in induction period in terms of C=C consumption from 1 day at 20°C to ~0 days at 40°C. Increasing the reaction temperature also decreases the induction period with respect to elongation at break from 1-2 days to less than 1 day as shown in Figure 27.

Degradation occurs preferentially in the amorphous phase of the polymer, producing oxygen containing compounds, low molecular weight polymer chains, hydroperoxides, peroxides, and peroxy, hydroxy and alkyl radicals. Elevated temperatures cause an increase in the rate of formation of oxygen containing groups and a decrease in the induction period. This is due to the increased diffusion properties of the chloride and hydroxy radicals through the polymer at the higher temperature as well as the temperature effect of the oxidation rate constant.

In summary, based on carbonyl, unsaturation and hydroperoxide content, crystallinity and elongation at break, increasing the reaction temperature from 20 to 40°C decreases the length of the observed induction period from 2 days to less than 1 day using a HOCl solution of 10ppm.

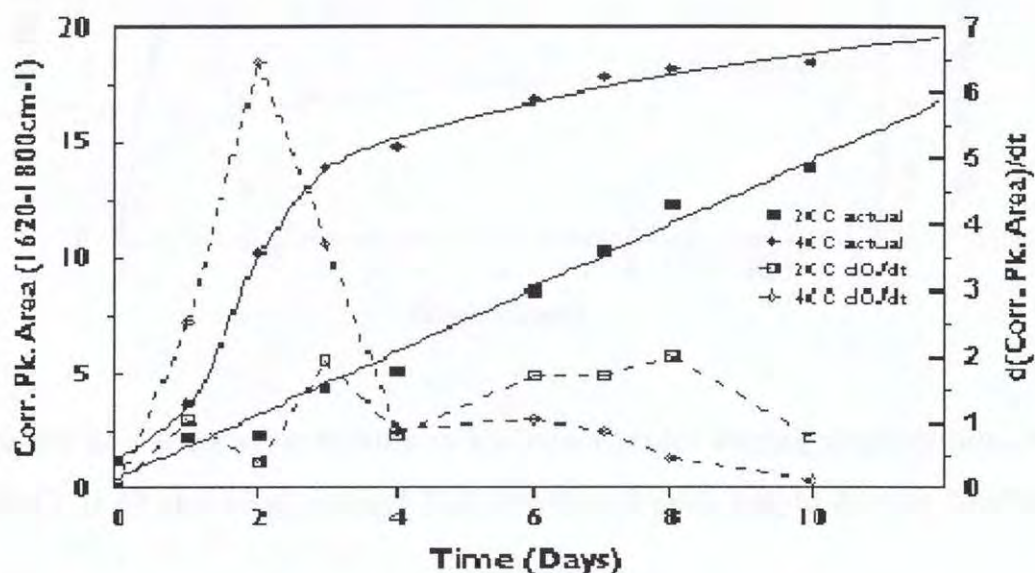


Figure 23 : Rate of formation of carbonyl groups during degradation, in 10ppm HOCl at 20 and 40°C, using FT-IR corrected peak area data in the region 1620-1800cm⁻¹.

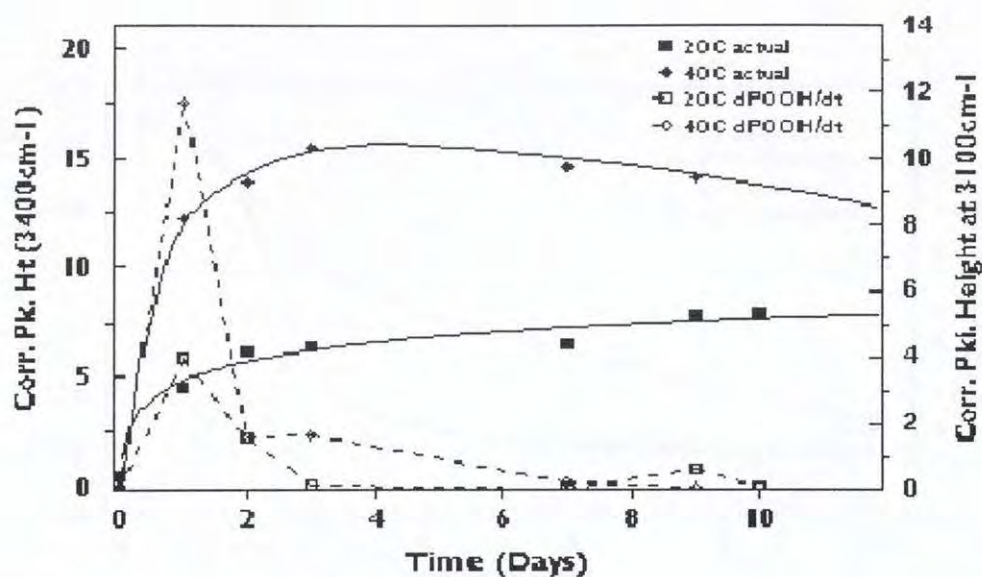


Figure 24 : Rate of formation of hydroperoxides during degradation, in 10ppm HOCl at 20 and 40°C, using FT-IR corrected peak height data at 3400cm⁻¹.

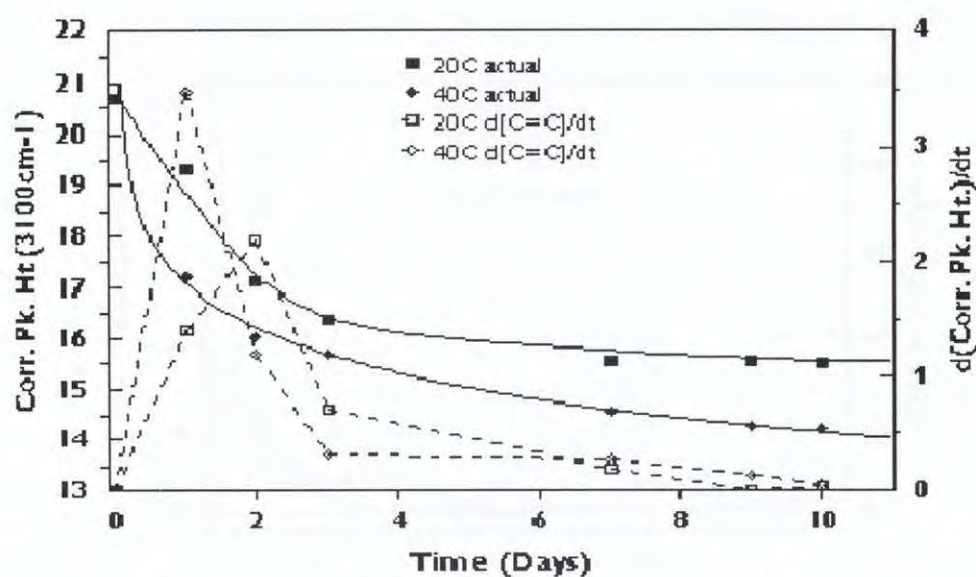


Figure 25 : Rate of consumption of C=C during degradation, in 10ppm HOCl at 20 and 40°C, using FT-IR corrected peak height data at 3100cm⁻¹.

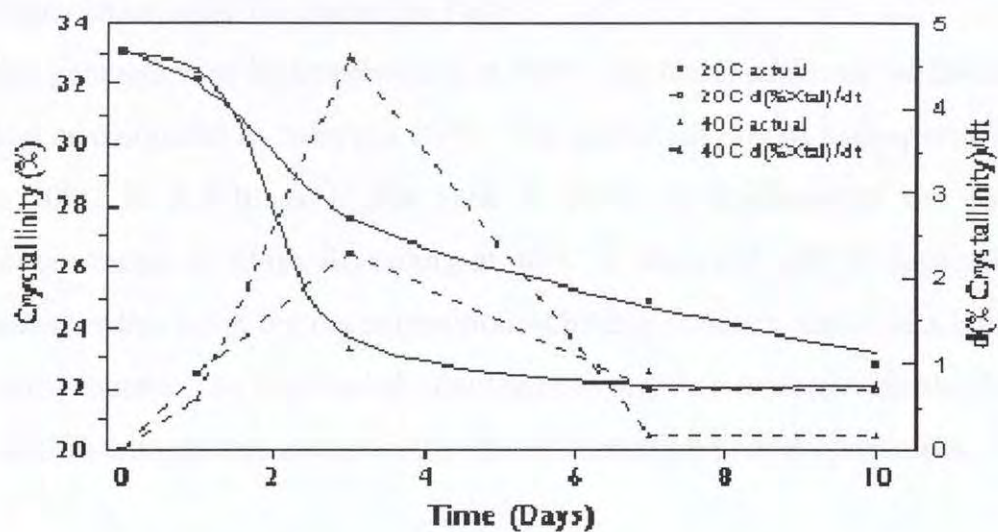


Figure 26 : Crystallinity time profile and rate of change of crystallinity during degradation at 20 and 40°C.

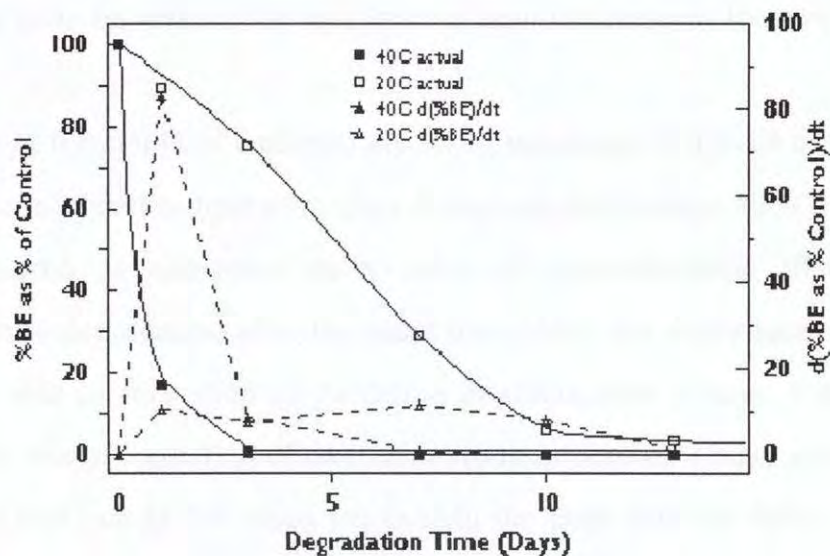


Figure 27 : % Break Extension time profile of degradation in 10ppm HOCl at 20 and 40°C

Degradation After the Induction Period

The generation of hydroperoxides at 40°C reaches a peak rate of formation after 1 day, as compared to 2 days at 20°C. The maximum rate of hydroperoxide formation at 40°C is 2.5 times higher than at 20°C. A decrease in the hydroperoxide concentration in fibres degrading at 40°C is observed after 3 days. This indicates that after this point the decomposition of hydroperoxides occurs at a higher rate than their generation by reaction of dissolved oxygen with tertiary radicals. So, increasing reaction temperature increases the rate of formation of hydroperoxides.

The consumption of unsaturated carbon-carbon groups reaches a peak rate after 1 day at 40°C as compared to 2 days at 20°C. The magnitude of the maximum C=C consumption rate at 40°C was 1.5 times that at 20°C. Unsaturated carbon-carbon bond consumption occurs by oxidation with dissolved oxygen. Increasing the reaction temperature increases the mobility of dissolved oxygen in the solution, resulting in an increase in the incidence of reaction between the two species.

In terms of formation of carbonyl products, measured by FT-IR as shown in Figure 23, at the elevated temperature after 3 days approximately 80% of the degradation has occurred as compared to a value of approximately 30% for the lower temperature degradation after the same time. Also, the degradation at 40°C reaches its peak rate of formation of oxidation products after 2 days. For degradations at 20°C the rate of formation of oxidation products reaches a peak after 3 days, and the value of this rate is 3.5 times lower than the peak rate for 40°C degradation. So, increasing reaction temperature increases rate of reaction and decreases the overall time of degradation in terms of formation of carbonyl compounds.

As degradation progresses the crystallinity decreases reflecting the changing chemical content of the polymer. This means that as the short chain radicals are formed in the bulk amorphous polymer they readily diffuse to the amorphous-crystalline boundary and attack the active sites, most probably highly stressed tie molecules. This results in an instantaneous drop in polymer crystallinity. At the lower temperature, the rate of decrease of crystallinity reaches a maximum at the same time (after 3 days) as at the elevated temperature. However, at 20°C the peak rate of decrease of crystallinity is approximately 2 times lower than at 40°C. In the period between 1 and 3 days at 40°C the polymer crystallinity decreases rapidly to almost its final value. This suggests that at 40°C the bulk of the crystalline rearrangement occurs in this time, as does most of the oxidation product formation as shown in Figure 23. After 3 days at 40°C the rate of decrease of crystallinity drops suddenly, indicating that the morphological rearrangement occurs at a high rate and then stabilises. It appears that the same overall process occurs at 20°C over a longer period of time due to the fact that at the lower temperature, chain scission is occurring at a lower rate compared to at 40°C, so the short chain fragments undergo morphological rearrangement as they are formed.

At the peak rate of decrease of crystallinity in the degradation at 20°C the formation of carbonyl groups has just begun as shown in Figure 23. So, the loss of crystallinity occurs at the start of chain scission. This means that the diffusion of short chain radicals through the amorphous region and their reaction at the crystalline-amorphous phase boundary is only slightly dependent on temperature.

Results from tensile measurements of these same fibres are not able to show the same detail as data from FT-IR and DSC studies. After 3 days at 40°C and 8 days at 20°C the break extensions for the fibres reached 0%. This means that no further

information can be obtained using the tensile technique once this limit has been reached. This is shown in Figure 27 for fibres degraded at 20°C and 40°C. Tensile strength measurements provide a good indication of the degradation process up to its limit of measurement when the break extension approaches zero.

After 10 days the formation of carbonyl products appears to be slowing down, as can be seen in the negative slope of 20C actual and 40C actual in Figure 23. So, after 10 days although the degradation is slowing down the fibre is still being oxidised. This is also observed in Figure 26 where the crystallinity content of the polymer approaches a constant level as the rate of degradation decreases. The crystallinity data plotted in Figure 26 differs slightly from the data plotted in Figure 22 for the same experimental conditions and is an indication of the variability of the technique. When measuring crystallinity only a small sample of fibres, <4mg, is required. This corresponds to approximately 5cm of fibre analysed per sample which represents less than 0.5% of the degraded polymer under the given experimental conditions. For each crystallinity analysis 3 replicates were measured to improve the accuracy, however it is obvious that some variability exists.

In summary, increasing reaction temperature increases the overall rate of degradation after the induction period. Increasing the reaction temperature from 20 to 40°C resulted in:

1. In terms of carbonyl content formation a decrease in the time to attain peak rate of carbonyl formation by one third, and an increase in the peak carbonyl formation rate by 350%.
2. The time required to attain peak rate of formation of hydroperoxide decreased by 50%, with a 250% increase in the magnitude of the rate.

3. The time required to attain maximum C=C consumption decreased by 50%, with a 150% increase in the magnitude of the rate.
4. In terms of crystallinity, no change was observed in the time to attain maximum loss of crystallinity, however approximately a 200% increase was observed in the maximum rate of loss of crystallinity.
5. In terms of elongation at break, no change was observed in the time to attain maximum loss of strength, but a 350% increase was observed in the time taken to reach zero elongation.

4.5.4.2 Hypochlorous Acid Concentration Effects.

Aqueous sodium hypochlorite (NaOCl) forms hypochlorous acid (HOCl) which is the active species in the degradation of polypropylene as discussed in Section 2.6. The HOCl solution acts as a source of i) chloride radicals by the reaction of hypochlorite ions with metallic impurities, or the reaction of chloride ions with hydroxy radicals present in active sites of the PP fibres and ii) dissolved oxygen decomposition of the HOCl solution.

The Induction Period

An increase in the HOCl concentration greatly accelerates the degradation process. Figure 28 shows the acceleration of decay in tensile strength for a degradation using 20ppm HOCl as compared to 10ppm at the same temperature (20°C) over a 72 hour period. Elongation at break data for a short time degradation under the same conditions is plotted in Figure 29. It appears that the induction period decreases from 30 hours at 10ppm, to 5 hours at 20ppm under the same conditions. This represents a loss of 85% suggesting that an increase in HOCl concentration has a large effect on degradation.

Doubling the HOCl concentration also increases the rate of loss of crystallinity of the PP fibres as shown in Figure 30. The induction period decreases from 29 hours at

10ppm HOCl to 1 hour at 20ppm. This sudden increase in rate of crystallinity loss using 20ppm HOCl is due to increased chain scission brought about by an increase in rate of formation of hydroperoxides, followed by their decomposition. Increasing the HOCl concentration decreases the induction period in terms of formation of hydroperoxides from 24 hours at 10ppm to 2 hours at 20ppm as shown in Figure 31.

Summarising, doubling the HOCl concentration resulted in a decrease in the induction period observed from elongation at break measurements by 85% from 30 to 5 hours. The induction period observed from crystallinity measurements decreased by 96% from 29 hours to 1 hour. A 92% reduction in induction period was observed from hydroperoxide formation data from 24 hours to 2 hours. Induction periods determined from crystallinity and hydroperoxide formation are most sensitive to HOCl concentration.

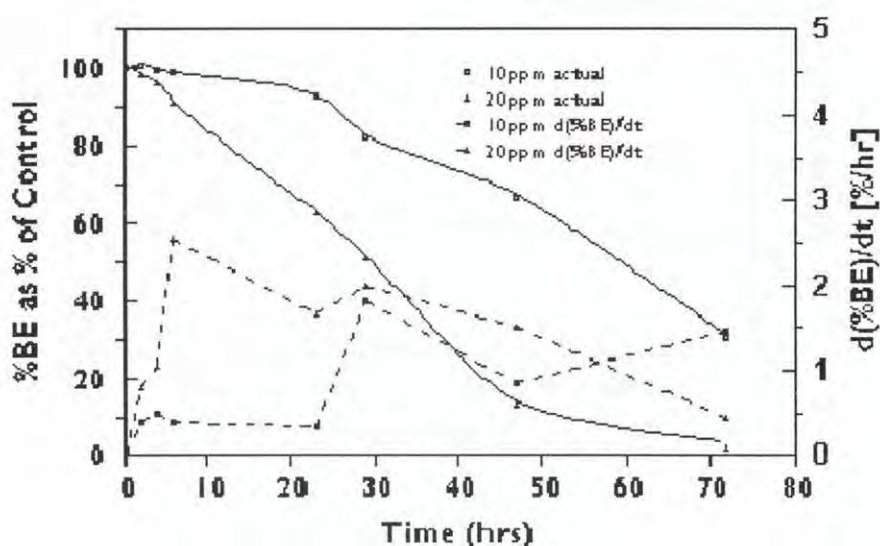


Figure 28 : Elongation at break time profile for PP degradation using 10 and 20ppm HOCl at 20°C.

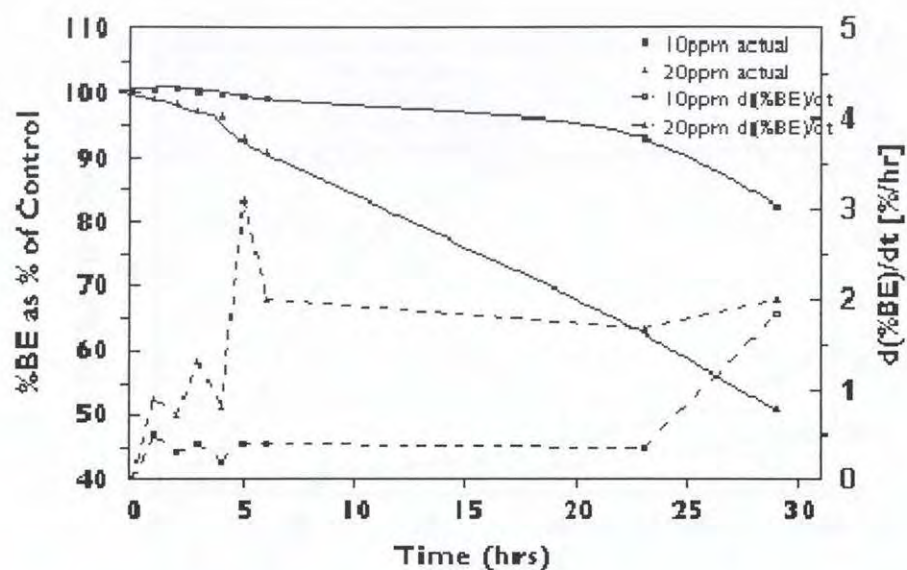


Figure 29 : Elongation at break 'close up' time profile for PP degradation using 10 and 20ppm HOCl at 20°C.

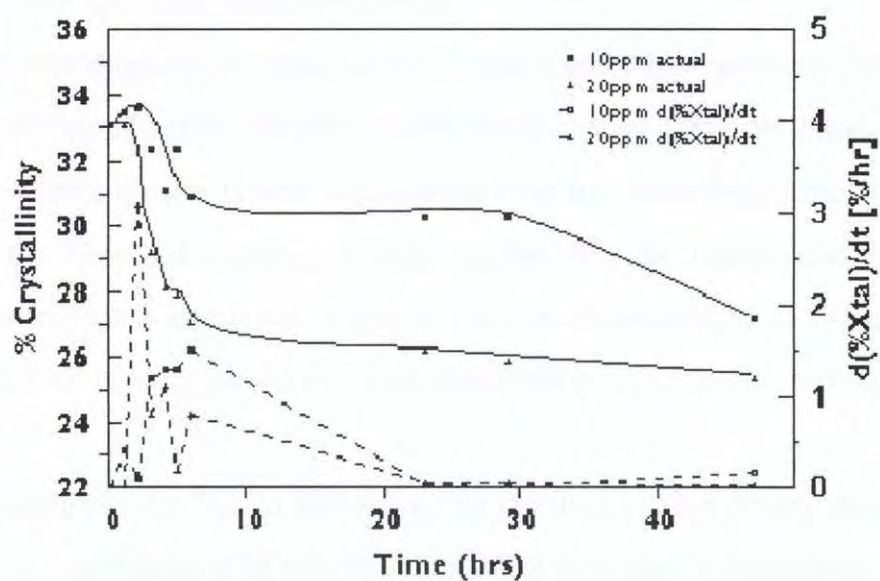


Figure 30 : Crystallinity time profile for PP fibres degrading in 10 and 20ppm HOCl at 20°C.

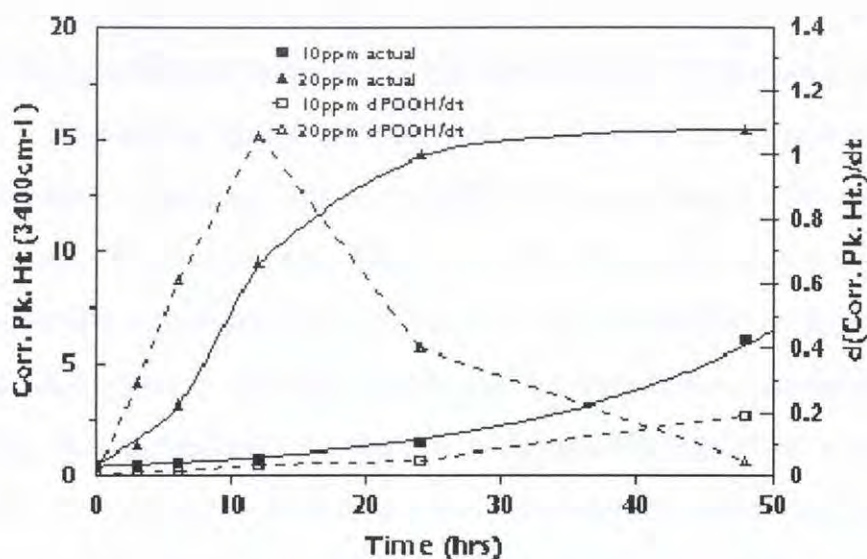


Figure 31 : Rate of formation of hydroperoxides during degradation, in 10 and 20ppm HOCl at 20°C, using FT-IR corrected peak height data at 3400cm⁻¹.

Degradation after the Induction Period

In terms of elongation at break, after the initial induction period of 5 hours at 20ppm, the fibres degrade fairly linearly at an overall rate of 1.8% per hour as compared to 0.9% per hour for the 10ppm degradation over the same time period (1/2 the overall rate of the 20ppm degradation). This suggests that the rate of chain scission in the polymer increases as a result of the increase in concentration of the active species in the HOCl solution: hypochlorite ions, dissolved oxygen and hypochlorous acid.

The crystallinity decline of the degrading polymer is also greatly accelerated by the higher concentration of HOCl. The maximum decrease in crystallinity occurs after 2 hours exposure at 20ppm as shown in Table 3. According to data in Figure 28 this is inside the induction period for the degradation as was also the case for degradation at elevated temperatures. At 20ppm the main loss of crystallinity occurs during the first 6 hours of degradation at an average loss of 1% per hour. From the data in

Table 3 the peak drop in crystallinity occurs after 47 hours exposure at 10ppm. The scatter of the crystallinity data during the first 6 hours of degradation, as seen in Figure 30, is responsible for the artificially high values of rate of loss of crystallinity during that period. The main loss of crystallinity occurs between 29 and 47 hours at an overall loss of 0.17% per hour. This means that the higher concentration of HOCl in solution creates a increased concentration of the active species: hypochlorite ions and dissolved oxygen in solution. These species generate an increased amount of hydroxy and chloride radicals by reaction with metallic impurities at active sites in the polymer. This results in an increase in oxidation rate, and hence chain scission. This improves the chances of chain scission of tie molecules occurring at the crystalline-amorphous boundary, thus increasing the rate of loss of crystallinity.

Time (Hrs)	d(%BE)/dt [%/hr] 10ppm	d(%BE)/dt [%/hr] 20ppm	d(%Xtal)/dt [%/hr] 10ppm	d(%Xtal)/dt [%/hr] 20ppm
0	0	0	0	0
1	0.5	0.9	-0.4	0
2	0.3	0.7	-0.1	3.1
3	0.4	1.3	1.2	0.8
4	0.2	0.8	1.3	1.1
5	0.4	3.1	-1.3	0.2
6	0.4	2.0	1.5	0.8
23	0.34	1.66	0.04	0.05
29	1.82	2	0	0.05
47	0.86	1.52	0.17	0.03

Table 3 : Time profile data for changes in %BE as % of Control and %Crystallinity for degradations at 10 and 20ppm at 20C.

Increasing the HOCl concentration significantly increases the rate of hydroperoxide formation as shown in Figure 31. A maximum rate of POOH formation is attained after 12 hours using 20ppm compared to 48 hours at 10ppm. The magnitude of the maximum POOH formation rate at 20ppm is 6 times the maximum observed at 10ppm. This data indicates that the increased concentration of dissolved oxygen, hypochlorous acid and hypochlorite ions increases the rate of generation of radicals at the active sites, increasing the rate of hydrogen abstraction and hence affecting the formation of hydroperoxides by reaction with dissolved oxygen.

In summary, doubling the concentration of the HOCl solution: i) Doubles the overall rate of loss of elongation at break, ii) Decreases the time to attain maximum loss of crystallinity by 93% from 29 hours at 10ppm HOCl to 2 hours at 20ppm, iii) Increases the magnitude of the maximum loss of crystallinity from 0.17% per hour at 10ppm to 3.1% per hour at 20ppm, iv) Decreases the time to attain maximum hydroperoxide formation from 48 hours at 10ppm to 12 hours at 20ppm, and increases the magnitude of this rate by 6 times. Increasing the HOCl concentration increases the concentration of dissolved oxygen, hypochlorous acid and hypochlorite ions in solution., thus increasing the rate of generation of radicals at active sites in the polymer. An increase in radical concentration increases the rate of hydrogen abstraction, generating macroradicals which then readily react with the high levels of dissolved oxygen generating hydroperoxides.

4.5.4.3 Conclusions

Generally speaking, increasing both temperature and HOCl concentration resulted in an overall increase in the rate of degradation. The degree of degradation of the PP hollow fibre membranes was determined using several techniques: i) Tensile strength to measure elongation at break, ii) DSC to measure crystallinity and iii) FT-

IR spectroscopy to measure carbonyl, hydroperoxide and unsaturation content. Degradation reactions were carried out using 10 and 20ppm HOCl at 20 and 40°C.

The induction period was defined as the period prior to the detection of formation of degradation products. The length of the observed induction period varied slightly depending on the analytical method being used. The length of the observed induction periods are shown in Table 4:

Property	Length of Induction Period (hrs)		
	10ppm 20°C	10ppm 40°C	20ppm 20°C
Elongation at Break	30	12	5
Crystallinity	29	24	1
Hydroperoxide Content	24	6	2
Carbonyl Content	30	24	n/a
Unsaturation Content	24	0	n/a

Table 4 : Summary induction period data.

Increasing degradation temperature most strongly affected the unsaturation and hydroperoxide content, significantly reducing the onset of observable change. Crystallinity and carbonyl content were least affected. This data indicates that the formation of hydroperoxides by the reaction of dissolved oxygen, from the HOCl solution, with either unsaturated carbon-carbon groups or tertiary radicals is strongly temperature dependent. Whereas, carbonyl decomposition forming carbonyls and low molecular weight fragments is less temperature dependent. The latter occurs in the bulk polymer, while the former occurs at the interface between the polymer and HOCl solution.

Increasing HOCl concentration resulted in a significant decrease in the induction period with respect to all properties. The HOCl solution provides the source of oxygen and free radicals for oxidation. Increasing their concentration results in an increase in the number of degradation reactions occurring, and hence a decrease in the time to observe chemical or physical change in the polymer.

Increasing temperature and HOCl concentration resulted in an overall increase in the rate of degradation after the induction period. The rate of change of the measured property reached a maximum value after a certain reaction time. These values are shown in as a percentage of the values obtained using 10ppm HOCl at 20°C.

Property	% Decrease in Time to Max. Rate*		% Increase in Max. Rate*	
	10ppm 40°C	20ppm 20°C	10ppm 40°C	20ppm 20°C
Elongation at Break	0	83	118	72
Crystallinity	0	50	109	138
Hydroperoxide Content	50	75	146	475
Carbonyl Content	33	n/a	225	n/a
Unsaturation Content	50	n/a	55	n/a

* Using the data for 10ppm at 20°C as a basis.

Table 5 : Summary data for degradation after the induction period.

Increasing the HOCl concentration most significantly increased the rate of hydroperoxide generation, as well as significantly decreasing degradation time. Hence, the formation of active chloride and hydroxy radicals from hypochlorous acid and hypochlorite ions, their abstraction of tertiary hydrogen atoms followed by reaction with dissolved oxygen is strongly dependent on HOCl concentration. The

increase in maximum rates observed by the other properties are a by-product of the increase in concentration of hydroperoxides generated at high HOCl concentrations.

Increasing the degradation temperature most strongly increased the rate of carbonyl formation, due to decomposition of the increased amount of hydroperoxides produced both during and after the induction period at the elevated temperature. Onset of loss of elongation at break and crystallinity were not temperature affected, however their rate of loss was.

The aqueous degradation of PP hollow fibre membranes using hypochlorous acid is strongly dependent on both HOCl concentration and reaction temperature. Temperature and HOCl concentration influence the degradation in two ways. An increase in the reaction temperature increases the overall reaction rate by increasing the mobility of all active species. Increasing HOCl concentration significantly increases the generation of hydroperoxides, which in turn increases the overall number of degradation reactions occurring, hence increasing the degradation rate.

4.5.5 Proof of the Infectious Spreading of Degradation

The ‘infectious’ model for the spreading of polypropylene degradation^{50,51,42} requires chemical attack of the polymer at certain active sites, followed by spreading of degradation by diffusion of active degradation products through the polymer and their reaction with the bulk polymer. Using polypropylene films pre-irradiated with γ -rays, Carlsson *et al*⁵² found that during storage at 23 and 60°C the films continued to undergo oxidation in the absence of an initiating source.

To test the nature of the spreading of the degradation process, polypropylene fibres were placed in 10ppm sodium hypochlorite at 20°C for 3 hours. The time of 3 hours

was chosen as it is approximately the length of the induction period for degradation under these conditions, while still exposing the polymer to an oxidising environment. After the 3 hours the fibres were placed in reverse osmosis (RO) water containing no contaminants for the duration of the experiments. Dissolved oxygen was removed from the solutions prior to reaction via regassing with UHP argon. This was to ensure that all oxygen consumed during degradation was generated during the reaction.

Fibres were sampled regularly and analysed by tensile strength, DSC and FT-IR. The results are shown in Figure 32 and Figure 33.

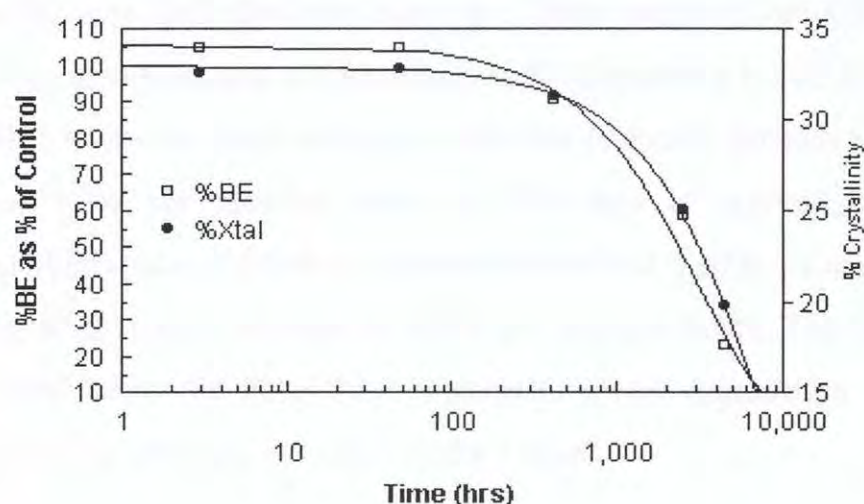


Figure 32 : Tensile strength and crystallinity trends showing the infectious nature of degradation.

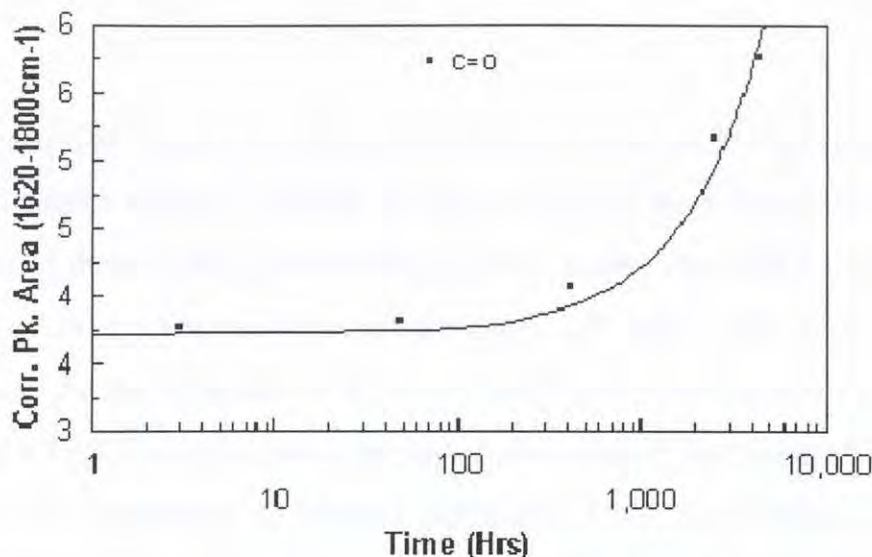


Figure 33 : Formation of carbonyl groups during degradation using FT-IR corrected peak area data in the region 1620-1800cm⁻¹.

It can be seen that after 409 hours the fibres begin to show signs of carbonyl formation as well as loss of crystallinity and elongation at break. Between 409 hours and 4465 hours the fibres undergo a 74% loss of tensile strength at an overall %BE rate of 1.7% per hundred hours, a 37% loss of crystallinity at an overall %crystallinity rate of 0.3% per hundred hours and a 51% increase in the oxygen content at an overall %O rate of 0.01% per hundred hours. This data suggests that after 4465 hours the fibres have undergone severe degradation, after only being exposed to an oxidising environment for 3 hours.

As shown in Section 4.5.4 fibres exposed to 10ppm HOCl for 3 hours undergo no observable change in polymer structure, however the formation of low levels of oxidation products occurs. HOCl solution in contact with PP hollow fibres generates chloride and hydroxy radicals as discussed in Section 2.6.2. These radicals initiate oxidation of PP, generating further hydroxy radicals and in addition macro radicals formed by abstraction of tertiary hydrogens. Removing the fibres from an oxidising environment after short time exposure to HOCl does not stop the degradation

process. Instead, the degradation proceeds with only those active species, chloride, hydroxy and macro radicals, already produced in the 3 hour exposure time. The concentration of these radical species being so low means that only a small amount of active sites in the polymer are attacked per unit time. This means that the induction time for the degradation is vastly increased, as compared to PP fibres degrading in a HOCl solution, until enough active sites in the polymer have been attacked for the degradation to become detectable. Once the overall degradation reaches detectable limits, it proceeds at a rate 100 times less than that which occurs in 10ppm HOCl under the same conditions.

4.5.5.1 Conclusions

In summary, PP hollow fibres exposed to an oxidising environment, such as 10ppm HOCl, for a short time and then exposed to a non-oxidising solution for an extended period undergo significant degradation. The induction period of the degradation is significantly increased, and the rate of oxidation is lower, approximately 100 times, than for fibres in an oxidising environment. This proves that the oxidation of PP spreads by an 'infectious' mechanism by diffusion of free radicals through the polymer. These radicals initiate further oxidation.

4.5.6 Effect of Dissolved Oxygen on Polypropylene Degradation.

The objective of this study was to evaluate the effect of dissolved oxygen only on the degradation of polypropylene hollow fibre membranes. PP fibre samples were placed in reverse osmosis (RO) water and oxygen was bubbled constantly through the solution at room temperature. Fibres were sampled regularly and their tensile strength measured to determine the extent of degradation. The oxygen content measured is that for water saturated with oxygen at 20°C - 9.1ppm. Degradation experiments were carried out at 20°C.

Time (Days)	%BE as % of Control
0	100
3	101.6
5	100.3
8	99.8
10	96.6
15	95.7
18	94.2

Table 6 : Tensile strength data for oxygen degradation at 20C.

The presence of low concentrations of dissolved oxygen in RO water did not significantly degrade the polypropylene fibres under the reaction conditions over an 18 day period as shown by the tensile strength data in Table 3. Dissolved oxygen present as a by-product of HOCl decomposition in HOCl solutions readily reacts with PP fibres by either reaction with unsaturated C-C groups or by oxidising tertiary radicals, producing hydroperoxides. The tertiary radicals are present in the polymer due to abstraction of tertiary hydrogen atoms by chloride and hydroxy radicals produced from the HOCl solution. So, in the absence of a radical initiator, the oxidation of PP fibres with dissolved oxygen does not occur by reaction with tertiary radicals. A slight decrease in the elongation at break is observed indicating that slight degradation has occurred. This is due to oxidation of C=C groups present in the polymer as a residual impurity from visbreaking. Hydroperoxides are produced as a result of this oxidation, which may undergo decomposition generating radicals. In this way, oxidation proceeds at a slow rate due to the low concentration of radicals generated.

4.5.6.1 Conclusion

PP hollow fibres immersed in reverse osmosis water saturated with dissolved oxygen (9.1ppm) undergo slight degradation as determined by the elongation at break. This is due primarily to the reaction of dissolved oxygen with residual C=C bonds, formed during visbreaking, generating hydroperoxides.

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Chapter 5 The Effect of Catalyst Residues and Other Impurities on the Oxidative Degradation of Polypropylene Membranes.

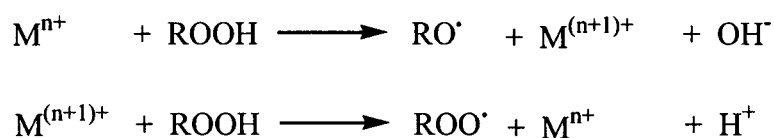
5.1 Introduction

After polymerisation and processing commercial polypropylene contains Ziegler-Natta catalyst residues, copper and iron from processing equipment, residual unsaturation and oxidised products from vis-breaking and oxidation products from degradation during pelletisation and extrusion. The formation of these products in commercial PP is discussed and the effect of these impurities on the degradation of polypropylene hollow fibre membranes by aqueous hypochlorous acid (HOCl) is investigated.

5.1.1 Transition Metals

Metal impurities present in polypropylene have been observed to accelerate the oxidation of the polymer^{1,2,6}. Typical metal impurities include titanium and aluminium, from Ziegler-Natta catalysts, and iron and copper from processing equipment³.

The initiation of oxidation of polypropylene normally occurs by decomposition of any hydroperoxides present in the polymer. Transition metal ions are important catalysts for the hydroperoxide decomposition process by reducing the activation energy as shown in Scheme 1. Transition metal is denoted by M:

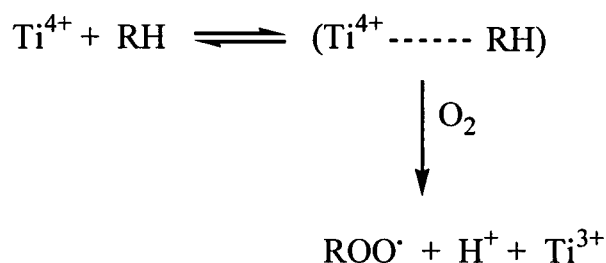


Scheme 1

The concentration of hydroperoxides in the polymer is low at the start of reaction, and as its concentration increases the rate of oxidation increases.

After polymerisation polypropylene contains Ziegler-Natta catalyst residues which consist of <50ppm titanium in the form of OTiCl_2 , TiO_2 , OTiCl(OR) , $\text{TiCl}_2(\text{OR})_2$, TiCl_4 , TiCl(OR)_3 and Ti(OR)_4 ⁴. Due to its variable valency titanium readily catalyses oxidation processes^{5,2}. Titanium (IV) compounds (n-butyl orthotitanate, n-octadecyl orthotitanate, titanium tetrastearate) have been found by Cicchetti *et al*⁶ to catalytically decompose hydroperoxides at low titanium concentrations, yielding t-alkyl peroxy radicals and t-alkoxy radicals. At high titanium concentrations, however, the compounds become oxidation inhibitors. Gijssman *et al*⁷ found that residual titanium impurities catalysed the decomposition of hydroperoxides at low temperatures but had no effect on the decomposition rate at elevated temperatures. Instead, at elevated temperatures the hydroperoxides undergo thermal decomposition.

A primary initiation reaction for polypropylene degradation was proposed by Cicchetti *et al*⁶. A complex formed between the polymer molecule and the Ti(IV) catalyst subsequently reacts with oxygen to give an alkylperoxy radical as shown in Scheme 2.



Scheme 2

This mechanism is analogous to a mechanism proposed by Bawn and Chaudri⁸ for the manganese catalysed oxidation of polypropylene.

Chromium(III) and iron(III) ions have been observed by Chirinos-Padron *et al*⁹ to have a stabilising effect on the thermal and photochemical degradation of stabilised polypropylene while copper(II) ions acted to catalyse the degradation.

Nickel, zinc and cobalt dithiocarbonates exhibit strong UV stabilising properties by inhibiting carbonyl and hydroperoxide formation¹⁰.

Some metal chelates act as UV stabilisers by causing the thermal decomposition of polymeric hydroperoxides. Carlsson and Wiles¹¹ observed that the thermal degradation of polypropylene can be inhibited by metal chelates of, in order of effectiveness, Ni(1) > Zn(1) > Ni(2) > P(7) > P(1) > Ni(3). Osawa and Saito¹² used metal chelates as inhibitors for thermal oxidation and found that only Al, Zn and V were effective, while Ti, Ni, Co, Cr, Fe, Mn and Cu all catalysed the oxidation. It is well known in the literature hydroperoxide activity may be reduced by the effect of the metal complexes of Ni and Co dithiocarbamates^{13,14}. A variety of nickel(II) chelates were found by Briggs and McKellar¹⁵ to be effective stabilisers for polypropylene photodegradation.

5.1.2 The Formation of Residual Unsaturation and Oxidised Products During Visbreaking.

Traditional Ziegler-Natta catalyst technology for the production of polypropylene produces impure polymer with a broad molecular weight distribution. Two methods are used for the modification of molecular weight: Thermal degradation and peroxide-promoted degradation.

Thermal degradation processes carried out in the absence of oxygen have high energy requirements due to the high temperatures (200-400°C) and long reaction times (upto 24 hours) required for molecular weight control¹⁶. This method also achieves only low degrees of molecular weight reduction as compared to peroxidic methods, and hence is not widely used.

Organic peroxides are most commonly used to modify polymer molecular weight after polymerisation in a process named viscosity breaking or 'vis-

breaking'. Molecular weight control is achieved by chain cleavage of high molecular weight polypropylene, resulting in the removal of the high molecular weight tail and a narrowing of the molecular weight distribution¹⁷. Molecular weight control is achieved using a common industrial organic peroxide. The organic peroxides most commonly used for polypropylene visbreaking are¹⁸:

DHBP : 2,5-dimethyl-2,5-di-(t-butylperoxy)-hexane

DTBP : di-t-butylperoxide

DIPP : di-(2-t-butylperoxypropyl-(2))-benzene

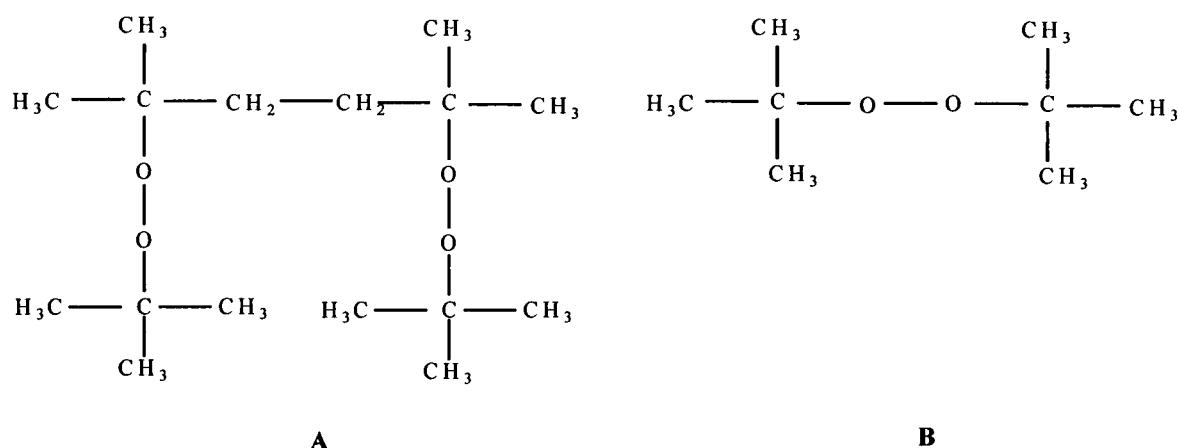


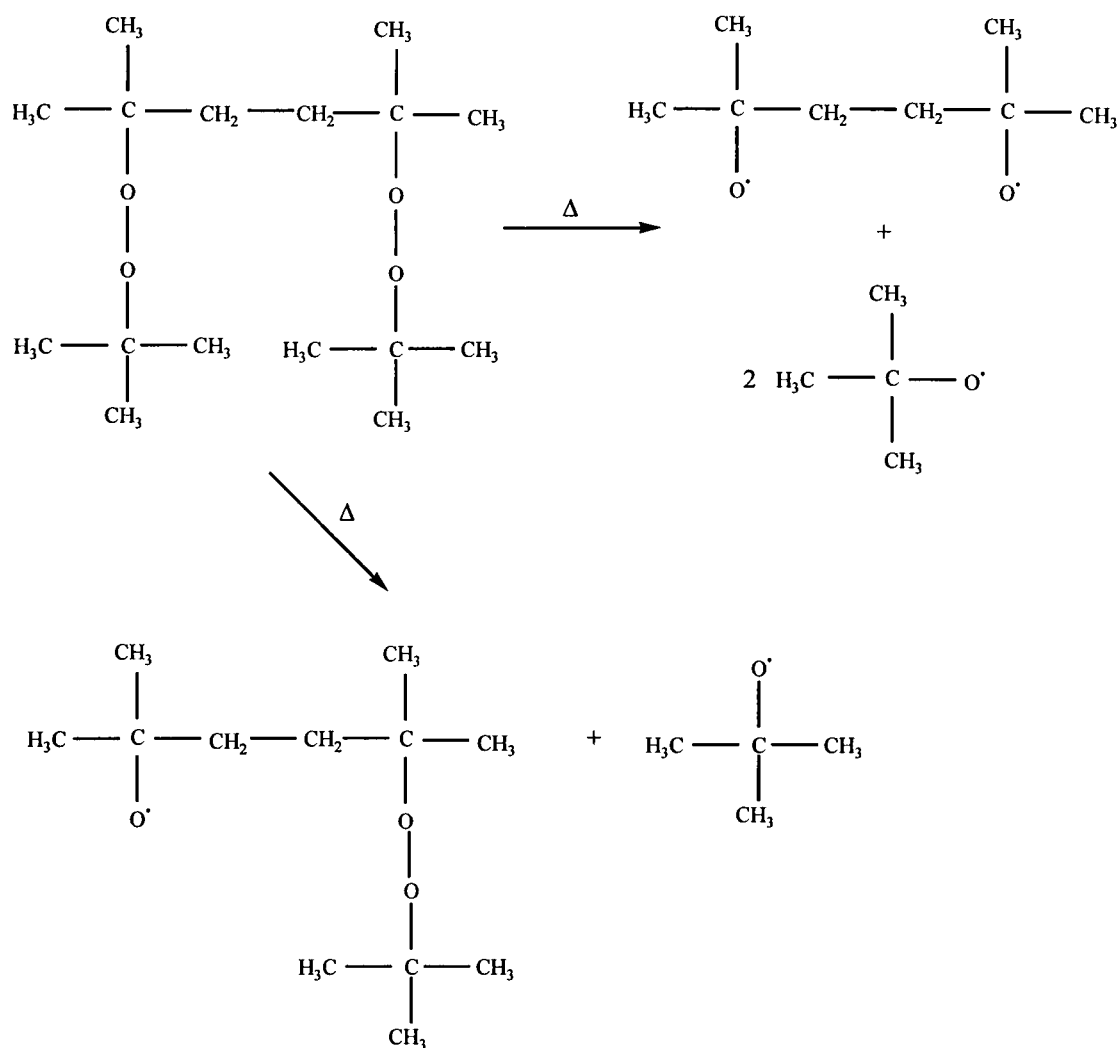
Figure 1: Structures for A: DHBP and B : DTPP

The organic peroxide DHBP exhibits first order decomposition kinetics with a half life of 5.9 seconds at 200°C. DHBP is a liquid with a boiling point of 249°C¹⁸.

Peroxidic-promoted degradation generally takes place in an extruder. The peroxides can either be premixed with the PP prior to being fed to the extruder or injected into the melt pumping zone¹⁶. Argon blanketing is used to reduce the amount thermooxidative degradation occurring.

As well as decreasing the polymer molecular weight the visbreaking process produces various impurities in the polymer either due to polymer chain scission or organic peroxide decomposition. Formation of radicals from the organic

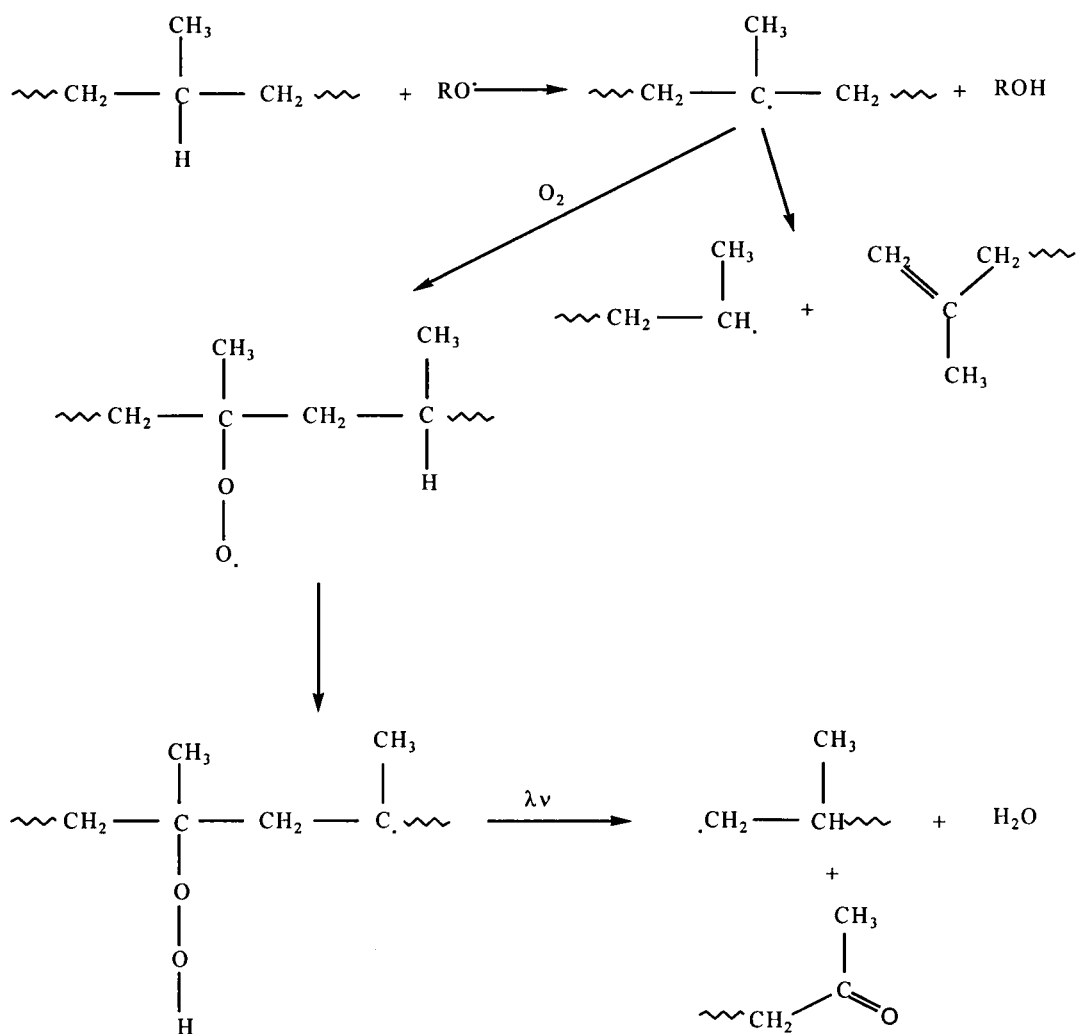
peroxide occurs by a decomposition reaction as shown in Scheme 3 for the most commonly used organic peroxide DHPB.



Scheme 3

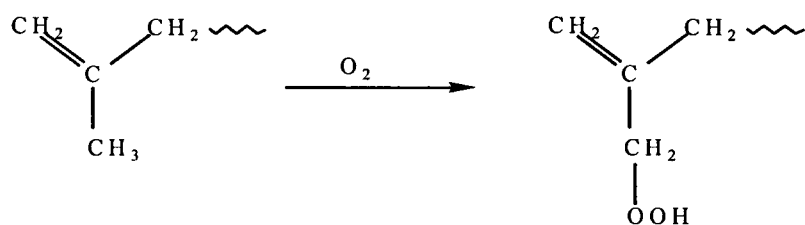
During molecular weight control the alkoxy radicals formed in Scheme 3 abstract a tertiary hydrogen atom from the polymer, deactivating the alkoxy radical by forming an alcohol. The resulting tertiary polymer radical behaves in 1 of 2 ways:

- 1) Reaction with oxygen forming a hydroperoxy radical which then abstracts a hydrogen forming a hydroperoxide and a tertiary radical. This product decomposes further producing a short chain radical and a carbonyl compound. In the presence of UV radiation the carbonyl compound undergoes further decomposition according to the Norrish Reaction, as discussed in Chapter 2, forming unsaturated C-C bonds, ketones and alcohols.



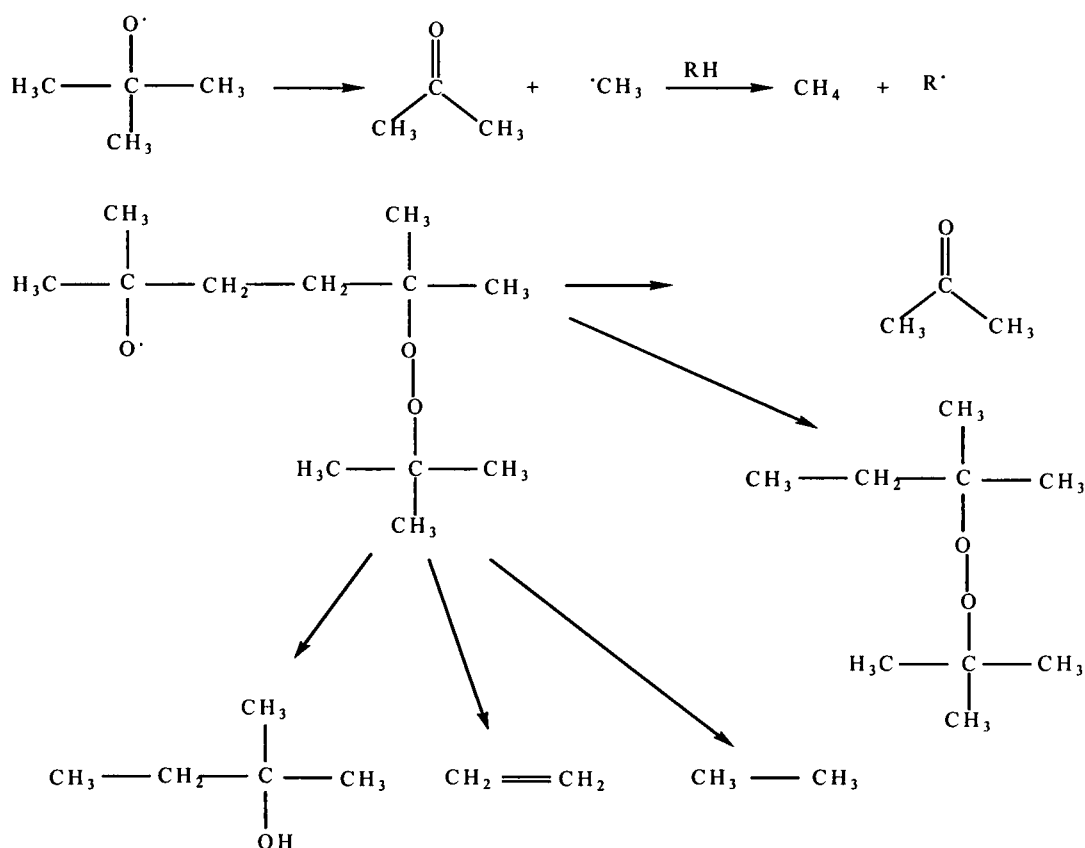
Scheme 4 :Molecular weight control using organic peroxides. The formation of unsaturated end-groups and carbonyl compounds.

2) Tertiary radical undergoes β -scission as shown in Scheme 4. This results in the formation of short chain radicals as well as unsaturated C-C bonds at the sites where scission occurred. These C=C bonds react readily with any oxygen present in an oxidising environment forming peroxides as is shown in Scheme 5 ¹⁹.



Scheme 5 : Oxidation across C-C double bonds.

During the visbreaking process the organic peroxides, as well as forming alcohols, undergo further decomposition to form residual impurities in the polymer. Scheme 6²⁰ shows the decomposition products formed from the initial peroxy radicals shown in Scheme 3. Not included here are the alcohols of the 3 peroxy radicals shown in Scheme 3, however they also contribute to the total impurity concentration. These impurities will affect the inherent structure of the polymer even though the total concentration of the impurities in the polymer is low. Of particular importance is the high surface area polypropylene membranes which may have a high local but a low total impurity concentration.

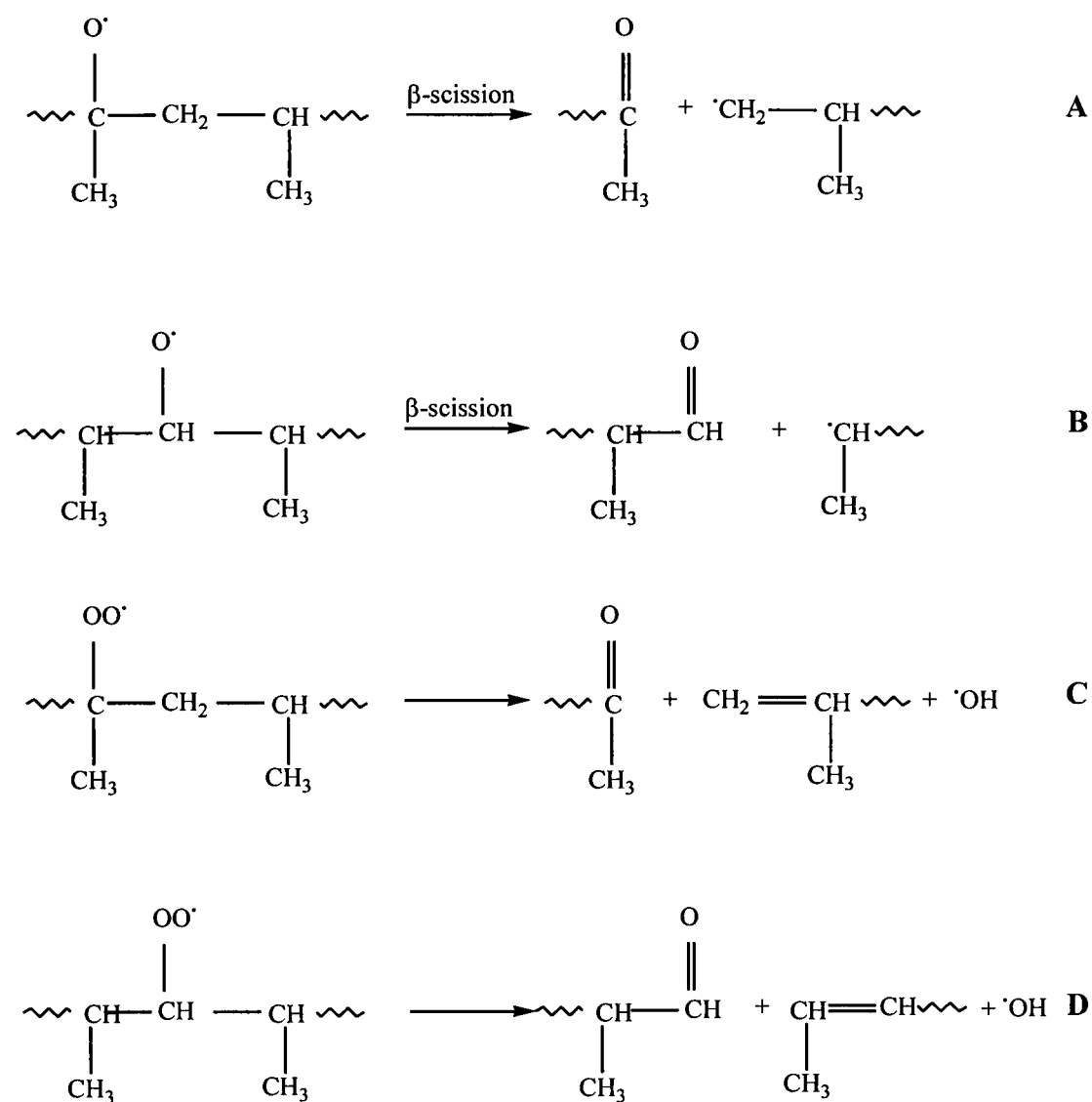


Scheme 6 : Formation of impurities by organic peroxide decomposition.

5.1.3 The Effect of Extrusion of Polypropylene

Generally, processing has an adverse effect on the structure of polypropylene due to chemical and structural changes which occur in the polymer eg, formation of oxygen containing groups such as carbonyls and peroxides as well as carbon-

carbon unsaturation^{21,22,23}. The processing of polypropylene also leads to a decrease in the molecular weight due to the breakdown of peroxy radicals resulting in chain scission²¹. Chakraborty and Scott^{24,25} showed that the rate of oxidation of polypropylene in the early stages is dependent on the concentration of hydroperoxides formed during processing. Hinsken *et al*²¹ showed that in the extrusion of polypropylene in air at 240°C the formation of aldehyde and ketone groups was due to the β -scission of alkoxy radicals as shown in Scheme 7.



Scheme 7 : The formation of aldehydes and ketones from the scission of alkoxy and peroxy radicals during polypropylene extrusion.

After polymerisation, raw polypropylene powder is converted to pellets by a compounding process in which the polymer is heated to a plastic state, then shear-mixed at high pressures²⁶. The extrusion of polypropylene pellets to hollow fibre membranes involves heating with a solvent to above the polymer crystallisation temperature (T_c). The polymer solution is mixed continuously with a twin screw which conveys it to the extrusion port. This process applies considerable shear on the polymer melt and may affect its inherent structure. Also, at the high extrusion temperature some thermal degradation is possible.

5.1.4 Objectives

The objectives of this study are threefold:

1. To determine the effect of processing on the content of commercial polypropylene.
2. To determine the effect of impurities present due to processing on the oxidation resistance of PP to hypochlorous acid.
3. To determine the effect of transition metals on the oxidation of PP using hypochlorous acid.

5.2 Experimental

The effect of processing on polypropylene was investigated by comparing the chemical structure of polypropylene fibres to that of polypropylene pellets and the unextruded form of polypropylene powder. The resistance to oxidation by hypochlorous acid was compared for polypropylene pellets and powder. The effect of the presence of transition metal ions Fe(III), Fe(II), Cu(II) and Co(II) on the degradation of polypropylene fibres by aqueous HOCl was investigated.

5.2.1 Materials

Polypropylene fibres, extruded by Memtec Ltd. from polypropylene pellets, were studied in the form of hollow fibre membranes. A detailed description of the membranes is given in Section 4.3.1. Polypropylene pellets and powder were

supplied by Hoechst. Films were pressed from pellets and powder using a heated press at 200°C with a 40 tonne load for 2 minutes. The resulting film thickness was 0.5mm. Some oxidation of the films may occur during heat pressing, however this thermal oxidation would be minimal compared to oxidation during processing. Degradations were carried out using sodium hypochlorite (Ajax Chemicals). Metal ions used were Cobalt (II) in the form of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ from Ajax Chemicals, Iron (III) as $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ from BDH Chemicals, Copper (II) as $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ from Ajax Chemicals and Iron (II) as $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ from Ajax Chemicals.

5.2.2 Method of Degradation

5.2.2.1 Oxidation Resistance of Polypropylene Pellets and Powder.

Films from the pellets and powder were cut into 3cm x 3cm squares for the degradation experiments. Oxidation was carried out using sodium hypochlorite solutions at 10, 20 or 80ppm. Prior to reaction the solutions were regassed with high purity argon. Films were immersed in this solution and placed in a sealed reactor at 20°C. HOCl concentration was maintained by controlled sodium hypochlorite dosing, see Section 1.3.2. Extent of degradation of the films was determined by FT-IR and DSC.

5.2.2.2 Effect of Transition Metals on Polypropylene Degradation.

Degradation solutions were prepared by dissolving known masses of the transition metal salts in 10ppm HOCl solutions. Fibres were then wet out with methanol and rinsed with RO water. Fibres were immersed in the solutions inside sealed reactors at 20°C. Solutions were replaced daily. Fibres were sampled regularly and the extent of degradation was determined using tensile strength and DSC methods.

5.3 Results and Discussion.

5.3.1 Degradation of Polypropylene During Processing.

Polypropylene pellets are extruded by the supplier from polypropylene powder at elevated temperatures. Prior to extrusion, a hindered phenol stabiliser is added to the polypropylene powder. After pelletisation, the pellets are then extruded at above 180°C into hollow fibres. FT-IR analysis of samples from each stage of processing : powder before pelletisation, PP pellets after pelletisation and PP fibres after extrusion, are compared to determine the presence of any impurities formed by oxidation.

A summary of the relevant FT-IR data for the 3 samples is shown in Table 1. Functional groups are identified by FT-IR wavenumber and the concentration of each group either the powder, pellets or fibre is represented by the peak height of the signal. It was found in Chapter 1 that either the peak height or peak area could be used interchangeably to represent concentration.

Waveno. (cm ⁻¹) ²⁷	Functional Group	Corrected Pk. Height PP Powder	Corrected Pk. Height PP Pellets	Corrected Pk. Height PP Fibre
3410	Hydroperoxides	0.6	0.85	1.6
3200	C=C	1.7	1.5	4.9
1705	Ketones	1.5	1.6	1.9
1633	vinyl C=C	3.4	4.8	5.9
1720	carboxylic acids	1.1	1.4	2.2
1735	aldehydes	0.5	0.8	1.6

Table 1 : FT-IR Data for undegraded PP powder, pellets and fibre.

It is evident from the FT-IR powder content that during the visbreaking process a significant amount of hydroperoxides and unsaturated carbon-carbon bonds are formed. This is consistent with the mechanism shown in Scheme 4 for the products of polypropylene visbreaking. The presence of ketones in the powder sample are due to the decomposition of hydroperoxides formed in the visbreaking process as depicted in Scheme 4. A small amount of propanone formed by decomposition of the organic peroxide, as seen in Scheme 6, also contributes to this signal.

During pelletisation at $> 160^{\circ}\text{C}$ the amount of mid-chain carbon-carbon double bonds decreases indicating oxidation occurs across the double bond resulting in the formation of hydroperoxides as shown in Scheme 5, while the amount of vinyl carbon-carbon groups increases as would be expected as a result of chain scission due to oxidation. Due to the stabilising action of the hindered phenol only a slight increase in the oxygen containing products, aldehydes and carboxylic acids occurs. A slight increase in the ketone content occurs due to peroxide decomposition.

During extrusion the formation of oxidised species continues with increases in carboxylic acids, aldehydes and ketones present. Oxidation proceeds resulting in the formation hydroperoxides and unsaturated carbon-carbon bonds as in Scheme 4.

In summary, polypropylene powder, pellets and fibres have significant differences in content due to oxidation occurring to varying extents during processing. Polypropylene powder contains a significant amount of hydroperoxides and unsaturated carbon-carbon bonds, residual products of visbreaking. The formation of these products appears to follow the proposed mechanism as shown in Scheme 4. Pelletisation results in a decrease in the

unsaturation content and increase in hydroperoxide content due to oxidation of C=C groups as described in Scheme 5. Extrusion results in a significant increase in concentration of all oxidation products. Unstabilised PP fibres also contain twice as many active hydroperoxides and unsaturated C-C bonds than PP powder and so will be significantly more susceptible to oxidation than PP powder.

5.3.2 Degradation of Pellets vs Powder.

Films pressed from PP pellets and powder were oxidised in HOCl solutions and their extent of degradation determined using crystallinity measurements from DSC and oxygen content data from FT-IR.

A general increase in crystallinity was observed with degradation for the films. This is contrary to the observed decrease in crystallinity observed for degrading polypropylene fibres. This difference in behaviour can be explained by the very high surface area of the fibres as compared to the relatively low surface area of the films. PP films immersed in the aqueous HOCl solution have essentially only two surfaces in contact with the solution. As discussed in Section 2.6, the active chloride radicals are formed by reaction of HOCl and OCl^- with the PP active sites containing metallic impurities or hydroxy or alkoxy radicals. So, the oxidation depends on the number of PP active sites in contact with the HOCl solution. This means that degradation occurs preferentially on the film surface in much the same way as in photodegradation. The resulting short chain radicals diffuse into the film and oxidise further reactive sites, however diffusion of the radicals limits the degradation mostly to the amorphous phase. Short chain fragments produced in the amorphous region align and recrystallise, increasing the polymer crystallinity.

Polypropylene fibres, on the other hand, have approximately 80% of the polymer in contact with the reacting HOCl solution. This means that the low molecular weight chloride radicals formed by the HOCl solution are able to react with all of

the active sites in the polymer, including 'tie molecules'. The decrease in crystallinity of polypropylene fibres was explained in Chapter 4 to be due to chain scission of these 'tie molecules', opening up the crystalline region and decreasing the overall crystallinity. Clearly, the mechanism of HOCl attack on polypropylene is dependent on reaction surface area. This means also that due to the high surface area of the membrane, the rate controlling process for the aqueous degradation is diffusion across phase boundaries.

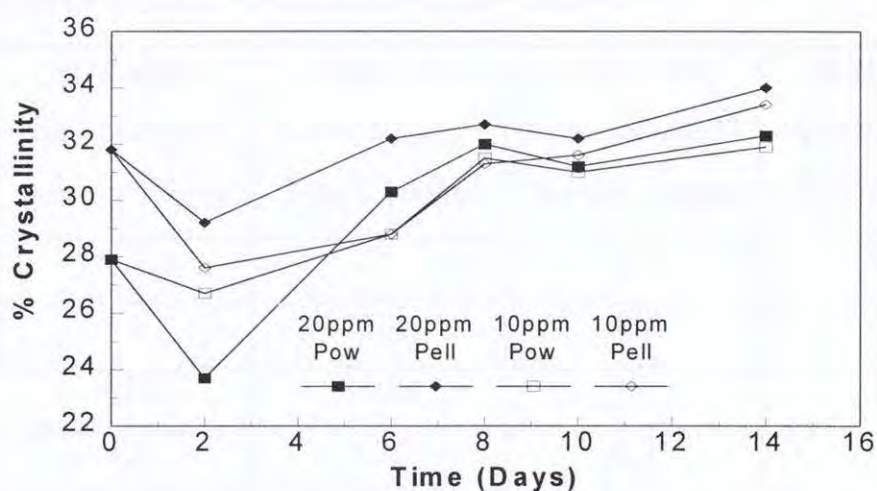


Figure 2 : %Crystallinity of films from PP pellets and powder degraded at 10 and 20ppm HOCl.

The films pressed from pellets contain more oxidised products such as aldehydes, ketones and unsaturated carbon-carbon bonds than films from powder, and as a result contain more short chain fragments due to chain scission. These short chains are most likely to exist in the crystalline region, so a higher crystallinity is expected for undegraded films from pellets than from powder, as is observed in Figure 2.

As one of the products of oxidation is chain scission, the rate of change of crystallinity indicates the rate of oxidation. The overall rate of change of crystallinity of films pressed from PP powder, 0.30%/day, was much higher than

that for films pressed from PP pellets, 0.13%/day. PP pellets contained a large amount of oxidised products prior to degradation, as shown in Table 1. So a decreased rate of oxidation is expected due to a decreased concentration of active sites for oxidation. From Figure 1, after 6 days the rate of change of crystallinity of films from powder approaches that of films from pellets. This implies that the rate of oxidation during this period is dependent on the active site concentration. This is supported by data in Table 2 which shows that the oxygen content of the degrading films reaches a constant level after 6 days.

Time (Days)	Peak Area 1620-1800cm ⁻¹ Powder 10ppm	Peak Area 1620-1800cm ⁻¹ Pellets 10ppm	Peak Area 1620-1800cm ⁻¹ Powder 20ppm	Peak Area 1620-1800cm ⁻¹ Pellets 20ppm
0	3.5	3.7	3.5	3.7
2	3.6	3.9	4.1	4.5
6	4.05	4.2	4.4	5
14	4.2	4.25	4.5	5

Table 2 : Oxygen content data for degrading films from pellets and powder.

After 14 days the films from pellets have a higher oxygen content than those from powder, by 11% at 20ppm HOCl and 1% at 10ppm. This shows that the formation of oxygen containing groups is dependent on HOCl concentration. Carbonyl compounds are formed by the decomposition of hydroperoxides. Table 3 shows that films from pellets have a high initial hydroperoxide content and this explains the high initial rate of formation of carbonyl compounds observed in Table 2.

Time (Days)	Peak Height 3410 cm ⁻¹ Powder 10ppm	Peak Height 3410 cm ⁻¹ Pellets 10ppm	Peak Height 3410 cm ⁻¹ Powder 20ppm	Peak Height 3410 cm ⁻¹ Pellets 20ppm
0	0.6	0.85	0.6	0.85
2	0.8	0.8	0.71	0.7
6	0.73	0.82	0.68	0.6
14	0.7	0.8	0.65	0.58

Table 3 : Hydroperoxide content data for degrading films from pellets and powder.

At 10ppm the concentration of hydroperoxides was higher in the film from both pellets and powder than those at 20ppm. This indicates that sufficient active sites in the polymer were still present to replace those hydroperoxides undergoing decomposing. At 20ppm the decrease in hydroperoxide contents in both the films from pellets and powder indicated a decrease in the rate of oxidation, as can be seen in oxygen content data for 20ppm samples in Table 2.

In summary, processing of PP powder into PP pellets increases the content of oxidised species. The presence of these oxidised species in films from PP pellets increases the initial rate of oxidation by decomposition of existing hydroperoxides and reaction with existing unsaturated groups. The overall rate of oxidation in both types of films depends on active site and oxidant concentration. The overall products of oxidation in films from PP pellets and PP powder are consistent and independent of initial PP composition. Degradation of PP films results in an increase in crystallinity while PP fibre degradation produces a decrease. This discrepancy is due to the much lower surface area of PP films compared to PP fibres.

5.3.3 The Transition Metal Ion Effect.

Polypropylene fibres were degraded in solutions containing transition metal salts dissolved in 10ppm HOCl. The extent of degradation of the fibres was determined using tensile strength measurements. Fibre degradation in the presence of the HOCl/metal ion solution was compared to degradation in HOCl only solutions. As shown in Figure 3 and Figure 4, of the transition metal ions tested Iron(III) as $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and Copper(II) as $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ accelerated the rate of oxidation by catalysing the decomposition of hydroperoxides by the mechanism shown in Scheme 1. Chirinos-Padron *et al*²⁸ observed similar results for copper(II) salts in stabilised polypropylene, however the presence of iron(III) salts did not effect the degradation of stabilised polypropylene due to interaction with the hindered phenol stabiliser.

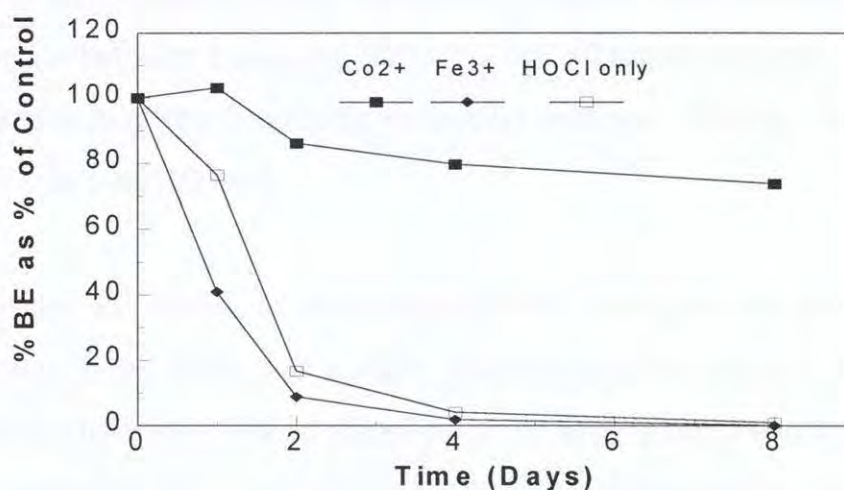


Figure 3 : Elongation at break time profile for PP fibres degraded in HOCl, HOCl + Co^{2+} (7200ppm), HOCl + Fe^{3+} (7275ppm).

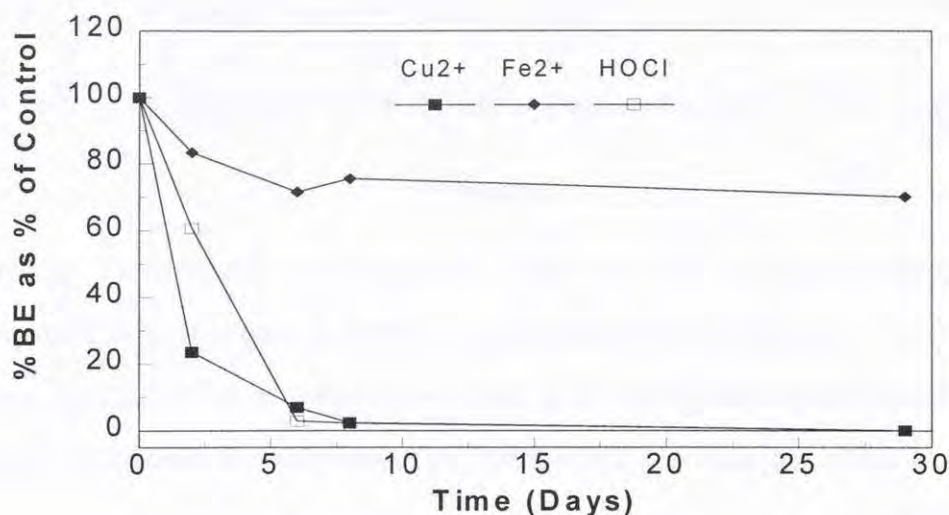
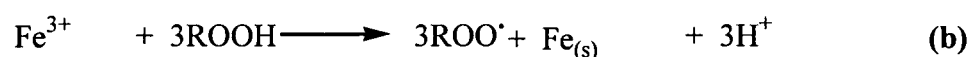
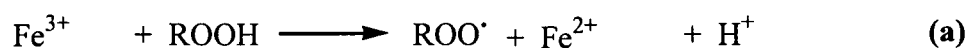


Figure 4: Elongation at break time profile for PP fibres degraded in HOCl, HOCl + Cu²⁺(7125ppm), HOCl + Fe²⁺(7125ppm).

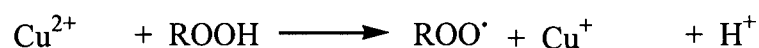
The iron(III) and copper(II) salts significantly reduced the induction period of degradation so that after 2 days the fibres had lost all tensile strength. The rate of degradation for solutions containing copper(II) ions was 40%/day, compared to 45%/day for the iron(III) ions.

Immersing the PP fibres in the iron(III)/HOCl solutions caused a yellow discolouration of the fibres and a slight precipitate in the solution. Fe(III) ions may accelerate hydroperoxide decomposition by undergoing reduction to Fe(II) as shown in Scheme 8(a). The standard electrode potential for the Fe(III)/Fe(II) oxidation reaction being 0.771V²⁹. As shown in Figure 4, Fe(II) ions present in solution were observed to stabilise the degradation. So, as the presence of Fe(III) ions accelerates the oxidation, most of the Fe(III) ions must be reduced to solid iron, forming the precipitate observed as shown in Scheme 8(b). This avoids the formation of the stabilising Fe(II) ions.



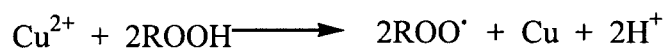
Scheme 8

According to Scheme 1 copper(II) ions should catalyse hydroperoxide decomposition as shown in Scheme 9, regenerating the Cu(II) ions. However, the Cu^+ ion does not exist in aqueous solution as it readily disproportionates. So, the copper(II) catalysed decomposition of hydroperoxides does not occur by Scheme 9.



Scheme 9

Copper(II) ions may catalyse hydroperoxide decomposition forming copper as shown in Scheme 10.

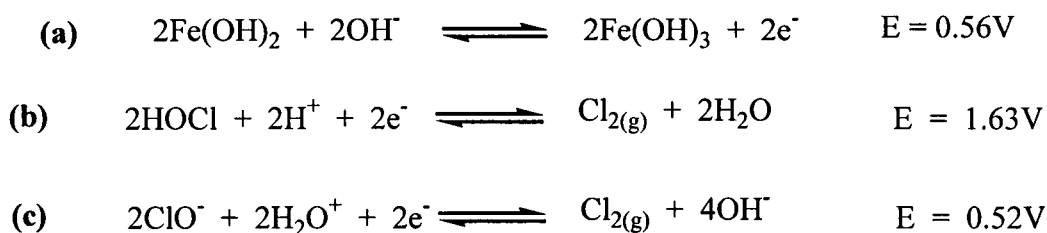


Scheme 10

Iron(III) ions catalyse POOH decomposition more effectively than copper(II) ions. Considering Scheme 8(b) and Scheme 10, one Fe(III) ion decomposes 50% more POOH groups than one copper(II) ion. Both mechanisms result in the formation of a solid product.

Both iron(II) and cobalt(II) ions have a stabilising effect on PP oxidation with HOCl as shown in Figure 3 and Figure 4. Only a slight loss of elongation at break is experienced by fibres in contact with either of these solutions over the same period: 3.1% per day for solutions containing Fe(II) and 2.5% per day for Co(II) containing solutions. This stabilising effect is due to the deactivation of the hypochlorous acid (HOCl) and the hypochlorite ion (OCl^-) by redox reaction.

Fe^{2+} in solution readily forms iron(II) hydroxide which subsequently reacts with HOCl or OCl^- forming inactive chlorine gas and iron(III) hydroxide as shown in Scheme 11. Solutions containing Fe(III) ions undergo preferential reduction and so are unable to deactivate the HOCl by undergoing oxidation as occurs with the $\text{Fe}(\text{OH})_2$ species as shown in Scheme 11(a).



Scheme 11

As discussed in Section 2.6 HOCl generates oxygen and chloride radicals while OCl^- generates chlorine radicals, all of which are the active species in PP oxidation using HOCl. Deactivation of the HOCl by iron(II) hydroxide forming chlorine gas removes these active species from solution, inhibiting oxidation.

Aqueous cobalt(II) ions exist as the octahedral species, $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$, which when dissolved in hypochlorous acid readily forms the blue tetrahedral complex $[\text{CoCl}_4]^{2-}$ as shown in Scheme 12.



Scheme 12

This removes the active chloride ions, critical to oxidation, from solution, thereby inhibiting the degradation. Cobalt(II) is a more effective inhibitor for PP oxidation than iron(II) as each Co(II) ion deactivates 4 chloride ions, while each Fe(II) ion deactivates only 1 HOCl or OCl^- species.

In summary, the presence of iron(III) and copper(II) ions in the HOCl solution accelerated the oxidation of PP fibres by significantly decreasing the induction

period. Iron(III) ions catalysed the decomposition of hydroperoxides to peroxy radicals by undergoing reduction to Fe. Copper(II) ions were reduced to Cu while accelerating the decomposition of hydroperoxides. Both iron(II) and cobalt(II) ions present in HOCl inhibited PP oxidation. Iron(II), in the form of iron(II) hydroxide, reduced the active HOCl and OCl⁻ species to chlorine gas preventing the formation of chloride radicals for oxidation. Cobalt(II), when dissolved in HOCl, formed a stable tetrahedral chlorine complex [CoCl₄]²⁻ by reacting with chloride ions present in HOCl, preventing their reaction with PP. So, it appears that the presence of transition metals in PP may either i) accelerate the oxidation by catalysing hydroperoxide decomposition; or ii) inhibit the oxidation by deactivating the HOCl solution.

5.4 Conclusions

The effect of processing on polypropylene was investigated by comparing the chemical structure of polypropylene fibres to that of polypropylene pellets and the unextruded form of polypropylene powder. The hydroperoxide, carbonyl and unsaturation content were determined using FT-IR spectroscopy. Crystallinity was determined using DSC measurements. It was found that polypropylene powder, pellets and fibres have significant differences in content due to oxidation during processing. Polypropylene powder contains a significant amount of hydroperoxides and unsaturated carbon-carbon bonds, residual products of visbreaking. The formation of these products appears to follow the proposed mechanism as shown in Scheme 4. Pelletisation results in a decrease in the unsaturation content and increase in hydroperoxide content due to oxidation of C=C groups as described in Scheme 5. Extrusion results in a significant increase in concentration of all oxidation products.

The resistance to oxidation by hypochlorous acid was compared for polypropylene pellets and powder. Degraded films were analysed by FT-IR and DSC. The presence of additional oxidised species in films from PP pellets

increased the initial rate of oxidation by decomposition of existing hydroperoxides and reaction with existing unsaturated groups. The overall rate of oxidation in both types of films depends on active site and oxidant concentration. The overall products of oxidation in films from PP pellets and PP powder are consistent and independent of initial PP composition.

The effect of the presence of transition metal ions Fe(III), Fe(II), Cu(II) and Co(II) on the degradation of polypropylene fibres by aqueous HOCl was investigated. Fibre degradation was determined by elongation at break. The presence of iron(III) and copper(II) ions in the HOCl solution accelerated the oxidation of PP fibres. Iron(III) ions catalysed the decomposition of hydroperoxides to peroxy radicals by undergoing reduction to Fe. Copper(II) ions were reduced to Cu while also accelerating the decomposition of hydroperoxides. Both iron(II) and cobalt(II) ions present in HOCl inhibited PP oxidation. Iron(II), in the form of iron(II) hydroxide, reduced the active HOCl and OCl⁻ species to chlorine gas preventing the formation of chloride radicals. Cobalt(II), when dissolved in HOCl, formed a stable tetrahedral chlorine complex [CoCl₄]²⁻ by reacting with chloride ions present in HOCl, preventing their reaction with PP.

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Chapter 6 The Effect of Stabilisers on the Oxidative Degradation of Polypropylene Membranes.

6.1 Introduction

The problem of stabilisation is significant for polypropylene fibres because of their high surface area to volume ratio. The term stabiliser, or antioxidant, is used to describe those compounds which inhibit the oxidative degradation of polymers at ambient and elevated. Since the purpose of stabilisers, or antioxidants, is to interfere with the oxidation process, their effect is measured by the extent to which oxidised products are formed in the stabilised sample. Stabilisers exist in the amorphous region of the polymer being excluded from the crystalline which has a much lower oxidation rate due to the impermeability of oxygen in the region.

Anti-oxidants may be classified generally as either primary or secondary, depending on the mechanism of stabilisation¹. Primary antioxidants are free radical scavengers which terminate chain reactions during oxidative degradation. Secondary antioxidants, also called synergists, destroy hydroperoxides which are the source of free radicals. Synergists convert hydroperoxides to stable non-radical products.

Anti-oxidant systems in technical use for polypropylene are composed of processing stabilisers, long term heat stabilisers, calcium or zinc stearate, and synergists². Typical processing stabilisers include hindered phenols, such as BHT, and phosphorous compounds, such as phosphites and phosphonites. These 2 stabilisers are always used together.

Much has been written in the literature about the stabilisation of polypropylene degraded thermally^{3,4}, mechanically⁵ and chemically⁵. An ideal stabiliser

should be sufficiently soluble in the polymer, compatible with the polymer matrix, resistant against volatilisation and extraction, and be able to migrate through the polymer⁶. Of these the solubility and the migration of the stabiliser are important in stabiliser effectiveness⁷.

6.2 Stabilisation of Thermally-Initiated Degradation.

Hydroperoxides are the main source of formation of further radicals during oxidation and as such are the most important factor. The most common stabilisers used in polypropylene fall under four categories⁸:

1. Chain-breaking donor anti-oxidants of which the phenol 'butylated hydroxytoluene' (BHT) is one (Figure 1). Sterically hindered phenolic antioxidants act by scavenging $\text{RO}\cdot$ and $\text{ROO}\cdot$ radicals via H-transfer from the OH group^{9,10,11}. Phenolic antioxidants act as primary antioxidants. The phenolic antioxidants are largely nonstaining and nondiscolouring, although upon oxidation they may form highly coloured quinoid structures.

The general structure for a phenolic anti-oxidant is shown in Figure 1-D. The activity of the anti-oxidant depends on the composition of X. Where X is electron releasing the anti-oxidant activity is increased. Where X is electron attracting the anti-oxidant activity is decreased. BHT inhibits the oxidation process by preferentially donating a proton to the reactive peroxy radicals present, preventing abstraction of hydrogen atoms from the polymer chain. A detailed outline of the reactions of BHT during stabilisation is given in Reference 11 page 7. BHT is commonly used as an anti-oxidant in the food industry. BHT is sanctioned by the FDA for use in foods, and considered to be nontoxic. This anti-oxidant however, is relatively volatile and so not used in polymers at high temperatures. BHT has been observed to be the most effective melt stabiliser for polypropylene¹¹. For use at elevated temperatures higher molecular weight phenolics were developed to eliminate problems with antioxidant volatility. These higher molecular weight phenolics include Irganox 1010 and Irganox 1076

as shown in Figure 1. Other stabilisers of this type include diphenylamine and the aminodiphenylamines.

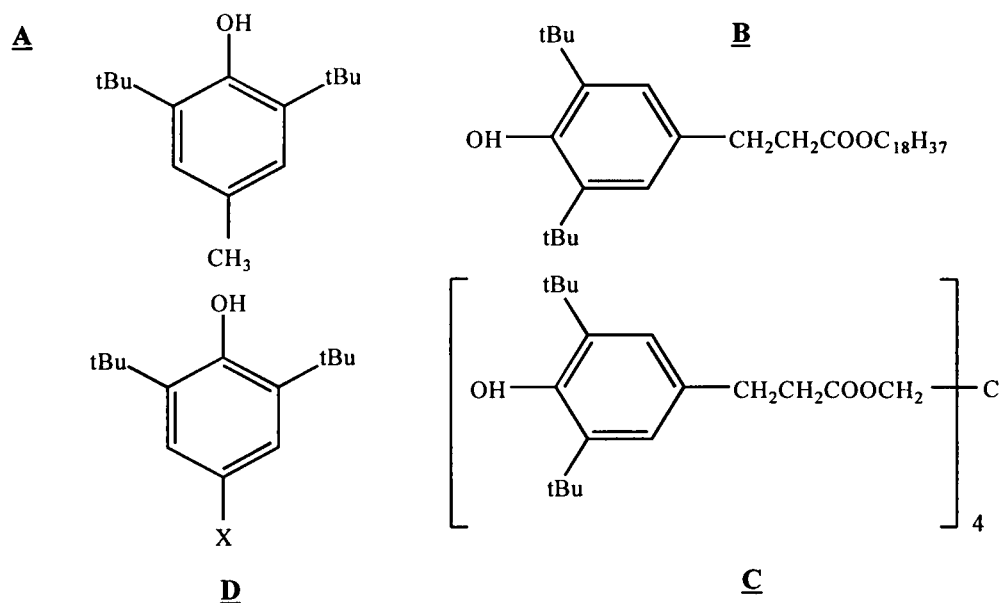


Figure 1 : Phenolic anti-oxidants A: BHT, B: Irganox 1010, C: Irganox 1076 D: General structure for phenolic anti-oxidants.

2. Peroxidolytic anti-oxidants. This class of compounds inhibit oxidation by deactivating hydroperoxides and reducing them to alcohols or catalytically decomposing them to inactive products¹⁰. As such they act as secondary antioxidants. High molecular weight phosphites such as tris-nonyl phenylphosphite and penta-erithritol distearile diphosphite are used for this purpose. Also sulfur compounds such as mercaptobenzthiazole (MBT) and dilaurylthiodipropionate (DLTP) catalyse the decomposition of hydroperoxides^{12,4}. Phosphites are commonly used with phenolic antioxidants as they inhibit the formation of quinoid products formed upon oxidation of phenolics¹.

3. Stearates and metal oxides which act as acid traps and remove catalyst residue from the polymer, hence slowing down the decomposition of hydroperoxides to shorter chain radicals.

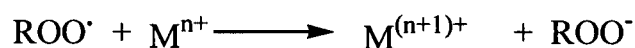
4. a) Metal ions which catalyse the deactivation of alkyl and peroxy radicals in the absence of excess oxygen. In 1971 Scott¹³ found that under conditions of low oxygen pressure copper functions as an anti-oxidant by a catalytic cyclical process in which it acts as a redox inhibitor oxidising alkyl radicals and reducing peroxy radicals alternately. This reaction occurs via a copper alkyl intermediate as shown in Scheme 1.



Scheme 1

This mechanism applies only when oxygen access to the site is limited, resulting in high rates of formation of $R^{\cdot}$ and $ROO^{\cdot}$. Also, the anti-oxidant must be capable of being reversibly oxidised and reduced.

b) Metal deactivators which act as chelating agents for active metal ions. The molecular decomposition of hydroperoxides into free radicals requires relatively high activation energies, and so only becomes effective at temperatures above 120°C². However, in the presence of small amount of certain metal ions, hydroperoxides decompose readily at room temperature by a redox reaction to radical products. The function of a metal deactivator is to form an inactive complex with the catalytically active metal species. Also, metal chelates may also catalyse the decomposition of hydroperoxides to non-radical products as shown in Scheme 2¹¹. (M indicates the metal chelate.) A chelating agent is used due to its polyfunctionality, meaning that it contains several ligand atoms such as N, O, S, P in combination with hydroxyl, carboxyl or carbamide groups².



Scheme 2

The stabilisation of oxidation of polypropylene occurs by several mechanisms as described above, and the activity of the stabilisers is dependent on temperature^{14,15}. During processing at high temperatures, often over 200°C, polypropylene is generally stabilised with a combination of high molecular mass phenolic anti-oxidants with phosphites or phosphonites¹⁶.

6.3 Stabilisation of Photo-Initiated Degradation.

Anti-oxidants that protect polymers against thermal oxidation rarely give protection against the effect of UV light. Much has been written in the literature about the stabilisation of photo-initiated degradation^{17,21,18,19,20}. The light resistance of polypropylene decreases with decreasing sample thickness, hence the UV stability of fibres critical. Photo-initiated degradation occurs because quantum energies associated with radiation in the UV parts of the spectrum are sufficient to break the chemical bonds present in polymers²¹. Photo-oxidation of polypropylene is initiated by the presence of chromophoric impurities such as carbonyl groups, transition metals, C-C unsaturation²² and charge transfer complexes formed between oxygen and the saturated polymer²³.

Stabilisers designed to protect polymers from UV degradation operate by a variety of mechanisms¹⁸:

1. UV absorption which involves the screening of incident UV radiation by chemical groups and the removal of the wavelengths detrimental to polypropylene as well as the quenching of photochemically excited states²⁴. UV absorbers absorb the detrimental radiation and dissipate it in a manner which does not lead to photosensitisation ie by dissipating as heat. Hydrobenzophenones are used for this purpose as are nickel complexes^{25,26}.
2. Hydroperoxide decomposition which causes the decomposition of -OOH groups resulting in no chain scission or free radical production. Metal complexes of sulfur-containing compounds or organic phosphites are used for this purpose^{25,2}.

3. Free radical scavengers to stop chain scission and regeneration of active radicals. These radical scavengers behave the same way as those used in thermal stabilisation.
4. Complexation of transition metal impurities which may otherwise catalyse the degradation²⁷.
5. Quenchers which take over the energy absorbed from UV radiation by chromophores and dissipate it as either heat or as fluorescent or phosphorescent radiation². The mode of action of these stabilisers is to deactivate the photoexcited chromophores before they undergo reactions that result in polymer degradation.
6. UV Screeners. These stabilisers function by reflecting the damaging incident UV radiation, limiting its contact with the bulk polymer. This is achieved either by coating the surface of the polymer or incorporating into the bulk polymer materials with high UV reflectance. Inorganic pigments are commonly used as UV screeners such as titanium dioxide, zinc oxide, magnesium oxide, calcium carbonate, chromium oxide and the iron oxides²⁸.

The effectiveness of an anti-oxidant in deactivating alkoxy and peroxy radicals depends on the mobility of the anti-oxidant through the polymer compared to the radicals²⁹. Hindered Amine Light Stabilisers (HALS) have been shown in the literature to be effective stabilisers for polypropylene^{16,30,20}. This is due to their large molecular size making them less volatile, more soluble in polypropylene and diffusing more slowly through the polymer than traditional stabilisers³¹. The competing reactions in this case are $IH + RO_2\cdot$ (or $RO\cdot$) which leads to retardation of polymer oxidation and $IH + O_2$ which involves unwanted side reactions between the anti-oxidant and oxygen. (IH signifies the anti-oxidant).

It has been observed in the literature that synergistic effects are observed for polymers containing both UV and thermal stabilisers. Chmela *et al*³² combined an organic phosphite with a Hindered Amine Light Stabiliser (HALS).

6.4 Objectives

The aim of this work is firstly to investigate the effect of the addition of a hindered phenol stabiliser prior to extrusion (processing) on the degradation properties of polypropylene fibres. Secondly, to investigate the effect of the common hindered phenol stabiliser butylated hydroxy toluene (BHT), added to the PP after extrusion, on the oxidative stability of polypropylene fibres.

6.5 Experimental

6.5.1 Materials

Polypropylene hollow fibre membranes were extruded by Memtec Ltd. from pellets supplied by Hoechst. The pellets contain a standard stabiliser package consisting of 2 chain breaking donor anti-oxidants, as well as a high molecular weight phosphite at approximately 0.9pph, a stearate at <0.1wt% and a metal oxide at approximately 0.05pph. The pellets prior to extrusion contain <5ppm heavy metals. Generally, prior to extrusion a stabiliser, Ethanox 330, is added to the polymer to prevent degradation during processing. This stabiliser is a standard hindered phenol anti-oxidant as is shown in Figure 2. For comparison purposes, the fibres used in this work are extruded either with the extra stabiliser added, A, or without, B, the extra stabiliser added for the extrusion process. Both types of fibre (A and B), however, will contain small amounts of residual stabilisers from the supplier's polymerisation and storage processes. The membranes produced have an inner diameter 250-290µm and outer diameter 650µm. The membranes are 81-94% isotactic, 30% crystalline, have a nominal pore size of 0.2µm, strand thickness of 0.02µm, density of 0.088g/cm³ and a specific mass of 0.046 m²/g. Degradation experiments were carried out using

chlorine in the form of aqueous sodium hypochlorite, NaOCl (Ajax Chemicals), 125g/l dissolved in reverse osmosis (RO) water.

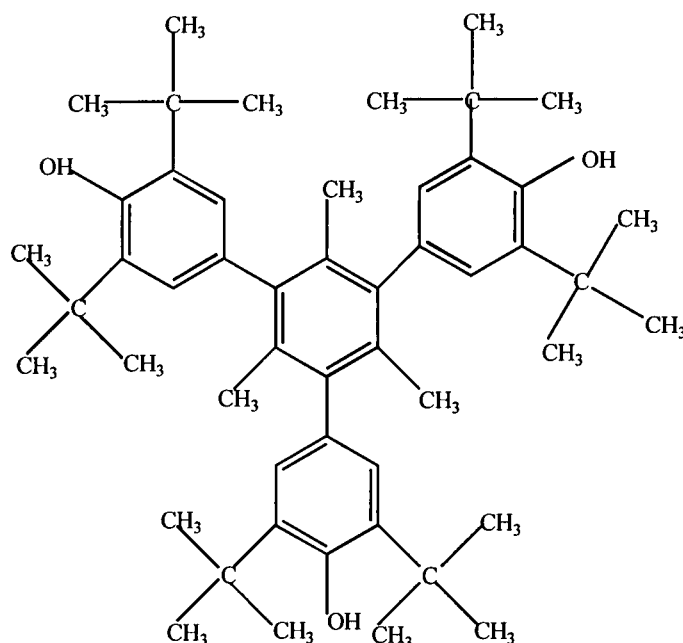


Figure 2 : Ethnox 330 – Hindered Phenol Antioxidant

For the butylated hydroxy toluene (BHT) experiments, BHT was sourced from Sigma Chemical. HPLC grade hexane (BDH chemicals) was used as a solvent for the stabiliser.

6.5.2 Experimental Method of Degradation

Polypropylene fibres were degraded in a sealed reactor with a controlled HOCl concentration as described by the method in Section 4.4.2.

6.5.2.1 Effect of Stabilisers Added Prior to Extrusion.

Fibres used in this work were of type A and type B. Fibres were first wet out with methanol and then degraded using aqueous sodium hypochlorite, 10ppm, at several reaction temperatures for 216 hours. The two types of fibres were degraded in separate reaction vessels but under identical conditions for comparison purposes. Fibres were sampled periodically. Fibre degradation was

classified using break extension measured using an Instron tensometer, and oxygen content as determined from FT-IR spectra. Both of these techniques are described in Section 4.4.3.1 and 4.4.3.2.

6.5.2.2 BHT Stabilisation Studies.

Fibres used in this work were of type A and type B. BHT was added to the fibres by first dissolving the required mass of BHT in a known volume of hexane resulting in BHT concentrations of either 534, 2000 or 50600ppm. The fibres were then immersed in this solution and left to soak for 3 hours. The fibres were then rinsed in RO water and wet out with methanol. Degradation was carried out using aqueous sodium hypochlorite at several concentrations at 20°C. Fibres were sampled periodically. Fibre degradation was classified using break extension as measured using an Instron tensometer, and oxygen content as determined from FT-IR spectra. Both of these techniques are described in Section 4.4.3.1 and 4.4.3.2.

6.6 Results and Discussion

6.6.1 The Effect of Hindered Phenol Stabilisers Added Prior to Extrusion.

In theory, the addition of the stabiliser prior to extrusion should act to increase the induction period of the degradation by deactivating any peroxy or alkoxy radicals present in the polymer. Induction time here is defined as the time after the start of degradation when visible changes occur in the polymer. In the case of fibre membranes a loss of tensile strength occurs when sufficient points of weakness are formed in the fibre structure. This means that when a decrease in tensile strength is observed, sufficient polymer chains have been broken to weaken the polymer web structure at one point. Understandably then, a proportionately small amount of chain scission must occur for a large observed loss of tensile strength.

The loss of break extension of both stabilised and unstabilised fibres, Figure 3, shows a drop in induction period from 2 days for the stabilised fibres to 1 day for the unstabilised fibres. It appears that in terms of PP fibre degradation the addition of a hindered phenol stabiliser prior to extrusion has increased the induction period in terms of elongation at break by preventing chain scission by deactivating radicals formed in the polymer.

As discussed in Chapter 4, increasing the reaction temperature increases the rate of oxidation of polypropylene fibres. The degradation of unstabilised fibres at 40°C proceeds with an induction period of less than 1 day. Data shown in Figure 4 indicates that the induction time for stabilised fibres is increased to approximately 1 day. At elevated temperatures the rate of formation of radicals increases so that the stabilisers present are able to deactivate only a percentage of the radicals formed. Also, the stabiliser is more quickly depleted due to the large volume of stabilisers formed over the same period. This means that while the stabiliser is present, the concentration of active radicals in the polymer is decreased and as a result the rate of oxidation decreases until the stabiliser concentration has been exhausted.

Carbonyl content data shows a decrease in the induction period from 2.5 days for stabilised PP fibres to 2 days for unstabilised fibres. For unstabilised samples during this 2 day induction period no carbonyl species are formed, however a significant loss of tensile strength due to chain scission is observed. This indicates that degradation involving the formation of alkyl, alkoxy and peroxy radicals and resulting in chain scission is occurring. A small loss of break extension is observed for stabilised fibres during the 2.5 day induction period due to the action of the stabiliser in deactivating the alkoxy, peroxy and alkyl radicals formed. The carbonyl content of unstabilised fibres increases slightly between 0

and 1 day due to the reaction of radicals, generated during extrusion, with the oxygen producing carbonyl products.

The addition of a hindered phenol stabiliser to PP prior to extrusion increases the observed induction time for PP fibre oxidation from 1 to 2 days in terms of break extension and from 2 to 2.5 days in terms of carbonyl content. A small loss of mechanical strength observed for stabilised fibres during the induction period compared to unstabilised fibres is due to alkyl, peroxy and alkoxy radical deactivation by the stabiliser, preventing chain scission.

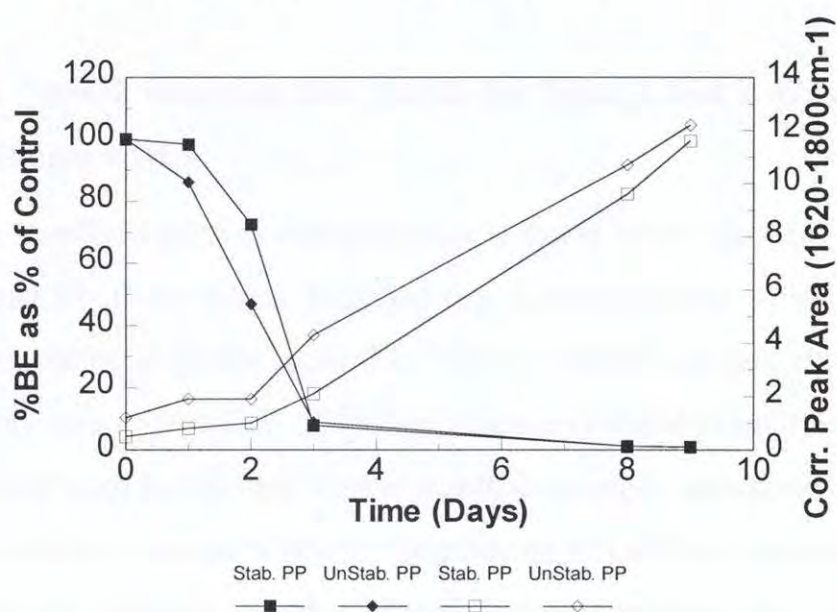


Figure 3 : Break extension and carbonyl content time profile for Type A and B fibres oxidising by HOCl (10ppm) at 20°C.

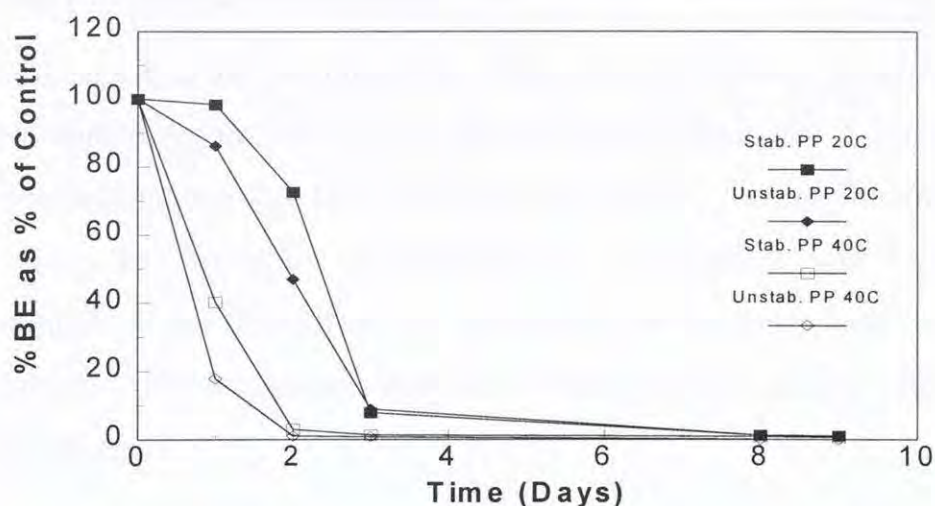


Figure 4 : Break extension time profile for Type A and B fibres at 20 and 40°C in 10ppm HOCl.

PP fibres stabilised prior to extrusion have a lower initial carbonyl content than unstabilised PP fibres which indicates that some oxidation of the unstabilised fibres has occurred during extrusion. After 3 days it appears that the overall increase in carbonyl content of the stabilised and unstabilised fibres follows a similar trend with the content for the stabilised sample consistently lower. This offset in carbonyl content is due to the presence of carbonyl compounds formed as a result of oxidation which occurred during extrusion. Once the stabiliser supply has been exhausted, the carbonyl content of the stabilised and unstabilised fibres increases similarly. It is expected that the carbonyl content for the stabilised and unstabilised samples would reach an equivalent level when oxidation of all active sites in the PP fibre is complete.

The addition of a hindered phenol stabiliser to PP prior to fibre extrusion prevents oxidation during processing. This is observed by an initial inhibition of formation of carbonyl species, and loss of break extension. After the stabiliser supply has been exhausted, degradation of the stabilised fibres occurs as in the unstabilised fibres.

6.6.2 BHT Stabilisation Studies

BHT was added to the polypropylene fibres prior to exposure to hypochlorous acid by immersing the fibres in a hexane/BHT solution for 3 hours. Three BHT/hexane solutions with BHT concentrations of 534, 2000 or 50600ppm were used. The effect of BHT concentration in this solution, and hence BHT concentration in the fibres, on the stabilisation of polypropylene fibres was investigated. Also, temperature and HOCl effects on the stabiliser effectiveness were investigated.

Butylated hydroxy toluene (2,6-di-tert-butyl phenol) is a chain breaking donor stabiliser which donates protons to active alkoxy and peroxy radicals deactivating them and inhibiting the oxidation. This process is not fully catalytic meaning that BHT is partially consumed during the inhibition process as shown in Figure 5. After deactivating one radical, the aryloxy radical is then able to either deactivate another radical or reform BHT or the quinoid compound **B**. The yellow colour observed to occur in the fibre samples containing high concentrations of BHT is due to the formation of the stilbene quinone (**F**) and the dibenzyl quinol (**G**).

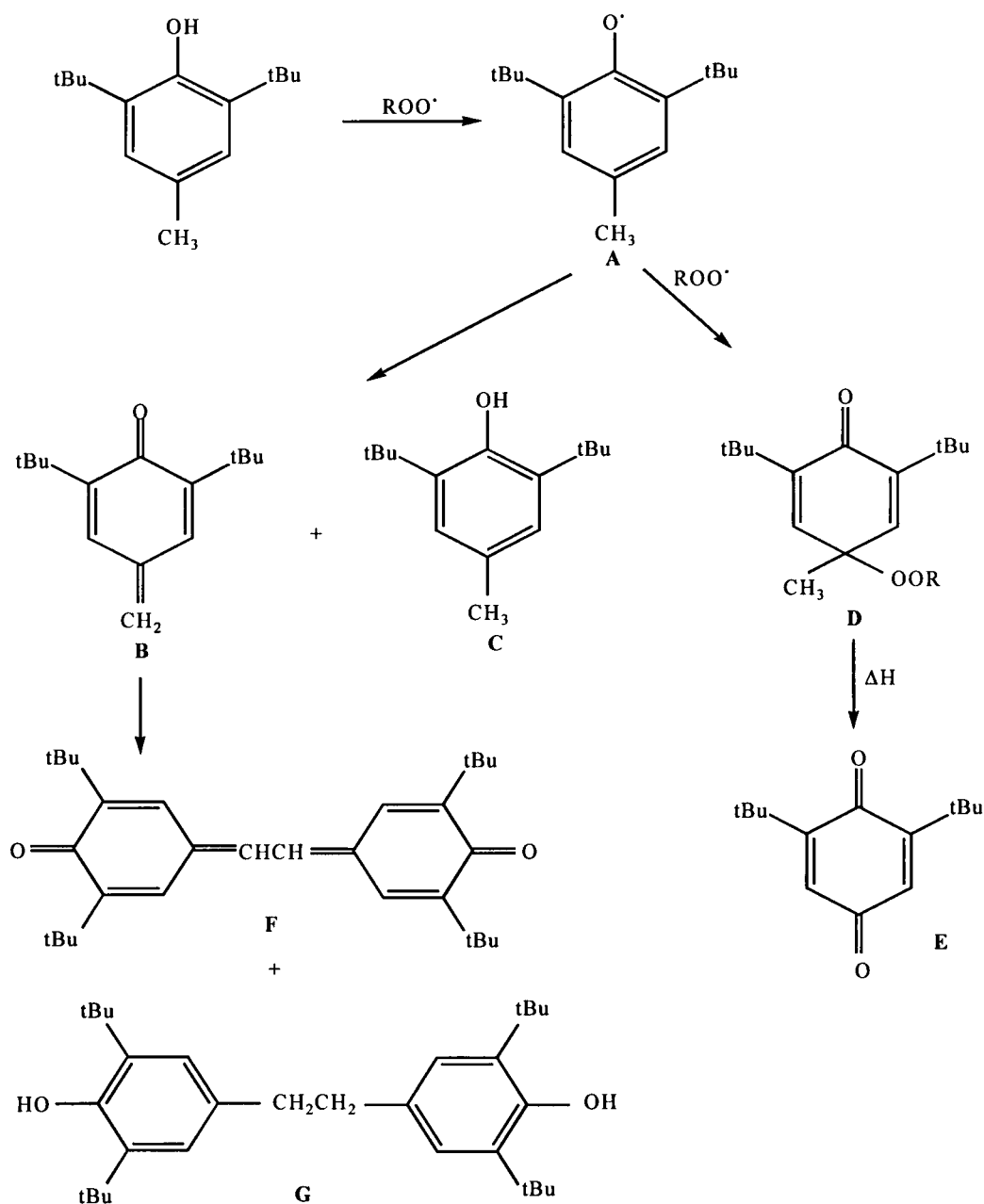


Figure 5 : Oxidative transformations of BHT ^{33,8}.

During degradation with HOCl , a yellow colour was observed to form on the PP fibres due to the formation of the stilbene quinone (**F**) and the dibenzyl quinol (**G**).

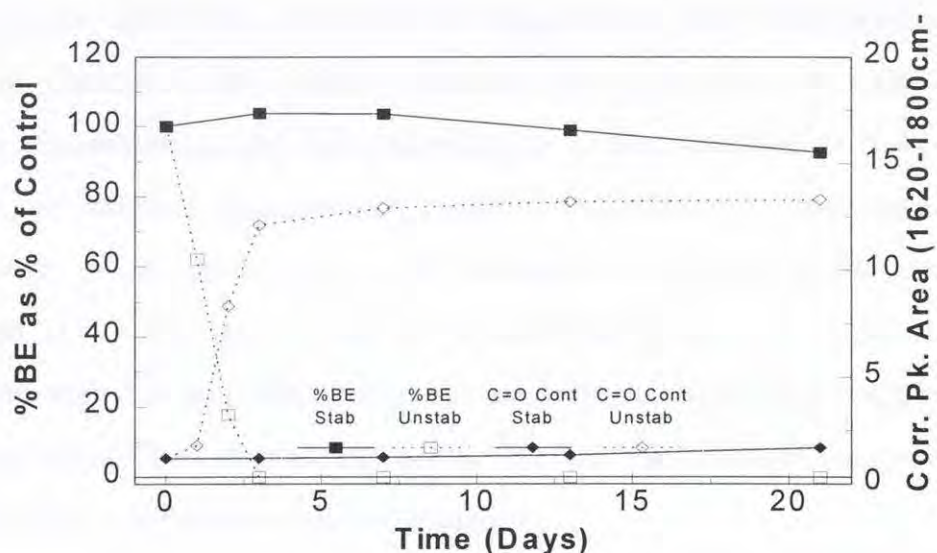


Figure 6 : Tensile strength and carbonyl content time profile for polypropylene fibres stabilised with excess BHT and degraded using 20ppm HOCl at 20°C.

Polypropylene fibres soaked in a saturated hexane/BHT solution for 3 hours and immersed in 20ppm HOCl for 21 days showed excellent degradation resistance, Figure 6. This data compared favourably to the results obtained from unstabilised fibres degraded under the same conditions. After 3 days in 20ppm at 20°C, unstabilised fibres showed a complete loss of tensile strength and a significant increase in carbonyl content. Clearly, the excess of BHT stabiliser was in sufficient concentration to deactivate all radicals formed during the 21 day period and significantly increase the lifetime of the fibres under these conditions.

Degradation was carried out on fibres with varied levels of BHT stabiliser added to determine the optimum concentration for oxidation inhibition. Fibres were degraded in 20ppm HOCl at 20°C. The BHT concentration is expressed as ppm in the hexane solution in which the fibres were soaked prior to oxidation. Degradation time profiles for fibres stabilised with 534, 2000 and 50600ppm BHT are shown in Figure 7. Fibre stabilisation with 50600ppm increased the induction period to seven times that of unstabilised fibres, while the low stabiliser

concentration gave little protection to degradation. The effectiveness of the stabiliser depends on the number of radicals being generated by oxidation, the oxidant concentration and the concentration of the stabiliser in the polymer. Insufficient stabiliser concentration results in deactivation of radicals at only a percentage of the active sites, and consequently polymer oxidation occurs although at a lower rate than in the unstabilised fibres. This occurs in fibres stabilised with 534 and 2000ppm where the induction period has been increased from the unstabilised degradation value, however the stabiliser concentration is insufficient to completely inhibit degradation.

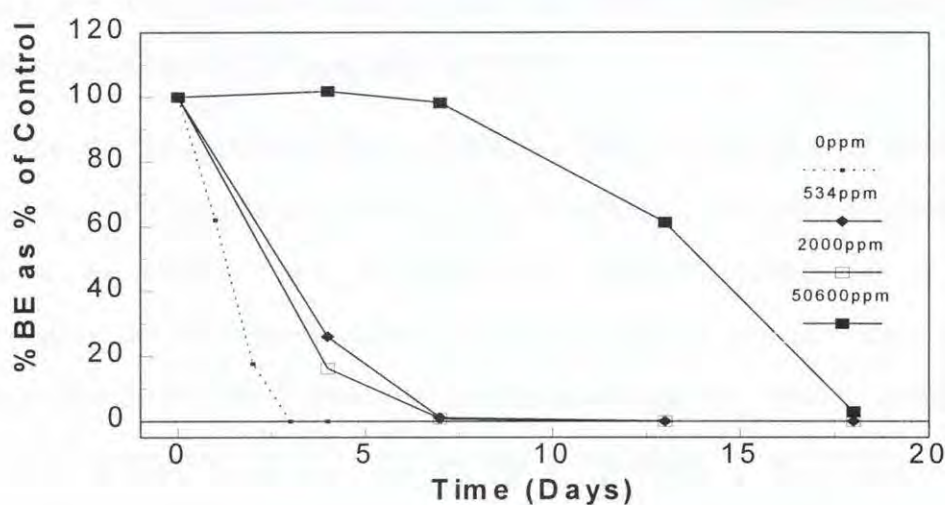


Figure 7 : Degradation time profile for PP fibres stabilised with BHT at varied concentrations degrading in 20ppm HOCl at 20°C.

As mentioned earlier the effectiveness of stabiliser depends on the oxidant concentration. As oxidant concentration increases, stabiliser effectiveness decreases due to the increase in radicals to be deactivated in the polymer. As shown in Figure 8 for fibres stabilised with BHT at 52000ppm, doubling the oxidant concentration reduces the induction period by approximately half. As discussed in Section 2.6, each HOCl molecule generates one chloride radical, hence halving the HOCl concentration halves the radical concentration diffusing through the polymer.

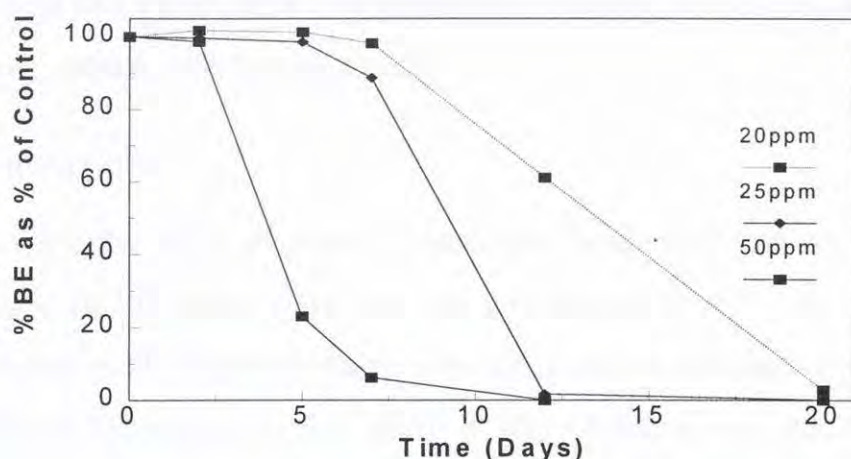


Figure 8 : Degradation time profile for BHT stabilised fibres, [BHT]= 52,000ppm, using 20, 25 and 50ppm HOCl.

In summary, the hindered phenol stabiliser BHT is effective in inhibiting the oxidation of polypropylene under certain conditions. The concentration of BHT required to stabilise the polypropylene fibres depends on degradation temperature, HOCl concentration and the presence of any additional stabilisers already added. The BHT stabiliser acts to scavenge any radicals formed in the fibre, thus increasing the induction period of oxidation by preventing reaction of these radicals with oxygen. A summary of the induction period data obtained for BHT stabilisation is given in Table 1.

[BHT] (ppm)	[HOCl] (ppm)	Induction Period (Days)
0	20	1
534	20	1-2
2000	20	4
50600	20	8
52000	20	8
52000	25	7
52000	50	2

Table 1 : Effect of BHT stabilisation on oxidation induction period.

It is evident that a high BHT concentration is required to significantly extend the induction period for PP fibre oxidation.

6.7 Conclusions

To determine the effect of adding a hindered phenol stabiliser on the oxidative degradation of PP fibres, stabilised and unstabilised fibres were oxidised with hypochlorous acid. Degraded fibres were analysed for carbonyl content and loss of mechanical strength. In this study it was observed that the addition of a hindered phenol stabiliser to PP prior to extrusion increased the observed induction time for PP fibre oxidation by HOCl from 1 to 2 days in terms of tensile strength and from 2 to 2.5 days in terms of carbonyl content. This initial inhibition of formation of carbonyl species, and loss of mechanical strength continued until the stabiliser supply was exhausted. At this point degradation of the stabilised fibres began as in the unstabilised fibres.

The effectiveness of BHT as a stabiliser for PP fibre oxidation was evaluated. The hindered phenol stabiliser BHT is effective in inhibiting the oxidation of polypropylene under certain conditions. At sufficiently high concentrations, BHT inhibits PP oxidation, increasing the induction period in terms of mechanical strength and carbonyl content. Using a BHT concentration of ~50,000ppm, the induction period was increased by seven times compared to oxidation of unstabilised fibres under the same conditions. So, the activity of the BHT stabiliser depends on its concentration in the fibre and the oxidant (HOCl) concentration.

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- ³²Chmela, S., Habicher, D., Hahner, U., Hrdlovic, P., *Polym. Deg. and Stab.*, **39** (1993) 367-371.
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Chapter 7 Degradation of Hollow Fibre Membranes from Metallocene Polypropylene and Ziegler-Natta Polypropylene.

7.1 Introduction

A new generation of catalysts for polyolefin polymerisation, metallocenes, remove the necessity for polymer visbreaking by their ability to engineer polymers to the desired molecular weight distribution. Being a very new technology, metallocene catalysed polypropylene is not widely commercially available. To date only Exxon US are supplying commercial customers, however several other companies are in the development stages¹. Metallocene polypropylene used in this experimental work was obtained from Exxon - US.

Metallocene catalysts are able to change each property of the polymer on the molecular level independent of each other. These properties are: 1) Degree of isotacticity. 2) Molecular weight and 3) Width and shape of molecular weight distribution. This technology is just beginning to become commercially available for polypropylene and is already so for polyethylene. For this work, hollow fibre membranes were extruded from metallocene polypropylene. The resistance to degradation of the fibres was evaluated and compared to fibres extruded from Ziegler-Natta catalysed polypropylene. As the metallocene polymerisation of PP is relatively new, no work has been published in the literature regarding its stability to degradation or its extrusion into fibres.

7.2 Metallocene Catalyst Development.

The first metallocene molecule 'ferrocene' was synthesised by Wilkinson and Fischer in 1952 (Figure 1A). The first metallocene to make isotactic polypropylene was published in 1985 by Kaminsky *et al*² and is shown in Figure 1B. This system showed high activity, but was not able to produce i-PP of high

molecular weight and high melting point eg 125⁰C for the metallocene PP compared to 160-165⁰C for conventional (Ziegler-Natta) PP^{3,12}.

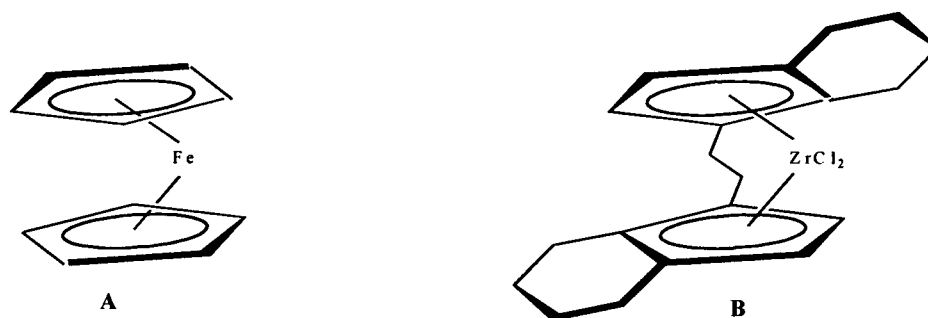


Figure 1 : Structure of the first metallocenes.

In recent years these performance deficits have been overcome by improved metallocene structures. Two of those are shown in Figure 2. The new metallocenes have common features in being fully aromatic bridged chiral systems with alkyl groups in neighbouring positions to the bridge. The one-membered silicon bridge is preferable to the two-membered ethylene bridge (Figure 1) as it adds rigidity to the molecule and induces higher isotacticity and molecular weight to the polymer. These metallocenes do not produce any atactic PP, but according to their substitution pattern produce a certain amount of irregularities in the chain which defines melting point and other polymer properties. Compared to Kaminsky's first molecule (Figure 1) the polymer molecular weight is more than 10 times higher and the melting point is more than 20⁰C higher. The new metallocene catalyst activity is 40 times more active than the conventional catalysts³. Performance data for the 3 catalysts in Figure 2 is given in Table 1⁴.

Species	Activity [kg PP/mmol Zr]	M _w [10 ³ g/mol]	M.P. (⁰ C)	% Isotactic
A	99	195	145	88.5
B	250	240	150	88.6
C	880	920	161	99.1

Table 1 :Polymerisation performances of advanced metallocene catalysts.

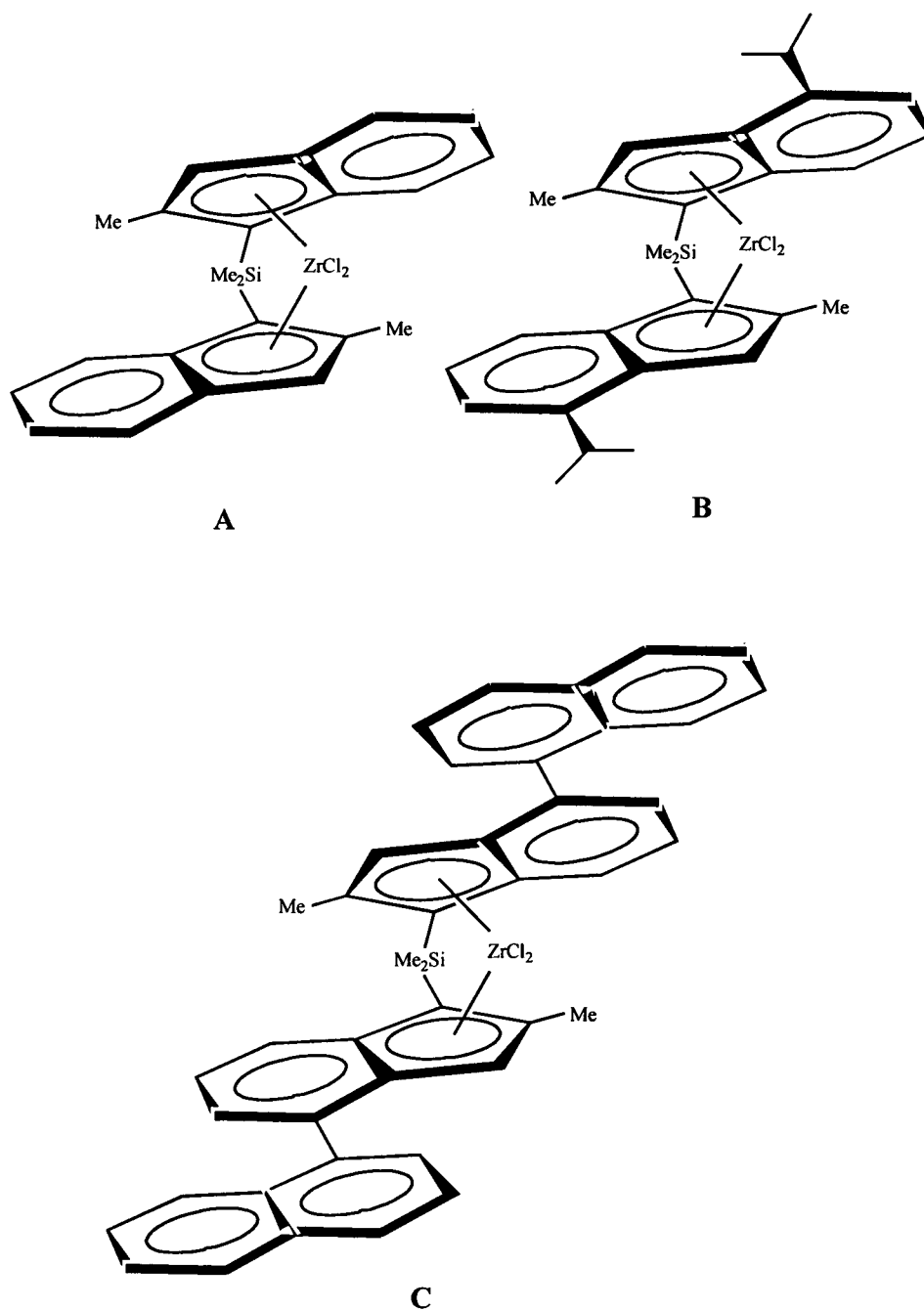


Figure 2 : Structure of three advanced metallocenes for isotactic PP polymerisation.

7.3 Metallocene Catalyst Polymerisation.

Like traditional Ziegler-Natta catalysts, metallocenes contain a metal atom, usually titanium or zirconium, which is linked to two rings of five carbon atoms

and to two other groups⁵. The rings play a key role by partly enclosing the metal atom. Electrons associated with the rings influence the metal, modifying its propensity to attack carbon-carbon double bonds.

For PP polymerisation a methylaluminoxane (MAO) cocatalyst was found to be most effective for the activation of the dichlorometallocene (as shown in Figure 1 and Figure 2). The metallocene/MAO system catalyses polymerisation upto 100 times faster than conventional catalysts⁶. The metallocene/MAO catalyst system is supported, with a low Zr:MAO ratio. These supported catalysts are free-flowing powders. TEAL is used as a scavenger for monomer impurities. As with the conventional Ziegler-Natta catalysts the molecular weight of the polypropylene is very high. Instead of molecular weight control by peroxidic degradation, hydrogen is used in metallocene PP polymerisation as a molecular weight regulator³. The mechanism of metallocene catalysed polymerisation for polyolefins has been described extensively in the literature^{7,8,9,10,11}, however is beyond the scope of this work.

7.4 Properties of Metallocene Polypropylene.

The typical molecular weight distribution of a metallocene polypropylene is very narrow, with a polydispersity index = 2.5¹². This is much lower than the conventional grades which are made by peroxidic degradation. Metallocene catalysed polypropylene also has a higher modulus and hardness than conventional PP.

Molecular weight of metallocene polymers is regulated using hydrogen, so metallocene PP has a much reduced amount of unsaturated C-C bonds and oxidised species. Also, a lower concentration of catalyst residue is expected compared to conventional Ziegler-Natta catalyst systems.

7.4 Experimental

7.4.1 Materials

Metallocene polypropylene (Exxpol Achieve 3844) was supplied in pellet form by Exxon US with a MFI of 22, melting temperature of 157.2°C and crystallinity of 31.4%. Conventional Ziegler-Natta polypropylene was supplied by Hoechst Germany with a MFI of 4, melting temperature of 155.6°C and crystallinity of 27.8%. Degradation was carried out using sodium hypochlorite supplied by Ajax Chemicals.

7.4.2 Fibre Extrusion

Fibres were extruded using a small scale twin screw extruder at 190°C. The polymer was not stabilised during extrusion. Fibres were extruded from both metallocene and conventional polypropylene to compare fibre resistance to degradation. The resulting fibres had an elongation at break of 99.5% for the metallocene fibres and 197% for the Ziegler-Natta fibres. The fibre structure is described in Section 4.3.1.

7.4.3 Degradation Procedure

Fibre degradations were carried out in 500mL sealed reactors at 20 and 50°C. Aqueous sodium hypochlorite, diluted to the required HOCl concentration, was regassed with high purity argon prior to degradation. Fibres were wet out with methanol, rinsed in RO water and then immersed in the HOCl solution. After sampling fibres from the reactors, the HOCl solutions were regassed with high purity argon. The extent of degradation of the fibres was determined using FT-IR and tensile strength measurements. Both of these techniques have been outlined in Section 4.3.3.

7.5 Results and Discussion

7.5.1 Ziegler-Natta PP vs Metallocene PP - A Chemical Comparison.

FT-IR and DSC studies were carried out on the undegraded mPP and Z-N PP. The resulting data is shown in Table 2. The polymerisation of mPP requires no peroxidic degradation for molecular weight control as discussed in Section 7.2. As a result metallocene polypropylene contains one third the unsaturated carbon-carbon bonds and hydroperoxides of Z-N PP. Both polymers, however contain similar levels of carbonyl compounds.

Property	Metallocene PP	Ziegler-Natta PP
Melting Temperature (°C)	157.2	155.6
Crystallinity (%)	31.4	27.8
MFI	22	4
Carbonyl Content Corrected Peak Area (1620-1800cm ⁻¹)	2.92	2.90
C=C Content Corrected Peak Area (3100-3220cm ⁻¹)	1.53	4.60
Hydroperoxide Content Corrected Peak Area (3320-3460cm ⁻¹)	0.59	1.90

Table 2 : Properties of mPP and Z-N PP.

7.5.2 The Induction Period

The existence of an induction period for the degradation of polypropylene fibres was proved in Chapter 4. The length of this induction period is representative of the polymer resistance to oxidative degradation and will be used in this work to compare the degradation properties of Ziegler-Natta (Z-N) polypropylene and metallocene polypropylene (mPP) fibres. The induction period was determined using carbonyl, hydroperoxide and unsaturation content data from FT-IR

measurements and break extension from tensile measurements. The effect of temperature and HOCl concentration on induction period will also be investigated.

In 0ppm HOCl at ambient temperatures (20°C), mPP and Z-N PP fibres have an induction period greater than 20 days. The increase in %BE of the mPP fibres shows the presence of a protective effect occurring. This is commonly observed at the beginning of the induction period of PP fibres prior to degradation. At elevated temperatures (50°C), both mPP and Z-N PP fibres undergo degradation after an induction period of 8 days, Figure 3. The elevated temperature significantly reduces the induction period by inducing thermal degradation of the fibres. It appears that the Z-N PP fibres are more susceptible to thermal degradation than the mPP.

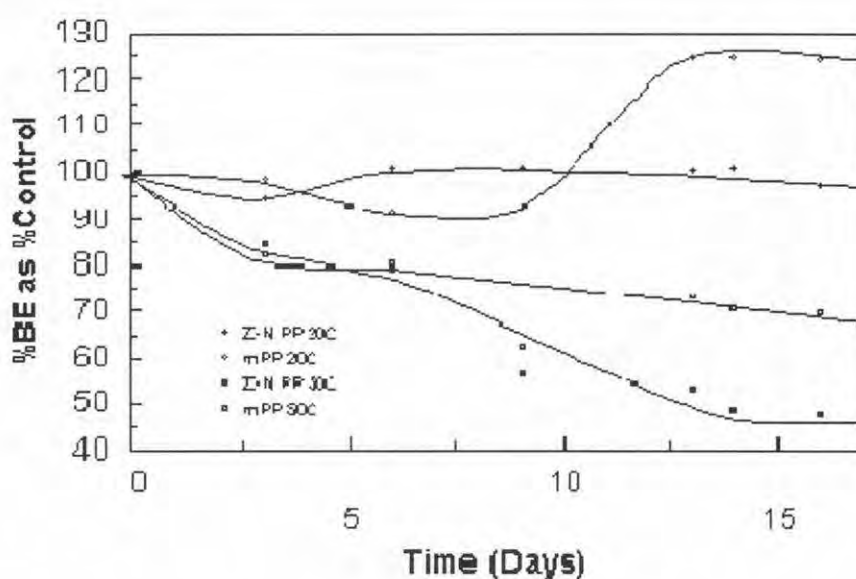


Figure 3 : %BE time profile for Z-N PP and mPP in 0ppm HOCl.

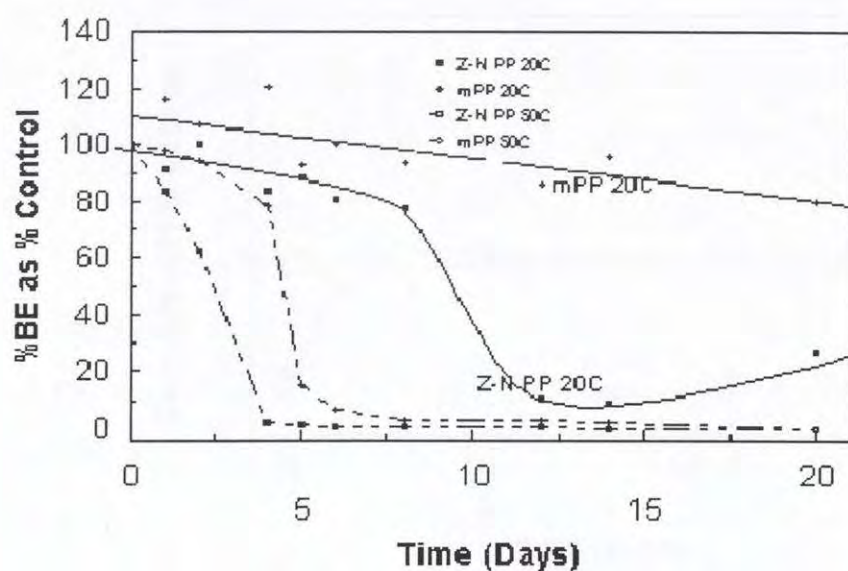


Figure 4 : %BE time profile for Z-N PP and mPP in 10ppm HOCl.

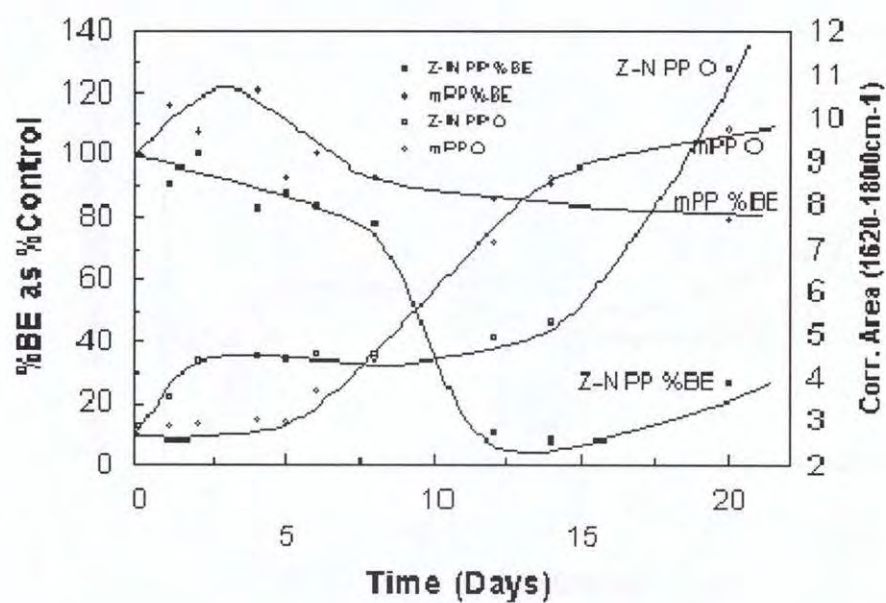


Figure 5 : Carbonyl content time profile for Z-N PP and mPP in 10ppm HOCl at 20°C.

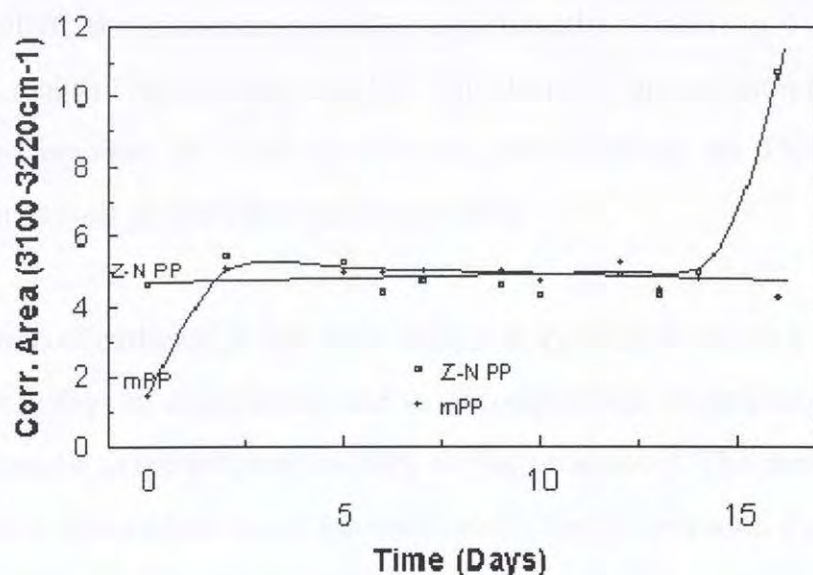


Figure 6 : Carbon-Carbon unsaturation content time profile for Z-N PP and mPP in 10ppm HOCl at 20°C.

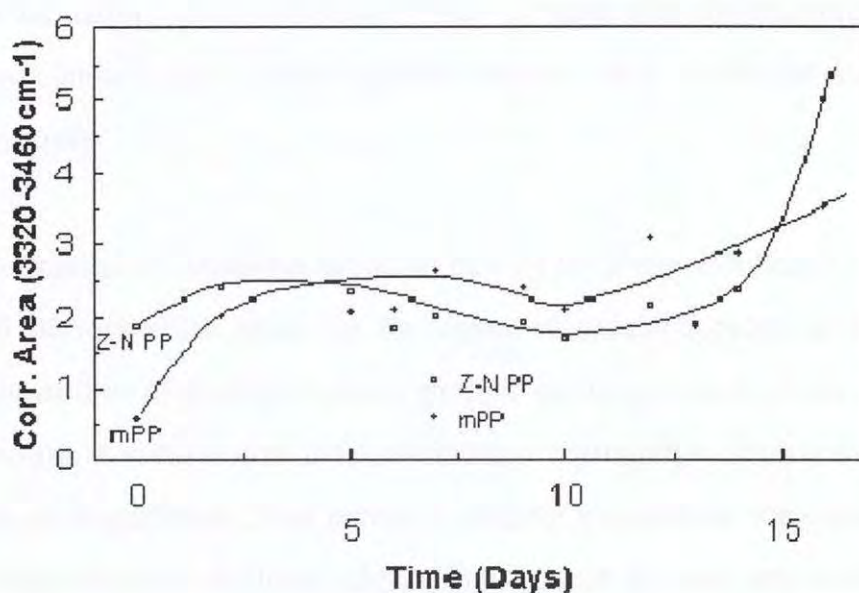


Figure 7 : Hydroperoxide content time profile for Z-N PP and mPP in 10ppm HOCl at 20°C.

In 10ppm HOCl the mPP fibres are more stable than fibres from Z-N PP as shown in Figure 4. In terms of mechanical strength, at 20°C the mPP fibres exhibit an induction period of 14 days as compared to 8 days for the Z-N PP

fibres. At 50°C the induction period is significantly reduced to 4 days for the mPP fibres and to 1 day for the Z-N PP. This decrease in induction period is due to increased amounts of chain scission as part of either the HOCl chemical degradation as well as some thermal degradation.

The formation of carbonyl compounds occurs, in Z-N PP fibres, to a small degree for the first 3 days of degradation due to decomposition of peroxides (shown in Figure 7) formed in the polymer initially during processing. The concentration of unsaturated carbon-carbon bonds increases in the first 3 days also, Figure 6. After this initial 3 day period, the rate of formation of carbonyl compounds decreases significantly as the formation of carbonyl groups depends on the concentration of hydroperoxides present in the polymer, Figure 5. The rate of formation of carbon-carbon double bonds also decreases due to a drop in the rate of chain scission and hence oxidation of the polymer. After 15 days the concentration of carbonyl groups, unsaturated carbon-carbon bonds and hydroperoxides increases significantly.

The formation of oxidation products in Z-N PP fibres exhibits a 3 day induction period during which time the formation of oxidised products is only due to decomposition of hydroperoxides present in the polymer as an impurity from processing. A similar slow decrease in tensile strength is observed during the first 8 days of degradation. This period is slightly longer than for oxidation products as a large amount of chain scission must occur for any noticeable decrease in polymer tensile strength. This 'induction period' is followed by a 12 day slow increase in oxidation product concentration due to a building up of hydroperoxides and their subsequent decomposition. Once the hydroperoxide concentration is sufficiently high the rate of chain scission and formation of carbonyl compounds increases significantly, as seen by the sudden increase after

15 days in Figure 5 and Figure 6. At this time the break extension is too low for any meaningful data to be obtained.

The formation of carbonyl groups in the mPP fibres shows a 5 day induction period, during which no oxidised species are formed, Figure 5. After this period the oxygen content steadily increases during degradation. However, both the hydroperoxide (Figure 7) and unsaturated carbon-carbon bond (Figure 6) concentration increase during the first 2 days followed by a slow increase hydroperoxide content, and a slow decrease in unsaturation content over the degradation period. This suggests that the hydroperoxides, when formed, rapidly decompose forming oxidation products. Unsaturated carbon-carbon bonds are formed by chain scission, then oxidised producing more hydroperoxides. The break extension does not decrease significantly even though oxidation of the mPP fibres is occurring. This suggests that oxidation must be occurring in many isolated areas in the polymer by only small amounts, producing insufficient chain scission to effect the fibre strength.

In summary, mPP fibres exhibit a 5 day induction period for the formation of oxidation products in the polymer. The resulting oxidation products are spread in low concentration in many isolated sites throughout the polymer, not detrimentally effecting the fibre strength.

In 20ppm HOCl at 50°C the mPP fibres are more resistant to degradation than the Z-N PP with an induction time of 2 days as compared to less than 1 day for the Z-N PP fibres (Figure 8). At 20°C the Z-N PP fibres show an induction period of 5 days as compared to 6 days for the mPP fibres. After 6 days, the mechanical strength of the mPP fibres decreases rapidly. So, the Z-N PP fibres are more susceptible to degradation at elevated temperatures than the mPP fibres,

while the mPP fibres are more susceptible to degradation at high HOCl concentrations when the temperature is low.

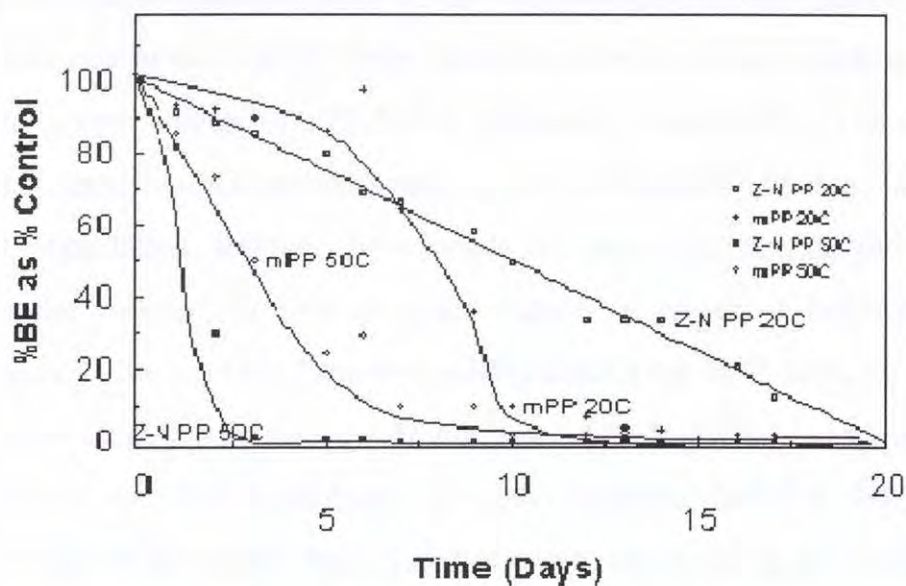


Figure 8 : %BE time profile for Z-N PP and mPP in 20ppm HOCl.

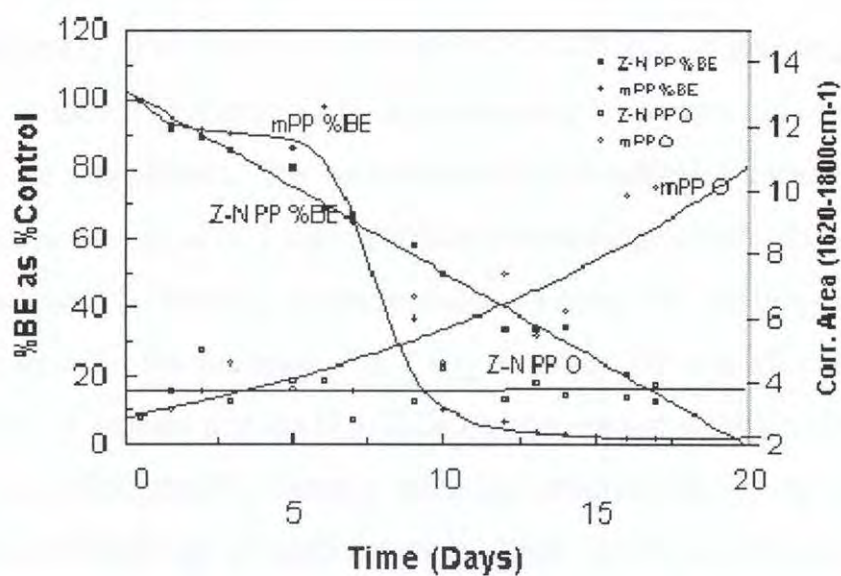


Figure 9 : Carbonyl content time profile for Z-N PP and mPP in 20ppm HOCl at 20°C.

In 20ppm HOCl, the formation of carbonyl compounds in mPP fibres shows a small increase during the first 3 days, followed by a slower increase during the rest of the degradation. After 15 days the oxygen content of the mPP fibres is 2.5 times that of the Z-N PP fibres oxidised under the same conditions and 2.6 times the oxygen content of mPP fibres oxidised at 10ppm HOCl. The concentration of unsaturated carbon-carbon bonds undergoes a sudden increase in the first 1 day of degradation, followed by a steady decrease over degradation (Figure 10). A similar increase in hydroperoxide content is observed followed by a steady increase. So, the HOCl solution readily attacks the mPP, forming hydroperoxides which readily decompose forming carbonyl compounds and resulting in chain scission and C=C formation. A 6 day induction period is observed for tensile strength of the fibres. This period is due to the build up of sufficient scissioned chains to noticeably effect the polymer strength. In summary, the formation of oxidised species on mPP shows a zero induction period, meaning that the HOCl solution diffuses and reacts instantly with the mPP.

The formation of carbonyl compounds on Z-N PP also occurs instantly in 20ppm HOCl, as shown in Figure 9, then maintaining a constant concentration for the rest of the degradation. The concentration of unsaturated carbon-carbon bonds increases suddenly after 1 day and then decreases gradually during degradation by consumption forming hydroperoxides, Figure 10. Hydroperoxide content undergoes a similar increase after 1 day followed by a small gradual decrease, Figure 11. It appears that the high HOCl concentration significantly decreases the induction period, rapidly forming oxidation products after 1 day of degradation. The gradual increase of carbonyl compounds is due to the decomposition of hydroperoxides formed early in the degradation. Mechanical strength of the Z-N PP fibres decreases linearly due to the slow build up of scissioned chains before noticeable loss of fibre strength is observed.

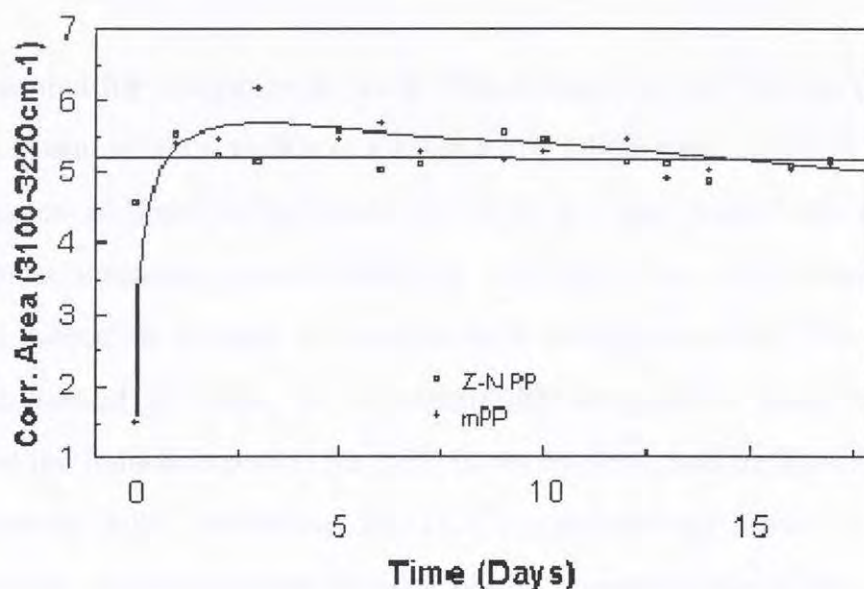


Figure 10 : Carbon-Carbon unsaturation content time profile for Z-N PP and mPP in 20ppm HOCl at 20°C.

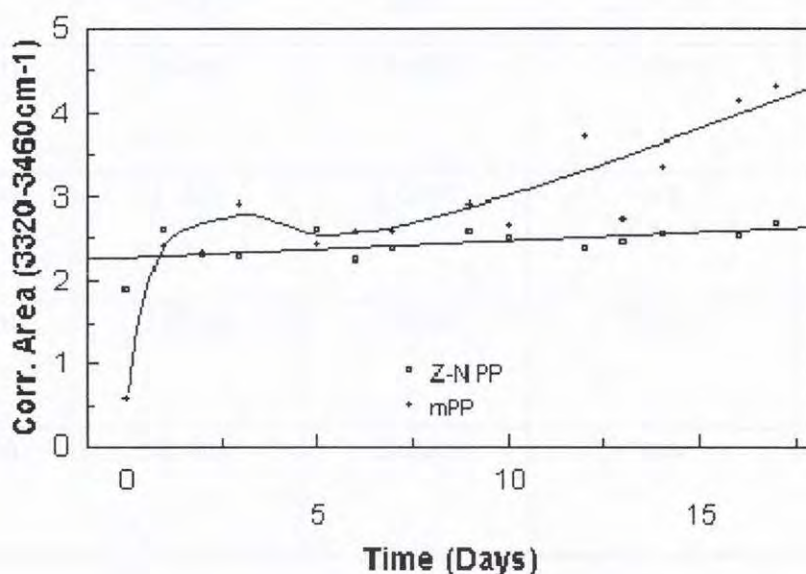


Figure 11 : Hydroperoxide content time profile for Z-N PP and mPP in 20ppm HOCl at 20°C.

In this work it was found that in terms of induction period, mPP fibres have a greater resistance to oxidation and oxidative degradation than Z-N PP fibres. The induction period in terms of formation of oxidation products was shorter in all

cases than that for elongation at break. This is because the build up of oxidation products is immediately visible as a change in FT-IR signal intensity. The change in elongation at break is dependent on chain scission. Significant numbers of chains must undergo scission before a noticeable loss of tensile strength is observed, hence an increase in the observed 'induction period'. The results are best summarised in Table 3. Increasing the temperature from 20 to 50°C decreased the induction period for mPP fibres by 70%, and for Z-N PP fibres by approximately 80%. Increasing the HOCl concentration from 10 to 20ppm decreased the induction period for mPP fibres by approximately 75%, and for Z-N PP by approximately 40%. So, mPP fibres are more sensitive to HOCl concentration than Z-N PP, which are more sensitive to temperature.

Conditions	Induct. Period wrt %BE Z-N PP	Induct. Period wrt %BE mPP	Induct. Period wrt Ox. Products Z-N PP	Induct. Period wrt Ox. Products mPP
10ppm 20°C	8 days	14 days	3 days	5 days
10ppm 50°C	1 day	4 days	n/a	n/a
20ppm 20°C	5 days	6 days	0 days	0 days
20ppm 50°C	<1 day	2 days	n/a	n/a

Table 3 : Summary of induction period data for mPP and Z-N PP fibres.

7.5.3 Rate of Oxidation

As an indicator of rate of oxidation, the rate of change of carbonyl, hydroperoxide and unsaturation content and elongation at break is monitored with degradation time.

The formation of carbonyl compounds on mPP fibres degrading in 10ppm HOCl exhibits a 5 day induction period as shown in Section 7.5.2. The production of carbonyl compounds increases significantly after 12 days, reaching an observed maximum after 16 days. In comparison, the formation of carbonyl compounds on Z-N PP fibres under the same conditions exhibits a 3 day induction period followed by a steady increase with maximum observed carbonyl production after 15 days (Figure 12). Doubling the HOCl concentration, Figure 13, results in maximum carbonyl production after 3 days for the Z-N PP, and after 8 days for mPP.

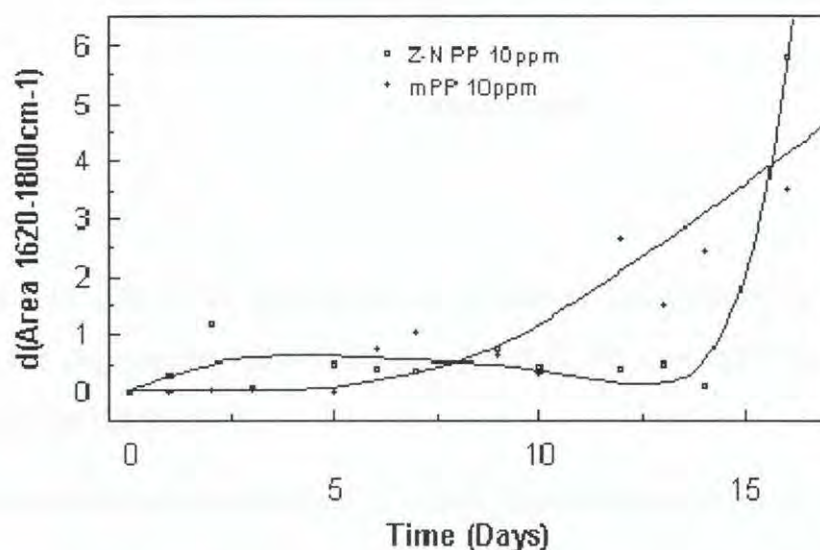


Figure 12 : Rate of formation of carbonyl compounds, using FT-IR peak area for the region 1620-1800cm⁻¹, for Z-N PP and mPP fibres degrading in 10ppm HOCl at 20°C.

This data suggests that after the induction period, the rate of carbonyl production for Z-N PP fibres is strongly dependent on HOCl concentration compared to the mPP fibres. Before degradation Z-N PP contains a large concentration of active impurities (eg catalyst residue, residual unsaturation and hydroperoxides)

compared to mPP so the rate of oxidation at these numerous sites is strongly dependent on oxidant concentration. Oxidation of mPP, containing fewer impurities, is observed to be slightly dependent on HOCl concentration.

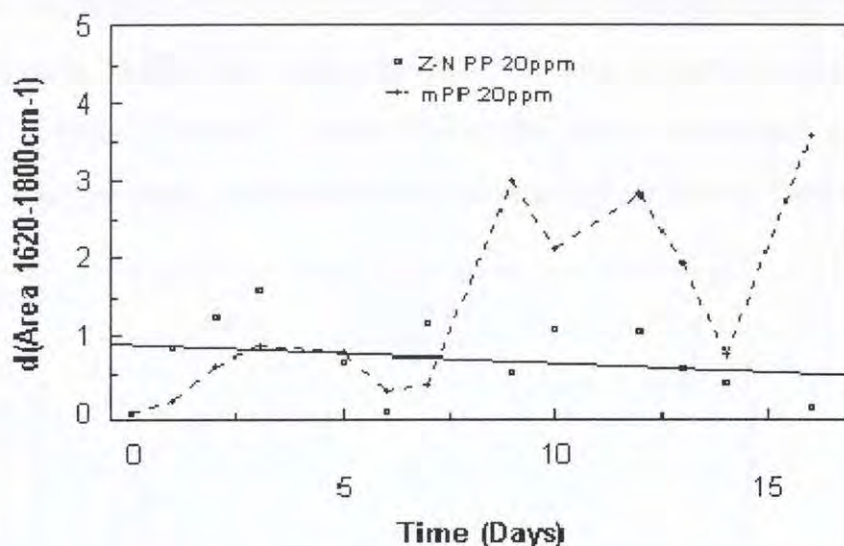


Figure 13 : Rate of formation of carbonyl compounds, using FT-IR peak area for the region $1620\text{-}1800\text{cm}^{-1}$, for Z-N PP and mPP fibres degrading in 20ppm HOCl at 20°C .

The maximum production rate of unsaturated carbon-carbon bonds in mPP fibres degrading in 10ppm HOCl occurs after 2 days as compared to 16 days for Z-N PP (Figure 14). Similarly, the maximum production rate of hydroperoxides occurs after 2 days in mPP fibres under the same conditions, and 16 days in Z-N PP fibres (Figure 16). Doubling the HOCl concentration has no effect on the time for maximum hydroperoxide or unsaturation increase in mPP. However, the maximum production rate of hydroperoxides and unsaturated C-C bonds occurs after 2 days in Z-N PP under these conditions.

This data suggests that Z-N PP shows an increased resistance to the formation of hydroperoxides and unsaturated groups at low HOCl concentrations compared to

mPP, while at high HOCl concentrations oxidation of both fibres occurs simultaneously. Prior to degradation, mPP contains a quarter of the concentration of hydroperoxides and a tenth the concentration of carbon-carbon double bonds found in Z-N PP. So, at low HOCl concentrations the mPP fibres undergo high rates of oxidation at the few active sites forming hydroperoxides and unsaturated C-C groups, while the numerous Z-N PP active sites undergo only partial oxidation forming some hydroperoxides and fewer unsaturated groups. At high HOCl concentrations, oxidation occurs at most active sites in both types of fibre.

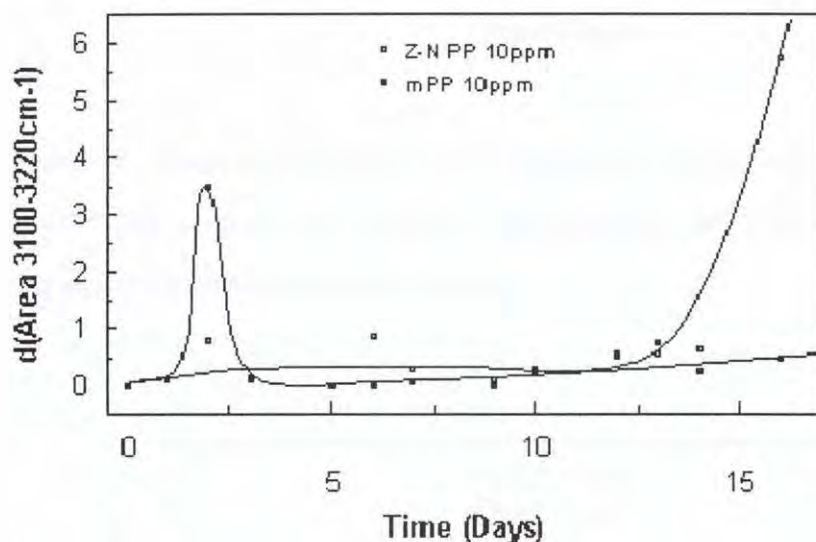


Figure 14 : Rate of formation of unsaturated carbon-carbon bonds, using FT-IR peak area for the region 3100-3220cm⁻¹, for Z-N PP and mPP fibres degrading in 10ppm HOCl at 20°C.

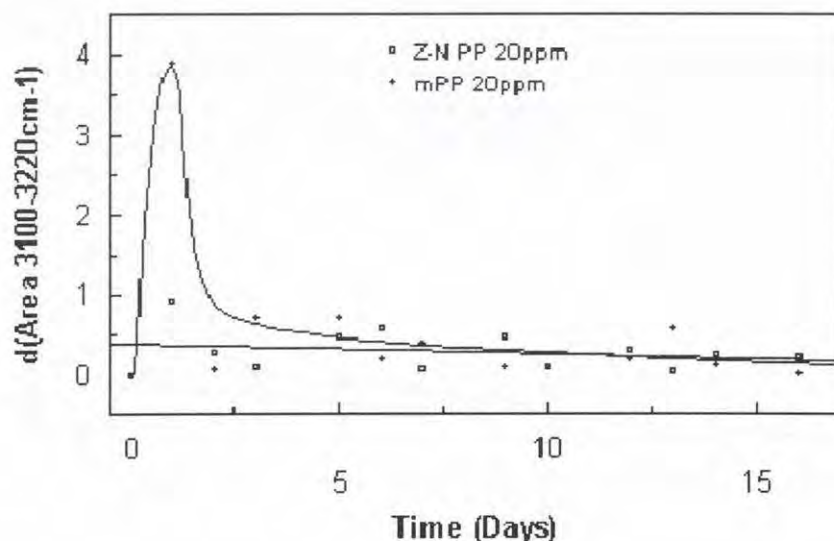


Figure 15 : Rate of formation of unsaturated carbon-carbon bonds, using FT-IR peak area for the region $3100\text{-}3220\text{cm}^{-1}$, for Z-N PP and mPP fibres degrading in 20ppm HOCl at 20°C .

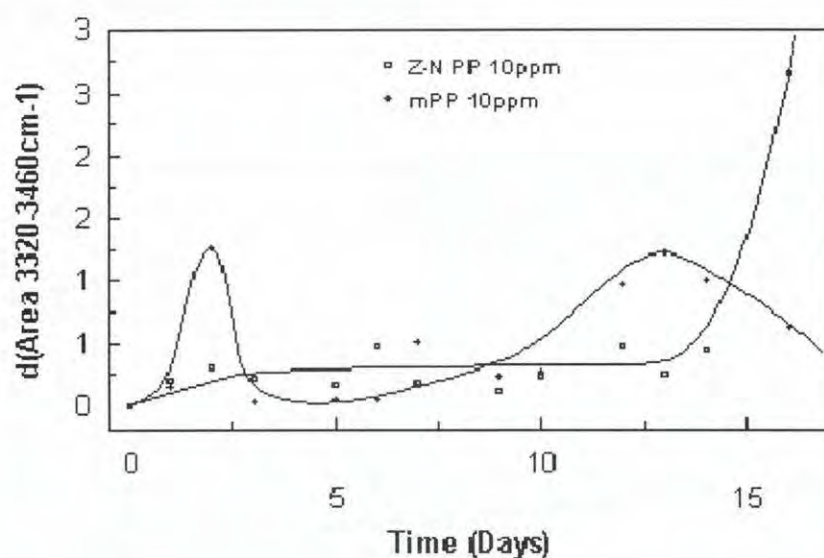


Figure 16 : Rate of formation of unsaturated carbon-carbon bonds, using FT-IR peak area for the region $3320\text{-}3460\text{cm}^{-1}$, for Z-N PP and mPP fibres degrading in 10ppm HOCl at 20°C .

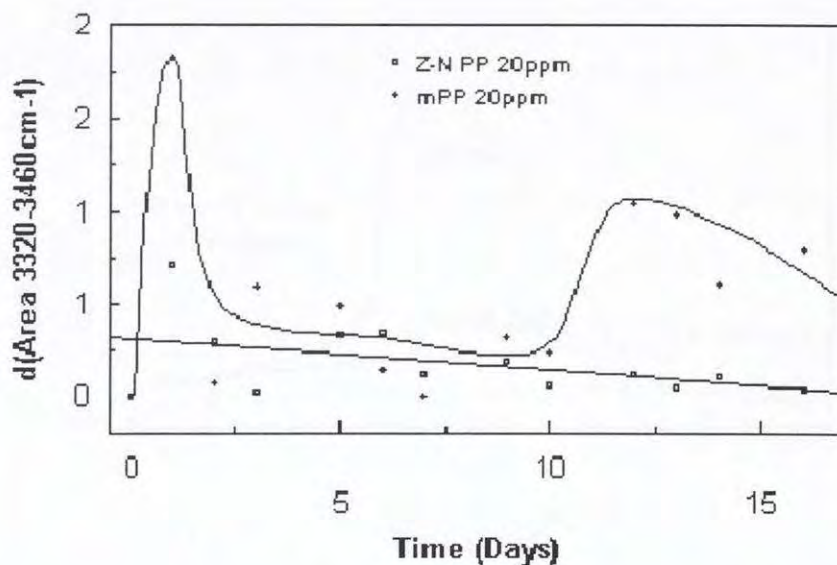


Figure 17 : Rate of formation of unsaturated carbon-carbon bonds, using FT-IR peak area for the region $3320\text{--}3460\text{cm}^{-1}$, for Z-N PP and mPP fibres degrading in 20ppm HOCl at 20°C .

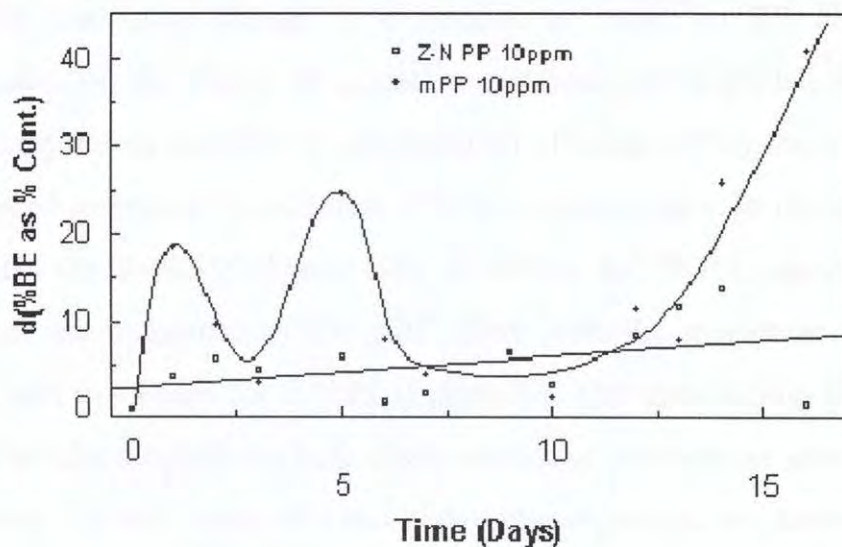


Figure 18 : Change in %BE for Z-N PP and mPP fibres degrading in 10ppm HOCl at 20°C .

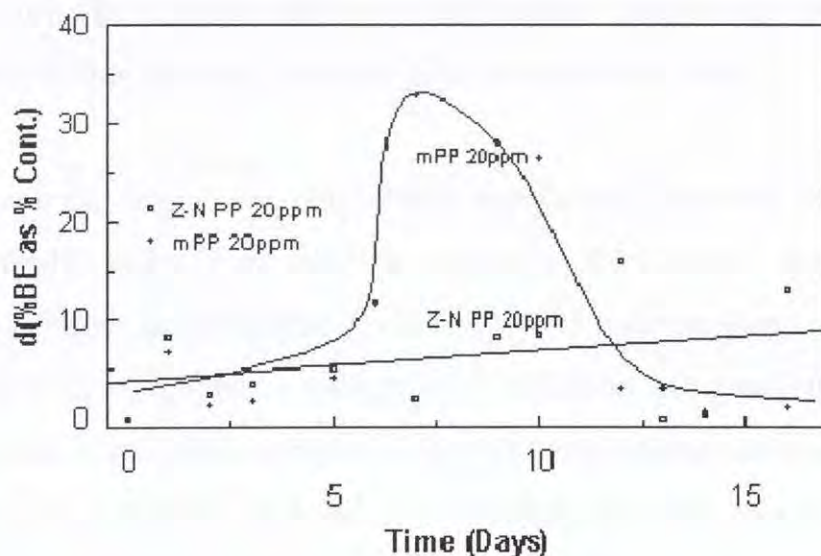


Figure 19 : Change in %BE for Z-N PP and mPP fibres degrading in 20ppm HOCl at 20°C.

Elongation at break is an indicator of chain scission occurring either on the polymer backbone or by the production of low short chain oxygenated species. So, the maximum change in elongation at break for PP fibres is strongly dependent on the degree of oxidation and hence on degradation conditions. At low temperature and HOCl concentration (10ppm, 20°C) the mPP fibres show improved resistance to oxidation with a maximum after 16 days as compared to 14 days for Z-N PP (Figure 18). Doubling the HOCl concentration rapidly reduces the resistance of the mPP fibres with the maximum after 7 days as compared to 12 days for Z-N PP (Figure 19). This data implies that at low HOCl concentrations significant bulk chain scission of mPP occurs after other oxidation products, eg hydroperoxides and carbonyl compounds, are formed. Metallocene PP contains few impurities from polymerisation and hence few active sites for degradation compared to Z-N PP which contains 7 times the number of active sites. Increasing the oxidant (HOCl) concentration rapidly increases the oxidation

at these few active sites producing a high local but low total degree of oxidation. This causes bulk chain scission at the isolated sites which is shown by the decrease in time for maximum change to elongation at break.

Increasing the degradation temperature significantly increases the oxidation rate in both mPP and Z-N PP fibres as shown by the time for onset of bulk chain scission, Figure 20 and Figure 21. In both HOCl concentrations at 50°C, the Z-N PP fibres show a lower resistance to oxidation compared to mPP. At this temperature the thermal stability of the polymers becomes an important factor. It was shown in Section 7.5.2 that Z-N PP fibres are more susceptible to thermal degradation than mPP, indicating that as well as chemical degradation the Z-N PP fibres are also influenced by thermally induced degradation.

In summary, the resistance of mPP to loss of tensile strength is strongly dependent on HOCl concentration. At low HOCl concentrations mPP fibres exhibit greater resistance to loss of tensile strength than Z-N PP fibres. Increasing HOCl concentration significantly reduces the resistance of mPP fibres to loss of tensile strength compared to Z-N PP. At elevated temperatures mPP fibres show a slight improvement in resistance to loss of tensile strength than Z-N PP fibres.

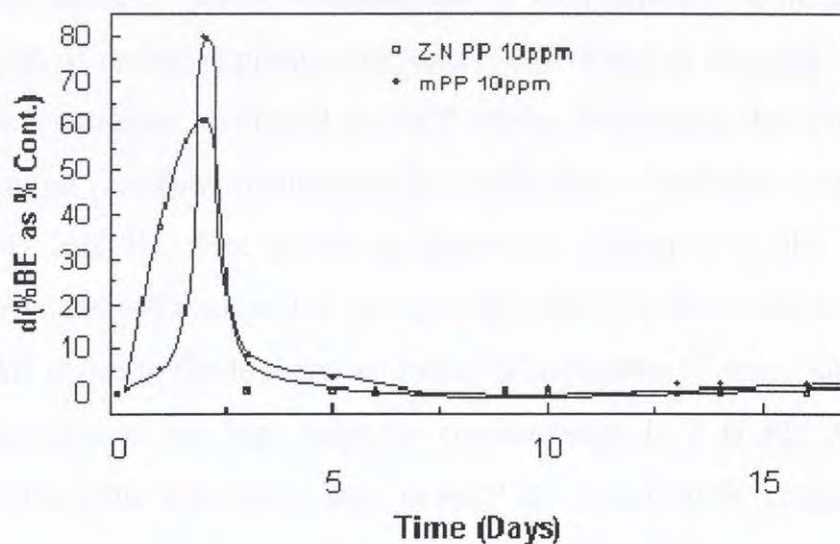


Figure 20 : Change in %BE for Z-N PP and mPP fibres degrading in 10ppm HOCl at 50°C.

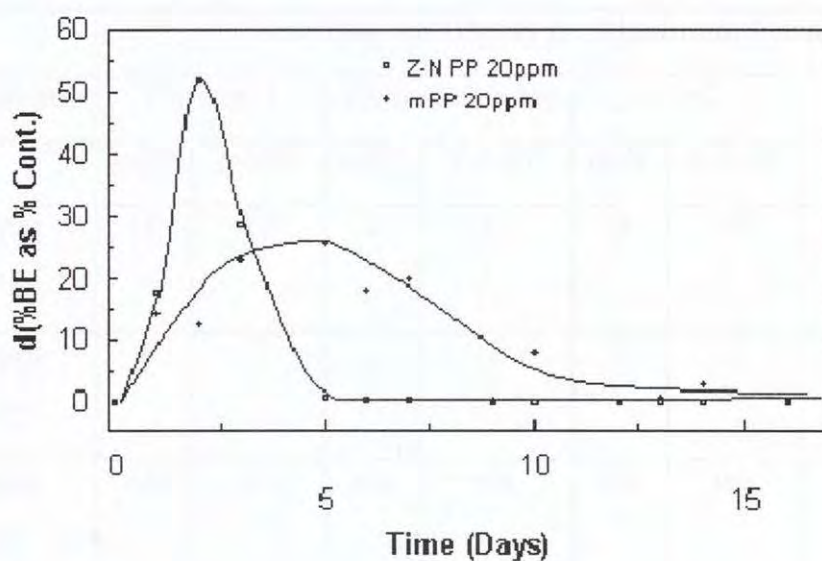


Figure 21 : Change in %BE for Z-N PP and mPP fibres degrading in 20ppm HOCl at 50°C.

The observations of rate of oxidation can be summarised by a number of points:

i) The rate of carbonyl production for Z-N PP fibres is strongly dependent on HOCl concentration compared to mPP fibres. Increasing the oxidant (HOCl) concentration significantly increases the production of carbonyl compounds in Z-N PP. ii) Z-N PP fibre shows an increased resistance to the formation of hydroperoxides and unsaturated groups at low HOCl concentrations compared to mPP. This is due to the low concentration of impurities ie active sites, present in mPP compared to the high impurity concentration in Z-N PP. At low HOCl concentrations the few active sites in mPP are significantly oxidised while the many active sites in Z-N PP are only partially oxidised. At high HOCl concentrations oxidation of both types of fibres occurs simultaneously. iii) The resistance of mPP to loss of tensile strength for mPP fibres is strongly dependent on HOCl concentration. Compared to Z-N PP fibres, increasing the HOCl concentration increases the relative resistance of the mPP fibres. These observations regarding rate of oxidation are summarised in Table 4.

Conditions	Time Elapsed (Days) for Maximum Change in:							
	Carbonyl		Hydroperoxide		C=C		%BE	
	mPP	Z-NPP	mPP	Z-NPP	mPP	Z-NPP	mPP	Z-NPP
10ppm 20°C	12	12	2	16	2	16	16	14
20ppm 20°C	8	3	2	2	2	2	7	12
10ppm 50°C	n/a	n/a	n/a	n/a	n/a	n/a	2	2
20ppm 50°C	n/a	n/a	n/a	n/a	n/a	n/a	2	3

Table 4 : Summary data for maximum oxidation of mPP and Z-N PP fibres.

7.6 Conclusions

A comparison was made between the properties of hollow fibre membranes from Ziegler-Natta (Z-N) PP and metallocene PP (mPP), and their relative stability to oxidative degradation using HOCl. Several conclusions were drawn:

1. In this work it was found that in terms of induction period, mPP fibres have a greater resistance to oxidation and oxidative degradation than Z-N PP fibres. The induction period was determined using hydroperoxide, carbonyl and C-C unsaturation content from FT-IR data and elongation at break from tensile strength data. For mPP fibres the duration of the induction period is strongly dependent on HOCl concentration, while for Z-N PP fibres the induction period is dependent on degradation temperature.
2. The rate of carbonyl production for Z-N PP fibres is strongly dependent on HOCl concentration compared to mPP fibres. Increasing the oxidant (HOCl) concentration significantly increases the production of carbonyl compounds.
3. Z-N PP fibres show an increased resistance to the formation of hydroperoxides and unsaturated groups at low HOCl concentrations compared to mPP.
4. The resistance of mPP fibres to loss of tensile strength is strongly dependent on HOCl concentration compared to Z-N PP.

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Chapter 8 Conclusions and Recommendations

The purpose of this chapter is to provide a summary of the conclusions reached in the 5 preceding chapters (Chapters 3 to 7), and to highlight some areas for further work. A comprehensive set of conclusions can be found at the end of each chapter pertaining to the specific area investigated. As mentioned, Section 8.1 is intended to be only a summary of these conclusions.

8.1 Conclusions

In Chapter 3 a study was carried out i) To determine whether or not oxidation of polypropylene occurs by hydrogen abstraction by a pure HOCl solution and ii) To determine whether terminal C=C bonds, present in commercial PP, undergo oxidation by a HOCl solution. Part i) was carried out using a low molecular weight compound, 2,4-dimethylpentane (DMP), as a model for tertiary carbon atoms present in polypropylene. Part ii) was carried out using low molecular weight compound, 2-methylbut-1-ene (2MB), as a model for terminal C=C groups present in commercial PP. Reaction of the PP model compound DMP with HOCl resulted in oxidation of less than 0.1% of the model compound. So, it was concluded that oxidation of polypropylene by HOCl does not occur to an appreciable degree due to hydrogen abstraction by the HOCl solution or by any species present in the pure HOCl solution. So, oxidation of commercial PP using HOCl must proceed by generating active species in either the HOCl or on the polymer to initiate oxidation. Reaction of the terminal C=C model compound 2MB with HOCl produced a wide variety of oxidation products in significant amounts. So, it appears that HOCl significantly oxidises terminal C=C groups in the 2MB model compound. It would be expected then that HOCl would react in a similar manner with terminal C=C groups in commercial PP.

In Chapter 4 several conclusions were drawn regarding the induction time of degradation and they may be summarised as follows: An overall induction period

of 2 days was observed for the generation of all oxidation products. During the first hour of degradation, no oxidation products were detected. After 1 hour a decrease in crystallinity was observed, indicating the onset of chain scission. After 4 hours a loss of mechanical strength was observed indicating the occurrence of sufficient chain scission to detrimentally effect the fibre mechanical strength. Between 1 and 2 days a decrease was observed in the unsaturated carbon-carbon (present as a by-product of visbreaking) content. This was due to oxidation of these C=C groups, forming hydroperoxides. A slight increase in hydroperoxide and carbonyl composition, from FT-IR measurements, and surface oxygen content, from XPS measurements, was observed during this time as a result of the C=C oxidation. After 2 days, a significant increase in carbonyl and hydroperoxide content, from FT-IR measurements, and total oxygen content, from XPS measurements, was observed indicating the onset of oxidation.

Also in Chapter 4 several conclusions were drawn regarding degradation after the induction period and these are summarised below.

1. After the induction period, the elongation at break for PP fibres undergoes a rapid decrease. This is due to a rapid increase in the rate of chain scission of the PP fibres. So, oxidation of PP fibres results in chain scission and radical generation.
2. The average molecular weight decreases during degradation due to chain scission. The appearance of a bimodal MWD in highly degraded samples indicates that chain scission is occurring at localised sites resulting in a high local but low total rate of degradation.
3. FT-IR studies of degraded PP fibres may be summarised as:

a. i) Hydroperoxide concentration increases linearly during oxidation. This increase in POOH concentration is due to hydroperoxide decomposition generating more than 1 active radical. ii) Radicals derived from hydroperoxide decomposition initiate oxidation at all sites throughout the polymer, not just at active sites.

3b. Carbonyl content increases linearly during degradation after the induction period. Carbonyl compounds, formed as a result of POOH decomposition, are a major oxidation product.

3c. Unsaturation content decreases significantly during degradation. C=C groups are generated by i) β -scission of tertiary radicals and ii) β -scission of carbonyl compounds.

4. XPS studies of oxygen content during PP degradation show an accelerating effect due to rapid oxidation of tertiary radicals and C=C groups, followed by a deceleration due to a decrease in the concentration of available oxidation sites.

5. Crystallinity of PP fibres decreases with degradation due to oxidation resulting in chain scission particularly of tie molecules. During degradation the crystallinity decrease undergoes a deceleration due to a decrease in rate of chain scission.

Using this information a basic oxidation mechanism was proposed and is summarised in Section 4.5.3.6.

In Chapter 4 the affect of temperature and hypochlorous acid concentration on PP fibre degradation was investigated and the conclusions are summarised below:

Generally speaking, increasing both temperature and HOCl concentration resulted in an overall increase in the rate of degradation. Increasing degradation temperature most strongly affected the unsaturation and hydroperoxide content, significantly reducing the onset of observable change. Crystallinity and carbonyl

content were least affected. This data indicates that the formation of hydroperoxides by the reaction of dissolved oxygen, from the HOCl solution, with either unsaturated carbon-carbon groups or tertiary radicals is strongly temperature dependent. Whereas, carbonyl decomposition forming carbonyls and low molecular weight fragments is less temperature dependent. Increasing the degradation temperature most strongly increased the rate of carbonyl formation, due to decomposition of the increased amount of hydroperoxides produced both during and after the induction period at the elevated temperature. Increasing the HOCl concentration most significantly increased the rate of hydroperoxide generation, as well as significantly decreasing degradation time. Hence, the formation of active chloride and hydroxy radicals from hypochlorous acid and hypochlorite ions, their abstraction of tertiary hydrogen atoms followed by reaction with dissolved oxygen is strongly dependent on HOCl concentration. The aqueous degradation of PP hollow fibre membranes using hypochlorous acid is strongly dependent on both HOCl concentration and reaction temperature. Temperature and HOCl concentration influence the degradation in two ways. An increase in the reaction temperature increases the overall reaction rate by increasing the mobility of all active species. Increasing HOCl concentration significantly increases the generation of hydroperoxides, which in turn increases the overall number of degradation reactions occurring, hence increasing the degradation rate.

In Chapter 5, the effect of catalyst residues and other impurities on degradation was investigated. The conclusions are summarised below:

1. It was found that polypropylene powder, pellets and fibres have significant differences in content due to oxidation during processing. Polypropylene powder contains a significant amount of hydroperoxides and unsaturated carbon-carbon bonds, residual products of visbreaking. Pelletisation results in

a decrease in the unsaturation content and increase in hydroperoxide content due to oxidation of C=C groups. Extrusion results in a significant increase in concentration of all oxidation products.

2. The presence of iron(III) and copper(II) ions in the HOCl solution accelerated the oxidation of PP fibres. Iron(III) ions catalysed the decomposition of hydroperoxides to peroxy radicals by undergoing reduction to Fe. Copper(II) ions were reduced to Cu while also accelerating the decomposition of hydroperoxides. Both iron(II) and cobalt(II) ions present in HOCl inhibited PP oxidation.

In Chapter 6 the effect of stabilisers on PP membrane degradation was investigated, and the conclusions are summarised below:

It was observed that the addition of a hindered phenol stabiliser to PP prior to extrusion increased the observed induction time for PP fibre oxidation by HOCl from 1 to 2 days in terms of tensile strength and from 2 to 2.5 days in terms of carbonyl content. This initial inhibition of formation of carbonyl species, and loss of mechanical strength continued until the stabiliser supply was exhausted. At this point degradation of the stabilised fibres began as in the unstabilised fibres. An alternative hindered phenol antioxidant (BHT) was added to the fibres after extrusion. It was observed that at sufficiently high concentrations, BHT inhibits PP oxidation, increasing the induction period in terms of mechanical strength and carbonyl content. Using a BHT concentration of ~50,000ppm in the solvent solution prior to addition to the fibres, the induction period was increased by seven times compared to oxidation of unstabilised fibres under the same conditions.

In Chapter 7 the performance of fibres from Ziegler Natta PP was compared to novel fibres extruded from metallocene catalysed PP. The conclusions are summarised below:

It was observed that in terms of induction period, the mPP fibres have a greater resistance to oxidation and oxidative degradation than Z-N PP fibres. Z-N PP fibres show an increased resistance to the formation of hydroperoxides and unsaturated groups at low HOCl concentrations compared to mPP. The resistance of mPP fibres to loss of tensile strength is strongly dependent on HOCl concentration compared to Z-N PP.

8.2 Recommendations

Based on the work carried out in this thesis, there are several areas for further study:

1. Only preliminary studies were carried out on metallocene polypropylene. Further studies are necessary to characterise the starting polymer in terms of catalyst residues and other impurities due to processing. Only 1 supplier of metallocene PP was used as it was the only commercially available polymer of this type at the time. Samples should be obtained from alternative suppliers and the polymers evaluated and the impurity levels compared to those for Ziegler-Natta polypropylene. For comparison further batches of metallocene PP fibre must be produced using the production process at USF Memcor. For this polymer the process parameters need to be modified to ensure the fibre has similar properties to the current Z-N fibre.
2. The possibility of using antioxidants to slow down the oxidation of PP is exciting, and in this work only BHT was trialled. Further work should involve a variety of hindered phenol antioxidants with more phenol groups per molecule. Obviously, as USF Memcor's products are commonly used in drinking water applications the antioxidant of choice must be FDA approved,

as is BHT. Also, only hexane was trialled as a solvent. Further work should involve trialling other organic solvents such as heptane or HCFC's which may also swell the polymer.

3. Based on the results in Chapter 6 it is recommended that the amount of antioxidants added to PP during the USF Memcor extrusion process be increased by a factor of 10. This will significantly improve the chlorine resistance of the fibres.
4. This work identified several transition metal ions that retard the oxidation process. Further work should involve investigating the dosing of these ions into chlorinated feed waters upstream of PP CMF units in industrial applications. This would be of use in industrial waste water applications.
5. Chlorine degradation of PP increases with temperature, and hence decreases with decreasing temperature. An investigation into PP degradation at low temperatures in laboratory and industrial applications should be carried out.
6. As part of these studies FT-IR was a useful tool for identifying oxidation products at reasonable concentrations. FT-IR microscopy may also be trialled for analysing oxidation products in low concentration on the fibre surface, and may provide useful information about oxidation product formation during the induction period.
7. Further analysis of the degrading metallocene PP using GC-MS is required to further clarify the improvement in oxidation resistance of this polymer.