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Surface Modification of Polyethylene Film by Catalytic Ozonation

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SURFACE MODIFICATION OF POLYETHYLENE FILM BY CATALYTIC OZONATION

By

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ABSTRACT

Surface modification of polyethylene film by catalytic ozonation

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The hydrophobicity of polymer surfaces limits their applications in many areas such as for use as biomaterials and in membrane filtration. One solution to this problem is to modify the polymer surface by ozonation. Ozonation introduces peroxide groups on polymer surface, which can initiate graft polymerization of monomers with hydrophilic groups, and thus improves the hydrophilicity of the polymer surfaces. The concentration of peroxide groups formed can be used to indicate the effectiveness of ozonation process.

In this study, the low cost polyethylene film was selected as a model polymer film to conduct the investigation. Ozonation treatment was carried out in both gaseous and aqueous phases, to study the contribution of hydroxyl radical in the generation of peroxide group. Results revealed that aqueous ozonation generated slightly less peroxide than gaseous ozonation. However, the addition of soluble catalyst, copper (II) sulfate, to the aqueous ozonation resulted in 18% more peroxide concentration than that yielded by gaseous ozonation. Further investigation indicated that 0.05 g/L copper (II) sulfate was the optimal catalyst dose, and the optimal pH was approximately 5.60. A 19% reduction in tensile strength of the film was observed after 120 minutes of catalytic ozonation.

Upon addition of a radical scavenger, tert-butyl alcohol (TBA), a decrease of 12% in the peroxide concentration was observed for catalytic ozonation with 0.1 mol/L TBA. This decrease indicated that both ozone and hydroxyl radical contributed to the peroxide generation in catalytic ozonation. A reaction mechanism for aqueous ozonation of polyethylene was proposed in this study by combining the reaction mechanism for gaseous ozonation of polyethylene and the decomposition mechanism of ozone in water. The experimental data found in this study verified the exponential function obtained for peroxide concentration. This verification was obtained for various ozonation time and dose ranging from 15 – 120 minutes and 1.0 – 3.0 wt%, respectively.

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First, I would like express my gratitude to my supervisor, Dr. Jiangning Wu, for her continuous guidance and encouragement, which have enabled me to develop an understanding of the subject. I would also like to sincerely thank my other supervisor, Dr. Huu Doan, for his "open-door" policy and infinite patience in answering my questions and inquiries about everything, be it related or unrelated to this study.

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DEDICATION

This thesis is dedicated to my parents. Without their support, patience, and understanding, the completion of this work would not have been possible. Also to my siblings who have never failed to inspire and encourage me throughout these years. I could not ask for a better family.

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NOMENCLATURES

[Peroxide]	Concentration of peroxide	mol/m^2
C	Concentration	g/L, mol/L
H	Henry's constant	(mol/L)/(mol/L)
h_G	Gas-specific parameter for Sechenov's relation	$m^3/kmol$
h_i	Ion-specific salting-out constant	$m^3/kmol$
h_T	Gas-specific parameter for Sechenov's relation	$m^3/(kmol\ K)$
k	Reaction rate constant	various
K_S	Sechenov's constant	$m^3/kmol$
M	Molarity	mol/L
MW	Molecular weight	g/mol
N	Normality	mol eq/L
n	Number of moles	mol
V	Volume	L
W	Weight (mass)	g
x_i	Index of ion in the chemical formula	–

GREEK SYMBOLS

α	Inverse of time constant for gaseous ozonation	s^{-1}
β	Inverse of time constant for aqueous ozonation	s^{-1}
λ	Proportionality constant between applied and dissolved ozone concentrations	–
γ		–

ACRONYMS

AA	Acrylic acid
AAm	Acryl amide

AFM	Atomic force microscopy
BIEA	2-(2-bromoisobutyryloxy)ethyl acrylate
CI	Confidence interval
DMAPS	*N*,*N'*-dimethyl (methacryloyloxyethyl) ammonium propanesulfonate
DMMCA	*N*,*N'*-dimethyl-*N*-methacryloyloxyethyl-*N*-(2-carboxyethyl) ammonium
DMMSA	*N*,*N'*-dimethyl-*N*-methacryloyloxyethyl-*N*-(3-sulfopropyl) ammonium
DPPH	2,2-diphenyl-1-picryl-hydrazyl
DS	Dextran sulfate
HDPE	High-density polyethylene
LDPE	Low-density polyethylene
LLDPE	Linear low-density polyethylene
MAA	Methacrylic acid
MADAME	*N*,*N'*-dimethylamino-2-ethylmethacrylate
MPC	2-methacryloyloxyethyl phosphorylcholine
PAN	Polyacrylonitrile
PCMS	Polychloromethylstyrene
PEGMA	Poly(ethylene glycol) methacrylate
PET	Poly(ethylene terephthalate)
PHBV	Poly(3-hydroxybutrate-co-3-hydroxyvalerate)
PMMA	Polymethyl methacrylate
PP	Polypropylene
PU	Polyurethane
SD	Standard deviation
SE	Standard error of the mean
SEBS	Styrene-ethylene/butylene-styrene copolymer
SEM	Scanning electron microscope
SPEU	Segmented poly(ether urethane)
TBA	Tert-butyl alcohol
VPA	Vinyl phosphonic acid
WSC	Water-soluble chitosan
XPS	X-ray photoelectron spectroscopy

1 INTRODUCTION

In this chapter, the problem related to the surface properties of polymer and its application would be discussed. The general application of ozone as oxidants in gaseous and aqueous phase would also be explained succinctly. In the last section, the objectives of this research would be introduced.

§ 1.1 Surface modification of polymer

Polymers have a wide range of applications because they are inexpensive and easily constructible. Polymers also have favourable properties such as good thermal stability, excellent chemical resistance, and outstanding mechanical properties, which make them desirable. However, the hydrophobic nature of polymer surface has been known to cause various compatibility problems in applications where interaction between polymer and other chemicals is an important consideration (Coombes et al., 1996; Robin, 2004; Guo et al., 2008).

The compatibility problem arising from hydrophobicity of polymers can be remedied by different surface modification methods. Surface modification of polymer allows changes to be made on the outermost layer of polymer surface, while still retaining its mechanical properties (Desai & Singh, 2004; Mao et al., 2004). There are many different possible surface modification methods currently being investigated in various studies. One of the most versatile methods to modify polymer surface is by graft polymerization. Graft polymerization does not affect the bulk properties of the polymer that is required in various applications. Grafting simply introduces hydrophilic monomer on the surface of polymer film; therefore, the surface properties would be

affected by the hydrophilic monomer, while keeping the desirable mechanical properties of the original hydrophobic polymer (Robin, 2004; Desai & Singh, 2004; Grace et al., 2007).

In order to initiate graft polymerization on polymer surface efficiently, different pre-treatment methods can be used, such as plasma discharge, ozonation, and UV radiation. These pre-treatment methods introduce active groups on polymer surface, which would act as initiator for the graft polymerization step. Moreover, since the grafting would only occur at the site where these initiators were introduced by the pre-treatment, grafting efficiency highly depends on the surface concentration of the initiators (Strobel et al., 1995; Wang et al., 2000). Due to the relatively low cost and its ability to introduce initiators on the polymer surface evenly, ozone pre-treatment has been chosen as the subject of this study.

§ 1.2 Ozone as oxidant

Ozone is a very powerful oxidant, shown by the high value of its electrochemical potential. Due to its reactivity, ozone is widely used in many different fields including drinking water and wastewater treatment as an alternative to chlorine (Gottschalk et al., 2000; Beltrán, 2004). Ozone treatment has also been subject of various studies as polymer surface modification method (Robin, 2004; Mao, 2004). To the best of the author's knowledge, not many studies have been done on aqueous ozonation for polymer surface modification methods. Most studies deal with ozonation of polymer film or powder in the gaseous phase.

The reaction between ozone and polyolefin in gaseous phase has been found to form various non-oxygenated and oxygenated functional groups. One of these oxygenated functional groups is the peroxide group, which can be thermally decomposed to form radicals. The radicals, located on the polymer surface, can then be used to initiate graft polymerization with hydrophilic monomers desired in order to improve hydrophilicity of the polymer (Kefeli et al., 1971; Desai & Singh, 2004; Mao, 2004; Robin, 2004).

The half-life of ozone in gaseous phase at 20°C is 2 days, while the half-life of ozone in aqueous phase is 20 minutes at the same temperature; therefore the decomposition of ozone in gaseous phase is negligible when compared to that in aqueous phase (Gottschalk et al., 2000; Lenntech, 2009). The decomposition of ozone in gaseous phase depends on the temperature and

humidity of the system. The decomposition of ozone in water is highly dependent on the water quality, temperature, and pH.

Ozone decomposes to form various radicals when dissolved in water. One of the ozone decomposition products is hydroxyl radical, which is an even stronger oxidant than ozone. The presence of hydroxyl radical has been found to enhance the oxidation of organic compounds in the wastewater treatment. Oxidation of solutes by hydroxyl radical, as secondary oxidant, is called indirect oxidation, while the oxidation by molecular ozone is commonly termed as direct oxidation. The direct oxidations are often solute-selective and slow, whereas the indirect oxidations are non-selective and fast (Gottschalk et al., 2000; Beltrán, 2004). Therefore, in using ozonation to modify polymer surface, the relative contribution of indirect oxidation on the generation of peroxide is of interest in order to optimize the results of this pre-treatment.

§ 1.3 Objectives

As previously mentioned, in order to graft hydrophilic monomers on the surface of polymers, ozonation can be used as pre-treatment method. Ozonation introduces initiators on polymer surface, by generating peroxide groups, which could be decomposed to form radicals. The grafting efficiency depends heavily on the concentration of the peroxide groups formed after ozonation (Strobel et al., 1995; Wang et al., 2000). The main objective of this experimental study was to maximize the generation of peroxide group after ozone pre-treatment.

Many studies have been conducted to investigate the peroxide generation on various polymer types via ozonation pre-treatment. However, the ozonation in most of these studies was conducted in gaseous phase. Lack of experimental studies was found in the literature for aqueous ozonation. Previous researchers, who explored aqueous ozonation as pre-treatment method for polymer surface modification, have reported an improvement in the peroxide generation (Gu, 2008; Patel, 2008). Therefore, the main focus in this research is to study the generation of peroxide by aqueous ozonation with the addition of soluble metal salts as catalyst.

The aforementioned objective was achieved by dividing it into several parts. The first was to investigate the difference between the concentration of peroxide generated after gaseous and aqueous ozonation. The effect of copper (II) sulfate in aqueous ozonation as catalyst was then

studied. The next step was to investigate the effect of operating parameters, namely initial pH, ozonation time and applied ozone dose on the concentration of peroxide.

In order to maximize the peroxide generation, knowledge of the reaction mechanism is needed. Therefore, the reaction mechanism of ozone treatment on polyethylene film was investigated in this study as well.

2 LITERATURE REVIEW

As mentioned in the previous chapter, polymer applications in areas such as membrane and biomaterial are limited by the hydrophobicity of its surface. In this chapter, more details on the polymer applications, methods for surface modification would be presented. Results of relevant previous studies on polymer surface modification would also be discussed.

§ 2.1 Limitation in polymer applications

Polymers are versatile materials due to its low cost, high chemical resistance, and the flexibility in its physical properties. The physical properties of polymers, such as tensile strength and ductility, can be easily tailored in order to meet the needs for many different applications (Coombes et al., 1996). For example, low-density polyethylene (LDPE) and linear low-density polyethylene (LLDPE) are often combined to take advantage of the specific properties of each material. LLDPE offers higher tensile strength, elongation, and better puncture and tear resistant than LDPE, but it is also harder to process than LDPE. By blending the two resins, the resulting film has higher processability, while still having relatively high tensile strength (Oh, 1998; Vasile & Pascu, 2005). The drawback in using polymer for particular applications is often due to the lack of required surface property. The hydrophobicity of polymer surface presents problems when polymers come into contact with other chemicals, hence limiting its applications (Coombes et al., 1996; Mao et al., 2004).

To better elucidate this problem, the application of polymer and its limitation for various application fields would be discussed. The use of polymer in membrane filtration is very

beneficial because it is relatively easy and inexpensive to construct polymeric membranes with specific pore sizes and shapes. Unfortunately, due to the hydrophobicity of polymeric membrane, it attracts organic materials; for example, a hydrophobic membrane is less resistant to protein fouling when compared to a hydrophilic membrane (Guo et al., 2008). The hydrophobic nature of polymer surface is also an indication of its low surface energy. The low value of surface energy presents problem in the adhesive technologies because of the poor adhesion of coatings (Bongiovanni et al., 2007).

Another application field where the surface property of polymer limits its application is for use as biomaterials. As organic material, polymer is an ideal candidate of construction materials for medical devices and artificial organs. For example in biomedical field, polyethylene is used as material for medical catheters, artificial blood vessels, and some blood-contacting materials in extracorporeal circulation equipment during operations (Coombes et al., 1996; Ratner et al., 2004). Unfortunately, when blood comes into contact with the hydrophobic polymer surface, the protein in blood is quickly adsorbed onto the surface of polymer. This protein adsorption would then lead to adhesion of platelet on polymer surface, and activation of components of the blood coagulation system. In other words, hydrophobic polymer is not biocompatible because blood clot would form when it comes into contact with blood. The addition of anti-coagulants into blood, such as heparin, to prevent clot formation is not satisfactory due to the possible side effects associated with its usage. Large doses of heparin can lead to excessive bleeding that can be fatal (Coombes et al., 1996; Lin et al., 2005).

As previously mentioned, one of the approaches that can be used to overcome the drawback related to surface properties of polymer is by means of surface modification. Despite all the researches done in this field, surface modification of polymer is still a developing field of study. Different methods are being investigated in order to improve the hydrophilicity of polymer surface. One of the most well-known and fundamental methods of surface modification for polymeric material is through graft polymerization of hydrophilic monomers on hydrophobic polymer backbone (Desai & Singh, 2004; Mao et al., 2004)

§ 2.2 Graft polymerization

A graft copolymer can be defined as the polymer comprising of molecules with different monomer species attached to the polymer backbone, where the monomer has different configurational features than those in the main chain (Desai & Singh, 2004). The structure of graft copolymer is illustrated in Figure 2-1, where M represents the monomer unit in the backbone, G is the monomer as the pendant chain (graft). This figure shows the versatility of graft polymerization in modifying polymer surface. To improve the hydrophilicity of polymer, the grafted monomer, G, would be chosen as the one with hydrophilic surface property. Moreover, the backbone, M, would be chosen based on the required physical properties.

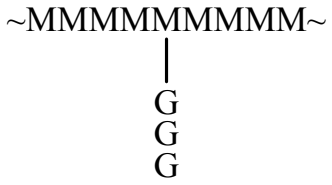

Figure 2-1: Structure of graft copolymer
(Adapted from: Desai & Singh, 2004)

Extent of grafting can be evaluated in several different ways. One of them is to calculate the extent of grafting by the weight increase of the polymer before and after graft polymerization, as shown by equation below (Hebeish et al., 1981; Karlsson et al., 1997):

$$\%\ \text{Extent of grafting} = \frac{\left(W_{\text{dry grafted sample}}\right) - \left(W_{\text{dry original sample}}\right)}{W_{\text{dry original sample}}} \times 100\%$$

The extent of grafting is also commonly expressed by the weight increase after grafting per unit area of polymer surface, instead of per original weight of the polymer sample, as shown by the equation below (Tu et al., 2006):

$$\text{Extent of grafting} = \frac{W_{\text{after grafting}} - W_{\text{before grafting}}}{\text{area of polymer surface}}$$

Another method to quantify extent of grafting, shown by Xu et al. (2003), is by calculating the ratio between the spectra peak areas from ATR-FTIR as the indication of the amount of monomer grafted onto the polymer surface. This method requires the polymer backbone and grafted monomers to have different functional groups (Xu et al., 2003). Partouche et al. (2006) calculated the grafting yield through elemental analysis result by X-ray photoelectron

spectroscopy (XPS) method for nitrogen and chloride atoms to represent the grafted polymers, polyacrylonitrile (PAN) and polychloromethylstyrene (PCMS). Several researchers used spectrometry method by utilizing addition of dye and its absorptivity to calculate the extent of grafting (Tesema et al., 2004; Lin et al., 2005).

Graft polymerization can be conducted by adding an initiator to polymer fiber and monomer solution as shown by the study done by Hebeish and colleagues (1981). In that experimental study, polyethylene terephthalate (PET) fiber was introduced into an aqueous solution containing methyl methacrylate, in the presence of hydrogen peroxide as the initiator. The percentage of homo-polymers formed in that study was calculated to be approximately 25% of the monomer supplied. The extent of grafting was found to be heavily dependent on the initiator concentration used during graft polymerization (Hebeish et al., 1981). Another common way to induce graft polymerization is through combination with other surface modification techniques, which are capable to produce active groups on polymer surface.

§ 2.3 Methods to introduce active groups for initiation of grafting

In this section, different methods that would work as pre-treatment for graft polymerization would be discussed. These methods are able to introduce active groups on polymer surface, which would act as initiator for the graft polymerization step. Some of the techniques commonly used for this purpose are plasma discharge, ultraviolet (UV), high-energy radiations, and ozonation (Desai & Singh, 2004; Mao et al., 2004). In these cases, the extent of grafting for graft polymerization depends on the concentration of active groups formed. By pre-treating polymer surface with ozone, plasma or other high-energy radiation, graft polymerization can be done in the absence of photo-initiator, while UV radiation would still require the addition of photo-initiator (Wang et al., 1998).

2.3.1 Plasma

Plasma can be defined more or less as ionized gas; therefore, even though it is considered electrically neutral, plasma is electrically conductive. It is generated by applying thermal energy, electric currents, or electromagnetic radiation to gas in order to generate excited species and ions. The temperature of plasma ranges from low temperature to the range of tens of thousands

Celsius (Tendero et al., 2006). Hence, it is important to choose plasma source for surface modification purpose with appropriate temperatures, especially for thermally sensitive polymer.

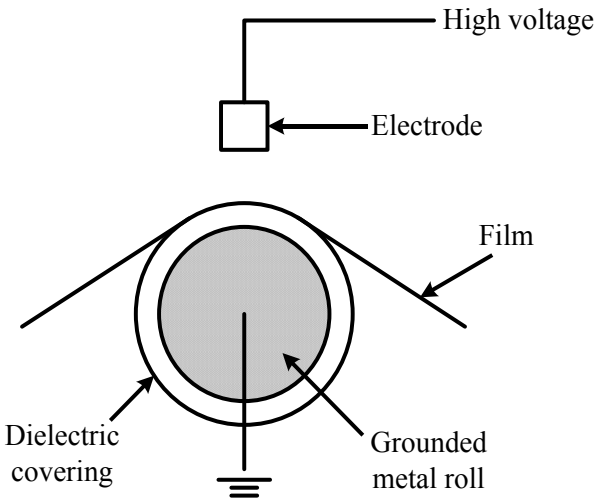

Figure 2-2: Schematic diagram of corona discharge treatment (Adapted from: Desai & Singh, 2004)

Plasma treatment on the polymer surface would result in surface activation by altering the surface energy of polymer. The effects of plasma modification are generally shallow, or limited only to the surface region of polymer (Strobel et al., 1995; Grace et al, 2007). The surface activation involves reaction of plasma active species on the polymer surface, which would result in functionalization process. This can be followed by grafting hydrophilic monomer onto the polymer surface. Therefore, the composition of gas feed used for plasma treatment influence the surface properties of the treated polymer. Numerous studies have been done in grafting polymer surface by using air, oxygen, hydrogen, nitrogen, ammonia, and argon plasma (Holländer et al., 1993; Geckeler et al., 1997; O'Hare et al., 2002; Tu et al., 2005; Tu et al., 2006; Lommatzsch et al., 2007).

Flame, corona discharge, and plasma jet treatments are the most widely studied plasma treatment types, classified by the electron density and temperature (Tendero et al., 2006; Lommatzsch et al., 2007). Flame treatment is one of the oldest methods used to modify polymeric surface in industry, especially to enhance ink permeability on the polymer surface. Corona discharge treatment is a continuous surface modification process mainly used in plastic industry to improve adhesion and printability of polyolefin films (Desai & Singh, 2004; Pascual et al., 2008). The assembly of corona discharge treatment is shown in Figure 2-2.

Some advantages of using plasma treatment to modify polymer surface are the high efficiency, short treatment time necessary to reach sufficient degree of surface modification, and slow hydrophobic recovery associated with this treatment. Plasma treatment also does not involve addition of toxic and/or hazardous chemicals, thereby making it environmentally friendly (Tu et al., 2005; Lommatzsch et al., 2007).

Some disadvantages of this type of surface treatment are its inability to generate active species uniformly on polymer with complicated shapes, hence it is only commonly used for polymer films, and the equipments for plasma treatment are usually expensive and of large scale (Fujimoto et al., 1993; Yanagisawa et al., 2006). Another major drawback of plasma treatment is it complexity; control of the molecular weights and well-defined macromolecular architectures are almost impossible while employing this technique (Tu et al., 2005).

2.3.2 High-energy radiation

For the purpose of surface modification, high-energy irradiation, or also known as ionization radiation, is mainly delivered by X-rays, γ-rays, electron-beams from cobalt (^{60}Co) and magnesium (^{58}Mg) sources (Desai & Singh, 2004). Surface modification with this technique is widely used in the design of biochips and in-situ photo-polymerizable bioadhesives (Mao et al., 2004).

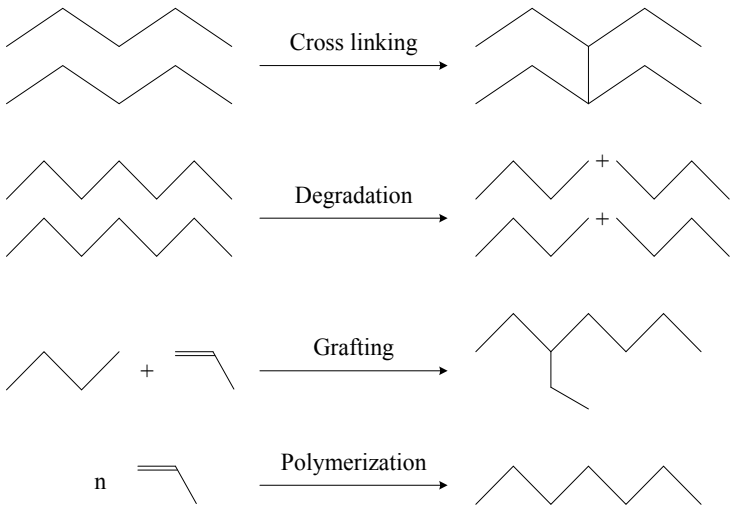

Figure 2-3: Modification produced at the polymer surface as a result of irradiation (Adapted from: Desai & Singh, 2004)

During exposure to such radiations, the molecules on the polymer backbone would be activated and react with other molecules in the surrounding. These activated molecules, which are stripped from electron, enable this treatment method to be combined with graft polymerization to improve the activity of polymer surface. High-energy radiation-induced grafting can be achieved by simultaneous or pre-irradiation techniques (Desai & Singh, 2004; Mao et al., 2004). Other chemical effects produced by high-energy radiation are degradation, cross-linking, and copolymerization in the presence of monomer as shown in Figure 2-3.

Main operating parameters that affect the efficiency of surface modification using irradiation technique are the radiation time, radiation dose, and its source. The main disadvantage of this method is its relatively high cost. Another disadvantage associated with this method is the hydrophobic recovery produced on polymer surface, which resulted due to configurational change (Desai & Singh, 2004; Mao et al., 2004).

2.3.3 UV radiation

In this method, grafting of polymers is done by exposing polymer substrates to UV radiation in a mixture of monomer and photo-initiator. Similar to other pre-treatment methods, this method promotes abstraction of hydrogen from polymer surface, which would generate radicals to act as initiator for graft polymerization. The photo-initiators that are commonly used for this purpose are benzophenone and its derivatives (Wang et al., 1998).

Surface modification through UV radiation can be combined with other methods to improve the efficiency of the process. This would also eliminate the need for photo-initiators. Several studies have been conducted by using UV radiation after plasma pre-treatment to alter surface properties of polymeric materials. Chen & Liu (2004), and Zhao et al. (2007) studied the effect of plasma pre-treatment and UV-induced graft polymerization on the antithrombogenicity properties of polyethylene surface. After graft polymerization, heparin was covalently immobilized onto the polyethylene surface. The mechanism of plasma pre-treatment and UV-induced graft polymerization used in that study is depicted in Figure 2-4.

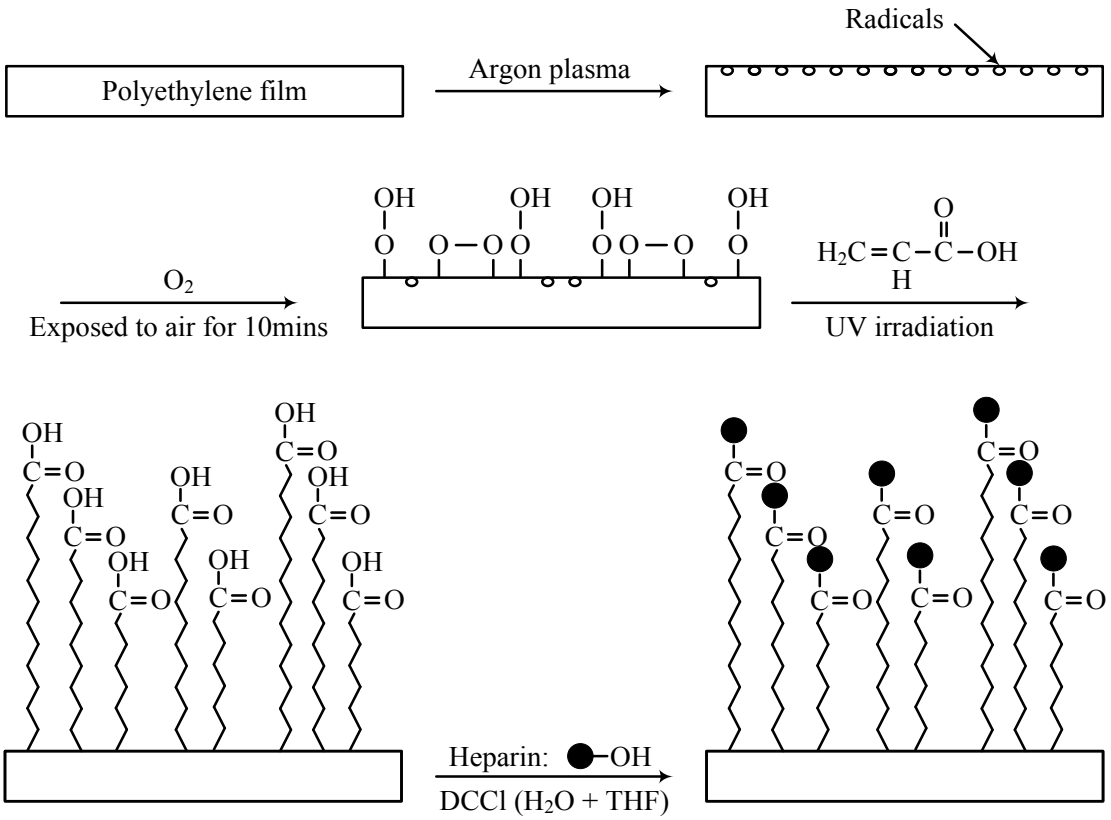

Figure 2-4: Mechanism of plasma, UV irradiation, and graft polymerization (Adapted from: Zhao et al., 2007)

The main advantage of this method is the low fabrication temperature, while the disadvantage of this method is its relatively high cost. Another drawback of this method is the necessary addition of photo-initiator for grafting step (Chen et al., 2004; Yanagisawa et al., 2006).

2.3.4 Ozonation

Ozonation works as pre-treatment method by attacking the surface of polymer and introducing peroxide groups. Aside from peroxide groups, ozonation of polymer can also form alcohol group and carbonyl groups such as carboxyl and ketone (Robin, 2004; Desai & Singh, 2004). Peroxides group formed on the polymer surface would break into radicals in the presence of reducing agent such as ferrous ion, Fe^{2+}, and at an elevated temperature. Therefore, by exposing polymer to ozone before graft polymerization, peroxides group generated can serve as an initiator to graft polymerization; hence eliminating the needs for initiator addition, as shown in Figure 2-5. The reducing agent also serves to strain homo-polymerization of the monomer (Robin, 2004; Zhou et

al., 2005). The common reducing agent used to initiate ozone-induced graft copolymerization is Mohr's salt, or also known as ammonium ferrous sulfate hexahydrate salt, $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$ (Fujimoto et al., 1993; Karlsson et al., 1997).

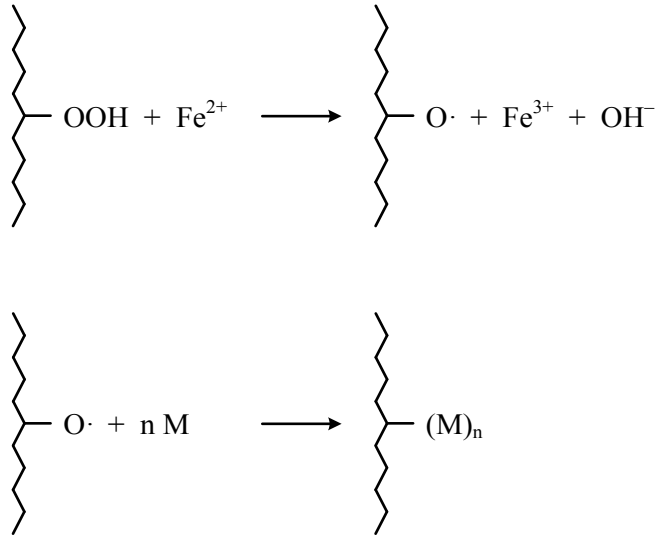

Figure 2-5: Graft polymerization by redox mechanism of peroxide group (Adapted from: Robin, 2004)

The results from studies done by Tu and colleagues (2005, 2006) show that ozonation alone could not modify the surface of polytetrafluoroethylene (PTFE). The resistance is due to the strong C–F bonds present in the structure of this polymer. Based on this study, the PTFE surface can still be modified by combining hydrogen plasma and ozonation as pre-treatment methods. The C–H groups would be incorporated in place of C–F groups after plasma treatment, thereby making this polymer surface accessible to ozone attack (Tu et al., 2005).

Aside from combination with plasma treatment, ozone treatment is also often combined with UV radiation (UVO treatment). This combination can be conducted by using only UV and oxygen as feed, or can also utilize an additional ozone generator to supply ozone to the reactor to reach higher oxidation extent (Macmanus et al., 1999). The common source of UV radiation used in UVO-induced grafting technique is mercury-based lamp, which has wavelengths of 185 nm and 254 nm, because at these wavelengths photolysis and generation of ozone occur simultaneously (Bablon et al., 1990). The effectiveness of photooxidation of UVO treatment depends on the UV-absorbing characteristics of the polymers (Strobel et al., 1995; Murakami et al., 2003; Yanagisawa et al., 2006).

According to study done by Murakami et al. (2003), the combination of ozone aeration and UV irradiation would be suitable for surface modification of polymers with aromatic rings, such as polystyrene (PS). On the other hand, this treatment combination did not significantly increase the extent of modification when compared to ozone treatment alone for poly(methyl methacrylate) (PMMA).

As shown by Yanagisawa et al. (2006), the liquid used as the media for UVO treatment would determine the functional groups formed on the polymer surface. They found carbonyl and hydroxyl groups were formed by using distilled water, while amide and amino groups were formed by using ammonia solution as the media (Yanagisawa et al., 2006). The apparatus used for this experimental study is shown in Figure 2-6 below.

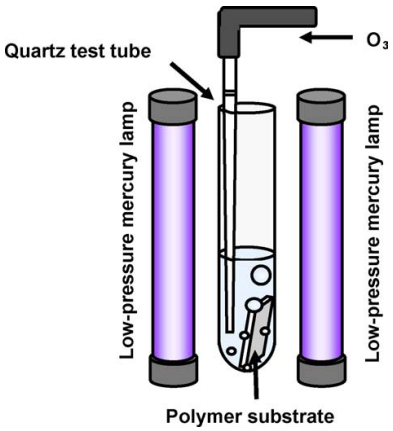

Figure 2-6: Apparatus for combination of ozone aeration and UV radiation (Yanagisawa et al., 2006)

Some of the advantages of using ozonation for surface modification are the relatively low operational cost, and its ability to introduce peroxide uniformly even on complicated 3-dimensional shapes. Ozone treatment also has simple and inexpensive apparatus, which makes it easy to operate. Because of the relatively fast decomposition of ozone, it does not form any toxic products, which is particularly important for application of treating polymer to be used in biomedical field. Moreover, no addition of toxic/strongly acidic material is required in ozone treatment (Mao et al., 2004; Robin, 2004).

The main disadvantages of ozone treatment are the long treatment time needed and the attack of ozone on the polymer backbone, which may cause the polymer to be mechanically fragile. Strobel et al. (1995) compared different gaseous phase technique for the modification of

polypropylene (PP) and PET surface properties, namely plasma, ozone and UV/ozone treatment. In that study, the oxidation target was set to be O/C atomic ratio of 0.10, determined by the peak ratio at the relevant binding energies obtained by using XPS. They found the time required for plasma treatment to be much less than that for UVO and ozone treatment to reach this target. They also found the oxidation to penetrate deeper to the bulk of polymer for UVO and ozone treatments (Strobel et al., 1995).

Table 2-1: Comparison of surface modification techniques

Treatments	Advantages	Disadvantages
Plasma	Short treatment time Slow hydrophobic recovery	Not applicable to thermally sensitive materials Complicated process Hard to control in large scale Will not work evenly on complicated 3D objects
High-energy radiation	Short treatment time	Costly Wetting instability (i.e. hydrophobic recovery)
UV radiation	Low fabrication temperature Can be combined with other methods to improve efficiency	Costly Requires the addition of photo-initiator
Ozone	Works for complicated 3D shape Simple and inexpensive Non toxic	Long treatment time May alter mechanical properties

For comparison purposes, the main advantages and disadvantages of each treatment method described above are summarized in Table 2-1. Based on the advantages of ozonation compared to the other pre-treatment methods listed above, ozone pre-treatment for initiating graft polymerization was chosen to be studied further in this research. More details on ozone treatment and the results obtained by previous researchers would be further discussed in the next section.

§ 2.4 Ozonation

As previously mentioned, ozonation is a simple, inexpensive, and non-hazardous treatment technique, which is able to generate peroxide uniformly on polymer surface. The concentration of peroxide groups generated after ozonation would determine the extent of graft polymerization (Strobel et al., 1995; Wang et al., 2000). The major drawback of ozonation is sometimes long treatment time is necessary; therefore, it is important to obtain faster generation rate of peroxide groups, to decrease the treatment time required.

The efficiency of ozone treatment depends on the ozonation time, ozone concentration, temperature, and reaction media. Based on the study conducted by Razumovskii et al. (1971), the result of gaseous ozonation also depends on the polymer types. The most susceptible type of polymers to ozone treatment is polyolefins due to its relatively weak C–H bonds (Robin, 2004). Polyolefin is widely used in various fields including membrane filtration and biomedical field due to its low cost and excellent mechanical properties (Coombes et al., 1996; Robin, 2004; Shan et al., 2006). Polyurethane (PU) is another polymer subjected to surface modification study for its applicability to wide range applications owning to its excellent chemical resistance (Coombes et al., 1996; Zhou et al., 2010).

One of the methods commonly used to characterize the surface property of treated polymer is by measuring the water contact angle as an indication of its hydrophilicity. Pull-out test may also be utilized to ensure strong adhesion properties of the polymer with another material immobilized onto it (Ferreira et al., 2005). The resistance to protein fouling or the blood compatibility of polymer can be investigated by utilizing scanning electron microscope (SEM) to observe any platelet adhesion on polymer surface (Xu et al., 2003; Mao et al., 2004; Lin et al., 2005; Zhou et al., 2005). Zhou et al. (2010) utilized SEM and atomic force microscopy (AFM) to observe the homogeneity of grafting with different pre-treatment methods. AFM is commonly used to calculate the root-mean-square (RMS) value of the surface roughness of the treated film (Ferreira et al., 2005; Zhou et al., 2010). XPS spectra analysis is usually conducted to quantify the atomic composition. This analysis is also able to give a depth profiling of the treated polymer film by angle-resolved analysis (Strobel et al., 1995; Ferreira et al., 2005).

The analysis of FTIR spectra of ozonated polymer films is also generally done after ozone exposure in order to identify new functional groups formed (Zhou et al., 2010). However, due to

the symmetrical nature of O–O bond in peroxide group, the presence of peroxide group cannot be determined directly through IR spectroscopy (Vacque et al., 1997). The concentration of peroxide groups can be quantified by utilizing its reactivity via chemical reaction, as will be discussed in § 2.5.

Ozone treatment can be conducted either in gaseous phase or in aqueous phase. Most of the previous studies done for ozonation as surface modification method were conducted in gaseous phase. Aqueous phase ozonation has a potential advantage over gaseous ozonation, because both direct and indirect oxidation can contribute to the generation of peroxide, compared to just direct oxidation in the gaseous ozonation. The next subsections would further discuss each ozonation media along with their advantages and disadvantages. Summary of several recent studies conducted on ozonation of various polymers can be found in Table 2-3 at the end of this chapter.

2.4.1 Gaseous ozonation

Many studies have been conducted to modify polymer surface by gaseous ozonation followed by graft polymerization. Some of these studies were conducted to focus on improving the ozone treatment. The reaction mechanism between ozone and different polymer was explored in order to enhance the peroxide generation rate.

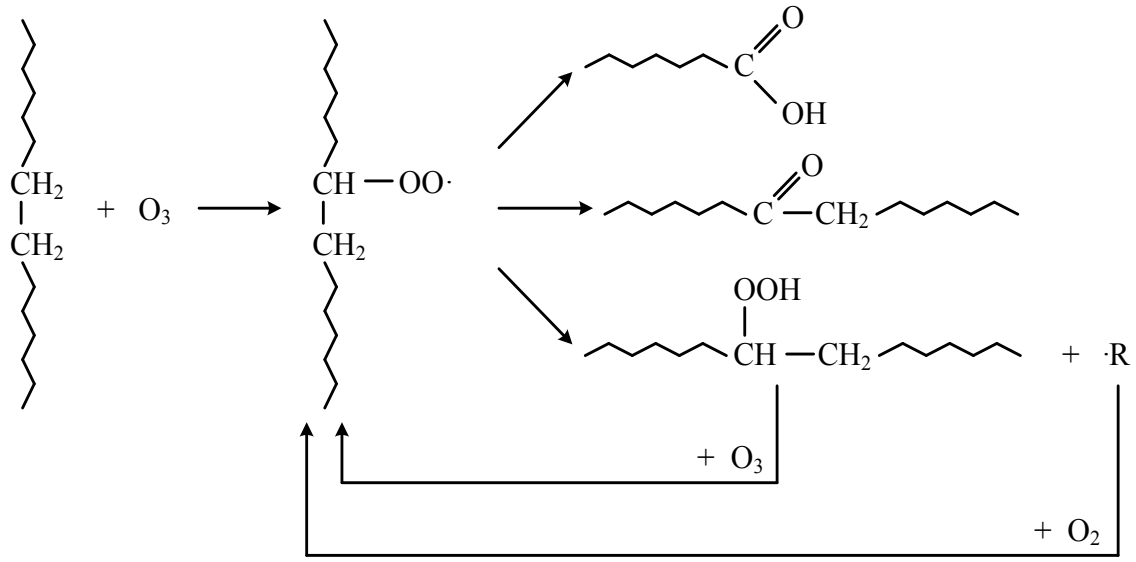

Figure 2-7: Reaction mechanism of ozone with polyethylene
(Adapted from: Razumovskii et al., 1971)

In 1971, Kefeli et al. studied the degradation of polyethylene due to the attack of ozone. This study was conducted mainly to determine the reaction mechanism involved between ozone and polyethylene. In this study, powder polyethylene was exposed to gaseous ozone in a thermostatically controlled fluidized bed reactor for up to 6 hours. The presence of polar functional groups, such as carbonyl and peroxide groups, on the polymer surface was evident from the experimental results obtained in that study (Kefeli et al., 1971).

Similar reaction mechanism was suggested by Razumovskii et al. (1971) for ozone and polyethylene powders. They proposed an initial stage of ozone reaction with polyethylene surface involving the formation of peroxy radicals, as shown in Figure 2-7 and Figure 2-8. As proposed by both of these studies, the peroxy radical is the common source for the formation of different functional groups, such as carboxyl, ketone, and peroxide groups.

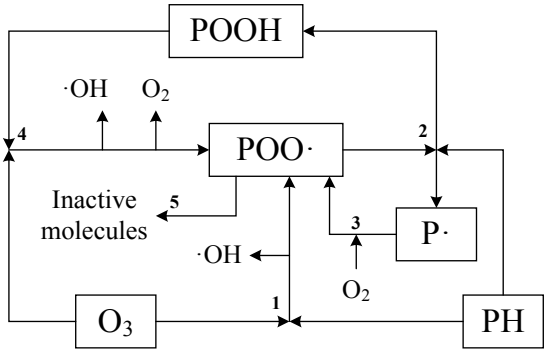

Figure 2-8: Reaction mechanism for gaseous ozonation of polyethylene (Adapted from: Kefeli et al., 1971)

The reaction numbers shown in Figure 2-8 correspond to the subscripts of the reaction rate constants, k. The polyethylene, polyethylene alkyl radical, polyethylene peroxy radical, and polyethylene peroxide are represented in Figure 2-8 by PH, P·, POO·, and POOH, respectively.

Initiation step:

$$O_3 + PH \xrightarrow{k_1} \cdot OH + POO\cdot \quad (2\text{-}1)$$

Propagation steps:

$$PH + POO\cdot \xrightarrow{k_2} P\cdot + POOH \quad (2\text{-}2)$$

$$O_2 + P\cdot \xrightarrow{k_3} POO\cdot \quad (2\text{-}3)$$

$$O_3 + POOH \xrightarrow{k_4} O_2 + \cdot OH + POO\cdot \quad (2\text{-}4)$$

Termination step:

$$POO\cdot \xrightarrow{k_5} \text{Inactive (carbonyl and alcohol groups)} \qquad (2\text{-}5)$$

Kefeli et al. (1971) obtained an expression for the concentration of peroxide generated as a function of treatment time from Reactions (2-1) to (2-5). The expression obtained in that study is shown in Equation (2-6).

$$[POOH] = \frac{k_1 k_2 [PH]^2 [O_3]}{\alpha k_5}(1 - e^{-\alpha t}) \qquad (2\text{-}6)$$

$$\text{where:} \quad \alpha = k_4 [O_3]\left(1 - \frac{k_2 [PH]}{k_5}\right)$$

From Equation (2-6), the peroxide concentration generated during ozonation increases with treatment time to a maximum value, while its generation rate decreases with respect to the treatment time. The experimental results, from study done by Kefeli et al. (1971), show a rapid decrease in the generation rate of peroxide groups with increasing ozonation time. The horizontal plateau observed in the concentration of peroxide generated for polyethylene was in agreement with the experimental results obtained for various polymers by other researchers (Ko et al., 2001; Xu et al., 2003; Tesema et al., 2004; Lin et al., 2005; Zhou et al., 2005; Shan et al., 2006).

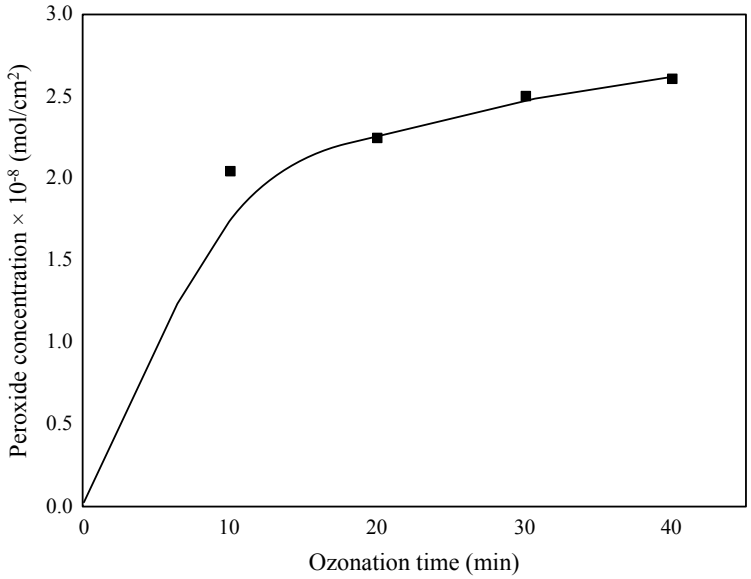

Figure 2-9: Peroxide concentration on silicone film for various ozonation time (Adapted from: Xu et al., 2003)

Xu et al. (2003) observed that the concentration of peroxide generated on silicone film increased rapidly with ozonation time at the initial stage. However, after 20 minutes of ozonation, there is a noticeable decrease in the generation rate of peroxide, where the peroxide concentration reached a plateau after approximately 30 minutes. The result obtained in that study for the relation between the concentration of peroxide and ozonation time is shown in Figure 2-9. Boutevin and colleagues (2002) obtained a rather similar trend for the ozonation of LDPE powders. They postulated a square-root relationship between the concentration of peroxide generated and the ozonation time.

As previously mentioned, the SEM images could be utilized in studying the platelet adhesion for blood compatibility or fouling test of the polymer (Xu et al., 2003; Mao et al., 2004; Lin et al., 2005; Zhou et al., 2005). An example of the images obtained after platelet adhesion test on treated and untreated cellulose surface is shown in Figure 2-10.

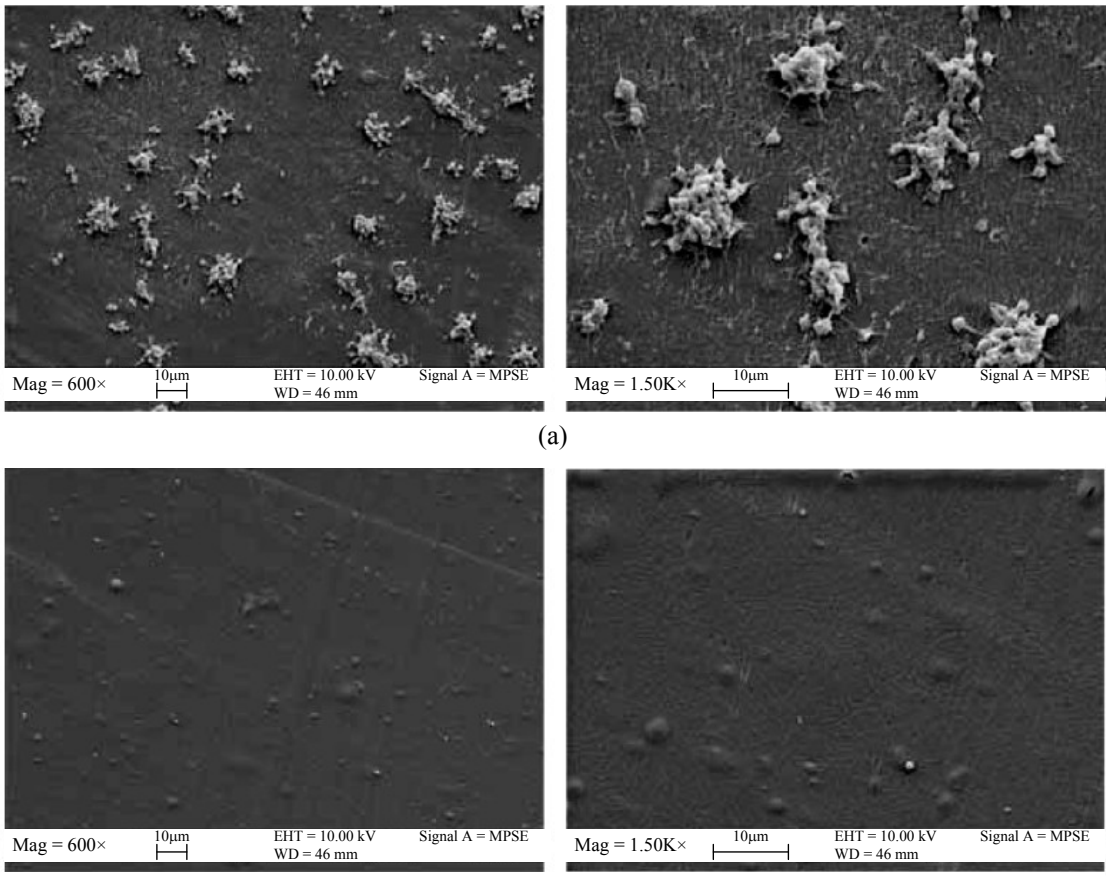

Figure 2-10: SEM images of the morphology of PRP-contacted surfaces (Left ×600; right ×1500): (a) blank cellulose; (b) grafted cellulose (Adapted from: Mao et al., 2004)

Comparison of SEM images also allows an observation of the uniformity of grafting. Zhou et al (2010) compared two different pre-treatment methods for surface modification of medical polyurethane: ozone and potassium peroxydisulfate. From Figure 2-11, it can be seen that the surface topography of PAA-*g*-PU film that was pre-treated by ozone was more homogeneous compared to the one pre-treated by peroxydisulfate.

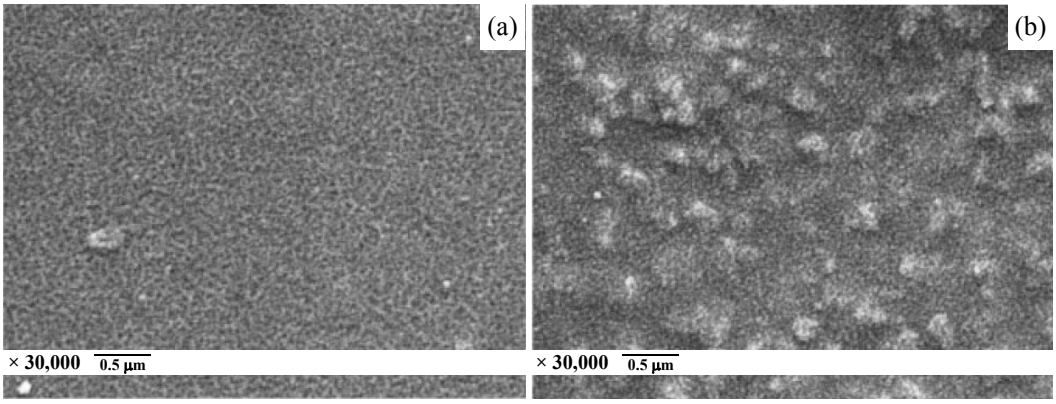

Figure 2-11: SEM images of PU film grafted with poly(acrylic acid)(PAA) with: (a) peroxydisulfate pre-treatment; (b) ozone pre-treatment (Adapted from: Zhou et al., 2010)

Kefeli and colleagues (1971) studied the effect of temperature on gaseous ozonation of polyethylene powder. They found that by increasing the reaction temperature from 30°C to 70°C, the maximum concentration of peroxide increased as well. Additionally, the time required to reach the equilibrium peroxide concentration decreases from tens of hours at 30°C to only a few hours at 70°C. Boutevin et al. (2002) also studied the effect of reactor temperature in the ozonation of LDPE and high-density polyethylene (HDPE). The experimental results show a positive correlation for temperature and peroxide concentration generated for the temperature range of 25°C to 45°C. Similar finding was also reported for ozonation of polyethylene and polystyrene films for temperature range of 25°C to 70°C by Kobayashi et al. (2007).

2.4.2 Aqueous ozonation

When ozone is dissolved in aqueous phase, it quickly decomposes to form different radicals, including hydroxyl radical. The hydroxyl radical is a stronger oxidant compared to molecular ozone; the oxidation by this secondary product is often referred to as indirect oxidation. On the other hand, the oxidation of other compounds by molecular ozone is called direct oxidation (Gottschalk et al., 2000).

In wastewater treatment, the decomposition rate of ozone is of interest due to the non-selectivity and higher reactivity of the hydroxyl radical, hence improving the oxidation of organic pollutants (Legube & Leitner, 1999; Gottschalk et al., 2000). The decomposition of ozone has been studied extensively over the last few decades for wastewater treatment purposes. Two of the most well-known models for the reaction mechanisms of ozone decomposition are models according to Staehelin, Hoigné, and Bühler (SHB model) and Tomiyasu, Fukutomi and Gordon (TFG model) (Bühler et al., 1984; Tomiyasu et al., 1985). The SHB model is generally accepted as the mechanism for ozone decomposition in pure water, while the TFG model represents the decomposition mechanism under alkaline condition (Gottschalk et al., 2000; Beltrán, 2004; Lovato et al., 2009). The reaction mechanism of ozone decomposition in pure water based on SHB model is depicted in Figure 2-12, showing the effect of hydroxide ions.

An important parameter that must be taken into consideration during aqueous ozonation is the pH of aqueous solution. Due to the catalyzing effect of hydroxide ions, the decomposition rate of ozone increases significantly in higher pH range (Gottschalk et al., 2000; Beltrán, 2004; Ershov & Morozov, 2008). Hence, the knowledge of which oxidation mode is the dominant mode is important in order to adjust the pH of solution accordingly to find the optimum value that would yield maximum peroxide generation.

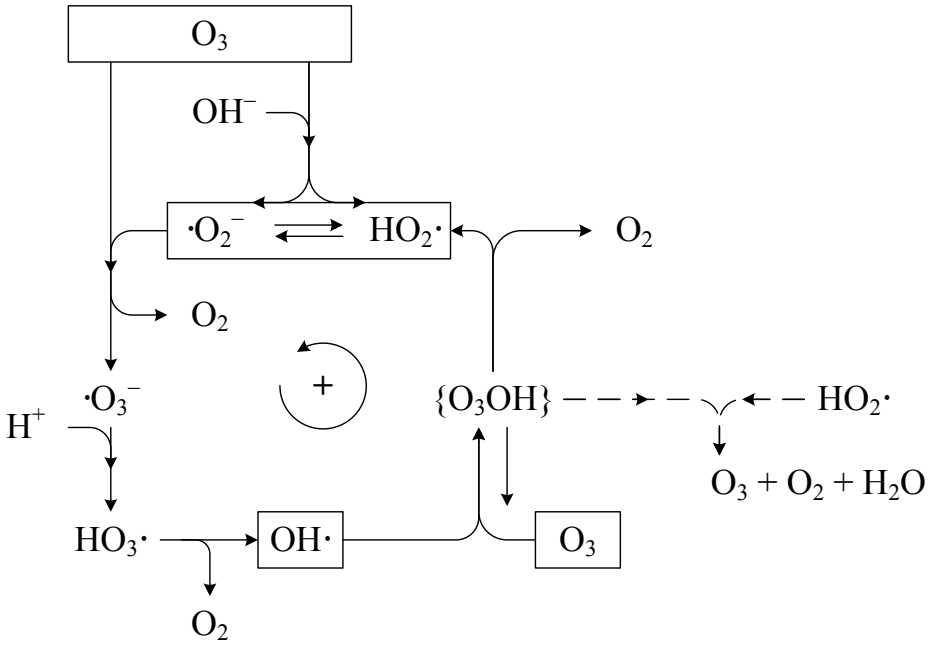

Figure 2-12: SHB reaction mechanism for decomposition of ozone in pure water (Adapted from: Staehelin & Hoigné, 1985)

Gu (2008) compared the peroxide concentration generated on HDPE, biaxial-oriented polypropylene (BOPP), and PET films during aqueous and gaseous ozonation. From that study, it was observed that the peroxide concentration formed on HDPE film was higher after aqueous ozonation than that after gaseous ozonation. On the other hand, opposite trend was observed for BOPP and PET films, with higher peroxide concentration formed after gaseous ozonation than after aqueous ozonation. This may be due to the contribution of indirect oxidation, which also depend on the polymer types, as is the case for direct oxidation shown by Razumovskii et al. (1971). However, the difference in the availability of ozone in gaseous and aqueous ozonation may also contribute to the difference in peroxide generated in both phases. Therefore, for HDPE, the indirect oxidation contributed to the peroxide generation, because regardless of the lower availability of molecular ozone in aqueous ozonation, the resulting peroxide concentration was found to be higher. On the other hand, for BOPP and PET films, no conclusion can be made from this result. The lower peroxide concentration cannot be interpreted as inexistent contribution from indirect oxidation on the peroxide generation. The availability of ozone in gaseous and aqueous ozonation may also be the reason of the results obtained.

Aside from the presence of hydroxyl radical, aqueous phase ozonation also enables the easy addition of other chemicals that could enhance or modify the reaction of ozone and polymer, and the decomposition reaction of ozone. The additives may serve as catalyst to improve the rate of peroxide generation during ozonation, or it can prevent ozone attack on the bulk polymer, hence reducing the effect of ozonation on the bulk properties of polymer.

The addition of transition metal salts is known to catalyze the oxidation of organic pollutants by ozone in wastewater treatment (Legube & Leitner, 1999; Lin et al., 2002). Patel (2008) conducted aqueous ozonation for blend of LDPE and LLDPE film in the presence of different transition metals and magnesium salts to test their effects on the peroxide generation. The peroxide generated on the polymer film after 120 minutes of ozonation with 1.0 wt% applied ozone dose was 0.120 mmol/m^2 without catalyst and 0.162 mmol/m^2 with the addition of 0.2 g/L iron (III) chloride, $FeCl_3$ (Patel, 2008).

Additionally, metal salts could also catalyze auto-oxidation of organic hydroperoxides, ROOH, to form radicals and oxygenated products such as alcohol and carbonyl functional

groups. Bhaduri & Mukesh (2000) proposed a reaction mechanism for this catalytic oxidation, shown by Reactions (2-7) to (2-13).

$$\text{Initiation}\begin{cases} \text{ROOH} + \text{M}^{n+} \longrightarrow \text{RO}\cdot + \text{HO}^- + \text{M}^{(n+1)+} & (2\text{-}7) \\ \text{ROOH} + \text{M}^{(n+1)+} \longrightarrow \text{ROO}\cdot + \text{H}^+ + \text{M}^{n+} & (2\text{-}8) \\ \text{RH} + \text{M}^{(n+1)+} \longrightarrow \text{R}\cdot + \text{H}^+ + \text{M}^{n+} & (2\text{-}9) \end{cases}$$

$$\text{Propagation}\begin{cases} \text{RO}\cdot + \text{RH} \longrightarrow \text{ROH} + \text{R}\cdot & (2\text{-}10) \\ \text{R}\cdot + \text{O}_2 \longrightarrow \text{ROO}\cdot & (2\text{-}11) \\ \text{ROO}\cdot + \text{RH} \longrightarrow \text{ROOH} + \text{R}\cdot & (2\text{-}12) \end{cases}$$

$$\text{Termination} \quad \text{ROO}\cdot \longrightarrow \text{Oxygenated products} \quad (2\text{-}13)$$

The possibility for improvisation is numerous in the field of aqueous ozonation. Yanagisawa and colleagues (2006) utilized UVO treatment in aqueous media to introduce various kinds of functional groups on polystyrene surface. The introduction of carbonyl and hydroxyl groups was accomplished by using distilled water as treatment medium, while the amide and amino groups were introduced by using ammonia solution as the medium (Yanagisawa et al., 2006). This eliminates the need of graft polymerization step, if these functional groups suffice for a specific application. Several studies have also been conducted to modify polymer surface by ozonation conducted in isopropanol (Tu et al., 2005; 2006; Ho et al., 2007).

Similar to gaseous ozonation, temperature is a parameter that may affect aqueous ozonation process. Temperature would affect aqueous ozonation in at least two different ways. Higher temperature would relate to a faster reaction rate, as governed by Arrhenius' equation, shown previously by the trend observed in gaseous phase ozonation. Another effect of higher temperature would be to lower the solubility of ozone in liquid phase, which would lower the available ozone concentration. To the best of the author's knowledge, no experimental data are available at elevated temperature for aqueous ozonation of polymer in the subject of surface modification.

Gu (2008) found that the changes observed in contact angle after ozone treatment are negligible compared to the changes observed after grafting the polymer films with hydrophilic

monomers. Table 2-2 shows the results obtained for the effect of ozone treatment and graft polymerization on the contact angle of HDPE films.

Table 2-2: Contact angle of HDPE films
(Adapted from: Gu, 2008)

Treatment on HDPE films	Contact angle
Untreated	74.92°
Ozonated for 1 hour with 1wt% O_3	70.71°
Ozonated for 1 hour with 3.7 wt% O_3	69.71°
Ozonated for 1 hour with 1wt% O_3 and grafted with AAm	38.55°
Ozonated for 1 hour with 3.7wt% O_3 and grafted with AAm	N/A

For HDPE films that were ozonated but not grafted with acrylamide (AAm), the decreases in contact angle observed were no more than 6°. The small change observed can be explained by the formation of polar groups, such as alcohol, carboxyl and ketone groups, on the surface of polymer after ozonation. Patel (2008) reported similar findings for blend of polyethylene films.

§ 2.5 Peroxide determination methods

The concentration of peroxide group generated after ozone exposure is of crucial importance because peroxide group acts as an initiator for graft polymerization. In other words, concentration of peroxide groups would determine the extent of grafting that would be achieved after ozone treatment (Strobel et al., 1995; Wang et al., 2000). It is considered as an indication of the degree of ozonation on the polymer (Ko et al., 2001). To determine the concentration of peroxide group formed on polymer surface during ozonation, different analytical chemistry methods have been employed in preceding experimental studies.

Some of the methods used to determine peroxide concentration in the literature are the DPPH, indirect titration by thiol, and standard iodometric methods (Gardette & Lemaire, 1986; Fujimoto et al., 1993; Ko et al., 2001; Boutevin et al., 2002). Determination methods involving spectroscopy is utilized by decomposing the peroxide groups on polymer surface. The decomposition products would be reacted with other chemicals, whose absorptivity could be

easily measured by means of spectroscopy (Fujimoto et al., 1993). Some of the methods used in the literature would be discussed and compared in the next subsections.

2.5.1 DPPH method

DPPH, or 2,2-diphenyl-1-picryl-hydrazyl, is a stable radical, which acts as radical scavenger by binding other radicals that are formed by the decomposition of peroxide groups. This method involves dissolving polymer and DPPH in a solvent such as benzene or o-xylene. The solution is then heated to a certain temperature, depending on the types of polymer and solvent involved, in order to decompose peroxide groups from the polymer surface. The residual amount of DPPH is then determined by the difference in absorbance of the treated and untreated polymer solution at 520 nm, with molar absorptivity of 1.8×10^4 L/(mol cm) (Fujimoto et al., 1993; Boutevin et al., 2002). The concentration of peroxide groups could then be calculated based on the stoichiometric ratio between DPPH and radicals formed from peroxides.

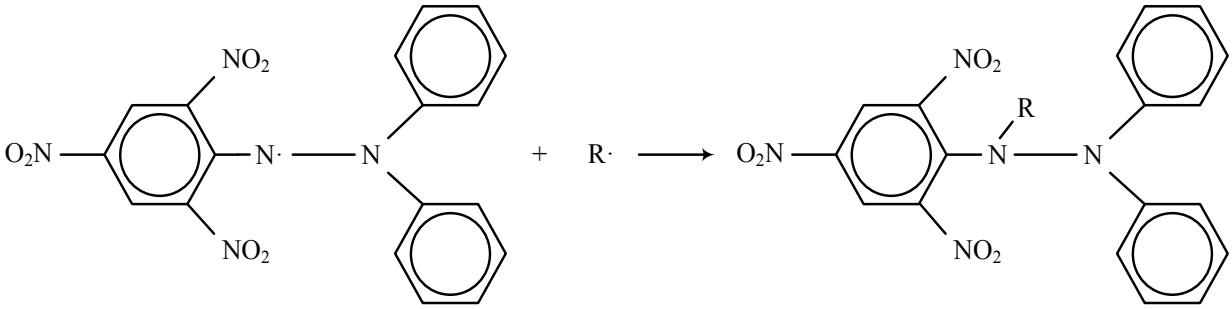

Figure 2-13: Binding reaction of DPPH with another radical
(Adapted from: Boutevin et al., 2002)

Based on the experimental results of Boutevin and colleagues in 2002, the use of DPPH method to determine the concentration of peroxide groups on ozonated polyethylene have low reproducibility, with ± 50% error. Non-reproducible results were also obtained when dealing with PP and polyvinylidene fluoride (PVDF). This non-reproducibility was not observed on ozonated ethylene-vinyl acetate (EVA) (Boutevin et al., 2002). Fujimoto et al. (1993) observed a lower measurement of peroxide concentration by using DPPH method on the ozonated PU film, compared to that obtained by iodometric method. They argued that DPPH could not react with all the radicals generated from the peroxides (Fujimoto et al., 1993)

2.5.2 Indirect titration by thiol

In indirect titration by thiol, solid polymer and a known amount of organic compound with sulfur-hydrogen bond, R_F–S–H, are dissolved in an organic solvent, such as o-dichloro-benzene. The solution is saturated with argon gas and placed at an elevated temperature of 130°C for 30 minutes. At this elevated temperature, the peroxide groups will decompose to form radicals. The organic compound, R_F–S–H, would then act as a transfer agent and stabilize these radicals by forming R_F–S·, which would then reacts with each other to form R_F–SS–R_F. The residual thiol, left unreacted from these reactions, can then be titrated by using iodine solution after quenching the solution in cold-water bath for 5 minutes (Boutevin et al., 2002).

$$ROOR \xrightarrow{\Delta} 2\,RO\cdot \quad (2\text{-}14)$$

$$RO\cdot + R_FSH \longrightarrow ROH + R_FS\cdot \quad (2\text{-}15)$$

$$2\,R_FS\cdot \longrightarrow R_FSSR_F \quad (2\text{-}16)$$

$$2\,R_FSH + I_2 \longrightarrow R_FSSR_F + 2\,HI \quad (2\text{-}17)$$

The reaction mechanism involved in this method, as explained by Boutevin and colleagues (2002), is shown by Reactions (2-14) to (2-17). They found the peroxide concentration measured by this method for ozonated HDPE and LDPE powders was in good agreement with the results obtained by the iodometric titration method (Boutevin et al., 2002).

2.5.3 Iodometric method

Aside from the two methods mentioned previously, measurement of organic peroxide concentration on solid polymer can also be accomplished through iodometric method. As the name suggested, the method utilizes the readiness of iodide ions, I^-, to be oxidized to form iodine, I_2. The procedure for the iodometric titration method has been investigated, modified, and followed by many other researchers (Kokatnur & Jelling, 1941; Radford, 1954; Gardette & Lemaire, 1986; Ko et al., 2001). This method is widely used to determine chlorine concentration in wastewater treatment based on the procedure published in 1989 by the American Public Health Association (APHA) including the procedure to standardize sodium thiosulfate solution (APHA, 1989). Similar to how chlorine liberates free iodine from iodide, peroxide groups from polymer act as an oxidizing agent under heat and in acidic condition (Kokatnur & Jelling, 1941).

This method involves using iso-propanol as the solvent medium, and addition of potassium iodide and glacial acetic acid. At an elevated temperature and under acidic condition, the peroxide groups present on the polymer would oxidize iodide ions to form iodine, which resulted in yellow colour of the solution. The concentration of iodine can then be determined by titrating the solution with a known concentration of sodium thiosulfate until the solution reverts to colourless (Kokatnur & Jelling, 1941). Some possible sources of error that can be associated with this method are the possibility of iodide ions being oxidized by other substances aside from peroxide, and the volatility of iodine formed (Radford, 1954).

This method determines the concentration of peroxide groups formed not only on the polymer surface, but also those formed in the bulk polymer (Ko et al., 2001). This method works for large range of peroxides concentration (Kokatnur & Jelling, 1941). High accuracy and reproducibility of peroxide concentration have been reported through the use of this specific method as shown by Xu et al. (2003) and Boutevin et al. (2002). Therefore, this method was chosen as the method to quantify peroxide concentration in this study.

Table 2-3: Several recent studies conducted for ozone treatment of various polymer

Year	Authors	Polymer	Grafted polymer	Notes[1]
2010	Zhou et al.	PU	AA	Comparison between a chemical method and ozonation as pre-treatment for grafting
2010	Peinado et al.	SEBS	–	The use of chemiluminescence analysis to reflect the concentration of peroxide groups
2009	Gu et al.	HDPE	AAm	Gaseous and aqueous ozonation (in distilled water) were tested
2008	Chang et al.	PVDF	PEGMA	
2007	Ho et al.	PLLA	RGDS	Aqueous ozonation in isopropanol
2006, 2005	Tu et al.	PTFE	AA, AAm, BIEA, NaSS, glycidyl methacrylate	Combination of hydrogen plasma and ozonation Aqueous ozonation in isopropanol
2006	Shan et al.	LDPE	DMAPS	Ozonation conducted at 30°C
2006	Yanagisawa et al.	PS	–	UVO treatment in distilled water and in ammonia solution
2006	Zouahri et al.	LDPE and HDPE powder	AA, MADAME, and VPA	Ozonation conducted at 50°C
2005	Ferreira et al.	PET	HEMA	Pull-out test was conducted to check the adhesion strength
2005	Lin et al.	PU	AA, DS, WSC	

[1] Ozonation was conducted in gaseous phase, unless otherwise noted

Year	Authors	Polymer	Grafted polymer	Notes[1]
2005	Zhou et al.	Silicone	DMMCA	
2003	Murakami et al.	PS and PMMA	–	UVO treatment in distilled water
2003	Xu et al.	Silicone	MPC	Ozonation conducted at 30°C
2003, 2002	Yuan et al.	SPEU	DMAPS, DMMSA	
2002	Boutevin et al.	HDPE and LDPE powders	–	Ozonation conducted at 25°C, 35°C, and 45°C
2001	Ko et al.	PU, PMMA, LDPE, and silicone	PEGA, and PEGA-SO_3	

3 EXPERIMENTAL

In this chapter, the equipment and chemicals used, and the detailed experimental procedures followed are presented. This chapter is divided based on the different processes involved, such as ozone treatment and various analytical techniques that were used to characterize treated polymer films. The last section describes the different part of experimental runs along with the specific operating parameters used.

§ 3.1 Ozonation

The surface modification of polymer through ozonation is a relatively simple and inexpensive process. This section is further divided into two subsections; the first part explains the equipment and chemicals chosen for this study, and the second describes the details of the ozonation.

3.1.1 Materials

The polymer film chosen for the purpose of this study was a blend of low-density polyethylene (LDPE) and linear low-density polyethylene (LLDPE), obtained from Exopack Ltd., Newmarket, ON, Canada. This particular film, LDPE+LLDPE, has no coating or co-extrusion layer, and it consists of 60:40 weight ratio of LDPE to LLDPE, with a thickness of 51 μm. LDPE and LLDPE are often combined to take advantage of the specific properties of each material. LLDPE offers higher tensile strength, elongation, and better puncture and tear resistant than LDPE, but it is also harder to process. By blending the two resins, the resulting film can be easily processed, while

still having relatively high tensile strength. Additionally, this polymer film was chosen due to its availability and the low cost.

Table 3-1: Equipment list for ozonation process

Equipment	Manufacturer
Ozone generator, GL-1	PCI – Wedeco Environmental Technologies, West Caldwell, NJ, USA
Ozone monitor, OzoMeterTM	Ozocan Corporation, Scarborough, ON, Canada
pH meter, SB70P	VWR Canada, Mississauga, ON, Canada
Ultrasonic cleaner, 50D	VWR International, West Chester, PA, USA
Reactor	Ryerson University, Toronto, ON, Canada
Gas diffuser	Refractron Technologies Corp., Newark, NY, USA

In this study, ozonation of LDPE+LLDPE film was conducted in aqueous phase, with and without the presence of additives acting as homogeneous catalyst, and also in gaseous phase. Oxygen gas used as the feed to ozone generator was supplied by Linde Industrial Gases. Details on the equipment used in the ozonation process, including their model and manufacturers, are listed in Table 3-1.

Table 3-2: Transition metal salts used as additives

Chemical Name	Supplier
Silver (I) acetate, $AgCH_3COO$	BDH
Copper (II) sulfate pentahydrate, $CuSO_4 \cdot 5H_2O$ (99.0%)	ScholAR Chemistry
Zinc (II) sulfate heptahydrate, $ZnSO_4 \cdot 7H_2O$ (99.6%)	J. T. Baker
Iron (III) chloride hexahydrate, $FeCl_3 \cdot 6H_2O$ (97 – 102%)	BioBasic Inc.
Iron (II) sulfate heptahydrate, $FeSO_4 \cdot 7H_2O$ (99.0%)	EMD Chemicals Inc.

In order to adjust the pH for aqueous ozonation process, concentrated sulfuric acid, hydrochloric acid, and nitric acid, obtained from J. T. Baker, BDH, and BDH, respectively, were added to the distilled water. Moreover, solution of sodium hydroxide, made from the pellets supplied by Sigma-Aldrich with 97.0% purity, was used in order to adjust the pH of solution to a

more basic condition. Five different transition metal salts were tested as catalyst candidates for the ozonation process. These transition metal salts, as listed in Table 3-2, were selected because of their relatively high solubility in water. The radical scavenger chosen for the purpose of this study is tert-butyl alcohol (TBA) supplied by BDH.

3.1.2 Procedures

In each run, six polymer films with dimension of 4 cm × 25 cm were cleaned by submerging in distilled water for 30 minutes. The dimension of the film was chosen based on the reactor dimension. These films were subjected to further cleaning via ultrasonic cleaner for an additional 3 minutes. The films were mounted equidistantly using nylon strings onto a stainless steel support, which was then placed inside the reactor. In each gaseous ozonation run, the polymer films were vacuum dried for 60 minutes before the ozonation process in order to reduce the error that could be introduced by the presence of water vapor in the system. In an aqueous ozonation run, 11 L of distilled water was used as the ozonation medium. The additions of other chemicals to alter the pH of solution, to act as radical scavenger, and/or to act as catalyst were done before placing the films inside the reactor. The experimental set-up for ozone process used in this study and the schematic diagram are shown in Figure 3-1 and Figure 3-2, respectively.

Figure 3-1: Experimental set-up for ozonation process

Ozone was produced by feeding pure oxygen gas through high electrical discharge inside the ozone generator. The concentration of ozone in the ozone-oxygen gas mixture was recorded by the percent weight of ozone shown on the ozone monitor. The gaseous mixture was fed from the bottom of the reactor through ceramic diffuser. The residual gas exited the reactor from the top, and was sent to exhaust after passing through a catalytic destructor.

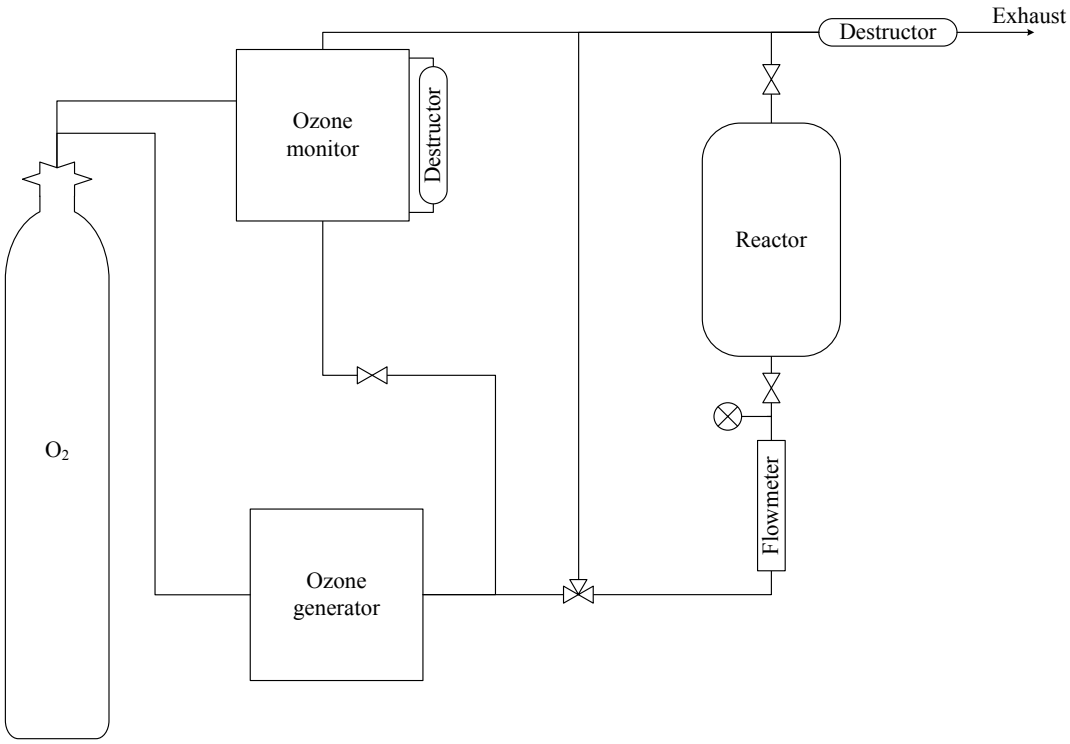

Figure 3-2: Schematic diagram of experimental set-up for ozonation process

The amount of ozone in the gaseous mixture was controlled by varying the electrical discharge of the ozone generator. The amount of oxygen passing the generator could also alter the concentration of ozone introduced to the system. Therefore, for all experimental runs conducted in this study, the volumetric flow-rate and the pressure of pure oxygen fed to the ozone generator were set to be 26 SCFH and 1.0 kg_f/cm^2, respectively, by adjusting the inlet valve of ozone generator. Other parameters such as the flow-rate and pressure of ozone-oxygen mixture entering the reactor were recorded through flowmeter and pressure gauge, which were installed at the reactor inlet. For all the runs conducted in this study, these two parameters were kept constant at 9.0 L/min and 25 kPa, respectively. In aqueous ozonation, the pH of the solution before and after ozone treatment were recorded. The temperature prior to and after ozonation

were also recorded, even though it was not controlled and left at room temperature (24.0 ± 3.0°C).

§ 3.2 Peroxide determination

Concentration of peroxide was determined by using the standard iodometric titration method (Kokatnur & Jelling, 1941). This method is simple, yet it provides accurate measurements of peroxide concentration, as proven by many studies. The following subsections describe the materials used and detailed methods followed in this study. Relevant equations and reactions involved in the preparation and standardization of sodium thiosulfate solution are included in Appendix A.

3.2.1 Materials

The chemicals used in the peroxide determination part of this study are listed in Table 3-3.

Table 3-3: Chemicals utilized in peroxide determination method

Chemical Name	**Manufacturer/Supplier**
Potassium iodide, KI (99%)	Sigma-Aldrich
Sodium thiosulfate-5-hydrate, $Na_2S_2O_3 \cdot 5H_2O$ (99.5%)	Sigma-Aldrich
Sulfuric acid, H_2SO_4 (98%)	J. T. Baker
Isopropanol, C_3H_7OH (99.7%)	J. T. Baker
Glacial acetic acid, CH_3COOH (99.5%)	BDH
Potassium dichromate, $K_2Cr_2O_7$ (99%)	Sigma-Aldrich

3.2.2 Procedures

Based on the literature review done, iodometric titration was selected as the method to determine the amount of peroxide group present on the polymer film. This method involves the use of dilute sodium thiosulfate solution, which is highly susceptible to chemical and bacterial decomposition, hence resulting in its unstable concentration. A common practice to ensure the accuracy of this method is by standardization of sodium thiosulfate solution every 1-3 days.

Therefore, this section is divided into two parts, the preparation and standardization of sodium thiosulfate solution, and the iodometric titration itself.

Preparation and standardization of sodium thiosulfate solution

The preparation of this solution involved making 0.1 N sodium thiosulfate solution by dissolving 24.82 g of sodium thiosulfate pentahydrate crystal in distilled water to make 1.0 L solution. The solution was then stored for two weeks to allow oxidation of any bisulfite ion, HSO_3^-, which may be present in the solution. This was done in order to achieve a steady concentration of sodium thiosulfate solution (Kassner & Kassner, 1940). Small amount of this solution was then diluted 100 times in a dark bottle to reach the desired normality of 0.001 N.

This solution was standardized regularly to maintain the accuracy of subsequent calculations. The standardization of this solution was done by potassium dichromate solution (APHA, 1989). For the standardization procedure, 1.0 mL of concentrated sulfuric acid was added to 80.0 mL of distilled water in a dark bottle. In addition to the sulfuric acid, 10.0 mL of potassium dichromate solution, with equal normality as the expected normality of sodium thiosulfate solution, and 1.0 g of potassium iodide were placed inside the dark bottle as well. This reaction mixture was placed in the dark for approximately 6 minutes to allow the reaction to complete. Upon completion of reaction, the mixture was transferred into an Erlenmeyer flask, followed by titration with sodium thiosulfate until the solution turned colourless.

Iodometric titration

In order to determine the peroxide concentration generated on the polymer surface, two films were cut into smaller pieces and placed inside a mixture of 50.0 mL solution of isopropanol and 2.0 mL of glacial acetic acid. Following this, 2.0 mL of freshly made saturated potassium iodide solution was added into the mixture. Upon this addition, some of the potassium iodide precipitated out of the solution, which was already expected due to its low solubility in isopropanol.

The mixture was subjected to incipient boiling (80.0 ± 1.0°C) for a certain period of time, which was determined in the preliminary stage of this study. Upon heating, the solution colour changed from colourless to yellow. Titration with sodium thiosulfate was done immediately after

incipient boiling, without cooling, until the solution reverted back to colourless. The titration was repeated once for every experimental run with another two polymer films in order to ensure the accuracy of the results obtained. Related equations and reactions for the iodometric titration can be found in the Appendix A section of this thesis.

§ 3.3 Tensile strength measurement

The tensile strength of polymer film in this research was tested according to ASTM D882-09 (ASTM, 2009), because the thickness of the polymer film used was less than 1.0 mm. The machine used to measure the tensile strength was Universal Testing Machine, model 4442 by Instron, Norwood, USA, shown in Figure 3-3.

Figure 3-3: Instron 4442

In order to determine some of the optimum operating parameters for this test, such as the testing speed and dimension of the sample needed, several preliminary tests were conducted. The percent elongation at break of untreated film was measured in order to determine the

corresponding standardized value of initial grip separation and the required initial strain rate. These values were then used to calculate the testing speed necessary for accurate measurement of tensile properties.

Based on the physical limitation of the machine and the readings obtained from the preliminary runs, the initial grip separation was set to be 2.0 cm. The length and width of the film sample were determined to be 5.0 and 1.0 cm, respectively. The length was chosen based on the initial grip separation and the height of top and bottom grips, while the width was chosen based on the width of the grips used. The appropriate testing speed was calculated to be 20.0 cm/min according to the ASTM standard mentioned above.

A set of preliminary tests was carried out to ensure the isotropy of this particular polymer film. In this test, the tensile strength of untreated films was measured on the transverse and machine directions. The difference between the two measurements was found to be not statistically significant (see § K.1 for relevant calculations). Because the film was found to be isotropic, the subsequent measurements were only taken for the transverse direction.

§ 3.4 FTIR spectra analyses

The FTIR spectra for polymer films were obtained by using Perkin-Elmer Spectrum-One, V3.01 spectrometer from Waltham, USA. These spectra were then analyzed in order to acquire information on the presence of different functional groups formed due to the exposure of films to ozone. From the literature review, some of the commonly investigated functional groups generated after the ozonation process are carboxyl, ketone, esters, and alcohol groups (Kefeli et al., 1971; Robin, 2004; Mao et al., 2004). Table 3-4 lists the frequencies and intensities of some of the functional groups of interest.

The oxidation of polyethylene initially resulted in the formation of peroxy radical, which further reacts to form different functional groups, such as carboxylic, ketone, alcohol, and peroxide groups (Razumovskii et al., 1971). The presence of peroxide groups on polymer film could not be confirmed directly by FTIR spectroscopy due to the O–O symmetric bond (Vacque et al., 1997). However, the formation of peroxide groups after ozonation could be confirmed through the presence of other functional groups such as carboxylic groups, since all the groups were formed from a common root, peroxy radical.

Table 3-4: Characteristic infrared frequencies of different functional groups (Adapted from: Socrates, 1994)

Functional groups		Wavenumber (cm^{-1})	Peak intensity[2]
Alcohol	O–H	3200 – 3600	S (br)
	O–H	3500 – 3700	S (sh)
	C–O	1050 – 1150	S
Alkane	C – C	955 – 1255	V
Alkene	=C–H	675 – 1000	S
	–C=C (tri-substituted)	790 – 850	W – M
	–C=C (polyene)	970 – 990	S
Carbonyl	C=O	1670 – 1820	S
Carboxyl	C=O	1700 – 1725	S
	O–H	2500 – 3300	S (very br)
	C–O	1210 – 1320	S
Ester	C=O	1735 – 1750	S
	C–O	1000 – 1300	2 bands or more
Ketone	acyclic	1735 – 1750	S

Aside from introducing different oxygenated functions, ozone exposure of polyolefin also causes reconstruction of the polymer structure (Michael et al., 2004). Chain scission on the backbone of the polymer would lead to cross-linking of the polymer. The reconstruction by chain scissions and cross-linking can be observed by comparing the FTIR spectra of treated and untreated film around 600 – 1300 cm^{-1} (Socrates, 1994).

§ 3.5 Contact angle

Contact angle is widely used as an indicator of the hydrophilicity/hydrophobicity of a material surface. Hydrophilicity signifies high surface free energy, which is associated to good

[2] W = weak, M = medium, S = strong, V = variable, sh = sharp, br = broad

adhesiveness and high degree of wetting, while hydrophobicity implies the opposite (Xu et al., 2003; Ferreira et al., 2005; Bongiovanni et al., 2007).

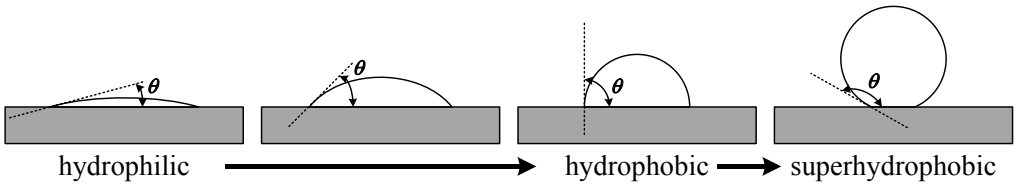

Figure 3-4: Schematic of different surface wettability levels
(Adapted from: Förch et al., 2009)

If water droplet is strongly attracted to the solid surface, in other words the surface is hydrophilic, the droplet will form contact angle that is close to 0°. On the other hand, for hydrophobic material, the contact angle of water and material would be greater than 90° and superhydrophobic materials exhibit contact angle greater than 150° (Förch et al., 2009).

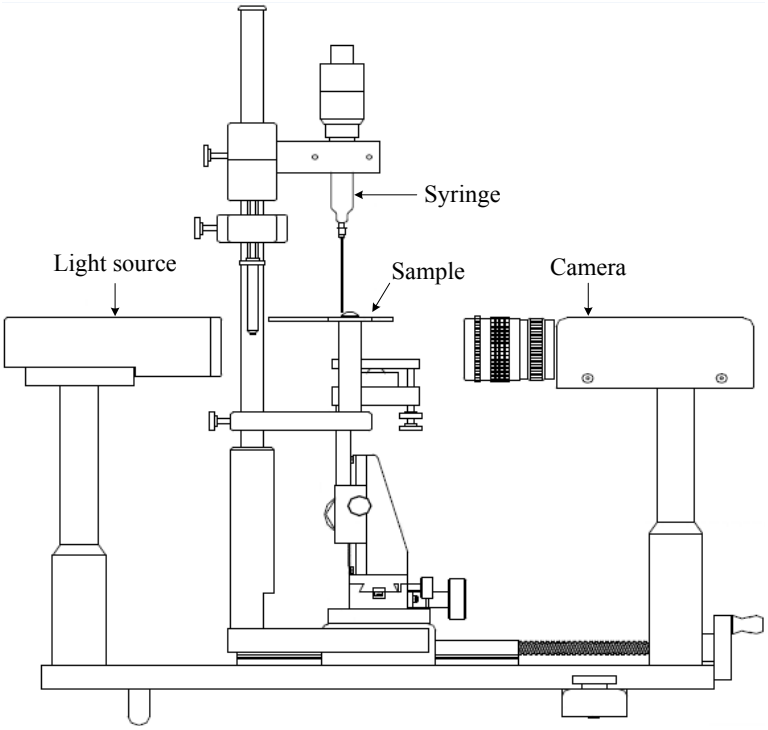

Figure 3-5: Goniometer from Ramé-Hart
(Adapted from: Ramé-Hart, 2010)

Contact angle between ultra-pure water and the LDPE+LLDPE film in this study was measured by using goniometer, model 100-00-115 manufactured by Rame-Hart (NJ, USA). The method used for contact angle measurement was the static sessile drop method. Ultra pure water

was obtained from the Analytical Chemistry Lab in Ryerson University. The volume of water drop used in this test method was chosen to be 2.0 μL. The contact angle of the film was obtained by taking the average of contact angle measurements of three different spots on each side of the film.

§ 3.6 Scanning electron microscope (SEM)

Surface morphology of polymer film was investigated by using SEM for untreated polymer film and for films treated under different operating conditions. High resolution images were obtained by using SEM model JSM-6380 LV, from JEOL, Oxford Instrument, U.K., at 15 kV. Samples were coated with gold at 0.2 Torr before the SEM analysis in order to increase its conductivity, thereby enhancing the resolution of the images. For comparison purposes, all the polymer film samples were observed under 5000 times magnification. The change in surface roughness of polymer film for different treatment condition was observed qualitatively.

§ 3.7 Experimental design

A set of preliminary runs was conducted to establish the length of incipient boiling time necessary for the determination of peroxide concentration. In the preliminary stage of this study, blank titration was also conducted by subjecting untreated polymer films to the same condition as the treated films, except the ozonation treatment part. This was done in order to determine the amount of potassium iodide reacting with impurities.

Operating parameters being studied in this research were the ozonation time, applied ozone dose, initial pH of solution for aqueous ozonation, the type and dose of catalyst for catalytic ozonation, and the presence of TBA as radical scavengers in catalytic ozonation. Table 3-5 summarizes the different operating conditions applied, where most of the runs were repeated at least twice in order to ensure reproducibility of the results. Even though the runs had to be done in certain order, the repeats of each run were done randomly. The sequence of these repeats was obtained by using a unique pseudo-random number generator. Moreover, the ozonated samples were always randomly chosen for the mechanical and chemical tests conducted in order to reduce the source of systematic error.

Table 3-5: Different operating conditions for ozone treatments

Phase	[Ozone] (wt%)	Time (minutes)	Initial pH[3]	Additives
gaseous	1.0	30	–	N/A[4,5,9]
aqueous	1.0	30	–	None[5]
aqueous	1.0	30	–	0.2 g/L of various transition metal salts[5]
aqueous	1.5	60	–	None[6,8]
aqueous	1.5	60	–	0.1 or 0.5 mol/L TBA, with 0.05 g/L copper (II) sulfate[7]
aqueous	1.5	60	–	0.02, 0.03, 0.05, 0.2, or 0.5 g/L of copper (II) sulfate[6]
aqueous	1.5	60	3.00, 4.00, and 5.00	Sulfuric, hydrochloric, and nitric acid for pH adjustment[8]
aqueous	1.5	60	7.00 and 10.00	Sodium hydroxide for pH adjustment[8]
aqueous	1.5	60	3.00 and 5.00	0.03 or 0.05 g/L copper (II) sulfate, with sulfuric acid[8]
aqueous	1.5	15 – 120	–	0.05 g/L of copper (II) sulfate[9]
gaseous	1.5	15 – 120	–	N/A[9]
aqueous	1.0 – 3.0	60	–	0.05 g/L of copper (II) sulfate[10]

[3] "–" indicates not applicable or not controlled
[4] For determination of incipient boiling time
[5] For catalyst candidate test; transition metal salts used are listed in Table 3-2
[6] For determination of optimum copper (II) sulfate dose
[7] For investigation of radical scavenger effect
[8] For investigation of initial pH effect
[9] For investigation of ozonation time effect
[10] For investigation of ozone dose effect

4 RESULTS AND DISCUSSIONS

In this chapter, the results obtained during this study are presented and discussed. The operating parameters investigated in this study were the type and dose of catalyst, the pH of solution, presence of scavenger, ozonation time, and ozonation dose. The sample calculation for concentration of peroxide can be found in Appendix B. Error bars shown in this study represent the 95% confidence interval. Sample calculation for the error bar is included in Appendix B.

§ 4.1 Preliminary runs and blank titration

Measurements of peroxide concentration formed on the polymer samples were done through the use of standard iodometric titration method (Kokatnur & Jelling, 1941). In this method, solution containing pieces of polymer films was subjected to incipient boiling (80.0 ± 1.0°C) for a period of time. Due to the unstable nature of potassium iodide, long incipient boiling time may introduce error, i.e. the iodide ions being oxidized by other substances. Another possible source of errors that can be associated with long incipient boiling time is due to the volatility of iodine. On the other hand, sufficient time must be given in order to allow all the peroxide groups formed on polymer surface to react with iodide ions. Therefore, in order to minimize the error at this stage, it is necessary to determine the optimum time necessary for the peroxide groups to react completely.

Experiments for this test were conducted in gaseous phase with 30 minutes ozonation time and ozone feed concentration of 1.000 ± 0.020 wt%. The peroxide concentrations detected were plotted against the incipient boiling time, as shown in Figure 4-1. This test was conducted by

subjecting two polymer films from each run to certain incipient boiling time. From this figure, it was obvious that the peroxide generated from ozonation was completely reacted with iodide ions after 7 – 8 minutes of incipient boiling time. Patel (2008) presented similar finding for the same polymer films with different peroxide concentrations, which were also treated with ozonation. The comparison of the results from these two sets of experiments suggests that the incipient boiling time needed is independent of the amount of peroxide.

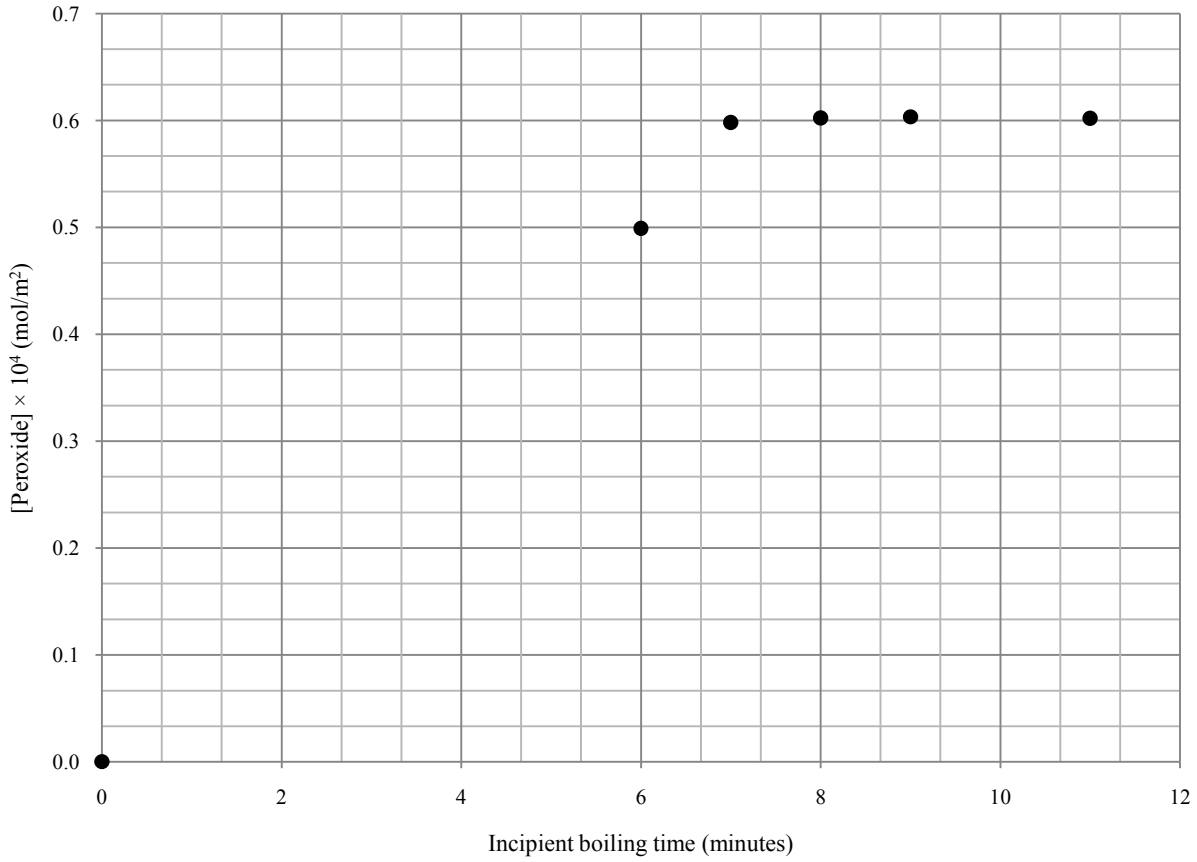

Figure 4-1: Peroxide detected on LDPE+LLDPE film at different incipient boiling time after 30 minutes gaseous ozonation with 1.0 wt% applied ozone dose

Comparison of the peroxide generated on films placed at different positions inside the reactor shows that film position has negligible effect on the amount of peroxide generated. Blank titrations were done by subjecting the untreated polymer samples through the same process as treated ones, except for the ozonation process. The blank titration was subtracted from the calculated peroxide determination of ozonated polymer films. This subtraction was necessary to account for the impurities reacting with iodide ions. The average value obtained from the blank

titrations for this particular polymer film was calculated to be equivalent to peroxide concentration of 0.064×10^{-4} mol/m^2. The raw data obtained from the incipient boiling time test and blank titration are provided in Appendix C.

§ 4.2 Effect of transition metal salts

Various transition metal salts, listed in Table 3-2, were tested as additives in the aqueous ozonation. In addition to comparing the effect of different additives, the peroxide generated by gaseous ozonation was compared to that generated by aqueous ozonation. This comparison is necessary because in aqueous ozonation, both direct and indirect oxidations could be responsible for the peroxide formation; while in gaseous ozonation, only direct oxidation is considered (Gottschalk et al., 2000; Beltrán, 2004; Yanagisawa et al., 2006; Gu, 2008).

In this section, ozonation runs were conducted under the same condition for gaseous phase and aqueous phase with and without additives. Ozonation time chosen was 30 minutes with ozone dose of 1.000 ± 0.020 wt%. Transition metal salts were added with the same anhydrous dose of 0.2 g/L for different runs. The concentrations of peroxide group generated from these runs were plotted and shown in Figure 4-2, and the raw data were tabulated in Appendix D.

From Figure 4-2, it can be observed that aqueous ozonation without any addition of transition metal salts yielded a slightly lower peroxide concentration when compared to gaseous ozonation. The ozone treatment in the presence of silver (I) acetate and iron (II) sulfate were not studied further due to the change observed in the transparency of polymer film. The surface of the films from runs with the silver salt was coated with oxidized silver, shown by the dark silver colour; while the films treated in the presence of iron (II) sulfate changed to orange colour.

On the other hand, the addition of iron (III) chloride, copper (II) sulfate, and zinc (II) sulfate enhanced the generation of peroxide to be higher than the gaseous ozonation, without any visible change in appearance. Copper (II) sulfate was chosen to be the catalyst further studied in the subsequent parts of this research, because the addition of iron (III) chloride on the ozonation of polyethylene has been studied. The average concentration of peroxide generated from 30 minutes ozonation runs using 0.2 g/L of copper (II) sulfate was found to be 0.71×10^{-4} mol/m^2, while gaseous ozonation produced 0.60×10^{-4} mol/m^2 for the same operating conditions. This translates to an approximately 18% increase in the amount of peroxide generated.

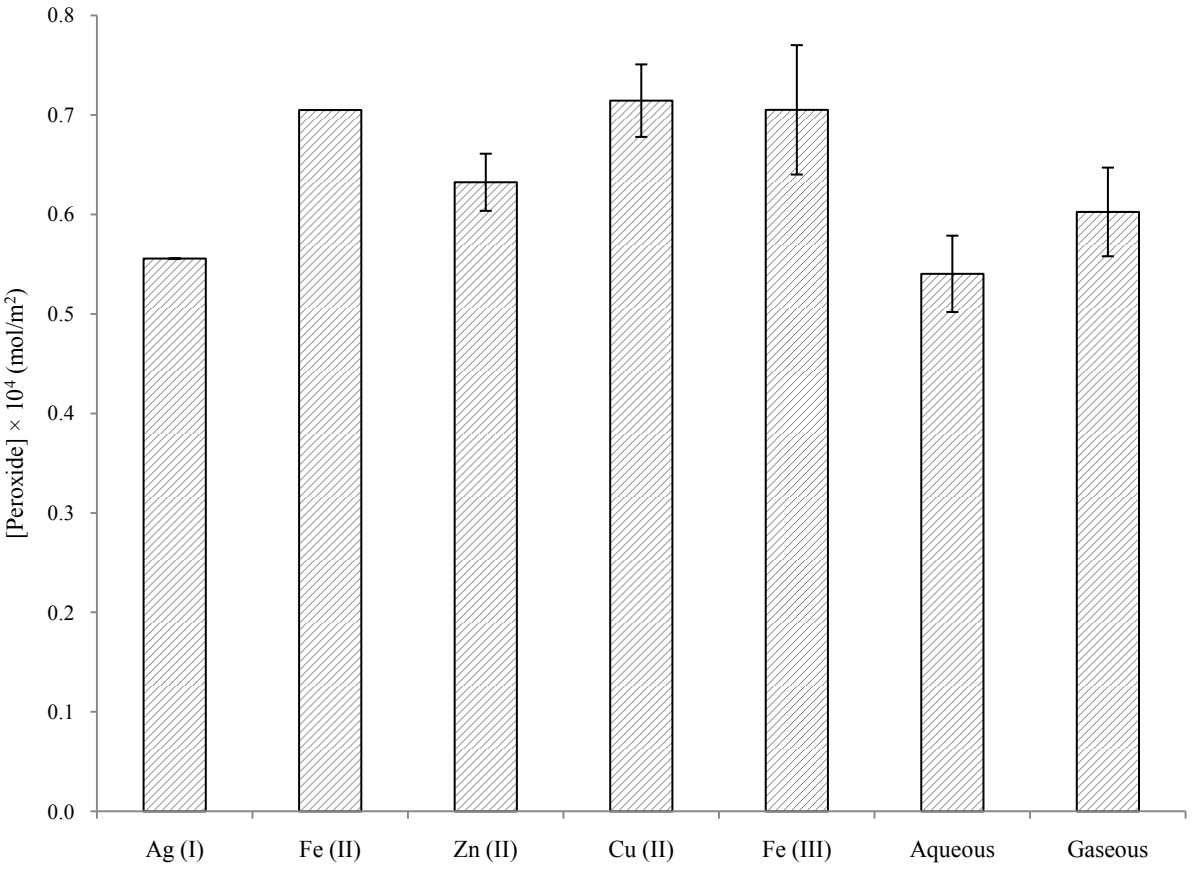

Figure 4-2: Peroxide generated on LDPE+LLDPE film after 30 minutes ozonation with 1.0 wt% applied ozone dose and 0.2 g/L anhydrous salt where applicable

The increase in the peroxide generation observed after the addition of soluble transition metal salts may be due to the alternative reaction pathways. Due to the large number of reactions occurring simultaneously in the oxidation of polymer in aqueous ozonation, the addition of these transition metal salts may catalyze different reactions. For example, the addition of transition metal salts in the wastewater treatment for ozonation process enhances the oxidation rate of various organic pollutants (Legube & Leitner, 1999; Lin et al., 2002). Another possible explanation is based on the catalyzing mechanism of metal salts in the auto-oxidation of organic peroxide groups, shown by Reactions (2-7) to (2-13).

§ 4.3 Optimal copper (II) sulfate dose

From the results shown in § 4.2, copper (II) sulfate was chosen as the catalyst to be studied in the subsequent parts of this research. An optimal dose of copper (II) sulfate was of interest in order

to minimize the cost of ozonation, while maximizing the peroxide generated. All the ozonation treatments for this section were conducted for 60 minutes with 1.500 ± 0.020 wt% of ozone dose. No other chemical was added in these experimental runs. In addition to the concentration of peroxide, the change in tensile strength and FTIR spectra of the polymer films were also studied with respect to different copper salt concentration.

4.3.1 Peroxide concentration

The concentration of peroxide generated from this test are shown in Figure 4-3, while the raw data can be found in Appendix E.

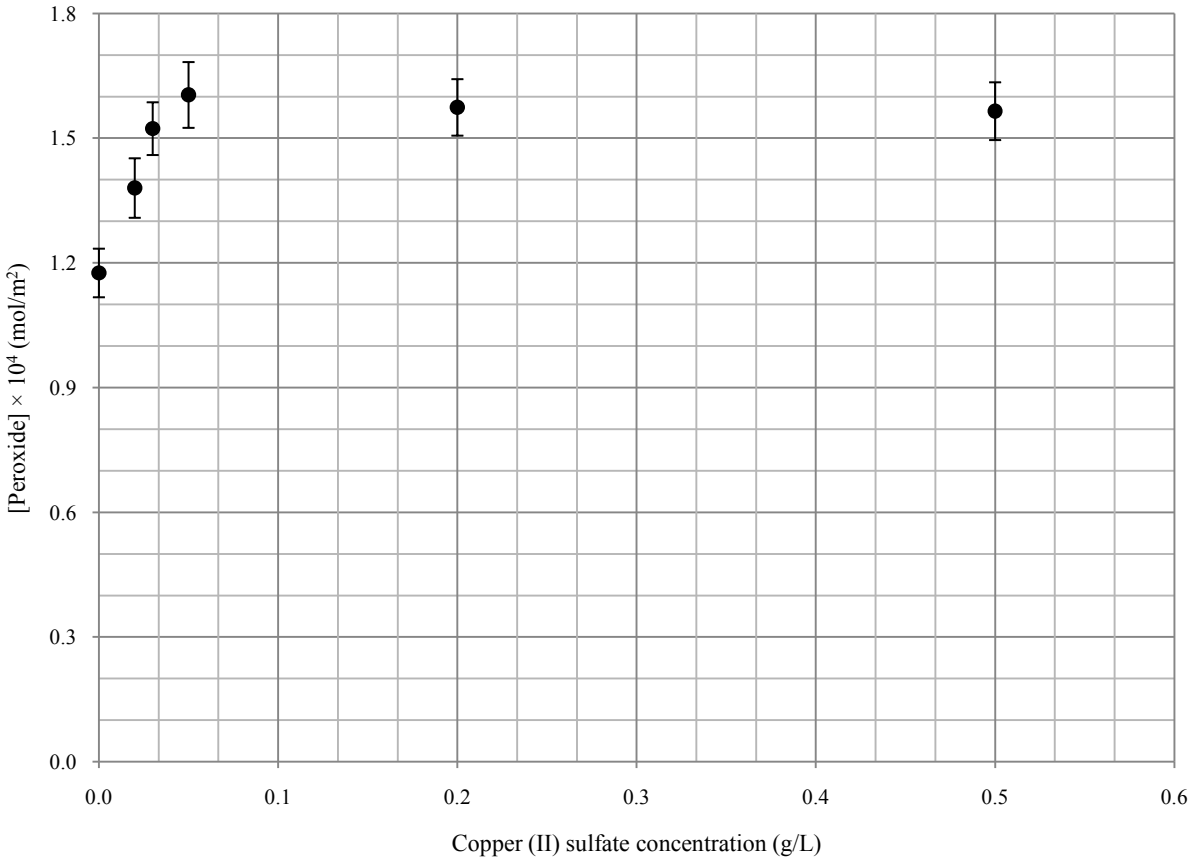

Figure 4-3: Peroxide generated on LDPE+LLDPE film after 60 minutes ozonation with 1.5 wt% applied ozone dose and various copper (II) sulfate concentration

Based on this figure, the optimal dose of copper (II) sulfate to produce maximum concentration of peroxide was 0.05 g/L. In other words, the concentration of peroxide generated increases with increasing copper (II) sulfate concentration up to 0.05 g/L, after which the

peroxide concentration remains approximately constant, even if higher concentration of copper (II) sulfate was present in the aqueous solution.

As explained in the previous section and in the literature review, transition metal salts may catalyze various reactions in ozonation process (Legube & Leitner, 1999; Lin et al., 2002). However, it is not possible to identify which reactions are being catalyzed by the copper (II) sulfate from the results obtained in this study alone. Further studies must be conducted in order to investigate this phenomenon in detail.

4.3.2 Tensile strength

Tensile strength measurements were done for polymer films subjected to 60 minutes ozonation with 1.500 ± 0.020 wt% ozone dose, and various copper (II) sulfate concentration. The results of these tensile strength measurements were tabulated in Appendix E, and plotted in Figure 4-4.

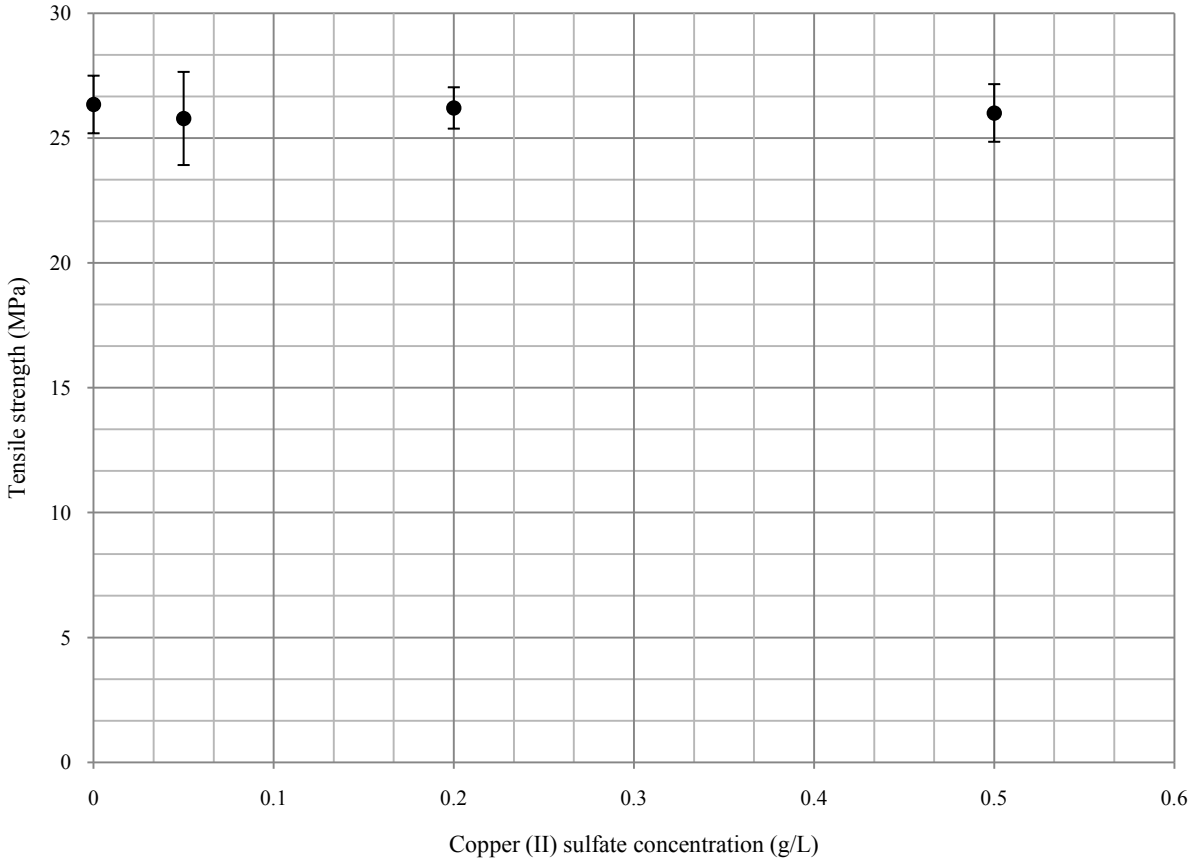

Figure 4-4: Tensile strength of LDPE+LLDPE film after 60 minutes ozonation with 1.5 wt% applied ozone dose and various copper (II) sulfate concentration

For comparison purposes, the tensile strength of untreated polymer film was measured to be 27 MPa. The tensile strength of polymer films treated in aqueous ozonation without the presence of copper (II) sulfate is represented by the data point at 0 g/L copper (II) sulfate in Figure 4-4. By comparing this value with the ones treated in the presence of copper (II) sulfate, it can be observed that the addition of copper (II) sulfate in ozonation does not have detrimental effects on the tensile strength of polymer film. This would mean that the same amount of peroxide concentration can be obtained with less reduction in tensile strength in the presence of copper (II) sulfate.

4.3.3 FTIR spectra analysis

The polymer films were also characterized by analyzing the FTIR spectra. The FTIR spectra obtained from polymer films before and after treatment were compared as shown in Figure 4-5. As previously mentioned, the presence of peroxide group can be determined through the analysis of FTIR spectra indirectly because ozonation does not only generate peroxide groups on the polymer surface (Kefeli et al., 1971; Vacque et al., 1997).

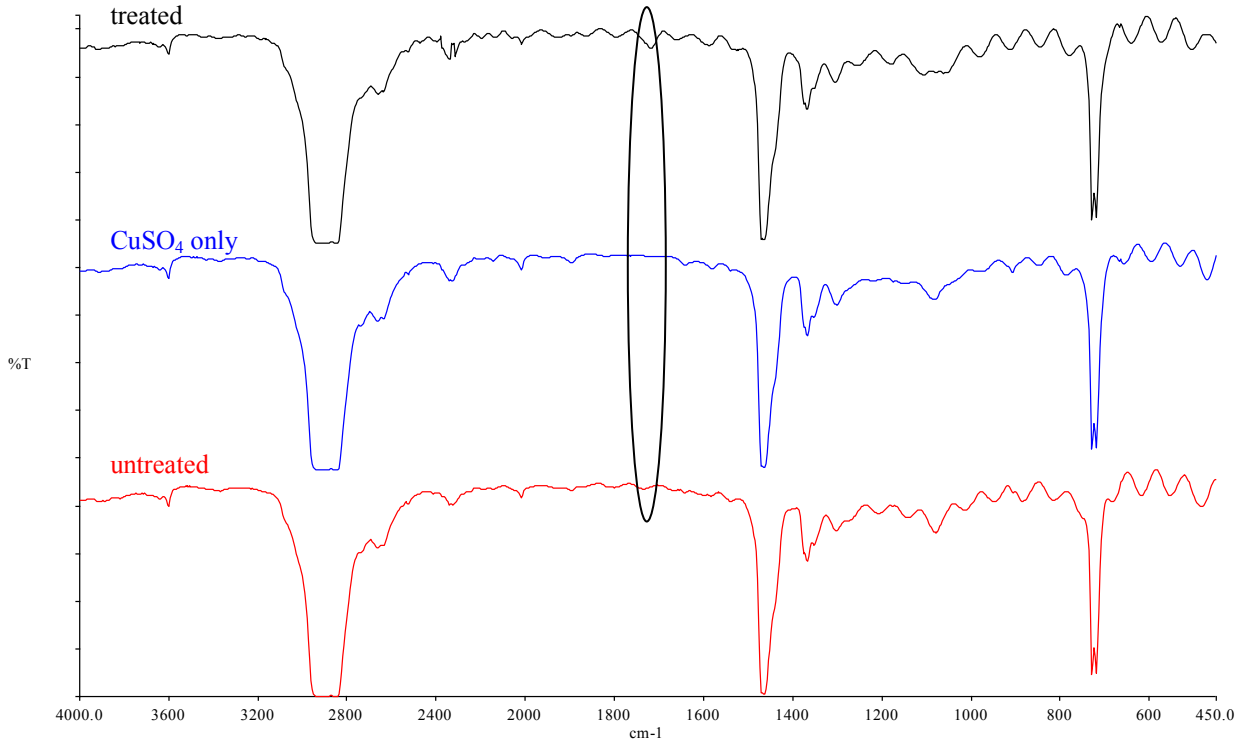

Figure 4-5: FTIR spectra of LDPE+LLDPE film before treatment and after 60 minutes ozonation with 1.5 wt% applied ozone dose and 0.05 g/L of copper (II) sulfate

For comparison purposes, polyethylene film was also subjected to a solution of 0.05 g/L copper (II) sulfate for 60 minutes, in the absence of ozone. The spectra obtained for this polymer sample shows no change when compared to the untreated polymer film. This shows that the polymer film is inert to the copper (II) sulfate presence.

The presence of other functional groups such as carboxylic, ketone, and alcohol groups, which were formed after ozonation, can be confirmed by analyzing the FTIR spectra. These functional groups served as evidence of oxidation reaction on polyethylene and of the formation of peroxide groups, because these functional groups, including peroxide groups, were formed by the reaction of peroxy radical, shown in Figure 2-7 (Razumovskii et al., 1971).

Based on Figure 4-5, the most noticeable difference between the IR spectra obtained from ozonated and untreated polyethylene films corresponds to a wavenumber of 1750 cm^{-1}, which represents the C=O bonds in carboxylic and ketone groups, as shown in Table 3-4. Moreover, the reconstruction of polymer film by chain scission and cross-linking can be observed from the peak variations between wavenumber of 600 cm^{-1} to 1300 cm^{-1} (Socrates, 1994). The formation of alcohol groups, which corresponds to wavenumber of 3200 cm^{-1} to 3700 cm^{-1}, was not detected from this spectra comparison. The absence of peak could be an indication of the low concentration of alcohol functional groups formed (Socrates, 1994).

§ 4.4 Effect of radical scavenger in catalytic ozonation

Several catalytic ozonation runs were conducted in the presence of a known hydroxyl radical scavenger, tert-butyl alcohol (TBA). The purpose of these runs was to explore more on the reaction mechanism of peroxide formation. The addition of TBA should reduce the contribution of hydroxyl radical, if any, in the peroxide generation. In other words, the presence of TBA limited the peroxide formation to be mainly from direct oxidation. These results provided experimental evidence on which species plays the major role in the peroxide formation during aqueous ozonation. The experimental data obtained from these runs were tabulated and plotted, as shown in Appendix F and Figure 4-6. Two different concentrations, 0.1 mol/L and 0.5 mol/L, of TBA were used in these runs.

From Figure 4-6, catalytic ozonation runs without the presence of TBA yielded higher concentration of peroxide when compared to the results obtained with the addition of TBA.

Based on this comparison, the formation of peroxide could be attributed to both direct and indirect oxidation.

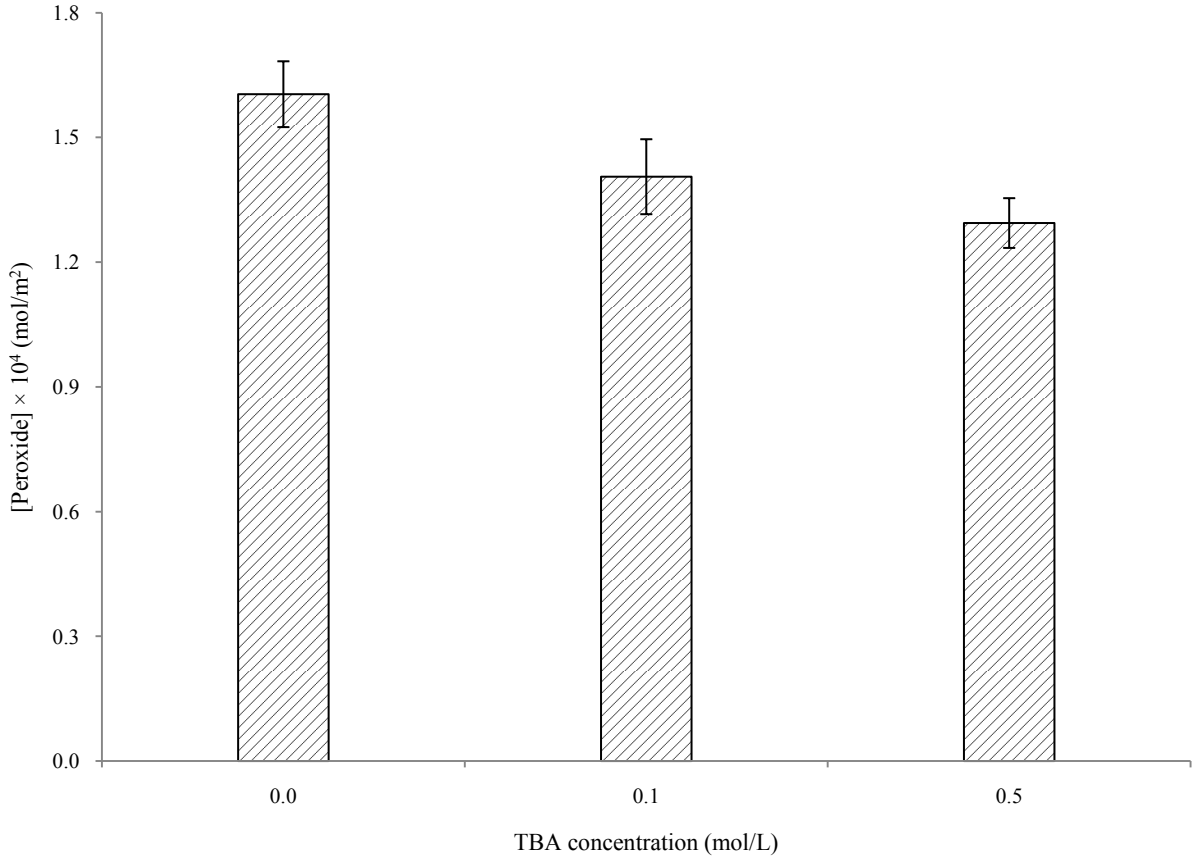

Figure 4-6: Peroxide generated on LDPE+LLDPE film after 60 minutes ozonation with 1.5 wt% applied ozone dose and 0.05 g/L copper (II) sulfate, with TBA

A decrease of approximately 12% in peroxide concentration generated was observed when 0.1 mol/L of TBA was introduced, as shown in Figure 4-6. The relatively small decrease in the concentration of peroxide generated in the presence of TBA could be due to the effect of TBA in the gas-liquid mass transfer rates. Studies have revealed that the addition of TBA enhances the mass transfer rates of ozone into the solution by decreasing the surface tension, which would in turn decrease the gas bubble size (López-López et al., 2007; Tizaoui et al., 2009). The reduction in bubble size would imply an increase in the mass transfer area, hence increasing the volumetric mass transfer rate. The increase in mass transfer rates of ozone into the solution suggests a higher availability of ozone in the solution, which would also affect the concentration of hydroxyl radical available in the system, hence affecting the peroxide generation rates.

§ 4.5 Effect of initial pH in aqueous ozonation

Another parameter that may affect the generation of peroxide on polymer surface by aqueous ozonation is the pH of the aqueous medium. As previously mentioned, both molecular ozone and hydroxyl radical could play role in the peroxide group formation during aqueous ozonation. The production of hydroxyl radical is accelerated under basic condition due to the catalyzing effect of hydroxide ions on ozone decomposition reaction.

Hydroxyl radical is formed as a product of ozone decomposition in water, and it has a stronger oxidation capacity than ozone itself. To the best of the author's knowledge, the effect of pH on the reaction rate constants of polyethylene with ozone and hydroxyl radical is still currently unknown. As explained in the experimental section, the pH of distilled water was adjusted prior to the start of ozonation treatment by the addition of acids or bases. The experimental data for peroxide groups generated for different initial pH values can be found in Appendix G.

4.5.1 Effect of initial pH in the absence of copper (II) sulfate

In Figure 4-7, data of peroxide generated from experimental runs with initial pH varying from 3 – 10 were plotted. The experimental runs with initial pH of 3, 4, and 5 were conducted by the addition of sulfuric acid only, while the ones with initial pH of 7 and 10 were conducted by the addition of sodium hydroxide only. The data point corresponding to initial pH of 5.60 ± 0.10 was obtained from runs conducted in distilled water as aqueous medium without pH adjustment. All of the plotted data were obtained from 60 minutes aqueous ozonation runs with ozone concentration of 1.500 ± 0.020 wt%.

By observing the trend shown in Figure 4-7, the optimal initial pH was found to be 5.60 ± 0.10. Moreover, the decrease in peroxide generated was observed to be much greater for aqueous ozonation under basic condition than that under the acidic condition. Based on this information and the trend observed, it would be tempting to conclude that direct oxidation is the dominating mode for peroxide formation; i.e., molecular ozone is the substance responsible for the majority of peroxide generation on polymer surface in aqueous ozonation, not the hydroxyl radical. However, this proposition contradicts with finding shown in acidic pH, where the amount of peroxide groups formed decreases as the pH decreases as well.

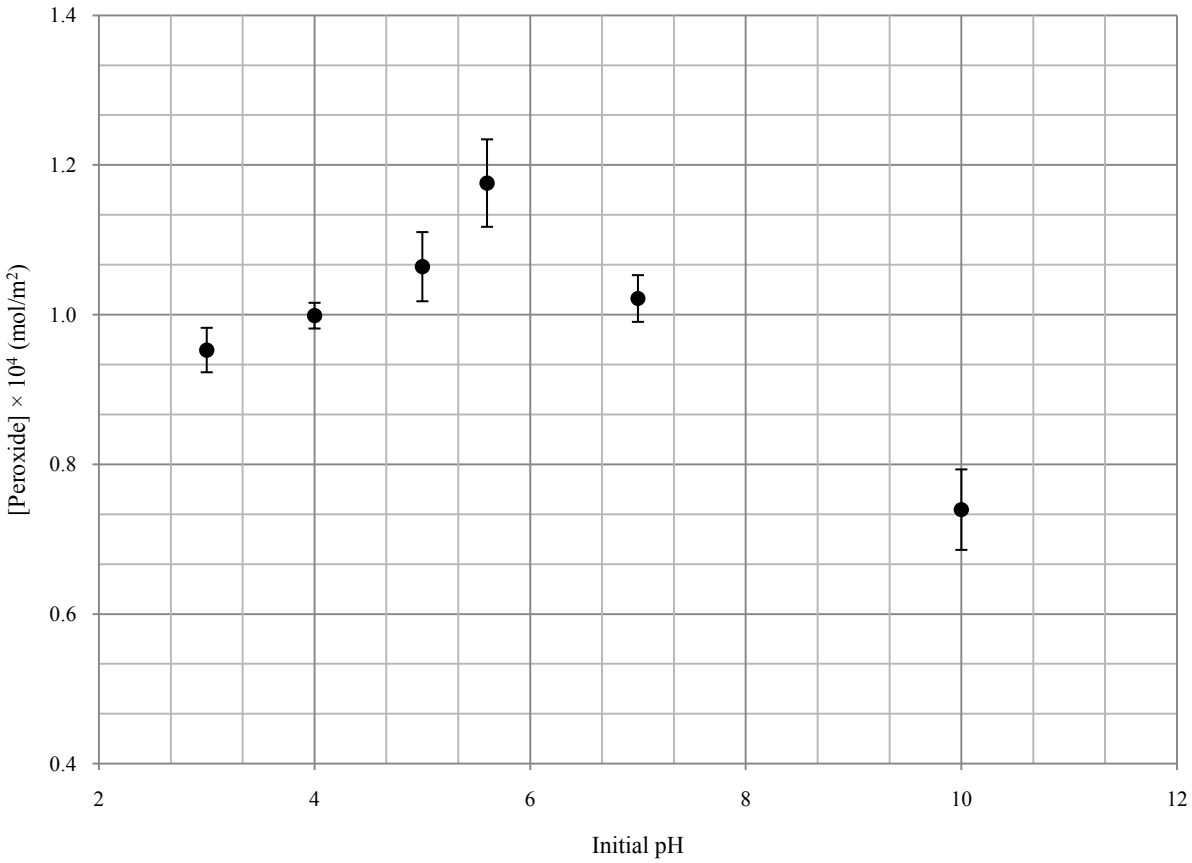

Figure 4-7: Peroxide generated on LDPE+LLDPE film after 60 minutes ozonation with 1.5 wt% applied ozone dose at different initial pH values adjusted by using sulfuric acid or sodium hydroxide

The decrease in the concentration of peroxide at lower initial pH for acidic condition could be explained by the slow decomposition rate of ozone. This implies lower hydroxyl radical concentration is present under acidic condition (Gottschalk et al., 2000). The low concentration of hydroxyl radical affects the abstraction rate of hydrogen from alkyl group (Billamboz et al., 2010), which in turn affects the initiation step of peroxide formation. This result agrees with the findings obtained in § 4.4, where the concentration of peroxide generated decreased in the presence of TBA as radical scavenger. However, this may seem to contradict previous experimental results showing that gaseous ozonation yielded slightly higher peroxide concentration than aqueous ozonation, even though there is negligible contribution from hydroxyl radical in gaseous ozonation. Careful consideration must be taken in comparing gaseous and aqueous ozonation, due to the different ozone concentration involved. The difference in peroxide generated may be due to the smaller quantity of dissolved ozone

concentration, which is responsible in aqueous ozonation, in comparison to the applied ozone dose, which is responsible in gaseous ozonation.

Lower peroxide concentration generated was also observed in Figure 4-7 when the initial pH was set to the more basic condition, namely 7 and 10. Even though higher pH enhances ozone decomposition to produce stronger oxidant, the hydroxyl radical, it could also reduce the reaction rate constants of one or more reaction steps involved in the generation of peroxides.

The effect of electrolyte concentration on the solubility of ozone have been the subject of many different research, mainly for environmental and health purposes. Levanov et al. (2008) concluded that ozone solubility decreases in solution involving different types of strong acid. Rischbieter et al. (2000) studied the effect of electrolytes on the Henry's constant of ozone. The effect of these chemicals on ozone solubility in aqueous solution is called salting-out effect, which has been found to follow Sechenov's relation by several experimental studies (Rischbieter et al., 2000; Bińi, 2006). In order to ensure the trend in Figure 4-7 was not observed due to the change in solubility of ozone, change in Henry's constant according to Sechenov's relation was calculated for several ozonation runs. Detailed calculation on the salting-out effect on the solubility of ozone for this study can be found in § K.2. Due to the low concentration of electrolytes involved in the aqueous ozonation conducted in this study, there is no significant reduction expected on the ozone solubility.

4.5.2 Investigation of peroxide generated using different acids

Due to the low solubility of copper (II) sulfate under basic condition, the subsequent parts of these studies were focused on the acidic pH range only. From the results obtained by Levanov et al. (2008), the decrease in ozone solubility depends on both the concentration and the type of acid present in the solution (Levanov et al., 2008). In order to observe any relation between the type of acid and the peroxide generated, further tests were conducted for acidic initial pH. The initial pH were adjusted by using two different types of strong acids, nitric acid and hydrochloric acid. These runs were conducted with the same experimental conditions as the runs with sulfuric acid. The data obtained from these runs were plotted in Figure 4-8, along with the results from runs with sulfuric acid for comparison.

From Figure 4-8, similar trends in concentration of peroxide generated were observed for different types of acid used. The peroxide generated for ozonation runs involving nitric acid and sulfuric acid were very close to each other, while data points with lower value but with similar trend were obtained from ozonation runs with hydrochloric acid.

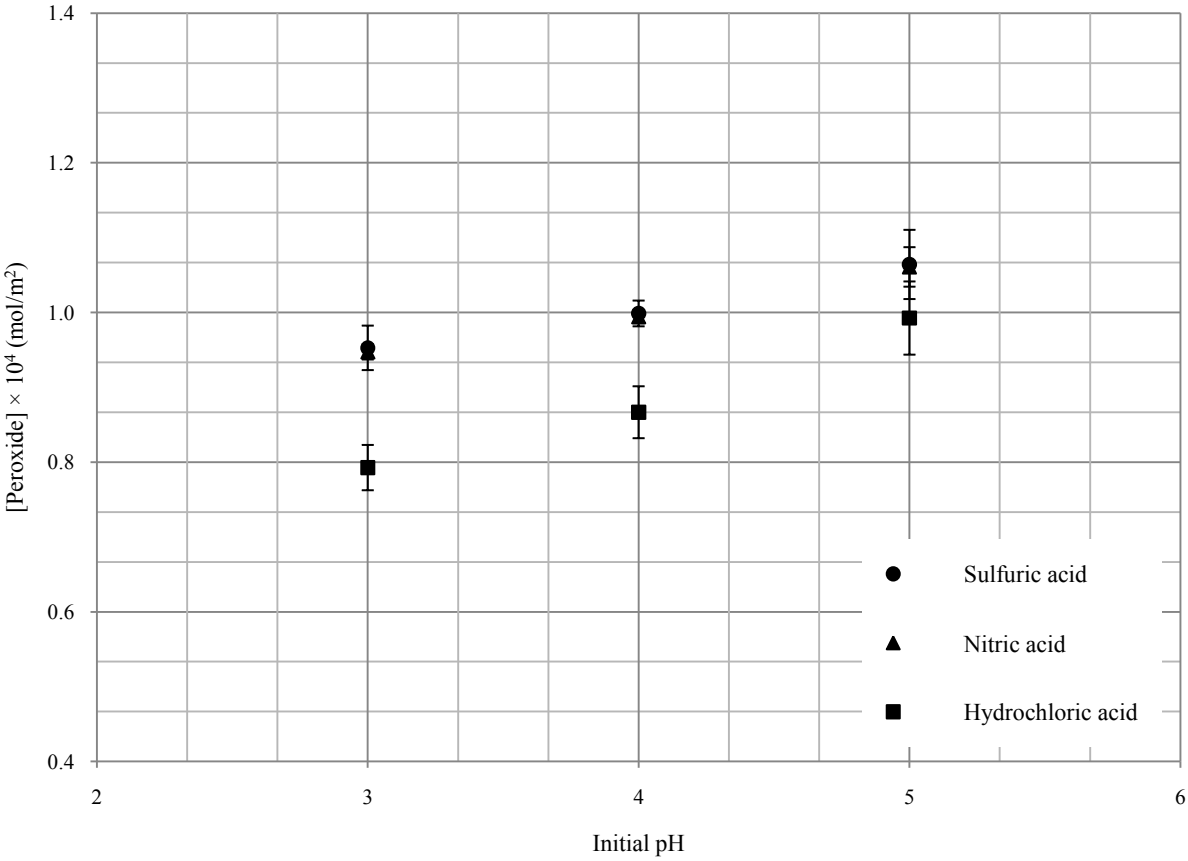

Figure 4-8: Peroxide generated on LDPE+LLDPE film after 60 minutes ozonation with 1.5 wt% applied ozone dose at different initial pH values adjusted by using sulfuric, nitric, or hydrochloric acid

Lower peroxide generation observed for runs in the presence of hydrochloric acid can be attributed to the reaction between molecular ozone and chloride ions in the aqueous medium (Levanov et al., 2002). The presence of the chloride ions created a competition between chloride ions and the polymer film for molecular ozone, hence lowering the availability of the molecular ozone to react with polymer film.

4.5.3 Effect of initial pH in the presence of copper (II) sulfate

As previously mentioned, this study focused only on the ozone treatment under acidic pH for catalytic ozonation in order to avoid precipitation of copper (II) sulfate. Several more experiments were conducted in order to see the interaction between pH and catalyst dose, if there is any, in order to maximize the amount of peroxide generated. This set of experiments were done by varying the concentration of copper (II) sulfate at 0 g/L, 0.03 g/L, and 0.05 g/L, which was the optimal catalyst dose found in § 4.3. The initial pH was adjusted by the addition of sulfuric acid. The results obtained from these experiments are shown in Figure 4-9.

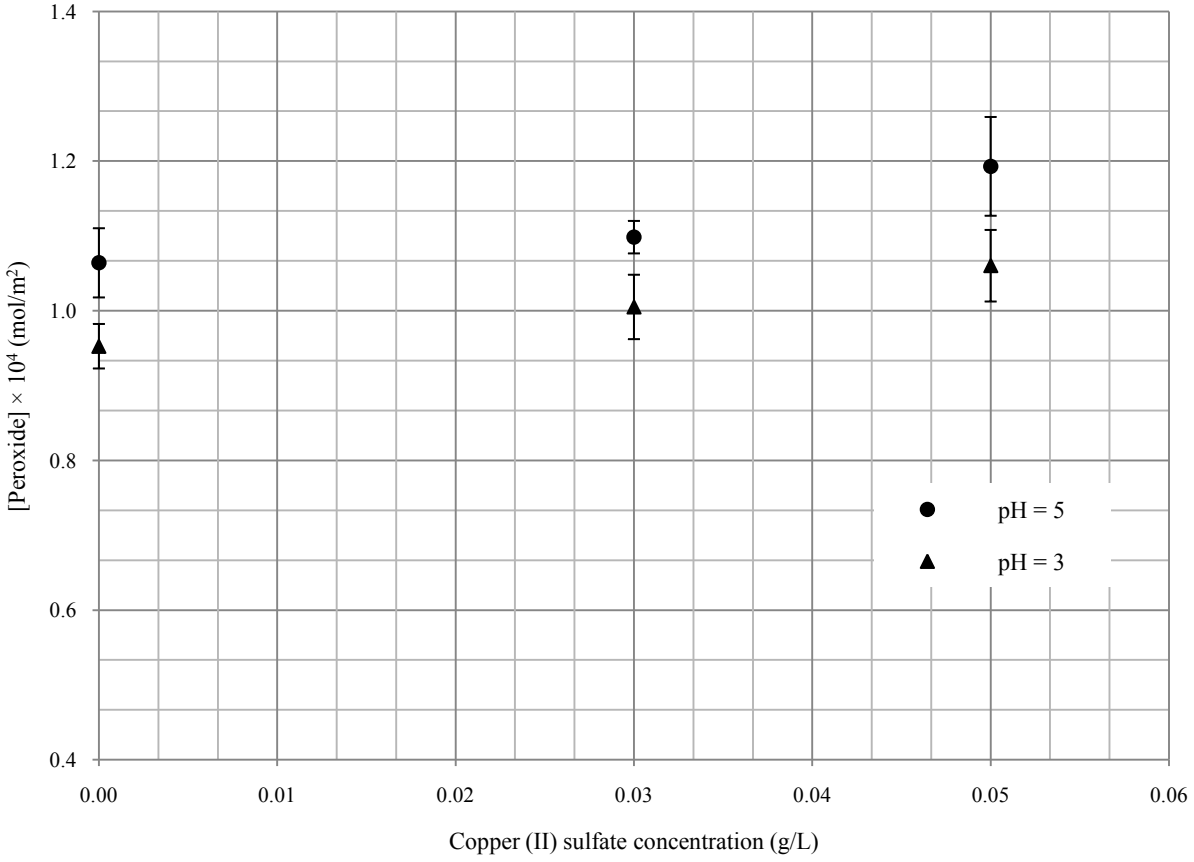

Figure 4-9: Peroxide generated on LDPE+LLDPE film after 60 minutes ozonation with 1.5 wt% applied ozone dose at initial pH of 3 and 5 adjusted by using sulfuric acid in the presence of various copper (II) sulfate concentration

The peroxide generated at pH 5 was always higher than that obtained at pH 3 regardless of the copper (II) sulfate dose used in the experiment. Based on the observation of Figure 4-9, it can

be suggested that there is no interaction between the effect of initial pH and the effect of copper salt concentration on the peroxide generation.

Consequently, based on the results obtained in this section, it was found that maximum amount of peroxide was generated at pH 5.60 for aqueous ozonation. In order to avoid precipitation of copper (II) sulfate, ozonation could not be conducted above pH 6; hence, it was decided not to adjust the pH of solution for the subsequent parts of this study.

§ 4.6 Effect of ozonation time in catalytic ozonation

Ozonation runs were conducted at various lengths of reaction time with 1.5 wt% ozone dose and the optimal catalyst dose. The experimental data for these runs are tabulated in Appendix H. In this section, the effect of ozonation time on peroxide concentration, tensile strength, contact angle, and SEM images of the polymer films are presented.

4.6.1 Peroxide concentration

For comparison purposes, another set of experiments were conducted in gaseous phase at different ozonation time with 1.5 wt% applied ozone dose. The peroxide concentration from these experimental runs were plotted on the same graph as the results obtained from catalytic ozonation runs, as illustrated in Figure 4-10. The raw experimental data for gaseous ozonation runs were tabulated in Appendix I.

It was found from Figure 4-10 that the amount of peroxide generated increased exponentially with increasing time. Initially, the peroxide generated on polymer films by ozone treatment increased rapidly, but the generation rate decreased over time. This trend was observed for ozone treatment conducted in both gaseous phase and in aqueous phase with catalyst. This finding agrees with experimental results obtained by other researchers for different types of polymer films, where the peroxide generated on the polymer surface reached a plateau after certain ozonation time (Ko et al., 2001; Xu et al., 2003; Tesema et al., 2004; Lin et al., 2005; Zhou et al., 2005; Shan et al., 2006).

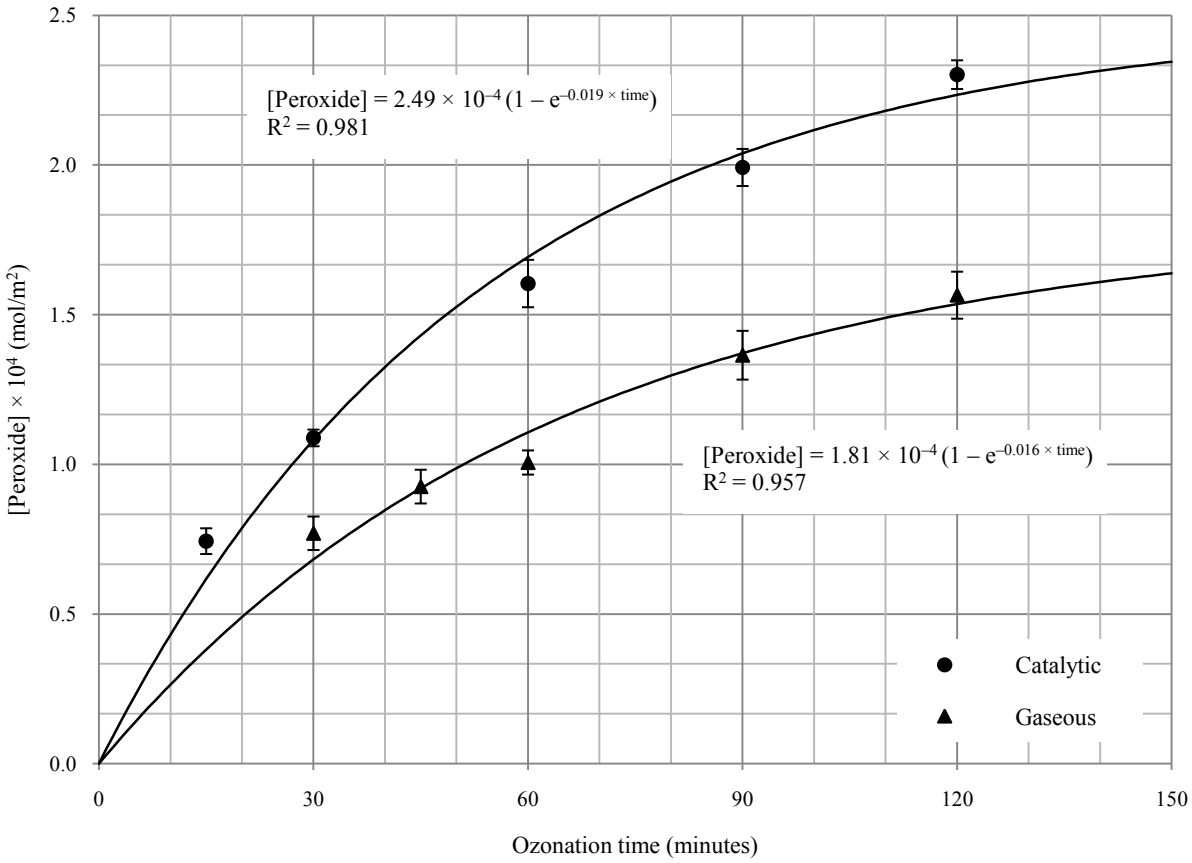

Figure 4-10: Peroxide generated on LDPE+LLDPE film after various ozonation time for catalytic ozonation with 1.5 wt% applied ozone dose and 0.05 g/L copper (II) sulfate, and for gaseous ozonation with 1.5 wt% applied ozone dose

The experimental results shown in Figure 4-10 for catalytic and gaseous ozonation were fitted to the same type of function, namely exponential rise to a maximum value, via SigmaPlot. The regressions show RMS values of 0.078×10^{-4} and 0.061×10^{-4} mol/m^2 for catalytic and gaseous ozonation, respectively.

4.6.2 Proposed reaction mechanism

Prior to proposing reaction mechanism for the aqueous ozonation, the reaction steps involved in the gaseous ozonation were assumed to be the same as that proposed by Kefeli et al. (1971). In that study, the reaction mechanism was used to express the concentration of peroxide generated with respect to time. The reaction steps from that study was illustrated by Figure 2-8, and also written as shown by Reactions (2-1) to (2-5). The experimental data obtained in this study for

gaseous ozonation confirmed the exponential function obtained from this reaction mechanism, shown by Equation (2-6) and Figure 4-10.

Reaction mechanism, as shown in Figure 4-11, for aqueous ozonation of polyethylene was proposed in this study by combining the SHB mechanism for decomposition of ozone in water and for gaseous ozonation of polyethylene found in the literature (Gottschalk et al., 2000; Staehelin & Hoigné, 1985; Kefeli et al., 1971). Additionally, the role of hydroxyl radical in oxidation of polyethylene was taken from the pulse radiolysis study done by Billamboz and colleagues (2010).

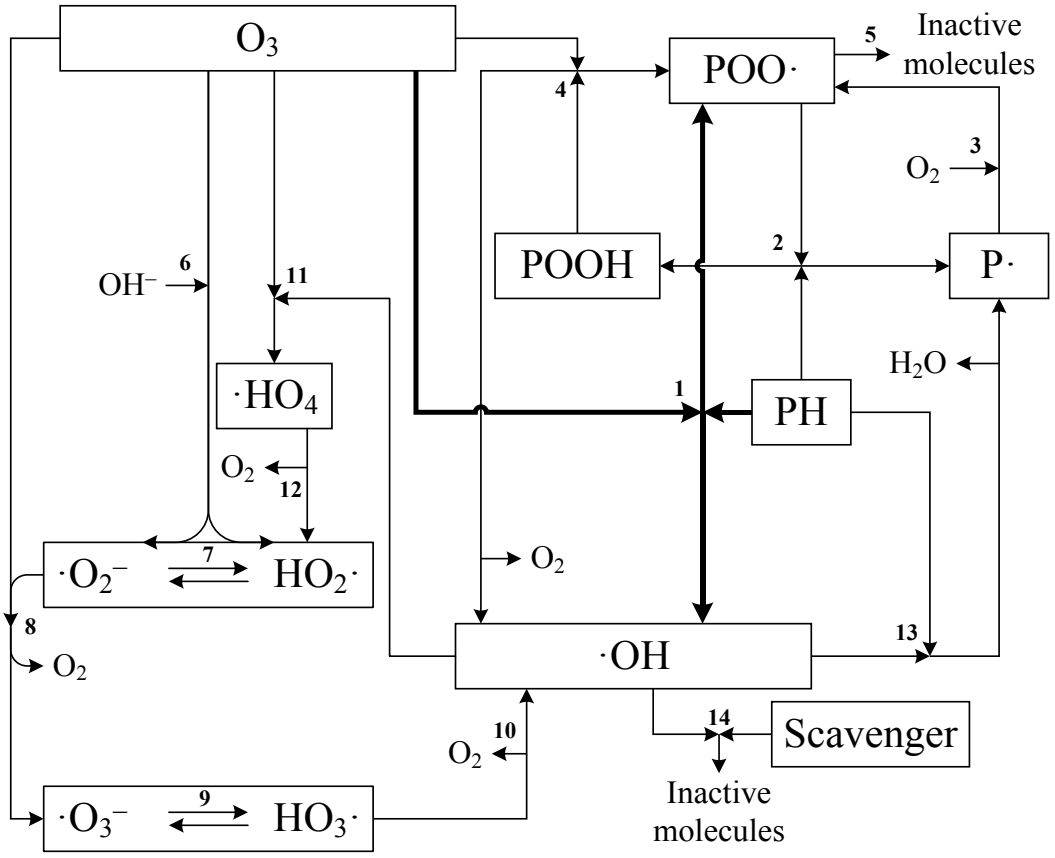

Figure 4-11: Proposed reaction mechanism for aqueous ozonation of polyethylene

The reaction numbers shown in Figure 4-11 correspond to the subscripts of the reaction rate constants, k. The initiation step by direct oxidation, propagation steps and termination step were taken from Reactions (2-1) to (2-5) shown for gaseous ozonation. It is known that the presence of catalyst only changes the value of reaction rate constants without affecting the order

of reaction (Kotz et al., 2009); therefore, reaction steps for peroxide generation would be the same for aqueous ozonation with or without the addition of catalyst. The decomposition steps of ozone are represented by Reactions (4-1) to (4-7), while the reaction steps involving hydroxyl radical are shown by Reactions (4-8) to (4-9).

Ozone decomposition:

$$O_3 + OH^- \xrightarrow{k_6} \cdot O_2^- + HO_2\cdot \quad (4\text{-}1)$$

$$\cdot O_2^- + H^+ \xleftrightarrow{K_7} HO_2\cdot \quad (4\text{-}2)$$

$$O_3 + \cdot O_2^- \xrightarrow{k_8} \cdot O_3^- + O_2 \quad (4\text{-}3)$$

$$\cdot O_3^- + H^+ \xleftrightarrow{K_9} HO_3\cdot \quad (4\text{-}4)$$

$$HO_3\cdot \xrightarrow{k_{10}} \cdot OH + O_2 \quad (4\text{-}5)$$

$$O_3 + \cdot OH \xrightarrow{k_{11}} HO_4\cdot \quad (4\text{-}6)$$

$$HO_4\cdot \xrightarrow{k_{12}} O_2 + HO_2\cdot \quad (4\text{-}7)$$

Indirect oxidation:

$$\cdot OH + PH \xrightarrow{k_{13}} H_2O + P\cdot \quad (4\text{-}8)$$

$$\cdot OH + \text{Scavenger} \xrightarrow{k_{14}} \text{Inactive} \quad (4\text{-}9)$$

In addition to the assumptions listed for gaseous ozonation, the following assumptions were made for aqueous ozonation in this study:

- Reactions (4-1) to (4-9) can be considered as elementary reactions
- Pseudo-steady state hypothesis (Fogler, 2006) is applicable for $POO\cdot$, $P\cdot$, and for $\cdot OH$

  Therefore: $r_{POO\cdot} = 0$, $r_{P\cdot} = 0$ and $r_{\cdot OH} = 0$
- Constant dissolved ozone concentration and scavenger concentration

  Assuming scavenger is present in an excess amount, the change in scavenger concentration can be neglected. Therefore: $\frac{d[O_3]}{dt} = 0$ and $\frac{d[S]}{dt} = 0$
- The reaction between peroxide group and hydroxyl radical is negligible

  Because the main role of hydroxyl radical is to abstract hydrogen from alkyl group (Billamboz, 2010)

- The reaction between alkyl radical and hydroxyl radical is negligible

  Which is evidenced by Figure 4-5, where no change in FTIR spectra could be observed between untreated and treated film for wavenumber 3200 cm^{-1} to 3700 cm^{-1}. This implies the alcohol group formed after ozonation is negligible

- The decomposition of ozone is of first-order with respect to ozone (Staehelin & Hoigné, 1985; Gottschalk et al., 2000; Beltrán, 2004).

  Consumption rate of ozone from decomposition reaction = $k_d\,[O_3]$

- Two moles of hydroxyl radical are formed from the decomposition of three moles of ozone (Gottschalk et al., 2000)

  Production rate of hydroxyl radical from ozone decomposition = $\frac{2}{3}k_d\,[O_3]$

The expression for ozone concentration, $[O_3]$, in the reaction rate laws of aqueous ozonation system represents the dissolved ozone concentration, not the ozone concentration in gas phase, as is the case for gaseous ozonation. The expression for peroxide concentration generated in aqueous ozonation was obtained from these assumptions in a similar manner as previously done for gaseous ozonation.

For alkyl radical, $r_{P\cdot} = 0$:

$$k_3[O_2][P\cdot] = k_{13}[\cdot OH][PH] + k_2[PH][POO\cdot] \tag{4-10}$$

For peroxy radical, $r_{POO\cdot} = 0$:

$$k_2[PH][POO\cdot] + k_5[POO\cdot] = k_1[O_3][PH] + k_3[O_2][P\cdot] + k_4[O_3][POOH] \tag{4-11}$$

For hydroxyl radical, $r_{\cdot OH} = 0$:

$$k_{13}[\cdot OH][PH] + k_{14}[\cdot OH][S] = \frac{2}{3}k_d[O_3] + k_1[O_3][PH] + k_4[O_3][POOH] \tag{4-12}$$

Combining Equations (4-10), (4-11), and (4-12):

$$[POO\cdot] = \frac{[O_3]}{k_5}\left\{k_1[PH] + k_4[POOH] + \frac{k_{13}[PH]}{k_{13}[PH] + k_{14}[S]}\left(\frac{2}{3}k_d + k_1[PH] + k_4[POOH]\right)\right\} \tag{4-13}$$

Rate of generation of peroxide groups:

$$\frac{d[POOH]}{dt} = k_2[POO\cdot][PH] - k_4[O_3][POOH] \tag{4-14}$$

Substituting Equation (4-13) into (4-14) and rearranging:

$$\frac{d[POOH]}{dt} = [O_3]\left\{\frac{k_2[PH]^2}{k_5}\left(k_1 + \frac{k_{13}}{k_{13}[PH] + k_{14}[S]}\left(\frac{2}{3}k_d + k_1[PH]\right)\right) - k_4[POOH]\left(1 - \frac{k_2[PH]}{k_5}\left(1 + \frac{k_{13}[PH]}{k_{13}[PH] + k_{14}[S]}\right)\right)\right\} \tag{4-15}$$

Integration of Equation (4-15) with zero initial value for [POOH] gives:

$$[POOH] = \frac{k_2[PH]^2[O_3]}{\beta_0 k_5}\left\{k_1 + \frac{k_{13}}{k_{13}[PH] + k_{14}[S]}\left(\frac{2}{3}k_d + k_1[PH]\right)\right\}(1 - e^{-\beta_0 t}) \tag{4-16}$$

$$\text{where:} \quad \beta_0 = k_4[O_3]\left\{1 - \frac{k_2[PH]}{k_5}\left(1 + \frac{k_{13}[PH]}{k_{13}[PH] + k_{14}[S]}\right)\right\}$$

Additional assumptions were made in an attempt to further simplify the expression for peroxide concentration shown in Equation (4-16).

CASE I: Presence of scavenger is negligible, [S] = 0

By assuming negligible concentration of scavenger is present in the system, Reaction (4-9) was no longer considered in the reaction mechanism. The final expression for peroxide groups would then be simplified as shown by Equation (4-17).

$$[POOH] = \frac{k_2[PH][O_3]}{\beta_1 k_5}\left\{2k_1[PH] + \frac{2}{3}k_d\right\}(1 - e^{-\beta_1 t}) \tag{4-17}$$

$$\text{where:} \quad \beta_1 = k_4[O_3]\left\{1 - \frac{2k_2[PH]}{k_5}\right\}$$

By comparing Equations (4-16) and (4-17), the absence of scavenger would yield higher peroxide concentration for runs under the same operating conditions. This is due to the higher available hydroxyl radical concentration to abstract hydrogen from alkyl group, as studied by Billamboz et al. (2010).

The ozonation runs conducted for various ozonation time in this section did not involve addition of any radical scavengers. Therefore, the experimental data for catalytic ozonation shown in Figure 4-10 were fitted into Equation (4-17). By comparing Equation (2-6) and Equation (4-17), it can be seen that regardless of the ozonation media, the concentration of peroxide generated follows the same trend with respect to the treatment time. The curve-fitting done for aqueous ozonation, shown in Figure 4-10, displays the experimental data confirmed the exponential function obtained for the peroxide concentration based on the proposed reaction mechanism.

Due to the similar trend in peroxide generated for aqueous and gaseous ozonation, the contribution of indirect oxidation in aqueous ozonation could not be observed from this comparison. The difference observed in the peroxide concentration after catalytic and gaseous ozonation could be due to the difference in the available ozone concentration and the presence of copper (II) sulfate. As previously mentioned, the available ozone concentration in the reaction rate laws of aqueous ozonation represents the dissolved ozone concentration, not the ozone concentration in gas phase, as is the case for gaseous ozonation.

CASE II: Hydroxyl radical formations from Reactions (2-1) and (2-4) are negligible

As is the case for gaseous ozonation, the hydroxyl radical formed by Reactions (2-1) and (2-4) are assumed to be negligible to initiate indirect oxidation. Applying the same assumption for aqueous ozonation, it can be said that the formation of hydroxyl radical from Reaction (2-1) and (2-4) are negligible when compared to that from ozone decomposition reactions. The final expression for peroxide concentration would then simplified to be Equation (4-18).

$$[POOH] = \frac{k_2[PH]^2[O_3]}{\beta_2 k_5}\left\{k_1 + \frac{2}{3}\left(\frac{k_{13}k_d}{k_{13}[PH] + k_{14}[S]}\right)\right\}(1 - e^{-\beta_2 t}) \qquad (4\text{-}18)$$

$$\text{where} \qquad \beta_2 = k_4[O_3]\left\{1 - \frac{k_2[PH]}{k_5}\right\}$$

The assumption made for this case would result in a lower calculated peroxide concentration due to lower hydroxyl radical concentration.

CASE III: Both the presence of scavenger, involved in Reaction (4-9), and the hydroxyl radical formations from Reactions (2-1) and (2-4) are negligible

By utilizing both assumptions in case I and II, the final expression for peroxide concentration would then simplified to be Equation (4-19).

$$[POOH] = \frac{k_2[PH]}{\beta_3 k_5}\left\{k_1[PH] + \frac{2}{3}k_d\right\}(1 - e^{-\beta_3 t}) \qquad (4\text{-}19)$$

$$\text{where:} \quad \beta_3 = k_4[O_3]\left\{1 - \frac{k_2[PH]}{k_5}\right\}$$

Equation (2-6) and Equation (4-19) could be compared as expressions of peroxide concentration generated in gaseous and aqueous ozonation, respectively. It would be tempting to conclude that no change could be observed in the expression for time constants, $1/\alpha$ and $1/\beta_3$, for gaseous and aqueous ozonation, respectively. However, careful observation must be done in comparing the two equations, since the values of reaction rate constants in aqueous and gaseous phase are not known to be equal. Moreover, the concentration of ozone used for Equation (2-6) represents the ozone dose in gaseous phase; while in Equation (4-19), it represents the dissolved ozone concentration.

In an attempt to explain the catalyzing role of copper in the peroxide generation, the reaction mechanism proposed by Bhaduri & Mukesh (2000) were used in this study. As previously mentioned, the addition of transition metal salts could catalyze the decomposition of organic peroxide according to the mechanism shown by Reactions (2-7) to (2-13). By using copper (II) sulfate as the catalyst, Reactions (2-8) and (2-9) were rewritten as Reactions (4-20) and (4-21), respectively. The formation of $RO\cdot$ in Reaction (2-7) was neglected because it would only react to form alcohol group, which was shown to be negligible by the lack of peak in the FTIR spectra at wavenumber of 3200 cm^{-1} to 3700 cm^{-1}, as shown in Figure 4-5 for this study.

$$POOH + Cu^{2+} \longrightarrow POO\cdot + H^+ + Cu^+ \qquad (4\text{-}20)$$

$$PH + Cu^{2+} \longrightarrow P\cdot + H^+ + Cu^+ \qquad (4\text{-}21)$$

Due to the lack of experimental data available in the literature for oxidation of copper ions by molecular ozone, the oxidation pathways of iron were assumed to be applicable for copper in this

study. Hart proposed reaction mechanism for the oxidation of iron (II) to iron (III) by ozone (Legube & Leitner, 1999). Reactions (4-22) and (4-23) were written for the oxidation of copper.

$$O_3 + Cu^+ \longrightarrow \cdot O_3^- + Cu^{2+} \quad (4\text{-}22)$$

$$\cdot OH + Cu^+ \longrightarrow OH^- + Cu^{2+} \quad (4\text{-}23)$$

Two of the steps in ozone decomposition mechanism, Reactions (4-4) and (4-5), could be combined with the Reactions (4-20) and (4-22) as shown below.

$$\begin{aligned} POOH + Cu^{2+} &\longrightarrow POO\cdot + H^+ + Cu^+ \\ O_3 + Cu^+ &\longrightarrow \cdot O_3^- + Cu^{2+} \\ \cdot O_3^- + H^+ &\longleftrightarrow HO_3\cdot \\ HO_3\cdot &\longrightarrow \cdot OH + O_2 \quad + \\ \hline O_3 + POOH &\xrightarrow{Cu} O_2 + \cdot OH + POO\cdot \end{aligned}$$

Moreover, Reactions (4-21) and (4-23) could also be combined.

$$\begin{aligned} PH + Cu^{2+} &\longrightarrow P\cdot + H^+ + Cu^+ \\ \cdot OH + Cu^+ &\longrightarrow OH^- + Cu^{2+} \quad + \\ \hline \cdot OH + PH &\xrightarrow{Cu} H_2O + P\cdot \end{aligned}$$

The two overall reactions found by these combinations were the same reactions proposed earlier, namely Reactions (2-4) and (4-8).

4.6.3 Tensile strength

The tensile strength of the polymer film treated by catalytic ozonation for various exposure time were tabulated and plotted, as shown in Appendix H and Figure 4-12, respectively. As previously mentioned, a disadvantage of ozone treatment is that it can potentially affect the bulk structure of polymer by attacking the backbone of the polymer. The change in polymer structure would cause changes in the mechanical properties of polymer film, which is undesirable for surface modification purposes. Therefore, the duration of ozonation time that can be conducted depends on the level of tensile strength reduction that is acceptable.

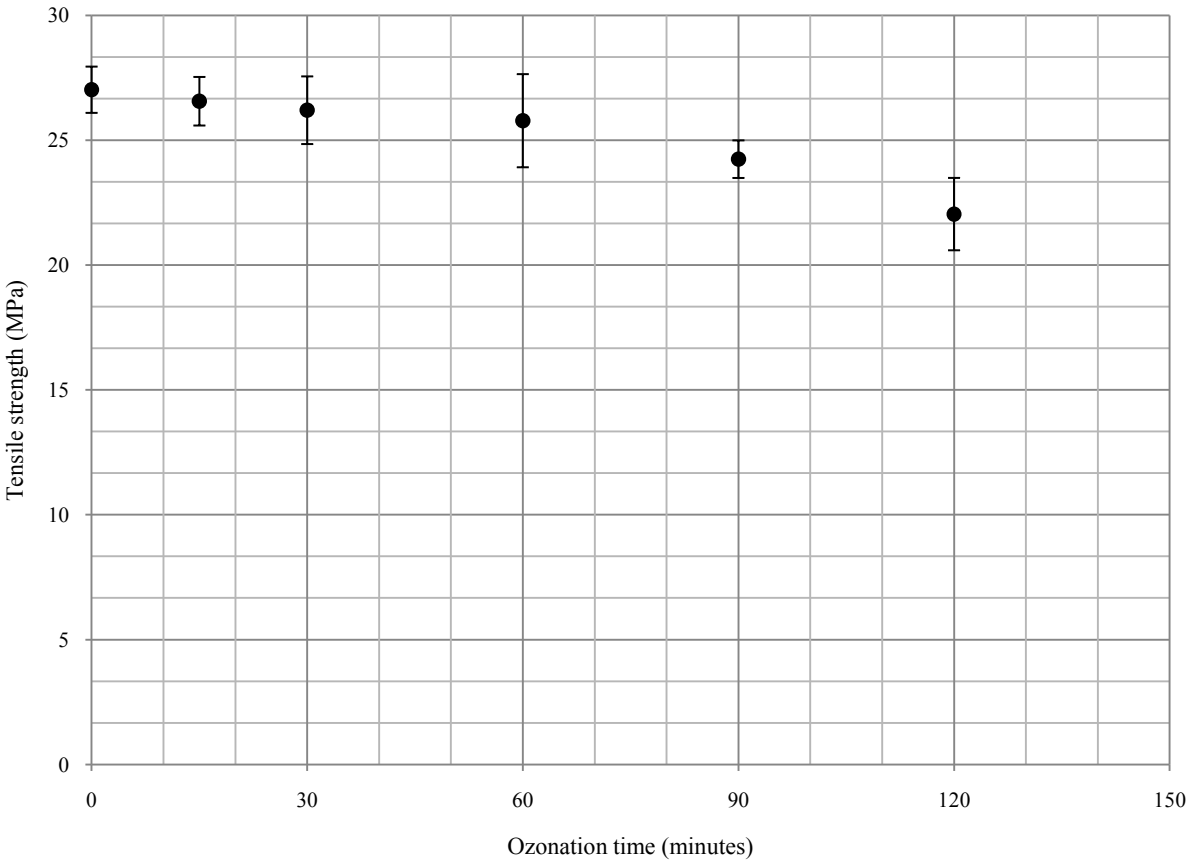

Figure 4-12: Tensile strength of LDPE+LLDPE film after various ozonation time for runs with 1.5 wt% applied ozone dose and 0.05 g/L copper (II) sulfate

The tensile strength of polymer films decreased from 27 MPa for untreated polyethylene film to approximately 22 MPa after 120 minutes of catalytic ozonation. This translates to an approximately 19% reduction in tensile strength. Patel (2008) presented similar finding as this study for the tensile strength measurement of LDPE+LLDPE film after catalytic ozonation with iron (III) chloride as the catalyst. From that study, a 15% reduction in the tensile strength was observed after 120 minutes of catalytic ozonation.

4.6.4 Contact angle

The data of water contact angle on the polymer films were also recorded for different ozonation time. The raw experimental data are shown in Appendix H, and illustrated in Figure 4-13. As have been mentioned, the water contact angle of a material is an indication of its hydrophilicity.

The polymer film used in this study, LDPE+LLDPE film, is highly hydrophobic, as shown by the high water contact angle that it exhibits. The untreated LDPE+LLDPE film was measured to have slightly more than 90° of contact angle with ultra-pure water. After 120 minutes of ozone treatment, the water contact angle for this polymer film decreased to approximately 78°, as shown in Figure 4-13. The decrease in water contact angle after ozone treatment could be attributed to the presence of polar functional groups formed, such as carboxylic and ketone groups.

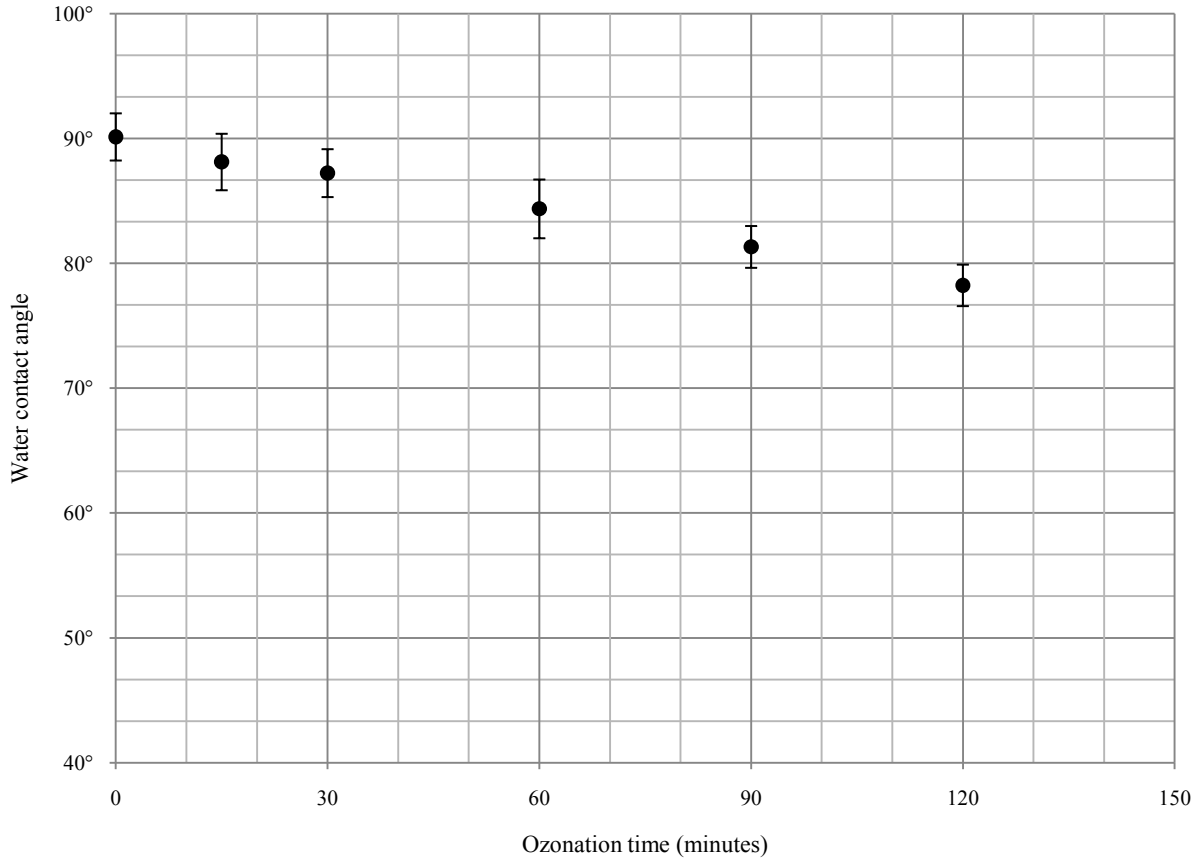

Figure 4-13: Water contact angle of LDPE+LLDPE film after various ozonation time for runs with 1.5 wt% applied ozone dose and 0.05 g/L copper (II) sulfate

The water contact angle slightly decreased after ozonation, but the value of this contact angle is still not showing the desirable hydrophilicity. For comparison purposes, the contact angle of polyethylene with ultra-pure water after ozonation followed by graft polymerization of hydrophilic monomer would fall below 40° (Gu, 2008). Change in hydrophilicity after ozone

treatment was not necessary, because as previously mentioned ozonation was conducted as pre-treatment to produce peroxides for graft polymerization.

4.6.5 Surface morphology

The change in surface morphology of the films after different treatment time is shown in Figure 4-14. This figure reveals 5000 times magnification of untreated LDPE+LLDPE film surface and the treated LDPE+LLDPE film surface for different treatment times, which were 15 and 90 minutes of catalytic ozonation.

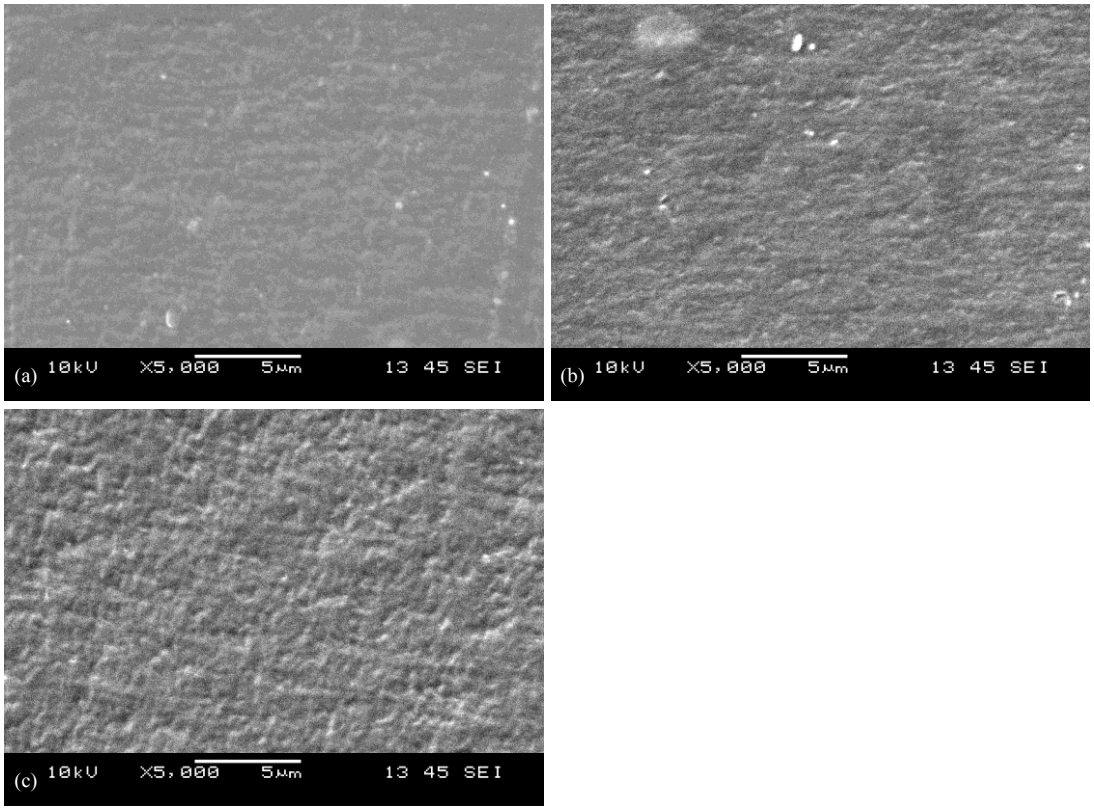

Figure 4-14: SEM images of LDPE+LLDPE film (a) before ozonation, (b) after 15 minutes of ozonation, (c) after 90 minutes of ozonation with 1.5 wt% applied ozone dose and 0.05 g/L copper (II) sulfate

By comparing these images, it can be qualitatively observed that the surface roughness of LDPE+LLDPE film increased with increasing ozone treatment time. This was due to the oxidation of LDPE+LLDPE films by ozonation, which led to the breaking down of polymer molecules.

§ 4.7 Effect of ozone concentration in catalytic ozonation

Several ozonation runs were conducted for 60 minutes with copper (II) sulfate at its optimal concentration and various ozone doses ranging from 1.0 – 3.0 weight percentage at 0.5 wt% interval. The experimental data were tabulated and can be found in Appendix J, while the calculated peroxide concentrations were plotted and shown in Figure 4-15. The value of ozone concentration used as the x-axis in Figure 4-15 is the applied ozone dose.

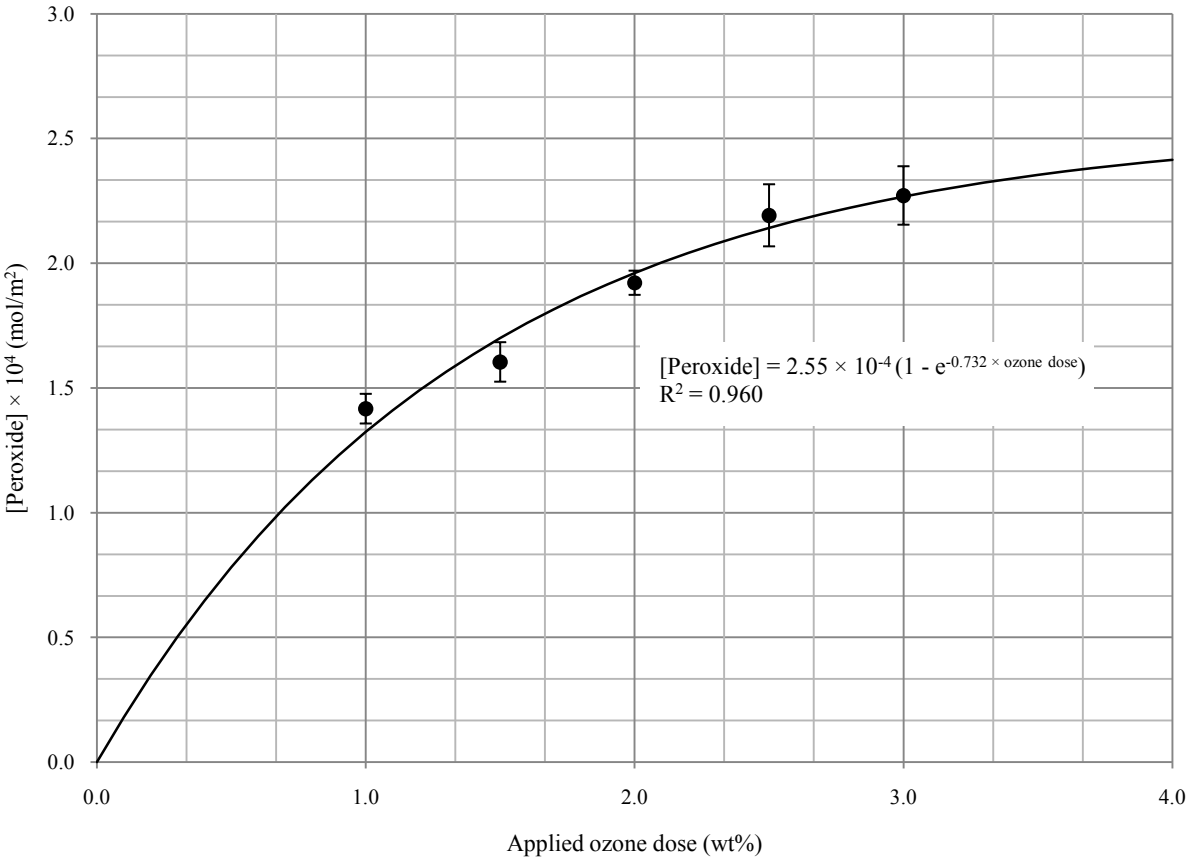

Figure 4-15: Peroxide generated on LDPE+LLDPE film after 60 minutes ozonation with various applied ozone doses and 0.05 g/L copper (II) sulfate

The results obtained in this section were fitted into the same type of equation obtained from the proposed reaction mechanism of catalytic ozonation, Equation (4-16). The dissolved ozone concentration was assumed to be linearly proportional to the applied ozone dose. Therefore, Equation (4-16) was re-written as Equation (4-24) for constant ozonation time and various applied ozone dose. The RMS value from this regression was calculated to be 0.066×10^{-4} mol/m^2.

$$[POOH] = \frac{k_2[PH]^2 \left\{ k_1 + \frac{k_{13}}{k_{13}[PH] + k_{14}[S]} \left(\frac{2}{3} k_d + k_1[PH] \right) \right\}}{k_4 k_5 \left\{ 1 - \frac{k_2[PH]}{k_5} \left(1 + \frac{k_{13}[PH]}{k_{13}[PH] + k_{14}[S]} \right) \right\}} (1 - e^{-\gamma C_{O_3}}) \qquad (4\text{-}24)$$

$$\text{where:} \quad \gamma = k_4 \lambda \left\{ 1 - \frac{k_2[PH]}{k_5} \left(1 + \frac{k_{13}[PH]}{k_{13}[PH] + k_{14}[S]} \right) \right\} t$$

In Equation (4-24), the applied ozone dose is denoted as C_{O_3}, while λ denotes the proportionality constant between applied ozone dose and the dissolved ozone concentration.

5 CONCLUSIONS

Ozonation of LDPE+LLDPE film was conducted in both gaseous and aqueous phases. Although the peroxide concentration generated by aqueous ozonation was found to be slightly lower than that obtained by gaseous ozonation, the aqueous ozonation enables addition of transition metal salts to act as catalyst. The catalyst chosen for this study was copper (II) sulfate. An 18% increase in peroxide concentration was obtained after catalytic ozonation when compared to what was observed after gaseous ozonation. There exists an optimum copper (II) sulfate dose, at 0.05 g/L, after which, increasing the concentration of the catalyst further did not result in a higher peroxide generation.

An optimum pH value for aqueous ozonation was found to be approximately 5.60. Subsequent catalytic ozonation runs were conducted at this optimum pH.

Radical scavenger, tert-butyl alcohol (TBA), was added in catalytic ozonation to investigate the contribution of hydroxyl radical in the formation of peroxide. A 12% decrease in peroxide concentration was observed in the presence of 0.1 mol/L of TBA, confirming the contribution of indirect ozonation.

The tensile strength of LDPE+LLDPE film was found to decrease slowly with prolonged ozonation time. If 19% reduction in tensile strength is tolerable, then 120 minutes of catalytic ozonation may be conducted for this polymer, producing a peroxide concentration of $(2.30 \pm 0.05) \times 10^{-4}$ mol/m^2.

The contact angle was found to decrease slightly after ozonation. This decrease may be due to the formation of various polar groups.

By combining the SHB mechanism for ozone decomposition in water and the mechanism of gaseous ozonation of polyethylene, a reaction mechanism for aqueous ozonation of polyethylene was proposed in this study. The experimental results obtained in this study for various ozonation time, ranging from 15 – 120 minutes, and applied ozone dose, ranging from 1.0 – 3.0 wt%, confirmed the exponential function for peroxide concentration obtained from the proposed reaction mechanism for catalytic ozonation.

6 RECOMMENDATIONS

Aqueous ozonation has a good potential to be used as a surface modification method for polymer films. There are many different subjects that have yet to be investigated in this field, for example the reaction mechanism and the effect of various operating parameters may be further studied. Some of the assumptions made in this study for the reaction mechanism may be eliminated by using experimental data. The knowledge of reaction mechanism would be very beneficial in determining the optimum operating conditions for catalytic ozonation in order to maximize the production of peroxide groups.

Parameter estimations can be used in order to obtain the magnitude of reaction rate constants involved. Sensitivity analyses of the peroxide concentration with respect to the temperature, polymer area, ozone concentration, ozonation time, etc. are also interesting to be investigated.

A comparison between the extent of grafting on the polymer treated by ozonation in different phases also needs to be done. This comparison could be conducted to ensure the catalyst addition does not have any detrimental effects on the grafting process. The application of catalytic ozonation of different types of polymer films may also shed lights on the reaction mechanism. This can be done in order to find which reaction is catalyzed by the addition of these transition metal salts. Other salts of iron (III), except for iron (III) chloride, can be tested for catalytic ozonation of polyethylene. The experimental result obtained for ozonation in the presence of iron (III) chloride in this study may be negatively affected by the reaction between chloride ions and ozone.

Other analytical methods can be used to further characterize the change in properties of ozonated polymer film. AFM method could be employed to conduct the roughness analysis. In order to determine the thickness of oxidized layer of ozonated film, XPS spectra with different electron take-off angles can be analyzed. This would allow the generation of a depth profile of the surface region of the ozonated film.

Another operating parameter that would be an interesting area of study is the temperature of the aqueous system. The change in temperature would affect both the reaction and the mass transfer rate of this oxidation system. The effect of different types of scavengers with various concentrations is also another insightful area of study, where the reaction rate constants between these scavengers and hydroxyl radical may be determined.

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APPENDIX A PEROXIDE DETERMINATION BY STANDARD IODOMETRIC METHOD

As mentioned in the Experimental section of this report, this titration method can be divided into the standardization of sodium thiosulfate solution and the iodometric titration for peroxide determination. The two reactions involved in the standardization procedure are:

$$K_2Cr_2O_7 + 6\,KI + 7\,H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 4\,K_2SO_4 + 7\,H_2O + 3\,I_2$$

$$2\,Na_2S_2O_3 + I_2 \rightarrow 2\,NaI + Na_2S_4O_6$$

On the other hand, the reaction between peroxide groups, liberated in acidic medium under heat, with the iodide ions present in the solution during iodometric titration is shown below:

$$O_2^{2-} + 2\,I^- + 2\,H^+ \rightarrow I_2 + 2\,H_2O$$

Similar to the standardization procedure, the iodine generated from this reaction would be determined by titration using sodium thiosulfate solution according to the following reaction:

$$2\,Na_2S_2O_3 + I_2 \rightarrow 2\,NaI + Na_2S_4O_6$$

§ A.1 Preparation and standardization of solutions

In order to prepare solutions of 0.1 N sodium thiosulfate and 0.1 N potassium dichromate, first the stoichiometric ratio between the two substances must be determined in order to obtain the relation between molarity and normality. Based on the reactions shown above for standardization procedure, a molar stoichiometric ratio of 1:6 can be observed between potassium dichromate, $K_2Cr_2O_7$, and sodium thiosulfate, $Na_2S_2O_3$. Therefore, the following relations can be established between the molarity and normality of each substance:

$$N_{Na_2S_2O_3} = M_{Na_2S_2O_3} \qquad N_{K_2Cr_2O_7} = 6 \times M_{K_2Cr_2O_7}$$

From this information, the amount of sodium thiosulfate pentahydrate, $Na_2S_2O_3 \cdot 5H_2O$, necessary to prepare 1.0 L solution of 0.1 N sodium thiosulfate, $Na_2S_2O_3$, was determined as follow:

$$W_{Na_2S_2O_3 \cdot 5H_2O} = M_{Na_2S_2O_3} \times MW_{Na_2S_2O_3 \cdot 5H_2O} = N_{Na_2S_2O_3} \times MW_{Na_2S_2O_3 \cdot 5H_2O}$$

$$W_{Na_2S_2O_3 \cdot 5H_2O} = 0.100\ N \times 248.19\ g/mol = \mathbf{24.82\ g}$$

This solution was further diluted to reach concentration of 0.001 N, to accurately titrate small concentration of peroxide in the iodometric titration part. The diluted solution of sodium thiosulfate was stored in dark bottle to mitigate the fast decomposition associated with this solution. Similarly, calculation for the potassium dichromate needed to prepare a 1.0 L solution with normality of 0.1 N is shown below:

$$W_{K_2Cr_2O_7} = M_{K_2Cr_2O_7} \times MW_{K_2Cr_2O_7} = \frac{N_{K_2Cr_2O_7}}{6} \times MW_{K_2Cr_2O_7}$$

$$W_{K_2Cr_2O_7} = \frac{0.100\ N}{6} \times 294.18\ g/mol = \mathbf{4.903\ g}$$

It is a common practice to standardize the sodium thiosulfate solution using potassium dichromate solution of the same normality; therefore, this solution was diluted further to 0.001 N. This is done in order to maintain the accuracy of the standardization procedure. Volume of sodium thiosulfate consumed to titrate all the iodine liberated by potassium dichoromate was used to calculate the standardized normality of sodium thiosulfate. Sample calculation to obtain the standardized normality of sodium thiosulfate solution is shown in § B.2.

$$N_{Na_2S_2O_3} \times V_{Na_2S_2O_3} = N_{K_2Cr_2O_7} \times V_{K_2Cr_2O_7}$$

§ A.2 Peroxide determination

From the reaction above, a molar ratio of 1:2 was observed for iodine to sodium thiosulfate, while iodine and peroxide have a molar ratio of 1:1. The number of moles of iodine liberated would be calculated as follow:

$$n_{I_2} = \frac{N_{Na_2S_2O_3} \times V_{Na_2S_2O_3}}{2}$$

Hence, the concentration of peroxide groups can be calculated as follow:

$$[\text{Peroxide}] = \frac{n_{\text{Peroxide}}}{\text{Area of films}} = \frac{n_{I_2}}{\text{Area of films}}$$

APPENDIX B SAMPLE CALCULATIONS

Operating conditions:

Ozonation phase: aqueous

Ozonation time: 60 minutes

Ozone dose: 1.500 ± 0.020 wt%

Catalyst dose: 0.05 g/L copper sulfate

Experimental results for the first run:

Volume of $Na_2S_2O_3$ solution used for titration (average of 2 trials): 16.85 mL

Volume of $Na_2S_2O_3$ solution used for standardization: 12.40 mL

Experimental results for the second run:

Volume of $Na_2S_2O_3$ solution used for titration (average of 2 trials): 15.50 mL

Volume of $Na_2S_2O_3$ solution used for standardization: 11.85 mL

Experimental results for the third run:

Volume of $Na_2S_2O_3$ solution used for titration (average of 2 trials): 14.70 mL

Volume of $Na_2S_2O_3$ solution used for standardization: 11.00 mL

Load at break for tensile strength measurement (average of 5 readings): 13.15 N

§ B.1 Weight of transition metal salt needed

The concentration of copper sulfate pentahydrate, $CuSO_4 \cdot 5H_2O$, required for this run was determined by using the chosen concentration of anhydrous copper sulfate, $CuSO_4$:

$$C_{CuSO_4 \cdot 5H_2O} = C_{CuSO_4} \times \frac{MW_{CuSO_4 \cdot 5H_2O}}{MW_{CuSO_4}}$$

$$C_{CuSO_4 \cdot 5H_2O} = 0.05 \text{ g } CuSO_4/\text{L} \times \frac{249.68 \text{ g } CuSO_4 \cdot 5H_2O/\text{mol}}{159.61 \text{ g } CuSO_4/\text{mol}} = 7.82 \times 10^{-2} \text{ g/L}$$

Therefore, the amount of $CuSO_4 \cdot 5H_2O$ needed for run involving 11-L distilled water with copper sulfate dose of 0.05 g/L would be:

$$W_{CuSO_4 \cdot 5H_2O} = C_{CuSO_4 \cdot 5H_2O} \times V$$

$$W_{CuSO_4 \cdot 5H_2O} = \left(7.82 \times 10^{-2} \text{ g/L}\right) \times 11 \text{ L} = \mathbf{0.8604 \text{ g}}$$

§ B.2 Concentration of peroxide generated

Each titration involves the use of two treated polymer films. The dimension of the polymer film used in this study, as mentioned previously, was 4 × 25 cm. All the steps for calculation of peroxide concentration for the first run are shown below.

Area of films = (4 cm × 25 cm)/side × (2 sides/film) × 2 films = 0.04 m^2

As explained in detail in previous sections, normality of sodium thiosulfate was determined from the volume consumed during the standardization procedure:

$$N_{Na_2S_2O_3} = \frac{N_{K_2Cr_2O_7} \times V_{K_2Cr_2O_7}}{V_{Na_2S_2O_3} \text{ for standardization}}$$

$$N_{Na_2S_2O_3} = \frac{10^{-3} \text{ N} \times 10.00 \text{ mL}}{12.40 \text{ mL}} = 8.06 \times 10^{-4} \text{ N}$$

The number of moles of iodine liberated for the first run was calculated:

$$n_{I_2} = \frac{N_{Na_2S_2O_3} \times V_{Na_2S_2O_3}}{2}$$

$$n_{I_2} = \frac{\left(8.06 \times 10^{-4} \text{ N}\right) \times 16.85 \text{ mL}}{2} = 6.79 \times 10^{-6} \text{ mol}$$

Therefore, concentration of peroxides generated during ozonation was calculated as follow, keeping in mind the stoichiometric ratio between peroxide group and iodide ion:

$$[\text{Peroxide}] = \frac{n_{I_2}}{\text{Area of films}} - \text{Blank titration}$$

$$[\text{Peroxide}] = \frac{6.79 \times 10^{-6} \text{ mol}}{0.04 \text{ m}^2} - 0.064 \times 10^{-4} \text{ mol/m}^2 = \mathbf{1.63 \times 10^{-4} \text{ mol/m}^2}$$

The peroxide concentrations of the ozonated polymer film on the second and third run were found to be 1.57 × 10^{-4} and 1.61 × 10^{-4} mol/m^2, respectively.

§ B.3 Tensile strength

The dimension of the sample for each reading is 5 cm × 1 cm × 51 μm. The tensile strength of polymer film could be easily obtained by dividing the load reading when polymer breaks by the

initial cross-sectional area. Due to the consistent sample size used, only one tensile strength calculation was necessary for each operating conditions.

$$\text{Tensile strength} = \frac{\text{Load at break}}{\text{Initial cross-sectional area}}$$

$$\text{Tensile strength} = \frac{13.15\ \text{N}}{1\ \text{cm} \times 51\ \mu\text{m}} = \mathbf{25.8\ MPa}$$

§ B.4 Error bars

The error bars shown in the graphs throughout this thesis represent the 95% confidence interval, calculated by assuming these variables obey t-distribution, for runs with the same operating condition. The standard error of the mean for runs with the same operating condition. The t-distribution was assumed instead of the normal distribution because of the small sample sizes involved in this study. Shown below is the sample calculation for the error bars for concentration of peroxide.

$$\overline{[\text{Peroxide}]} = \frac{\sum [\text{Peroxide}]_i}{N} = \left(\frac{1.63 + 1.57 + 1.61}{3}\right) \times 10^{-4} = 1.60 \times 10^{-4}\ \text{mol/m}^2$$

Based on the definition, standard deviation, SD, was calculated as follow:

$$\text{SD} = \sqrt{\frac{\sum \left([\text{Peroxide}]_i - \overline{[\text{Peroxide}]}\right)^2}{N - 1}}$$

$$\text{SD} = \sqrt{\frac{(1.63 - 1.60)^2 + (1.57 - 1.60)^2 + (1.61 - 1.60)^2}{3 - 1} \times 10^{-8}} = 3.19 \times 10^{-6}\ \text{mol/m}^2$$

Standard error of the mean, SE, was then obtained from the standard deviation:

$$\text{SE} = \frac{\text{SD}}{\sqrt{N}} = \frac{3.19 \times 10^{-6}}{\sqrt{3}} = 1.84 \times 10^{-6}\ \text{mol/m}^2$$

By using t-distribution table, a t-value of 4.303 was obtained for sample size 3 and 95% confidence level. therefore, the confidence interval was calculated as follow:

$$\text{Confidence interval} = 4.303 \times \text{SE}$$

$$\text{Confidence interval} = \mathbf{7.91 \times 10^{-6}\ mol/m^2}$$

Hence, the value of peroxide concentration would be reported as $(1.60 \pm 0.08) \times 10^{-4}$ mol/m^2. Similar calculations were done for the error bars for tensile strength and contact angle measurements. The t-value used for tensile strength and contact angle measurements were 2.776 and 2.571, respectively.

APPENDIX C BLANK TITRATION AND INCIPIENT BOILING TIME

The raw experimental data obtained from runs in the preliminary stages, namely blank titration and incipient boiling time test, would be presented in this section.

§ C.1 Blank titration

Blank titration resulted in:

Volume of $Na_2S_2O_3$ solution used for titration (average of 2 trials): 0.58 mL

Volume of $Na_2S_2O_3$ solution used for standardization: 11.20 mL

Therefore, by doing similar calculations as shown in § B.2, without the blank subtraction, the blank titration was found to be equivalent to 0.064×10^{-4} mol/m^2.

§ C.2 Incipient boiling time

Operating conditions:

Ozonation phase: gaseous

Ozonation time: 30 minutes

Ozone dose: 1.000 ± 0.020 wt%

Table C-1: Peroxide detected on LDPE+LLDPE film at different incipient boiling time after 30 minutes gaseous ozonation with 1.0 wt% applied ozone dose

Incipient boiling time (minutes)	**$Na_2S_2O_3$ consumed (mL)**		**[Peroxide] × 10^4 (mol/m^2)**
	titration	**standardization**	
6	5.45	12.10	0.50
7	6.25	11.80	0.60
8	6.45	12.10	0.60
9	6.30	11.80	0.60
11	6.50	12.20	0.60

APPENDIX D CATALYST CANDIDATE TEST

Operating conditions:

Ozonation phase: aqueous

Ozonation time: 30 minutes

Ozone dose: 1.000 ± 0.020 wt%

Catalyst dose: 0.20 g/L anhydrous salt

Table D-1: Peroxide generated on LDPE+LLDPE film after 30 minutes ozonation with 1.0 wt% applied ozone dose and 0.2 g/L anhydrous salt where applicable

Ozonation state	**$Na_2S_2O_3$ consumed (mL)**		**[Peroxide] × 10^4 (mol/m^2)**	**SD × 10^4 (mol/m^2)**
	titration	**standardization**		
Gaseous	6.45	12.10	0.60 ± 0.04	0.02
	6.20	11.95		
	6.05	11.05		
Aqueous	5.40	11.50	0.54 ± 0.04	0.02
	5.70	11.70		
	5.60	11.35		
Fe (III)	7.50	11.75	0.71 ± 0.07	0.03
	6.80	11.15		
	7.05	11.80		
Cu (II)	7.50	11.80	0.71 ± 0.04	0.01
	7.00	11.30		
	7.20	11.75		
Zn (II)	6.20	11.15	0.63 ± 0.03	0.01
	6.80	12.00		
	6.25	11.40		
Fe (II)	7.75	12.60	0.70	–
Ag (I)	5.70	11.50	0.56	–

APPENDIX E OPTIMAL COPPER (II) SULFATE DOSE

Operating conditions:

Ozonation phase: aqueous Ozonation time: 60 minutes

Ozone dose: 1.500 ± 0.020 wt%

Table E-1: Peroxide generated on LDPE+LLDPE film after 60 minutes ozonation with 1.5 wt% applied ozone dose and various copper (II) sulfate concentration

$CuSO_4$ dose (g/L)	$Na_2S_2O_3$ consumed (mL)		[Peroxide] × 10^4 (mol/m^2)	SD × 10^4 (mol/m^2)	Initial pH
	titration	standardization			
0.00	11.90	11.80	1.18 ± 0.06	0.02	5.60
	11.90	12.25			
	11.55	11.60			
0.02	13.20	11.20	1.38 ± 0.07	0.03	5.53
	13.25	11.70			
	13.05	11.30			
0.03	14.60	11.30	1.52 ± 0.06	0.03	5.45
	14.90	11.90			
	14.10	11.15			
0.05	16.85	12.40	1.60 ± 0.08	0.03	5.39
	15.50	11.85			
	14.70	11.00			
0.2	15.20	11.80	1.57 ± 0.07	0.03	5.25
	15.05	11.30			
	14.95	11.40			
0.5	15.15	11.40	1.56 ± 0.07	0.03	5.11
	15.50	12.00			
	14.50	11.25			

Table E-2: Tensile strength of LDPE+LLDPE film after 60 minutes ozonation with 1.5 wt% applied ozone dose and various copper (II) sulfate concentration

$CuSO_4$ dose (g/L)	Tensile strength (MPa)					Average (MPa)	SD (MPa)
	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5		
0	26.0	26.4	27.9	25.9	25.5	26.3 ± 1.2	0.9
0.05	27.6	25.4	23.5	26.3	26.1	25.8 ± 1.9	1.5
0.2	26.0	26.8	25.7	27.0	25.5	26.2 ± 0.8	0.7
0.5	26.9	25.0	25.9	27.0	25.2	26.0 ± 1.2	0.9

APPENDIX F EFFECT OF RADICAL SCAVENGER IN CATALYTIC OZONATION

Operating conditions:

Ozonation phase: aqueous

Ozonation time: 60 minutes

Ozone dose: 1.500 ± 0.020 wt%

Catalyst dose: 0.05 g/L copper sulfate

Table F-1: Peroxide generated on LDPE+LLDPE film after 60 minutes ozonation with 1.5 wt% applied ozone dose and 0.05 g/L copper (II) sulfate, with TBA

[TBA] (mol/L)	$Na_2S_2O_3$ consumed (mL)		[Peroxide] × 10^4 (mol/m^2)	SD × 10^4 (mol/m^2)
	titration	standardization		
0.0	16.85	12.40	1.60 ± 0.08	0.03
	15.50	11.85		
	14.70	11.00		
0.1	13.80	11.65	1.41 ± 0.09	0.04
	14.15	11.80		
	12.58	11.00		
0.5	12.55	11.60	1.29 ± 0.06	0.02
	12.35	11.15		
	12.63	11.80		

APPENDIX G EFFECT OF INITIAL pH

Operating conditions:

Ozonation phase: aqueous Ozonation time: 60 minutes

Ozone dose: 1.500 ± 0.020 wt%

Table G-1: Peroxide generated on LDPE+LLDPE film after 60 minutes ozonation with 1.5 wt% applied ozone dose at different initial pH adjusted by using sulfuric acid or sodium hydroxide

Initial pH	pH change	$Na_2S_2O_3$ consumed (mL)		[Peroxide] × 10^4 (mol/m^2)	SD × 10^4 (mol/m^2)
		titration	standardization		
3.00	–0.01	9.40	11.70	0.95 ± 0.03	0.01
		9.50	11.55		
		9.20	11.30		
4.00	–0.01	10.35	12.25	1.00 ± 0.02	0.01
		10.10	11.80		
		9.60	11.30		
5.00	0.30	10.60	11.55	1.06 ± 0.05	0.02
		11.10	12.50		
		10.10	11.20		
5.60	0.82	11.90	11.80	1.18 ± 0.06	0.02
		11.90	12.25		
		11.55	11.60		
7.00	1.16	10.75	12.35	1.02 ± 0.03	0.00
		9.58[11]	11.05		
10.00	0.05	7.23	11.30	0.74 ± 0.05	0.01
		8.40[11]	13.00		

[11] Conducted in the presence of 1.0 g/L sodium sulfate

Table G-2: Peroxide detected on LDPE+LLDPE film after 60 minutes ozonation with 1.5 wt% applied ozone dose at different initial pH adjusted by using nitric acid or hydrochloric acid

Acid used	Initial pH	$Na_2S_2O_3$ consumed (mL)		[Peroxide] × 10^4 (mol/m^2)	SD × 10^4 (mol/m^2)
		titration	standardization		
Nitric acid	3.00	9.95	12.35	0.95 ± 0.01	0.00
		9.95	12.25		
		9.55	11.80		
	4.00	9.55	11.25	0.99 ± 0.01	0.00
		9.70	11.50		
		10.00	11.80		
	5.00	10.23	11.50	1.06 ± 0.03	0.01
		10.40	11.45		
		9.90	11.00		
Hydrochloric acid	3.00	8.23	12.15	0.79 ± 0.03	0.01
		7.90	11.35		
		7.65	11.20		
	4.00	8.63	11.40	0.87 ± 0.04	0.01
		8.65	11.65		
		8.30	11.30		
	5.00	10.25	11.90	0.99 ± 0.05	0.02
		10.00	12.05		
		9.50	11.25		

Table G-3: Peroxide generated on LDPE+LLDPE film after 60 minutes ozonation with 1.5 wt% applied ozone dose at initial pH of 3 and 5 adjusted by using sulfuric acid in the presence of various copper (II) sulfate concentration

$CuSO_4$ dose (g/L)	Initial pH	$Na_2S_2O_3$ consumed (mL)		[Peroxide] × 10^4 (mol/m^2)	SD × 10^4 (mol/m^2)
		titration	standardization		
0.03	3.00	10.00	11.50	1.01 ± 0.04	0.02
		9.85	11.70		
		9.70	11.35		
	5.00	10.90	11.75	1.10 ± 0.02	0.01
		11.00	11.90		
		10.55	11.25		
0.05	3.00	11.05	12.05	1.06 ± 0.05	0.02
		10.00	11.20		
		9.95	11.20		
	5.00	11.35	11.45	1.19 ± 0.07	0.03
		12.00	11.65		
		11.25	11.30		

APPENDIX H EFFECT OF OZONATION TIME IN CATALYTIC OZONATION

Operating conditions:

Ozonation phase: aqueous Ozone dose: 1.500 ± 0.020 wt%

Catalyst dose: 0.05 g/L copper sulfate

Table H-1: Peroxide generated on LDPE+LLDPE film for various ozonation time with 1.5 wt% ozone dose and 0.05 g/L copper (II) sulfate

Ozonation time (minutes)	**$Na_2S_2O_3$ consumed (mL)**		**[Peroxide] × 10^4 (mol/m^2)**	**SD × 10^4 (mol/m^2)**
	titration	**standardization**		
15	8.20	12.40	0.74 ± 0.04	0.02
	7.55	11.90		
	7.35	11.45		
30	11.55	12.40	1.09 ± 0.03	0.01
	10.60	11.60		
	10.35	11.25		
60	16.85	12.40	1.60 ± 0.08	0.03
	15.50	11.85		
	14.70	11.00		
90	20.65	12.40	1.99 ± 0.06	0.02
	19.10	11.75		
	18.40	11.20		
120	23.50	12.40	2.30 ± 0.05	0.02
	21.20	11.30		
	21.45	11.25		

Table H-2: Tensile strength of LDPE+LLDPE film after various ozonation time for runs with 1.5 wt% ozone dose and 0.05 g/L copper (II) sulfate

Ozonation time (minutes)	Tensile strength (MPa)					Average (MPa)	SD (MPa)
	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5		
0	27.2	27.5	26.3	27.9	26.2	27.0 ± 0.9	0.7
15	26.0	26.4	27.9	26.0	26.5	26.6 ± 1.0	0.8
30	27.9	25.4	26.3	26.3	25.1	26.2 ± 1.4	1.1
60	27.6	25.4	23.5	26.3	26.1	25.8 ± 1.9	1.5
90	24.5	24.2	23.9	23.5	25.1	24.2 ± 0.8	0.6
120	23.0	22.5	21.6	22.9	20.2	22.0 ± 1.5	1.2

Table H-3: Water contact angle of LDPE+LLDPE film after various ozonation time for runs with 1.5 wt% ozone dose and 0.05 g/L copper (II) sulfate

Ozonation time (minutes)	Contact angle						Average	SD
	Spot 1	Spot 2	Spot 3	Spot 4	Spot 5	Spot 6		
0	87.7°	88.6°	90.6°	90.8°	90.4°	92.8°	90.1 ± 1.9°	1.8°
15	86.9°	89.4°	88.1°	85.7°	87.0°	91.7°	88.1 ± 2.3°	2.2°
30	86.4°	89.1°	88.0°	86.5°	89.0°	84.4°	87.2 ± 1.9°	1.8°
60	85.8°	83.0°	85.8°	85.7°	85.6°	80.4°	84.4 ± 2.4°	2.2°
90	82.3°	81.6°	81.7°	81.4°	82.7°	78.2°	81.3 ± 1.7°	1.6°
120	79.3°	77.8°	79.7°	79.0°	78.5°	75.3°	78.2 ± 1.7°	1.6°

APPENDIX I EFFECT OF OZONATION TIME IN GASEOUS OZONATION

Operating conditions:

Ozonation phase: gaseous Ozone dose: 1.500 ± 0.020 wt%

Table I-1: Peroxide generated on LDPE+LLDPE film for various ozonation time with 1.5 wt% ozone dose in gaseous phase

Ozonation time (minutes)	**$Na_2S_2O_3$ consumed (mL)**		**[Peroxide] × 10^4 (mol/m^2)**	**SD × 10^4 (mol/m^2)**
	titration	**standardization**		
30	7.60	11.05	0.77 ± 0.06	0.02
	7.85	11.95		
	7.35	11.20		
45	9.00	11.55	0.93 ± 0.06	0.02
	9.40	12.00		
	9.10	11.20		
60	10.00	11.70	1.01 ± 0.04	0.02
	10.35	11.90		
	10.00	11.85		
90	13.40	11.50	1.36 ± 0.08	0.03
	13.20	11.85		
	13.10	11.40		
120	14.05	11.00	1.57 ± 0.08	0.03
	15.20	11.65		
	16.00	12.05		

APPENDIX J EFFECT OF APPLIED OZONE DOSE IN CATALYTIC OZONATION

Operating conditions:

Ozonation phase: aqueous

Ozonation time: 60 minutes

Catalyst dose: 0.05 g/L copper sulfate

Table J-1: Peroxide generated on LDPE+LLDPE film for 60 minutes ozonation with various applied ozone dose and 0.05 g/L copper (II) sulfate dose

Ozone dose (wt %)	$Na_2S_2O_3$ consumed (mL)		[Peroxide] × 10^4 (mol/m^2)	SD × 10^4 (mol/m^2)
	titration	standardization		
1.0	14.83	12.40	1.42 ± 0.06	0.02
	13.45	11.25		
	13.60	11.70		
1.5	16.85	12.40	1.60 ± 0.08	0.03
	15.50	11.85		
	14.70	11.00		
2.0	19.85	12.40	1.92 ± 0.05	0.02
	17.93	11.25		
	17.75	11.30		
2.5	22.03	12.40	2.19 ± 0.12	0.05
	21.00	11.75		
	20.73	11.20		
3.0	23.25	12.40	2.27 ± 0.12	0.05
	22.35	11.75		
	21.20	11.60		

APPENDIX K OTHER PERTINENT CALCULATIONS

In this section, the data and calculations for the isotropic test of polymer film, the carbonate and bicarbonate equilibrium, and the ionic strength of solution are presented in detail.

§ K.1 Isotropic test

The tensile strength of untreated polymer film was measured on transverse and machine directions, in order to ensure its isotropy. Five readings were taken in each direction, and the results were compared by using t-distribution test at 95% confidence level. Table K-1 shows the readings and the average of tensile strength for each direction.

Table K-1: Tensile strength measurement of untreated LDPE+LLDPE film

Directions	**Tensile strength (MPa)**					**Average (MPa)**	**SD (MPa)**
	Trial 1	**Trial 2**	**Trial 3**	**Trial 4**	**Trial 5**		
Transverse	27.2	27.5	26.3	27.9	26.2	27.0	0.5
Machine	27.0	28.0	27.6	28.0	27.2	27.6	0.7

The standard deviations of these readings were found to be 0.5 and 0.7 MPa for transverse and machine direction, respectively. By assuming these readings are normally distributed and that the population standard deviations are approximately equal, the t-test was used to compare these two averages. The combined standard deviation was calculated to be 0.621 as shown below:

$$SD_{combined} = \sqrt{\frac{\left((n-1)\times SD^2\right)_{transverse} + \left((n-1)\times SD^2\right)_{machine}}{(\sum n) - 2}}$$

$$SD_{combined} = 0.621$$

The value of t for these combined readings was calculated as follow:

$$t = \frac{|\,27.0 - 27.6\,|}{SD_{combined}\sqrt{\frac{1}{5} + \frac{1}{5}}} = 1.914$$

At 95% confidence level, the corresponding t-value, with degree of freedom equal to 8, is 2.306; therefore, the tensile strength of LDPE+LLDPE film on transverse and machine directions can be considered equal. In another words, the polymer film is isotropic.

§ K.2 Salting-out effect

Sechenov's relation can be applied for ozone system to explain the change in Henry's constant with respect to the concentration of electrolytes. The equation describes only the effect of electrolytes' concentration on gas solubility, while excluding the effect of pH change or any other parameters (Rischbieter et al., 2000; Bin, 2006).

$$\log\left(\frac{H}{H_0}\right) = K_S\, C_S$$

Where: H is the Henry's constant in solution; C_S is the concentration of ions

H_0 is the Henry's constant in pure water; K_S is the Sechenov's constant

$$K_S = \Sigma\left(x_i\,(h_i + h_G)\right) \qquad h_G = h_{G,0} + h_T\,(T - 298.15)$$

Where: h_i is the ion-specific salting-out constant; T is the absolute temperature

h_G, $h_{G,0}$, and h_T are the gas-specific parameters

x_i is the index of ion in the chemical formula

Since the temperature is approximately 25°C, the last term in the expression of h_G was ignored. From the results obtained by Rischbieter et al. (2000), the $h_{G,0}$ value for ozone at temperature range 278 K to 298 K is 3.96 m^3/kmol. The h_i values for different types of cations and anions were tabulated in Table K-2. These values were obtained from various sources as seen from Weisenberger and Schumpe (1996).

Table K-2: Ion-specific salting-out constants for Sechenov's relation for 273 K to 363 K (Adapted from: Weisenberger & Schumpe, 1996)

Cations	**h_i (m^3/kmol)**	**Anions**	**h_i (m^3/kmol)**
H^+	0	OH^-	0.0839
Na^+	0.1143	SO_4^{2-}	0.1117
Cu^{2+}	0.1675		

The changes in Henry's constants for several ozonation runs conducted in this study were calculated as shown below. For ozonation run with initial pH of 3.00, the amount of sulfuric acid added was estimated from the pH change. Similar calculation was done for sodium hydroxide run with initial pH of 10.00. The changes in Henry's constant for these runs were tabulated as shown in Table L-3.

Table K-3: Increase in Henry's constant for different ozonation runs conducted

Run conditions	**Increase in Henry's constant**
Initial pH = 3.00, adjusted using sulfuric acid	0.014%
Initial pH = 10.00, adjusted using sodium hydroxide	0.005%
Copper (II) sulfate dose of 0.5 g/L	0.133%
1.0 g/L sodium sulfate runs at initial pH = 10.00	0.573%