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# An Investigation Into Surface Modificatin Of Polyethylene Film By Ozonation

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2008

**AN INVESTIGATION INTO SURFACE  
MODIFICATION OF POLYETHYLENE FILM  
BY OZONATION**

by

Dipak P. Patel

Bachelor of Chemical Engineering, Gujarat University, India, 1991

A thesis

presented to Ryerson University

in partial fulfillment of the requirements for the

degree of Master of Applied Science in

the program of Chemical Engineering

Toronto, Ontario, Canada, 2008

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Dipak P. Patel



# **ABSTRACT**

## **An Investigation into Surface Modification of Polyethylene Film by Ozonation**

**Dipak P. Patel**

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Ryerson University, Toronto, 2008

The aim of this study was to investigate the hydrophilic modifications of the polymer films by ozonation. In this study, the polymer films (LD+LLDPE) were ozonated in gas phase and in aqueous phase, respectively. The surfaces of the polymer films were investigated in terms of peroxide generation, contact angle measurement, Fourier transform infrared (FTIR) spectroscopy and tensile strength measurements.

Experimental results indicated that the amount of peroxide groups generated increased with ozonation time and applied ozone dose. It was also observed that the efficiency of ozonation was similar for gas phase ozonation, and aqueous ozonation. Catalyst screening revealed that Fe (III) and Cu (II) were both effective in accelerating peroxide generation.

The hydrophilicity improvement of the film after ozonation was confirmed by contact angle measurements and Fourier transform infrared measurements. The LD+LLDPE films kept good tensile strength after ozonation. Even after 120 min ozonation at 1.0 wt% applied ozone dose, 85% of the tensile strength still remained.

The application of catalyst to modify polymer film is the first of its kind. In this study, the approach proved to be successful for LD+LLDPE films.

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## **DEDICATION**

Attribute to my father and mother for the bestowal of a beautiful life to me, dedicated to my lovely wife, Jignasha for her consistent support and encouragement during this study, also dedicated to my dearest daughters, Niyatee and Sakshi.

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## NOMENCLATURE

<b>Symbols</b>	<b>Description</b>
me	milliequivalents
N	Normality

<b>Abbreviations</b>	<b>Description</b>
AAm	Acrylamide
ATR- FTIR	Attenuated total reflectance Fourier transform infra-red
ASTM	American society for testing and materials
BIEA	2-(2- bromoisobutyryloxy) ethyl acrylate
DMAPS	N-N-dimethyl (methacryloyloxyethyl) ammonium propanesulfate
DMMCA	N-N-dimethyl-N-methacryloyloxyethyl-N-(2-carboxyethyl) ammonium
DMMSA	N-N-dimethyl-N-methacryloyloxyethyl-N-(3-sulfopropyl) ammonium
DPPH	1, 1 diphenyl-2- picrylhydrazyl
ESCA	Electron Spectroscopy for Chemical Analysis
GSH	Glutathione
HEMA	2-hydroxyl-ethyl methacrylate
IgK	bromine X-globulin
LDPE	Low density polyethylene
LLDPE	Linear low density polyethylene
LD+LLDPE	Consists of low density polyethylene and linear low density polyethylene
NADPH	Nicotinamide adenine dinucleotide phosphate

OBCS	<i>O</i> -butyrylchitosan
PBS	Phosphate buffer saline
PE	Polyethylene
PEGA	Poly (ethylene glycol) mono-acrylate
PEG-SO <sub>3</sub>	Sulfonated polyethylene glycol
PET	Polyethylene terephthalate
PMMA	Poly methyl methacrylate
PLLA	Poly-L-lactic acid
PP	Polypropylene
PRP	platelet- rich plasma
PS	Polystyrene
PU	Poly urethane
SEM	Scanning Electronic Microscopy
SPEU	Segment poly (ether-urethane)

# 1. INTRODUCTION

## 1.1 Background

Polymers are being extensively used in biomedical fields because they are relatively inexpensive, chemically nonreactive and have excellent thermal and mechanical properties. Polymers are used in biomedical fields for medical devices, artificial organs, and disposable clinical apparatuses such as vascular prostheses, blood pumps, artificial kidney, heart valves, intra-aortic balloon, artificial hearts, dialyzers and plasma separators (Ishihara et al., 1999). But most polymers are hydrophobic, and have chemically inert surface and poor biocompatibility, which limit their applications in many of areas (Dasgupta, 1990; Zhou et al., 2005). The hydrophobicity of polymers causes anticoagulation, adhesion and coating problems when used as biomaterials. Polyolefins such as polypropylene and polyethylene have non-polar and highly hydrophobic properties which limit their applications in the biomedical area. Because of poor biocompatibility of polymers, biomedical applications of polymeric material have faced many critical obstacles such as undesirable protein adsorption and cell adhesion. When a polymer surface comes into contact with fresh blood, the blood proteins adsorb onto it rapidly, followed by clotting factors activation, platelet adhesion, activation and finally thrombus formation (Sharma, 2001). Therefore, it is very important to modify polymer surface to change their biocompatibility, wettability, adhesion, cell attachment, and many other properties which are vital to modern engineering and medical applications of polymers (Kulik et al., 1997).

Polymers are also used in membrane bioreactors (MBR) for anaerobic biological wastewater treatment. The loss of membrane permeability is caused by membrane fouling as the results of inorganic precipitation, adsorption of organic compounds, and attachment of cells (Kayawake et al., 1991). Surface modification of polymer can reduce fouling caused by hydrophobic adsorption and increase hydrophilicity (Sainbayar et al., 2001). In short, modification of the polymer surfaces can improve properties of polymers for applications in the above two fields.

## 1.2 Surface Modification

Surface modification is an effective way to modify the surface of polymers. It can be accomplished by various methods (Kulik et al., 1997; Sainbayar et al., 2001; Ferreira et al., 2005) such as:

Table 1.1 The methods for surface modification

Method for Surface Modification	Advantages or Disadvantages
Corona discharge	Low capital cost, Only effective on surface of polymer
Glow discharge	Increase surface energy, Only effective on surface of polymer
Ultraviolet (UV) radiation	Costly method, More maintenance cost
Gamma-rays irradiation	Costly method
Flame treatment	Increase wettability, Complicated process
Activated gas-plasma	More reduction in platelet adhesion, Not good for complicated shapes
UV/Ozone treatment	Better reactivity than ozone, Maintenance costly
Ozonation	Simple and inexpensive, Suitable for complicated shapes

### 1.3 Advantages of Ozonation

By ozonation, peroxide groups are generated onto the polymer surfaces. The peroxides generated are capable of initiating graft radical polymerization of hydrophilic vinyl monomers onto the polymeric materials. Ozonation is a relatively simple and inexpensive method. It is suitable for mass production of modified polymers. Ozone method also has an advantage in terms of uniformity of peroxides on surface of polymers even with complicated shapes (Ko et al., 2001). Oxidation of polymeric films by ozonation occurs not only on the surface but penetrates deeply inside surface due to the diffusion of ozone into the film. The reactivity of the hydroperoxidized materials with hydrophilic monomers depends on the following factors: the kinetics of the thermal decomposition of peroxide, the nature of the radicals generated, the accessibility of peroxide sites and monomer diffusion (Gatenholm et al., 1997).

Ozonation can be conducted either in gas phase or aqueous phase. In gas phase ozonation, ozone gas reacts with substrate. In aqueous phase ozonation, dissolved ozone and ozone gas bubbles both react with the substrate. It is convenient and has more options to use catalyst/ additive to accelerate the reaction in aqueous phase than in gas phase. Active oxygen species (superoxide  $\text{HO}_2^\bullet$ , and Hydroxyl radical  $\text{OH}^\bullet$ ) can be generated when ozone is dissolved in water. These radicals are stronger oxidants than ozone molecules and are intrinsic chemical species in the human body. Thus, ozone treatment is recognized as a safe treatment for biomaterials, the treated polymer introduced into the body is not contaminated with toxic chemicals because only ozone and water are used as the chemical substances. Consequently, ozonation is considered to be more suitable for

modifying the surface of polymers, especially biomaterials, than the conventional chemical methods (Murakami et al., 2003).

#### **1.4 Research Objectives**

The research objectives are to compare ozonation efficiency in gas phase and aqueous phase for polyethylene film in terms of peroxide generation, to examine the effect of different pH value, to accelerate reaction by using suitable homogeneous catalysts and to examine effect of process parameters on peroxide generation with selected catalyst.

## 2. THEORY AND MECHANISM OF OZONATION

### 2.1 Properties of Ozone

Ozone acts as a very powerful oxidation agent and is capable of cleaving double bonds in a selective and fast way. Ozone, which is commonly written as  $O_3$  for simplification, is easily produced and does not need sophisticated apparatus that could be totally unacceptable for normal use. This gas is relatively stable up to  $70\text{ }^\circ\text{C}$  and can decompose in ionic species or other excited species when increasing temperature. Ozone destruction is relatively simple and does not require specific and expensive plants (Robin, 2004).

Ozone reactivity is due to the structure of the molecule. The ozone molecule consists of three oxygen atoms. Each oxygen atom has the following electronic configuration surrounding the nucleus:  $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$ , i.e., in its valence band it has two unpaired electrons, each one occupying one  $2p$  orbital. In order to combine the three oxygen atoms and yield the ozone molecule, the central oxygen rearranges in a plane  $sp^2$  hybridization from the  $2s$  and two  $2p$  atomic orbitals of the valence band. With this rearrangement the three new  $sp^2$  hybrid orbitals form an equilateral triangle with an oxygen nucleus in its center, i.e., with an angle of  $120^\circ$  between the orbitals. However, in the ozone molecule this angle is  $116^\circ 49'$ . The other  $2p$  orbital of the valence band stays perpendicular to the  $sp^2$  plane, as Figure 2.1 shows, with two coupled electrons. Two of the  $sp^2$  orbitals from the central oxygen, forming the angle indicated above, combine with one  $2p$  orbital (each containing one electron) of the other two adjacent oxygen atoms in the ozone molecule, while the third  $sp^2$  orbital has a couple of nonshared electrons.

Finally, the third 2p orbital of each adjacent atomic oxygen, which has only one electron, combines with the remaining 2p<sup>2</sup> orbital of the central oxygen to yield two  $\pi$  molecular orbitals that move throughout the ozone molecule (Beltran, 2004). As a consequence, the ozone molecule represents a hybrid formed by the four possible structures shown in Figure 2.2.

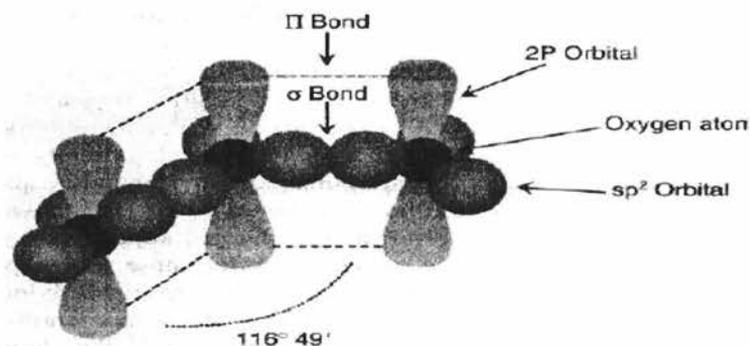


Figure 2.1 The molecular structure of ozone (Beltran, 2004)

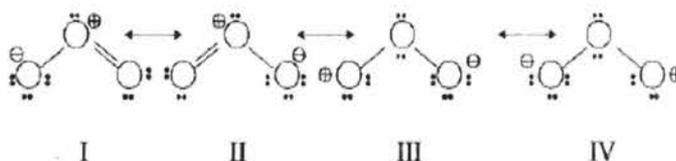


Figure 2.2 Resonance forms of the ozone molecule (Beltran, 2004)

The high reactivity of ozone can then be attributed to the electronic configuration of the molecule. Thus, the absence of electrons in one of the terminal oxygen atoms in some of the resonance structures confirms the electrophilic character of ozone. Conversely, the excess negative charge present in some other oxygen atom imparts a

nucleophilic character. These properties make ozone an extremely reactive compound (Beltran, 2004). Table 2.1 presents some physico-chemical properties of ozone.

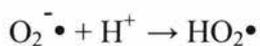
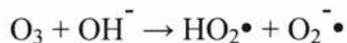
Table 2.1 Physico-chemical properties of ozone (Perry and Green, 1997)

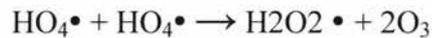
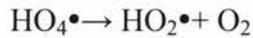
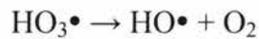
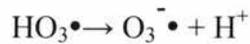
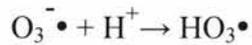
Property	Value
Melting point, °C	-251
Boiling point, °C	-112
Critical pressure, atm	54.62
Critical temperature, °C	-12.1
Specific gravity	1.658 higher than air 1.71 gcm <sup>-3</sup> at -183°C
Critical density, kgm <sup>-3</sup>	436
Heat of vaporization, calmol <sup>-1</sup> <sup>a</sup>	2,980
Heat of formation, calmol <sup>-1</sup> <sup>b</sup>	33,880
Free energy of formation, calmol <sup>-1</sup> <sup>b</sup>	38,860
Oxidation potential, V <sup>c</sup>	2.07

<sup>a</sup> At the boiling point temperature. <sup>b</sup> At 1 atm 25°C. <sup>c</sup> At pH =0.

## 2.2 Mechanism of Ozone Decomposition in Water

Stahelin et al. (1984) suggested following mechanism of ozone decomposition in water.





The reactions of ozone with the hydroxide and hydroperoxides ions can be considered the main initiation reactions of the ozone decomposition mechanism in water. There are other reactions that lead to the decomposition or stabilization of ozone in water. Thus, substances of different nature can also contribute to the appearance or inhibition of free radicals. These substances are called initiators, inhibitors and promoters of the reaction. The initiators are those substances, such as the hydroxides ion that directly react with ozone to yield the superoxide ion radical ( $\text{HO}_2^{\cdot}$ ). The superoxide ion radicals is the key to propagating free radical species because it rapidly reacts with ozone to yield free radicals such as ozonide ion radical that eventually leads to the hydroxyl radicals ( $\text{HO}^{\cdot}$ ). Promoters are those species that, through their reaction with the hydroxyl radicals, propagate the radical chain to yield the key free radical: the superoxide ion radical. Finally, inhibitors of the ozone decomposition are those species that while reacting with the hydroxyl radicals terminate the radical chain. In last two reactions, reaction products were tentatively proposed (Beltran, 2004).

The stability of dissolved ozone is readily affected by pH, ultraviolet (UV) light, ozone concentration, and the concentration of radical scavengers (Langlais et al., 1991).

Ozone decomposition rate is first order with respect to both ozone and hydroxide ions, resulting in an overall equation as mentioned in Equation (1) (Langlais et al., 1991).

$$-\frac{d[O_3]}{dt} = k [O_3] [OH^-] \text{-----} \quad (1)$$

$k$  = Rate-constant

$$-\frac{d[O_3]}{dt} = k' [O_3] \text{-----} \quad (2)$$

$$k' = k [OH^-]$$

$k'$  = Pseudo first-order rate constant for given pH value when  $[OH^-]$  is a constant.

### 2.3 Ozone Reaction with Polyolefins

The reactions of ozone onto polymers lead to numerous chemical modification. The chemical reaction occurred at the surface of the polymer as well as in the depth of material. The main functional groups appeared during the treatment are unsaturated compounds, ketones, aldehydes, acids, esters, hydroxyl groups, peroxides and hydroperoxides.

As shown in Figure 2.3, the species  $R\cdot$ ,  $HO\cdot$  and  $HOO\cdot$  are responsible for the further abstraction of hydrogen from polypropylene leading to alcohol functions by abstractions of hydrogen from a neighbouring chain of polymer, but also and mainly, to the  $\beta$ -scissions. Moreover, the radicals obtained can react with oxygen giving hydroperoxides on the other hand; intramolecular rearrangement produces different species leading to esters and ketones (Robin, 2004).



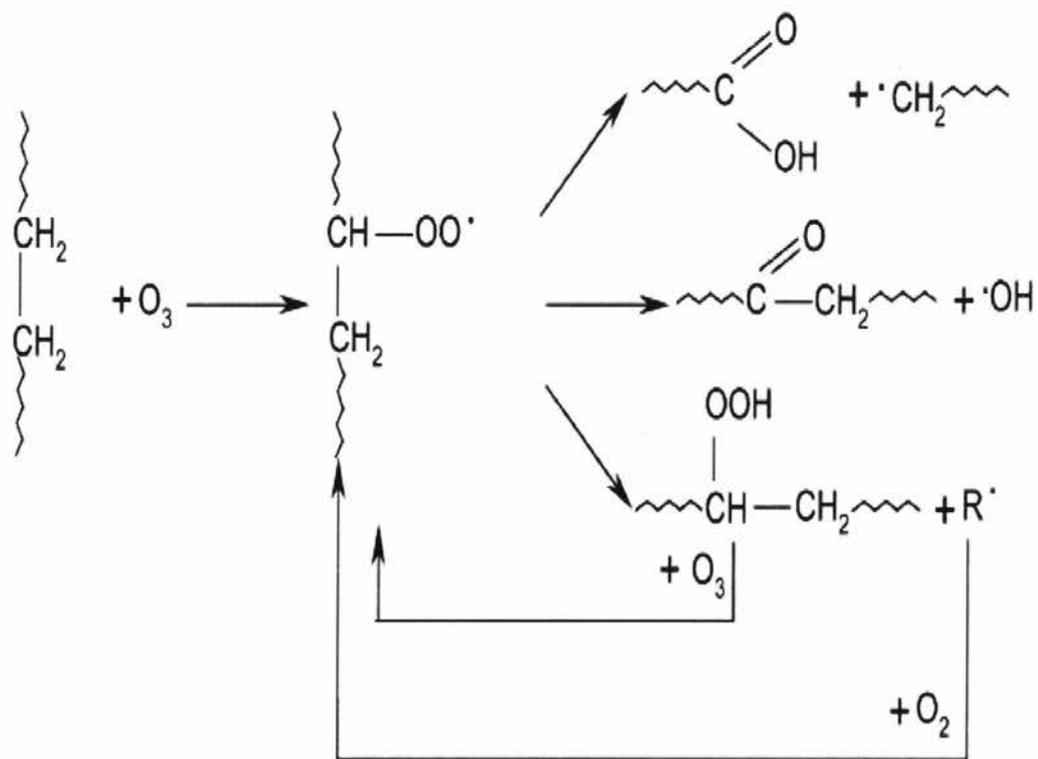


Figure 2.4 The reaction of ozone with polyethylene (Robin, 2004)

### 3. LITERATURE REVIEW

#### 3.1 Process of Ozonation

Fujimoto et al.(1993) used apparatus as shown in Figure 3.1 for ozonation of polyurethane(PU), silicone, poly methacrylate(PMMA), high density polyethylene (PE), poly hexafluoro propylene(6F),vinyl alcohol ethylene copolymer(VAECO), polyethylene terephthalate (PET) & poly tetrafluoroethylene (Teflon).

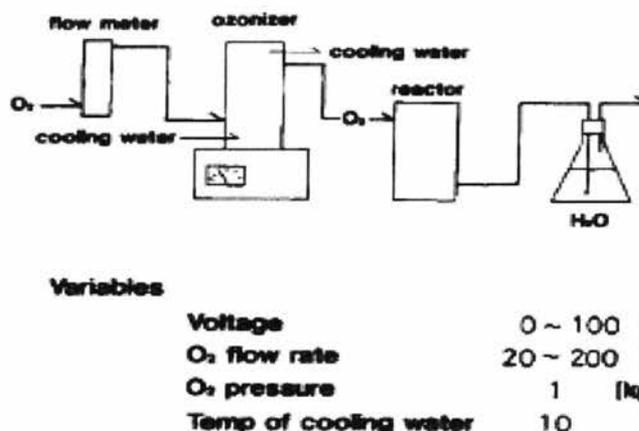


Figure 3.1 Experiment setup for ozonation (Fujimoto et al., 1993)

Ozone was generated by passing dried oxygen gas through a generator (ozonizer). The ozone concentration in gas was varied by changing the generator voltage and the oxygen flow rate. Then ozone gas was passed to a reactor where polymer films were placed. Polymer films were treated in a pyrex vessel for desirable time and process conditions. After ozone treatment, the films were degassed under vacuum for several hours to remove ozone absorbed in the films.

Wang et al. (2000) used experiment setup as shown in Figure 3.2 for ozonation of polypropylene microfiltration membranes. The ozone gas was passed through a water bath whose temperature was maintained at 30 °C and then was supplied to the ozonation reactor, where the membrane sheets were placed.

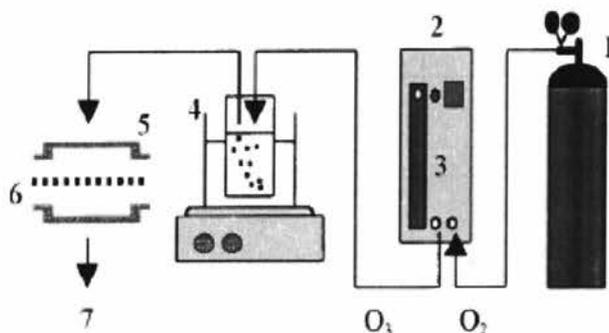


Figure 3.2 Experiment setup for ozonation of membranes. (1) Oxygen tank (2) Ozone generator (3) Flow meter (4) Water bath (5) Ozonation reactor (6) Membrane (7) Ozone trap with KI (Wang et al., 2000)

Gatenholm et al. (1997) used experimental setup as shown in Figure 3.3 for ozonation of microporous polypropylene film.

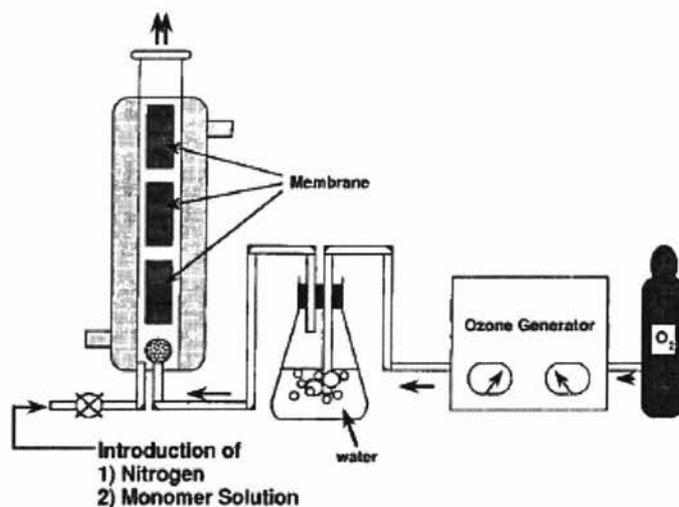


Figure 3.3 Schematic layout of the experimental setup for ozonation (Gatenholm et al., 1997)

Yuan et al. (2002) used thermostatic bath and sodium thiosulfate solution as shown in Figure 3.4 for ozonation of silicon rubber.

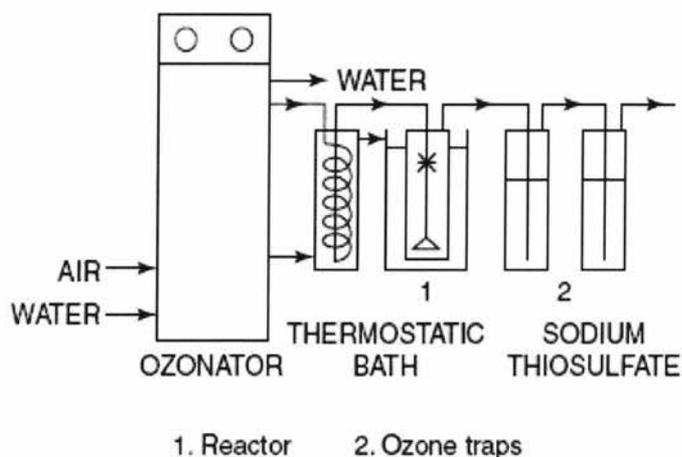


Figure 3.4 Flow diagrams for ozonation of polymer film (Yuan et al., 2002)

For above different processes of ozonation, reaction time and ozone concentration were varied and dependent on selection of polymers. The ozonation process described in Figure 3.1 was easy to handle. By ozonation, we can introduce peroxide function groups on the surface of polymers. The longer the reaction time, the more peroxides can be generated. But excessive ozone treatment can make the polymer mechanically fragile.

### 3.2 Gas Phase Ozonation Versus Aqueous Phase Ozonation

Most of researchers worked on gaseous phase ozonation. For aqueous ozonation, there is little information available in the literature. Kulik et al. (1997) gave comparison

of ozone in gas with aqueous solution for polypropylene (PP) and low density polyethylene (LDPE) as shown in Table 3.1.

Table 3.1 Peroxide concentration of ozonated PP and LDPE (Kulik et al., 1997)

Sample	Peroxide, (nmole/cm <sup>2</sup> )
PP	
5 min ozone in oxygen	11.3± 0.7
20 min ozone in oxygen	22.3± 1.2
20 min ozone in DI water, 43 °C	25.5± 1.5
LDPE	
5 min ozone in oxygen	12.4± 0.8
20 min ozone in oxygen	27.2± 1.2
30 min ozone in DI water, 43 °C	32.3± 1.4

From Table 3.1, we can conclude that peroxide generation increased with reaction time. It was slightly increased for ozonated PP films in aqueous media compare to gaseous counterpart. However, above results are applicable for the tested polymers only.

### 3.3 Effects of Additives and Catalysts on Ozonation

Effects of some additives as well as some catalysts on ozone reaction to enhance the generation of functional groups are an open area for further study (Dasgupta, 1990).

### 3.4 Polymers Ozonated by Other Researchers

Following are polymers which were ozonated by other researchers for surface modification.

- Polystyrene (PS) film, aqueous phase ozonation (Murakami et al., 2003)
- Polyurethane (PU) film, gas phase ozonation (Fujimoto et al., 1993), Thermoplastic Polyurethane (TPU) membrane, gas phase ozonation (Lin et al., 2005)
- Polypropylene (PP) films and PP microfiltration membrane, gas phase ozonation (Gatenholm et al., 1997), PP fibers and powder, aqueous phase ozonation (Dasgupta, 1990)
- Polyethylene (PE) film, gas phase ozonation (Fujimoto et al., 1993) , PE fibers and powder, aqueous phase ozonation (Dasgupta, 1990)
- Low density polyethylene (LDPE) film, gas phase ozonation and aqueous phase ozonation (Kulik et al., 1997)
- Poly-L-lactic Acid (PLLA) film, gas phase ozonation (Suh et al., 2001)
- Polytetrafluoroethylene (PTFE) film, aqueous phase ozonation (Tu et al., 2005)
- Silicone rubber film, gas phase ozonation (Zhou et al., 2005)
- Polyethylene terephthalate (PET) film and microfibres, gas phase ozonation (Ferreira et al., 2005)
- Polymethylmethacrylate (PMMA) film, gas phase ozonation (Ko et al., 2001)

### 3.5 Process of Graft Polymerization

The peroxides generated by ozonation are capable of initiating radical polymerization of monomers resulting graft polymerization onto the polymeric materials. Yuan et al. (2003) grafted N-N-dimethyl-N-methacryloyloxyethyl-N-(3-sulfopropyl) ammonium (DMMSA) onto the surface of Segment poly (ether-urethane) (SPEU) film as shown in Figure 3.5.

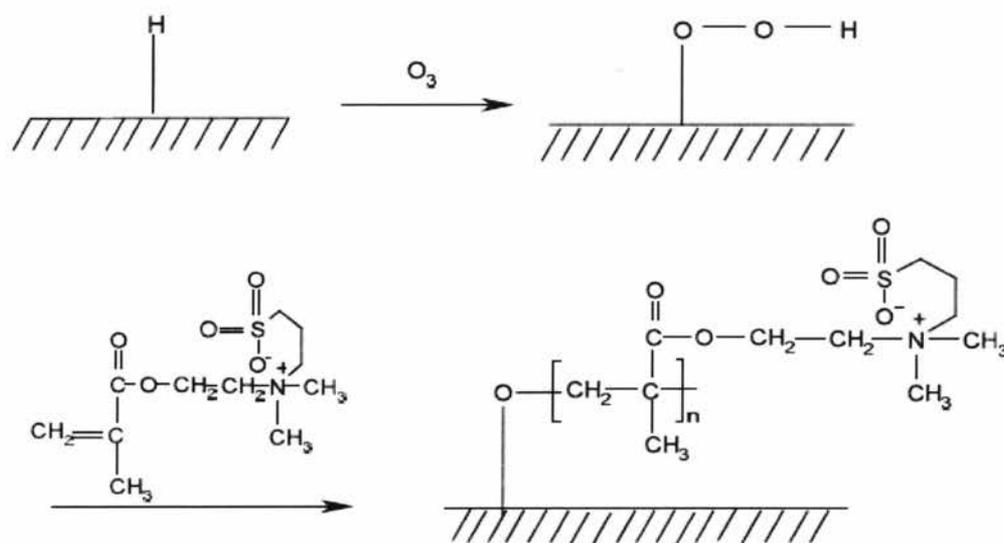


Figure 3.5 Scheme illustration of surface graft polymerization with DMMSA monomer (Yuan et al., 2003)

Graft copolymerization onto SPEU film was carried out at a set temperature with a deaerated aqueous solution of DMMSA of certain weight percent concentration (1, 3, 5, 8 and 10%). The grafting reaction is initiated by adding  $Fe^{2+}$  ions in order to decompose peroxides and reduce homopolymerization. Reaction time was 24 hrs. Reaction temperature, time, conc. of  $Fe^{+2}$  and concentration of monomer were varied to maximize the efficiency of DMMSA. To remove the homopolymer from the grafted film, the

grafted film is first washed with 40-50 °C saline water and immersed in saline water kept at 50 °C overnight under continuous stirring until constant weight (Yuan et al., 2002). The amount of DMMSA grafted monomer was determined by measuring the film weight before ( $W_0$ , g) and after ( $W_1$ , g) graft copolymerization. The graft yield is calculated according to formula equation-1.  $A$  is the area of film ( $\text{cm}^2$ ). Reported amounts are mean values of measurements on four specimens.

$$\text{Graft yield (g cm}^{-2}\text{)} = \frac{W_1 - W_0}{A} \times 100 \quad \text{----- (1)}$$

Zhou et al. (2005) grafted DMMCA onto the surface of silicon rubber film.

Kulik et al. (1997) used reducing agent such as ferrous ions, vitamin C and sodium borohydride to reduce the surfaces after ozone treatment and carried out free radical graft polymerization of soluble monomers (40 wt% distilled acrylic acid or methoxy (poly ethylene glycol 230) methacrylate) onto the ozonated LDPE film with the use of ceric ions.

Wang et al. (2000) performed hydrophilic modification of polypropylene micro filtration membranes with the introduction of peroxide onto the membrane surface by ozone treatment followed by graft polymerization with hydroxyethyl methacrylate (HEMA). Figure 3.6 shows above graft polymerization of HEMA onto the membrane surface.

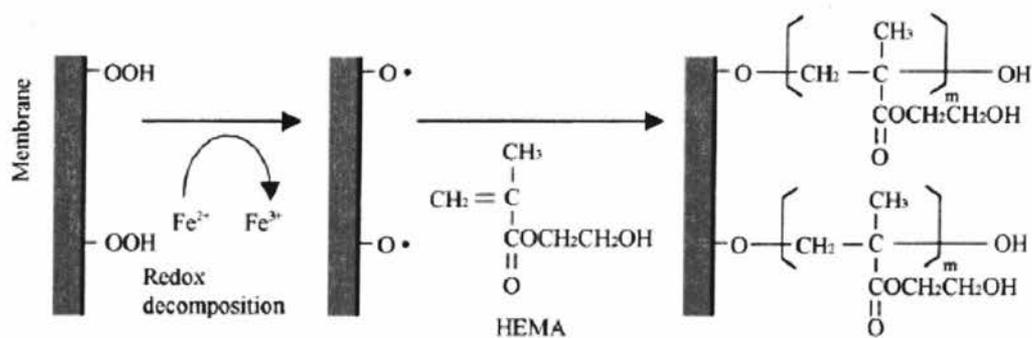


Figure 3.6 Scheme illustration of ozone-induced graft polymerization with HEMA monomer (Wang et al., 2000)

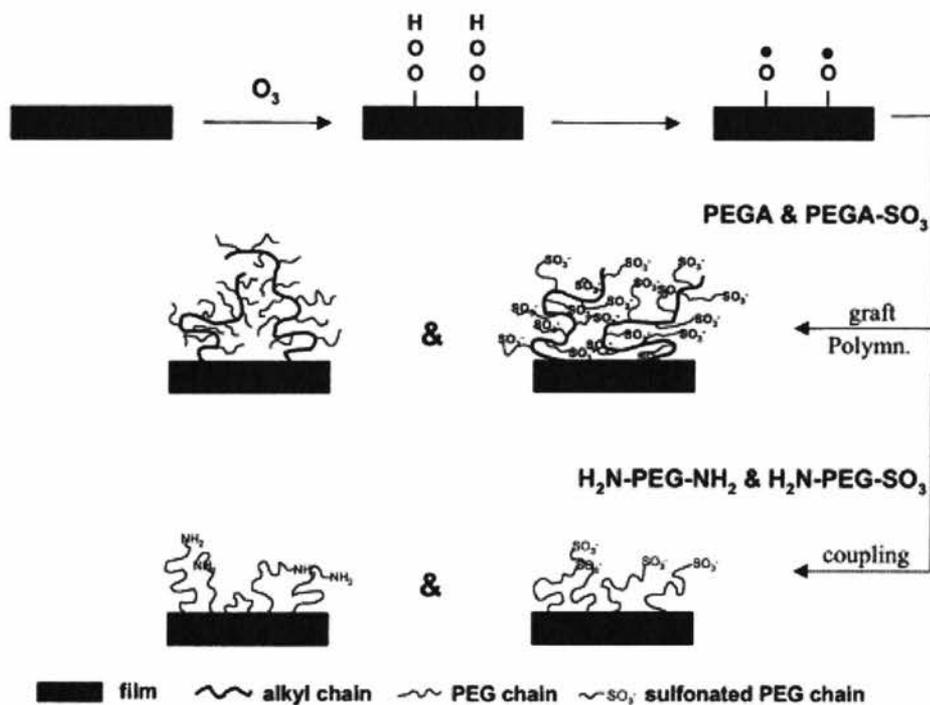


Figure 3.7 Immobilization of poly(ethylene glycol) or its sulfonate onto polymer surface (Ko et al., 2001)

Ko et al., (2001) developed a novel surface modification method for immobilization of poly(ethylene glycol) or its sulfonate onto PU, PMMA and PE polymers surfaces by ozone oxidation as shown in Figure 3.7.

### **3.6 Monomers used by Other Researchers**

Following are monomers which were attached by other researchers during Graft polymerization.

- Acrylic acid (Tu et al., 2005)
- Acrylamide (Tu et al., 2005)
- 2-hydroxy-ethyl methacrylate (HEMA) (Gatenholm et al.,1997)(Wang et al., 2000)
- Glycidyl methacrylate (Tu et al., 2005)
- N-N-dimethyl(methacryloyloxyethyl) ammonium propane sulfonate (DMAPS) (Yuan et al., 2002)
- O-butyrylchitosan (OBCS) (Mao et al., 2005)
- N-N-dimethyl-N-methacryloyloxyethyl-N-(3-sulfopropyl)ammonium (DMMSA) (Zhou et al., 2005) (Yuan et al., 2003)
- Sulfonated polyethylene glycol (PEG-SO<sub>3</sub>) (Ko et al., 2001)
- 2-(2- bromoisobutyryloxy)ethyl acrylate (BIEA) (Tu et al., 2005)
- N-N-dimethyl-N-methylloxyethyl-N-(2-carboxyethyl)ammonium (DMMCA) (Zhou et al., 2005)

### **3.7 Analytical Methods**

#### **3.7.1 Determination of peroxides generated on polymers**

Amount of peroxides produced on the treated films can be determined by the following four methods.

#### 3.7.1.1 Iodide method

This method involves an oxidation of sodium iodide by peroxides in the presence of ferric chloride. The treated films are kept at 60°C for 10 min in benzene-isopropyl alcohol (1:6, by vol.) solution containing saturated sodium iodide and 1 ppm ferric chloride. After addition of water to stop the reaction, the oxidized iodine is measured as triiodide anion from the absorbance of the solution at 360 nm with the molar absorptivity of  $2.3 \times 10^4$  l/mol cm (Fujimoto et al., 1993).

#### 3.7.1.2 DPPH method

The treated films are put in benzene solution of 1, 1-diphenyl-2-picrylhydrazyl (DPPH, radical scavenger) and kept at 70°C for 24 h to decompose the peroxides. The DPPH molecules consumed by binding to the radicals formed are quantified from the difference in transmittance at 520 nm between the virgin and the treated film using  $1.8 \times 10^4$  L mol<sup>-1</sup> cm<sup>-1</sup> as the molar absorptivity of DPPH. Based on this measurement, the amount of hydroperoxide consumed is calculated (Fujimoto et al., 1993).

#### 3.7.1.3 Peroxidase method

The reduction of by glutathione (GSH), catalyzed by glutathione peroxidase, is followed by measuring the coupled oxidation of nicotinamide adenine dinucleotide phosphate (reduced) (NADPH) in the presence of glutathione reductase. An aqueous solution is prepared from reduced GSH, GSH reductase, NADPH, and GSH peroxidase, and then flushed with nitrogen to minimize the autooxidation of GSH. The treated films are placed in the solution at 25°C for 30 min and the extent of NADPH oxidation is

determined from the absorption at 340 nm with the molar absorptivity of NADPH at  $6.2 \times 10^3$  l/mol cm (Fujimoto et al., 1993).

#### 3.7.1.4 Standard Iodometric Method

In this method, 25 ml iso-propanol is added to the sample, followed by 1 ml of saturated potassium iodide and 1 ml of glacial acetic acid. Dried sample is immersed into solution and the mixture is heated almost to boiling, kept at incipient boiling for 2-5 min with occasional swirling and without cooling, titrated with standard sodium thiosulfate until the yellow color disappeared (Kokatnur and Jelling, 1941). It is possible to titrate solutions containing a peroxygen as low as  $10^{-4}$  N to with 0.1 ml using 0.005 N thiosulfate. This method is able to report small amounts of peroxides to big amounts of peroxides (Yuan et al., 2003).

#### 3.7.2 Contact angle

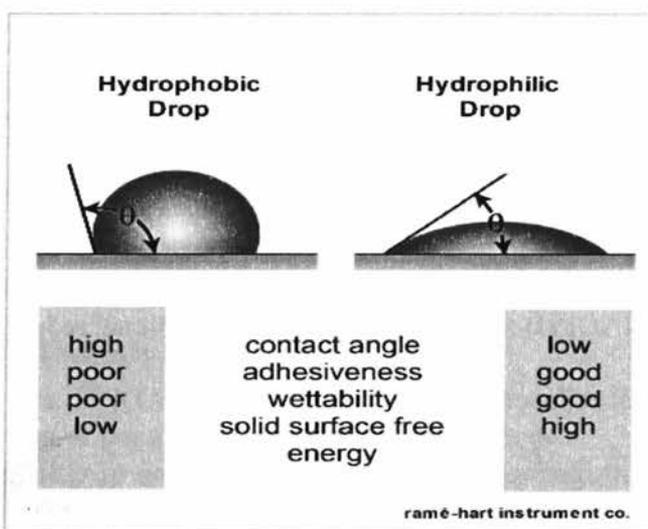


Figure 3.8 Contact angle measurement

The contact angle ( $\theta$ ) of the polymeric surface is measured to quantify the change in its hydrophilicity. Large value of contact angle indicates hydrophobic surface while small contact angle means hydrophilic surface as shown in Figure 3.8. Hydrophilic surface has low contact angle, good adhesiveness, good wettability and high solid surface free energy. While hydrophobic surface has high contact angle, poor adhesiveness, poor wettability and low solid surface free energy.

Contact angle measurements are performed using an optical contact angle goniometer (Rame- Hart 100) or Data Physics equipped with video CCD-camera and software (Mao et al., 2005, Ferreira et al., 2005).

Ferreira et al. (2005) studied contact angle measurement of ozonated PET films. Untreated or ozonated PET films ( $2 \times 2 \text{ cm}^2$ ) were placed in a closed, thermostated chamber ( $25^\circ\text{C}$ ) saturated with water in order to prevent its evaporation. Static contact angles were measured by placing purified water droplet ( $3 \mu\text{L}$ ) onto sample surface from a glass syringe. The readings were stabilized and taken after 1 min of water contact with sample. Subsequently, the water droplet was slowly increased or decreased in volume in order to obtain the advancing or receding water contact angles, respectively. Every contact angle was determined at four different spots on the sample. It is generally known that advancing angles indicate hydrophobicity while receding ones express hydrophilicity of surfaces.

Mao et al. (2005) measured contact angle measurements of OBCS grafted nylon films using a goniometer (Rame – hart-100). The water contact angle for each OBCS grafted nylon sample was measured five times by a sessile drop method at room temperature. Drops of purified water ( $3 \mu\text{l}$ ) were deposited onto the modified nylon films,

and the readings were stabilized and taken in 60s after dropping. Water sessile drops were deposited from a glass syringe onto the samples surfaces, and the water contact angle was measured after a defined period of time, in order to allow the establishment of equilibrium.

### **3.7.3 Mechanical strength measurement**

Mechanical measurements including tensile strength and percentage elongation at break were measured and evaluated for the treated samples using a Universal Testing Machine. The tensile strength is the stress at the maximum on the stress-strain curve. The tensile strength was determined at a cross-head speed of 5 mm/min. The measurements were carried out according to ASTM D638 type V for membranes (Wang et al., 2000) as well as Standard Method 2000, D 3822-96 for polymeric fabrics (Michael et al., 2004).

### **3.7.4 Attenuated Total Reflection Infrared Spectroscopy (ATR-IR)**

The purpose of this analysis was to examine effect of graft polymerization and to introduce function groups during ozonation. Attenuated total reflection infrared spectroscopy (ATR-IR) is used for analysis of the surface functional groups of materials. Ferreira et al. (2005) performed this analysis for PET films with a spectrophotometer (Perkin-Elmer, model 2000) coupled with an ATR (split-pea) and a nitrogen cooled mercury cadmium telluride (MCT) detector. One hundred scans were performed with a resolution of 4  $\text{cm}^{-1}$ . In ATR-IR measurements, the penetrations depth (DP) of the radiation within the polymer film was calculated according to Harrick equation:

$$DP = \frac{1}{2\pi\nu N_c (\sin^2 \theta - N_{sc}^2)^{1/2}}$$

Where  $\nu$  is the wave number ( $\text{cm}^{-1}$ ).  $N_c$  is the refraction index of the crystal (silicon, 3.42),  $\theta$  is the incidence angle of the infrared radiation into the crystal ( $45^\circ$ ),  $N_{sc}$  is the ratio between the refraction index of PET sample (1.64) and the crystal.

Gatenholm et al. (1997) had done this analysis for PP films and microporous membranes with a Perkin – Elmer 1720X Fourier transform infrared spectrometer, equipped with a liquid nitrogen cooled mercury/cadmium/telluride (MCT) detector with a resolution of  $2 \text{ cm}^{-1}$ . One hundred scans were recorded on each sample.

Tu et al. (2005) were taken ATR-FTIR spectra with a Perkin-Elmer spectrum One FTIR equipped with a multiple internal reflectance apparatus and a ZnSe prism as an internal reflection element.

### 3.7.5 Electron Spectroscopy for Chemical Analysis (ESCA)

Surface compositions determined from ESCA spectra were used to examine the oxygen content of the ozone-treated surfaces. Gatenholm et al.(1997) performed this analysis for PP films and microporous membranes with an SSX-100 spectrometer (Surface Science Instruments, Mountain View, CA) using a monochromatic AlK X-ray source, a detection system with a  $30^\circ$  solid angle acceptance, and a hemispherical analyzer. A 5 eV flood gun was applied to compensate for the surface charging of polymer samples. The x- ray spot size (analyzing area) on the sample surfaces was about  $1000 \mu\text{m}$  in diameter. A standard  $55^\circ$  take-off angles (the angle between the surface

normal and the axis of the analyzer lens) was used for surface scans. The hydrocarbon peak in high resolution  $C_{1s}$  spectra was assigned at 285 eV.

### **3.7.6 Protein adsorption test**

Protein adsorption test were carried out to learn the extent of interaction of the treated surface with protein in aqueous solution. Bovine fibrinogen was used for preparing protein solution in PBS (Phosphate buffer saline, PH 7.4).  $^{125}I$ -fibrinogen was added to pure fibrinogen solution and then protein concentrations were adjusted with phosphate buffer saline to 3 and 1  $mg\ ml^{-1}$  for adsorption of Bovine fibrinogen. Protein adsorption was carried out at 37°C by placing five pieces of treated polymer film of 1 × 1 cm in 2 ml of protein solution for each experiment. After allowing the adsorption to proceed for 3 h, the films were first rinsed with PBS without taking them out from the protein solution and then blotted with tissue paper. The radioactivity of the protein-adsorbed films was measured with a  $\gamma$ -ray scintillation counter. Generally three-four readings were performed on the different pieces cut from the same film (Fujimoto et al., 1993).

### **3.7.7 Platelet adhesion test**

In order to determine the potential blood compatibility of the materials, platelet adhesion study is conducted since platelet adhesion is one of the most important steps during blood coagulation on artificial surfaces. The grafted films were rinsed with PBS first and contacted at 37 °C, respectively, with freshly prepared PRP (Platelet- rich plasma) of human blood for 300 min and with fresh blood activated by  $CaCl_2$  for 60 and

120 min. Samples were rinsed with PBS and treated with 2.5% glutaraldehyde for 30 min at room temperature. Then the samples were rinsed with PBS and dehydrated by systemic immersion in a series of ethanol-water solutions [50, 60, 70, 80, 90, 95, 100% (v/v)] for 30 min each and allowed to evaporate at room temperature. Then sample surfaces are gold deposited in vacuum and examined by scanning electron microscopy. Experiments were done three times (Yuan et al., 2003).

In other method, 0.6 mL PRP was placed on polymeric films and allowed to stand for 1 h at 37 °C. Then the films was washed with PBS and put into 2 mL of 0.1 M phosphate buffer containing 0.5% Triton-X 100 to lyse the adhered platelets. Lactic acid dehydrogenase (LDH) activity of the lysate was determined with an enzymatic method to count the adhered platelets. Experiments were done five times for same film using different PRP (Fujimoto et al., 1993).

As per specific requirements, following analysis done for polymer films and membranes.

- Time-of-flight secondary ion mass spectroscopy (Kulik et al., 1997 )
- Molecular weight determination (Gatenholm et al., 1997)
- Differential scanning calorimetry (Gatenholm et al., 1997)
- Streaming potential measurement (Fujimoto et al., 1993)
- Scanning electron microscopy ( Sainbayar et al., 2001)
- Bubble point measurement (Wang et al., 2000)

### 3.8 Effect of Ozonation on Polymer Surfaces

#### 3.8.1 A concentration of peroxide as a function of ozonation time

Fujimoto et al. (1993) studied the concentration of peroxide on the PU films at different voltages of ozonizer as shown in Figure 3.9. From Figure 3.9, it is observed that the concentration of peroxides monotonously increased with the treatment time and application of higher voltage for ozone generation produced a higher density of peroxides. This was because the concentration of ozone increased with the increasing voltage of the ozoniser. But the excessive ozone treatment could make the polymer mechanically fragile. So ozone oxidation time should be optimized such a way to get better efficiency of ozone treatment. It follows that the peroxide production can be readily controlled by the ozone concentration & the ozone exposure time (Fujimoto et al., 1993).

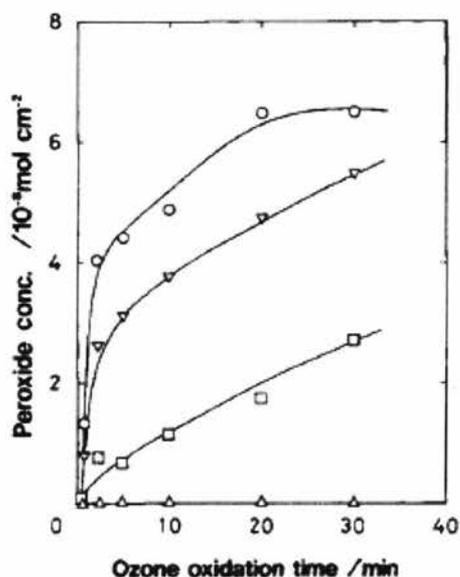


Figure 3.9 Formation of peroxide on the PU film by ozone oxidation at different voltages (iodide method): (Δ) 20, (□) 30, (▽) 60, (○) 100 V (Fujimoto et al., 1993)

Peroxide concentrations determined with different methods as shown in Table 3.2.

From Table 3.2, it was concluded that Iodide method gave the highest concentration (Fujimoto et al., 1993).

Table 3.2 Peroxide concentrations determined with Iodide, Peroxidase and DPPH methods (Fujimoto et al., 1993)

Applied Voltage* (V)	Method	Oxidation Time (min)	Peroxide Concentration ( $\times 10^8 \text{ mol cm}^{-2}$ )
30	Iodide	3	0.7
		30	3.0
	Peroxidase	3	0.1
		30	0.4
60	Iodide	3	2.6
		30	8.0
	Peroxidase	3	0.8
		30	1.2
	DPPH	20	1.4

\* For ozone generation.

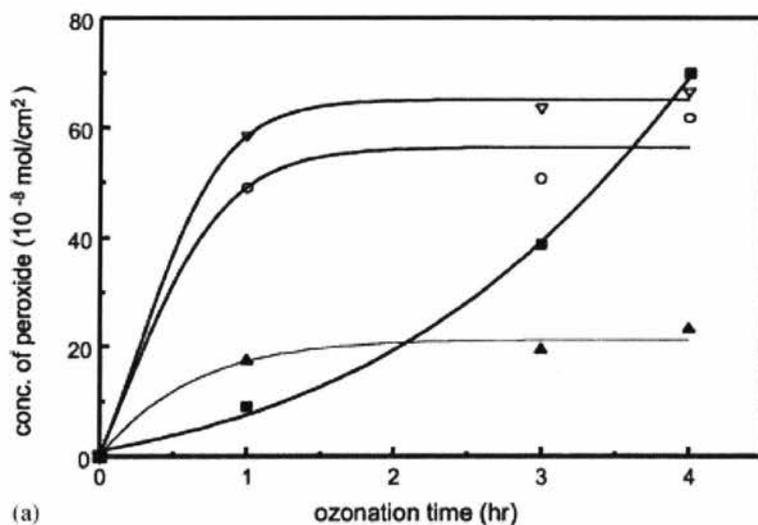


Figure 3.10 Concentration of peroxide generated at various ozonation time: ( $\nabla$ ) PU, ( $\circ$ ) silicone, ( $\blacksquare$ ) PMMA, ( $\blacktriangle$ ) PE (Ko et al., 2001)

Ko et al. (2001) studied concentration of peroxide on the PU, Silicone, PMMA and PE films at various ozonation times as shown in above Figure 3.10. They observed that concentration of peroxides increased fast at first one hour, then slowly increased, atleast did not change for PU, Silicone and PE films. This might be due to that the film surfaces were almost saturated by the hydroperoxide groups. PU, silicone exhibited a high concentration of peroxide and fast increased as they are soft materials having high ozone permeability. But PE showed low peroxide concentration due to hard and crystalline. The peroxides increased gradually in PMMA film because of an amorphous polymer.

### 3.8.2 Contact angle of modified polymer surfaces

Ko et al. (2001) studied receding contact angles of ozonated PU, Silicone, PMMA and PE polymers at various ozonation times as shown in Figure 3.11.

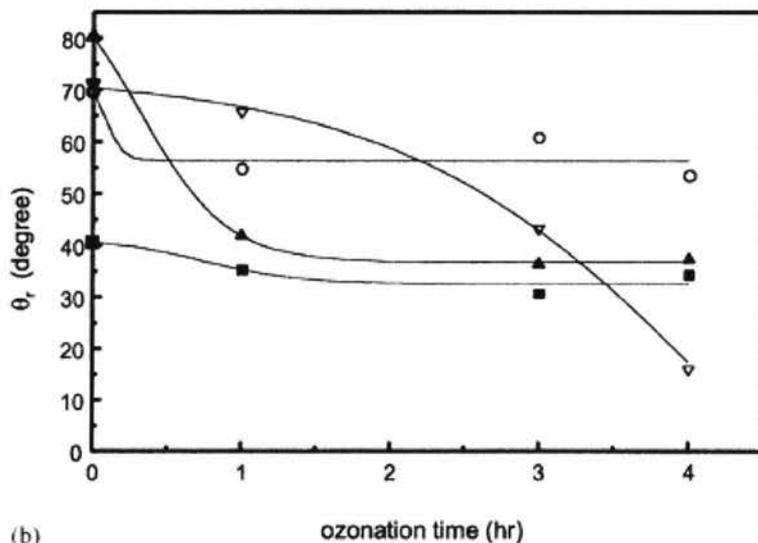


Figure 3.11 Receding contact angles,  $\theta_r$ , of ozonated polymers at various ozonation times: ( $\nabla$ ) PU, ( $\circ$ ) silicone, ( $\blacksquare$ ) PMMA, ( $\blacktriangle$ ) PE (Ko et al., 2001)

Figure 3.12 shows receding contact angles of PEGA grafted above PMMA, PU, Silicone films for 24 h after various ozonation times. In case of PMMA and PU, the receding angle decreased substantially with increased ozonation time & reached to complete wet state after 4 & 3 h treatment respectively (Ko et al., 2001). Similar behaviour was observed on silicone although plateau value was relatively high (around 30°).

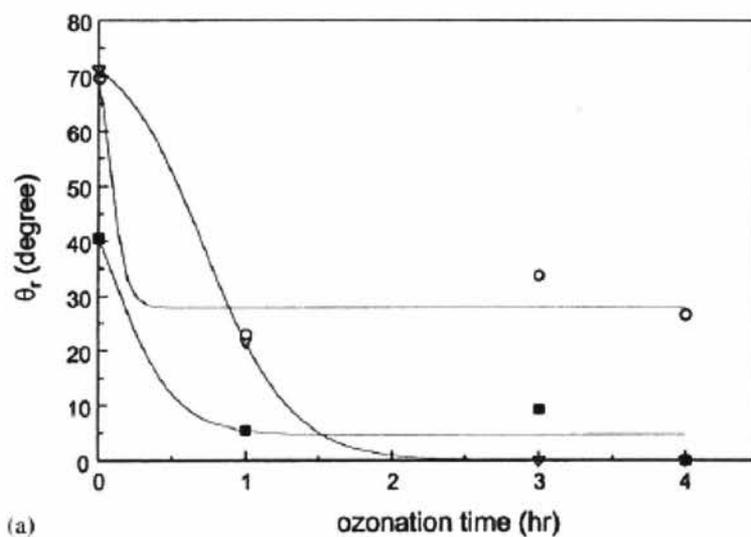


Figure 3.12 Receding contact angle of PEGA grafted polymers for 24 h after various ozonation time: ( $\nabla$ ) PU, ( $\circ$ ) silicone, ( $\blacksquare$ ) PMMA (Ko et al., 2001)

Table 3.3 Contact angles of ozone treated PET films (Ferreira et al., 2005)

Ozonation time (h)	Treatment	$\theta$ static (°)	$\theta$ advancing (°)	$\theta$ receding (°)
0	Unwashed	$72.5 \pm 2.9$	$78.4 \pm 1.4$	$51.1 \pm 2.1$
1		$68.1 \pm 1.1$	$74.5 \pm 0.8$	$42.2 \pm 1.8$
3		$60.6 \pm 0.3$	$66.0 \pm 2.6$	$36.2 \pm 1.1$
6		$50.1 \pm 1.0$	$54.1 \pm 0.8$	$20.7 \pm 2.5$
1	Washed	$66.4 \pm 0.9$	$70.3 \pm 1.0$	$44.1 \pm 2.4$
3		$61.6 \pm 1.8$	$67.7 \pm 1.4$	$36.0 \pm 1.8$
6		$57.4 \pm 1.5$	$61.9 \pm 1.1$	$23.3 \pm 3.2$

Ferreira et al. (2005) studies contact angle measurements of pHEMA hydrogels by treating PET with ozone. The ozone treatment of PET was followed by static or dynamic (advancing & receding) water contact angle measurement. The advancing water contact angle is most sensitive to the low-energy (unmodified) components of the surface. The receding contact angle tends to be more sensitive to the high – energy, oxidation groups introduced by the surface treatment (Andrade et al., 1985). From Table 3.3, as expected the wettability of PET surface increases as a function of ozonation time as shown by the decrease in static, advancing & receding contact angles.

### 3.8.3 Mechanical strength of modified polymer surfaces

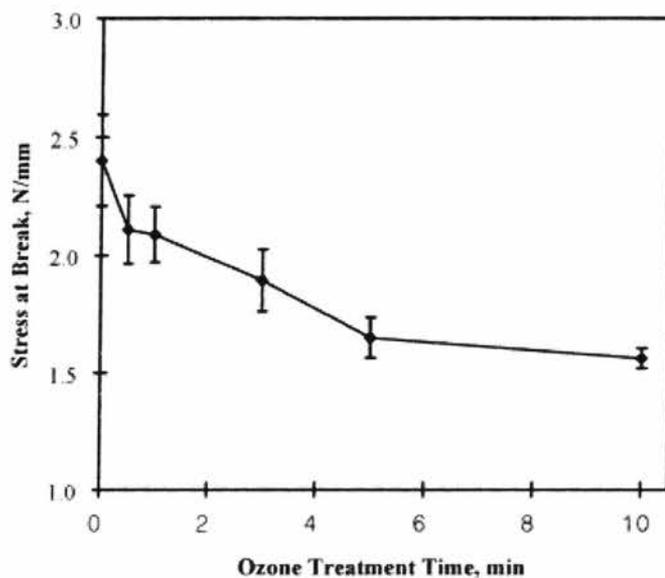


Figure 3.13 Effect of ozone treatment time on tensile strength (Wang et al., 2000)

Wang et al. (2000) studied effect of ozone treatment time on tensile strength of ozone treated PP membrane as shown in Figure 3.13. In this figure, the maximum stress

at break steadily decreased as the ozone treatment time increased that mean tensile strength of treated film was wool decreased by approximately 40% compared to that of the virgin membrane. Longer ozonation time made the membrane mechanically fragile since ozone attacked the backbone of the PP membrane

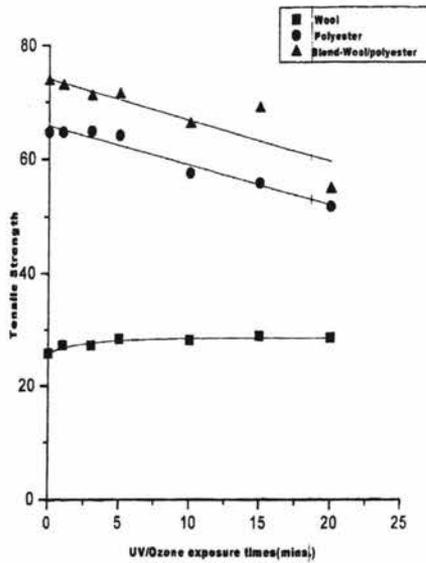


Figure 3.14a

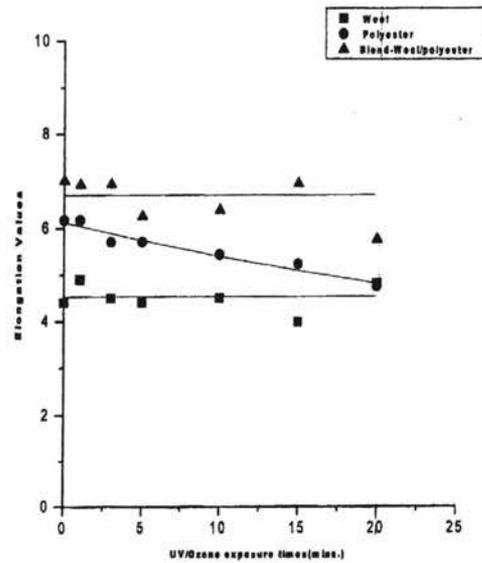


Figure 3.14b

Figure 3.14 a-b. The change in the tensile strength values and change in elongation values with different UV/Ozone times for three examined fabrics (Michael et al., 2004)

Michael et al. (2004) studied the changes in the mechanical properties of tensile strength, percentage elongation at break of the examined fabrics at different UV/Ozone exposure times as shown in Figures 3.14a and 3.14b. Results shown that tensile strength of polyester and blended wool/polyester decreased with UV/ozone exposure times increased. Elongation values of polyester decreased with UV/ozone exposure times increased while elongation values of wool and blended wool/polyester remained same.

### 3.8.4 Effect of ozonation on FTIR spectrum

Wang et al. (2000) studied FT-IR spectra of virgin and HEMA grafted Polypropylene microfiltration as shown in above Figure 3.15. They were observed that the presence of HEMA graft on the membrane surface was confirmed by the C=O vibration peak at  $1725\text{ cm}^{-1}$ . The peak intensity at  $1725\text{ cm}^{-1}$  was increased with increasing the ozone treatment time suggesting that a larger amount of HEMA was grafted with larger ozonation time.

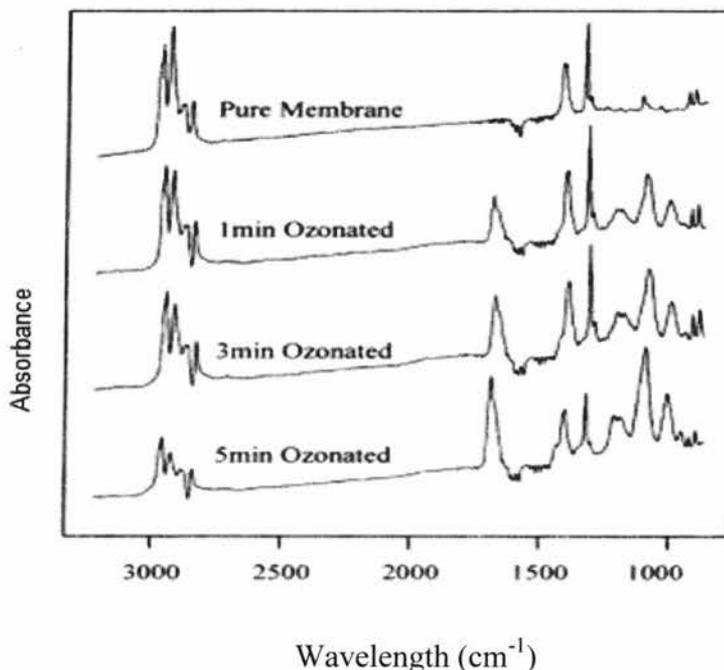


Figure 3.15 FT-IR spectra of virgin and grafted membranes (Wang et al., 2000)

Yanagisawa et al. (2006) studied ATR/IR spectra of PS film surface with and without the modification by the  $\text{O}_3/\text{UV}$  treatment in aqueous phase as shown in Figure 3.16. When compared with the spectrum of the non-treated PS film(c), the spectrum of the PS film modified in water (PS-W film) had two peaks at  $3400$  and  $1715\text{ cm}^{-1}$  assigned to OH and C=O groups (arrows in (a)), respectively. The PS film modified in the aqueous

ammonia solution (PS-A film) had two new peaks at 3333 and 1673  $\text{cm}^{-1}$  assigned to NH and CONH groups (arrows in (b)). These functional groups on both films were introduced by the reaction of original PS films with reactive radical species generated in the  $\text{O}_3/\text{UV}$  treatment (Yanagisawa et al., 2006).

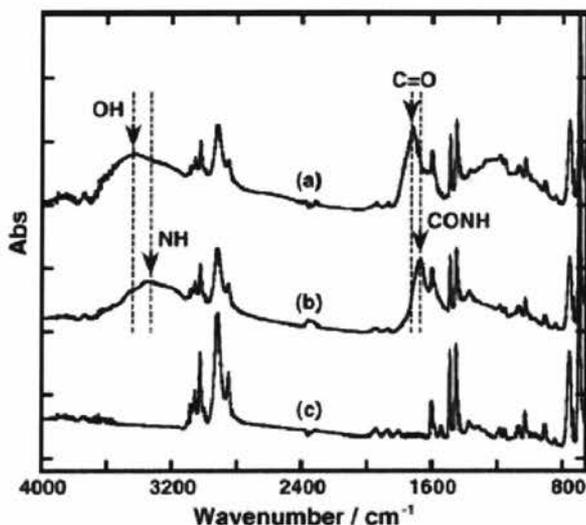


Figure 3.16 ATR/IR spectra of (a) PS-W, (b) PS-A and (c) original PS films (Yanagisawa et al., 2006)

Yuan et al. (2003) gave ATR-FTIR spectra of SPEU film (a) and SPEU-g-PDMMSA film (b) as shown in Figure 3.17. It could be seen from spectrum of the SPEU film, the NH absorption appeared at 3325.7 and 1535.6  $\text{cm}^{-1}$ .

The urethane -  $\text{NHCOO}$  - carbonyl absorption was split into two peaks 1731.3  $\text{cm}^{-1}$  (free carbonyl) and 1704.9  $\text{cm}^{-1}$  (bonded carbonyl). The peaks at 1080.4 and 1110.7  $\text{cm}^{-1}$  were the absorption of stretching of the C-O-C band. The NCO adsorption (2250.0  $\text{cm}^{-1}$ ) and the OH in polyether absorption (3500.0  $\text{cm}^{-1}$ ) all disappeared. It indicated the completion of the reaction. From AIR-FITR spectrum (b) of SPEU-g- PDMMSA film, the absorptions of  $\text{SO}_3^-$  (1180.2, 1037  $\text{cm}^{-1}$ ),  $-\text{N}^+(\text{CH}_3)_2\text{CH}_2^-$

( $965.1\text{ cm}^{-1}$ ) and  $\text{-COO-}$  ( $1723.8\text{ cm}^{-1}$ ) were detected. It could be confirmed that DMMSA had been grafted onto the SPEU film surface (Yuan et al., 2003).

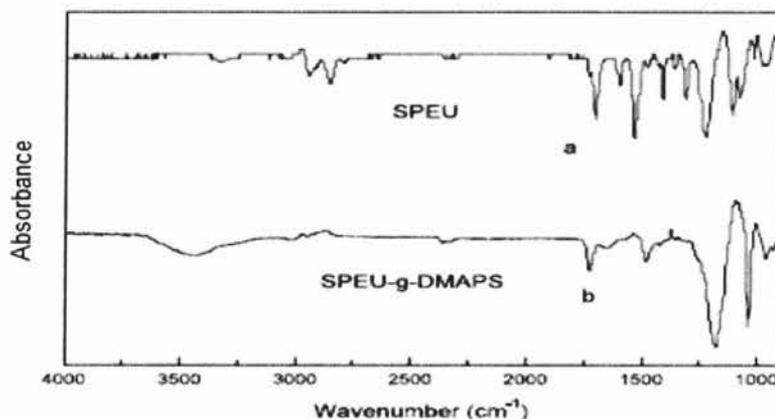


Figure 3.17 ATR-FTIR spectra of SPEU film (a) and SPEU-g- PDMMSA film (b) graft copolymerization condition: 10% DMMSA, 24 h and 37 °C (Yuan et al., 2003)

Gatenholm et al. (1997) reported the effect of ozonation time on the chemical composition by FT-IR shown in Figure 3.18. They were observed that the peak at 1680-1760  $\text{cm}^{-1}$ , characteristic for carbonyl absorption increased in intensity as ozonation time increased.

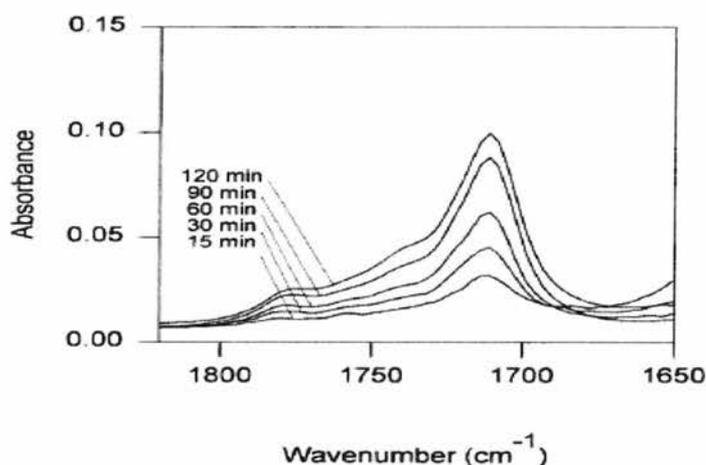


Figure 3.18 Effect of ozonation time on films shown by FT-IR (Gatenholm et al., 1997)

### 3.8.5 The influence of various conditions on graft yield

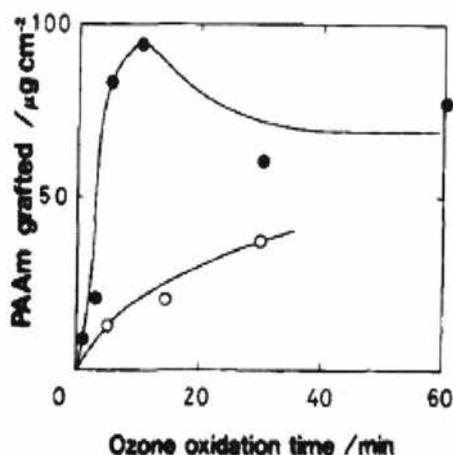


Figure 3.19 Effect of the ozone oxidation time on the density of PAAm grafted : (○) PE (100 V, 120 L h<sup>-1</sup>), (●) PU (50 V, 50 L h<sup>-1</sup>) (Fujimoto et al., 1993)

Fujimoto et al. (1993) showed the effect of ozone treatment time on the graft polymerization of AAm onto PU and PE films shown in Figure 3.19. They were observed that lower graft densities were obtained on the PE film (higher ozone voltage) than on the PU film (lower ozone voltage). They also observed that ozone treatment gave higher graft densities than plasma treatment when comparison was made on graft polymerization performed under the most optimal conditions. However polymer degradation caused by the ozone attack must be taken into account, because the PU film became opaque when oxidized with ozone at 50 v for 60 min. The deterioration of PU by the ozone attack may give an explanation for the decrease in graft density at prolonged ozone treatment (Fujimoto et al., 1993).

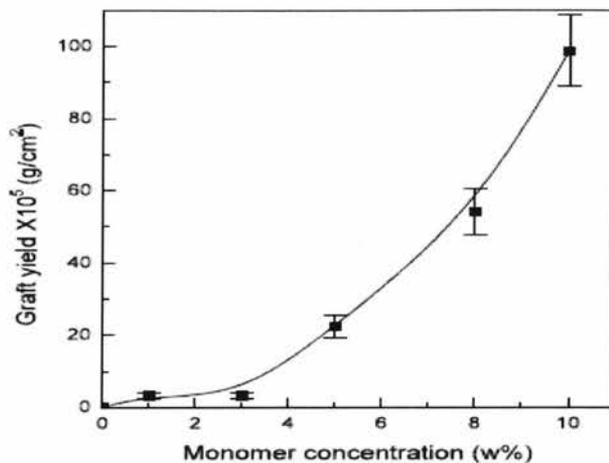


Figure 3.20 Effect of DMMSA concentrations on graft yield at 24 h and 37 °C (Yuan et al., 2003)

Yuan et al. (2003) studied the influence of graft copolymerization conditions such as monomer solution concentration, graft copolymerization time and temperature on graft yield. Figure 3.20 showed the amount of DMMSA grafted onto segmented poly (ether urethane) films against various DMMSA concentrations (wt %). Graft copolymerization took place in high yields with increasing DMMSA concentration.

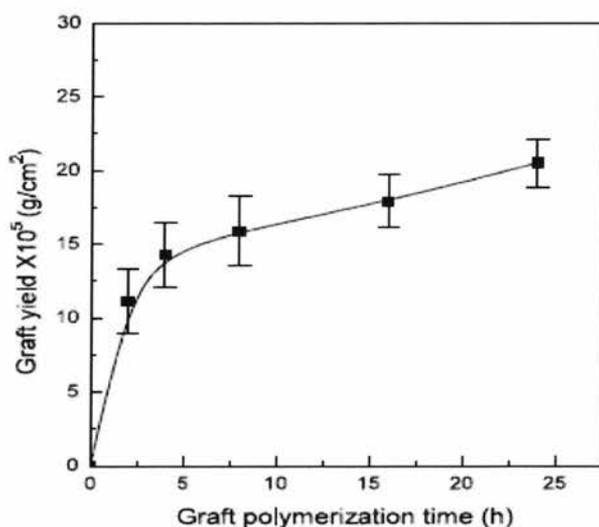


Figure 3.21 Effect of graft copolymerization time on graft yield at 5% DMMSA and 37°C (Yuan et al., 2003)

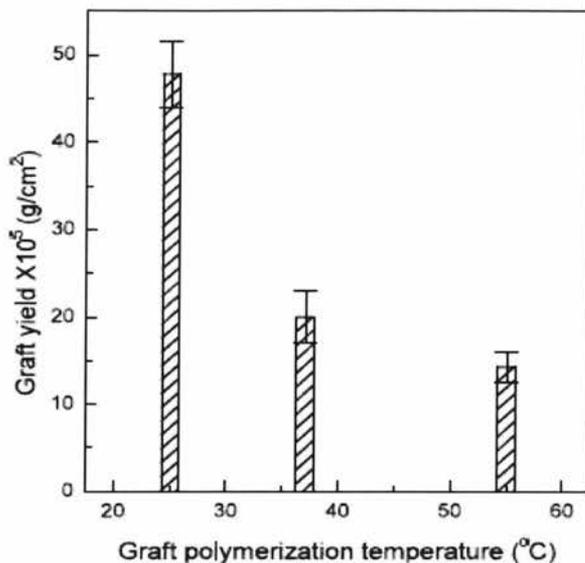


Figure 3.22 Effect of graft copolymerization temperature on graft yield at 5% DMMSA and 24 h (Yuan et al., 2003)

The effect of graft copolymerization time and temperature was showed in Figures 3.21 and 3.22. It could be detected from Figure 3.21 that the great yield increased rapidly at the first 4 h, the graft yield increased with the increase of the copolymerization time. After 8 h, the graft yield increased slowly. It could be found from Figure 3.22 that graft yield were high at 25°C copolymerization temperature and low at 55°C. This might be due to that the chain termination reaction on the film surface and the homopolymerization of monomer in solution increased with increasing copolymerization temperature.

### 3.8.6 Effect of protein adsorption on modified surface

Zhou et al. (2005) studied protein adsorption on DMMCA grafted silicone surface under series of monomer concentration as shown in Figure 3.23. Results shown that adsorption of protein decreased drastically at the beginning (2-5 wt% of DMMCA); the amount of protein adsorption decreased slightly when DMMCA concentration increased

from 5 to 15%. But when the DMMCA concentration increased from 15 to 20%, the amount of protein absorbance increased on the contrary, it was like that excessive grafting caused protein diffusion into the thick grafted layer region.

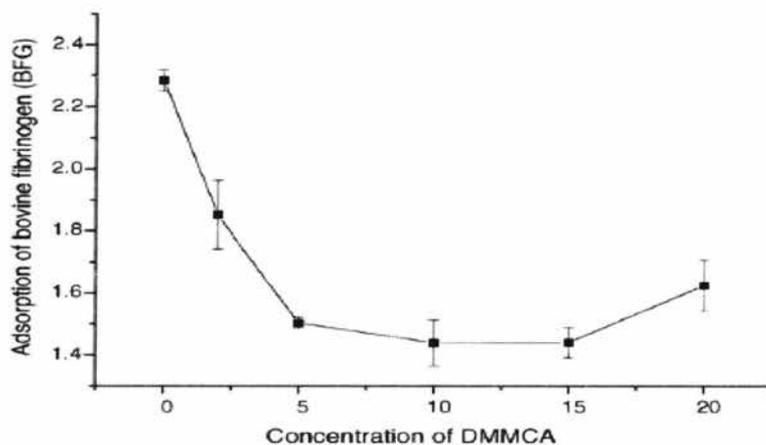


Figure 3.23 Comparison of bovine fibrinogen adsorption by blank silicone and grafted silicone under series of monomer concentration ( Zhou et al., 2005)

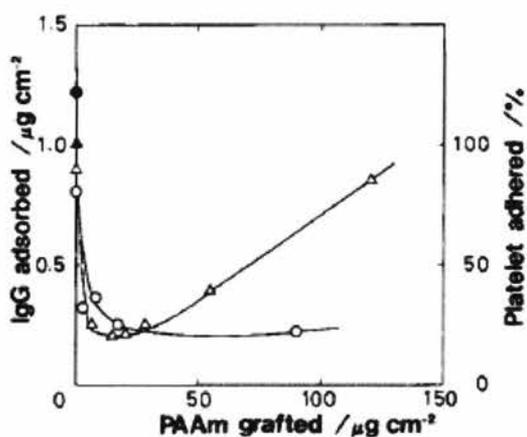


Figure 3.24 Adsorption of  $^{125}\text{I}$ -labeled IgG and adhesion of platelet to the grafted PU film as a function of graft density: ( $\Delta$ ) IgG [( $\blacktriangle$ ) virgin], ( $\circ$ ) platelet [( $\bullet$ ) virgin] (Fujimoto et al., 1993)

Same thing was happened in studied of Fujimoto et al. (1993) as shown in Figure 3.24. This finding indicates that it is important to select the condition for graft polymerization to minimize the protein adsorption. Figure 3.25 shown that protein adsorption decreased with the ozone oxidation time.

### 3.8.7 Effect of platelet adhesion on modified surface

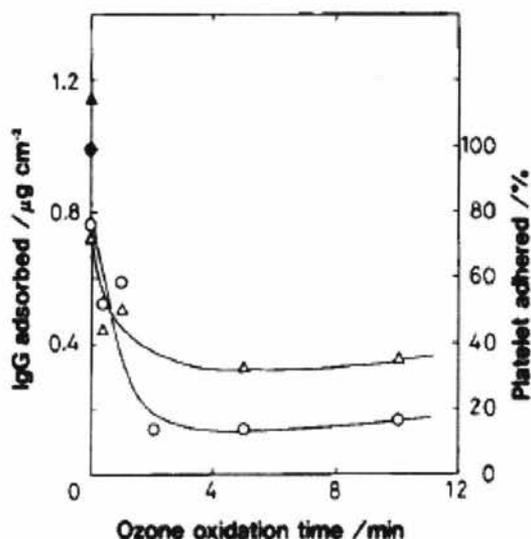


Figure 3.25 Adsorption of  $^{125}\text{I}$ -labeled IgG and adhesion of platelet to the PU film grafted with AAm at 60 °C for 1 h after ozone oxidation at 30 V: ( $\Delta$ ) IgG [( $\blacktriangle$ ) virgin], ( $\circ$ ) platelet [( $\bullet$ ) virgin] (Fujimoto et al., 1993)

When materials contact with blood, protein are first adsorbed instantaneously onto surface & deformed, then platelets are adsorbed, activated & aggregated so that platelet play a major role in the thrombus formulation. Therefore a study on platelet adhesion is the first step to evaluate the blood compatibility of materials. In general, human plasma proteins are a mixture of at least 200 kinds of proteins with different molecular weights and properties, including both platelet adhesion promoting proteins such as fibrinogen, fibronectin, and platelet adhesion inhibiting proteins such as albumin, immunoglobulin G

and high molecular weight kininogen (HMWK) (Lin et al., 2005). Lee et al. (1998) observed the degree of platelet adhesion on wettability gradient surface in the absence & presence of plasma proteins, platelet adhesion increased with increasing wettability. In contrast platelet adhesion was suppressed on hydrophilic surface in the presence of plasma proteins (Schmaier et al., 1984).

Fujimoto et al. (1993) studied platelet adhesion on the ozone induced modified polymeric surface as shown in Figures 3.24 and 3.25. From Figure 3.24, it was observed that platelet adhesion drastically decreased with increasing grafted density. From Figure 3.25, it was observed that platelet adhesion was decreased with increasing ozone oxidation time.

From literature review, it was concluded that peroxide groups were generated during ozonation which grafted with hydrophilic vinyl monomers during graft polymerization. Therefore, surface properties of polymer films were modified. Ozonation can be conducted either in gas phase or aqueous phase. For aqueous phase, there is little information available in the literature. Aqueous phase has potential to add catalyst/additive to enhance the reaction which an open area for further study.

## 4. EXPERIMENTAL METHODOLOGY

### 4.1 Materials

#### 4.1.1 Polyethylene film

Polyethylene (LD+LLDPE) film with a thickness of 51  $\mu\text{m}$  from Exopack Ltd., Newmarket, Ontario was selected for this study. LD+LLDPE film is manufactured by blending two resins, one is low density polyethylene (LDPE), and another is linear low density polyethylene (LLDPE). The ratio of LDPE and LLDPE is 60:40. No coating or co-extrusion layer exists.

LDPE film has weak strength while LLDPE has an excellent strength and impact as well as puncture resistance. By blending both resins, overall film has good mechanical strength which is an important for ozonation. Therefore, LD+LLDPE film was selected for this research. This film was readily available and cheaper than other polymers so LD+LLDPE film was selected for this research.

#### 4.1.2 Other chemicals

##### 4.1.2.1 Chemicals used for determination of peroxides

- Iso-propanol alcohol (99.7%) and concentrated sulphuric acid 98% were obtained from J.T. Baker, Toronto, Ontario.
- Glacial acetic acid (99.5%) was obtained from BDH, Toronto, Ontario.

- Potassium iodide (99%), Sodium thiosulfate (99.5%), Potassium dichromate (Reagent grade) and Starch (Analytical grade) were supplied by Sigma-Aldrich.

#### 4.1.2.2 Chemicals used for ozonation process

- Ferric chloride (minimum 98%), Cobalt nitrate (99%), Manganese chloride (99%), Magnesium sulphate (99%), Nickel sulphate (98%), Copper sulfate (99%) and Sodium hydroxide (97%) were supplied by Sigma-Aldrich.
- Concentrated sulphuric acid 98% were obtained from J.T. Baker, Toronto, Ontario.
- For an aqueous medium, distilled water was used.

#### 4.1.2.3 Chemical used for advanced oxidation process with ozonation process

- Hydrogen peroxide (50% w/w) and Ferric chloride (minimum 98%) were supplied by Sigma-Aldrich.
- For an aqueous medium, distilled water was used.

## 4.2 Experiment Set-up

### 4.2.1 Experiment set-up for ozonation process

Figure 4.1 shows a picture of experimental set-up for ozonation and Figure 4.2 represents a schematic diagram of the experimental set-up for ozonation used in this research. Table 4.1 describes the equipments used in ozonation process.

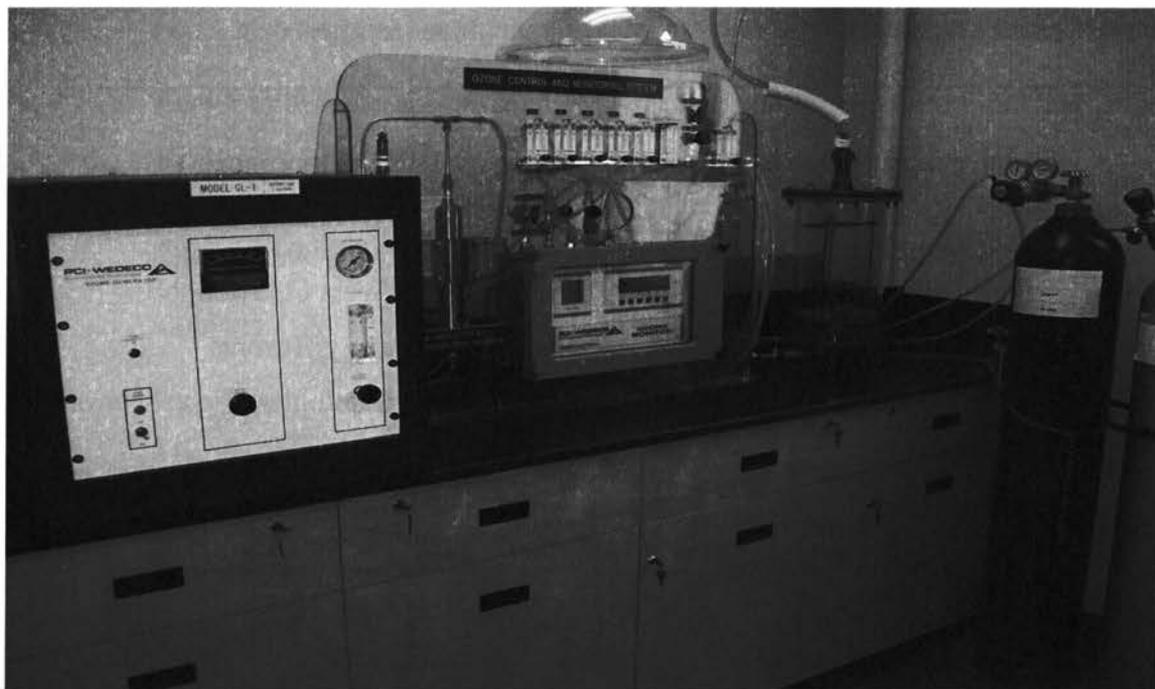


Figure 4.1 Experimental set-up for ozonation process on polyethylene film

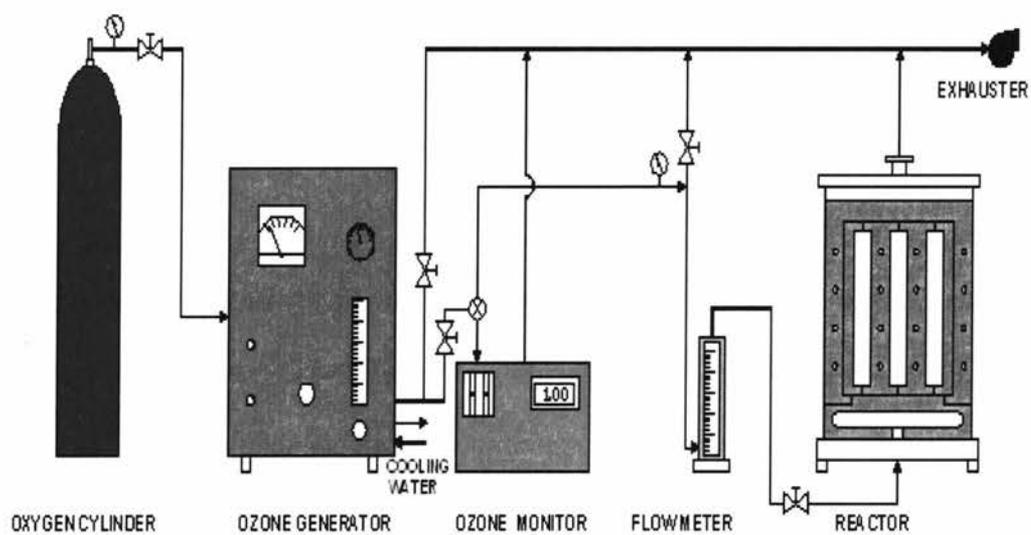


Figure 4.2 Schematic diagram of experimental set-up for ozonation

Table 4.1 The description of the equipments used in ozonation process

Equipment	Manufacturer
Ozone generator, model GL-1	PCI – WEDECO Environmental Technologies, West Caldwell, NJ
Ozone monitor, HC 400	PCI – WEDECO Environmental Technologies, West Caldwell, NJ
Reactor, Acrylic	Ryerson University, Toronto
Diffuser	Refractron Technologies Corp., Newark, NY
pH Meter, SB70 P	VWR, Mississauga, ON
Sonicator, model 50 D	VWR International, West Chester, PA

### 4.3 The Procedure of Ozonation Process

- Polymer films were cut into 1.5 inch × 10 inch strips, cleaned with distilled water in sonicator for 3 min and degassed by vacuum for 30 min;
- Three strips in a row were hanged vertically on stainless steel frame. The strips were tightened by strings from top and bottom supports. The distance between two strips was 1.5 cm. Total six strips were fixed in the reactor prior to the start of the reaction;
- Compressed oxygen gas was supplied to ozone generator (PCI-WEDECO Environmental Technologies, Model GL-1) from the oxygen cylinder.
- Ozone was produced from ozone generator; flow of oxygen was controlled by flow meter and pressure gauge; cooling water was fed to ozone generator continuously in order to remove heat from the generator;

- The rate of ozone generation was controlled by adjusting the output power knob; generated ozone oxygen mixture was released in three directions: to the reactor (flow rate and pressure was measured and adjustable), another to be released to exhaust system, and the third to the ozone concentration monitor (PCI-WEDECO); The concentration of ozone was recorded from ozone monitor;
- Oxygen and ozone mixture with 9 L/min flow rate and 14 psig input pressure was fed to the reactor through the diffuser which uniformly diffused in the gas phase or an aqueous in the reactor;
- In the reactor, strips were reacted with ozone at room temperature for set ozone concentrations and for set reaction times;
- After finishing reaction, samples were taken out and degassed by vacuum for 60 min at room temperature.

## **4.4 Experimental Design**

### **4.4.1 Ozonation in gaseous phase**

In order to generate peroxides into the surface of polymer, ozonation was conducted in gaseous phase first. Initially sample strips were cleaned with distilled water in sonicator for 3 minutes and degassed by vacuum for 30 minutes. Then cleaned six strips were fixed to stainless steel frame to avoid overlapping with each other. Then

polymer films were ozonated for desired process conditions according to the ozonation procedure.

After ozonation, the strips were taken out and degassed by vacuum at room temperature (23°C – 25°C) for 60 min. After drying, samples were tested for surface analysis.

#### **4.4.2 Ozonation in aqueous phase**

In order to generate peroxides into the surface of polymer, ozonation was conducted in aqueous phase as well. For aqueous phase ozonation, the procedure was analogous to gaseous phase except that films were immersed in 11 L of distilled water, and ozone gas was sparged into the water.

#### **4.4.3 Effect of pH on generation of peroxides**

The purpose of this study was to investigate effect of various pH on generation of peroxides in aqueous phase. The reaction was carried out with 1.0 wt % applied ozone dose and 120 min reaction time for various pH from 1.5 to 10, and the result were studied for effect of different pH on generation of peroxides.

#### 4.4.4 Effect of catalyst on generation of peroxides

Since an aqueous phase has the potential to add catalyst to accelerate the reaction, different catalysts were tested with 1.0 wt % applied ozone dose and 120 min reaction time, and the results were studied to find out which catalyst was effective.

In the presence of selected effective catalyst, the effects of the process conditions on peroxide generation were investigated as listed below.

##### 4.4.4.1 Effect of different reaction times

The purpose of study was to examine effect of different reaction times on generation of peroxides. For homogenous catalytic ozonation, applied ozone dose was set at 1.0 wt %, and different reacting times from 30 minutes to 120 minutes were studied to examine the yield of generation peroxide and effect of ozonation on mechanical strength.

##### 4.4.4.2 Effect of catalyst dosage

For homogenous catalytic ozonation, reaction time was set at 120 min and applied ozone dose at 1.0 wt %, and dosage of catalyst was optimized to minimize the amount of catalyst.

#### 4.4.4.3 Effect of applied dosage of ozone

The purpose of study was to examine effect of applied dosage of ozone on generation of peroxides. Ozone reaction time was set at 60 min and applied dosage of ozone, from 0.5 % to 3.5 % were applied to study which concentration would effective to generate more peroxides and maintain the mechanical strength.

#### 4.4.4.4 Effect of an advanced oxidation process (AOP) on generation of peroxides

The purpose of study was to examine effect of an advanced oxidation process (AOP) on generation of peroxides. The ozonation was carried out with hydrogen peroxide alone and combined with the selected catalyst, to study the effect of an advanced process (AOP) with different concentration of hydrogen peroxide and 1.0 wt % applied ozone dose.

Table 4.2 describes the outline of experimental design.

Table 4.2 The description of experimental design of ozonation with the process conditions

Reaction condition	Catalyst	Dosage of catalyst (g/l)	Applied Ozone dose (wt %)	Reaction time (min)
Gas phase	-	-	1.0	15 to120
Aqueous phase	-	-	1.0	15 to120
Aqueous with diff. pH – 1.5 to 10	-	-	1.0	120

Catalyst screening	Mg (II)	0.2	1.0	120
	Mn (II)	0.2		
	Co (II)	0.2		
	Ni (II)	0.2		
	Cu (II)	0.2		
	Fe (III)	0.2		
Different reaction times	selected catalyst	0.2	1.0	30 to120
Minimum dosage of catalyst	selected catalyst	0.005 to 0.5	1.0	120
Different applied dose of ozone	selected catalyst	0.04	0.5 to 3.5	60
AOP with H <sub>2</sub> O <sub>2</sub> (0.005 to 0.045 M)	-	-	1.0	60
AOP with H <sub>2</sub> O <sub>2</sub> (0.005 to 0.045 M)	selected catalyst	0.04	1.0	60
All the reactions were carried out at room temperature (23-25° C) with 9 l/min gas flow rate, and 14 psi gas input pressure.				

## 4.5 Analytical Methods

### 4.5.1 Determination of Peroxides

#### 4.5.1.1 Titration method

The Standard Iodometric method is a quantitative method for determination of peroxides. 50 ml iso-propanol was added to cutting pieces of ozonated films (two pieces of the film with the dimensions of 1.5 inch × 10 inch), followed by 2 ml of saturated KI and 2 ml of glacial acetic acid. The mixture was heated almost to boiling temperature (80±1°C) with stirring, kept at incipient boiling for 7 minutes with occasional swirling and without cooling, titrated with 0.001N standard sodium thiosulfate solution until the yellow colour disappeared. The consumption of 0.001N standard Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> was recorded. The generation of peroxides was calculated.

Peroxide/hydroperoxide reacts with iodide to produce iodine in acidic environment, and iodine can be precisely titrated with sodium thiosulfate solution. Detailed calculation mentions in Appendix I.

#### 4.5.1.2 Optimizing incipient boiling time for titration procedure

Different incipient boiling times were examined in this study. They were set-up at 2, 5, 7, 9 and 11 min. Figure 4.3 presents the results for different incipient boiling times with 1.0 wt % applied ozone dose and 60 min reaction time. It is obvious that boiling the sample for 7 min is enough.

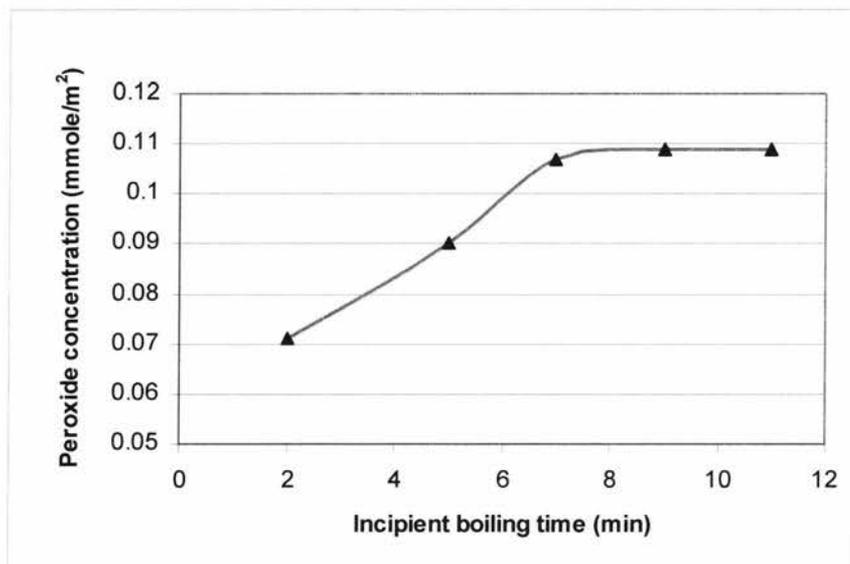


Figure 4.3 Optimization of incipient boiling time for titration procedure with 1.0 wt% applied ozone dose, 9 L/min gas flow rate, 14 psig input gas pressure for 60 min reaction time

#### 4.5.2 Contact angle measurement



Figure 4.4 Goniometer

The contact angle of ozonated film was measured by the goniometer (Rame Hart, Model 100.00 115 NJ, USA) as shown in Figure 4.4. The sample films were placed on a sample holder, a drop of pure water ( $3\mu\text{l}$ ) was placed on the sample, took picture of drop by high resolution camera and then, the static angle was measured. Goniometer is equipped with Dropimage program (software) which calculates the value of contact angle as per picture (image) of drop.

### 4.5.3 FTIR (Fourier Transform Infrared)



Figure 4.5 FTIR Instrument

FTIR spectra of untreated and treated films were measured by Perkin Elmer spectra one, V3.01 equipment as shown in Figure 4.5. It is chemical analytical technique which measured the infrared intensity versus wave length of light. FTIR detects the vibration characteristics of chemical functional groups in a sample. By FTIR spectra, we can know which functional groups induced on the films during ozonation.

- The peaks of C=O between  $1710$  to  $1750\text{ cm}^{-1}$  for R(C=O)-H, R(C = O)-R
- The peaks of C-O-C are at  $1080$  to  $1110\text{ cm}^{-1}$
- O-H peaks occur around  $3300\text{ cm}^{-1}$
- C-H stretching and vibration are from  $2850$  to  $3300\text{ cm}^{-1}$

(Kulik et al., 1997; Gatenholm et al., 1997; Sainbayar et al., 2001; Yuan et al., 2002)

#### 4.5.4 Mechanical strength measurement



Figure 4.6 Instron Machine

Instron machine (3367) as shown in Figure 4.6 was used to measure tensile strength measurements of untreated and ozonated polyethylene films. By this analysis, we can know effect of ozonation on tensile strength of polymers. For the procedure of testing, speed of cross-head was 10 in/min and followed ASTM D882-02 standard. There are two directions on films, one is machine direction (MD) and other is traverse direction (TD). So five measurements of both directions were taken and average of total ten measurements considered for results.

## 5. RESULTS AND DISCUSSION

### 5.1 Gaseous and aqueous ozonation of LD+LLDPE Film

#### 5.1.1 Peroxide generation on film ozonated in gaseous and aqueous phases

The LD+LLDPE films were ozonated in ozone-oxygen gas mixture and in distilled water respectively. For both phases, reaction time was set at 15, 30, 45, 60, 90 and 120 minutes. Six LD+LLDPE strips (1.5 in × 10 in) were fixed in the reactor. The applied ozone dose was 1.0 wt% for both gaseous and aqueous ozonation. The ozonation was conducted at room temperature (23- 25°C) with 9 L/min gas flow rate and 96.5 KPa (14 psig) gas input pressure. The details of process conditions and the results of peroxide concentration are mentioned in Table-1 of Appendix VI (for gaseous phase) and Table-1 of Appendix VII (for aqueous phase), respectively. For titration, the standard Iodometric method was followed.

Figure 5.1 presents the results of peroxide concentration generated in both gas and aqueous phases. Figure 5.1 also presents error bars for each ozonation time with standard deviation. The concentration of peroxide was determined under different ozonation times with 1.0 wt % applied ozone dose. The results show that the concentration of peroxides increased with increasing ozonation time. It was increased rapidly in first one hour and then slowed down. The concentration of peroxide can be controlled by reaction time.

From Figure 5.1, it was concluded that similar results for generation of peroxide were observed for gaseous and for aqueous phase. The peroxide groups were generated

on the surface during ozonation in both phases. Those peroxides provide active species which initiate graft polymerization with vinyl functional group monomers. It is known that in gas phase, only molecular ozone exists, while in aqueous phase, both molecular ozone and ozone radicals are present. The similar results in gas and aqueous phase in terms of peroxide generation indicate that molecular ozone should be the oxidant responsible for the surface oxidation.

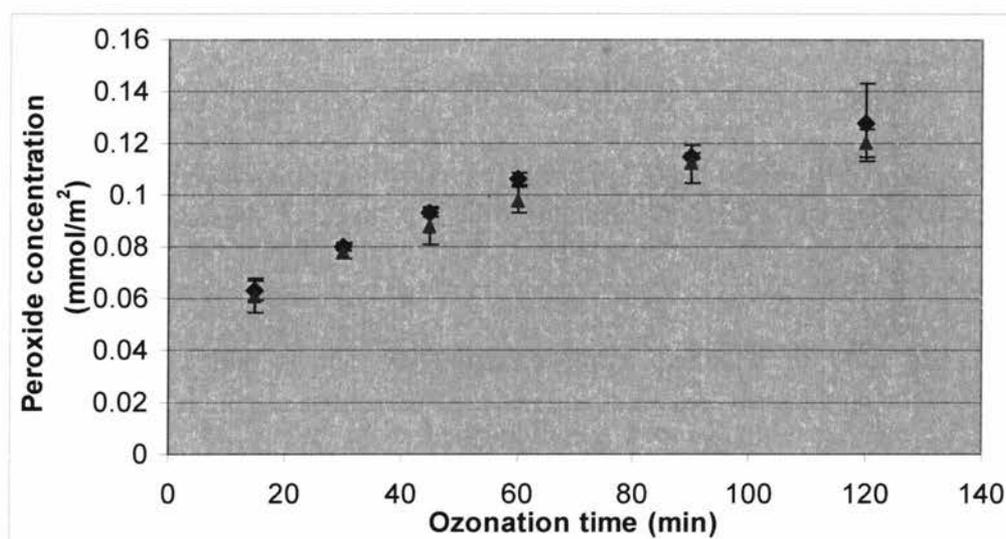


Figure 5.1 Peroxide generation on LD+LLDPE films ozonated with 1.0 wt % applied ozone dose, 9 L/min gas flow rate and 96.5 KPa (14 psig) gas input pressure in: (◆) gaseous phase, (▲) aqueous phase

### 5.1.2 Contact angle of LD+LLDPE film ozonated in gaseous and aqueous phases

The results of measurement of contact angle are shown in Table –2 (for gaseous phase) of Appendix VI and Table-2 (for aqueous phase) of Appendix VII, respectively.

Figure 5.2 presents the results of contact angles of films, which were ozonated in gaseous phase with 1.0 wt % applied ozone dose. The contact angle on the LD+LLDPE films monotonically decreased with ozonation time up to 60 min and remained almost constant afterwards. Initially virgin (untreated) film had 91.05 degree contact angle. After 120 min gaseous ozonation, the contact angle reduced upto 71.15 degree.

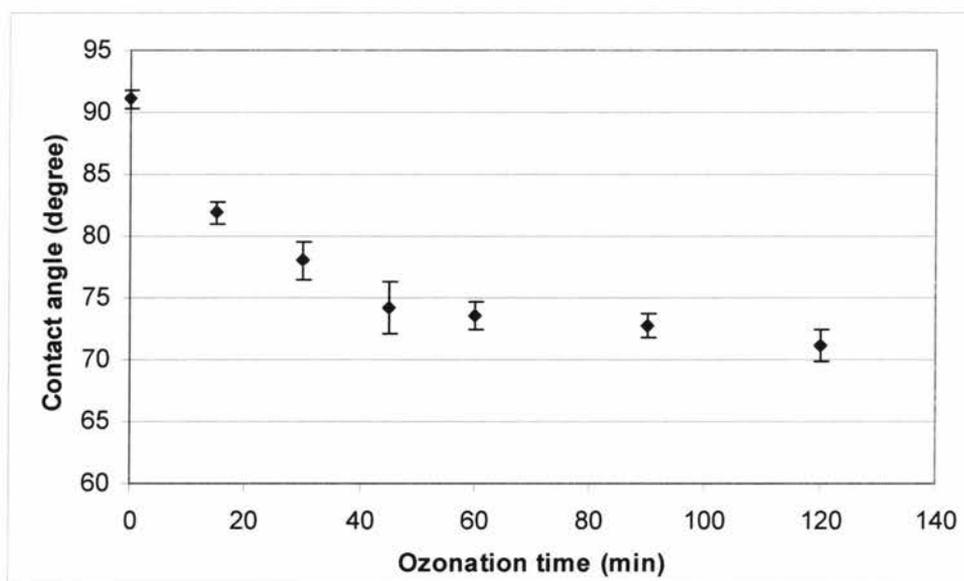


Figure 5.2 Contact angles of virgin and ozonated LD+LLDPE films with 1.0 wt % applied ozone dose, 9 L/min gas flow rate and 96.5 KPa (14 psig) in gaseous phase

Figure 5.3 presents the results of contact angles of films, which were ozonated in aqueous phase with 1.0 wt % applied ozone dose. The contact angle on the LD+LLDPE films monotonically decreased with ozonation time up to 60 min and remained almost constant afterwards. Initially virgin (untreated) film had 91.05 degree contact angle. The contact angle reduced up to 72.80 degree after 120 min ozonation. Figures 5.2 and 5.3 present error bars with standard deviation.

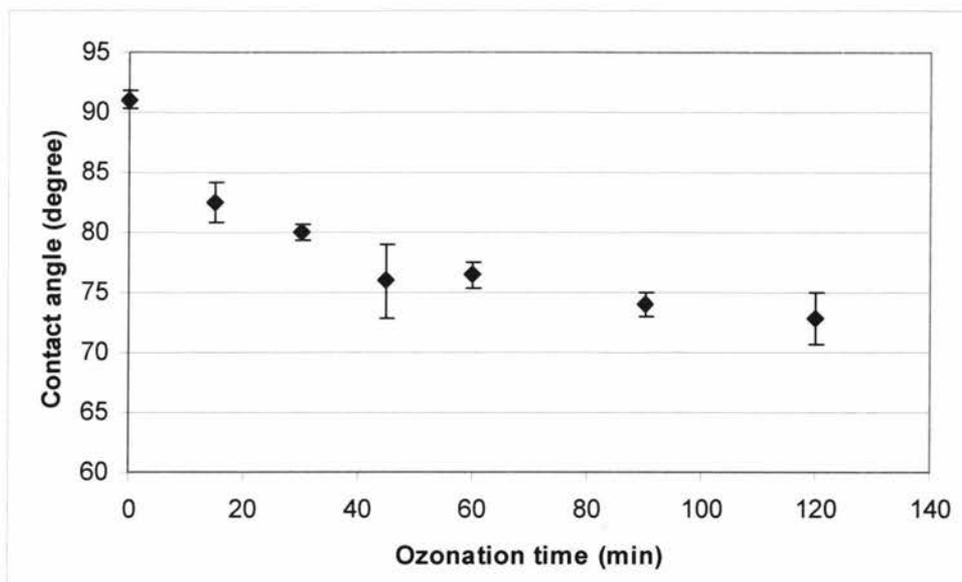


Figure 5.3 Contact angles of virgin and ozonated LD+LLDPE films with 1.0 wt % applied ozone dose, 9 L/min gas flow rate and 96.5 KPa (14 psig) in aqueous phase

The contact angle of the polyethylene films ozonated in both phases was measured to quantify the change in its hydrophilicity. From Figures 5.2 and 5.3, it was concluded that hydrophilicity of films improved in both phases after ozonation. Similar results for contact angles were observed for both phases. After 60 min ozonation, even though peroxides were still increasing as shown in Figure 5.1, the contact angle was almost a constant. Perhaps the effect of surface roughness on contact angle was opposite to that of the peroxides because the surface roughness changed after ozonation.

### 5.1.3 FTIR analysis of LD+LLDPE film

Infrared is a form of radiation that can travel through a vacuum, while heat is associated with the motion and kinetic energy of molecules. Infrared spectroscopy is used

to study how molecules absorb infrared radiation and ultimately convert it to heat. By examining the infrared spectra obtained, we gained information about the functional groups in the polymer molecules and learned about the molecular structure.

#### 5.1.3.1 FTIR analysis of LD+LLDPE film ozonated in gaseous phase

Figure 5.4 presents the infrared spectra obtained for virgin, 60 min ozonated and 120 min ozonated LD+LLDPE film in gaseous phase with 1.0 wt % applied ozone dose. A peak of hydrophilic group C=O for R-(C=O)-R, R-(C=O)-H occurs at  $1715\text{ cm}^{-1}$  (Kulik et al., 1997) which was created by ozonation and enhanced with ozonation time.

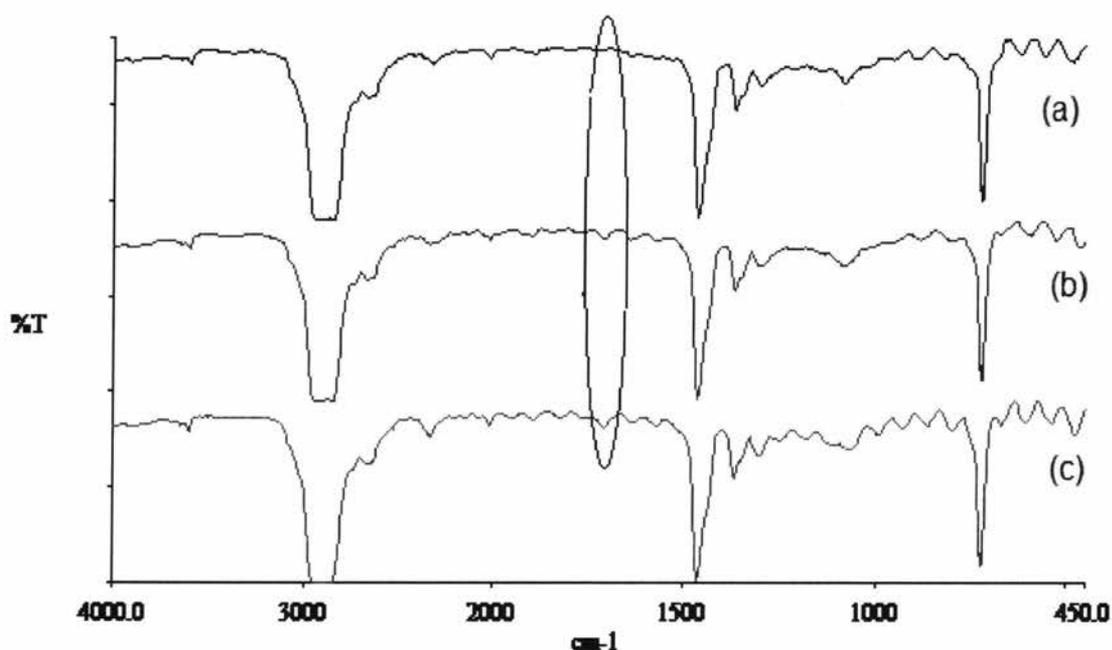


Figure 5.4 Infrared spectra of LD+LLDPE films ozonated with 1.0 wt % applied ozone dose , 9 L/min gas flow rate and 96.5 KPa(14 psig) gas input pressure in gaseous phase, spectra (a) for virgin film, spectra (b) for 60 min ozonation and spectra (c) for 120 min ozonation

Figure 5.5 and 5.6 are the enlargement of spectra (a) and (c) of Figure 5.4, respectively. After comparing these two spectra, the following results were concluded.

- The peak for C=O is created at  $1715\text{ cm}^{-1}$  (Kulik et al., 1997) and its value increased with increasing reaction time.
- Some peaks, between  $850\text{ cm}^{-1}$  and  $1250\text{ cm}^{-1}$ , show variation, indicating the chain scission and reconstruction.
- Peroxides could be determined neither by contact angle nor by spectroscopy, they quantitatively determined with chemical methods (Fujimoto et al., 1993).

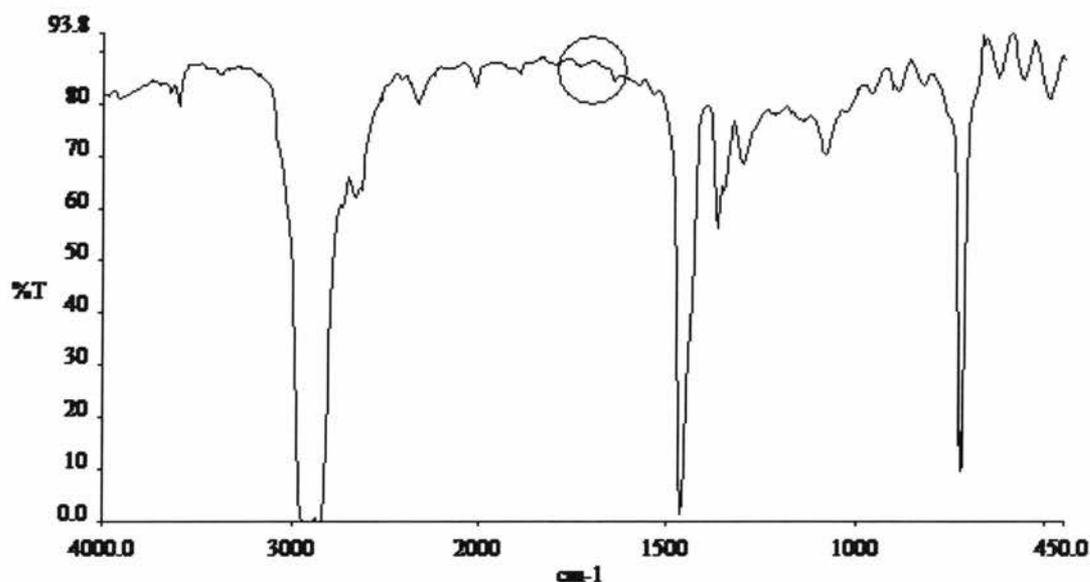


Figure 5.5 Infrared spectra of untreated LD+LLDPE film (enlargement of spectra (a) of Figure 5.4

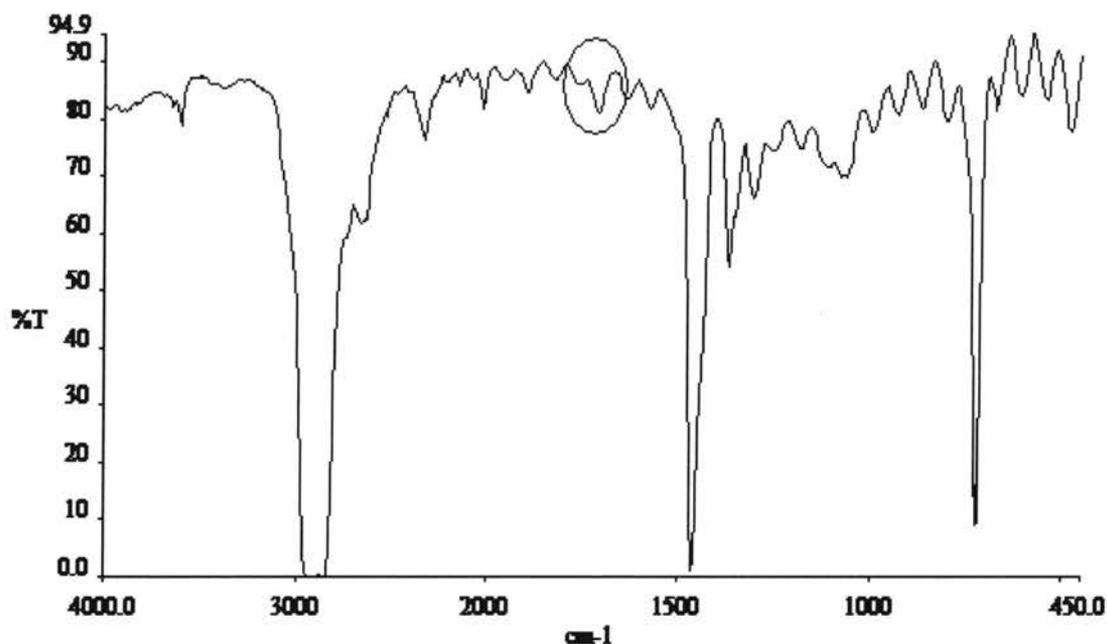


Figure 5.6 Infrared spectra of LD+LLDPE film after 120 min ozonation with 1.0 wt% applied ozone dose, 9 L/min gas flow rate and 96.5 KPa (14 psig) gas input pressure in gaseous phase (enlargement of spectra (c) of Figure 5.4

### 5.1.3.2 FTIR analysis of LD+LLDPE film ozonated in aqueous phase

Figure 5.7 presents the infrared spectra obtained for virgin, 60 min ozonated and 120 min ozonated LD+LLDPE film in aqueous phase with 1.0 wt % applied ozone dose. A peak of hydrophilic group C=O for R-(C=O)-R, R-(C=O)-H occurs at  $1716\text{ cm}^{-1}$  (Kulik et al., 1997) which was created by ozonation and enhanced with ozonation time.

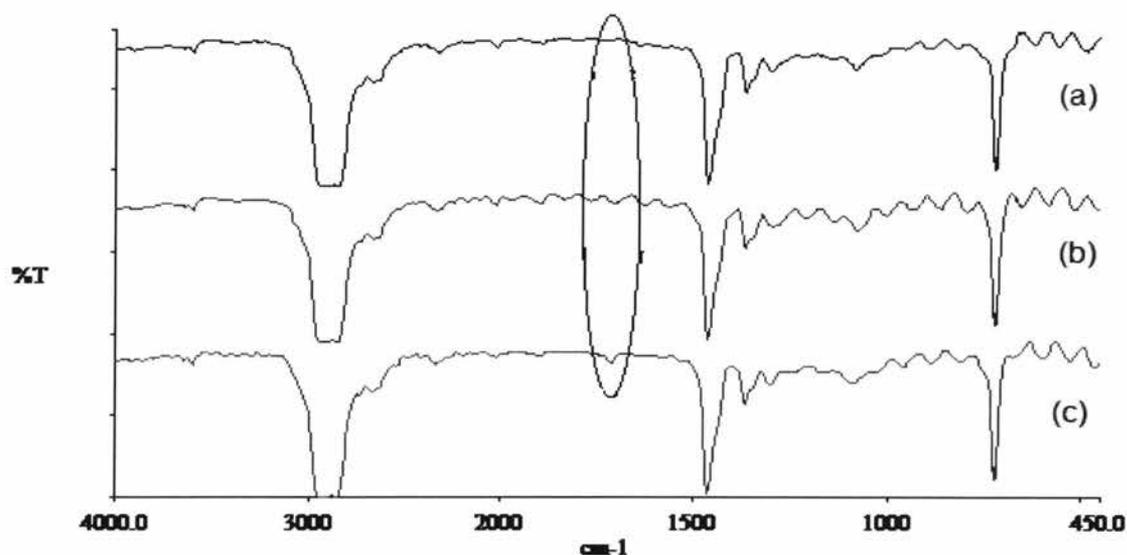


Figure 5.7 Infrared spectra of LD+LLDPE films ozonated with 1.0 wt % applied ozone dose, 9 L/min gas flow rate and 96.5 KPa (14 psig) gas input pressure in aqueous phase, spectra(a) for virgin film, spectra (b) for 60 min ozonation and spectra (c) for 120 min ozonation

#### 5.1.4 Tensile strength of LD+LLDPE film ozonated in gaseous and in aqueous phase

The details of testing methods and the results of tensile strength are given in Table-3 of Appendix VI (for gaseous phase) and in Table-3 of Appendix VII (for aqueous phase), respectively.

Figure 5.8 presents the results of tensile strength of LD+LLDPE films ozonated in gaseous phase with applied 1.0 wt% applied ozone dose. Figure 5.9 presents the results of tensile strength of LD+LLDPE films ozonated in aqueous phase with applied 1.0 wt% applied ozone dose. The tensile strength of virgin (untreated film) is 24.71 MPa. The tensile strength was slightly decreased when reaction time increased from 0 min (virgin) to 120 min in both phases. After 120 min gaseous ozonation, the tensile strength of films

is 21.73 MPa. After 120 minutes aqueous ozonation, the tensile strength of films is 21.23 MPa.

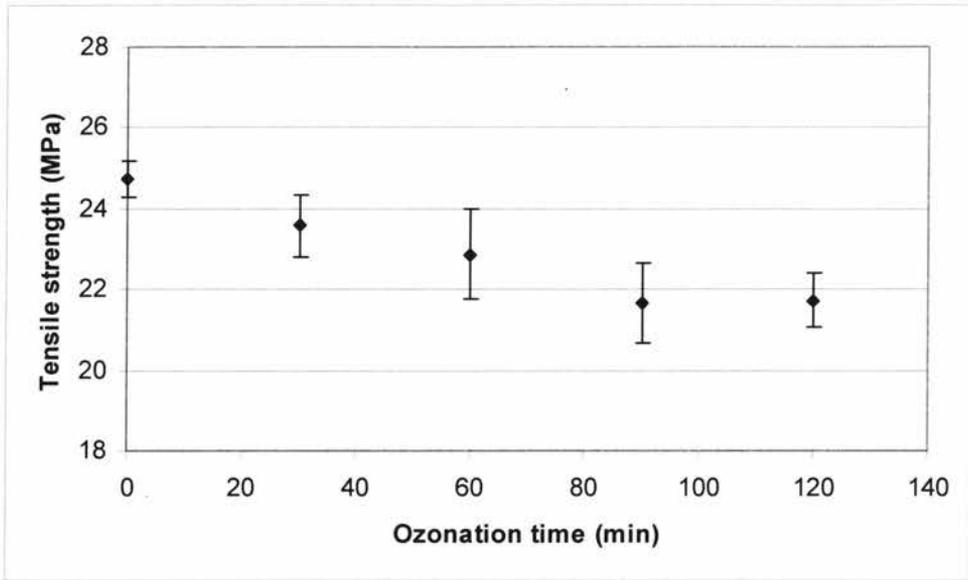


Figure 5.8 Tensile strength of virgin and ozonated LD+ LLDPE films with 1 wt% applied ozone dose, 9 L/min gas flow rate and 96.5 KPa(14 psig) gas input pressure, in gaseous phase

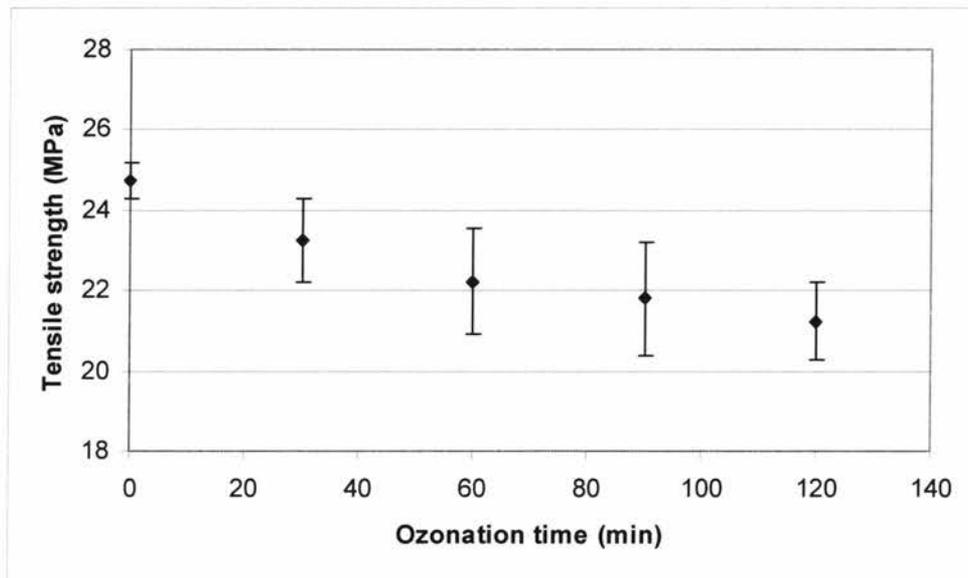


Figure 5.9 Tensile strength of virgin and ozonated LD+ LLDPE films with 1 wt% applied ozone dose, 9 L/min gas flow rate and 96.5 KPa(14 psig) gas input pressure, in aqueous phase

Gu (2008) observed 38% reduction of tensile strength of HDPE films after 60 min ozonation with 1 wt % ozone.

Wang et al. (2000) found that tensile strength of PP membrane decreased with increasing ozonation time. The excessive ozone treatment made the membrane mechanically fragile since ozone attacked back bone of the polymer.

The tensile strength data showed similar trends in gaseous phase and in aqueous phase. It was decreased 12-14% after 120 min ozonation in both phases. It was concluded that the ozonation in both phases does not affect significantly on the tensile strength of films. Figures 5.8 and 5.9 present error bars with standard deviation.

## **5.2 Effect of Different pH on Generation of Peroxide**

The effect of different pH on LD+LLDPE film was examined. The pH values were 1.6, 3.0, 5.7, 7.9 and 9.9 respectively. The pH of distilled water was adjusted by concentrated  $H_2SO_4$  and NaOH respectively. The effect of pH was examined with 1.0 wt % applied ozone dose for 120 min.

Figure 5.10 presents the results of peroxides generation at various pH values. In acidic pH, the peroxide concentration was higher. In more alkaline pH, the peroxide concentration was lower. It is known that ozone decomposes more into ozone radicals in more alkaline pH. In acidic pH, decomposition of ozone decreased. The fact that in acidic pH, more peroxide generated indicates that the ozone induced peroxide generation was

mainly caused by ozone molecules instead of ozone radicals. This observation is in agreement with that in Section 5.1.1.

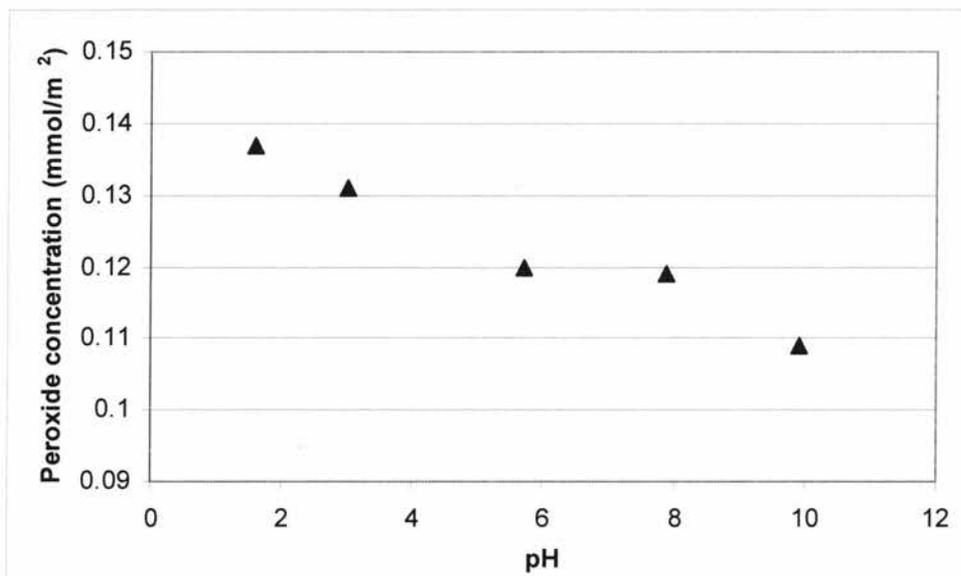


Figure 5.10 The effect of different pH on generation of peroxides on LD+LLDPE with 1.0 wt% applied ozone dose, 9 L/min gas flow rate, 96.5 KPa (14 psig) gas input pressure and 120 min reaction time

## 5.3 Homogeneous Catalytic Ozonation

### 5.3.1 Catalyst screening

The films were ozonated in presence of different homogeneous catalysts including salts of group VII to VIII transition metals, as well as magnesium. The details of process conditions and the results of generation of peroxide are given in Table-1 of Appendix IX.

Homogeneous catalytic ozonation was carried out with 1.0 wt % applied ozone dose and 120 min reaction time. The ozonation was conducted at room temperature (23-25°C) with 9 L/min gas flow rate and 96.5 KPa (14 psig) gas input pressure. Table 5.1

presents the results of the generation of peroxides of homogeneous catalysts ozonation with different catalysts. From above results, it was concluded that Mg (II), Mn (II), Ni (II) and Co (II) did not enhance reaction. But the reaction was accelerated by Fe (III) and Cu (II) as shown in Table- 5.1.

Table 5.1 The concentration of peroxide of homogeneous catalytic ozonation with different catalysts

Catalyst	Chemical	Dosage of Catalyst, g/L	Concentration of peroxide, m mol/m <sup>2</sup>
Without catalyst	-	-	0.120
Mg(II)	MgSO <sub>4</sub>	0.2	0.116
Mn(II)	MnCl <sub>2</sub>	0.2	0.116
Ni(II)	NiSO <sub>4</sub>	0.2	0.121
Co(II)	Co(NO <sub>3</sub> ) <sub>2</sub>	0.2	0.119
Cu(II)	CuSO <sub>4</sub>	0.2	0.140
Fe(III)	FeCl <sub>3</sub>	0.2	0.162

### 5.3.2 Effect of different reaction times on the generation of peroxides in presence of Fe (III) catalyst

Initially 3.67 g FeCl<sub>3</sub>•6H<sub>2</sub>O was dissolved in 11 L distilled water. The dosage of FeCl<sub>3</sub> catalyst was 0.2 g/L. Then six strips of LD+LLDPE film were fixed in reactor. Homogeneous catalytic ozonation was carried out with 1.0 wt % applied ozone dose for different reaction times. The reaction times were set at 30, 60, 90 and 120 min. The pH of solution before ozonation and after ozonation was recorded. After ozonation, the films were degassed for 60 min in order to remove absorbed ozone on films.

Since FeCl<sub>3</sub> has better solubility in acidic pH, catalytic ozonation in presence of Fe (III) was conducted at pH 2.9. As indicated by our results in section 5.2, acidic pH

itself enhance peroxide generation as well, therefore, Figure 5.11 presents the results of the peroxides generated with Fe (III) catalyst, without catalyst at 3.0 pH, and aqueous phase with distilled water (without catalyst), respectively. During homogeneous catalyst reaction, Fe (III) solution was at 2.9 pH before and after ozonation. Curve (1) presents the results of the generation of peroxides of homogeneous catalytic ozonation with Fe (III) catalyst. Curve (3) presents the results of the generation of peroxides without catalyst.

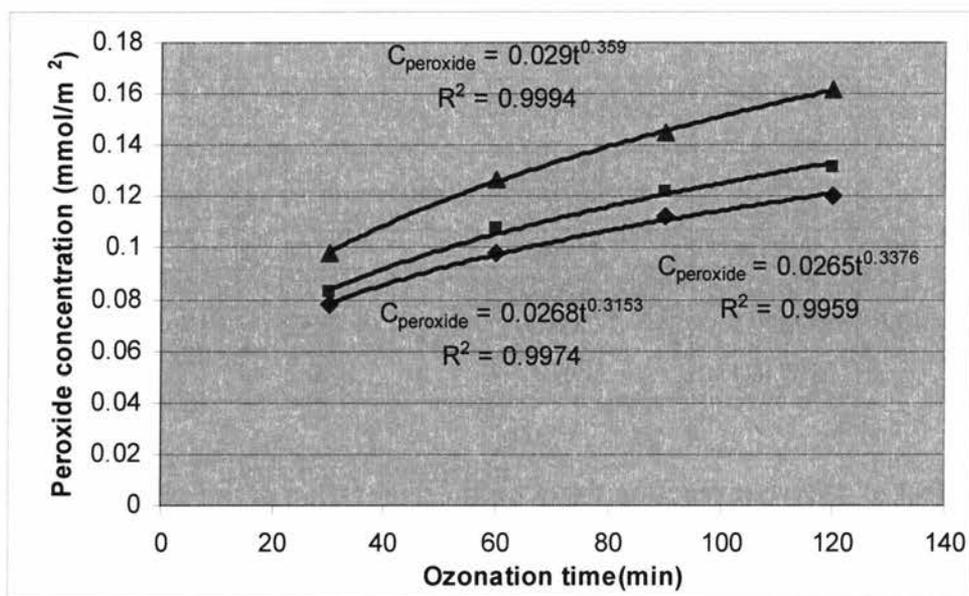


Fig 5.11 The generation of peroxide on LD+LLDPE films ozonated with 1.0 wt% applied ozone dose, 9 L/min gas flow rate with 0.2 g/L dosage of  $\text{FeCl}_3$  (▲)[curve(1)], at 3.0 pH without catalyst (■)[curve(2)], without catalyst at 5.7 pH (◆)[curve(3)]

In catalyst ozonation, the generation of peroxides increased from 0 to 0.162  $\text{mmol/m}^2$  while reaction time increased from 0 min (virgin film) to 120 min. In aqueous phase, without catalyst, the generation of peroxides was 0.12  $\text{mmol/m}^2$  after 120 min ozonation. At 3.0 pH, without catalyst, the generation of peroxides was 0.1317  $\text{mmol/m}^2$  after 120 min ozonation. Peroxides generation increased by 25.3% with Fe (III) catalyst

while the effect of pH increased peroxides generation by 9.7%. In short, Fe (III) catalyst is effective in generating more peroxides into the surface of LD+LLDPE films.

Homogeneous catalysts are generally well-defined chemical compounds or coordination complexes, which, together with the reactants, are molecularly dispersed in the reaction medium. Due to their high degree of dispersion, homogeneous catalysts exhibit a higher activity per unit mass. The high mobility of the molecules in the reaction mixture results in more collisions with substrate molecules. The reactants can approach the catalytically active center from any direction, and a reaction at an active center does not block the neighbouring centers. This feature allows the use of lower catalyst concentrations and milder reaction conditions (Hagen, 2006).

The relationship between peroxides concentration ( $C_{\text{peroxide}}$ ) and ozonation time ( $t$ ) fits a power function well as shown in Figure 5.11 for catalytic ozonation with Fe (III).

### **5.3.3 Effect of different reaction times on the contact angles in presence of Fe (III) catalyst**

The contact angles of LD+LLDPE ozonated with Fe (III) catalyst with different reaction times was examined. The average of four measurements was taken. The Details of process conditions and results of contact angles are given in Table- 4 of Appendix IX.

The contact angle is measured to quantify change in hydrophilicity of films. If angle is large, then surface is hydrophobic, and angle is small, then surface is more hydrophilic. Hydrophilic surface has low contact angle, good adhesiveness, good wettability and high solid surface free energy. While hydrophobic surface has high contact angle, poor adhesiveness, poor wettability and low solid surface free energy.

Figure-5.12 represents the results of the contact angles of LD+LLDPE ozonated with Fe (III) catalyst for different reaction times. Initially virgin (untreated) film was 91.05 degree contact angle. Contact angle of film decreased with increasing reaction times. After 120 min ozonation, contact angle reduced up to 67.68 degree.

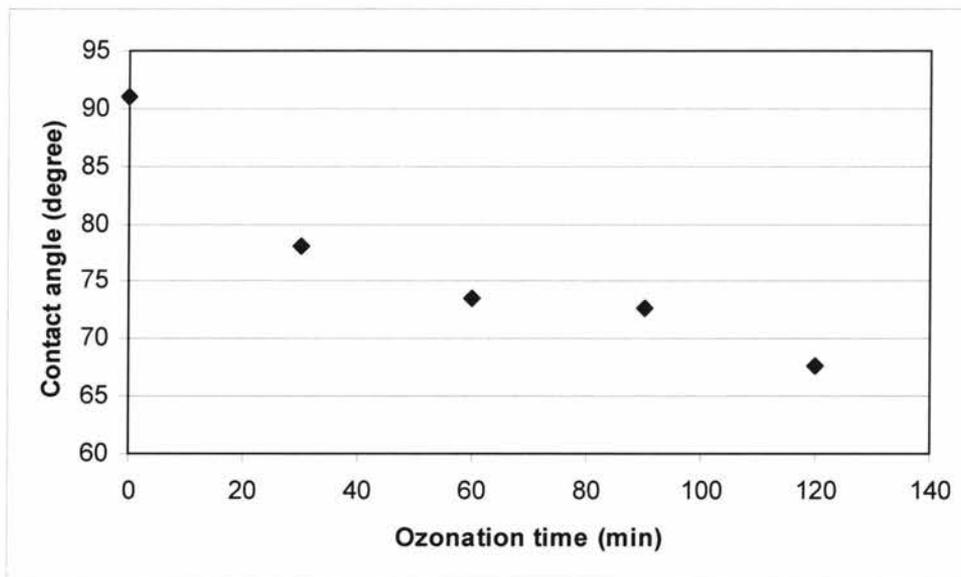


Figure 5.12 Contact angle measurements of LD+LLDPE ozonated with 0.2 g/L dosage of  $\text{FeCl}_3$ , 9 L/min gas flow rate and 1.0 wt% applied ozone dose for different reaction times

It was concluded that hydrophilicity of films improved by catalytic ozonation. We could get better effect in grafting process by reacting hydrophilic monomers with peroxides which generated during ozonation.

### 5.3.4 Effect of different reaction times on the FTIR analysis in presence of Fe (III) catalyst

Figure 5.13 presents the infrared spectra obtained for virgin (a), 60 min (b) and 120 min (c) ozonated LD+LLDPE film with Fe (III) catalyst and 1.0 wt % applied ozone dose. The peaks for C=O of R-(C=O)-R, R-(C=O)-H groups occur at  $1716\text{ cm}^{-1}$  (Kulik et al., 1997) which was created by ozonation and enhanced with ozonation time.

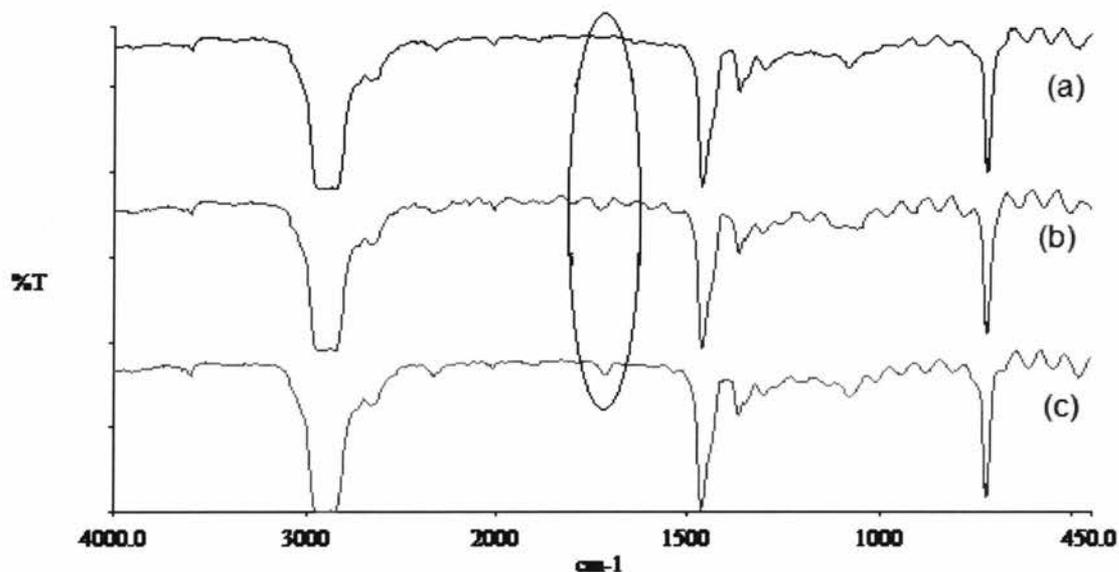


Figure 5.13 Infrared spectra of LD+LLDPE films ozonated with 0.2 g/L dosage of  $\text{FeCl}_3$ , 9 L/min gas flow rate, 1.0 wt % applied ozone dose, spectra(a) for virgin, spectra (b) for 60 min ozonation and spectra (c) for 120 min ozonation

Figure 5.14 and 5.15 present enlarged spectrum for parts (a) and (c) in Figure 5.13, Figure 5.14 is for virgin film, Figure 5.15 is for 120 min ozonated with Fe (III) catalyst. After comparing these spectra, the following results were concluded.

- The peak at  $1716\text{ cm}^{-1}$  indicates C=O (Kulik et al., 1997) was created and its value increased with increasing reaction time.
- Some peaks, between  $950\text{ cm}^{-1}$  and  $1250\text{ cm}^{-1}$ , show variation, indicating the chain scission and reconstruction.

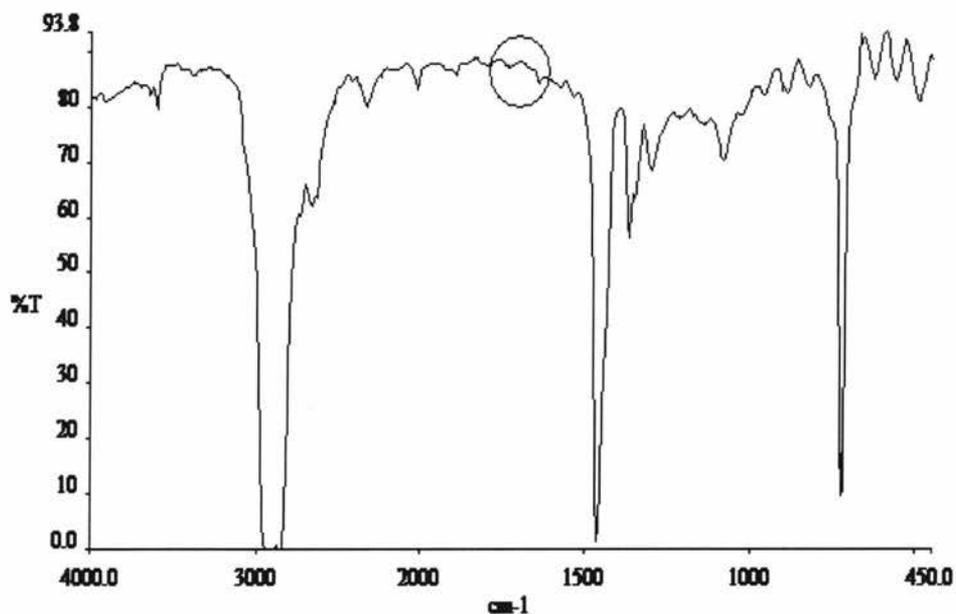


Figure 5.14 Infrared spectra of untreated LD+LLDPE film (enlargement of spectra (a) of Figure 5.13)

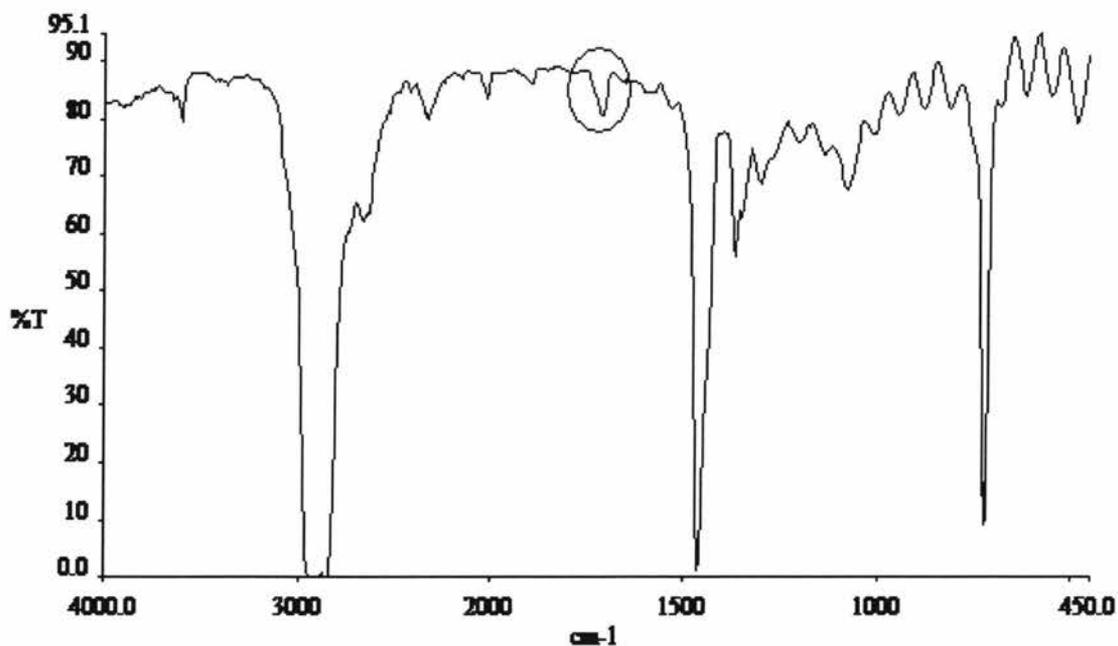


Figure 5.15 Infrared Spectra of LD+LLDPE film after 120 min ozonation with 0.2 g/L dosage of FeCl<sub>3</sub>, 9 L/min gas flow rate and 1.0 wt% applied ozone dose (enlargement of spectra (c) of Figure 5.13)

### 5.3.5 Effect of different reaction times on the tensile strength in presence of Fe (III) catalyst

The tensile strength of ozonated LD+LLDPE films with Fe (III) for various reaction times was tested. The details of testing method and the results of tensile strength are given in Table-5 of Appendix IX. Five measurements in machine direction and five measurements in traverse direction were taken. The average of total ten reading was considered.

Figure 5.16 presents the results of tensile strength of LD+LLDPE film ozonated with Fe (III) catalyst, 1.0 wt % applied ozone dose and different reaction times. The tensile strength of virgin (untreated film) is 24.71 MPa. The tensile strength was rather slightly decreased when reaction time increased from 0 min to 120 min. The tensile strength of films is 21.00 MPa after 120 min ozonation. The tensile strength of films decreased 15% even after 120 min ozonation.

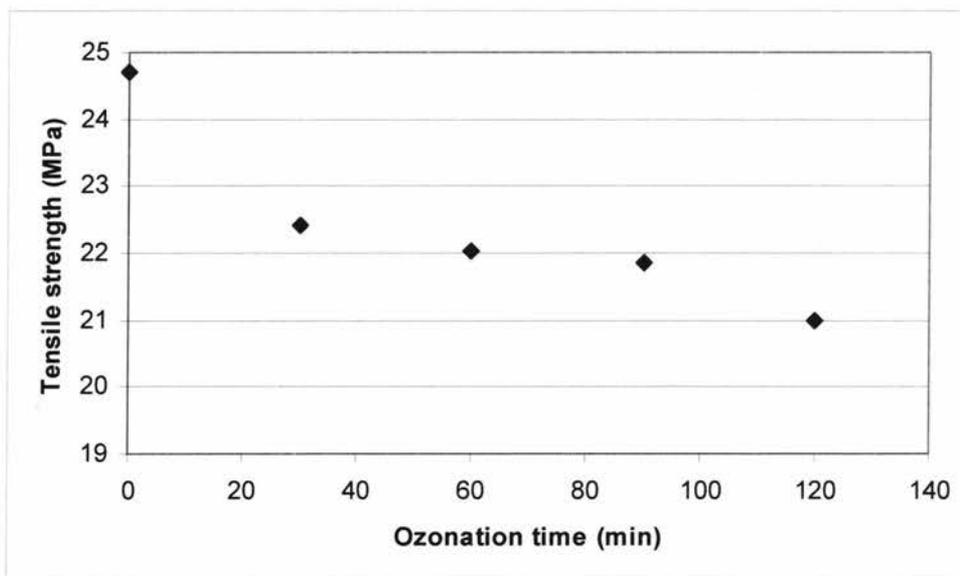


Figure 5.16 Tensile strength of LD+LLDPE ozonated with 0.2 g/L dosage of  $\text{FeCl}_3$ , 1.0 wt % applied ozone dose, 9 L/min gas flow rate for different reaction times

It was concluded that the catalytic ozonation does not affect significantly on the tensile strength of films. Therefore, the LD+LLDPE film is suitable as a substrate for surface modification by ozone.

### 5.3.6 Optimization of the dosage of Fe (III) catalyst

For catalytic ozonation conducted so far, excess amount of catalyst was used to explore the effectiveness of catalyst. From economic point view, the optimization of the dosage of Fe (III) catalyst is necessary. Different dosages of catalyst were examined. The details of process conditions and the results of generation of peroxides are given in Table-6 of Appendix IX.

Figure 5.17 presents the results. It is observed that the peroxide generation stopped increasing beyond catalyst concentration of 0.04 g/L. Therefore, the optimal dosage of  $\text{FeCl}_3$  was 0.04 g/L with 1.0 wt% applied ozone dose.

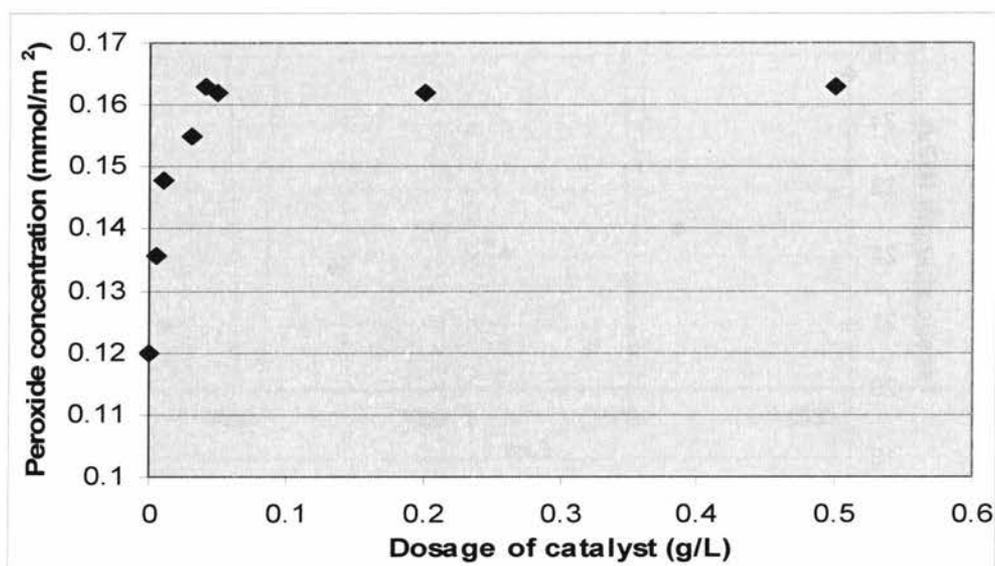


Figure 5.17 The effect of the dosage of Fe (III) catalyst (1.0 wt% applied ozone dose, 120 min reaction time and 9 L/min gas flow rate)

### 5.3.7 Effect of applied ozone dosage in the presence of Fe (III) Catalyst

#### 5.3.7.1 Effect of applied ozone dosage on the generation of peroxides of films

Homogeneous catalytic ozonation with Fe (III) catalyst at different applied dosage of ozone was examined. Initially, 0.733 g  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  was dissolved in 11 L distilled water to make 0.04 g/L dosage of catalyst. Then six strips of LD+LLDPE film were fixed in reactor. Catalytic ozonation was carried out for 60 min at different applied dosage of ozone. The pH of the solution before and after ozonation was recorded. The change in pH before and after ozonation was negligible. After ozonation, the films were degassed for 60 min. The applied dosage of ozone was set at 0.5, 1, 2, 3 and 3.5 wt %, respectively. The details of process conditions and the results of generation of peroxides are given in Table-7 of appendix IX.

Figure 5.18 presents the results of the peroxides concentration generated with Fe (III) catalyst at different applied dosage of ozone. The generation of peroxides increased with applied dosage of ozone. The generation of peroxides increased from 0 to 0.22  $\text{mmol/m}^2$  while applied dosage of ozone increased from 0 wt % (virgin film) to 3.5 wt %. It was also observed that the generation of peroxides increased faster initially, from 0  $\text{mmol/m}^2$  to 0.125  $\text{mmol/m}^2$  while the applied dosage of ozone increased from 0 wt % to 1 wt %. Increased ozone dosage could increase peroxide generation, however, the excessive ozone treatment could make the PP membrane mechanically fragile since ozone attacked backbone of the films (Wang et al., 2000).

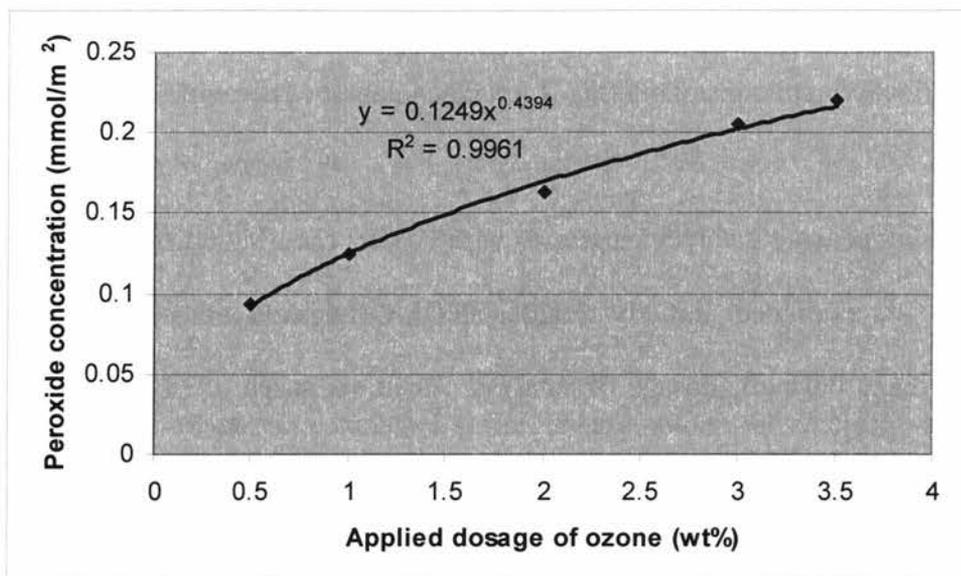


Figure 5.18 The effect of different applied dosage of ozone on peroxide generation with 0.04 g/L dosage of FeCl<sub>3</sub>, 60 min reaction time and 9 L/min gas flow rate

The relationship between peroxides concentration and applied dosage of ozone fits a power function well as shown in Figure 5.18.

#### 5.3.7.2 Effect of applied ozone dosage on contact angle of films

The contact angles of LD+LLDPE ozonated with Fe (III) catalyst with different applied dosage of ozone was measured. The static contact angle was examined using a drop of pure water (3μl). The details of process conditions and the results of contact angles are given in Table-8 of Appendix IX.

Figure 5.19 presents the results of contact angle measurements with Fe (III) catalyst and different applied dosage of ozone. The contact angle of virgin film was 91.05 degree and the contact angle of the films decreased when concentration of ozone increased. With 3.5 wt % ozone and 60 min ozonation, contact angle reduced to 66.95

degree. It is noticed that even though peroxide concentration kept increasing with ozone applied dose (Figure 5.18), the contact angle of the LD+LLDPE film is almost a constant beyond ozone concentration 2.0 wt%.

Contact angle indicates the characteristic of the outermost surfaces while the concentration of peroxide included those inside the material as well as on the surface (Ko et al., 2001). Therefore, it is possible that peroxides were not generated only from the surface but throughout the whole specimen. Another possible reason for the different trends in peroxide concentration and contact angle with ozone dosage could be that when ozone dosage at certain level, the surface roughness played negative role in the decrease the contact angle.

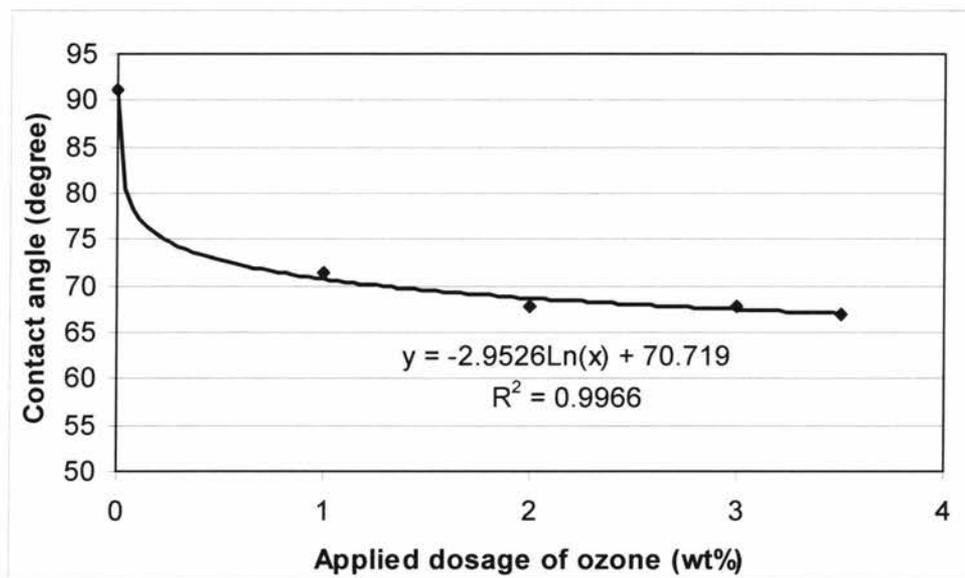


Figure 5.19 Contact angle measurements of LD+LLDPE ozonated with 0.04 g/L FeCl<sub>3</sub>, 60 min reaction time, and 9 L/min gas flow rate with different applied dosage of ozone

The relationship between contact angle and applied dosage of ozone fits a logarithmic function well as shown in Figure 5.19.

### 5.3.7.3 FTIR spectra of the films for different applied dose of ozone

Figure 5.20 presents the infrared spectra obtained from virgin and ozonated LD+LLDPE films. The peaks of hydrophilic group C=O for R-(C=O)-R, R-(C=O)-H, R-(C=O)-OH groups occur at  $1716\text{ cm}^{-1}$  (Kulik et al., 1997) which was created by ozonation and enhanced with concentration of ozone.

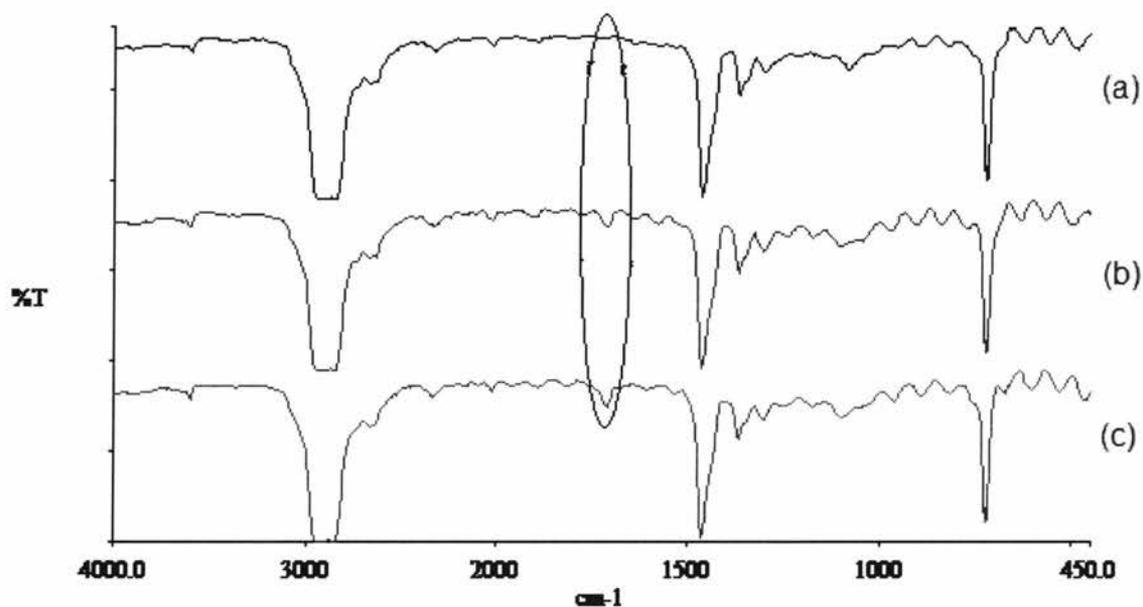


Figure 5.20 Infrared spectra of LD+LLDPE films ozonated with 0.04 g/L  $\text{FeCl}_3$ , 60 min reaction time and 9 L/min gas flow rate, spectra (a) for virgin film, spectra (b) for 2 wt% applied ozone dose and spectra(c) for 3.5 wt% applied ozone dose

Figures 5.21 and 5.22 presents the infrared spectra obtained for untreated LD+LLDPE film and infrared spectra of LD+LLDPE ozonated for 3.5 wt % ozone with

60 min reaction time. After comparing these spectra, the following results were concluded.

- The peak at  $1716\text{ cm}^{-1}$  indicates C=O (Kulik et al., 1997) was created and its value increased with increasing concentration of ozone. More molecular of ozone reacted with higher concentration of ozone. Thus, the value of peak increased.
- The small peaks of O-H groups occur at around  $3300\text{ cm}^{-1}$  (Sainbayar et al., 2003).
- Some peaks, between  $950\text{ cm}^{-1}$  and  $1250\text{ cm}^{-1}$ , show variation, indicating the chain scission and reconstruction.

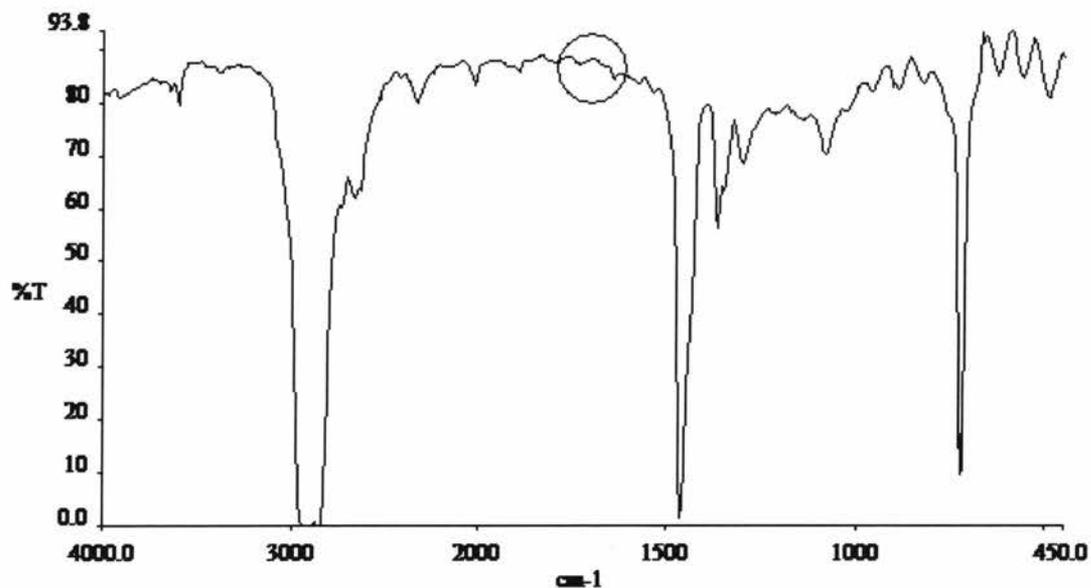


Figure 5.21 Infrared Spectra of untreated LD+LLDPE film (enlargement of spectrum (a) in Figure 5.20)

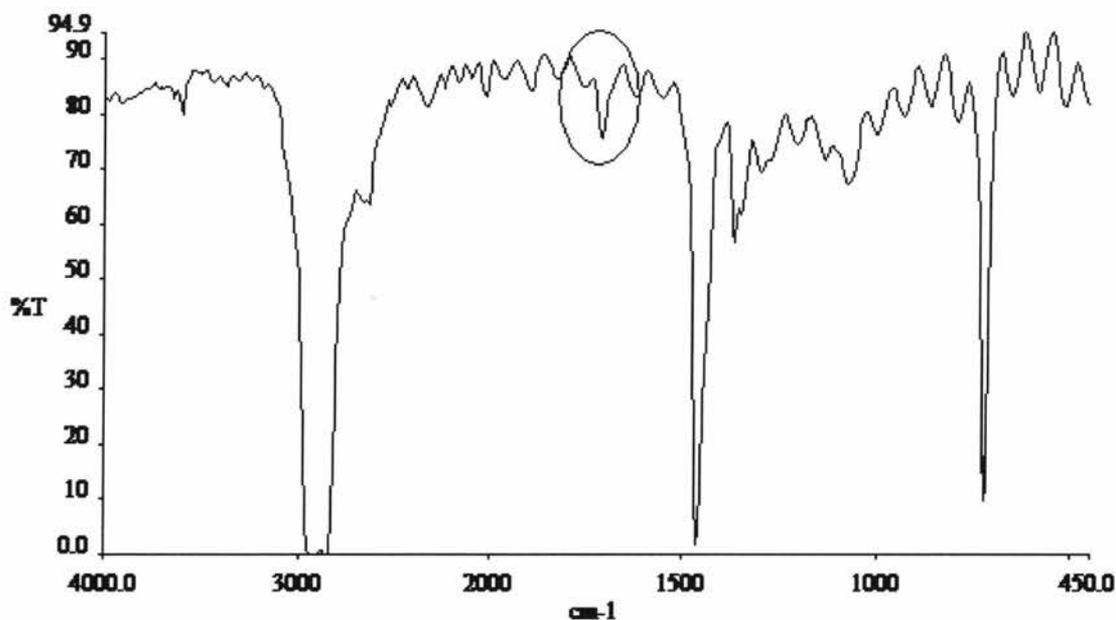


Figure 5.22 Infrared spectra of LD+LLDPE film ozonated with 0.04 g/L  $\text{FeCl}_3$ , 9 L/min gas flow rate and 3.5 wt % applied ozone dose (enlargement of spectrum (c) in Figure 5.20)

#### 5.3.7.4 Effect of applied ozone dosage on tensile strength of films

The tensile strength of ozonated LD+LLDPE films with Fe (III) catalyst and various applied dosage of ozone were tested. The details of testing method and the results of tensile strength are given in Table-9 of Appendix-IX. Five measurements in machine direction (MD) and five measurements in traverse direction (TD) were recorded. The average of total ten reading was recorded.

Figure 5.23 presents results of tensile strength measurements. The tensile strength of the virgin film is 24.71 MPa. The tensile strength was gradually decreased when concentration of ozone increased from 0 wt % (virgin film) to 3.5 wt %. The tensile strength of films ozonated with 3.5 wt % ozone and 60 min decreased up to 18.31 MPa.

The tensile strength of films was decreased by 25.9% when ozonation concentration was 3.5 wt %. Combining results in Figure 5.18 and 5.23, it looks like that ozonation of the film at 2.0 wt% for 60 min is appropriate both in generating peroxides and maintaining good mechanical strength. At this point, tensile strength decreased only by 14.6%.

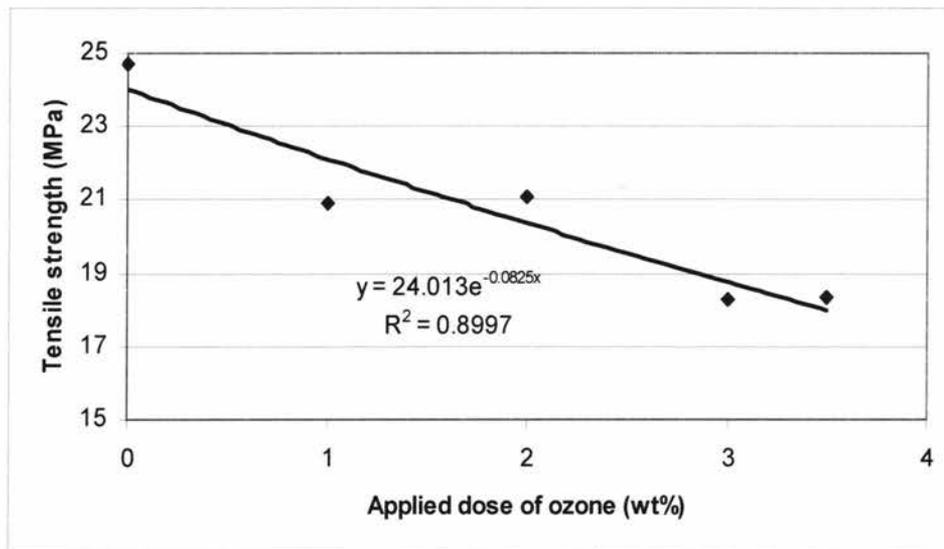


Figure 5.23 Tensile strength of LD+LLDPE ozonated with 0.04 g/L FeCl<sub>3</sub>, 60 min reaction time and 9 L/min gas flow rate for different applied dosage of ozone

As shown in Figure 5.23, the relationship between tensile strength and applied dose of ozone fits an exponential function well.

### 5.3.8 Ozonation with Advanced Oxidation Process (AOP)

The advanced oxidation processes (AOPs) are responsible for generating more OH• radicals when reacts with ozone during ozonation. O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub>/UV and O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>/UV are well known advanced oxygen processes (AOPs). In this study, hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) was dissolved in distilled water to conduct advanced ozonation. The

AOP process was conducted in absence of catalyst first. The applied ozone dose was 1 wt % and the reaction time was 60 min. Molar concentration (or molarity) of  $\text{H}_2\text{O}_2$  was set to be 0.005, 0.023 and 0.045 M, respectively. Calculation of molar concentration of  $\text{H}_2\text{O}_2$  is given in Appendix X. The details process conditions and the results of generation of peroxides are given in Appendix XI.

Figure 5.24 presents the results of the generation of peroxides with different molar concentration of  $\text{H}_2\text{O}_2$ . When concentration of  $\text{H}_2\text{O}_2$  increased from 0 to 0.045 M, the concentration of peroxide decreased from 0.098  $\text{mmol/m}^2$  to 0.047  $\text{mmol/m}^2$ .

The advanced ozonation was also carried out with  $\text{H}_2\text{O}_2$  and Fe (III) catalyst together. The details of process conditions and the results of peroxides generated are given in Appendix XII. It was found that (data not shown) when concentration of peroxide with constant 0.4 g/L dosage of Fe (III) catalyst increased from 0.005 M to 0.045 M, the concentration of peroxide decreased from 0.11  $\text{mmol/m}^2$  to 0.062  $\text{mmol/m}^2$ .

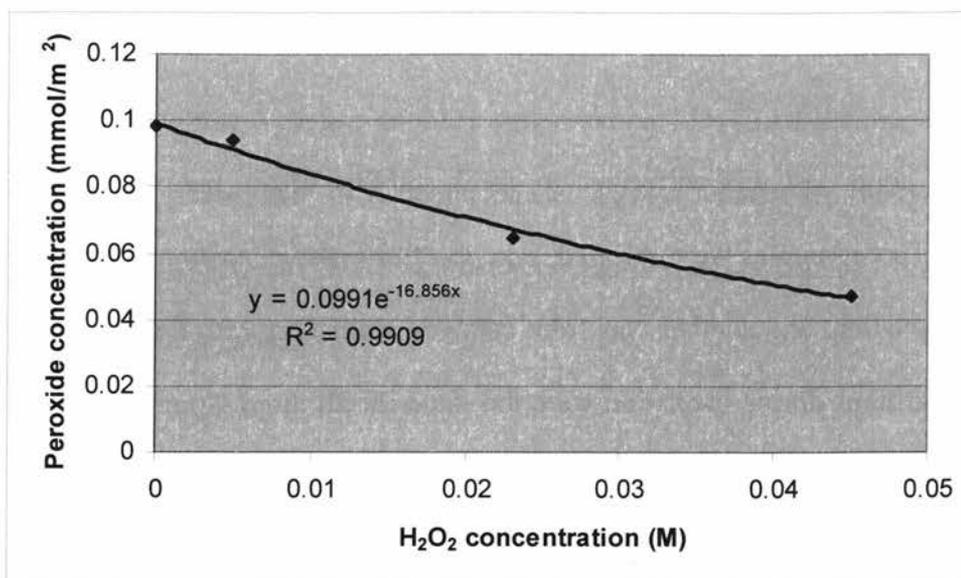


Figure 5.24 The generation of peroxide of films ozonated with 1.0 wt% applied ozone dose, 9 L/min ozone rate and 60 min reaction time for different molar of H<sub>2</sub>O<sub>2</sub>

In the ozonation with hydrogen peroxide, ozone decomposed and reacted with hydrogen peroxide ultimately, generated hydroxyl radicals. These radicals might be effective for ozonation of waste water, but might not effective for ozonation of polymer films. As discussed earlier, molecular ozone is responsible for generating peroxides into the polymer surface during ozonation. With higher concentration of H<sub>2</sub>O<sub>2</sub>, more molecular of ozone reacted with hydrogen peroxide and generated more hydroxyl radicals resulting lower peroxides generation. So above results of AOP are in agreements with our previous results.

The relationship between peroxides generation and concentration of hydrogen peroxide fits an exponential function well as shown in Figure 5.24.

## 5.4 Aging Test on the Treated LD+LLDPE Films

The aging test was performed to check stability of the peroxides generated by ozonation. Three samples were selected, one was from gaseous ozonation, one was from aqueous ozonation, and another was from catalytic ozonation with Fe (III) catalyst. The process conditions during ozonation were the same for all three samples. The films were examined for the concentration of peroxide immediately after ozonation, and 30 days after ozonation. Table 5.2 presents the results for aging test. It can conclude that the generated peroxides were stable.

Table 5.2 Results of aging test on treated films

Ozonation	Checking time	Peroxide concentration (mmol/m <sup>2</sup> )	Reduction in peroxide concentration (%)
Gas	Zero days after ozonation	0.1279	2.9
	30 days after ozonation	0.1242	
Aqueous	Zero days after ozonation	0.1201	3.1
	30 days after ozonation	0.1164	
With Fe(III)	Zero days after ozonation	0.1615	3.2
	30 days after ozonation	0.1563	

## 6. CONCLUSIONS

Peroxide groups were successfully generated on LD+LLDPE films by ozonation both in gaseous phase and in aqueous phase. The efficiency of the generation of peroxides had no significant difference between gas phase and aqueous ozonation with 1.0 wt% applied ozone dose.

pH was found to have effect on ozonation. In aqueous ozonation, lowering the pH enhanced peroxide generation by 14 %.

In aqueous phase ozonation, addition of soluble catalysts increased the generation of peroxides. Catalyst screening from salts of transitional metals of group VII and group VIII as well as magnesium, resulted in two effective catalysts, Fe (III). The minimum dosage of  $\text{FeCl}_3$  was found to be 0.04 g/L with 1.0 wt% applied ozone dose.

In addition to the direct peroxide concentration measurement, FTIR analyses, and contact angle measurements were conducted. The FTIR spectra demonstrated that hydroxyl and carbonyl groups were added onto the polymer films by ozonation. The density of these groups increased with the treatment time and applied dosage of ozone. The results of contact angle measurements demonstrated the improvement of hydrophilicity of films.

Tensile strength measurements were also conducted. Ozonation did not significantly affect the mechanical strength of the tested films. Even after 120 min

ozonation at 1 wt% applied ozone dose, 85% of the tensile strength still remained. The combination of 2.0 wt % and 60 min ozonation seems optimal for a good balance of peroxides generation and the film mechanical strength.

A novel approach of treat LD+LLDPE film, i.e., aqueous ozonation in presence of catalyst was applied successfully in this study.

## 7. RECOMMENDATIONS

- LD+LLDPE (Polyethylene) films ozonated by homogeneous catalytic ozonation with Fe (III) catalyst should be grafted with monomers in graft polymerization. These results should be compared with the results obtained through ozonation in aqueous phase (without catalysts) and its graft polymerization.
- Our preliminary results showed Cu (II) was effective to accelerate the reaction. The effect of different process parameters could be studied for ozonation of LD+LLDPE films with Cu (II) catalyst.
- Other catalysts like as Ag (I), Ti (II) and Zn (II) could be studied for homogeneous catalytic ozonation.
- UV could be combined with ozone treatment, and could be studied for ozonation with Fe (III) catalyst.
- Other polymer films such as PET, PU, PP and HDPE could be ozonated with Fe (III) catalyst.
- The protein adsorption test and the platelet adhesion test are most important for biomedical applications. So, these tests could be studied for catalytic ozonation followed by graft polymerization.

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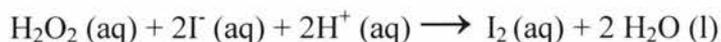
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## Appendix I

### Calculation of Peroxide Generation by Standard Iodometric Method:

The hydrogen peroxide reaction with iodide in acidic medium:



The created  $\text{I}_2 (\text{aq})$  can be investigated by the titration of a standard  $\text{S}_2\text{O}_3^{2-} (\text{aq})$  solution



Here we assume that the R-OOH has the same function as the  $\text{H}_2\text{O}_2$  in this reaction.

So 1 mole  $\text{H}_2\text{O}_2$  or R-OOH reacts with 2 mole  $\text{S}_2\text{O}_3^{2-}$

For example, the determination of peroxide of polyethylene (LD+LLDPE) film ozonated with 1 wt % ozone and 120 min reaction time in aqueous phase is as below,

No. of strips for titration: 2

Size of each strip: 1.5 inch  $\times$  10 inch

Total area of strips: No. of sides  $\times$  No. of strips  $\times$  Width  $\times$  Length

$$= 2 \times 2 \times (1.5\text{inch} \times 0.0254\text{m}) \times (10 \text{ inch} \times 0.0254\text{m})$$

$$\text{Total area} = 0.038710 \text{ m}^2$$

Volume of  $\text{Na}_2\text{S}_2\text{O}_3$  Consumed in titration: 9.3 ml

Normality of  $\text{Na}_2\text{S}_2\text{O}_3 = 0.001 \text{ N}$

So, no. of milliequivalents of  $\text{Na}_2\text{S}_2\text{O}_3 = \text{Normality} \times \text{Volume}$

$$= 0.001 \times 9.3 \text{ me}$$

$$= 0.0093 \text{ me}$$

As per general chemistry and above reaction,

$$2 \times \text{no. of milliequivalents of } \text{Na}_2\text{S}_2\text{O}_3 = \text{no. of milliequivalents of R-OOH}$$

Also, as per definition of normality,

$$2 \times \text{number of equivalent of Na}_2\text{S}_2\text{O}_3 = \text{no. of equivalents of R-OOH}$$

Therefore,

$$\text{Normality of R-OOH} = \frac{0.0093}{2} \text{ me}$$

$$= 0.00465 \text{ me}$$

$$\text{Molarity} = \frac{\text{Normality}}{n} \quad (n = \text{the number of protons exchanged in a reaction})$$

n = 1 in this reaction

Therefore, Molarity of R-OOH:  $0.00465 \div 1 = 0.00465 \text{ mmol}$

Here, unit of normality is milliequivalents, so unit of molarity is millimole (mmol),

Concentration of peroxide (R-OOH) = Molarity of peroxide/ Area of strips

$$\text{Concentration of peroxide (R-OOH)} = 0.00465 \text{ mmol} \div 0.038710 \text{ m}^2$$

$$\text{Concentration of peroxide (R-OOH)} = 0.120 \text{ mmol/ m}^2$$

## Appendix II

### Preparation of Standard Sodium Thiosulfate Solution:

For 0.1N  $\text{Na}_2\text{S}_2\text{O}_3$ : Dissolved 25 g  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  (Sodium Thiosulfate Pentahydrate) in a 1.0 litre freshly boiled distilled water and standardized against  $\text{K}_2\text{Cr}_2\text{O}_7$  (Potassium dichromate) solution after at least 2 weeks storage. This solution diluted necessary to make 0.001N  $\text{Na}_2\text{S}_2\text{O}_3$  for titration.

Above Sodium thiosulfate solutions must be calibrated by standard  $\text{K}_2\text{Cr}_2\text{O}_7$  solution.

## Appendix III

### Preparation of Standard Potassium dichromate ( $K_2Cr_2O_7$ ) Solution:

Standard 0.1N  $K_2Cr_2O_7$  - Dissolved 4.904 g anhydrous potassium dichromate in 1.0 liter distilled water .Then stored in a glass-stopper bottle.

For 0.01N  $K_2Cr_2O_7$ : Diluted 10 times 0.1N  $K_2Cr_2O_7$  (Above solution) with distilled water.

For 0.001N  $K_2Cr_2O_7$ : Diluted 10 times 0.01N  $K_2Cr_2O_7$  (Above solution) with distilled water.

## Appendix IV

### Calibration of Standard Sodium Thiosulfate solution

In 80.0 ml distilled water, added 1.0 ml concentrated  $H_2SO_4$ , precisely measured 10 ml standard  $K_2Cr_2O_7$  solution added in the solution, then added 1.0 g solid crystals of KI, stirred and kept in dark for 6 minutes. Titrated with  $Na_2S_2O_3$  solution and recorded burette reading [APHA. 1992].

Calculation:  $N_1 \times V_1 = N_2 \times V_2$

$$N_1 = N_2 \times V_2 / V_1$$

Here,  $N_1$  = Normality of sodium thiosulfate (N)

$N_2$  = Normality of potassium dichromate consumed (N)

$V_1$  = Volume of sodium thiosulfate (Burette reading, ml)

$V_2$  = Volume of potassium dichromate consumed (ml)

## Appendix V

### Calculation for Amount of Fe (III) Catalyst as per dosage

Molecular weight of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O} = \text{Fe} + 3(\text{Cl}) + 12(\text{H}) + 6(\text{O})$

Atomic weight of Fe = 55.85 g

Atomic weight of Cl = 35.45g

Atomic weight of H = 1.00 g

Atomic weight of O = 16.00 g

So, MW of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O} = 55.85 + 3(35.45) + 12(1) + 6(16)$

$$= 55.85 + 106.35 + 12 + 96$$

$$= 270.20 \text{ g}$$

MW of  $6\text{H}_2\text{O} = 12(\text{H}) + 6(\text{O})$

$$= 12(1) + 6(16)$$

$$= 108 \text{ g}$$

MW of  $\text{FeCl}_3 = \text{M.W of } \text{FeCl}_3 \cdot 6\text{H}_2\text{O} - \text{M.W of } \text{H}_2\text{O}$

$$= 270.20 - 108$$

$$= 162.20 \text{ g}$$

% weight of  $\text{FeCl}_3$  in  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O} = 162.2/270.2$

$$= 0.60$$

$$= 60 \%$$

For 0.2 g/L dosage of  $\text{FeCl}_3$ , weight of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O} = 0.2/0.6$

$$= 0.33 \text{ g/L}$$

For 11 liters reactor's volume, weight of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O} = 0.33 \times 11$

$$= 3.666 \text{ g}$$

Accordingly, for 0.1 g/L dosage of  $\text{FeCl}_3$  and 11 liters reactor's volume,

$$\text{Weight of } \text{FeCl}_3 \cdot 6\text{H}_2\text{O} = 1.83\text{g}$$

For 0.05 g/L dosage of  $\text{FeCl}_3$  and 11 liters reactor's volume,

$$\text{Weight of } \text{FeCl}_3 \cdot 6\text{H}_2\text{O} = 0.916\text{ g}$$

For 0.04 g/L dosage of  $\text{FeCl}_3$  and 11 liters reactor's volume

$$\text{Weight of } \text{FeCl}_3 \cdot 6\text{H}_2\text{O} = 0.733\text{ g}$$

For 0.03 g/L dosage of  $\text{FeCl}_3$  and 11 liters reactor's volume

$$\text{Weight of } \text{FeCl}_3 \cdot 6\text{H}_2\text{O} = 0.55\text{ g}$$

For 0.01 g/L dosage of  $\text{FeCl}_3$  and 11 liters reactor's volume

$$\text{Weight of } \text{FeCl}_3 \cdot 6\text{H}_2\text{O} = 0.183\text{ g}$$

For 0.005 g/L dosage of  $\text{FeCl}_3$  and 11 liters reactor's volume,

$$\text{Weight of } \text{FeCl}_3 \cdot 6\text{H}_2\text{O} = 0.091\text{ g}$$

## Appendix-VI Experimental Data Tables of LD+LLDPE Ozonated in Gaseous Phase

Table -1 Peroxide data table of LD+LLDPE film ozonated in gaseous phase

Material	LD+LLDPE	Size	1.5 inch × 10 inch	No. of films	06
Applied ozone dose	1.0 wt %		Gas flow rate	9 l/min	
Reaction temperature	23-25°C (Room Temperature)		Gas Pressure	96.5 KPa (14 psig)	
Titration Solution	50 ml Iso-propanol + 2 ml Saturated KI + 2 ml Glacial Acetic Acid				
Titration Procedure	Cutting pieces of 2 ozonated films soaked in above solution, heated up to boiling temperature with stirring, kept 7 min incipient boiling without cooling, titrated with 0.001N Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>				
Films were degassed by vacuum for 60 min after ozonation					

Ozonation time (min)	Consumption of 0.001N Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> (ml)		Molarity of Peroxide (mmol)		Area of Sample (m <sup>2</sup> )	Concentration of peroxide (mmol/m <sup>2</sup> )		
	Test-1	Test-2	Test-1	Test-2		Test-1	Test-2	Average
15	5	4.7	0.0025	0.0024	0.0387	0.065	0.061	0.063
30	6.2	6.1	0.0031	0.0031	0.0387	0.080	0.079	0.080
45	7.2	7.1	0.0036	0.0036	0.0387	0.093	0.092	0.093
60	8.3	8.1	0.0042	0.0041	0.0387	0.107	0.105	0.106
90	8.9	8.8	0.0045	0.0044	0.0387	0.115	0.114	0.115
120	9.3	10.5	0.0047	0.0053	0.0387	0.120	0.136	0.128

Ozonation time (min)	Standard Deviation	Standard Error	Error (95 % Confidence)
15	0.003	0.002	0.004
30	0.001	0.001	0.002
45	0.001	0.001	0.002
60	0.002	0.001	0.003
90	0.001	0.001	0.002
120	0.011	0.008	0.015

Following equations are used error analysis.

$$(1) \quad \text{Standard Deviation (S.D.)} = \sqrt{\frac{\sum_{s=1}^m \sum_{i=1}^n (x_i - \bar{X})^2}{N - 1}}$$

where:

s = series number

i = measurement number in series s

m = number of series

n = number of measurements

$x_i$  = measurement value and the ith point

$\bar{X}$  = Average

N = Total measurements in all series

$$(2) \quad \text{Standard Error} = \frac{S.D.}{\sqrt{N}}$$

$$(3) \quad \text{Error (with 95% confidence)} = 1.96 \frac{S.D.}{\sqrt{N}}$$

## Appendix VI Experimental Data Tables of LD+LLDPE Ozonated in Gaseous Phase

Table-2 Measurements of contact angle of virgin and ozonated LD+LLDPE film in gaseous phase

Material	LD+LLDP E	Size	1.5 inch × 10 inch	No. of films	06
Applied ozone dose	1.0 wt %	Gas flow rate	9 l/min	Gas Pressure	96.5 KPa (14 psig)
Pure distilled water	3.0 µl	Reaction Temperature	23-25°C (Room Temperature)	Contact angle	Static
Films were degassed by vacuum for 60 min after ozonation					

Ozonation Time (min)	Contact Angle (Degree)					Standard Deviation	Standard Error	Error (95 % confidence)
	Spot-1	Spot-2	Spot-3	Spot-4	Average			
Virgin	91.3	92	90.3	90.6	91.05	0.759	0.380	0.744
15	80.9	83	82.2	81.4	81.88	0.922	0.461	0.903
30	78.4	75.8	79.3	78.5	78.00	1.521	0.761	1.491
45	71.2	76.1	75.1	74.4	74.20	2.118	1.059	2.076
60	74.7	73.9	73.4	72	73.50	1.134	0.567	1.112
90	73.3	71.5	72.5	73.6	72.73	0.939	0.470	0.921
120	69.4	71.5	72.5	71.2	71.15	1.292	0.646	1.267

## Appendix VI Experimental Data Tables of LD+LLDPE Ozonated in Gaseous Phase

Table -3 Tensile strength data table of LD+LLDPE in gaseous phase

Material	LD+LLDPE	Size	1.5 inch × 10 inch	No. of films	06
Applied ozone dose	1.0 wt %	Gas flow rate	9 L/min	Gas Pressure	96.5 KPa
Equipment	Instron	Cross-head speed	10 in/min		
Standard Testing Method	ASTM D882-02	Width	5 mm		
Films were degassed by vacuum for 60 min after ozonation					

Ozonation time (min)	Tensile Strength (MPa)					
	Machine Direction					
	Test -1	Test-2	Test-3	Test-4	Test-5	Ave. - MD
Virgin	24.94	24.70	23.47	23.70	24.41	24.24
30	24.68	20.72	24.52	23.47	23.84	23.45
60	21.45	22.99	23.92	22.89	24.66	23.18
90	22.10	21.44	22.62	20.57	20.37	21.42
120	21.10	22.67	21.56	19.79	21.97	21.42

Ozonation time (min)	Tensile Strength (MPa)					
	Traverse Direction					
	Test -1	Test-2	Test-3	Test-4	Test-5	Ave. - TD
Virgin	25.02	25.47	25.79	24.40	25.22	25.18
30	24.25	23.63	22.72	23.03	24.90	23.70
60	22.90	18.65	24.83	23.06	23.31	22.55
90	22.42	23.11	22.22	23.59	18.25	21.92
120	22.07	21.77	22.48	20.36	23.51	22.04

Ozonation time (min)	Average (MPa)	Standard Deviation	Standard Error	Error (95 % confidence)
Virgin	24.71	0.738	0.233	0.457
30	23.58	1.229	0.389	0.762
60	22.87	1.771	0.560	1.098
90	21.67	1.576	0.499	0.977
120	21.73	1.098	0.342	0.681

## Appendix VI Experimental Data Tables of LD+LLDPE Ozonated in Gaseous Phase

Table- 4 Peroxide data table of LD+LLDPE film for optimizing incipient boiling time

Material	LD+LLDPE	Size	1.5 inch × 10 inch	No. of films	06
Applied ozone dose	1.0 wt %	Gas flow rate	9 L/min	Gas Pressure	96.5 KPa (14 psig)
Reaction temperature	23-25°C (Room Temperature)		Reaction time	60 min	
Titration Solution	50 ml Iso-propanol + 2 ml Saturated KI + 2 ml Glacial Acetic Acid				
Titration Procedure	Cutting pieces of 2 ozonated films soaked in above solution, heated up to boiling temperature with stirring, kept 7 min incipient boiling without cooling, titrated with 0.001N Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>				
Films were degassed by vacuum for 60 min after ozonation					

Incipient boiling time (min)	Consumption of 0.001N Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> (ml)	Molarity of Peroxides (mmol)	Area of sample (m <sup>2</sup> )	Concentration of peroxide (mmol/m <sup>2</sup> )
2	5.5	0.00275	0.0387	0.071
5	7.0	0.0035	0.0387	0.090
7	8.1	0.00405	0.0387	0.105
9	8.2	0.00410	0.0387	0.106
11	8.1	0.00405	0.0387	0.105

## Appendix VII Experimental Data Tables of LD+LLDPE Ozonated in Aqueous Phase (without catalyst)

Table -1 Peroxide data table of films ozonated in aqueous phase (without catalyst)

Material	LD+LLDPE	Size	1.5 inch × 10 inch	No. of films	06
Applied ozone dose	1.0 wt %		Gas flow rate	9 l/min	
Reaction temperature	23-25°C (Room Temperature)		Gas Pressure	96.5 KPa (14 psig)	
Titration Solution	50 ml Iso-propanol + 2 ml Saturated KI + 2 ml Glacial Acetic Acid.				
Titration Procedure	Cutting pieces of 2 ozonated films soaked in above solution, heated up to boiling temperature with stirring, kept 7 min incipient boiling without cooling, titrated with 0.001N Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>				
Films were degassed by vacuum for 60 min after ozonation					

Ozonation time (min)	Consumption of 0.001N Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> (ml)		Molarity of Peroxide (mmol)		Area of Sample (m <sup>2</sup> )	Concentration of peroxide (mmol/m <sup>2</sup> )		
	Test-1	Test-2	Test-1	Test-2		Test-1	Test-2	Average
15	5	4.5	0.0025	0.0023	0.0387	0.064	0.058	0.061
30	6.1	5.9	0.0031	0.0030	0.0387	0.079	0.076	0.078
45	6.5	7.1	0.0033	0.0035	0.0387	0.084	0.091	0.088
60	7.8	7.4	0.0039	0.0037	0.0387	0.100	0.096	0.098
90	9.0	8.4	0.0045	0.0042	0.0387	0.116	0.108	0.112
120	9.5	9.1	0.0048	0.0046	0.0387	0.123	0.117	0.120

Ozonation time (min)	Standard Deviation	Standard Error	Error (95 % Confidence)
15	0.005	0.004	0.007
30	0.002	0.001	0.003
45	0.006	0.004	0.008
60	0.004	0.003	0.006
90	0.006	0.004	0.008
120	0.004	0.003	0.006

## Appendix VII Experimental Data Tables of LD+LLDPE Ozonated in Aqueous Phase (without catalyst)

Table-2 Measurements of contact angle of virgin and ozonated LD+LLDPE film in aqueous phase (without catalyst)

Material	LD+LLDPE	Size	1.5 inch × 10 inch	No. of films	06
Applied ozone dose	1.0 wt %	Gas flow rate	9 l/min	Gas Pressure	96.5 KPa (14 psig)
Pure distilled water	3.0 µl	Reaction Temperature	23-25°C (Room Temperature)	Contact angle	Static
Films were degassed by vacuum for 60 min after ozonation					

Ozonation Time (min)	Contact Angle (Degree)					Standard Deviation	Standard Error	Error (95 % confidence)
	Spot-1	Spot-2	Spot-3	Spot-4	Average			
Virgin	91.3	92	90.3	90.6	91.05	0.759	0.380	0.744
15	81	81	84.2	83.6	82.45	1.692	0.846	1.658
30	79.5	80.8	80.1	79.5	79.98	0.619	0.309	0.606
45	76.3	71.4	78.4	77.7	75.95	3.157	1.578	3.093
60	77.8	75.6	75.4	76.9	76.42	1.133	0.566	1.110
90	73.7	72.8	74.2	75.2	73.98	1.001	0.501	0.981
120	73.3	70.1	72.1	75.4	72.80	2.219	1.110	2.174

## Appendix VII Experimental Data Tables of LD+LLDPE Ozonated in Aqueous Phase (without catalyst)

Table – 3 Tensile strength data table of LD+LLDPE in aqueous phase (without catalyst)

Material	LD+LLDPE	Size	1.5 inch × 10 inch	No. of films	06
Applied ozone dose	1.0 wt %	Gas flow rate	9 L/min	Gas Pressure	96.5 KPa
Equipment	Instron	Cross-head speed	10 in/min		
Standard Testing Method	ASTM D882-02	Width	5 mm		
Films were degassed by vacuum for 60 min after ozonation					

Ozonation time (min)	Tensile Strength (MPa)					
	Machine Direction					
	Test -1	Test-2	Test-3	Test-4	Test-5	Ave.-MD
Virgin	24.94	24.70	23.47	23.70	24.41	24.24
30	22.84	22.34	20.63	21.75	23.79	22.27
60	22.87	22.14	23.02	21.20	19.70	21.78
90	24.21	19.38	20.88	21.71	19.11	21.06
120	21.47	20.59	20.35	21.98	19.20	20.72

Ozonation time (min)	Tensile Strength (MPa)					
	Traverse Direction					
	Test -1	Test-2	Test-3	Test-4	Test-5	Ave.-TD
Virgin	25.02	25.47	25.79	24.40	25.22	25.18
30	23.99	21.63	25.31	24.60	25.57	24.22
60	25.77	22.54	19.78	20.20	25.04	22.67
90	23.07	18.79	24.29	24.76	21.66	22.51
120	18.79	22.23	21.78	24.11	21.73	21.73

Ozonation time (min)	Average (MPa)	Standard Deviation	Standard Error	Error (95 % confidence)
Virgin	24.71	0.738	0.233	0.457
30	23.25	1.667	0.527	1.033
60	22.23	2.086	0.660	1.293
90	21.79	2.246	0.710	1.392
120	21.22	1.554	0.491	0.963

**Appendix VIII Experimental Data Table of LD+LLDPE Ozonated  
with different pH (without catalyst)**

Table-Peroxide data table of LD+LLDPE film ozonated for different pH (without catalyst)

Material	LD+LLDPE	Size	1.5 inch × 10 inch	No. of films	06
Applied ozone dose	1.0 wt %	Gas flow rate	9 L/min	Gas Pressure	96.5 KPa (14 psig)
Titration Solution	50 ml Iso-propanol + 2 ml Saturated KI + 2 ml Glacial Acetic Acid			Reaction Time	120 min
Titration Procedure	Cutting pieces of 2 ozonated films soaked in above solution, heated up to boiling temperature with stirring, kept 7 min incipient boiling without cooling, titrated with 0.001N Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>				
Films were degassed by vacuum for 60 min after ozonation					

pH value	Consumption of 0.001N Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> (ml)			Molarity of peroxides (mmol)	Area of Sample (m <sup>2</sup> )	Concentration of peroxide (mmol/m <sup>2</sup> )
	Test-1	Test-2	Average			
1.6	10.6	-	10.6	0.0053	0.0387	0.137
3.0	10.4	10.3	10.3	0.0051	0.0387	0.132
5.7	9.5	9.1	9.3	0.00465	0.0387	0.120
7.9	9.2	-	9.2	0.0046	0.0387	0.119
9.9	8.4	-	8.4	0.0042	0.0387	0.109

## Appendix IX Experimental Data Tables of LD+LLDPE Ozonated for Homogeneous Catalytic Ozonation

Table-1 Peroxide data table of LD+LLDPE film ozonated in presence of different catalysts

Material	LD+LLDPE	Size	1.5 inch × 10 inch	No. of films	06
Applied ozone dose	1.0 wt %	Gas flow rate	9 L/min	Gas Pressure	96.5 KPa (14 psig)
Reaction time	120 min	Reaction temperature	23-25°C (Room Temperature)		
Titration Solution	50 ml Iso-propanol + 2 ml saturated KI + 2ml Glacial Acetic Acid				
Titration Procedure	Cutting pieces of 2 ozonated films soaked in above solution, heated up to boiling temperature with stirring, kept 7 min incipient boiling without cooling, titrated with 0.001N Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>				
Films were degassed by vacuum for 60 min after ozonation					

Catalyst	Chemical	Dosage of catalyst (g/L)	Consumption of 0.001N Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> (ml)			Molarity of peroxides (mmol)	Area of Sample (m <sup>2</sup> )	Concentration of peroxide (mmol/m <sup>2</sup> )
			Test-1	Test-2	Ave.			
Without Catalyst	-	-	9.5	9.1	9.3	0.0047	0.0387	0.120
Mg (II)	MgSO <sub>4</sub>	0.2	9.0	-	9.0	0.0045	0.0387	0.116
Mn (II)	MnCl <sub>2</sub>	0.2	9.0	-	9.0	0.0045	0.0387	0.116
Ni (II)	NiSO <sub>4</sub>	0.2	9.4	-	9.4	0.0047	0.0387	0.121
Co (II)	Co(NO <sub>3</sub> ) <sub>2</sub>	0.2	9.2	-	9.2	0.0046	0.0387	0.119
Cu (II)	CuSO <sub>4</sub>	0.2	10.9	-	10.9	0.00054	0.0387	0.140
Fe (III)	FeCl <sub>3</sub>	0.2	12.4	12.6	12.5	0.0063	0.0387	0.162

## Appendix IX Experimental Data Tables of LD+LLDPE Ozonated for Homogeneous Catalytic Ozonation

Table -2 Peroxide data table of ozonated LD+LLDPE film with Fe (III) catalyst for different reaction times

Material	LD+LLDPE	Size	1.5 inch × 10 inch	No. of films	06
Applied ozone dose	1.0 wt %	Gas flow rate	9 L/min	Gas Pressure	96.5 KPa (14 psig)
Reaction Temperature	23-25°C (Room Temperature)	Catalyst	Fe(III)	pH	2.9
Chemical	FeCl <sub>3</sub>	Dosage of Catalyst	0.2 g/L		
Titration Solution	50 ml Iso-propanol + 2 ml saturated KI + 2ml Glacial Acetic Acid				
Titration Procedure	Cutting pieces of 2 ozonated films soaked in above solution, heated up to boiling temperature with stirring, kept 7 min incipient boiling without cooling, titrated with 0.001N Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>				
Films were degassed by vacuum for 60 min after ozonation					

Reaction time (min)	Consumption of 0.001N Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> (ml)			Molarity of peroxides (mmol)	Area of Sample (m <sup>2</sup> )	Concentration of peroxide (mmol/m <sup>2</sup> )
	Test-1	Test-2	Average			
30	7.6	-	7.6	0.0038	0.0387	0.0981
60	9.6	10.0	9.8	0.0049	0.0387	0.1266
90	11.2	-	11.2	0.0056	0.0387	0.1447
120	12.4	12.6	12.5	0.0063	0.0387	0.1620

## Appendix IX Experimental Data Tables of LD+LLDPE Ozonated for Homogeneous Catalytic Ozonation

Table – 3 Peroxide data table of LD+LLDPE ozonated into the distilled water with 3.0 pH and without catalyst

Material	LD+LLDPE	Size	1.5 inch × 10 inch	No. of films	06
Applied ozone dose		1.0 wt %	Gas flow rate	9 L/min	
Reaction Temperature		23-25°C (Room Temperature)	Gas Pressure	96.5 KPa (14 psig)	
Titration Solution	50 ml Iso-propanol + 2 ml saturated KI + 2ml Glacial Acetic Acid				
Titration Procedure	Cutting pieces of 2 ozonated films soaked in above solution, heated up to boiling temperature with stirring, kept 7 min incipient boiling without cooling, titrated with 0.001N Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>				
Films were degassed by vacuum for 60 min after ozonation					

Reaction Time (min)	Consumption of 0.001N Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> ( ml)	Molarity of peroxide (mmol)	Area of sample (m <sup>2</sup> )	Concentration of peroxide (m mol/m <sup>2</sup> )
30	6.4	0.0032	0.0387	0.0827
60	8.3	0.0042	0.0387	0.1072
90	9.4	0.0047	0.0387	0.1215
120	10.2	0.0051	0.0387	0.1317

## Appendix IX Experimental Data Tables of LD+LLDPE Ozonated for Homogeneous Catalytic Ozonation

Table- 4 Contact angle measurements of LD+LLDPE ozonated with Fe (III) catalyst for different reaction times

Material	LD+LLDPE	Size	1.5 inch × 10 inch		No. of films	06
Applied ozone dose		1.0 wt %	Gas flow rate		9 L/min	
Reaction Temperature		23-25°C (Room Temperature)	Gas Pressure		96.5 KPa (14 psig)	
Contact angle	Static	Catalyst	Fe (III)	Chemical	FeCl <sub>3</sub>	
Pure distilled water		3μl	Dosage of catalyst		0.2 g/L	
Films were degassed by vacuum for 60 min after ozonation						

Reaction Time (min)	Contact Angle (degree)				
	Spot-1	Spot-2	Spot-3	Spot-4	Average
Virgin	91.3	92.0	90.3	90.6	91.05
30	78.5	77.5	77.1	79.3	78.10
60	73.7	73.5	70.2	76.9	73.57
90	70.5	69.6	75.5	74.9	72.62
120	67.2	67.0	70.0	66.5	67.68

## Appendix IX Experimental Data Tables of LD+LLDPE Ozonated for Homogeneous Catalytic Ozonation

Table-5 Tensile strength data table of LD+LLDPE films ozonated with Fe (III) catalyst for different reaction times

Material	LD+LLDPE	Size	1.5 inch × 10 inch		No. of films	06
Applied ozone dose		1.0 wt %		Gas flow rate		9 L/min
Equipment	Instron	Cross-Head speed	10 in/min	Standard Testing Method	ASTM D882-02	
Films were degassed by vacuum for 60 min after ozonation						

Reaction time (min)	Tensile Strength (MPa)					
	Machine Direction					
	Test -1	Test-2	Test-3	Test-4	Test-5	Ave.-MD
Virgin	24.94	24.70	23.47	23.70	24.41	24.24
30	23.95	23.03	21.49	21.01	21.90	22.28
60	21.38	22.98	22.33	22.88	20.91	22.09
90	23.17	20.97	19.13	24.04	20.83	21.63
120	19.94	20.46	20.05	21.22	21.86	20.71

Reaction time (min)	Tensile Strength (MPa)					
	Traverse Direction					
	Test -1	Test-2	Test-3	Test-4	Test-5	Ave.-TD
Virgin	25.02	25.47	25.79	24.40	25.22	25.18
30	24.29	25.13	18.96	22.70	21.91	22.60
60	24.76	21.86	18.09	23.37	21.79	21.97
90	23.35	22.22	23.16	19.53	-	22.06
120	22.26	21.35	19.02	20.73	23.09	21.29

Reaction time (min)	Average (MPa)
Virgin	24.71
30	22.43
60	22.03
90	21.84
120	20.99

## Appendix IX Experimental Data Tables of LD+LLDPE Ozonated for Homogeneous Catalytic Ozonation

Table-6 Peroxide data table of homogeneous catalytic ozonation on LD+LLDPE film to optimize dosage of Fe (III) catalyst

Material	LD+LLDPE	Size	1.5 inch × 10 inch		No. of films	06
Applied ozone dose		1.0 wt %		Gas flow rate		9 L/min
Reaction Temperature		23-25°C (Room Temperature)		Gas Pressure		96.5 KPa (14 psig)
Reaction Time		120 min		Chemical		FeCl <sub>3</sub>
Titration Solution		50 ml Iso-propanol + 2 ml saturated KI + 2ml Glacial Acetic Acid				
Titration Procedure		Cutting pieces of 2 ozonated films soaked in above solution, heated up to boiling temperature with stirring, kept 7 min incipient boiling without cooling, titrated with 0.001N Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>				
Films were degassed by vacuum for 60 min after ozonation						

Dosage of catalyst(g/L)	pH of solution	Consumption of 0.001N Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> (ml)			Molarity of peroxides (mmol)	Area of Sample (m <sup>2</sup> )	Concentration of peroxide (mmol/m <sup>2</sup> )
		Test-1	Test-2	Average			
0.005	4.1	10.5	-	10.5	0.0053	0.0387	0.136
0.01	3.8	11.4	-	11.4	0.0057	0.0387	0.148
0.03	3.6	11.9	-	11.9	0.0060	0.0387	0.155
0.04	3.1	12.8	12.6	12.7	0.0063	0.0387	0.163
0.05	3.2	12.3	12.7	12.5	0.0062	0.0387	0.162
0.2	2.9	12.6	12.4	12.5	0.0062	0.0387	0.162
0.5	2.7	12.6	-	12.6	0.0063	0.0387	0.163

## Appendix IX Experimental Data Tables of LD+LLDPE Ozonated for Homogeneous Catalytic Ozonation

Table-7 Peroxide data table of ozonated LD+LLDPE film with Fe (III) catalyst for different applied dosage of ozone

Material	LD+LLDPE	Size	1.5 inch × 10 inch	
Nos. of films		06	Gas flow rate	9 L/min
Reaction Temperature		23-25°C (Room Temperature)	Gas Pressure	96.5 KPa (14 psig)
Catalyst	Fe (III)	Chemical	FeCl <sub>3</sub>	
Reaction Time		60 min	Dosage of catalyst	0.04 g/L
Titration Solution	50 ml Iso-propanol + 2 ml saturated KI + 2ml Glacial Acetic Acid			
Titration Procedure	Cutting pieces of 2 ozonated films soaked in above solution, heated up to boiling temperature with stirring, kept 7 min incipient boiling without cooling, titrated with 0.001N Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>			
Films were degassed by vacuum for 60 min after ozonation				

Applied dosage of ozone (wt%)	Consumption of Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> solution (ml)	Molarity of Peroxides (mmol)	Area of sample (m <sup>2</sup> )	Concentration of peroxide (m mol/m <sup>2</sup> )
0.5	7.2	0.00360	0.0387	0.093
1.0	9.7	0.00485	0.0387	0.125
2.0	12.6	0.00630	0.0387	0.163
3.0	15.9	0.00795	0.0387	0.205
3.5	17.1	0.00855	0.0387	0.220

## Appendix IX Experimental Data Tables of LD+LLDPE Ozonated for Homogeneous Catalytic Ozonation

Table- 8 Contact angle measurements of LD+LLDPE ozonated with Fe (III) catalyst with different applied dosage of ozone

Material	LD+LLDPE	Size	1.5 inch × 10 inch	No. of films	06
Pure water	3μl	Gas flow rate	9 L/min	Gas Pressure	96.5 KPa (14 psig)
Reaction Temperature	23-25°C (Room Temperature)	Reaction time	60 min	Contact angle	Static
Chemical	FeCl <sub>3</sub>	Dosage of Catalyst		0.04 g/L	
Films were degassed by vacuum for 60 min after ozonation					

Applied dosage of ozone (wt %)	Contact Angle measurement (degree)				
	Spot-1	Spot-2	Spot-3	Spot-4	Average
Virgin	91.3	92.0	90.3	90.6	91.05
1	72.6	70.3	70.1	72.8	71.50
2	69.7	69.1	68.8	63.6	67.80
3	67.3	68.0	69.0	66.8	67.70
3.5	67.3	67.2	66.8	66.5	66.95

## Appendix IX Experimental Data Tables of LD+LLDPE Ozonated for Homogeneous Catalytic Ozonation

Table-9 Tensile strength data table of LD+LLDPE ozonated with Fe (III) catalyst and different applied dose of ozone

Material	LD+LLDPE	Size	1.5 inch × 10 inch	No. of films	06
Cross-head speed		10 in/min	Gas flow rate		9 L/min
Reaction Temperature		23-25°C (Room Temperature)	Gas Pressure		96.5 KPa
Instrument	Instron	Reaction Time	60 min	Dosage of catalyst	0.04 g/L
Films were degassed by vacuum for 60 min after ozonation					

Applied dose of ozone (wt %)	Tensile Strength (MPa)					
	Machine Direction					
	Test -1	Test-2	Test-3	Test-4	Test-5	Ave.-MD
Virgin	24.94	24.70	23.47	23.70	24.41	24.24
1	19.27	18.34	21.63	22.50	20.48	20.44
2	21.30	20.53	19.75	22.15	22.17	21.18
3	20.07	17.96	18.49	13.89	20.04	18.09
3.5	16.55	17.28	15.55	18.42	21.44	17.85

Applied dose of ozone (wt %)	Tensile Strength (MPa)					
	Traverse Direction					
	Test -1	Test-2	Test-3	Test-4	Test-5	Ave.-TD
Virgin	25.02	25.47	25.79	24.40	25.22	25.18
1	22.21	20.02	19.94	22.61	21.86	21.33
2	18.67	22.13	21.26	20.93	22.22	21.04
3	20.31	16.96	17.27	20.10	17.74	18.48
3.5	16.95	17.19	20.13	19.09	20.54	18.78

Applied dose of ozone (wt%)	Average (MPa)
Virgin	24.71
1	20.90
2	21.10
3	18.28
3.5	18.31

## Appendix IX Experimental Data Tables of LD+LLDPE Ozonated for Homogeneous Catalytic Ozonation

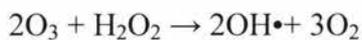
Table -10 Peroxide data table of homogeneous catalytic ozonation on LD+LLDPE film with Cu (II) catalyst

Material	LD+LLDPE	Size	1.5 inch × 10 inch	No. of films	06
Applied ozone dose	1.0 wt %	Gas flow rate	9 L/min	Gas Pressure	96.5 KPa (14 psig)
Reaction Temperature	23-25°C (Room Temperature)	Catalyst	Cu (II)	pH	5.3
Chemical	CuSO <sub>4</sub>	Dosage of Catalyst	0.2 g/L		
Titration Solution	50 ml Iso-propanol + 2 ml saturated KI + 2ml Glacial Acetic Acid				
Titration Procedure	Cutting pieces of 2 ozonated films soaked in above solution, heated up to boiling temperature with stirring, kept 7 min incipient boiling without cooling, titrated with 0.001N Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>				
Films were degassed by vacuum for 60 min after ozonation					

Reaction time (min)	Consumption of 0.001N Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> (ml)			Molarity of peroxides (mmol)	Area of Sample (m <sup>2</sup> )	Concentration of peroxide (mmol/m <sup>2</sup> )
	Test-1	Test-2	Average			
60 (without catalyst)	7.8	7.4	7.6	0.00380	0.0387	0.098
120 (without catalyst)	9.5	9.1	9.3	0.00465	0.0387	0.120
60	8.6	9.1	8.85	0.0044	0.0387	0.114
120	10.9	-	10.9	0.0054	0.0387	0.140

## Appendix X

### Calculation of Amount of Hydrogen Peroxide ( H<sub>2</sub>O<sub>2</sub>)



2 mole O<sub>3</sub> required 1 mole H<sub>2</sub>O<sub>2</sub>

Atomic weight of O = 16.00 g

Atomic weight of H = 1.00 g

M.W of H<sub>2</sub>O<sub>2</sub> = 2(H) + 2(O)

$$= 2(1) + 2(16)$$

$$= 34 \text{ g}$$

So, 48 g O<sub>3</sub> required  $0.5 \times 34 \text{ g H}_2\text{O}_2$

Weight ratio of H<sub>2</sub>O<sub>2</sub> /O<sub>3</sub> = 17/48

$$= 0.35$$

Our reaction conditions are

O<sub>3</sub> = 1.0 wt%

Reaction time = 60 min

Flow rate = 9 L/min

Density of ozone = 1.31 g/l

Pressure, at flowmeter standardized (P<sub>o</sub>) = 14.07 psig

$$\text{Pressure correction factor (pf)} = \sqrt{\frac{P_o + P_g}{P_o}}$$

Operating pressure (P<sub>g</sub>) = 14 psig

Molecules correction factor = 0.95

Actual O<sub>3</sub> input corrected flow = flow rate × pressure correction

× molecular correction factor

$$= 9 \text{ L/min} \times \sqrt{\frac{P_o + P_g}{P_o}} \times 0.95$$

$$= 9 \text{ L/min} \times \sqrt{\frac{14.7 + 14}{14.7}} \times 0.95$$

$$= 9 \times 1.396 \times 0.95$$

Actual flow of O<sub>3</sub> = 11.94 l/min

O<sub>3</sub> input mass = Actual flow of O<sub>3</sub> × Reaction time × Density of O<sub>3</sub> × Applied dose of ozone

$$= 11.94 \text{ l/min} \times 60 \text{ min} \times 1.31 \text{ g/l} \times \frac{1}{100} \text{ (calculated as per formula given by manufacture flow meter)}$$

O<sub>3</sub> input mass = 9.39 g

$$\text{For } 0.045 \text{ M H}_2\text{O}_2 \rightarrow 0.045 \frac{\text{mole}}{\text{litre}}$$

For 11 liters reactor's volume = 0.045 × 11

$$= 0.5 \text{ mole H}_2\text{O}_2$$

For 0.5 mole H<sub>2</sub>O<sub>2</sub>, weight ratio of  $\frac{H_2O_2}{O_3} = \frac{0.5 \times 34}{48}$

$$= 0.35$$

For 9.39 g O<sub>3</sub> input, Qty of H<sub>2</sub>O<sub>2</sub> = 9.39 × 0.35

$$\text{Qty of H}_2\text{O}_2 = 3.28 \text{ g}$$

$$\text{Qty of } 50 \% \text{ H}_2\text{O}_2 = 6.57 \text{ gm} = 7 \text{ g}$$

## Appendix XI Experimental Data Table of LD+LLDPE Ozonated with $H_2O_2$

Table - Peroxide data table ozonated LD+LLDPE film with  $H_2O_2$

Material	LD+LLDPE	Size	1.5 inch × 10 inch	No. of films	06
Applied ozone dose	1.0 wt %		Gas flow rate	9 L/min	
Reaction Temperature	23-25°C (Room Temperature)	Reaction time	60 min	Gas Pressure	96.5 KPa (14 psig)
Titration Solution	50 ml Iso-propanol + 2 ml Saturated KI + 2ml Glacial Acetic Acid				
Titration Procedure	Cutting pieces of 2 ozonated films soaked in above solution, heated up to boiling temperature with stirring, kept 7 min incipient boiling without cooling, titrated with 0.001N $Na_2S_2O_3$				
Films were degassed by vacuum for 60 min after ozonation					

Concentration of $H_2O_2$ (M)	Consumption of 0.001N $Na_2S_2O_3$ (ml)			Molarity of peroxides (mmol)	Area of Sample ( $m^2$ )	Concentration of peroxide (mmol/ $m^2$ )
	Test-1	Test-2	Average			
Aqueous without $H_2O_2$	7.8	7.4	7.6	0.0038	0.0387	0.0980
0.005	7.3	-	7.3	0.00365	0.0387	0.0943
0.023	5.0	-	5.0	0.0025	0.0387	0.0646
0.045	3.8	3.5	3.65	0.00183	0.0387	0.0472

## Appendix XII Experimental Data Table of LD+LLDPE Ozonated with H<sub>2</sub>O<sub>2</sub> and Fe (III) catalyst

Table - Peroxide data table ozonated LD+LLDPE film with H<sub>2</sub>O<sub>2</sub> and Fe (III)

Material	LD+LLDPE	Size	1.5 inch × 10 inch	No of films	06
Applied ozone dose	1.0 wt %		Gas flow rate	9 L/min	
Reaction Temperature	23-25°C (Room Temperature)	Reaction time	60 min	Gas Pressure	96.5 KPa (14 psig)
Titration Solution	50 ml Iso-propanol + 2 ml saturated KI + 2ml Glacial Acetic Acid				
Titration Procedure	Cutting pieces of 2 ozonated films soaked in above solution, heated up to boiling temperature with stirring, kept 7 min incipient boiling without cooling, titrated with 0.001N Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>				
Films were degassed by vacuum for 60 min after ozonation					

Dosage of FeCl <sub>3</sub> (g/L)	Concentration of H <sub>2</sub> O <sub>2</sub> (M)	Consumption of 0.001N Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> (ml)			Molarity of peroxides (mmol)	Area of Sample (m <sup>2</sup> )	Concentration of peroxide (mmol/m <sup>2</sup> )
		Test-1	Test-2	Average			
-	-	7.8	7.4	7.6	0.0038	0.0387	0.098
0.04	0.005	8.7	-	8.7	0.00435	0.0387	0.112
0.04	0.045	4.8	-	4.8	0.0024	0.0387	0.062