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Surface modification of selected polymer films by ozonation

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SURFACE MODIFICATION OF SELECTED

POLYMER FILMS BY OZONATION

By

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ABSTRACT

Surface Modification of Selected Films by Ozonation

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In this study, three polymer films – high density polyethylene (HDPE), biaxial oriented polypropylene (BOPP) and biaxial oriented polyethylene terephthalate (PET) were oxidized by ozone in distilled water and in the gaseous phase in a specially designed reactor. Ozonation was conducted using different reaction times, applied ozone doses and pH values. Peroxides were generated by ozonation on the surfaces of polymers. Then the peroxide-induced graft polymerization of hydrophilic monomers improves the biocompatibility of the polymer surfaces. These three films are currently in extensive use, the modified polymer films can be applied more in organic materials packaging and medical fields.

These three films were all found to react with ozone to generate peroxides both in distilled water and in gaseous phase. When comparing the peroxide generation rates in distilled water and in ozone gas mixture, it was found that the peroxide generation rates of BOPP and PET in the gaseous phase ozonation were faster than the peroxide

generation rates in the aqueous phase ozonation; but the peroxide generation rate of HDPE showed a different trend: its peroxide generation rate in distilled water was faster than when using the ozone mixture in the gaseous phase. Further, among the three polymer films, HDPE obtained the fastest peroxide generation rate in distilled water, while BOPP has the fastest peroxide generation rate in gas phase.

The tensile strength and elongation of untreated and ozone treated films were examined. The tensile strength and elongation decreased with increasing ozonation time. For both the aqueous and ozone gas mixtures, the order in which the three polymer films decreased in tensile strength and elongation were: HDPE > BOPP > PET; but the tensile strength and elongation of BOPP and PET dropped faster when using the ozone gas mixture than when using the aqueous ozone. The results were the opposite for HDPE.

After the reaction conditions were investigated, that using the 1.0-wt% applied ozone dose and 1.0-hr reaction time was found to be optimal, both to obtain peroxides and to maintain good mechanical strength. After investigation of the reactions with different pH values, it was found that the peroxide density decreased slightly as the pH volume increased.

Finally, the ozone-induced graft polymerization of Acrylamide (AAm) significantly increased the hydrophilicity of HDPE films, the FTIR and SEM analysis confirmed the successful graft polymerization of AAm.

ACKNOWLEDGEMENTS

DEDICATION

Attribute to my father and mother for the bestowal of a beautiful life to me, attribute to my family members who support me all the time, tolerant my bad motion and unhappiness when I faced difficulty ; and for those unconditional love, consistent encouragement and forgiveness throughout my whole life, wherever I am.

Dedication also to Exopack Canada, which supported me a lot, included free samples, tensile strength testing machine and flexible time.

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CHAPTER 1

INTRODUCTION

1.1 Background

Polymeric materials are widely used in biomedical fields for blood and protein packaging materials and containers, artificial organs, medical devices and disposable clinical apparatuses [Xu et al., 2003]. They are chemically nonreactive, and have remarkable mechanical and thermal properties; however, their surfaces are usually hydrophobic and non bondable, which limit their applications in many areas [Dasgupta, 1990]. Hydrophobic surfaces cause anticoagulation, adhesion and coating when they come into contact with biomedical materials [Murakami et al., 2003]. For example, polyolefins, such as polypropylene and polyethylene, are very popular packaging materials; but they have non-polar and highly hydrophobic properties that severely limit their use in the biomedical area. Polyurethane and silicone rubbers are ideal polymer materials with a wide variety of applications, especially in the biomaterial fields; however, some of their surface conditions, such as antithrombogenic properties, limit their applications. Polymer fibers and membranes also have some surface property limits that decrease the number of their applications. The surface modification of polymers becomes important when polymeric material comes into contact with physiological components, such as blood and living tissues [Lin et al., 2005].

Methods used to modify polymer surfaces include UV radiation, corona-discharge treatment, activated gas plasma treatment, glow discharge treatment, surface oxidation – acid treatment, immobilization of the polymers by use of coupling reactions, γ-ray irradiation, flame treatment, etc. [Wang et al., 2000]. The chemical modification of polymers in order to obtain particular

structures or to embed specific properties in materials remains a fundamental topic of research. It is necessary from the viewpoint of green chemistry to modify the polymer surface easily and under mild conditions, such as using low temperature and neutral media [Murakami et al., 2003]. Besides the widespread conventional chemical ways of synthesis, new kinds of chemical reactions, based on the modification of conventional polymers, have emerged. Ozone appears to be a very interesting and cheap reagent. Surface ozonation is being widely applied in polymer research areas, because it has the advantage of uniformly introducing peroxides onto the polymer surface, even with complicated shapes, and involves an easy-to-handle, inexpensive technique [Yuan et al., 2002].

When polymers are exposed to ozone, mainly peroxides are formed, in addition to carbonyl and carboxyl groups. The peroxides generated are capable of initiating polymerization of vinyl monomers, resulting in polymer grafting onto the ozonated polymeric material. The ozonation of polymers usually occurs through three different events: (1) chain scission (2) cross-linking (3) recombination of broken chains [Michael et al., 2004]. The reactivity of the hydroperoxidized materials with the monomers depends on the following factors: the kinetics of the thermal decomposition of peroxide, the nature of the radicals generated the accessibility of peroxide sites and monomer diffusion [Gatenholm, 1997].

Using a water medium not only maintains uniform treatment over the bulk of the material and enhances the generation of hydroperoxide needed for the grafting process, but it also has the potential of finding additives or catalysts to accelerate the reaction. Active oxygen species (hydroxyl radical $\bullet OH$, superoxide $\bullet O_2^-$, and peroxide radical $\bullet OOH$) can be generated when

ozone is present in the water, and they can enhance the reaction and lead to peroxide generation. These radicals are intrinsic chemical species in the human body and also are generated by the reduction of oxygen in mitochondria (an organic activity in a cell). Thus, ozone treatment is recognized as a safe treatment method for biomaterials. Furthermore, the treated polymer surface introduced into the body is not contaminated with toxic chemicals, because the only chemical substances used are ozone, oxygen and water [Murakami, 2003]. Consequently, this method is considered to be suitable for modifying the surface of polymers, especially in biomaterials.

1.2 Research objectives

The research objective is to compare ozonation efficiency in gas and water media for selected films, to study the effects of the operating parameters, and to investigate the graft polymerization of hydrophilic monomers onto ozonized film.

CHAPTER 2

LITERATURE STUDY

2.1 Mechanism of ozonation

2.1.1 Description of ozone

Ozone is most often produced by electronic discharge, using a flow of air or pure oxygen through electrodes. Oxygen is then decomposed into different species: negative ions: O^-, O_2^-, O_3^- and O_4^-; positive ions: O^+, O_2^+, O_3^+ and O_4^+; and neutral molecules: O, O_2 and O_3. A mixture of active oxygen is called ozone (O_3) [Robin, 2004]. Figure 2.1 shows the conjugated schematic of ozone.
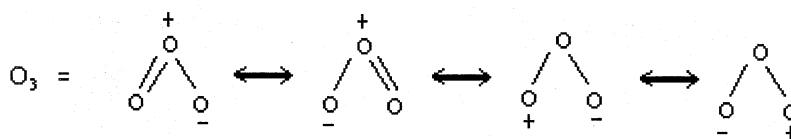
Figure 2.1 Schematic of ozone [Robin, 2004].

2.1.2 Reaction with polyolefins

The reactions of ozone on polymers lead to numerous chemical modifications. The application of ozone to polymers rapidly leads to formation of oxygenated functional groups, and chemical reactions occur at the surface of the polymer as well as below the surface of a material. The main functional groups produced during treatment are unsaturated compounds, ketones, acids, esters, hydroxyl groups, peroxides and hydroperoxides [Robin, 2004].

As shown in Figures 2.2 and 2.3, the species R•, HO• and HOO• are responsible for the further abstraction of hydrogen from polyolefins, leading to alcohol functions by abstraction of hydrogen from a neighboring chain of polymer, but also and mainly, to the β-scissions (the second carbon from the activated location). Moreover, the radicals obtained can react with oxygen giving hydroperoxides. On the other hand, intermolecular rearrangement produces different species, leading to esters and ketones.

Compounds can generate alcohol functions by the usual combination of hydroxyl-radical and carbon-radical.
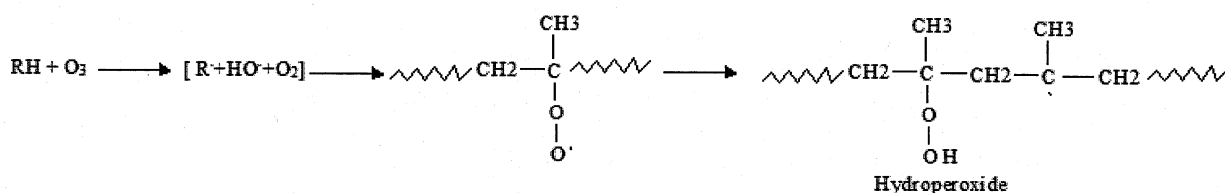
Figure 2.2 Ozone reacting with polyolefin to create hydroperoxide [Robin, 2004].
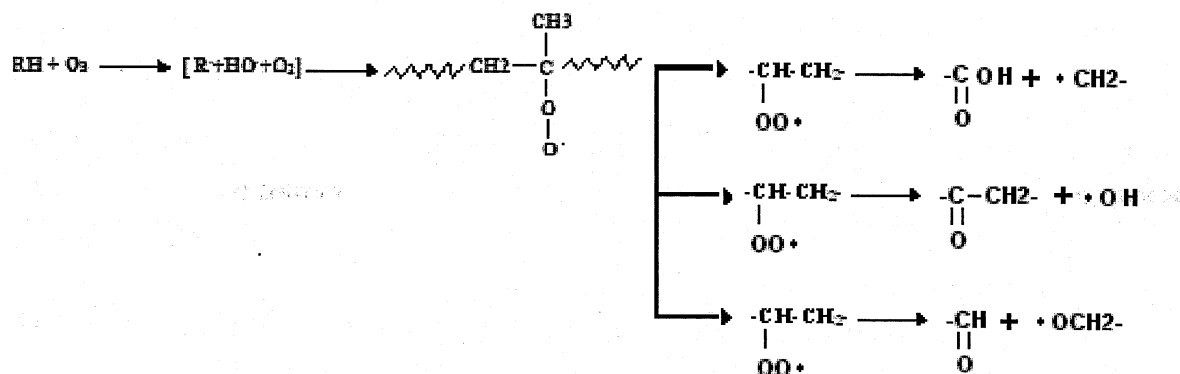
Figure 2.3 Ozone react with polyolefin to create carbonyl/carboxyl by chain scission [Robin, 2004].

2.1.3 Reaction with polydienes

Polydienes are very sensitive to ozone. A rapid decrease in molecular weights can be correlated with the number of unsaturations in the polymer backbone. The products obtained are mainly carbonyl groups, but also ozonides and peroxides, as shown in Figure 2.4 [Robin, 2004].
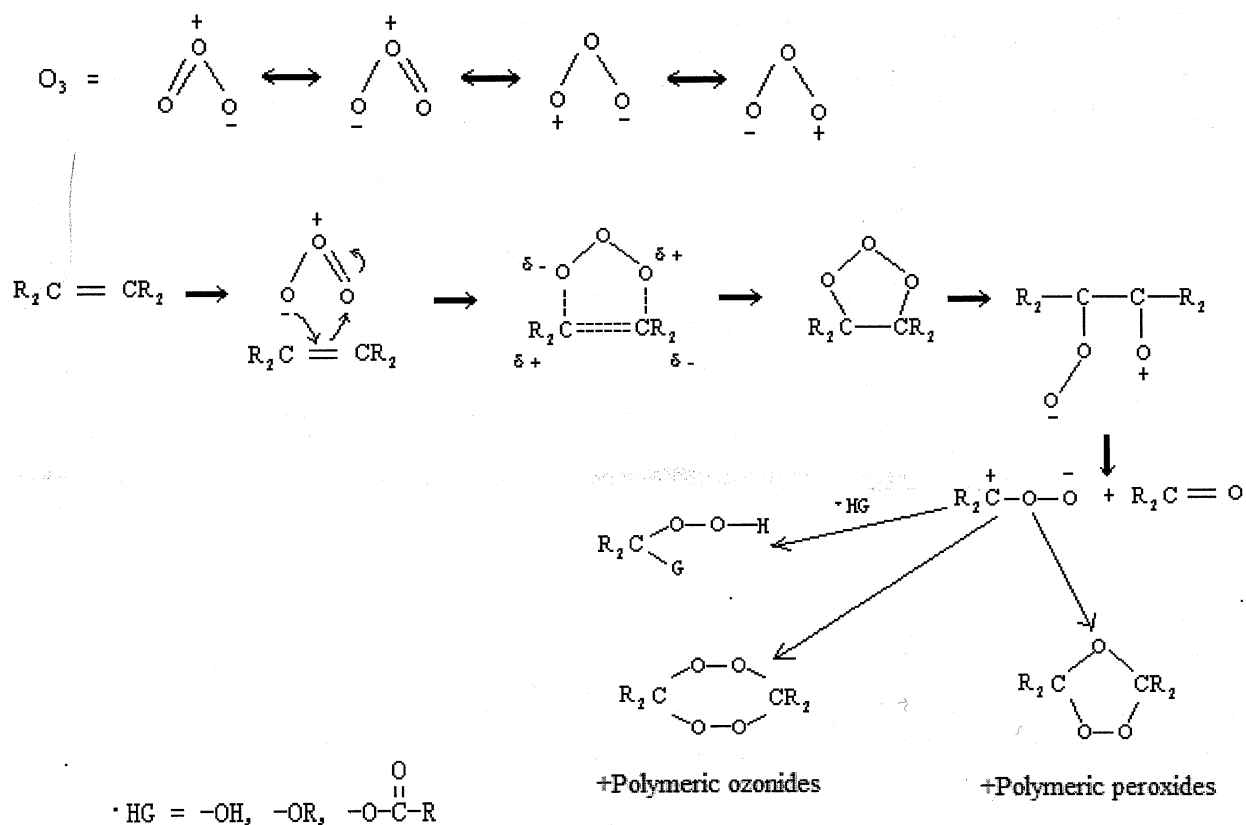
Figure 2.4 Ozone reacts with polydienes to create carbonyl/carboxyl and peroxide by chain scission [Robin, 2004].

2.1.4 Reaction with aromatic polymers

In the most frequently encountered cases, aromatic cycles are attacked in a second step after ring substituents. Further, different experimental conditions (ozonation in the solid phase or in dilute solution) lead to different products, and the appearance of cross linking is specific to solid phase ozonation. Radical formation occurred in the degradation of aromatic polymers. The tertiary carbon is the most favored site for O3 to attack. Figure 2.5 shows the schematic of ozone reaction with aromatic cycles.

Addition of O_3 to double bond
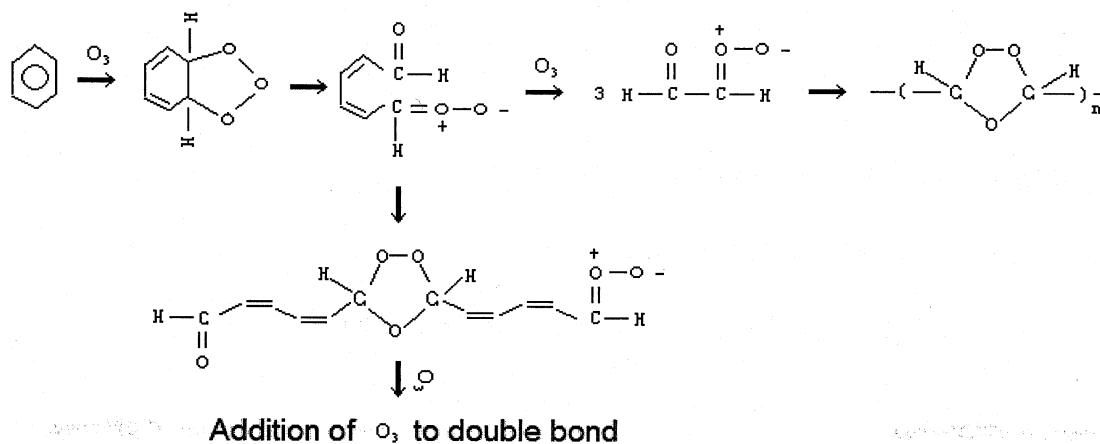
Figure 2.5 Ozonation of aromatic cycles [Robin, 2004].

2.1.5 Reaction with halogenated polymer

As an example, PVC is widely studied. The sensitivity of this polymer depends closely at first on the temperature, and also on the structure of the starting polymer, and thus, on its way of synthesis. Hydrogen atoms in the allylic position are favorite sites for hydroperoxidation of chains. The double bond provides a weak position at which to degrade the chains. In the second step, hydroperoxides lead to intermolecular rearrangements [Robin, 2004]. Figure 2.6 shows the ozonation of PVC.
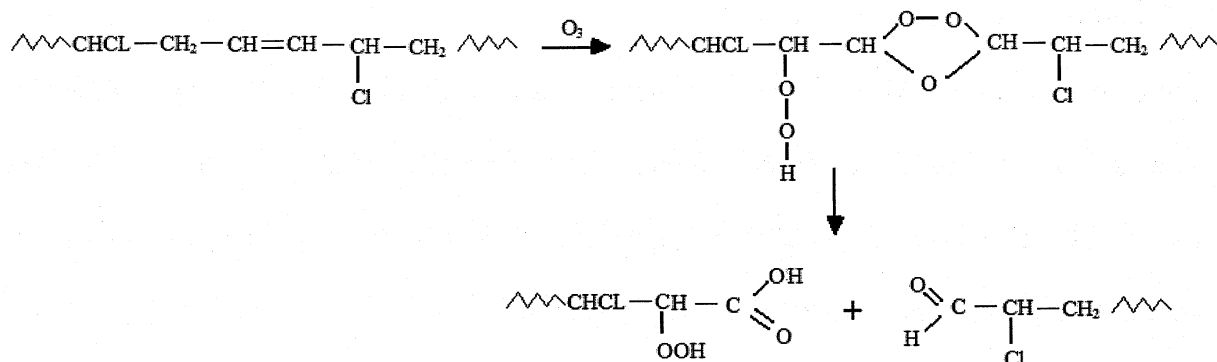
Figure 2.6 Ozone reacts with halogenated polymers to create carbonyl/carboxyl and peroxide by chain scission [Robin, 2004].

2.2 Materials, reaction systems and methods

2.2.1 The substrates that other researchers have studied:

- Polyolefin-polyethylene, polypropylene films and powders [Dasgupta, 1990]

- Polypropylene microfiltration membrane [Wang et al, 2000]

- Hybrid biomaterials, microporous polypropylene [Gatenholm, 1997]

- Silicone film, silicone rubber [Xu et al, 2003]

- Thermoplastic polyurethane membrane and film [Lin et al, 2005]

- Polyethylene terephthalate (PET) fiber and film [Ferreira, 2005]

- Poly(tetrafluoroethylene) (PTFE) film [Tu et al, 2005]

- Polystyrene (PS) film and powder [Murakami, 2003]

- Poly(methyl methacrylate) (PMMA) film [Ko et al, 2001]

- Poly(ethylene-co-vinyl alcohol) (EVA) film [Matsumura, 2004]

- Poly-L-lactic acid (PLLA) film [Suh, 2001]

2.2.2 Reaction systems

The main components of a reaction system are oxygen/air cylinder, ozone generator, flow rate and pressure control system, ozone concentration monitor, stainless steel or Pyrex vessel reactor, and ozone consumption detector.

Fujimoto (1993) used the reacting system shown in Figure 2.7.
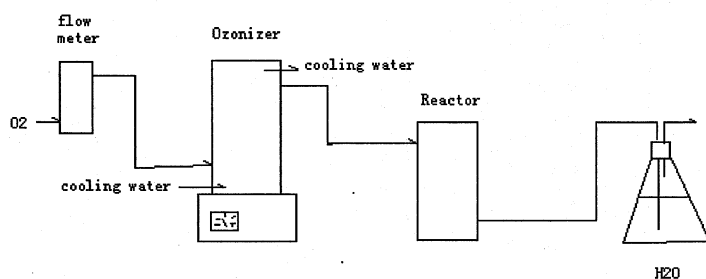
Variables: Voltage: 1~100 [V], O_2 flow rate: 20~200 [lh^{-1}]

O_2 pressure: 1 [$kgcm^{-2}$], Temp. of cooling water: 10 [^{o} C]

Figure 2.7 The apparatus for ozone oxidation. [Fujimoto, 1993]

Yuan and Lin (2002) used a thermostatic bath to keep the reacting temperature constant. The apparatus is shown in Figure 2.8.
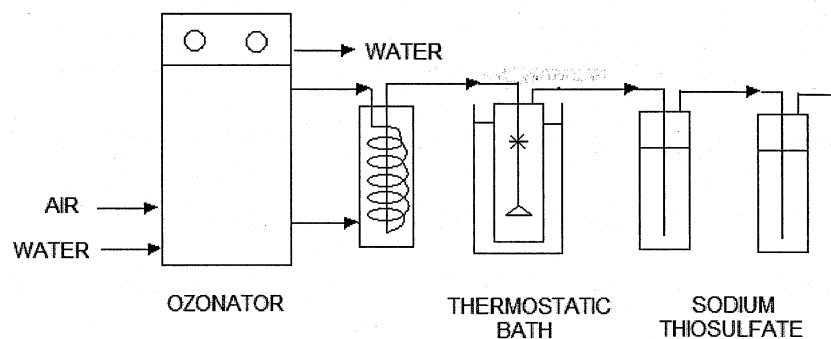
Figure 2.8 Flow diagram for ozonation of polymer film [Yuan et al., 2002].

Murakami and his group (2003) used a combination of ozone aeration and UV irradiation in an aqueous phase reaction system. Figure 2.9 illustrates the apparatus.
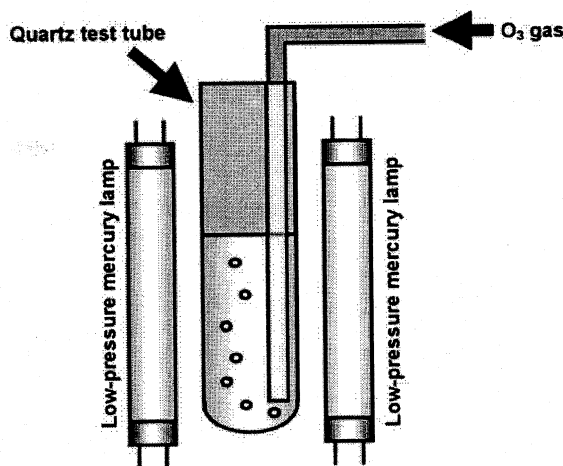
Fig 2.9 The active oxygen generator using a combination of ozone aeration and UV irradiation. Aeration of ozone with 300 ppm at $1.0 \, l \, min^{-1}$ flow rate and irradiation from both sides with two 6 W low-pressure mercury lamps (UV lamps) at $\lambda = 254$ nm were carried out in the system. [Takurou N. 2003]

2.2.3 Ozonation Methods and Results

2.2.3.1 Polyurethane (PU) and polyethylene (PE) reacted with gas ozone mixture

Fujimoto and his group (1993) investigated ozone-induced AAm graft polymerization onto PU and PE surfaces with gas ozone mixture and plasma oxidization. They found the contact angles (contact angle is a method used to detect the wettability of substrates and smaller contact angle indicates a better wettability) of PU and PE were decreased by the oxidation and plasma exposure as shown in Figure 2.10.

The surface concentration of peroxide generated on various polymer films was precisely detected.

Table 2.1 shows the surface concentration of peroxide generated on various polymer films.

Fujimoto's group found that peroxide concentration increased with ozone oxidization time, as shown in Figure 2.11.
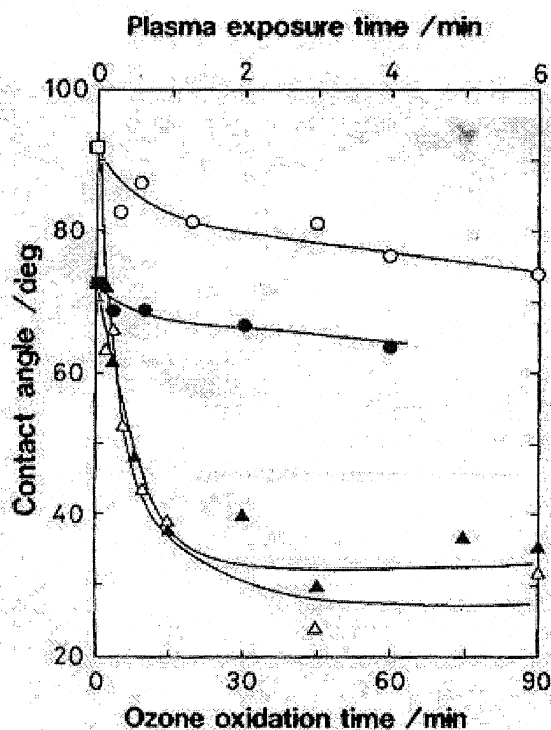
Fig 2.10 . Decrease in contact angle of PE and PU films by ozone oxidation and plasma exposure. Ozone (60 V, 50 L h^{-1}): (O) PE, (●) PU. Plasma (Ar, 24 W): (△) PE, (▲) PU. Virgin: (□) PE, (■) PU. [Fujimoto, 1993]

The interesting thing is that different peroxide concentration monitoring methods were used, and it was found that the Iodide method detected the highest concentration, as shown in Table 2.2 [Fujimoto, 1993].

Table 2.1 The peroxide concentration generated on various polymer films[a]. [Fujimoto, 1993]

Polymer	Peroxide $(mol\ cm^{-2})$
Silicone	8.7×10^{-8}
PU	6.2×10^{-8}
PU[b]	2.5×10^{-9}
PMMA	1.2×10^{-8}
PE	1.3×10^{-9}
PET	0.7×10^{-9}
VAECO	0.6×10^{-9}
6F	undetectable
Teflon	undetectable
[a]. Ozonation voltage: 100 V, oxidation time: 20 min, O2 flow rate: 50 lh^{-1}.	
[b]. Plasma exposure: 24 W, 20 s	

The contact angles of different virgin PU films, ozone oxidized films, and AAm grafted films were checked and they found that the surface of the PU film became hydrophilic upon graft polymerization by AAm. The virgin PU had the highest contact angles, with 89° as the advancing $(\theta\alpha)$ and 58° as the receding contact angle (θr), respectively. The ozone treatment at 60 V for 30 min without any graft polymerization resulted in contact angles of 90° $(\theta\alpha)$ and 51° (θr). After AAm grafting, the film contact angles decreased to 75° $(\theta\alpha)$ and 35° (θr) [Fujimoto, 1993]. The relationship between contact angle and PAAm grafting was researched, and the results are shown in Figure 2.12.
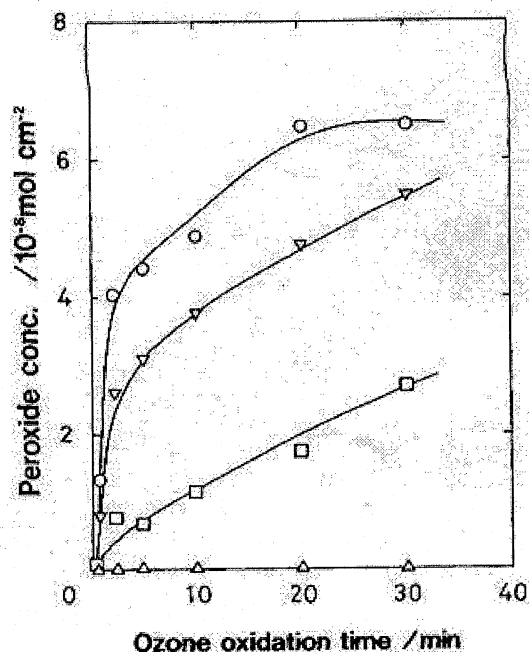
Figure 2.11 Formation of peroxide on the PU film by ozone oxidation at different voltages (iodide method): (△) 20, (□) 30, (▽) 60, (○) 100 V. [Fujimoto,1993]

Table 2.2 . Peroxide Concentrations Determined with Iodide and Peroxidase Methods

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

[a] For ozone generation.

[Fujimoto, 1993]

After the AAm was graft-polymerized, the film was checked by Fourier Transform Infrared (FTIR) spectra. The peaks at 1650-1700 cm^{-1} were found for the AAm grafted films. Figure 2.13 shows the results.
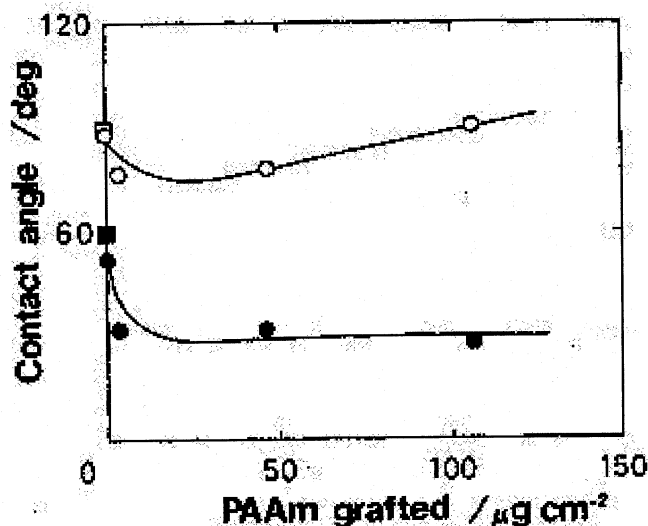
Figure2.12 Dependence of the contact angle of AAm- grafted PU film on the graft density: (O) θ_a [(□) virgin], (●) θ_r [(■) virgin]. [Fujimoto,1993]

2.2.3.2 Silicone, poly (ether-urethane), and low density polyethylene reacted with ozone gas mixture

Research has also been done on ozonation of silicone film, silicone rubber, segmented poly (ether-urethane) (SPEU) and LDPE films [Shan et al., 2006; Xu et al., 2003; Zhou et al., 2005]. After ozonation, Methacryloyloxyethyl phosphorylcholine (MPC), 2-(Dimethylamino) ethyl methacylate (DMMCA), and N,N'-dimethyl (methacyloyloxyethyl) ammonium propanesulfate (DMAPS) were graft-polymerized to the polymer substrates. Then surface conditions and biocompatibility were tested.

It was found that the concentration of peroxides evolved on the surface of the silicone film increased quickly with the ozonation time. However, after about 20 min, the peroxide

concentration increased slowly; and at around 30 min, it reached a plateau. The researchers think the concentration of peroxides may have become saturated on the silicone surface. Figure 2.14 shows the results.
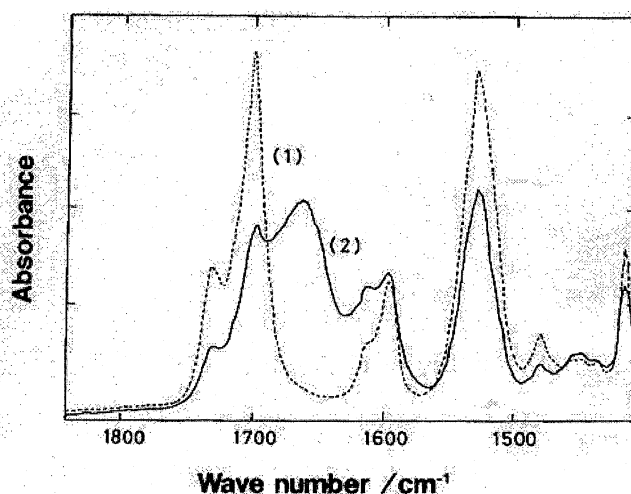
Figure 2.13 ATR-IR spectra for the virgin and an AAm- grafted PU film: (1) virgin, (2) AAm-grafted (graft density = 28 $\mu g \ cm^{-2}$). [Fujimoto, 1993]

The mechanism of peroxide inducing grafting polymerization was discussed by the Lin group. They think that POOH is decomposed by heat to produce PO· and OH·. PO· induces copolymerization, while OH· induces homopolymerization. Fe^{2+} ion was used as an agent to accelerate the reaction [Xu et al., 2003]:

$$POOH + Fe^{3+} \xrightarrow{k1} PO· + OH^- + Fe^{2+} \qquad PO· + Fe^{2+} \xrightarrow{k2} PO- + Fe^{3+}$$
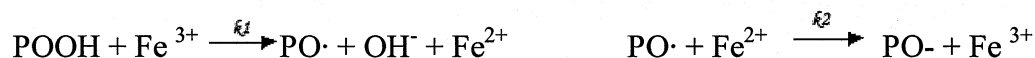
POOH represents polymeric peroxide. The homopolymerization is restrained because of *k2<<k1*.
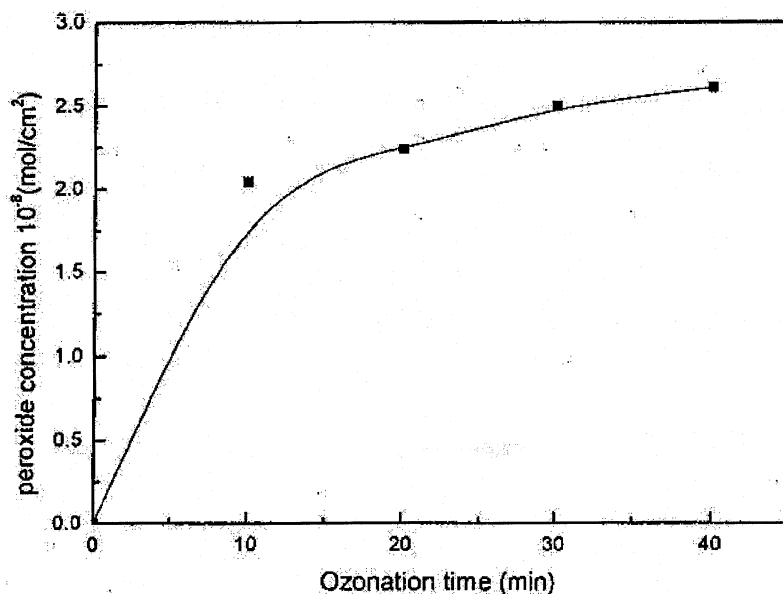
Fig 2.14 Relationship between peroxide concentration on silicone film and ozonization time [Xu et al., 2003].

According to the contact angle measurement, the grafted film's hydrophilicity increased with increasing MPC concentration. Table 2.3 shows the results.

Table 2.3 The contact angle measurement of the grafted silicone with different MPC concentrations [Xu et al., 2003].

MPC concentration (wt%)	0	1.0	2.0	5.0	8.0	10.0
Contact angle Measurement ($\pm$ 3°)	102.9	66.8	60.4	53.9	45.2	43.2

2.2.3.3 Poly(ethylene terephthalate) (PET) films and fibers reacted with ozone gas mixture

Ferreira and his colleagues (2005) improved the adhesion of PET fibers to poly(hydroxyethyl

methacrylate) (HEMA) hydrogels by treatment with ozone gas, and checked surface characterization and pull-out tests.

Ozone treatment introduces several polar groups into the surface of PET through oxidation and chain scission, resulting in increased wettability. [Ferreira, 2005]

Contact angle measurements were performed using the sessile drop method with a contact angle measuring system from Data Physic (Model OCA 15), equipped with a video CCD-camera and SCA 20 software. Static contact angles were measured by placing a water droplet [3.0 μl] onto the sample surface with an electronic control syringe. The angle was measured after 1 min of water contact with sample. Every contact angle was determined at four different spots on the sample. As expected, the wettability of PET surface increased as a function of ozonation time, as exhibited by the decrease in the static contact angle.

A major difference between the Infrared spectra of untreated and ozone-treated PET is related to the ratio between the bands at 1738 ($\upsilon_{C=O}$) (region from 1800 to 1650 cm^{-1}) and 1410 ($\upsilon_{C-H, \text{aromatic}}$) cm^{-1}. According to Table 2.4, this ratio is higher for ozone treated PET than for the untreated PET, thus showing that ozonation increased the –C=O group content in PET. Further, the treated films washed by distilled water and ethanol showed a lower ratio compared to the unwashed films, which meant solvents may extract components out of the samples. The ratio increased as a function of ozonation time. Changes in the IR spectrum of ozone-treated PET film were also observed in the range between 4000-3000 cm^{-1}, with the peak at 3550 cm^{-1}; this is assigned to the stretching of the terminal hydroxyl groups of PET. This peak overlaps with the

peak at 3430 cm^{-1}. The peak of 3290 cm^{-1} is assigned to the carboxylic O-H stretching vibration. The ratio increases for the first 3 h, thus showing that an increasing number of carboxyl groups are formed [Ferreira, 2005]. Results are shown in Figure 2.15.
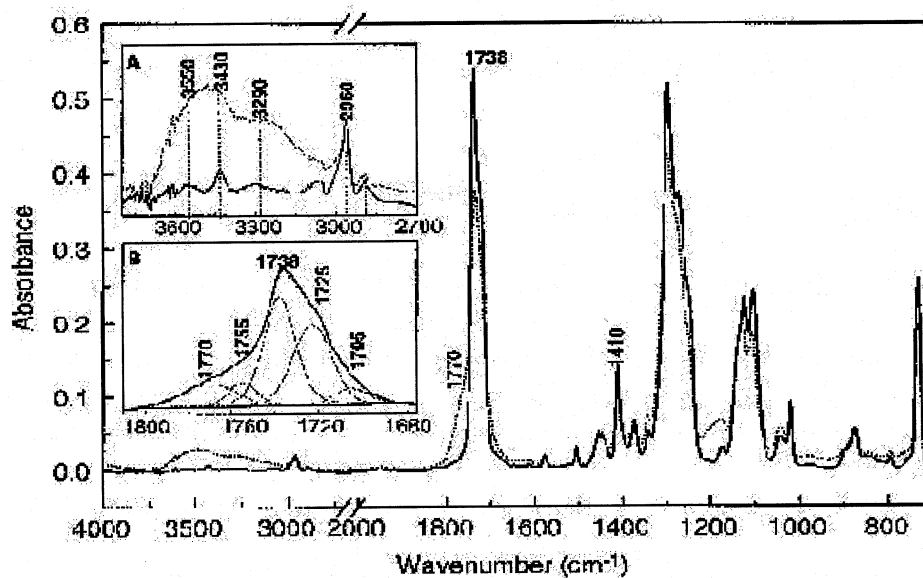
Figure 2.15 IR spectra of untreated and ozone treated PET film for 6 h [Ferreira, 2005].

2.2.3.4 Poly(tetrafluoroethylene) (PTFE) films reacted with hydrogen plasma and ozone gas mixture

Tu and Liu (2005) investigated surface grafting polymerization and modification on PTFE films by means of ozone gas treatment.

PTFE is extremely hydrophobic, with poor adhesive properties. Because of the strong bond of CF, hydrogen plasma treatment had to be applied to the PTFE film surface to break it, and then ozone treatment was conducted to bring the alkylperoxide and hydroperoxide to the surface in order to induce polymerization. Using this method, AAm monomers were grafted to the

ozonized films [Tu et al., 2005].

Table 2.4 Variation of normalized –C=O and COOH absorptions for ozone-treated PET films as measured by Infrared spectra [Ferreira, 2005].

Ozonation time (h)	(A1738/A1410) ozonated/ (A1738/A1410) untreated		(A3290/A2960) ozonated/ (A3290/A2960) untreated	
	Unwashed films	Washed films	Unwashed films	Washed films
1	1.088	1.083	4.491	1.747
3	1.170	1.128	6.838	2.407
6	1.295	1.212	6.571	3.554

Through the use of FTIR-ATR spectra, the grafted polymers were detected. The acrylamide structure in the resulting PTFE-g-PAAm film was characterized as having the absorption peak of the carbonyl group in amide (- NH-C=O), at 1662 cm^{-1}.

2.2.3.5 Other substrates reacted with ozone gas mixture

Wang and Kim's group (1999) researched hydrophilic modification of polypropylene microfiltration membranes by ozone-induced graft polymerization.

Suh et al. (2001) investigated the behavior of osteoblasts on a type I atelocollagen grafted ozone oxidized poly L-lactic acid membrane.
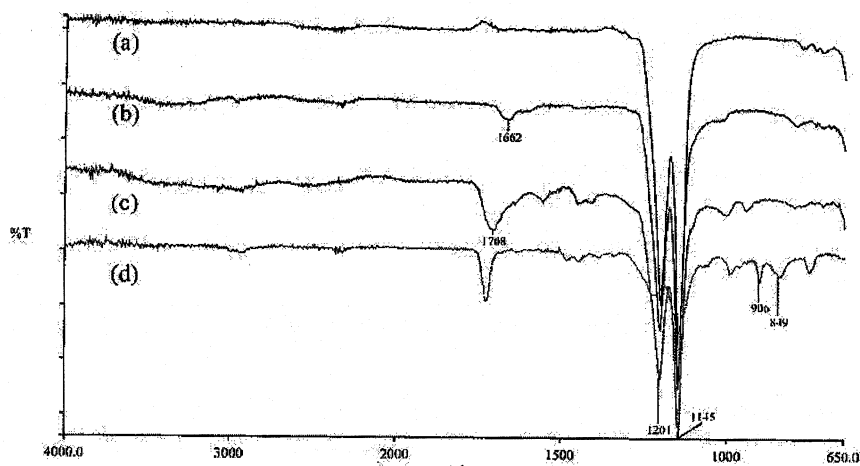
Figure 2.16 FTIR-ATR spectra of PTFE films, showing (a) pristine film; and grafted copolymerization with: (b) AAm; (c) AAc; and (d) GMA [Tu et al., 2005].

Matsumura et al. (2004) studied the surface modification of poly(ethylene-co-vinyl alcohol): hydoxyapatite immobilization and control of periodontal ligament cells differentiation through ozone exposure.

Kulik et al. (1993) studied Trypsin immobilization on to polymer surface through grafted layer and its reaction with inhibitors by ozonation.

Ko et al. (2001) studied immobilization of poly(ethylene glycol) or its sulfonate onto polymer surfaces by ozone oxidation.

Davidson et al. (2005) investigated surface studies of low molecular weight photolysis products from UV-ozone oxidized polystyrene, and also examined UV-ozone modification of plasma-polymerized acetonitrile films for enhanced attachment.

2.2.3.6 Polyolefins reacted with O_3 in aqueous phase

Dasgupta and his group (1990) investigated surface modification of polyolefins using ozone in aqueous phase for hydrophilicity and bondability. The relationship between ozone uptake (percent) and the intrinsic viscosity were studied. It was found that when the uptake increased, the intrinsic viscosity decreased; which meant that the molecular weight decreased and polymer chain scission had occurred. Figures 2.17 and 2.18 show the results.

On the other hand, carbonyl content (percent) increased [Dasgupta, 1990]. Figures 2.19 and 2.20 show the results.

The carbonyl and carboxyl contents generated with the ozone uptake were also studied, and were found to have increased with the ozone uptake percent.

The mechanism of ozone reaction was thought to be as follows [Dasgupta, 1990]:

$$O_3 \longrightarrow O_2 + O\cdot$$

$$O\cdot + O_3 \longrightarrow 2\,O_2\cdot$$

$$O\cdot + 2\,O_2 \longrightarrow O_3 + O_2\cdot$$

$$RH + O_3 \longrightarrow RO_2\cdot + HO\cdot$$

$$RO_2\cdot + RH \longrightarrow ROOH + R\cdot$$

$$R\cdot + O_2 \longrightarrow RO_2\cdot$$

$$ROOH + O_3 \longrightarrow RO_2\cdot + O_2 + HO\cdot$$
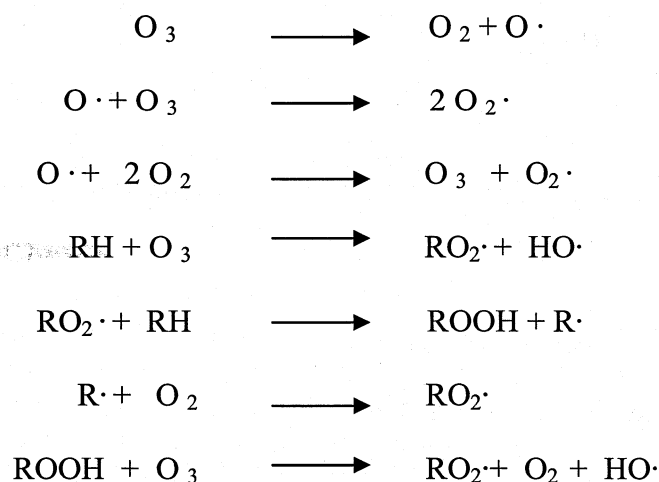
Radical ions can induce polymerization and can lead to chain scission.

The rate equation for the well-stirred batch reactor model may be expressed as [Dasgupta, 1990]:

$$\frac{dX}{dt} = K(1\text{-}E)\,[O] \qquad (2.1)$$

Where X = ozone uptake, g O_3 consumed / g pulp; t = time, min; K = rate constant, liter gas / g pulp min; E = efficiency, g O_3 consumed / g O_3 in feed; and [O] = concentration of ozone in feed gas, g O_3 / L gas at reaction temperature. Thus (1-E) [O] is the concentration of ozone in the gas leaving the reactor, which in the case of a well-stirred reactor model, is assumed to be equal to the concentration of ozone in the gas phase throughout the reactor.

The rate constant was calculated from experimental data using the equation:

$$K = \frac{X}{t(1-E)[O]} \qquad (2.2)$$

2.2.3.7 Polystyrene(PS), and poly(methyl methacrylate) (PMMA) substrates reacted with O_3 in aqueous phase

Takurou N. Murakami, Yoshinori Fukushima and their group (2003) investigated the possibility of the surface modification of hydrophobic PS and PMMA by ozone aeration, UV irradiation and combination of ozone aeration and UV irradiation (ozone/UV) in distilled water. The PS or PMMA was placed in a quartz test tube in the active oxygen generator for surface modification.
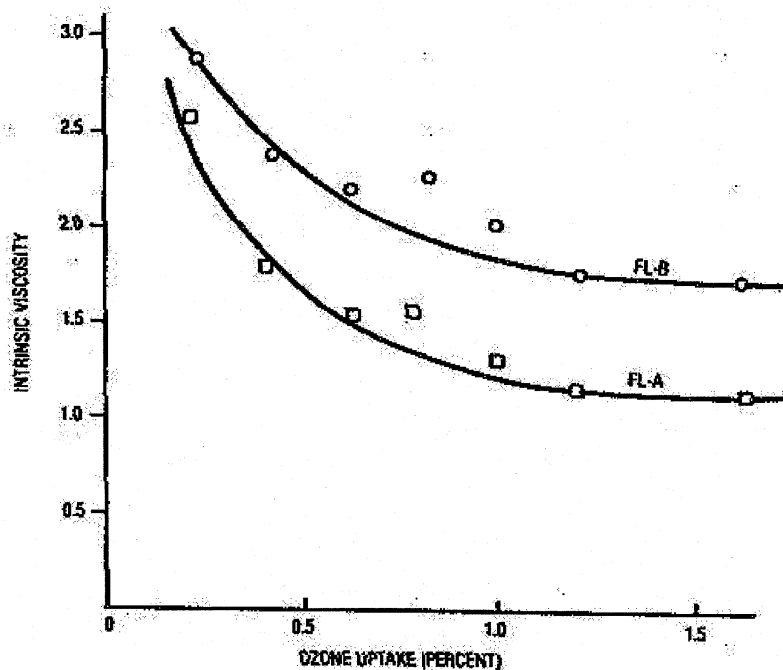
Fig 2.17 Intrinsic viscosity of polypropylene flake at various levels of ozone treatment. Flake FL-A and FL-B, which is FL-A-treated with a phenolic antioxidant stabilizer, are Hercules products. [Dasgupta, 1990]
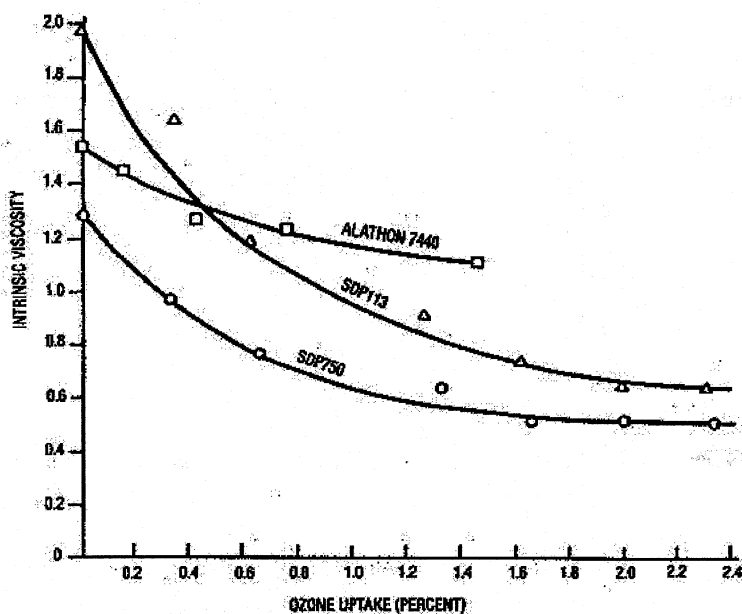
Fig 2.18 Intrinsic viscosity of polyethylene flake at various levels of ozone treatment. Alathon 7440 (DuPont) SPD-113 and SPD-750 (ARCO) have different molecular weights represented by intrinsic viscosity values.

[Dasgupta, 1990]
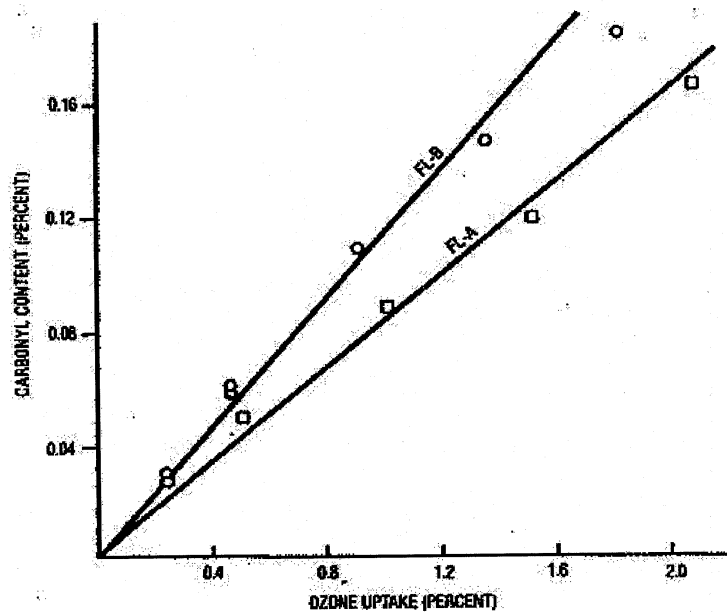
Fig 2.19 Carbonyl contents of ozonized stabilized and unstabilized polypropylene flake, FL-B and FL-A respectively.

[Dasgupta, 1990]
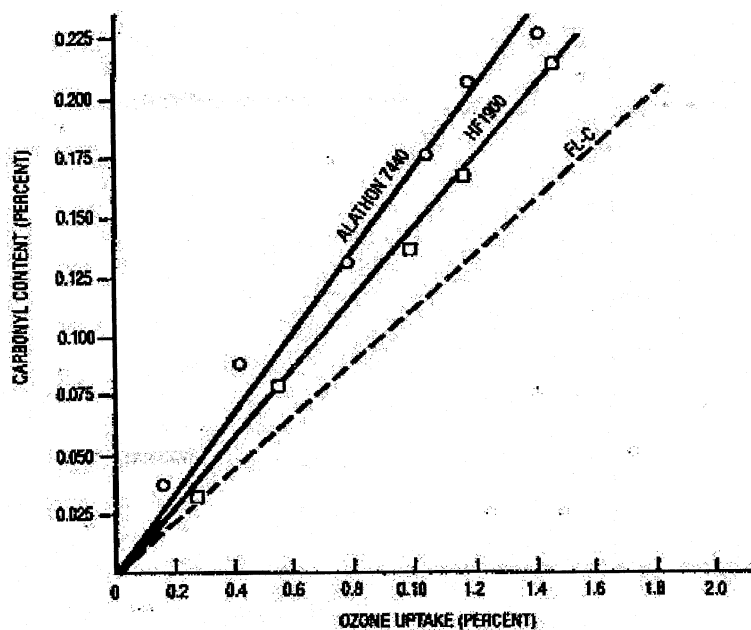
Fig 2.20 Carbonyl contents of ozonized polyethylene flake. Similar data for FL-C, a polypropylene flake provide a reasonable comparison.

[Dasgupta, 1990]

The contact angles of the treated samples were examined, and the contact angles of the treated PS films decreased with an increase in the treatment time. The most remarkable decrease was seen in the ozone/UV treatment. On the other hand, the contact angle on the treated PMMA film surfaces slightly increased to an equal extent after all three types of treatment [Murakami et al., 2003]. Figures 2.21 and 2.22 show the results.

The roughness of the virgin and treated film surfaces was examined by Atom Force Microscopy (AFM). The surface roughness of the PS film seemed to increase in the order of ozone, UV and ozone/UV treatments. Only slight roughness was observed on the PMMA film surfaces after treatments [Murakami, 2003]. The roughness increased because of the chain scission. Figures 2.23 and 2.24 show the results.
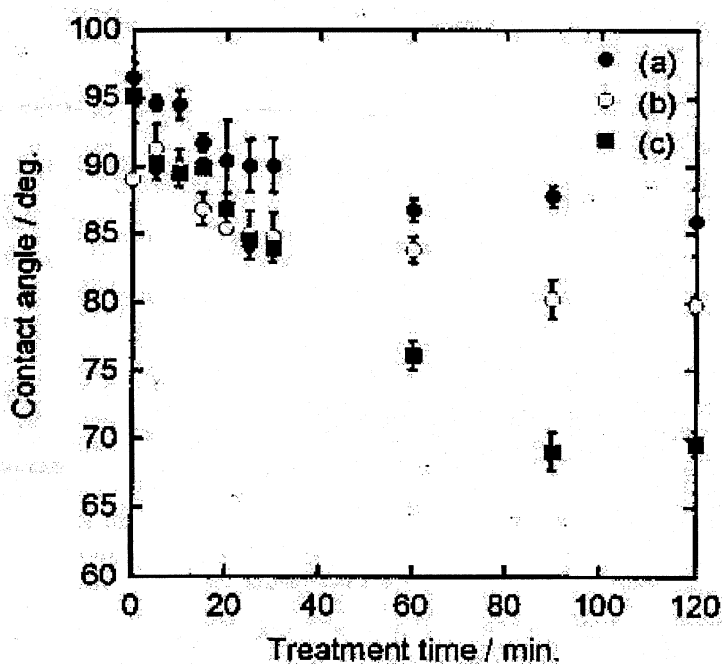
Fig 2.21 The contact angle of ultrapure water on PS films plotted against treatment time: (a), (b) and (c) correspond to ozone, UV and ozone/UV treatments, respectively. [Murakami, 2003]
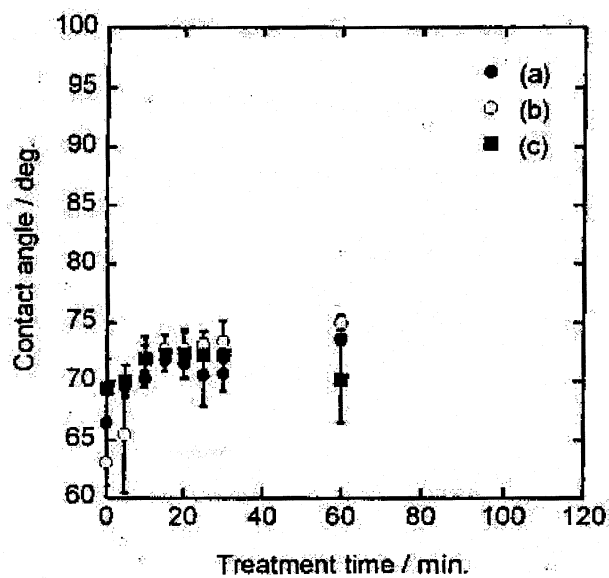
Fig 2.22 The contact angle of ultrapure water on PMMA films plotted as a function of treatment time: (a), (b) and (c) correspond to ozone, UV and ozone/UV treatments, respectively. [Murakami, 2003]
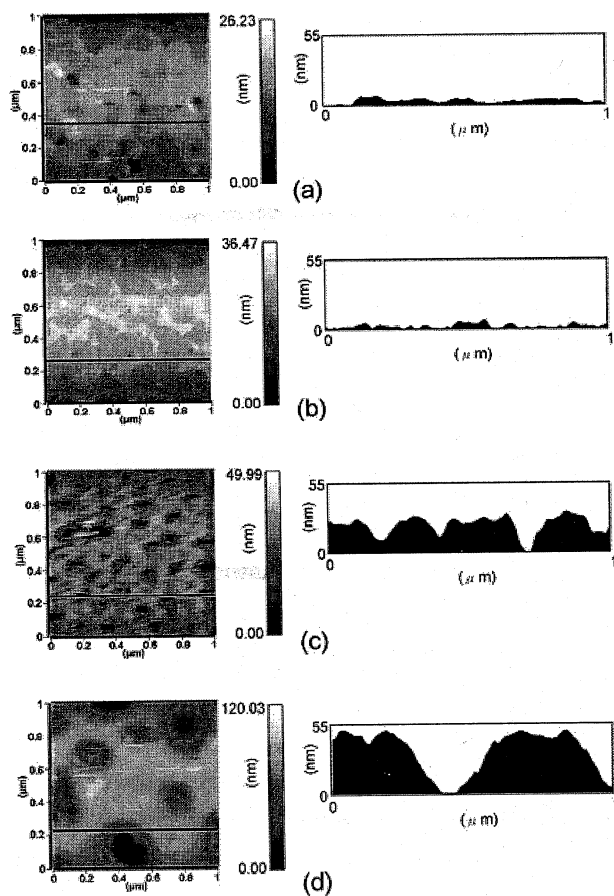
[Yuan et al., 2003]

Fig 2.23 AFM images of treated PS films with a height profile across the line shown in the image. (a) Freshly-prepared film before treatment. (b), (c) and (d) correspond to the images of the films after ozone, UV and ozone/UV treatments for 60 min, respectively. The measured area was 1 × 1 μm².
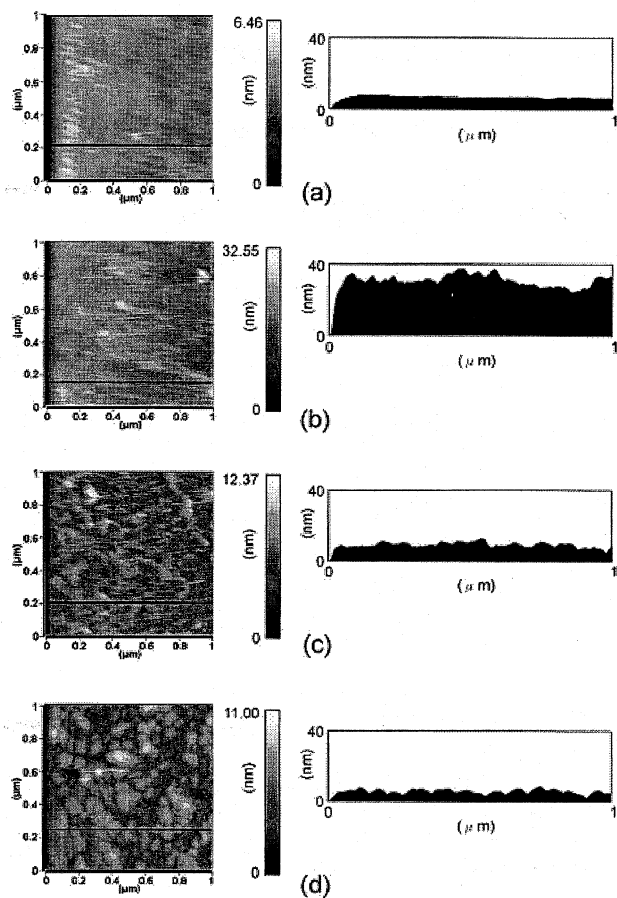
[Yuan et al., 2003]

Fig2.24 AFM images of treated PMMA films with a height profile across the line shown in the image. (a) Freshly-prepared film before treatment. (b), (c) and (d) correspond to the images of the films after ozone, UV and ozone/UV treatments for 60 min, respectively. The measured area was 1 × 1 μm².

2.3 Analysis methods

2.3.1 Peroxide measuring

2.3.1.1 Iodometric method

The concentration of peroxide introduced on and in the treated films was determined by the following method: 25 ml isopropanol was added to the sample, followed by 1 ml of saturated

potassium iodide and 1 ml of glacial acetic acid. The mixture was heated almost to the boiling point and kept there for 2-5 min, and titrated with standard sodium thiosulfate solution until the yellow color disappeared. It is possible to titrate solutions containing peroxides in as low of concentrations as 10^{-4} N to with 0.1 ml using 0.005N thiosulfate – for PU treatment [Yuan et al., 2003].

The concentration of peroxide introduced on and in the treated films was also determined spectrophotometrically by the following three methods:

2.3.1.2 Spectrophotometric iodide method

The treated films are put in benzene-isopropyl alcohol (1:6 by vol). Solution containing saturated Sodium iodide and 1 ppm ferric chloride is added, and kept at 60°C for 10 min. After addition of water to stop the reaction, the oxidized iodine is measured as triiodide anion from the absorbance of the solution at 360nm of UV [Ko, 2001].

2.3.1.3 DPPH method

The treated films are put in a benzene solution of 1,1-diphenyl-2-picrylhydrazyl (DPPH, radical scavenger) and kept at 70°C for 24 h to decompose the peroxides. The DPPH molecules consumed by binding to the radicals formed are quantified from the difference in transmittance at

520 nm between the virgin and the treated film using 1.18×10^4 Lmol^{-1} cm^{-1} (the absorption coefficient) as the molar absorptivity of DPPH [Wang et al., 2000].

2.3.1.4 Peroxidase method

The reduction of by glutathione (GSH), catalyzed by glutathione peroxidase, is followed by measuring the coupled oxidation of nicotinamide adenine dinucleotide phosphate (reduced) (NADPH) in the presence of glutathione reductase. The reaction scheme is represented as [Fujimoto, 1993]:

$$2\,GSH + ROOH \xrightarrow{\;GSHperoxidase\;} ROH + GSSG + H_2O$$

$$GSSG + NADPH + H^+ \xrightarrow{\;GSSGreductase\;} 2\,GSH + NADP^+$$
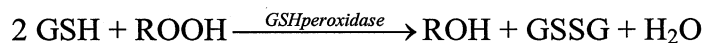
The treated films are placed in the solution at 25°C for 30 min, and the extent of NADPH oxidation is determined from the absorption at 340 nm with the molar absorptivity of NADPH of 6.2×10^3 L mol^{-1} cm^{-1}.

The peroxide concentrations determined with the iodide and peroxidase methods are shown in Table 2.2. And it was found that the iodide method detected the highest concentrations.

2.3.2 IR – ATR-FTIR measurement

Infrared (IR) spectroscopy is a chemical analytical technique, which measures the infrared intensity versus wavelength (wave number) of light. Infrared spectroscopy detects the vibration characteristics of chemical functional groups in a sample [www.nuance.northwestern.edu].

Attenuated total reflection infrared spectroscopy (ATR-IR) is used for analysis of the surface of materials. It is also suitable for characterization of materials which are either too thick or too

strongly absorbing to be analyzed by transmission spectroscopy. For bulk material or thick film, no sample preparation is required for ATR analysis. ATR-IR was performed on a spectrophotometer (Perkin-Elmer, Model 2000) coupled with an ATR (split-pea) and a nitrogen-cooled mercury cadmium telluride (MCT) detector. One hundred scans were performed with a resolution of 4 cm^{-1}. In ATR-IR measurements, the penetration depth (Dp) of the radiation within the PET film was calculated according to Harrick equation:

$$Dp = \frac{1}{2\pi N_C (\sin^2 \theta - N_{sc}^{~2})^{1/2}}$$
(2.3)

Where υ is the wave number (cm^{-1}), N_c is the refraction index of the crystal, θ is the incidence angle of the infrared radiation into the crystal (45°), and N_{sc} is the ratio between the refraction index of the PET sample and the crystal [Ferreira, 2005].

A Fourier transform spectrometer is usually used to measure the spectrum of the light transmitted through a laboratory sample. FTIR spectra were taken on a Bomem MB-100 Spectrometer (Canada) equipped with a DTGS detector in the micro-ATR mode. A germanium cell was used as the internal reflection element, and incident angle was fixed at 45°.

2.3.3 Electronic microscopy – SEM (scanning electron microscopy)

The scanning electron microscope (SEM) is a type of electron microscope capable of producing high-resolution images of a sample surface. Due to the manner in which the images are created, SEM images have a characteristic two or three-dimensional appearance and are useful for judging

the surface structure of the sample [http://en.wikipedia.org].

The instruments used in the reference are:

A JSM-35 microscope (JEOL, Japan) at 25 kV. Samples were dried and pre-coated with gold at 0.2 Torr before the SEM analysis; or a JOEL JSM 5300 SEM operated at 10-15 kV was used to analyze fracture surfaces of untreated membrane and the freed in liquid nitrogen [Gatenholm, 1996].

2.3.4 Contact angle test

The contact angle is the angle at which a liquid interface meets the solid surface. Contact angle measurements were performed using the sessile drop method with a contact angle measuring system (goniometer) from Data Physics equipped with a video camera and software in a computer.

Untreated or treated films (2 x 2 cm^2) were placed in a closed, thermostatic chamber (25°C) saturated with water in order to prevent evaporation. Static contact angles were measured by placing a water droplet (3 µl) onto the sample surface with an electronically regulated syringe. The angle was measured after 1 min of water contact with the sample. Subsequently, the water droplet was slowly increased or decreased in volume in order to obtain the advancing or receding water contact angle [Ferreira, 2005].

The contact angle concept is of fundamental importance in all solid-liquid interfacial phenomena. The contact angle that a liquid makes with an ideal solid surface is termed the intrinsic contact angle. The first equation that was developed for the intrinsic contact angle was the well-known

Young equation, which reads [Wolansky, 1998]:

$$\cos\theta_Y = \frac{\sigma_{sf} - \sigma_{sl}}{\sigma_{lf}} \qquad\qquad (2.4)$$

Where θ_Y is the Young contact angle (i.e., the intrinsic contact angle as calculated from the Young equation), and σ_{lf}, σ_{sl}, and σ_{sf} are the liquid-fluid, solid-liquid and solid-fluid interfacial tensions, respectively.

2.3.5 X-ray – photoelectron spectroscopy (XPS) analysis.

XPS, also known as ESCA, an abbreviation for Electron Spectroscopy for Chemical Analysis, is a surface chemical analysis technique that can be used to analyze the surface chemistry of a material in its "as received" state [http://en.wikipedia.org].

Using a monochromatic AIK x-ray source, a detection system with a 30° solid angle acceptance and a hemispherical analyzer in an SSX-100 spectrometer (Surface Science Instruments; Mountain View, CA), a 5 eV flood gun was applied to compensate for the surface charging of polymer samples. The X-ray spot size (analyzing area) on the sample surfaces was about 1000 μm in diameter. A standard 55° take-off angle (the angle between the surface normal and the axis of the analyzer lens) was used for surface scans. Surface compositions determined from ESCA spectra were used to examine the oxygen content of the ozone-treated surfaces. The hydrocarbon peak in high-resolution Cls spectra was assigned at 285 EV [Gatenholm, 1996].

2.3.6 Differential scanning calorimeter (DSC)

DSC is a thermoanalytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference are measured as a function of temperature [http://en.wikipedia.org].

Using a Perkin-Elmer DSC 7 calorimeter, the heating rate employed was 10° C/min, and typical sample weights were about 10 mg. A reference value of Δ H of 165 J/mol (for 100% crystalline PP) was used for the calculations of degree of crystallinity [Gatenholm, 1996].

2.3.7 Carbonyl content: An infrared method

The ozonized samples are pressed into 10 mil films with a 25-ton (Model M) Carver press at 190° C. The percent carbonyl is calculated from the height of the carbonyl band (1710-1720cm^{-1}) using Beer's law (shown in appendix XII). An average C=O is determined from a series of standards, such as stearic acid, in solution [Dasgupta, 1990].

2.3.8 Carboxyl content

Carboxyl content was examined by a titration method [Dasgupta, 1990].

The ozonized samples were weighed to the nearest 0.0001g and dissolved in picoline, heated to reflux and then titrated with sodium laurylate in o-dichlorobenzene, using a potentiometric titrator.

2.4 Grafting polymerization

The grafting of monomers with a vinyl function groups to ozonized polyethylene, polypropylene and other materials was studied previously. There are several routes one may follow to achieve this goal, and the grafting steps may be carried out under various ambient conditions. The monomers may be used in the vapor phase, liquid phase, in pure or solution, possibly with dry substrates, and the medium may be either organic, aqueous, or a mixture of the two [Dasgupta, 1990]. The grafting reaction was initiated by heat or the addition of $FeCl_2 \cdot 2H_2O$ to discompose the peroxide into the radicals O· and ·OH, which induce the polymerization.

Generally, the ozonation of polymers and grafting polymerization can be illustrated by the following schematic drawing [shown in Figure 2.25]

:
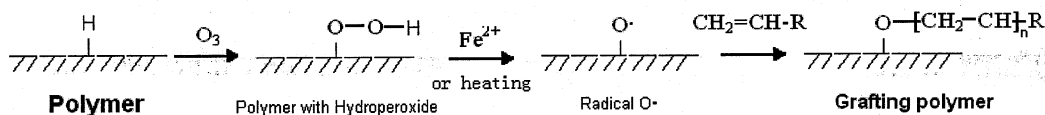
Fig 2.25 Schematic drawing of ozonation and grafting process [Robin, 2004].

2.4.1 The monomers for grafting polymerization

Monomers used for graft polymerization/immobilization were:

- Acrylamide, Acrylic acid [Dasgupta, 1990] [Tu et al., 2005]

- Maleic anhydride [Dasgupta, 1990]

- Vinyl chloride [Robin, 2004]

- HEMA-2-hydroxylethyl methacrylate [Gatenholm, 1997]

- 2-methacyloxylethyl phosphorylchotine (MPC) [Xu et al., 2003]

- N,N-dimethyl-N-methacryloyloxyethyl-N-(3-sulfopropyl)-

  ammonium (DMMSA) [Zhou et al., 2005]

- H2N-PEG-NH2, PEG, PEG-SO3 [Ko et al., 2001]

2.4.2 Grafting methods

2.4.2.1 Grafting AAc, AAm onto ozonized substrates

Kulik et al. (1997) studied the monomers grafted to ozonized LDPE film. Ozonized LDPE films were washed in DI water for 2 hrs to remove ozone absorbed into films. Reducing agents, such as ferrous sulfate, ascorbic acid, and sodium borotetrahydride were employed to reduce the surfaces after ozone treatment. Free radical graft polymerization of water soluble monomers to ozonized films was carried out with the use of ceric ions. Grafting solution (40 wt. % of distilled acrylic acid or methoxy(polyethylene glycol 230)methacrylate) was degassed with nitrogen bubbling prior to graft polymerization, which was carried out under a nitrogen atmosphere for 40 min at room temperature. Grafted polymer films were washed in water for 4 h at 70°C and then in isopropyl alcohol at 40°C for 2 hrs.

Tu et al. (2005) and his group studied the AAm monomers grafted to poly (tetrafluoroethylene) films. The ozonized, activated films immersed in 50 ml solutions of AAm monomers in isopropanol (IPA), the monomer concentrations were 20 wt% for AAm. The solutions were degassed by argon purge and frozen degas process. The reaction system was heated to 80°C and reacted at 80°C for 24 h, and then was quenched in an ice bath. Films were drawn out, washed with water and acetone in an ultrasonic washer and dried at room temperature under vacuum.

2.4.2.2 2-(Dimethylamino) ethyl methacylate (DMMCA) grafting polymerization

The ozonized films were degassed under the vacuum at room temperature for 60 min. Graft polymerization onto silicone film was carried out at 50°C with a deaerated, specific concentration aqueous solution of DMMCA and 3.0×10^{-4} mol/l Fe^{2+} ion in the sealed tube. The role of the Fe^{2+} ion was to strain homopolymerization. The polymerization time was 24 h. To remove the homopolymer from grafted films, the grafted films were first washed with 40-50°C saline water, and then washed by ultrasonic for another hour [Zhou et al., 2004]. Figure 2.26 illustrates the procedure.
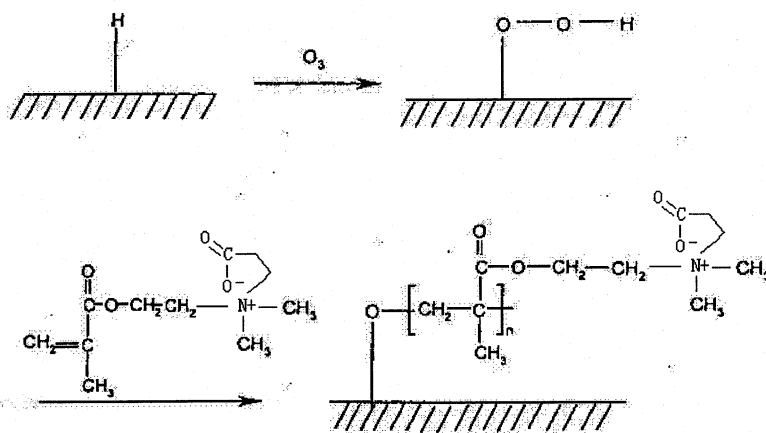
Fig. 2.26 Schematic Illustration of DMMCA grafting onto and modifying polymer surface [Zhou et al., 2004].

DMMSA and MPC graft polymerization was also studied by the Lin's groups using this grafting method.

2.4.2.3 HEMA grafting polymerization

The ozone-treated polypropylene membrane was soaked in ethanol for 10 min and placed in HEMA solution. The grafting reaction was initiated by the addition of $FeCl_2·2H_2O$. Graft

polymerization was allowed to proceed in a shaking incubator at 40°C with a shaking speed of 150 rpm for 2-12 h. The overall concentrations of HEMA and the catalyst ($FeCl_2\cdot2H_2O$) were 5% (v/v) and 10^{-4}M, respectively. When the polymerization was finished, the membrane was washed in a Soxhlet extraction apparatus with hot methanol to remove residual monomers and homopolymers. Figure 2.27 illustrates the procedure.
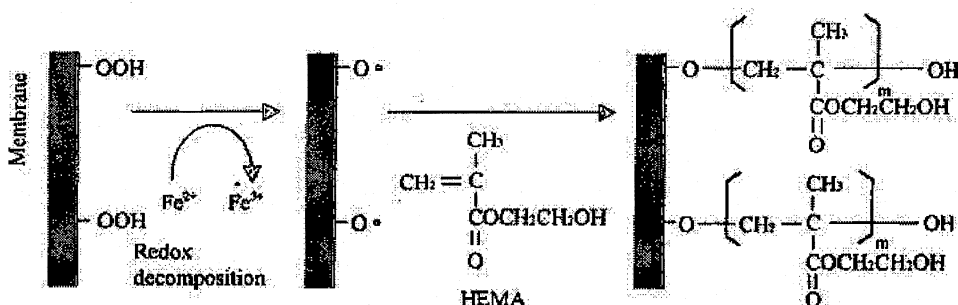
Fig. 2.27 Schematic illustration of ozone-induced graft polymerization [Wang et al., 1999].

2.4.2.4 PEG, PEG-SO₃, H2N-PEG-NH2, and H2N-PEG-SO₃ immobilization

Immobilization is another grafting method induced by peroxide, the difference with other grafting polymerization is the large molecules directly connected to the films instead of monomers polymerization.

After ozonation, the films were immersed immediately into 20 wt. % aqueous solution of PEG, PEG-SO₃, H2N-PEG-NH2, or H2N-PEG-SO₃ in glass ampoule. After vigorous degassing by purging N_2, the ampoule was sealed and kept at 60°C for given periods of time. The PEG-immobilized films were washed by super pure distilled water for 3 days to remove the untreated PEG derivatives. Figure 2.28 illustrates the procedure.
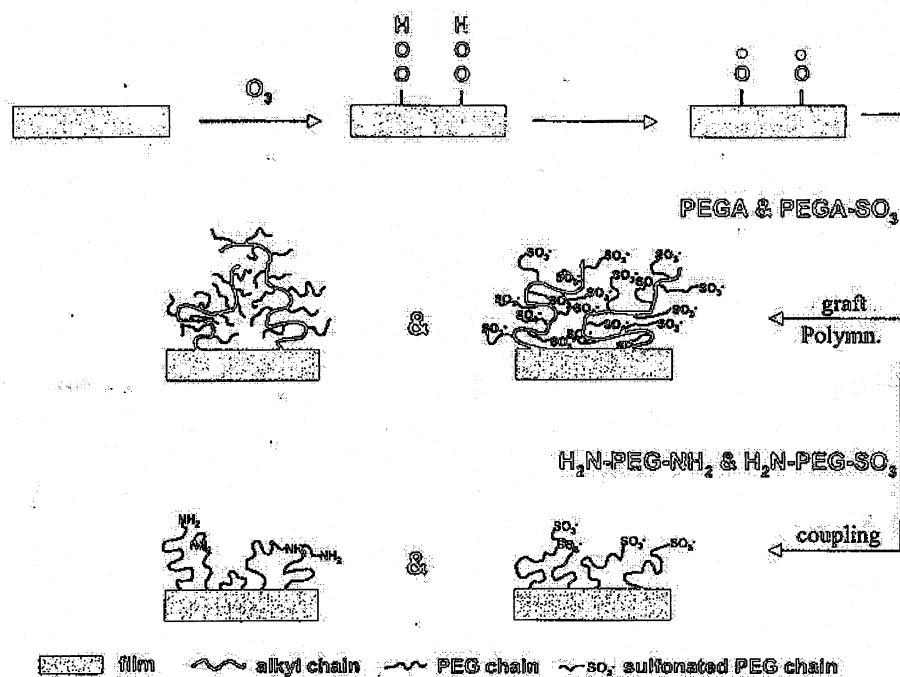
Fig. 2.28 Schematic Illustration of PEG immobilizing onto and modifying polymer surface [Ko et al., 2000].

CHAPTER 3

EXPERIMENTAL METHODOLOGY

3.1 Materials

3.1.1 Selected polymer films

- Biaxial oriented polypropylene (BOPP) film, 20 μm, T523-3 from AET film Co. Ltd.

- High density polyethylene (HDPE) blowing film, 15 μm, Exopack – Newmarket, Ltd.

- Biaxial oriented polyethylene terephthalate (PET) film, 12 μm, from Pilcher Hamilton Corporation, South Carolina, USA

The BOPP and PET are biaxial oriented film, HDPE is blown film, all commercial, and no coating or co-extrusion layer. Density of BOPP is 0.905 g/mm^3, PET is 1.41g/mm^3, and HDPE is 0.96g/mm^3. In this study polymer films cut into 1.5 x 10-inch strips for ozonation.

According to the Plastic News report, the BOPP global demand in 2001 was 6.1 billion pounds total[www.plasticsnews.com]; global demand for polyester film was over 1.5 million metric tons (eg. 3.3 billion pounds) in 2004 [www.sriconsulting.com]; by 2006, global PE productivity have reached 78.5 million tons, and demand, 62.92 million tons[www.wanfangdata.com]. These three films covered the most in application, which is the reason they are chosen in this study.

3.1.2 Other materials

- Distilled water used as an aqueous medium

- Acrylamide in isopropanol alcohol (IPA) solution, used for graft polymerization of monomers

- 99.7% isopropanol alcohol and glacial acetic acid, solid potassium iodate, and solid sodium thiosulfate were used as titration reagents. All were analytical grade and were obtained from Sigma-Aldrich (Toronto, Ontario).

- Other organic and inorganic materials used in this study were reagent grade and supplied by Sigma-Aldrich.

3.2 Experiment set-up

3.2.1 Experiment set-up for film ozonation

Figure 3.1 is a picture of the ozone generation and reaction system, and Figure 3.2 shows a schematic diagram of the ozonation reactor set-up used in this project. Table 3.1 describes the equipment of the ozone reaction system.

Fig. 3.1 Picture of the ozone generation and reaction system

3.2.2 Experiment set-up for graft polymerization

Figure 3.3 illustrates the AAm graft polymerization system, and Table 3.2 lists the equipment

used in graft polymerization
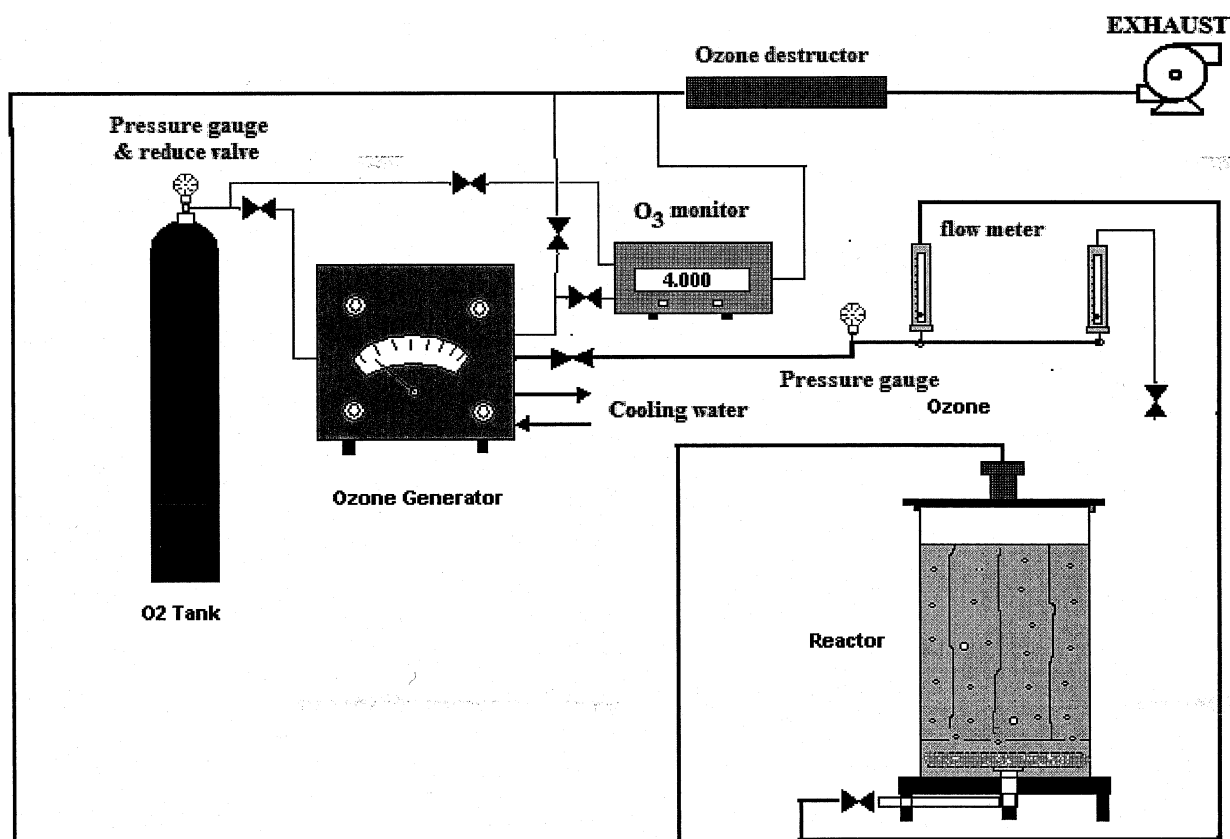
Fig 3.2 Schematic illustration of the ozone generation and reactor system

3.3 Experimental procedure

3.3.1 The ozonation procedure:

- Compressed oxygen gas was released from the O_2 cylinder, and pressure was reduced to

  20 psi by pressure reducing valve;

- Compressed oxygen gas was fed to the ozone generator (PCI-WEDECO Environmental Technologies, Model GL-1); flow was controlled by flow meter and pressure gauge;

- Cooling water was used to remove the heat from the generator;

Table 3.1 Description of the equipment used in the ozone generation and reaction system

Equipment	Description
Oxygen Cylinder	Steel cylinder, regular size, from BOC Canada
Pressure meter	Anti-corrosion
Pipes	PTFE 1/4"
Ozone generator	PCI-WEDECO Environmental Technologies OZONE GENERATOR, Model GL-1
Adjustable valve	Stainless steel
Three-way valve	Stainless steel
Ozone monitor	PCI-WEDECO Environmental Technologies ozone monitor
Ozone flow meter	0-10 l adjustable, anti-corrosion
Ozone pressure meter	0-50 psi
Adjustable valve	Stainless steel
Pipes	PTFE 1/4"
Diffuser	Ceramic, 2-5μ porous hole size, 7.5-inch diameter
Reactor vessel	12.6 L, transparent
Exhaust pipes	1/4" and 3"
Exhaust catalyst	Ozone decomposition
Exhaust fan	Anti-corrosion

- Ozone was generated at a controlled rate to ensure that it was a certain percentage of the oxygen gas mixture (rate was controlled by adjusting the output power knob) in the generator and was released in three directions: to the reactor (flow rate and pressure was measured and adjustable), another to be released, and the third to the ozone concentration monitor (PCI-WEDECO Environmental Technologies OZONE MONITOR);

- Controlled ozone and oxygen gas mixture flow led to the reactor through the diffuser (ceramic, 2-5μ porous hole size, 7.5-inch diameter), through which it was uniformly diffused in the aqueous phase or gas phase in the reactor.

- Pretreated, precisely cut, specific samples were fixed in the reactor prior to the start of the reaction. Samples reacted with ozone at set concentrations and for set reaction times.
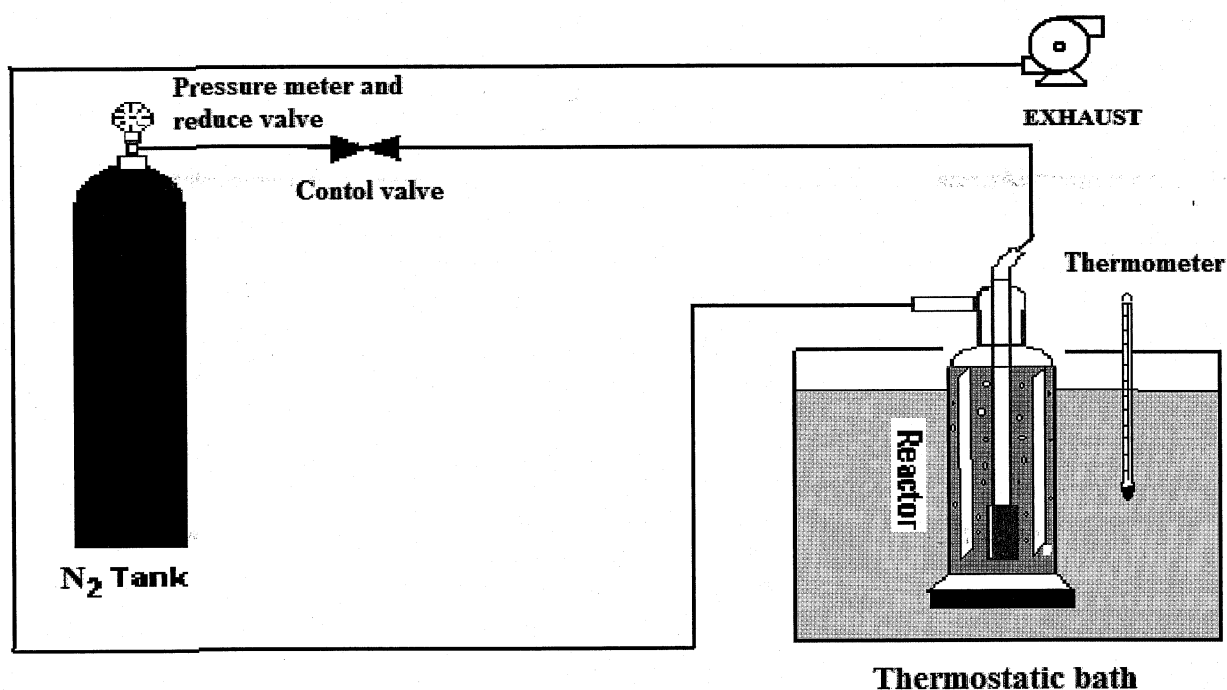
Fig 3.3 Schematic illustration of AAm grafting polymerization system

Table 3.2 Description of the equipment used in graft polymerization reactor system

Equipment	Description
Nitrogen cylinder	Steel cylinder, regular size, From BOC Canada
Pressure meter and pressure reducing valve	Special for N_2, Ar_2 application
Pipes	PTFE 1/4"
Adjustable valve	Stainless steel
Thermostatic bath	VWR Scientific Products, Model 1187
Reactor	600 ml washing bottle, glass vessel, ceramic diffuser
Exhauster	Share with the O_3 exhauster fan
Thermometer	0-100°C
Ultrasonic cleaner	VWR International, Model 50D

- Samples were taken out when the reaction was finished. Samples were vacuum dried at room temperature;

- Dried samples were sent to be analyzed;

- Dried samples were sent to the next step for graft polymerization.

3.3.2 The six steps of the procedure:

The experiments were implemented using the following six steps:

Steps I : Ozonate selected polymer films at room temperature (22-25°C) using ozone in aqueous phase, and analyze the peroxide groups generated and the mechanical strength effects.

Steps II: Ozonate selected polymer films in the gaseous phase and analyze the peroxide and mechanic strength.

Table 3.3 shows the reaction conditions for the above-mentioned steps.

Table 3.3 Description of experimental steps in this research

Step	Reaction medium	Substrate	Applied ozone dose (wt%)	Gas flow rate (L/min)	Gas pressure (psi)	Reaction time (hr)	Reactor volume (L)
Step I	Aqueous (DW)	HDPE, PET, BOPP	3.7	10	14	15 min to 5 h	10.5
Step II	Gaseous	HDPE, PET, BOPP	3.7	10	14	15 min to 4 h	12.6
Step III	Aqueous (DW)	HDPE	1.0 to 4.0	10	14	1.0	10.5
	Gaseous	HDPE	1.0 to 4.0	10	14	1.0	12.6
Step IV	Aqueous (DW)	HDPE	1.0	10	14	15 min to 2.5 h	10.5
Step V	Solution pH: 2 to 11	HDPE	1.0	10	14	1.0	10.5
Step VI	AAm solution	HDPE	1.0	10	14	1.0	500 ml
Remark:	All the reactions except graft polymerization were carried out at room temperature. DW indicates the distilled water						

Step III: Based on the above experimental results, study the effect of the applied dose.

Step IV: Based on the result of step III, select a suitable ozone dose, study the effect of reaction time.

Step V: Investigate the effects of pH at the selected applied ozone dose from Step III and the ozonation time from IV.

Step VI: Investigate the effect of graft polymerization. The monomer used was AAm.

3.4 Experimental design

3.4.1 Ozonation in aqueous phase

Pretreatment: sample strips were washed with distilled water, and soaked in distilled water for half an hour, then dried at room temperature.

10.5 L distilled water was placed in the reactor. Prewashed pieces of film were fixed to the stainless steel frame to avoid sticking to or overlapping with one another, and put into the aqueous reactor; polymer films reacted with ozone according to the ozonation procedure.

After ozonation, the samples were taken out according to the desired reaction time. The water was removed with clear tissue paper and samples were vacuum dried at room temperature (22-25°C) for one hour. Dried samples were sent for analysis and further treatment.

The ozone applied doses were all set at 3.7wt% both in aqueous and gaseous phases' ozonation. In the study we first wanted to obtain the maximum effects of ozonation, 3.7wt% applied ozone dose is the maximum concentration the generator can provide stable and keep long time running under the set-up flow rate and pressure.

3.4.2 Ozonation in gaseous phase

For gaseous phase ozonation, the procedure was analogous to aqueous phase ozonation, except that there was no water inside the reactor.

3.4.3 Investigation of the ozone dose and pH value effects on specific films

The results of samples reacted with ozone in the aqueous and gaseous phases at the same O_3 applied dose and for the same treatment time were compared. It was determined which specific film had the fastest reaction rate of peroxide production and the slowest rate of decrease in mechanical strength in the aqueous phase.

The investigation of the reaction conditions were as follows:

3.4.3.1 The study of the effect of applying different ozone doses

Both in the aqueous phase and the gaseous phase, treatment time was set at one hour, and different applied ozone doses, from 0.5 wt% to 4.0 wt% were studied to determine which dose would result in the highest peroxide content and maintain the highest mechanical strength. The results were compared.

3.4.3.2 The study of the effect of applying different ozonation times at 1.0 wt% ozone dose

Based on the results of section 3.4.3.1 above, the O_3 concentration was set at 1.0%wt, and different reaction times, from 15 min to 2.5 hrs, were used, to study the results to determine which reaction time yielded the highest peroxide content and maintained the highest mechanical strength.

3.4.3.3 The study of the effect of varying pH value in aqueous phase reactions

In aqueous phase reactions, O_3 concentration was set at 1.0%wt and treatment time at one hour, and pH value was varied from 2 to 11, and the results were studied.

3.4.4 Graft polymerization of the specific film under optimized conditions

The activated films ozonized under the optimal conditions were immersed in 500 ml solutions of AAm monomers in IPA. The monomer concentration was 20%wt of AAm. The solution was degassed by Nitrogen purging and frozen degassing process. The reaction and cleaning methods were according to Tu et al. (2005) and his group's method introduced in 2.4.2.1.

Dried samples were taken to examine by means of FTIR, contact angle and scanning electron microscope.

3.5 Analytical methods

The following analytical methods were used in this study:

3.5.1 Standard metric iodide method

Solutions were prepared using these ratios: 25 ml isopropanol : 1 ml glacial acetic acid + excess solid KI. Solutions were stirred enough to make sure KI dissolved to saturate the solution. 50 ml

of solution was added to the samples (three pieces of film with the dimensions of 1.5 in x 10 in). The mixture was heated almost to boiling (83-84°C) for 2-5min, and then titrated with 0.001N standard sodium thiosulfate solution until the yellow color disappeared. The consumption of 0.001N standard sodium thiosulfate was recorded, and the peroxide content was calculated.

Peroxide/hydroperoxide reacts with sodium iodate to produce iodine in acidic environment, and iodine can be precisely titrated with standard sodium thiosulfate solution. Detailed calculations can be found in Appendix I. Figure 3.4 exhibits the iodometric titration method. Figure 3.4 illustrates the equipment.

3.5.2 Tensile strength and elongation

A Universal Testing Machine (UTM, LLYOD Instrument LR 5K, UK) was used to measure tensile strength and elongation. Samples were prepared as ASTM D638 Type V, and the tensile strength was determined at a cross-head speed at 10 in/min. Sample width was 1 inch, jaw distance was 1 inch, and speed was 10 in/min. The top, middle, and bottom positions of the samples were checked each time.

Figures 3.5 and 3.6 are photos of the Universal Testing Machine.
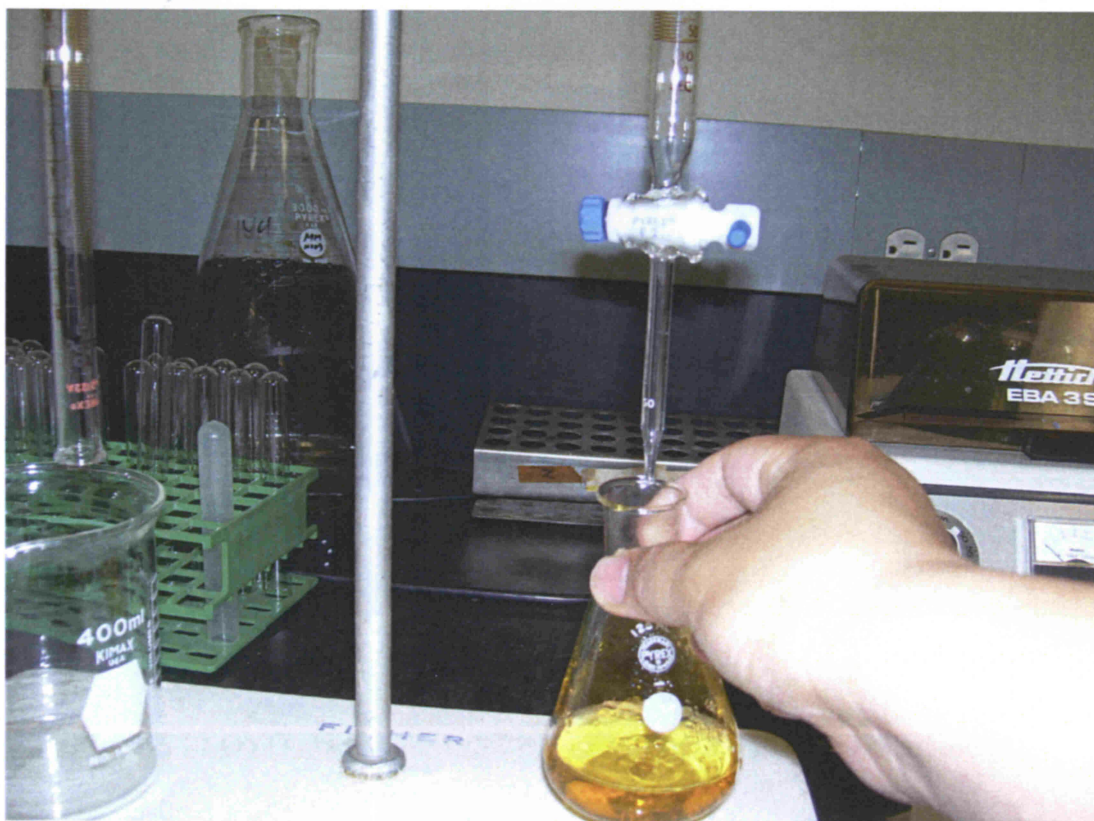
Fig. 3.4 Iodometric titration

3.5.3 FTIR

FT-IR (Perkin Elmer Spectrum One, V3.01 instrument) was used to examine functional groups on the surface of polymer films. The wavelength scanned was 450nm-4000nm.

- For Polyolefin, the peaks of C=O are at 1710 to 1750 cm^{-1}; and C-O-C are at 1080 to 1110 cm^{-1};

- C-H stretching and vibration are from 2850 to 3300 cm^{-1}

- For Polyester, peaks of C=O are at 1800 and 1650 cm^{-1}; aromatic C-H at 1410 cm^{-1};

- O-H peak at 3290 cm^{-1} [carboxyl] and 3550 cm^{-1} [hydroxyl]

- Other functional group peak values are shown in Appendix V.

[Yuan et al., 2002] [Mitchell et al., 2005] [Davidson et al., 2004]

Fig. 3.5 LLOYD machine   **Fig. 3.6** LLOYD machine
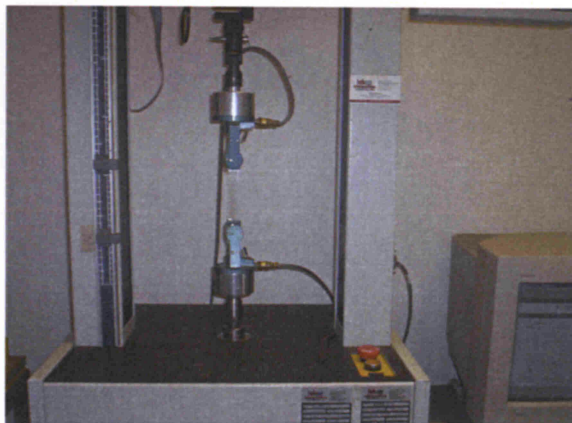
3.5.4 Contact Angle

The contact angle of the film surface was measured to quantify the change in its hydrophilicity. The film samples were placed on a goniometer (Rame Hart, Model 100-00-115, NJ, USA), a sessile drop of super-pure water was placed on the film sample, and then the static angle was measured. Figures 3.7 and 3.8 are photos of the goniometer.

3.5.5 SEM

Scanning Electron Microscope (SEM) pictures of the virgin, oxidized and grafted film samples were taken with a JSM-35 microscope (JEOL, Japan) at 10-15kV. Samples were precoated with gold at 0.2 Torr before the SEM analysis. Samples were observed under 2500 and 5000 times magnification.
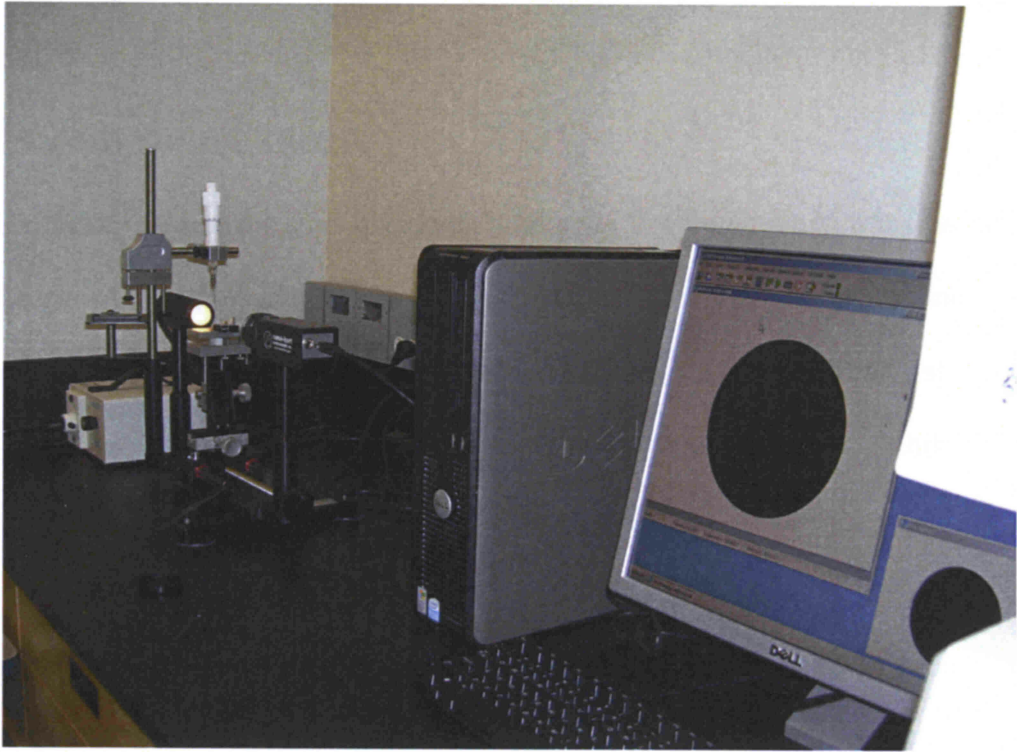
Fig. 3.7 Goniometer

Fig. 3.8 Goniometer

CHAPTER 4

RESULTS AND DISCUSSION

The main and most important results presented in this work were obtained from ozone treatment of selected films in an aqueous medium. Some of the results obtained from ozone gas mixture treatment were obtained just for comparison. HDPE became the main substrate studied here for effects of operating parameters and for graft polymerization, because it exhibited a unique character compared to the other two films.

Through inducing oxidization by ozone to modify film surfaces, peroxide groups are easily generated on the surface. Those peroxides provide active species which initiate graft polymerization with vinyl functional group monomers. Consequently, hydroxyl, carboxyl or amine groups can be brought to the surfaces of the polymers. The ozone oxidation time and applied ozone dose can readily control the amount of peroxide production. Different polymer substrates respond to ozone oxidation differently. The results will be presented one by one in the following paragraphs.

The different tensile strengths and percentages of elongation at break for the blank and treated samples follow a certain order for different film substrates. Generally, the decrease in tensile strength and the decrease in elongation at break result from cross-linking reactions that occur as a result of ozone exposure, causing molecular chains to be stiffened. Also, the increase in crystal structure is the main factor in the stiffer, more brittle character of the films; and the reverse holds true for the increase in amorphousity [Michael, 2004].

4.1 Ozone oxidation of HDPE

4.1.1 Peroxide generation in aqueous and gaseous phase ozonation

The HDPE films were ozonated in distilled water and in ozone-oxygen gas mixture, respectively. HDPE strips (1.5 in x 10 in) were fixed in the reactor. For aqueous ozonation, and reaction time was set at 15 min, and 0.5, 1.0, 1.5, 2.0, and 2.5 hrs.

For gaseous ozonation, reaction time was set at 15 min, and 0.5, 1.0, 1.5, 2.0, 2.5 and 3.5 hrs.

The applied ozone dose was 3.7 wt% for both aqueous and gaseous ozonation, and ozonation was conducted under room temperature (22-25°C).

Figure 4.1 presents the results of the peroxide concentration generated. The results show that the peroxide content per area increased from 0.021 $mmol/m^2$ to 0.125$mmol/m^2$ when the treatment time increased from 15 min to 2.5 hrs in aqueous solution, and increased from 0.026$mmol/m^2$ to 0.070$mmol/m^2$ when the treatment time increased from 15 min to 2.5 hrs in gas phase. Obviously, peroxide content was generated faster in aqueous solution than in the gas phase. The reason may explain as active oxygen species (hydroxyl radical $\cdot$OH, superoxide $\cdot O_2^-$, and peroxide radical $\cdot$ OOH) in water helped the reaction, especially with the loose molecular status, semi crystal-amorphous blown film HDPE.

The peroxide generation rate of HDPE in aqueous phase was slower under 1.0 hour ozonation, probably because the small molecules reacted with ozone and dissolved in the water. Lino

Ferreira studied the PET film ozonation and found the washed film measured a less C=O and COOH concentration [Ferreira, 2005].

4.1.2 Tensile strength of HDPE

The tensile strength of HDPE decreased from 70.95 Mpa to 3.42 Mpa when the treatment time increased from 0 min (virgin film) to 2.5 hrs in aqueous solution. For gaseous ozonation, the tensile strength decreased from 70.95 Mpa to 5.30 Mpa when the treatment time increased from 0 min (virgin film) to 2.5 hrs. Tensile strength data showed very similar trends in aqueous solution and in the gaseous phase; however, the rate dropped a little faster in aqueous solution. Figure 4.2 shows the trends.
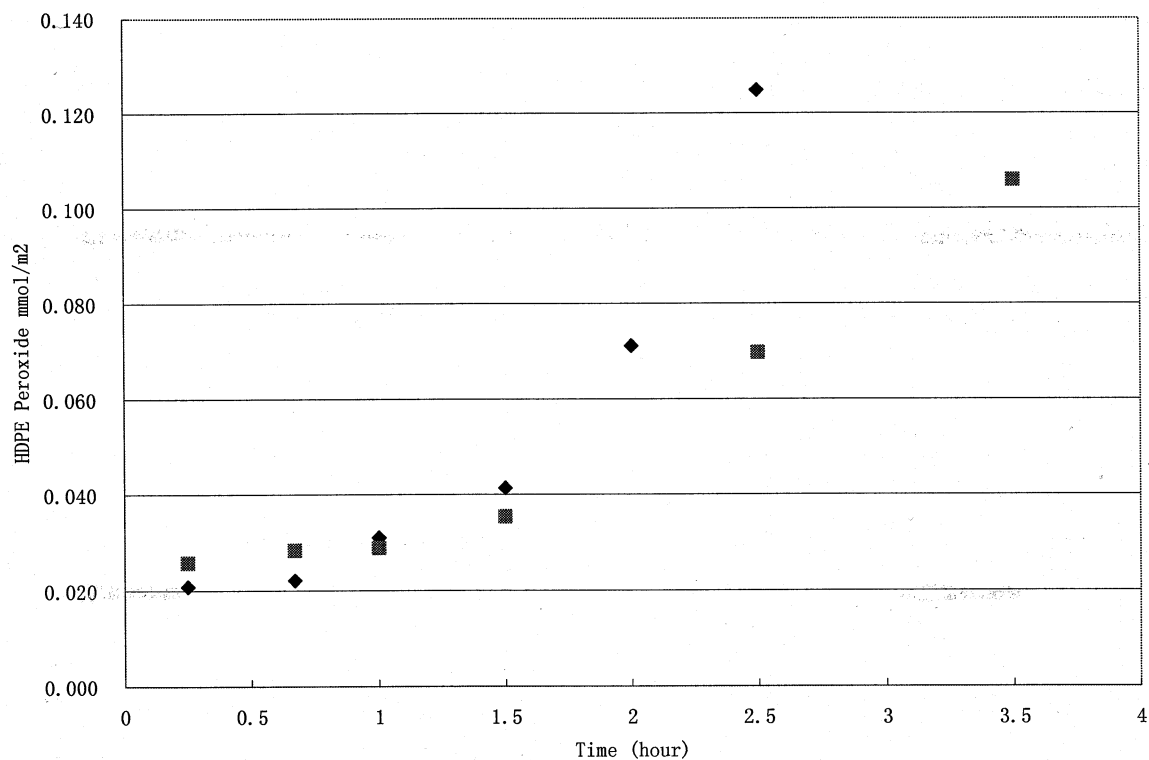
Fig. 4.1 Peroxide generation of HDPE with 3.7wt% ozone in: ◆ aqueous phase, ■ gaseous phase.

4.1.3 Elongation of HDPE

Elongation of HDPE decreased from 409% to 0% (brittle) when the treatment time increased from 0 min (virgin film) to 2.0 hrs in aqueous solution, and the decreased from 406% to 0% (brittle) when the treatment time increased from 0 min (virgin film) to 2.0 hrs in the gaseous phase. The data for elongation showed very similar trends both in aqueous solution and in the gas phase, as shown in Figure 4.3.
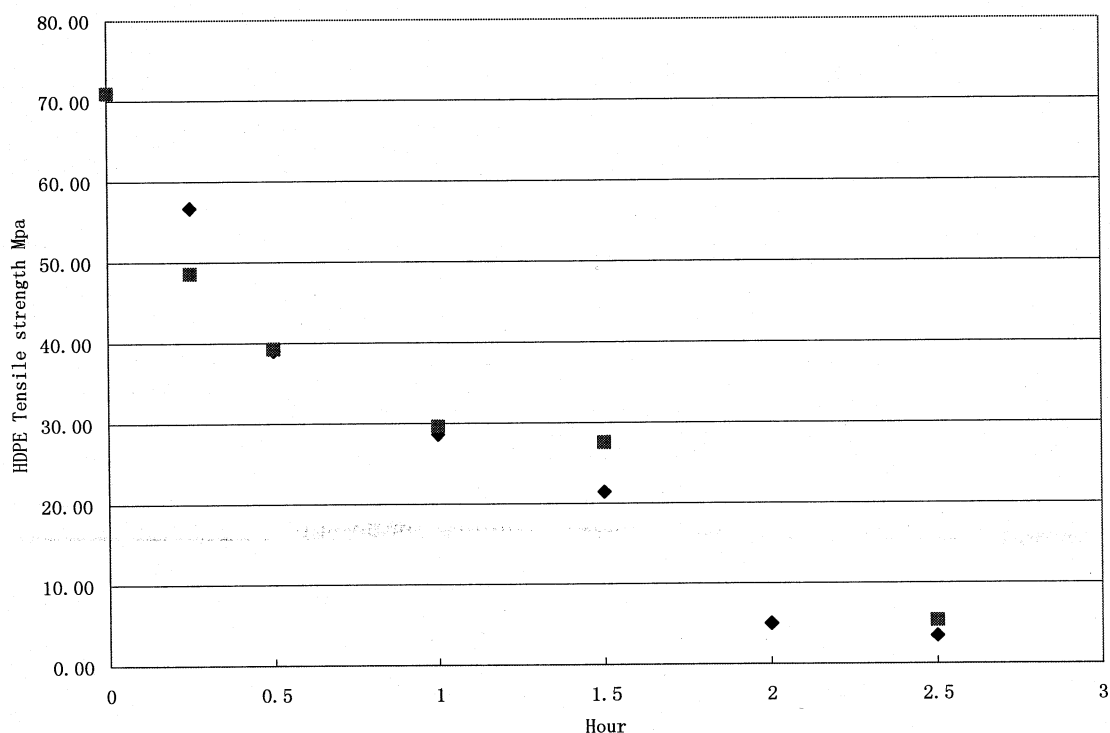
Fig. 4.2 Tensile strength of HDPE with 3.7wt% ozone in: ◆ aqueous phase, ■ gaseous phase.

4.2 Ozone oxidation of BOPP

4.2.1 Peroxide generation in aqueous and gaseous phasse ozonation

The BOPP films were ozonated in distilled water and in ozone-oxygen gas mixture, respectively. BOPP strips (1.5 in x 10 in) were fixed in the reactor for aqueous ozonation, and reaction time was set at 0.5, 1.5, 2.0, 2.5, 3.0, 4.0, and 5.0 hrs.

For gaseous ozonation, reaction time was set at 1.0, 1.7, 2.5, 2.7, and 3.5 hrs. The applied ozone dose was 3.7 wt% for both aqueous and gaseous ozonation.
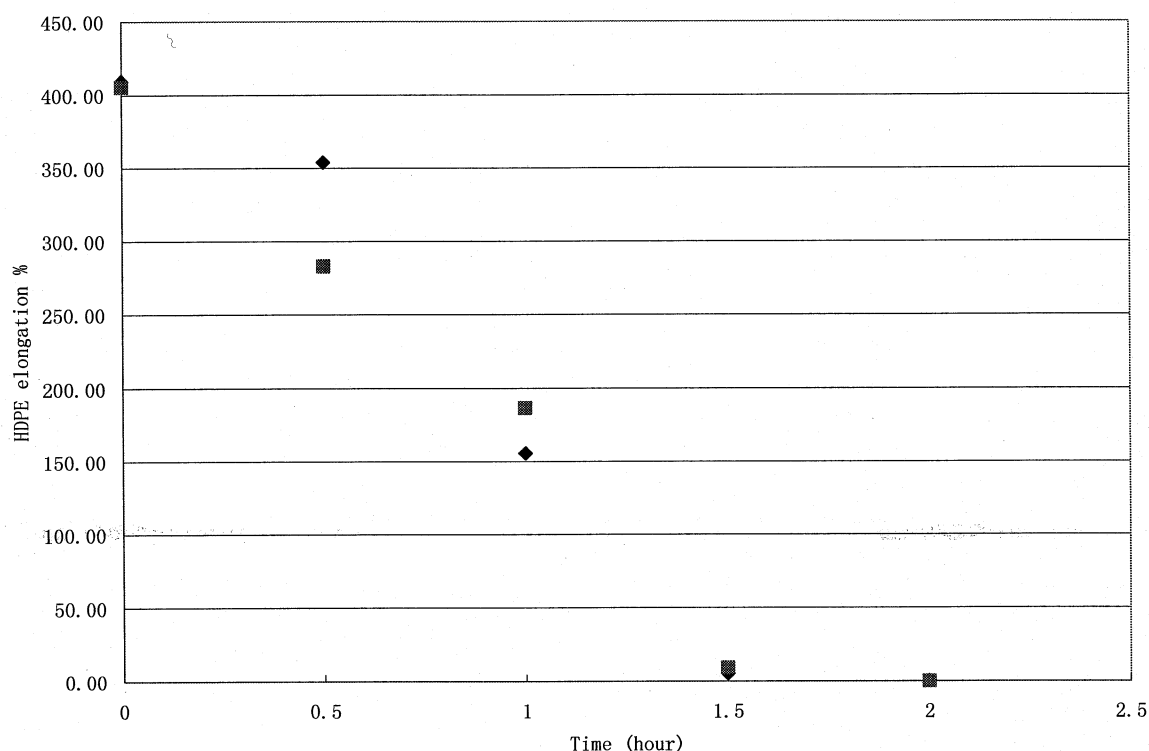
Fig. 4.3 Elongation of HDPE with 3.7wt% ozone in: ◆ aqueous phase, ■ gaseous phase.

Figure 4.4 presents the results of the peroxide concentration generated. The results show that the peroxide content per area increased from 0.025mmol/m^2 to 0.148 mmol/m^2 when the treatment time increased from 0.5 hrs to 4.0 hrs in aqueous solution, and increased from 0.044mmol/m^2 to 0.168mmol/m^2 when the treatment time increased from 1.0 hr to 3.5 hrs in the gas phase.

Peroxide content was generated slower in aqueous solution than in the gaseous phase after 2 hrs ozonation. The reason can be explained as the chain scission occurs more after 2 hrs ozonation in aqueous solution, this phenomenon can be read from the tensile strength chart---the tensile strength dropped significantly after 2 hrs ozonation as shown in Figure 4.5.
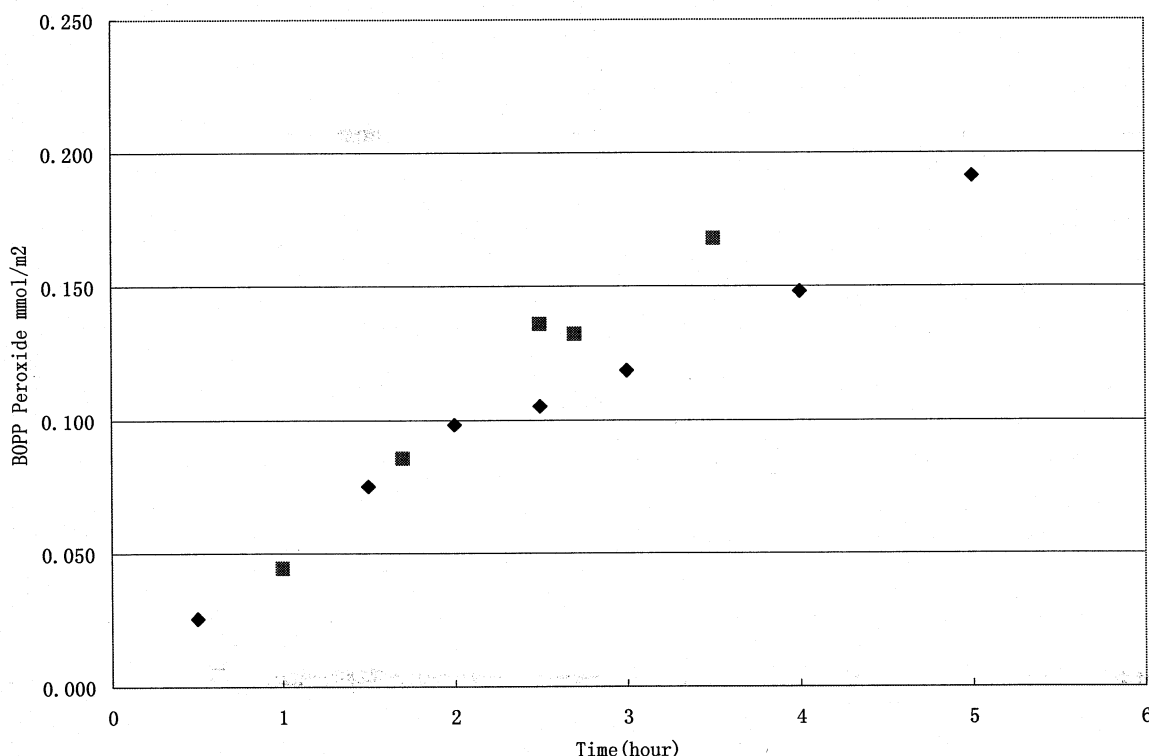
Fig. 4.4 Peroxide generation of BOPP with 3.7wt% ozone in: ◆ aqueous phase, ■ gaseous phase.

4.2.2 Tensile strength of BOPP

As shown in Figure 4.5, the tensile strength of the film decreased with ozonation. For ozonation conducted in distilled water, it decreased from 187.03 Mpa to 65.70 Mpa when the treatment time increased from 0 min (virgin film) to 4.0 hrs, and decreased from 187.03 Mpa to 66.46 Mpa when the treatment time increased from 0 min (virgin film) to 3.5 hrs in gaseous phase. The

tensile strength, both in the aqueous and gaseous phases, underwent a period of dramatic decrease with time. This occurred between 2 and 2.5 hrs in the aqueous phase and between 0 and 1 hrs in the gaseous phase. During the other periods of time, it maintained a slowly declining trend.
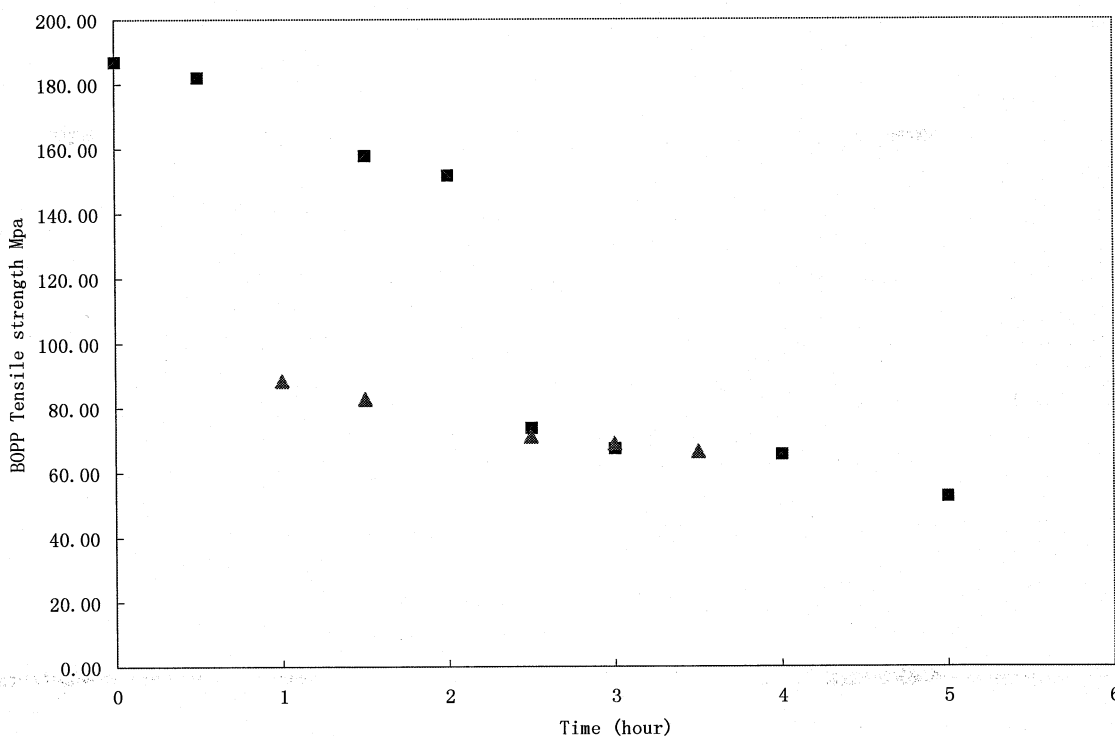
Fig. 4.5 Tensile strength of BOPP with 3.7wt% ozone in: ■ aqueous phase, ▲ gaseous phase.

4.2.3 Elongation of BOPP

It can be observed from Figure 4.6 that elongation decreased from 156.26% to 56.56% when the treatment time increased from 0 min (virgin film) to 4.0 hrs in aqueous solution, and decreased from 156.26% to 53.87% when the treatment time increased from 0 min (virgin film) to 3.5 hrs in the gas phase. The elongation dropped more slowly in aqueous solution than in the gaseous phase; and in the first hr, elongation also underwent a period of dramatic decrease.
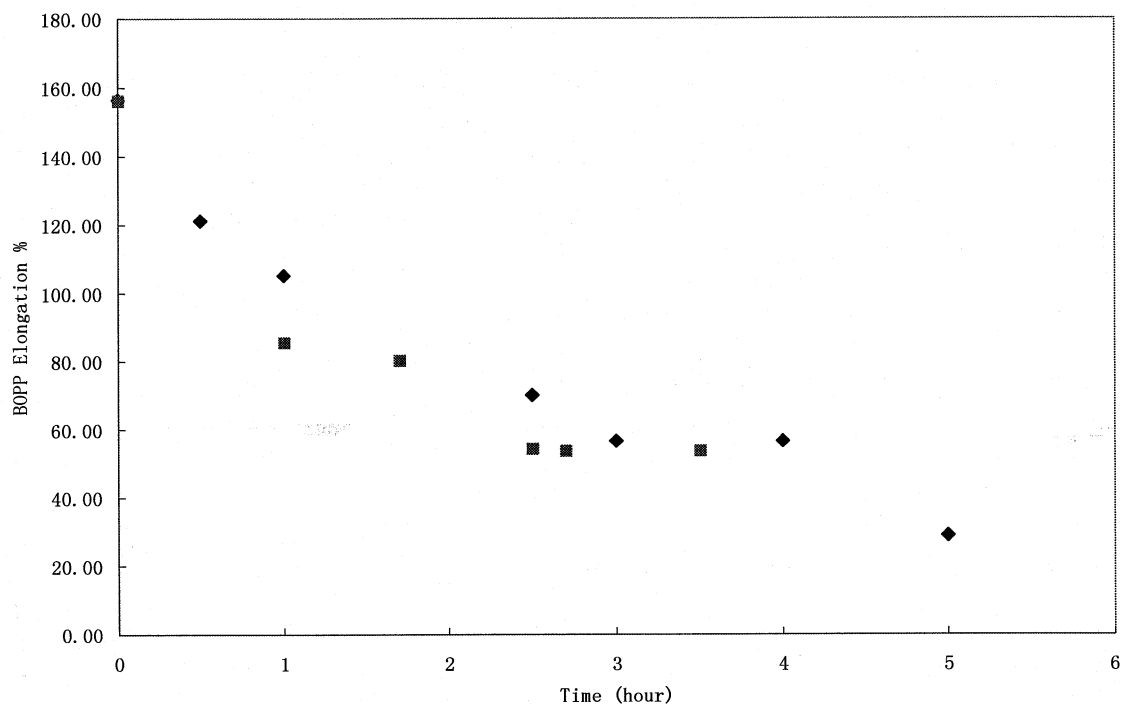
Fig. 4.6 Elongation of BOPP with 3.7wt% ozone in: ◆ aqueous phase, ■ gaseous phase.

4.3 Ozone oxidation of PET

4.3.1 Peroxide generation in aqueous and gaseous phases ozonation

The PET films were ozonized in distilled water and in ozone-oxygen gas mixture, respectively.

PET strips (1.5 in x 10 in) were fixed in the reactor for aqueous ozonation, and reaction time was

set at 0.5, 1.0, 2.0, 3.0, 3.5, 4.0, and 5.0 hrs.

For gaseous ozonation, reaction time was set at 1.0, 1.7, 2.5, 2.7, and 4.0 hrs. The applied ozone

dose was 3.7 wt% for both aqueous and gaseous ozonation.
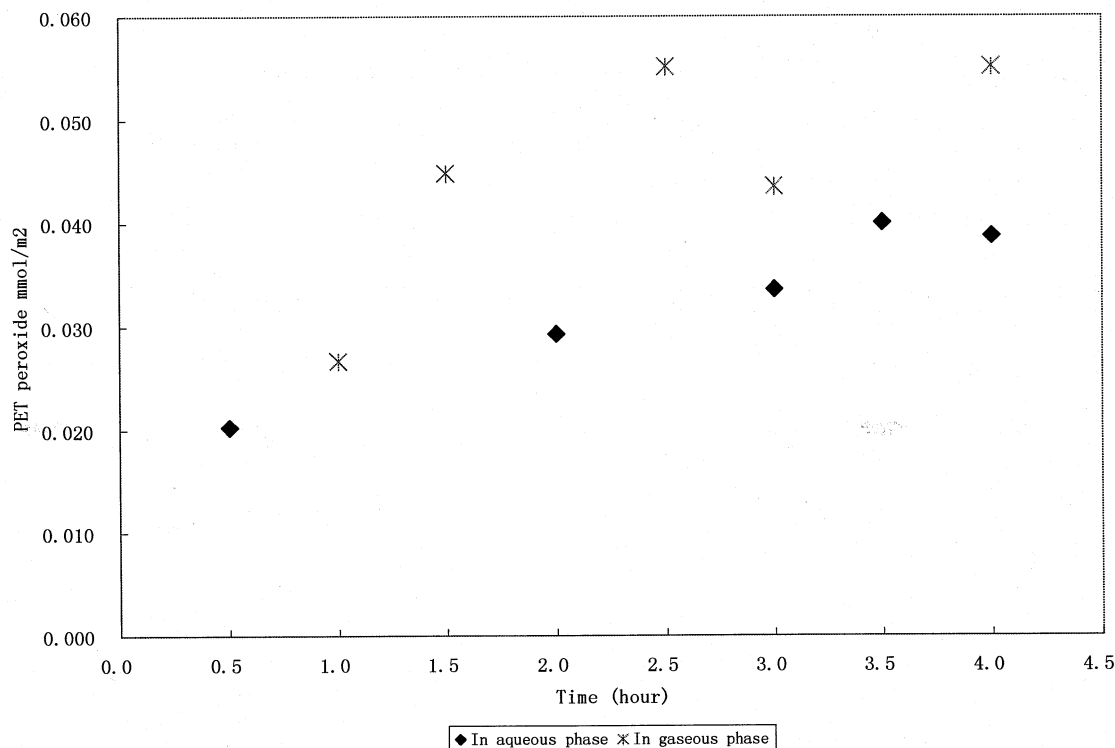
Fig. 4.7 Peroxide of PET with 3.7wt% applied ozone dose in aqueous and gaseous phases

Figure 4.7 presents the results of the peroxide concentration generated. The results show that the peroxide content per area increased from 0.020mmol/m^2 to 0.040mmol/m^2 when the treatment time increased from 0.5 hr to 3.5 hr in aqueous solution, and increased from 0.027mmol/m^2 to 0.055mmol/m^2 when the treatment time increased from 1.0 hr to 4.0 hrs in the gaseous phase. Obviously, peroxide content was generated more slowly in aqueous solution than in the gaseous phase. The rate of increase in peroxide content of PET film was the slowest among the three substrates in this work (as shown in Figure 4.10). And when the treatment time was longer, the peroxide content increased even more slowly, till it reached a plateau. This result corresponds to the aromatic groups in the molecular chain which have a slower ozonation rate.

4.3.2 Tensile strength of PET

As shown in Figure 4.8, the tensile strength of the film decreased with ozonation. For ozonation conducted in the aqueous phase, it decreased from 208.26 Mpa to 183.73 Mpa when the treatment time increased from 0 min (virgin film) to 4.0 hrs; while it decreased from 208.26 Mpa to 150.28 Mpa when the treatment time increased from 0 min (virgin film) to 4.0 hrs in the gaseous phase. However, the values in aqueous medium remained larger than those in the gas phase.
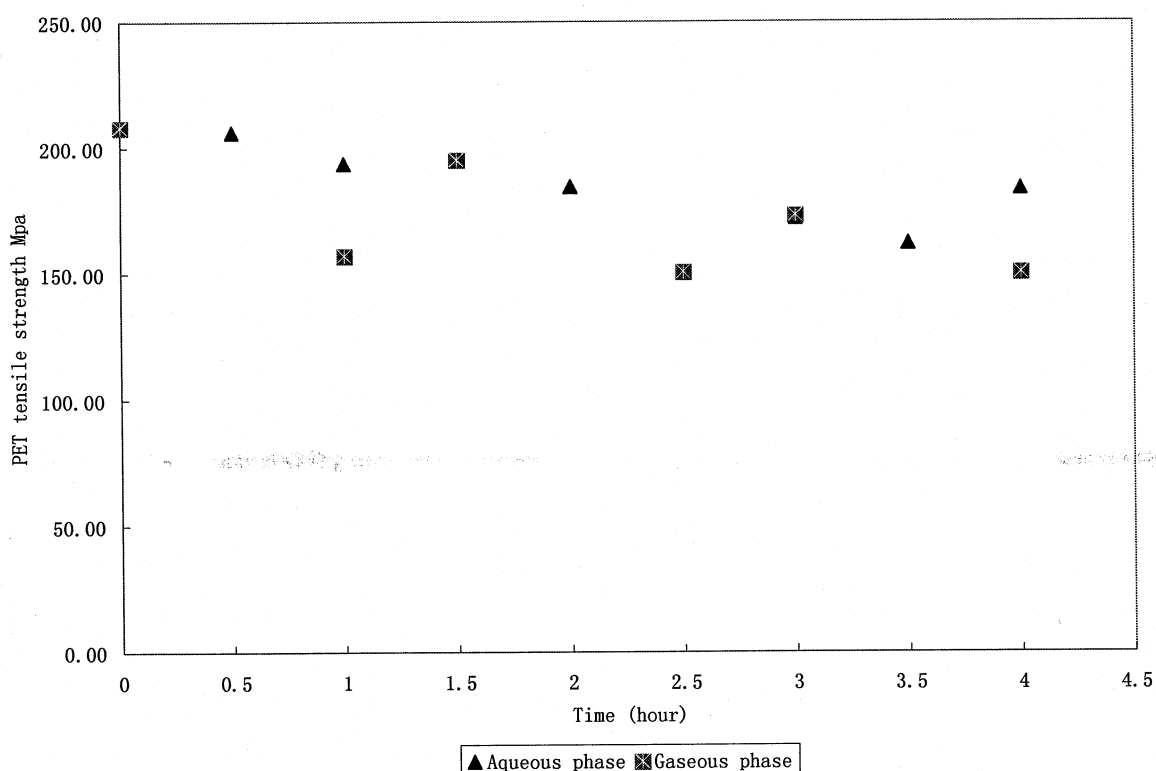
Fig. 4.8 Tensile strength of PET with 3.7wt% applied ozone dose in aqueous and gaseous phases

4.3.3 Elongation of PET

As shown in Figure 4.9, it can be observed that elongation decreased from 125.22% to 113.46% when the treatment time increased from 0 min (virgin film) to 4.0 hrs in aqueous solution and

decreased from 125.22% to 60.09% when the treatment time increased from 0 min (virgin film) to 4.0 hrs in the gaseous phase. The data for elongation show it decreased more slowly in the aqueous phase than in the gaseous phase.
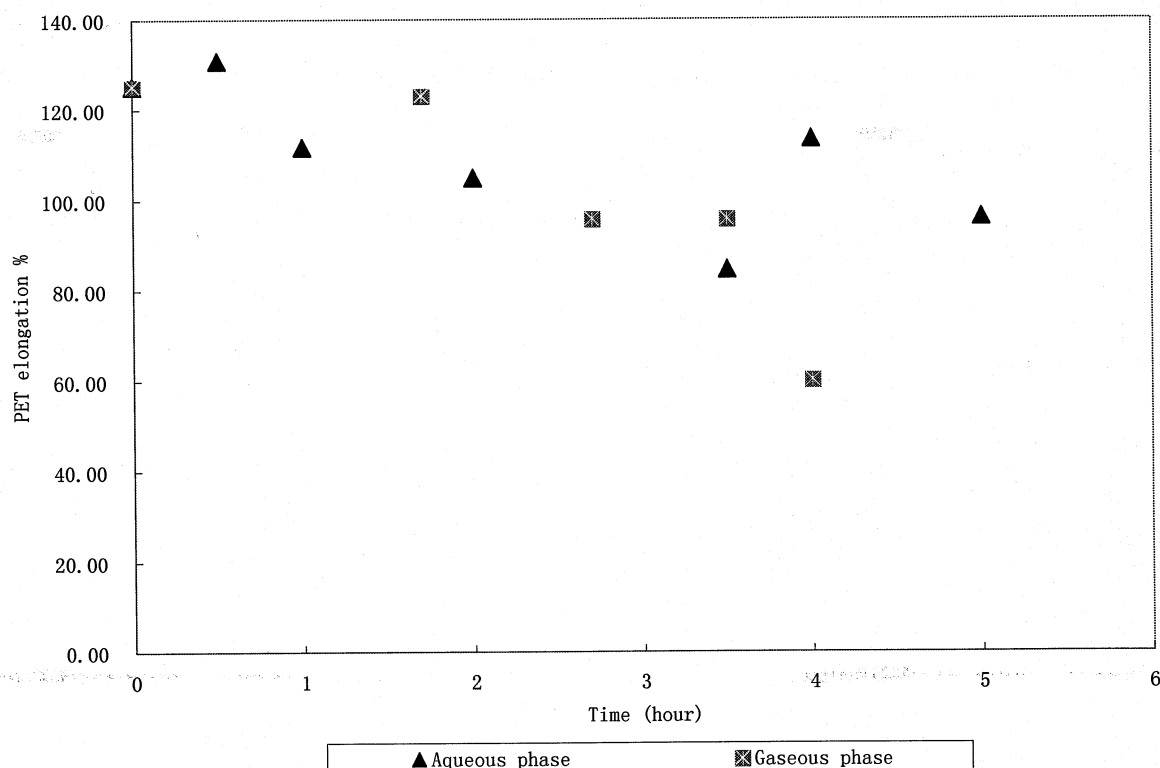
Fig. 4.9 Elongation of PET with 3.7wt% applied ozone dose in aqueous and gaseous phases

4.4 Comparison of peroxide generation and tensile strength at 3.7wt% applied ozone dose in aqueous phase

As shown in Figure 4.10 and Figure 4.11, comparing the three selected films with 3.7wt% applied ozone dose in aqueous phase, it was found that the PET film maintained the highest tensile strength and obtained the lowest peroxide content. BOPP and HDPE peroxide generation rates were much faster than PET, simultaneously, their mechanic strength dropped faster. BOPP

kept good mechanic strength in the first two hours of ozonation and obtained a fastest peroxide generation rate. HDPE was very brittle after 2.5 hour ozonation, but the peroxide generation speed showed an accelerating trend.

These charts showed the alkyl polymer molecules had a faster ozonation rate, the difference in behavior of both peroxide generation and mechanical properties of BOPP and HDPE probably were due to the $-CHCH_3-$, which has a different character compared to $-CH_2-$; and the aromatic groups in the molecular chain effected the reaction. The aromatic ring has a slower ozonation rate had been widely studied [Robin, 2004], the tensile strength dropped the least because of the slower ozonation.
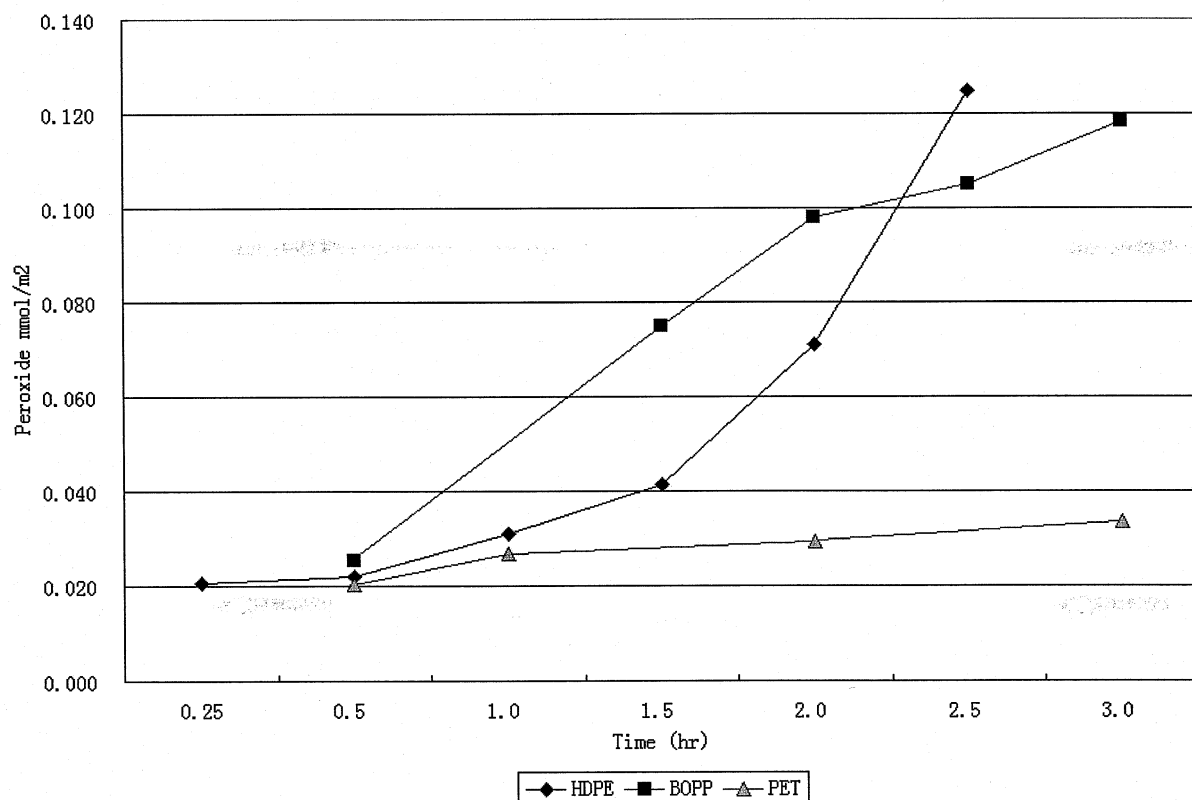
Fig. 4.10 Peroxide generation of selected films with 3.7wt% applied ozone dose in aqueous phase

4.5 Effects of operating parameters on polymer surface modification by ozone

For film surface modification, operation parameters, such as applied ozone dose and ozonation time, affect the efficacy significantly. In an aqueous medium, pH value is another important factor in the reaction. Therefore, these parameters were investigated for HDPE films, and the results are described below.
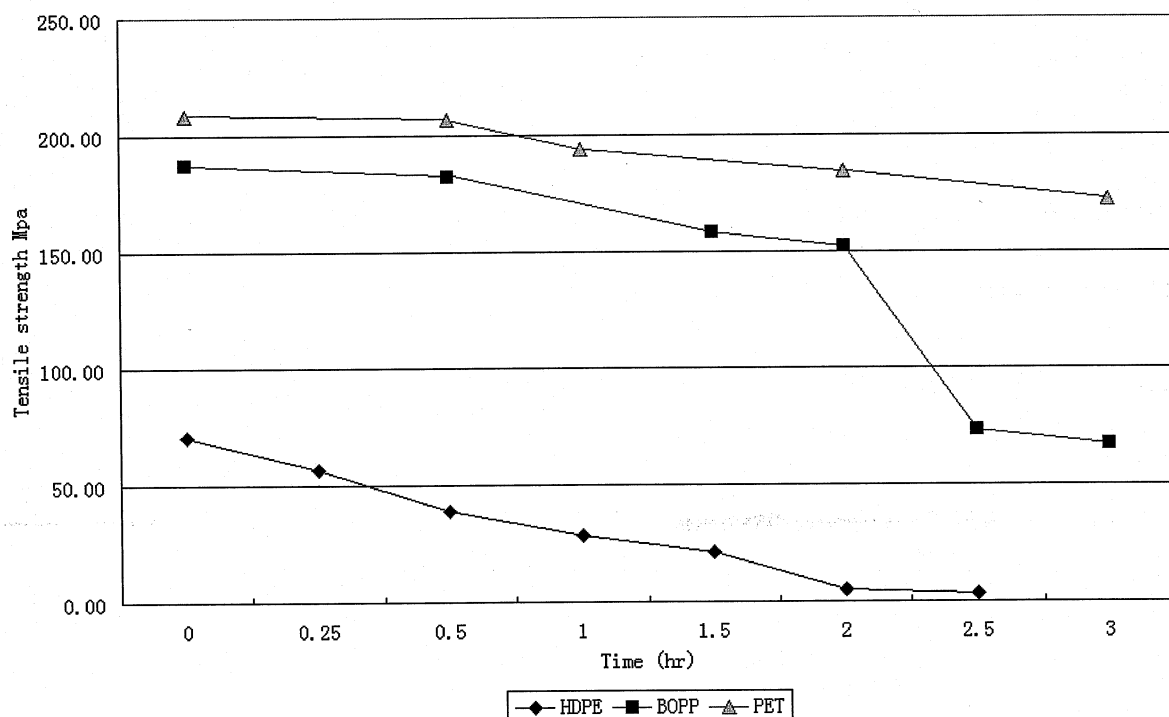
Fig. 4.11 Tensile strength of selected films with 3.7wt% applied ozone dose in aqueous phase

4.5.1 Effect of applied ozone dose

4.5.1.1 Peroxide generation of HDPE using different applied ozone doses in aqueous medium and gaseous phase

Attracted by the fact that peroxide was produced faster in HDPE in aqueous solution, we further studied the effect of the applied ozone dose. The reaction time was set at one hour. Figure 4.12

shows the results. The ozone concentration in the gas mixture was varied from 1.0 wt% to 4.0 wt%, both in the aqueous and gaseous phase reactions. The peroxide content per area increased with the ozone dose applied from 0.0245mmol/m^2 to 0.0362mmol/m^2 in aqueous medium, and from 0.0224mmol/m^2 to 0.0306mmol/m^2 in the gaseous phase.

It was observed that the peroxide content obtained more in aqueous medium than in gaseous phase.

$$y = 0.0027x + 0.0198$$
$$R^2 = 0.9548$$
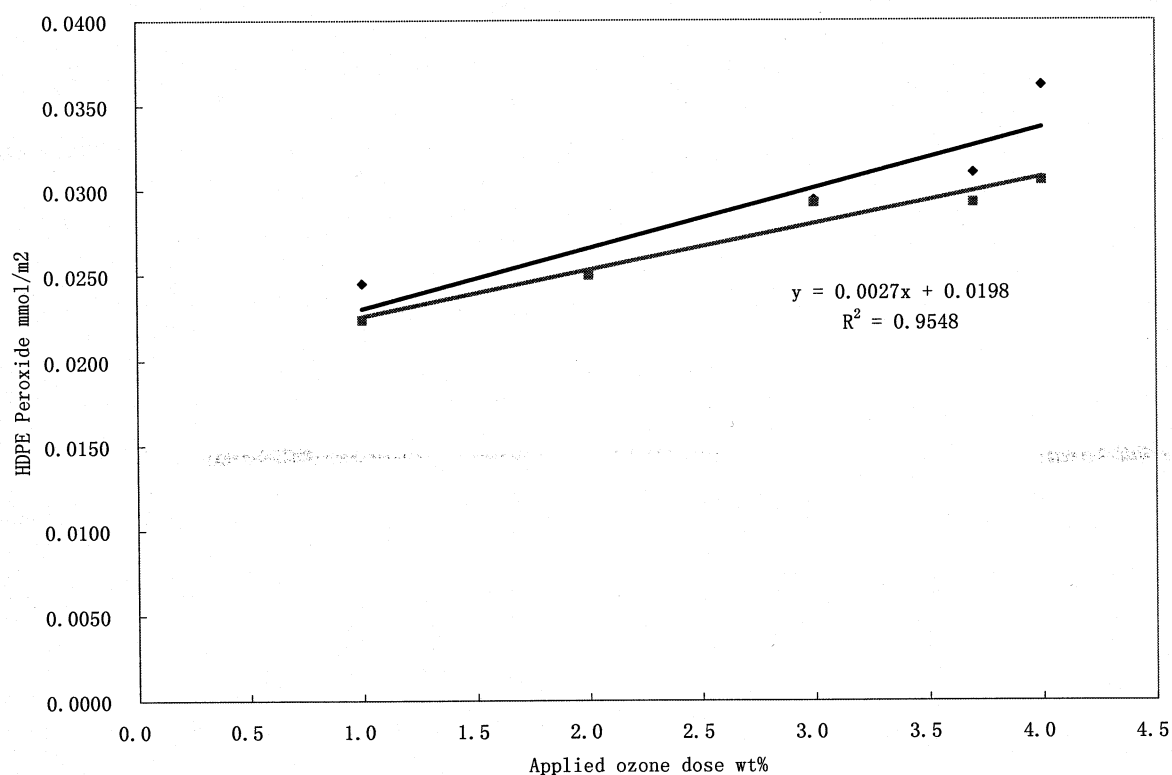
Fig. 4.12 Peroxide of HDPE using different O$_3$ doses and 1-hr reaction time in: ◆ aqueous phase, ▧ gaseous phases.

4.5.1.2 Tensile strength of HDPE with different applied ozone dose in aqueous and gaseous phase

Figure 4.13 shows the variation of tensile strength with ozone dose applied. The reaction time was one hour. The tensile strength decrease in aqueous solution was slightly less than that in gaseous phase with the ozone dose. The ozone dose applied in the gas mixture was set from 1.0%wt to 4.0%wt both in the aqueous and gaseous phase reaction, the tensile strength decreased from 70.95 Mpa to 29.39 Mpa in aqueous medium, and the tensile strength decreased from 70.95 Mpa to 29.04 Mpa in gaseous phase.

4.5.1.3 Elongation of HDPE with different applied ozone doses in aqueous and gaseous phases

As shown in Figure 4.14, when the reaction time was one hour, it can be observed that elongation decreased from 409.39% to 119.99% in aqueous solution, and from 409.39% to 21.53% in the gaseous phase when the applied ozone dose increased from 1.0 wt% to 4.0 wt%. When the film was ozonized for one hour with between 0 and 1.0 wt% applied ozone dose, there was no or only a minor decrease in elongation, both in the aqueous and gaseous phases. However, when the ozone dose was further increased, the elongation dropped linearly. Elongation decreased more slowly in the aqueous medium than in the gas phase.

4.5.2 Effect of ozonation time using 1 wt% applied ozone dose in aqueous phase

4.5.2.1 Effect of ozonation time on peroxide generation

Considering that there was more than 50% of tensile strength was lost after one hour of ozone treatment for HDPE when O_3 concentration was more than 1.5 wt%, the effect of ozonation time was investigated at the lower ozone dose of 1.0 wt% in aqueous phase.

Figure 4.15 shows the results. It can be observed that the peroxide content per area increased with ozonation time. For example, it increased from $0.0267 mmol/m^2$ to $0.0344 mmol/m^2$ as ozonation time increased from 0.5 hrs to 2.5 hrs.
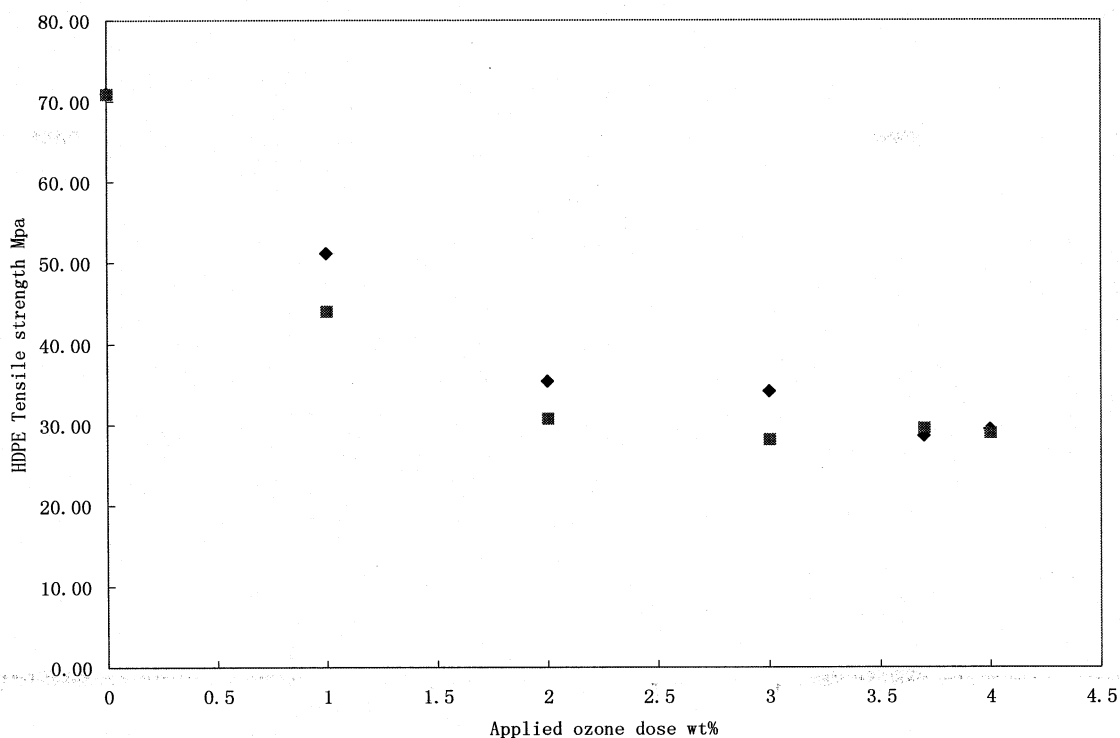
Fig. 4.13 Tensile strength of HDPE using different O_3 doses and 1-hr reaction time in: ◆aqueous phase; ■gaseous phases.

4.5.2.2 Effect on ozonation time on tensile strength of HDPE in aqueous phase

Figure 4.14 shows the variation of tensile strength with ozonation time. The applied ozone dose was 1.0 wt%. The tensile strength decreased in aqueous phase from 70.95 Mpa to 32.61 Mpa when the treatment time increased from 0 min (virgin film) to 2.5 hrs.

4.5.2.3 Effect on ozonation time on elongation of HDPE in aqueous phase

As shown in Figure 4.17, the applied ozone dose was 1.0 wt%, it can be observed that elongation decreased from 409.4% to 255.4% when the treatment time was increased from 0 min (virgin film) to 2.5 hrs in aqueous solution.
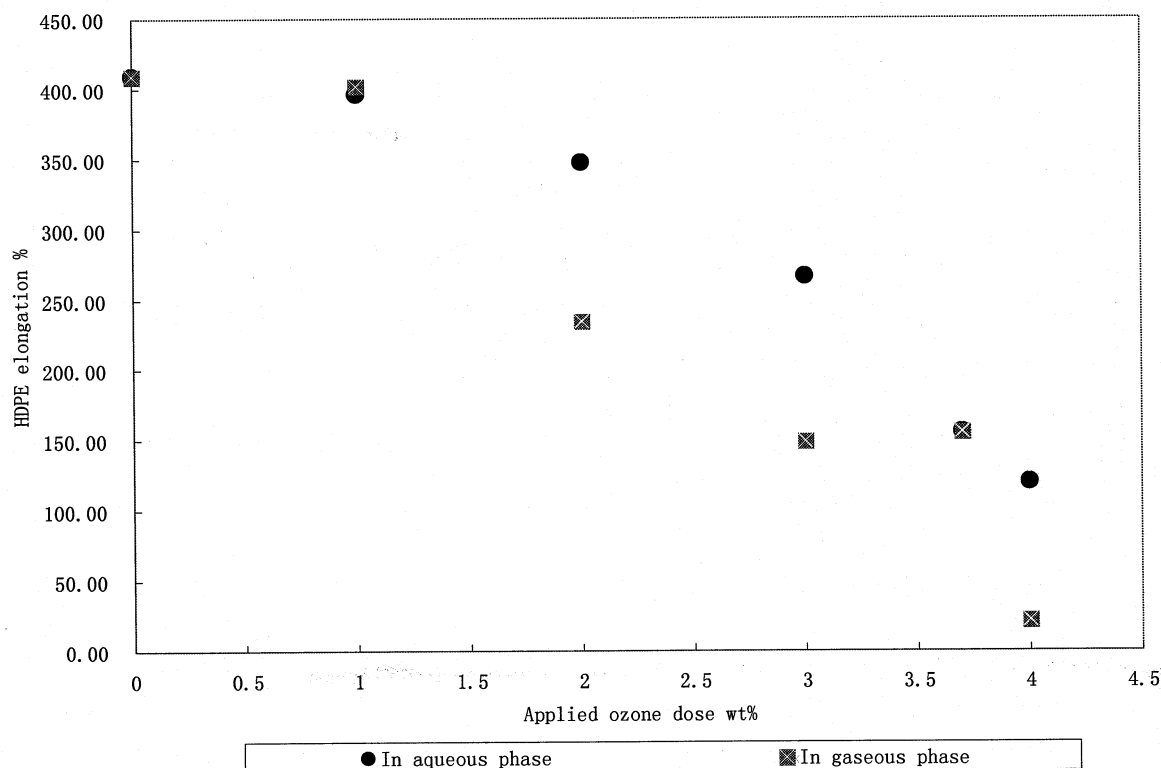
Fig. 4.14 Elongation of HDPE with different O_3 doses and 1-hr reaction time in aqueous and gaseous phases.

4.5.3 Effect of pH on ozonation in aqueous solution

The effect of pH on HDPE ozonation was also examined. The pH of the distilled water was adjusted by H_2SO_4 and NaOH. The range of pH examined was from 2 to 11. The ozonation parameters were 1.0wt% applied ozone dose and 1 hr, based on the above studies.

4.5.3.1 Effect of pH on peroxide generation

The pH values were 2.4, 4.4, 6.6, 7.5, 9.7, and 10.6, respectively. As can be observed from Figure 4.18, when pH increased, the peroxide concentration decreased slightly. Because ozone decomposes into ozone radicals in water, and the decomposition increased with increasing pH [Hoigne, J., 1982], it is possible that the ozone-induced peroxide generation was mainly caused by molecular ozone instead of ozone radicals.
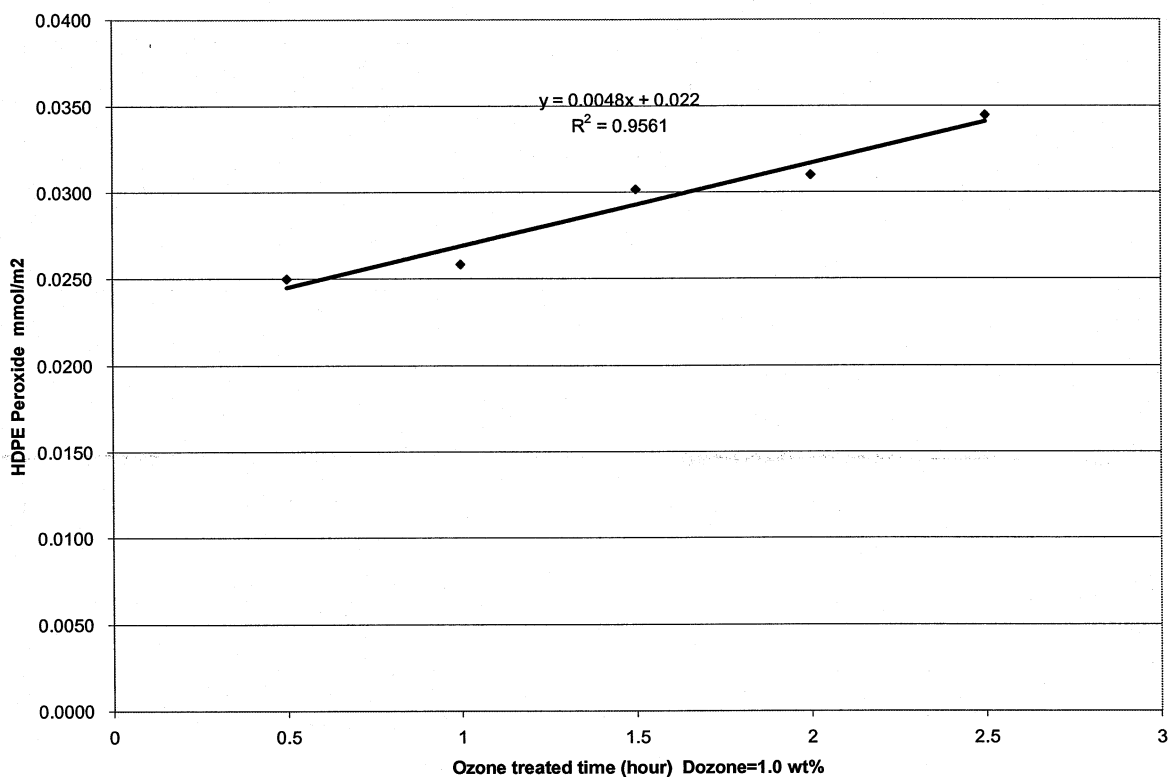
Fig. 4.15 Peroxide generation of HDPE with variable reaction time and 1.0 wt% O_3 dose in aqueous phase

4.5.3.2 Effect of pH on tensile strength

The pH values were 2.4, 4.4, 6.6, 7.5, 9.7, and 10.6, respectively. The reaction conditions were 1.0%wt ozone and 1.0 hr treatment time for HDPE. As can be observed from Figure 4.19, as pH increased, the tensile strength increased from 40.89 Mpa to 53.54 Mpa.

The figure contains the equation:

$$y = 4.2842x^2 - 25.576x + 69.676$$
$$R^2 = 0.9702$$
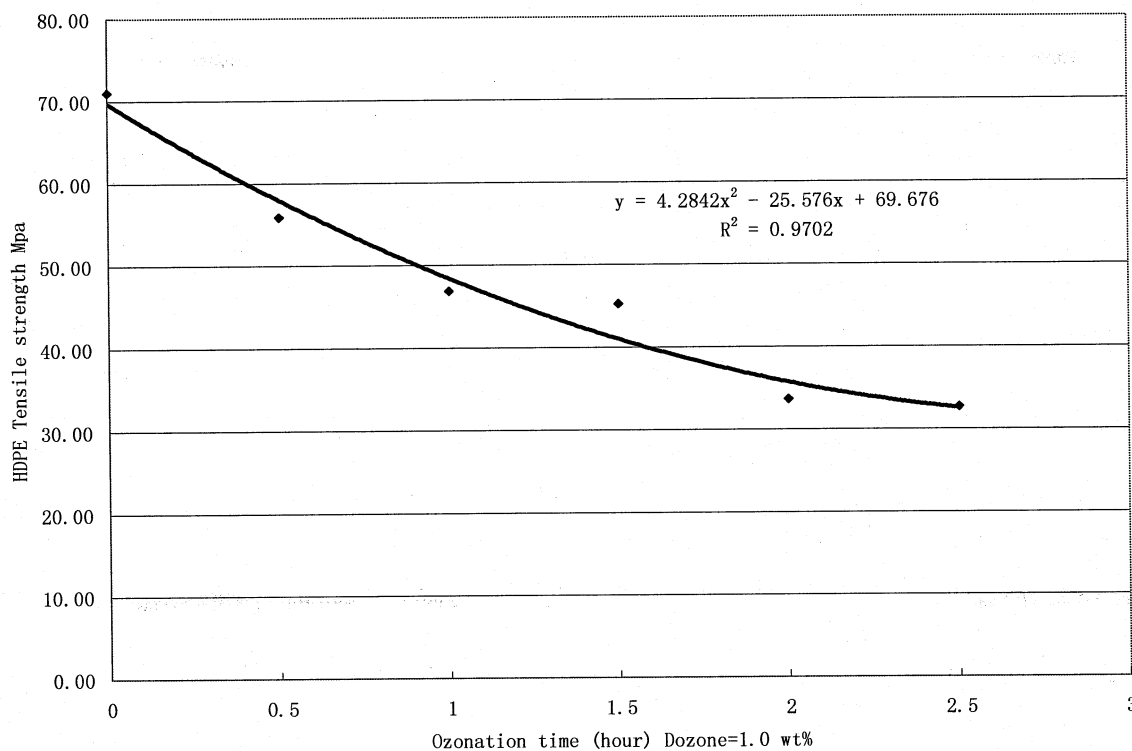
Fig. 4.16 Tensile strength of HDPE with variable reaction times and 1.0%wt O_3 concentration in aqueous phase

4.6 Aging tests on the treated HDPE films, both in the aqueous and gaseous phases

To study the stability of the peroxide content generated on the films, the aging test was performed for HDPE reacted with ozone, both in the aqueous and gaseous phases. For each

experimental run, the reaction time was one hour and the applied ozone dose was controlled at 1.0, 2.0, 3.0 and 4.0 wt%. The films were examined for their peroxide concentration immediately after ozonation; and after 15 days, it was found that the peroxide residue averages remaining were as follows: for the aqueous phase samples, it was 91.43%; and for the gas phase samples, it was 96.75%. Therefore, it was determined that the peroxide content for both phases decayed very slowly.

The chart shows HDPE Elongation % (y-axis, 0.0 to 450.0) versus Ozonation time (hour) Dozone=1.0 wt% (x-axis, 0.0 to 3.0). The fitted curve equation:

$$y = -31.784x^2 + 12.188x + 415.98$$
$$R^2 = 0.9781$$
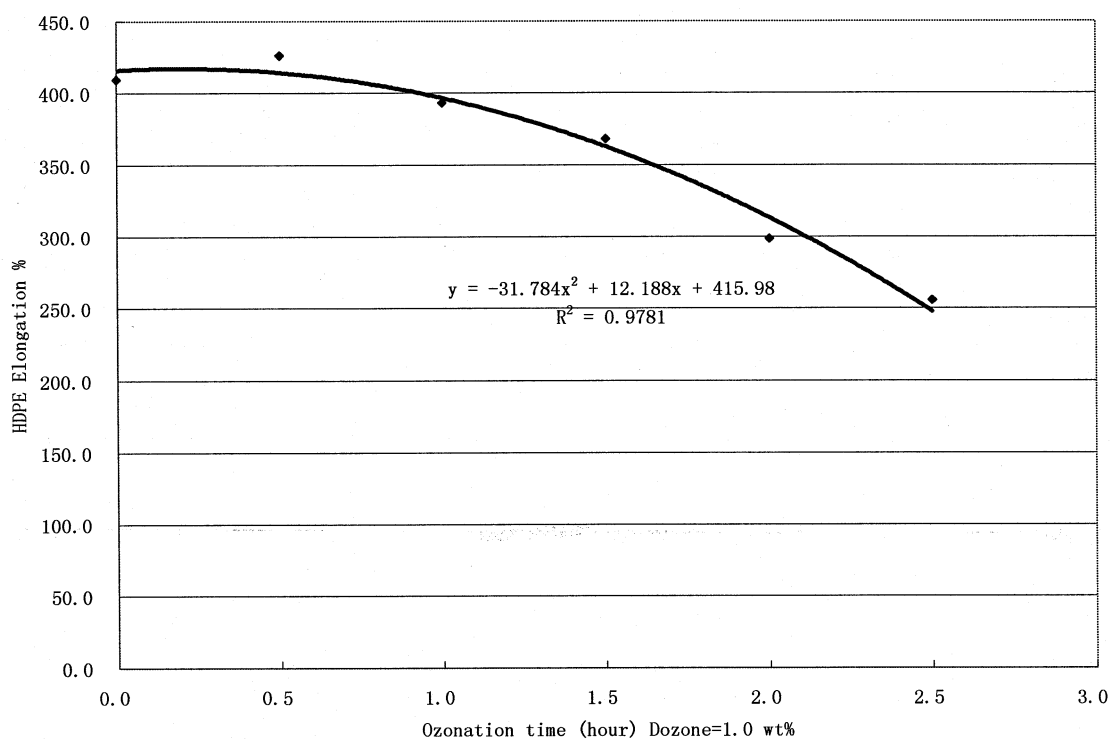
Fig. 4.17 Elongation of HDPE with variable reaction time and 1.0%wt O_3 concentration in aqueous phase

4.7 FTIR analysis

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

absorb infrared radiation and ultimately convert it to heat. By examining the infrared spectra obtained, we gained information about the functional groups in the polymer molecules and learned about the molecular structure [*Infrared Spectroscopy*, pp. 1-26, 2006].
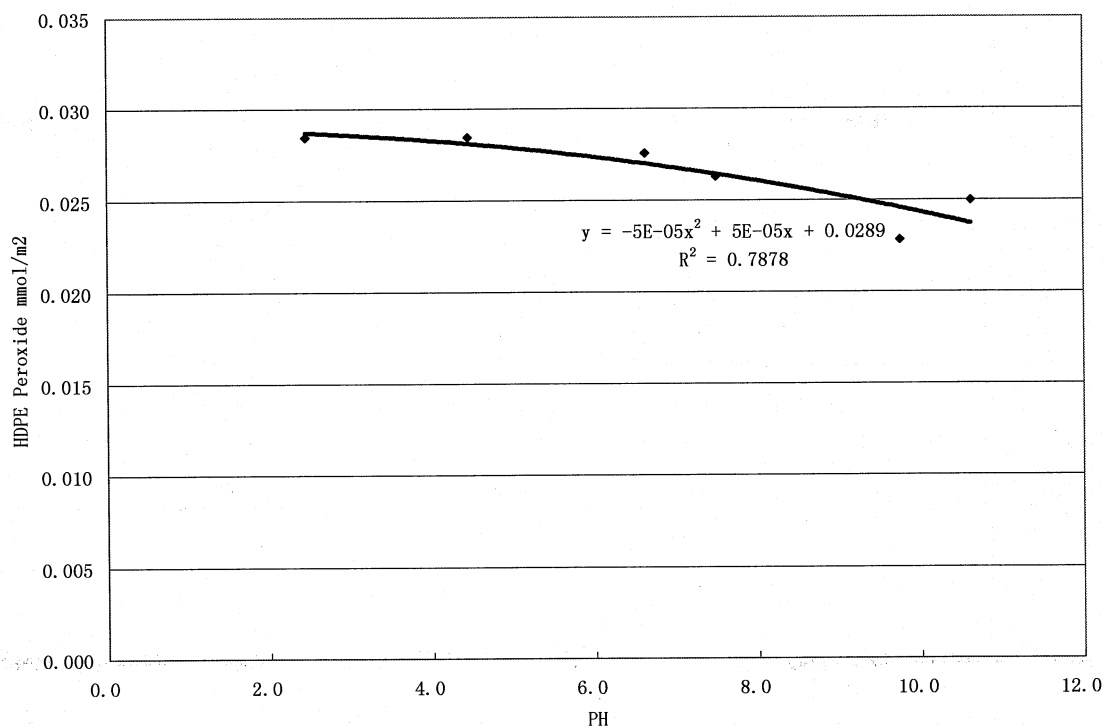
Fig 4.18 Peroxide in HDPE15 films with variable pH values in aqueous medium with 1.0%wt ozone and 1.0 hr treatment time

4.7.1 FTIR analysis of HDPE film

4.7.1.1 Ozonation of HDPE in the aqueous phase

Figure 4.20 presents the infrared spectra obtained from virgin HDPE film ozonized with 3.7 wt% applied dose in aqueous medium for 1.0 hrs, 1.5 hrs, 2.0 hrs, 2.5 hrs and 3.5 hrs. An obvious

peak of C=O of R-(C=O)-H, R-(C=O)-R, R-(C=O)-OH groups occurs at 1716 cm^{-1} (Figure 4.21 shows the peak value), which was created by ozonation and enhanced with ozonation time.
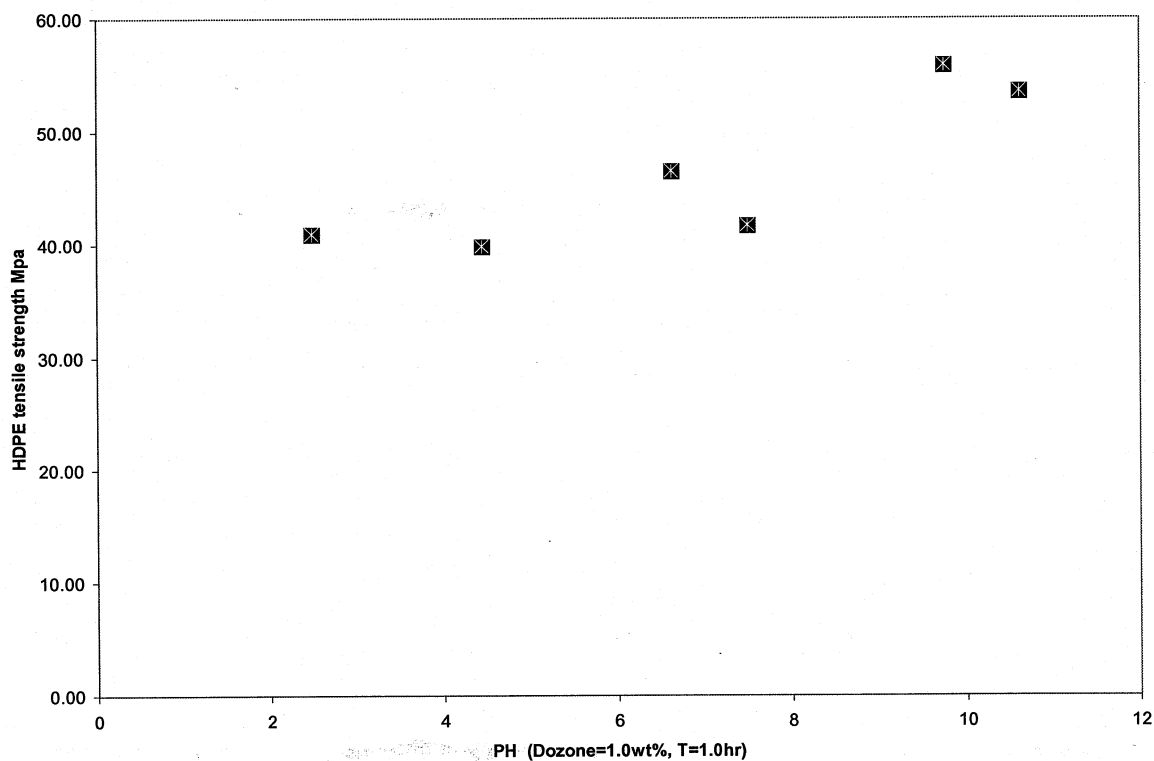
Fig. 4.19 Tensile strength of HDPE15 films with different pH values in aqueous medium

4.7.1.2 Ozonation of HDPE in the gaseous phase

Figure 4.21 presents the infrared spectra of virgin HDPE film ozonized with 3.7 wt% applied dose in gaseous phase for 0.5 hrs, 1.0 hrs, 1.5 hrs and 3.5 hrs. Also an obvious peak of C=O of R-(C=O)-H, R-(C=O)-R, R-(C=O)-OH groups occurs at 1716 cm^{-1} (Figure 4.23 shows the peak value), which was created by ozonation and enhanced with ozonation time.
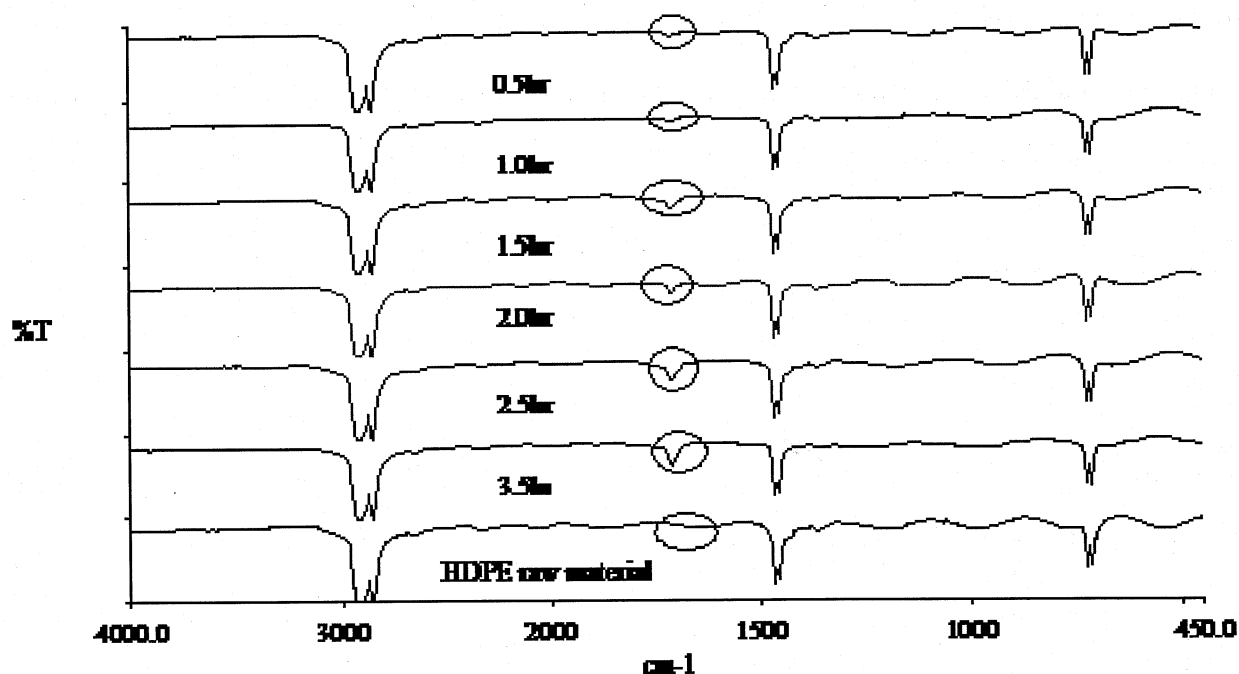
Fig. 4.20 Infrared spectra of HDPE with 3.7 wt% applied ozone dose in aqueous medium
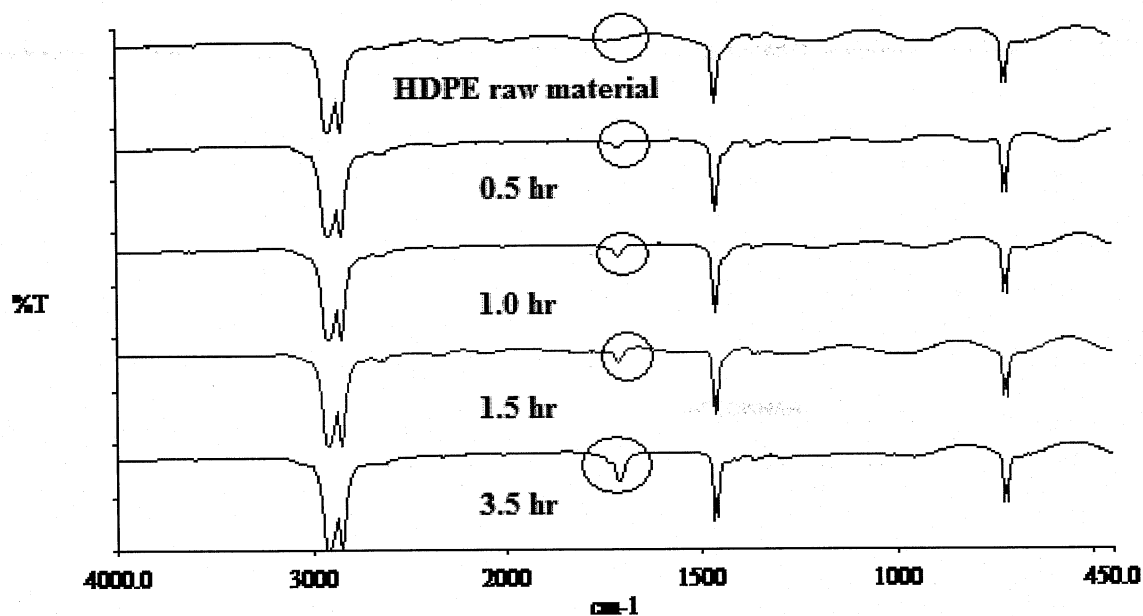
Fig 4.21 Infrared spectra of HDPE with 3.7 wt% applied ozone dose in the gaseous phase

4.7.1.3 Functional groups of HDPE infrared spectra

Figure 4.22 presents the infrared spectrum of raw material HDPE, and Figure 4.23 presents the infrared spectrum of HDPE ozonized for 3.5 hrs with 3.7 wt% applied ozone dose in the gaseous phase. After comparing these two charts, the following results were found:

- There is C-H stretching and vibration from 2850 to 3300 cm^{-1} [*Infrared Spectroscopy*, pp. 1-6, 2006];

- Carbonyl absorption was split into two peaks occurring between 1750 cm^{-1} and 1700 cm^{-1} because of free carbonyl and bonded carbonyl [Yuan et al., 2003].

- The peak at 1716 cm^{-1} indicates that C=O was created.

- A hydroxyl group (–OH) absorption peak occurs at around 3450 cm^{-1} (Murakami et al., 2003), and only small peaks at these values in the spectra can be observed.

- Some peaks, between 940 cm^{-1} and 1450 cm^{-1}, show variation, indicating the chain scission and reconstruction.
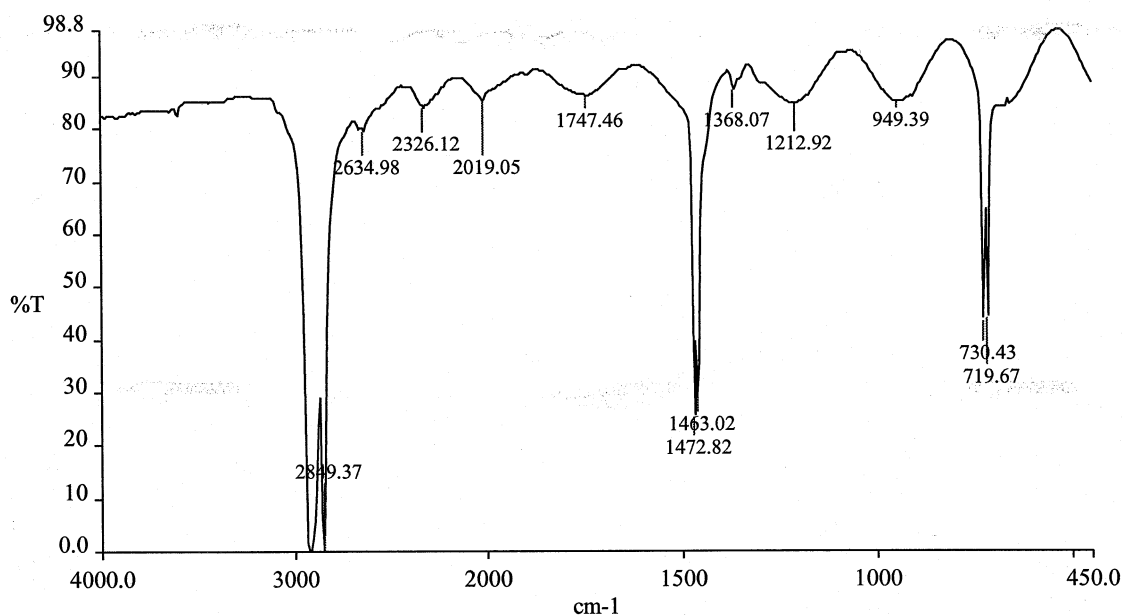
Fig. 4.22 Infrared spectrum of raw material HDPE

- 76 -
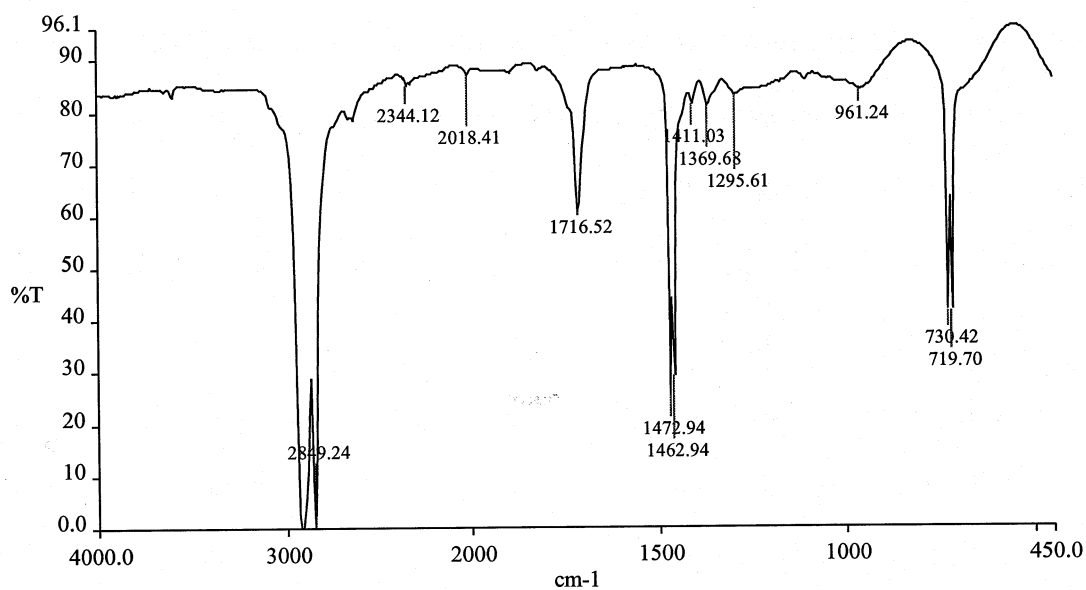
Fig. 4.23 Infrared spectrum of HDPE after 3.5 hrs treatment with 3.7 wt% ozone in gaseous phase

4.7.2 FTIR analysis of BOPP film
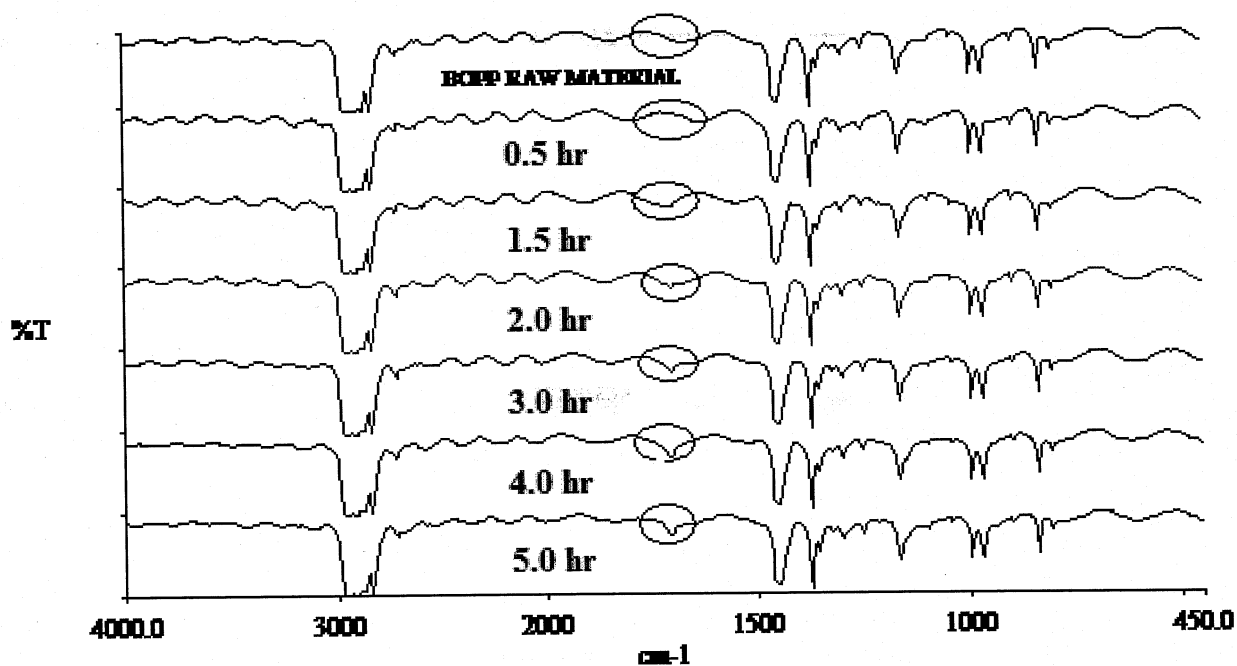
Fig. 4.24 Infrared spectra of BOPP treated with 3.7 wt% ozone dose in aqueous medium

4.7.2.1 Ozonation of BOPP in aqueous medium

Figure 4.24 presents the infrared spectra of virgin BOPP film ozonized with 3.7 wt% applied dose in aqueous medium for 0.5 hrs, 1.0 hr, 2.0 hrs, 3.0 hrs, 4.0 hrs and 5.0 hrs. An obvious peak of C=O of R-(C=O)-H, R-(C=O)-R, R-(C=O)-OH groups occurs at 1709 cm^{-1} (Figure 4.27 shows the peak value), which was created by ozonation and enhanced with ozonation time.

4.7.2.2 BOPP reacted with ozone in gaseous phase

Figure 4.25 presents the infrared spectra of virgin BOPP film ozonized with 3.7 wt% applied dose in gaseous phase for 1.0 hr, 1.7 hrs, 2.7 hrs and 3.5 hrs. Also an obvious peak of C=O of R-(C=O)-H, R-(C=O)-R, R-(C=O)-OH groups occurs at 1709 cm^{-1} (Figure 4.27 shows the peak value), which was created by ozonation and was enhanced with ozonation time.
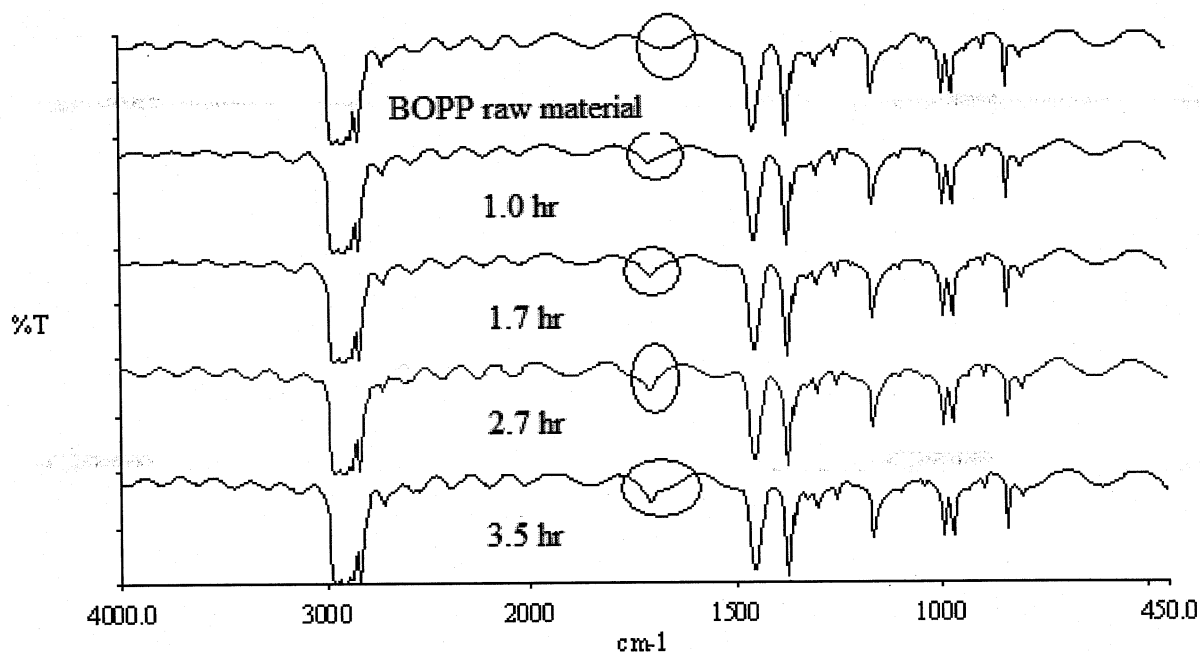
Fig. 4.25 Infrared spectra of BOPP with 3.7 wt% applied ozone dose in the gaseous phase

4.7.2.3 Functional groups of the BOPP infrared spectra
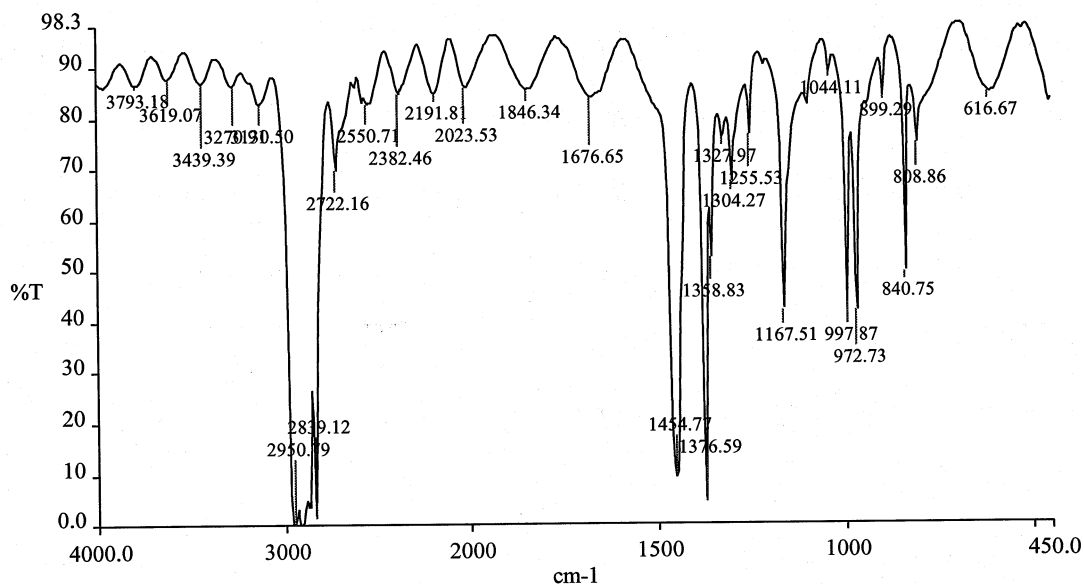
Fig. 4.26 Infrared spectrum of raw material BOPP
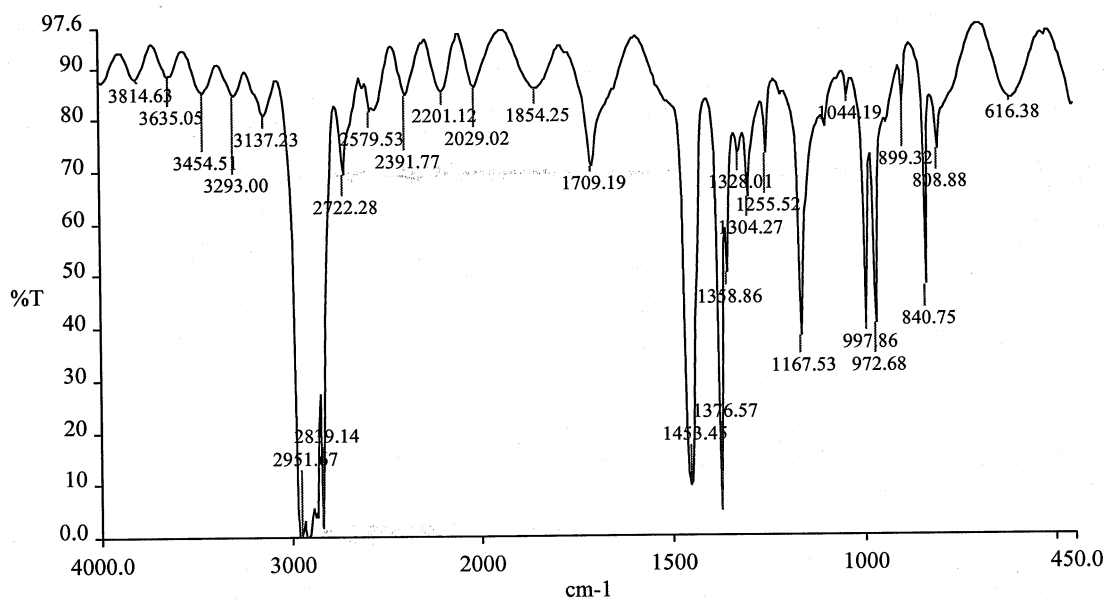
Fig. 4.27 Infrared spectrum of BOPP at 3.5 hrs and 3.7 wt% applied ozone dose in the gaseous

phase

Figure 4.26 presents the infrared spectra of raw material BOPP, Figure 4.27 presents the infrared spectra of ozone-oxidized BOPP after 3.5 hrs ozonation time and 3.7 wt% applied ozone dose in the gaseous phase. Comparing these two charts, the following results were found:

- A peak of C=O at 1706 cm^{-1} is created, and its value increases with reaction time; therefore, its surface becomes more hydrophilic with reaction time.

- Hydroxyl group (–OH) absorption peaks at around 3450 cm^{-1} (Murakami et al., 2003); also, the peaks between 3130 and 3650 cm^{-1} are enhanced and their positions moved, showing that – OH groups have been generated.

4.7.3 FTIR analysis of PET film

4.7.3.1 Ozonation of PET in aqueous medium

Figure 4.28 presents the infrared spectra of virgin PET film ozonized with 3.7 wt% applied dose in aqueous medium for 0.5 hrs, 1.0 hr, 2.0 hrs, 3.0 hrs, 4.0 hrs and 5.0 hrs. No obvious peaks were created, but the existing peaks between 1680 cm^{-1} and 1750 cm^{-1} were enhanced with ozonation time (Figure 4.31 shows the peaks).

4.7.3.2 PET reacted with ozone in the gaseous phase

Figure 4.29 presents the infrared spectra of virgin PET film reacted with 3.7 wt% applied ozone dose in the gaseous phase for 1.0 hr, 1.7 hrs, 2.5 hrs and 4.0 hrs. No obvious peaks were created, but the existing peaks between 1680 cm^{-1} to 1750 cm^{-1} were enhanced with ozonation time (Figure 4.31 shows the peak value).
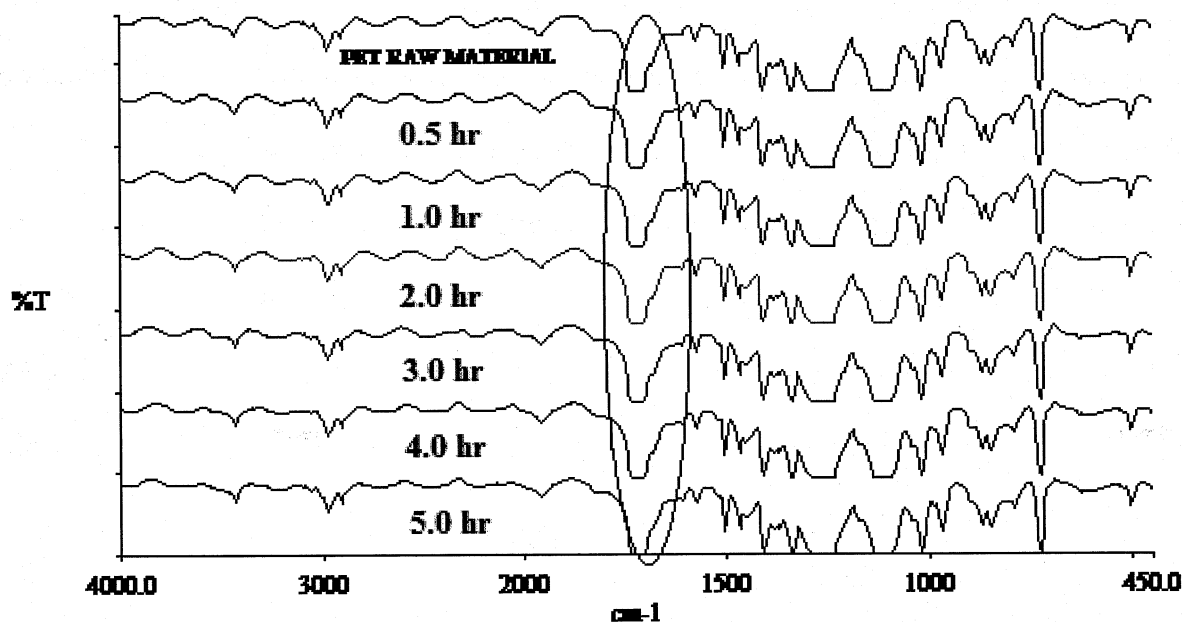
Fig. 4.28 Infrared spectra of PET with 3.7 wt% applied ozone dose in aqueous medium
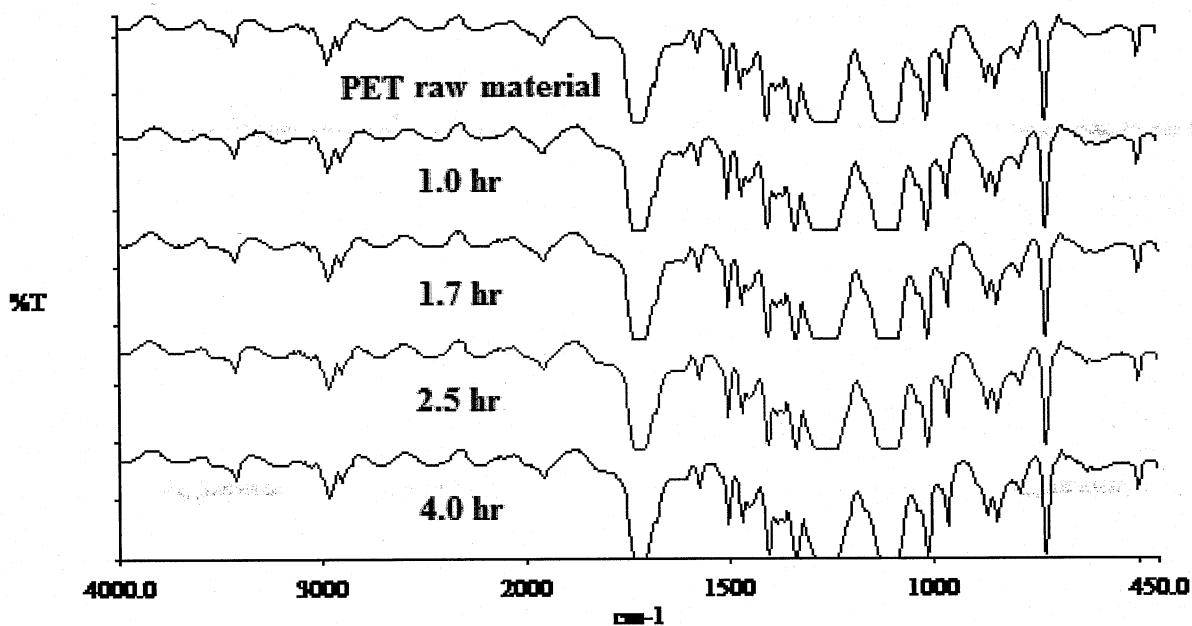
Fig. 4.29 Infrared spectra of PET with 3.7 wt% ozone applied dose in gaseous phase

4.7.3.3 Functional groups of the PET infrared spectrum

Figure 4.30 presents the infrared spectrum of raw material PET, and Figure 4.31 presents the infrared spectra of ozonized PET after 3.5 hrs ozonation time and 3.7 wt% applied ozone dose in the gaseous phase. After comparing these two charts, the following results were found:

- The broad band with a peak at 1738 cm^{-1} suggests contributions by several different components of $-C=O$ groups at 1770, 1755, 1738, 1725 and 1705 cm^{-1} [Ferreira, 2005];

- The peak at 1705 cm^{-1} represents the stretching of $-C=O$ in the carboxylic groups,

- The peaks at 1725 and 1738 cm^{-1} represent the stretching of the $-C=O$ in the original ester group,

- The peaks at 1755 and 1770 cm^{-1} are the vibrations of two $-C=O$ groups in the anhydride groups.

- The hydroxyl groups (–OH) absorption peaks occur at around 3450 cm^{1} (Murakami et al., 2003); and the fact that the peaks between 3130 and 3650 cm^{-1} are enhanced and their positions have moved shows that $-OH$ groups have been generated.

No new peaks were observed in the spectra. However, there was a major difference between the FTIR spectrum of the ozone-treated PET and the FTIR spectrum of the untreated PET, which was related to the values of the peaks in the bands at around 1738 cm^{-1} (the region from 1650 to 1800 cm^{-1}) and 1410 cm^{-1} [Ferreira, 2005]. According to the spectra shown above, the values of these peaks were higher, or the peaks were more enhanced, in the ozone-treated PET than in the untreated PET, which shows that the ozonation process increased the –C=O groups content.
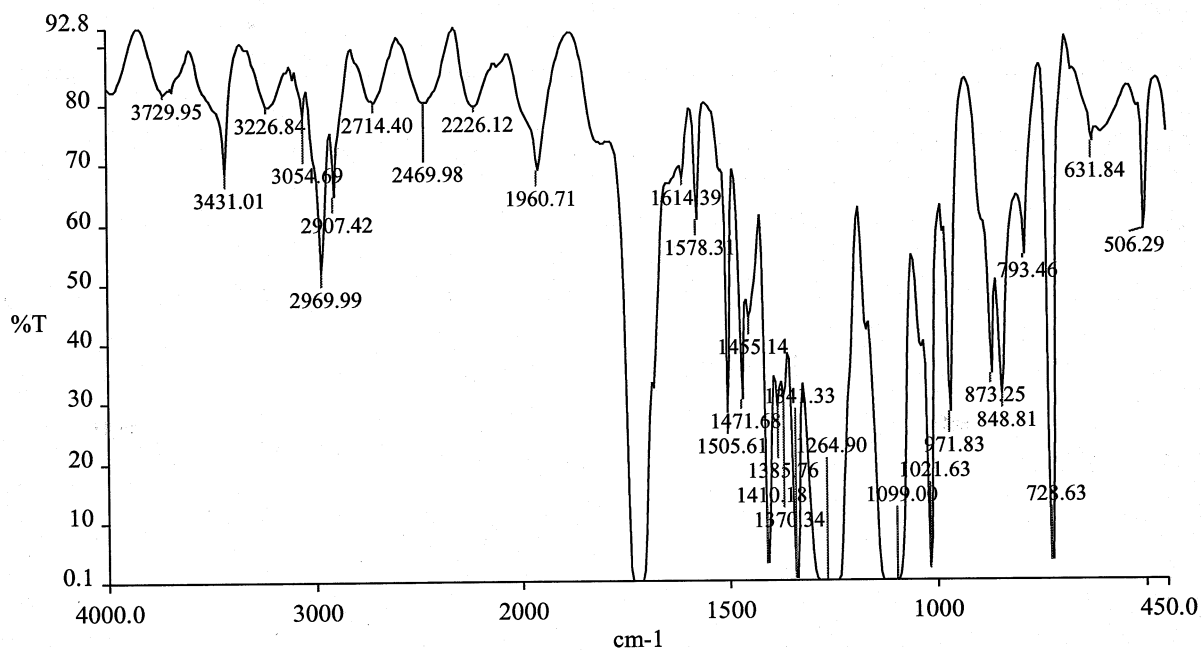
Fig. 4.30 Infrared spectrum of raw material PET
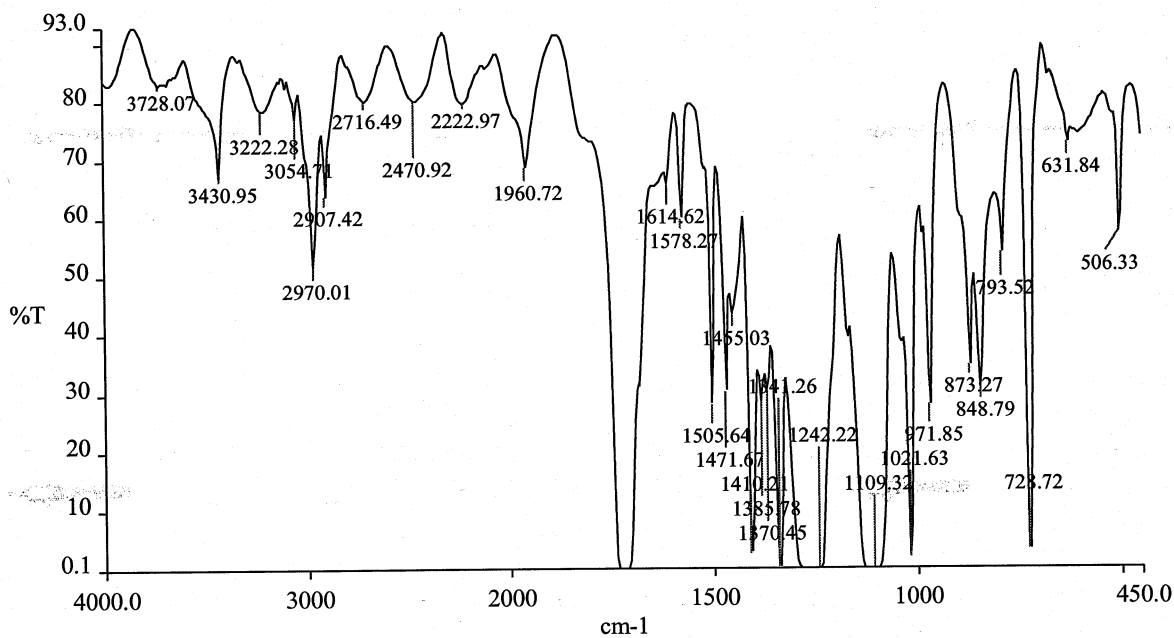
Fig. 4.31 Infrared spectrum of PET at 3.5 hrs and 3.7 wt% applied ozone dose in the gaseous phase

4.8 Graft polymerization

For the ultimate improvement of the polymer surface hydrophilicity, graft polymerization of acrylamide (AAm) on ozonated HDPE films was conducted. Based on the study results of the effects of the operating parameters, 1.0 wt% applied ozone dose and 1.0 hr treatment time were employed in the ozonation of HDPE film in aqueous medium. In order to better analyze and compare the results, another group of HDPE samples was treated at 3.7 wt% applied ozone dose and 1.0 hr treatment time in aqueous phase. All the samples after ozonation were dried and degassed for 1.0 hr under vacuum at room temperature.

Samples were graft polymerized by 20% AAm IPA solution according to the method introduced in 3.4.4. homopolymers were removed by ultrasound cleaning in distilled water and acetone, and dried 1.0 hr under vacuum at room temperature. The analytical results were discussed from 4.8.1 to 4.8.3.

4.8.1 Contact angle analytical results of grafted polymer films

Ozone treatment of films resulted in a small increase in the wettability of HDPE samples. However, there were significant changes in wettability of AAm-grafted HDPE films. Table 4.18 displays the results of contact angle of virgin HDPE film, ozonized film, and AAm-grafted film. The testing method was described in 3.5.4. The static contact angle was examined using a sessile drop of super pure water. Ten values were measured at each position, and 2 to 4 positions on each side of the sample film were examined. The results are shown in Table 4.18.

Apparently, the graft polymerization improved the hydrophilicity of the polymer films significantly. AAm-grafting on 1.0 wt% O_3, 1.0 hr ozonated HDPE films decreased the contact angle by 49.5%.

Table 4.1 Contact angle of virgin, ozone treated and AAm-grafted HDPE films

Contact Angle of HDPE					
Item	virgin	1.0%wt 1.0 hour ozonized	3.7%wt 1.0 hour ozonized	1.0%wt 1.0 hour ozonized and AAM grafted	3.7%wt 1.0 hour ozonized and AAM grafted
Contact angle (Average)	74.92	70.71	69.71	38.55	samples wrinkle

4.8.2 SEM analytical results

Samples were examined according to the method introduced in 3.5.3. Samples were pre-coated with gold at 0.4-0.5 Torr and observed under 2500 times and 5000 times magnification at 10-15 kV.

Figures 4.32 and 4.33 present the SEM results under 2500 times and 5000 times magnification.

HDPE oxidized by ozone led to molecules breaking down and surfaces becoming rougher. This fact was exhibited in the SEM pictures. Grafted AAm polymers filled in the gaps and covered the rough surface, leading to the surface being smooth. Moreover, with the hydrophilic molecular AAm connected to the backbone of the PE molecules, the film became hydrophilic and biocompatible.

4.8.3 FTIR analytical results of the grafted HDPE films

Figure 4.34 to Figure 4.37 present the FTIR analytical results of virgin, ozone oxidized and AAm-grafted HDPE films. Two new absorption peaks were observed from the AAm-grafted film, when the virgin and ozone oxidized film spectra were compared: 1667 cm^{-1} and 3202~3356 cm^{-1}, which represent two new functional groups: -NH-C=O and RN-H$_2$ [Fujimoto, 1993]; [Tu et al., 2005]; [Infrared Spectroscopy, pp. 1-26], which also meant the AAm monomer successfully graft polymerized onto the HDPE films.
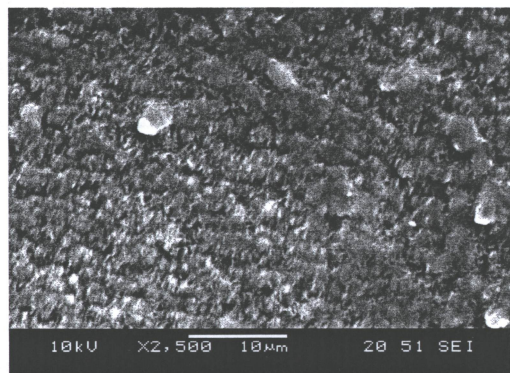
[a]
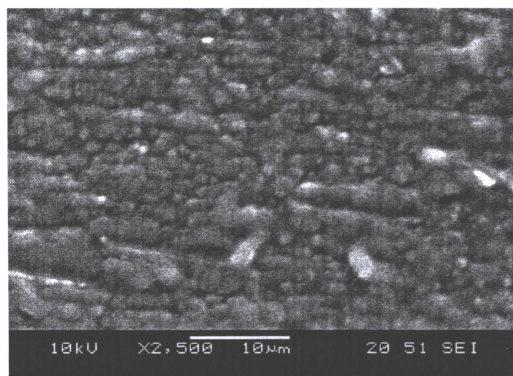
[b]
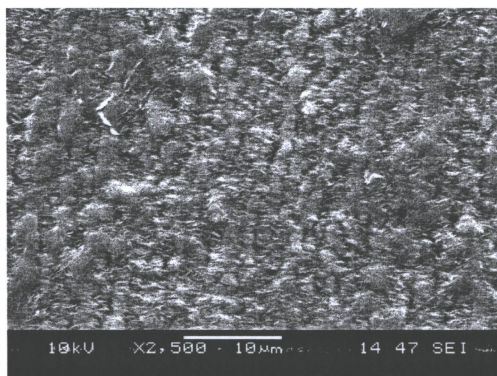
[c]
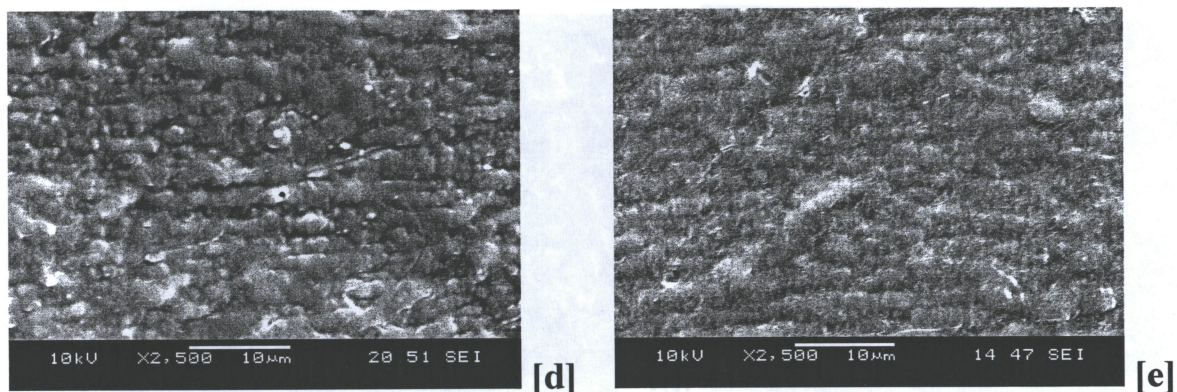
Fig. 4.32 SEM pictures under 2500 times magnification

[a] HDPE raw material; [b] HDPE oxidized by 1.0 wt% ozone, 1.0 hr in aqueous medium; [c] HDPE oxidized by 1.0 wt% ozone, 1.0 hr in aqueous medium; [d] AAm-grafted on 1.0 wt% O_3, 1.0 hr ozonated HDPE; [e] AAm-grafted on 3.7 wt% O_3, 1.0 hr ozonated HDPE
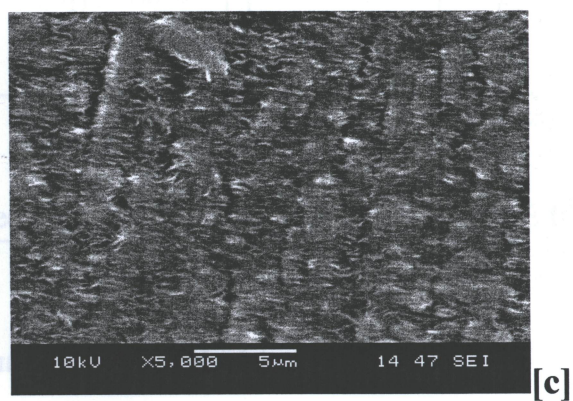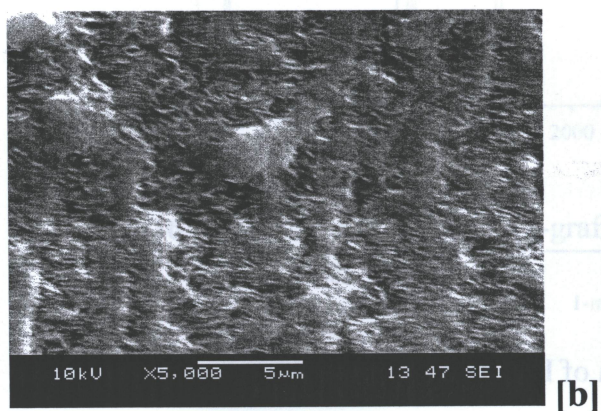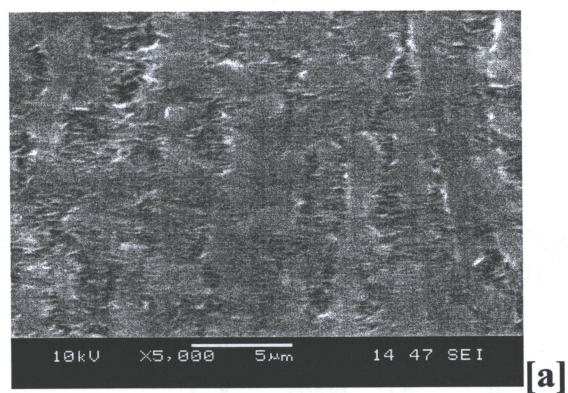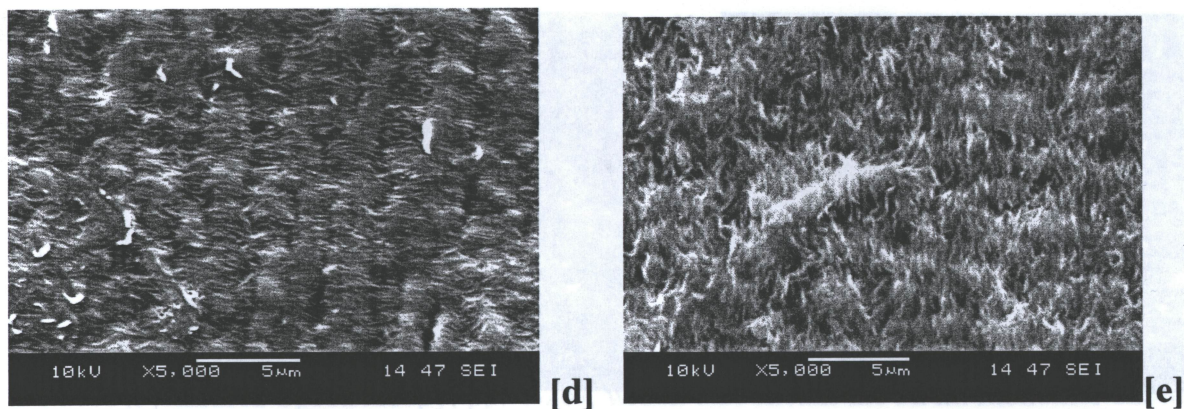
Fig. 4.33 SEM pictures under 5000 times magnification

[a] HDPE raw material; [b] HDPE oxidized by 1.0 wt% ozone, 1.0 hr in aqueous medium; [c] HDPE oxidized by 1.0 wt% ozone, 1.0 hr in aqueous medium; [d] AAm-grafted on 1.0 wt% O_3, 1.0 hr ozonated HDPE; [e] AAm-grafted on 3.7 wt% O_3, 1.0 hr ozonated HDPE
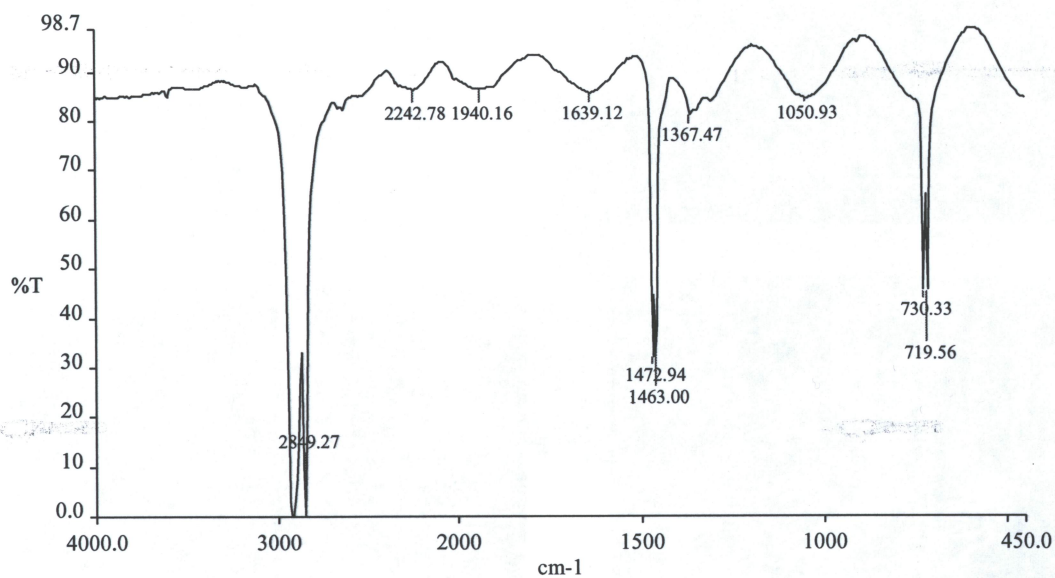
Fig. 4.34 Infrared spectrum of HDPE raw material
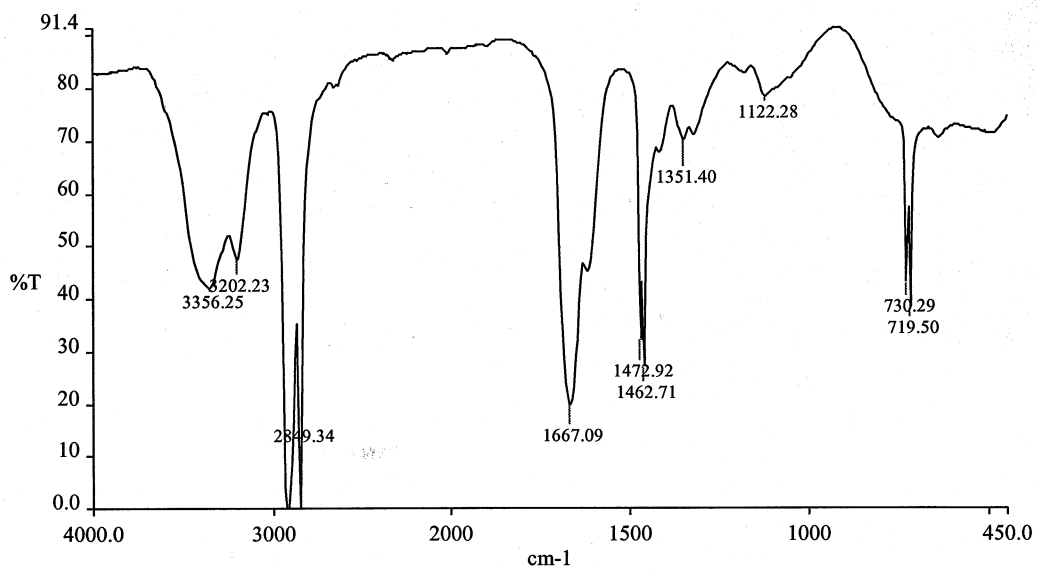
Fig. 4.35 Infrared spectrum of AAm-grafted on 1.0 wt% 1.0 hr ozone treated HDPE film
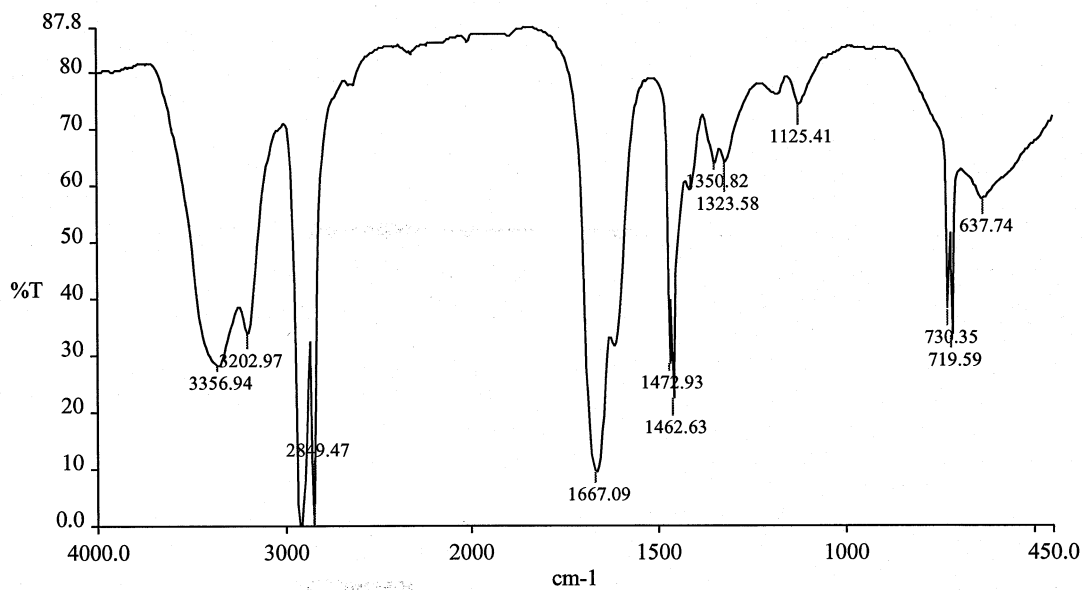
Fig. 4.36 Infrared spectrum of AAm-grafted on 3.7 wt% 1.0 hr ozone treated HDPE film
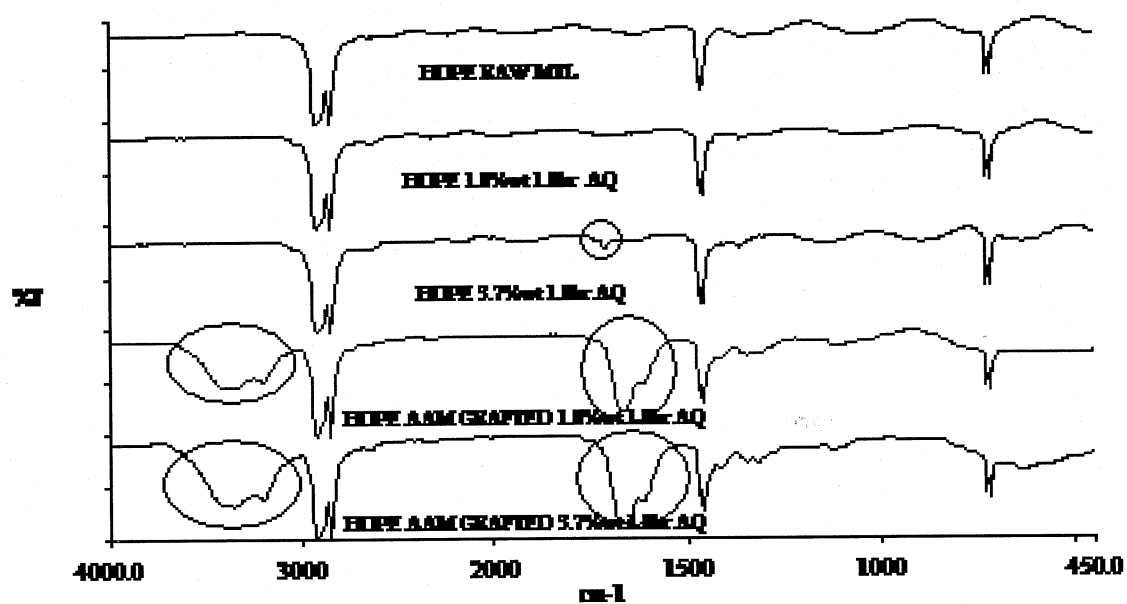
Fig. 4.37 Combination of infrared spectra of raw material/oxidized/AAm-grafted film

CHAPTER 5

CONCLUSIONS

The ozonation of three different films – HDPE, BOPP and PET – was successfully performed in aqueous solutions, and the treatment of the same films with ozone in the gaseous phase was implemented. The results were compared. The peroxide content generated and the changes in mechanical strength were measured after ozone treatment under both conditions. Through these experiments, we found that the peroxide generation rate varied in the aqueous and gaseous phases.

The peroxide generation rate also varied for different polymer films, but similar functional groups were generated. HDPE obtained a faster peroxide generation rate in the aqueous phase.

The peroxide content increased with the applied ozone dose, and increased with the treatment time as well. The mechanic strength displayed an opposite trend. The pH value was found to have some effect on ozonation; also, the amount of peroxide generation became less when the pH value increased. The pH value effect to the peroxide generation was minor.

The optimal parameter point (1.0 wt% and 1.0 hr) has been confirmed to create a good balance of mechanical strength and peroxide content created on HDPE film. A novel approach to treatment of these three films was successfully carried out through utilization of ozone treatment in aqueous medium.

AAm monomers were incorporated onto the HDPE film by peroxide-initiated graft polymerization. Grafted HDPE films exhibited a smaller contact angle of 49.5%, a decrease from that of the virgin HDPE; so a much better surface hydrophilicity was obtained. Considering that the grafted AAm introduced the biocompatible groups onto the HDPE surface, the film biocompatibility was significantly improved.

The FTIR spectra demonstrated the carbonyl, carboxyl and hydroxyl groups that were added onto the polymer films by ozonation. The density of these groups increased with the treatment time; and the AAm functional group was examined in the graft polymerized HDPE film by FTIR spectroscopy.

The SEM pictures show the differences in surface roughness and the changes in molecular structure in the virgin, ozonated and AAm-grafted HDPE films.

The contact angle test demonstrated the differences in surface conditions in the virgin HDPE film, ozonized films, and AAm-grafted films. Whereas ozone treatment of films resulted in a small increase in the wettability of HDPE film, AAm graft polymerization significantly improved the wettability of HDPE film.

RECOMMENDATIONS

Other substrates, such as PU, silicone, PMMA, EVA, etc, could be studied by ozonation in aqueous medium to compare the results with those obtained through ozonation in the gas phase.

Temperature is an important factor in ozonation. Investigation of the effect of temperature on the reaction and finding a suitable temperature range will be another area of study.

Other monomers, or macromolecules – for instance, PEG, DMMSA and Citrosan – could be employed in graft polymerization or immobilization. The protein adsorption test and the platelet adhesion test will be applied to surface modified polymers.

UV lamps and plasma methods can be combined with ozone treatment, and these combined methods can be used for films that have anti-ozonation properties.

This study will further lead to projects that broaden biomedical applications.

NOMENCLATURE

Symbol	Description
AAm	Acrylamide
AAc	Acrylic acid
ATR-IR	Attenuated total reflection infrared
BOPP	20 μ biaxial oriented polypropylene film
C=O	Carbonyl
DI	Distilled
DW	Distilled water
DMMCA	2-(Dimethylamino) ethyl methacrylate
DMAPS	N,N'-dimethyl (methacyloyloxyethyl) ammonium propanesulfate
DPPH	1,1-diphenyl-2-picrylhydrazyl
EVA	Poly(ethylene-co-vinyl alcohol) film
FTIR	Fourier transfer infrared
GSH	Glutathione
h (hr)	Hour
HAc	Glacial acetic acid
H_2SO_4	Sulphuric Acid
HDPE	15 μ blowing high density polyethylene film
HEMA	2-hydroxylethylmethacrylate
IPA	Isopropanol
$K_2Cr_2O_7$	Potassium dichromate
KI	Potassium iodide

LDPE	Low density polyethylene film
Mpa	Tensile strength unit, 10^6 N/m^2
MPC	Methacryloyloxyethyl phosphorylcholine
NADPH	Nicotinamide adenine dinucleotide phosphate
NaOH	Sodium hydroxide
Na$_2$S$_2$O$_3$	Sodium Thiosulfate
Nylon	Polyamide film
OBCS	*O*-butyrylchitosan
O-C=O	Carboxyl
O$_3$	Ozone
PET	12 μ biaxial oriented polyethylene terephthalate film
PLLA	Poly-L-lactic acid film
PMMA	Poly (methyl methacrylate) film
PS	Polystyrene film and powder
Psi	Pressure unit, pounds per square inch
PTFE	Poly (tetrafluoroethylene) film
PVC	Poly (vinyl chloride)
ROOH	Peroxide/hydroperoxide
SEM	Scanning Electronic Microscopy
SPEU	Segment Poly (ether-urethane)
VAECO	Vinyl alcohol-ethylene copolymer
wt%	weight percentage in the gas mixture
6F	Poly (hexafluoropropylene)

θ_Y	Young contact angle
σ_{lf}	liquid-fluid interfacial tensions
σ_{sl}	solid-liquid interfacial tensions
σ_{sf}	solid-fluid interfacial tensions
MCT	nitrogen-cooled mercury calmium telluride detector
DP	penetration depth
υ	wave number (cm^{-1})
Nc	refraction index of the crystal
θ	incidence angle of the infrared radiation into the crystal
Nsc	ratio between the refraction index
X	ozone uptake
t	time, min
K	rate constant
E	efficiency
[O]	concentration of ozone in feed gas

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Scanning electron microscope

http://en.wikipedia.org/wiki/Scanning_electron_microscope

Beer-Lambert law

(http://en.wikipedia.org/wiki/Beer-Lambert_law)

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SRI Consulting

http://www.sriconsulting.com/CEH/Public/Reports/580.1170/

Wanfang Data

http://www.wanfangdata.com/report/vpro.asp?id=582

Appendix I

Calculation of titration

The hydrogen peroxide reaction with iodide in acidic medium:

$$H_2O_2\ (aq) + 2I^-\ (aq) + 2H^+\ (aq) \longrightarrow I_2\ (aq) + 2\ H_2O\ (l)$$
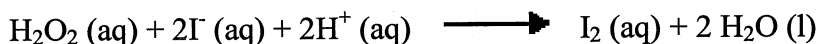
The created I_2 (aq) can be investigated by the titration of a standard $S_2O_3^{2-}$ (aq) solution

$$I_2 + 2\ S_2O_3^{2-} \longrightarrow 2\ I^- + S_4O_6^{2-} \qquad \text{[APHA, 1992, Iodometric Method I, pp 4-38]}$$

We assume the R-OOH has the same function as the H_2O_2 in this reaction, according to this formula, the consumption is:

$$1MMOL\ R\text{-}OOH\ =\ 2MMOL\ S_2O_3^{2-}$$
$$\text{TITRATION}$$
$$\text{CONSUMPTION}$$
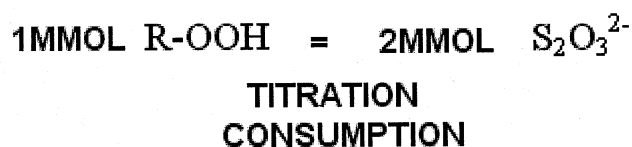
As an example, calculate the peroxide content of HDPE reacting with ozone at 3.7%wt, 1.0 h in aqueous medium:

Samples: 3 strips of 1.5" x10" HDPE film

Area: 2 (sides) x 3 (strips) x (1.5 inch x 25.4 mm) x (10 inch x25.4 mm) = 58064.4 mm^2

$\qquad\quad$ = 0.0580644 m^2

0.001N standard $Na_2S_2O_3^{2-}$ (aq) solution titration consumption: 3.6 ml

Consumption normality of $S_2O_3^{2-}$: 3.6 ml x 0.001 N = 0.0036

R-OOH normality = normality of $S_2O_3^{2-}$ = 0.0036

Where Normality = molality x n (where n = the number of protons exchanged in a reaction)

n = 2 in this reaction

R-OOH mmol: 0.0036 ÷ 2 = 0.0018

R-OOH (peroxide) density: 0.0018 mmol ÷ 0.0580644 m^2 = 0.031 mmol / m^2

Appendix II

Standard Sodium thiosulfate solution preparation:

0.1N: Dissolve 25.000 g $Na_2S_2O_3 \cdot 5H_2O$ in a 1.000 liter freshly boiled distilled water and standardized against potassium dichromate after at least 2 weeks storage.

0.01N: Dilute 10 times with freshly boiled distilled water, standardized against potassium dichromate.

0.001N: Dilute 100 times with freshly boiled distilled water, standardized against potassium dichromate.

Sodium thiosulfate solution must be calibrated by standard $K_2Cr_2O_7$ solution.

Appendix III

Calibration of Sodium Thiosulfate solution

In 80.0 ml distilled water slowly add in 1.0ml smoking H_2SO_4 and stirred, then added in 1.0g KI·5H$_2$O, precisely measured 10.00ml 0.1000 N $K_2Cr_2O_7$ solution add in the solution, shook and kept in dark for reaction of 6 minutes. Use sodium thiosulfate solution to titrate, record the consumption [APHA. 1992].

Standard 0.1000N $K_2Cr_2O_7$ making: dissolve 4.904 g anhydrous potassium dichromate of primary standard quality in distilled water and diluted to 1000ml to yield a 0.1000N solution. Then stored in a glass-stopper bottle.

Calculation is:

Normality of sodium thiosulfate = 0.1 x 10 ml of $K_2Cr_2O_7$/ consumption of sodium thiosulfate solution

Appendix IV

Calculation of tensile strength and elongation

Calculation of tensile strength

As an example of calculation tensile strength, use raw material HDPE analysis data.

The tensile strength checking data were 2.885, 2.784, 2.69, 2.677 kg/in at the different points of the sample. Average was 2.759 kg/in.

Force = 2.757 kg = 2.757 x 9.8 N = 27.0186 N

Area = (1 inch x 0.0254 m/inch) x (15 μ x 10^{-6} m) = 0.381 x 10^{-6} m^2

         Width   Thickness

Tensile strength = Force ÷ Area = 27.0186 N ÷ (0.381 x 10^{-6} m^2) = 70.91496 x 10^6 pa

                = 70.91496 Mpa

The thickness of BOPP is 20 μ, and thickness of PET is 12 μ, which is different from HDPE, so we must use the 20 μ replace of 15 μ when calculate the tensile strength of BOPP, and use 12 μ replace of 15 μ when calculate the PET.

Calculation of elongation

As an example of calculation elongation, use raw material HDPE analysis data.

The data of stretching length at break were 115.6, 81.24, 107.1, 112.0 mm at the different points of the sample. Average was 103.983 mm.

Sample set-up length was 1 inch, e.g., 25.4 mm,

Elongation = stretching length at break ÷ Sample set-up length x 100% = 103.983 mm ÷25.4 mm

          x 100%

          = 409. 389764 %

Appendix V
A summary of the principle infrared bands and their assignments.

R is an aliphatic group.

[Infrared Spectroscopy pp11 of 26, http://www.umsl.edu/~orglab/documents/IR/IR2.html]

Functional Group	Type		Frequencies cm-1	Peak Intensity
C–H	sp3 hybridized	R_3C-H	2850–3000	M(sh)
	sp2 hybridized	$=CR-H$	3000–3250	M(sh)
	sp hybridized	C–H	3300	M–S(sh)
	aldehyde C–H	H–(C=O)R	2750, 2850	M(sh)
N–H	primary amine, amide	$RN-H_2$, $RCON-H_2$	3300, 3340	S, S(br)
	secondary amine, amide	RNR–H, RCON–HR	3300–3500	S(br)
	tertiary amine, amide	$RN(R_3)$, $RCONR_2$	none	
O–H	alcohols, phenols	free O–H	3620–3580	W(sh)
		hydrogen bonded	3600–3650	S(br)
	carboxylic acids	R(C=O)O–H	3500–2400	S(br)
CN	nitriles	RCN	2280–2200	S(sh)
CC	acetylenes	R–CC–R	2260–2180	W(sh)
		R–CC–H	2160–2100	M(sh)
C=O	aldehydes	R(C=O)H	1740–1720	S(sh)
	ketones	R(C=O)R	1730–1710	S(sh)
	esters	$R(CO_2)R$	1750–1735	S(sh)
	anhydrides	$R(CO_2CO)R$	1820, 1750	S, S(sh)
	carboxylates	$R(CO_2)H$	1600, 1400	S, S(sh)
C=C	olefins	$R_2C=CR_2$	1680–1640	W(sh)
		$R_2C=CH_2$	1600–1675	M(sh)
		$R_2C=C(OR)R$	1600–1630	S(sh)
–NO2	nitro groups	RNO_2	1550, 1370	S, S(sh)

Intensities as follows: w =weak, m =medium, s =strong, **sh** =shoulder.

Appendix VI

Experimental Data Tables of HDPE reaction with ozone

Table VI-1 Peroxide data table of HDPE in aqueous medium

Ozone treated:	Sample pieces fixed in reactor, ozone bubbled through the diffuser					
Solution:	50 ml (Isopropanol : Glacial Acetic Acid = 25 : 1 + Potassium Iodide saturated in solution)					
Treated:	3 pieces of 1.5 in x 10 in of ozone oxidized films soaked in solution, heated nearly to boiling, stirred and kept 2-5 min					
Titration:	0.001 N Na$_2$S$_2$O$_3$ solution					
Material:	HDPE 15		Distilled Water (AQUEOUS PHASE)		10.5 liter	
Ozone flow rate:	10 l/min		Ozone pressure:		12 psi	
HDPE samples 1.0hr vacuum degassed and dried after ozone oxidization						
Ozone %wt	Time hr	0.001N Na$_2$S$_2$O$_3$ Titration consumption ml	Repeatable experiments	Molality of peroxide mmol	Area of samples m^2	mmol/m^2
3.7	0.25 hr	2.4		0.001	0.058	0.021
3.7	0.5 hr	2.5	2.2	0.001	0.058	0.022
3.7	1.0 hr	3.6		0.002	0.058	0.031
3.7	1.5 hr	4.8	4.6	0.002	0.058	0.041
3.7	2.0 hr	8.3		0.004	0.058	0.071
3.7	2.5 hr	14.5	13.8	0.007	0.058	0.125

Appendix VI

Experimental Data Tables of HDPE reaction with ozone

Table VI-2 Peroxide data table of HDPE in gas mixture

Ozone treated:	Sample pieces fixed in reactor, ozone diffused through the diffuser		
Solution:	50 ml(Isopropanol : Glacial Acetic Acid = 25 : 1 + Potassium Iodide saturated in solution)		
Treated:	3 pieces of 1.5 in x 10 in of ozone oxidized films soaked in solution, heated nearly to boiling, stirred and kept 2-5 min		
Titration:	0.001 N Na$_2$S$_2$O$_3$ solution		
Material:	HDPE 15	Reactor volume (GASEOUS PHASE)	12.5 liter
Ozone flow rate:	10 l/min	Ozone pressure:	13 psi
HDPE samples 1.0hr vacuum degassed and dried after ozone oxidization			

Ozone %wt	Time hr	0.001N Na$_2$S$_2$O$_3$ Titration consumption ml	Repeatable experiments	molality of peroxide	Area of samples m^2	mmol/m^2
3.7	0.25	3		0.002	0.0581	0.026
3.7	0.7	3.3		0.002	0.0581	0.028
3.7	1	3.4	3.6	0.002	0.0581	0.029
3.7	1.5	4.1		0.002	0.0581	0.035
3.7	2	12.2		0.006	0.0581	
3.7	2.5	8.1		0.004	0.0581	0.07
3.7	3			0	0.0581	
3.7	3.5	12.3	12.7	0.006	0.0581	0.106

Appendix VI

Experimental Data Tables of HDPE reaction with ozone

Table VI-3 Tensile strength data table of HDPE in aqueous medium

Machine	LLOYD LR 5K		Speed	10 in/min
1 in(w) x 1 in(L) sample gap of the clamps				
HDPE samples 1.0hr vacuum degassed and dried after ozone oxidization				
Ozone flow rate	10 l/min	Distilled water (aqueous medium)		10.5 l
Material:	HDPE 15	Ozone pressure:		13 psi

tensile strength	raw mat kgf/in	0.25 hr 3.7% Gas Ozone kgf/in	0.5 hr 3.7% Gas Ozone kgf/in	1 hr 4.0% Gas Ozone kgf/in	1.5 hr 3.7% Ozone kgf/in	2 hr 3.7% Ozone kgf/in	2.5 hr 4.0% Ozone kgf/in
	2.885	2.123	1.487	1.104	0.931	0.183	0.402
	2.784	2.102	1.503	1.092	1.047	0.262	0.130
	2.690	2.167	1.560	1.131	0.492	0.137	0.000
	2.677	2.370	1.475	1.114	0.851		0.000
		2.254	1.549				
Avg	2.759	2.203	1.515	1.110	0.830	0.194	0.133
Mpa (MN/m²)	70.948	56.656	38.953	28.550	21.353	4.995	3.421

Appendix VI

Experimental Data Tables of HDPE reaction with ozone

Table VI-4 Tensile strength data table of HDPE in gas mixture

Machine	LLOYD LR 5K	Speed		10 in/min
1 in(w) x 1 in(L) sample gap of the clamps				
HDPE samples 1.0hr vacuum degassed and dried after ozone oxidization				
Ozone flow rate	10 l/min	Reactor volume (gaseous medium)		12.5 l
Material:	HDPE 15	Ozone pressure:		13 psi

tensile strength	raw mat kgf/ in	0.25 hr 3.7% Ozone kgf/ in	0.7 hr 3.7% Ozone kgf/ in	1 hr 3.7% Ozone kgf/ in	1.5 hr 3.7% Ozone kgf/ in	2.5 hr 3.7% Ozone kgf/ in	3.5 hr 3.7% Ozone kgf/ in
	2.885	1.953	1.470	1.123	0.978	0.204	0.000
	2.784	1.897	1.564	1.179	1.080	0.172	0.116
	2.690	1.769	1.526	1.154	1.029	0.210	
	2.677	1.874	1.514	1.144	1.077	0.238	
		1.955	1.555	1.161	1.142		
					1.113		
Avg	2.759	1.890	1.526	1.152	1.070	0.206	0.058
Mpa(MN/m²)	70.948	48.591	39.236	29.629	27.509	5.296	1.494

Appendix VI

Experimental Data Tables of HDPE reaction with ozone

Table VI-5 Elongation data table of HDPE in aqueous medium

Machine	LLOYD LR 5K		Speed	10 in/min
1 in(w) x 1 in(L) sample gap of the clamps				
HDPE samples 1.0hr vacuum degassed and dried after ozone oxidization				
Ozone flow rate	10 1/min		Distilled water (aqueous medium)	10.5 1
Material:	HDPE 15		Ozone pressure:	13 psi

Elongation	raw mat mm	0.25 hr 3.7% Ozone mm	0.5 hr 3.7% Ozone mm	1 hr 3.7% Ozone mm	1.5 hr 3.7% Ozone mm	2 hr 3.7% Ozone mm
	115.6	102.0	87.8	34.6	1.5	0.0
	81.2	89.8	80.2	36.4	1.4	0.0
	107.1	88.9	91.0	47.3	2.3	0.0
	112.0	105.6	87.8		0.0	
		98.9	102.6			
Avg	104.0	97.0	89.9	39.5	1.3	0.0
%	409.4	382.0	353.8	155.4	5.1	0.0

Appendix VI

Experimental Data Tables of HDPE reaction with ozone

Table VI-6 Elongation data table of HDPE in gas mixture

Machine	LLOYD LR 5K		Speed		10 in/min	
1 in(w) x 1 in(L) sample gap of the clamps						
HDPE samples 1.0hr vacuum degassed and dried after ozone oxidization						
Ozone flow rate	10 1/min		Reactor volume (gaseous medium)		12.5 1	
Material:	HDPE 15		Ozone pressure:		13 psi	

Elongation	raw mat mm	0.25 hr 3.7% Ozone mm	0.7 hr 3.7% Ozone mm	1 hr 3.7% Ozone mm	1.5 hr 3.7% Ozone mm	2 hr 3.7% Ozone mm
	115.6	94.01	68.19	39.21	2.226	0
	81.24	93.27	73.79	57.93	1.71	0
	107.1	80.29	71.04	46.99	2.328	0
	112	97.03	71.17	40.3	2.783	0
	108	93.41	75.14	52.37	2.496	0
	97.88					
	99.33					
Avg	103.02	91.60	71.87	47.36	2.31	0
%	405.60	360.64	282.94	186.46	9.09	0

Appendix VII

Experimental Data Tables of BOPP reaction with ozone

Table VII-1 Peroxide data table of BOPP in aqueous medium

Ozone treated:	Sample pieces fixed in reactor, ozone diffused through the diffuser		
Solution:	50 ml (Isopropanol : Glacial Acetic Acid = 25 : 1 + Potassium Iodide saturated in solution)		
Treated:	3 pieces of 1.5 in x 10 in of ozone oxidized films soaked in solution, heated nearly to boiling, stirred and kept 2-5 min		
Titration:	0.001 N Na$_2$S$_2$O$_3$ solution		
Material:	BOPP20	Distilled water (AQUEOUS PHASE)	10.5 liter
Ozone flow rate:	10 l/min	Ozone pressure:	13 psi
BOPP samples 1.0hr vacuum degassed and dried after ozone oxidization			

Ozone %wt	Time hr	0.001N Na$_2$S$_2$O$_3$ Titration consumption ml	Repeatable experiments	Molality of peroxide mmol	Area of samples m^2	mmol/m^2
3.7	0.5 hr	3	2.9	0.001475	0.058064	0.025
3.7	1.5 hr	8.7		0.00435	0.058064	0.075
3.7	2 hr	11.4	10.9	0.0057	0.058064	0.098
3.7	2.5 hr	12.2		0.0061	0.058064	0.105
3.7	3 hr	13.8		0.006875	0.058064	0.118
3.7	4 hr	17.2	17.5	0.0086	0.058064	0.148
3.7	5 hr	22.2		0.0111	0.058064	0.191

Appendix VII

Experimental Data Tables of BOPP reaction with ozone

Table VII-2 Peroxide data table of BOPP in gas mixture

Ozone treated:	Sample pieces fixed in reactor, ozone diffused through the diffuser		
Solution:	50 ml(Isopropanol : Glacial Acetic Acid = 25 : 1 + Potassium Iodide saturated in solution)		
Treated:	3 pieces of 1.5 in x 10 in of ozone oxidized films soaked in solution, heated nearly to boiling, stirred and kept 2-5 min		
Titration:	0.001 N $Na_2S_2O_3$ solution		
Material:	BOPP 20	Reactor volume (GASEOUS PHASE)	12.5 liter
Ozone flow rate:	10 l/min	Ozone pressure:	13 psi
BOPP samples 1.0hr vacuum degassed and dried after ozone oxidization			

Ozone %wt	Time hr	0.001N $Na_2S_2O_3$ Titration consumption ml	Repeatable experiments	molality of peroxide	Area of samples m^2	$mmol/m^2$
3.7	0.5			0	0.058064	
3.7	1	5.2	5.7	0.002575	0.058064	0.044
3.7	1.7	10		0.004975	0.058064	0.086
3.7	2		12.2	0	0.058064	
3.7	2.5	15.8		0.0079	0.058064	0.136
3.7	2.7	15.4		0.007675	0.058064	0.132
3.7	3.5	19.5		0.00975	0.058064	0.168

Appendix VII

Experimental Data Tables of BOPP reaction with ozone

Table VII-3 Tensile strength data table of BOPP in aqueous medium

Machine	LLOYD LR 5K		Speed	10 in/min
1 in(w) x 1 in(L) sample gap of the clamps				
BOPP samples 1.0hr vacuum degassed and dried after ozone oxidization				
Ozone flow rate	10 l/min		Distilled water (aqueous medium)	10.5 l
Material:	BOPP 20		Ozone pressure:	13 psi

tensile strength	raw mat kgf/in	0.5 hr 3.7% Ozone kgf/in	1.5 hr 3.7% Ozone kgf/in	2.0 hr 3.7% Ozone kgf/in	2.5 hr 3.7% Ozone kgf/in	3 hr 3.7% Ozone kgf/in	4 hr 3.7% Ozone kgf/in	5 hr 3.9% Ozone kgf/in
	8.83	10.20	8.31	7.50	3.14	2.17	3.14	3.39
	8.66	8.82	7.80	8.44	3.96	3.71	3.49	3.19
	10.17	9.34	8.57	7.44	4.08	3.83	3.53	2.48
	11.13		8.09	8.14	3.95	3.88	3.49	2.34
					3.98	3.90	3.39	2.09
								2.89
Avg	9.70	9.45	8.19	7.88	3.82	3.50	3.41	2.73
Mpa (MN/m^2)	187.03	182.31	158.00	151.98	73.74	67.45	65.70	52.65

Appendix VII

Experimental Data Tables of BOPP reaction with ozone

Table VII-4 Tensile strength data table of BOPP in gas mixture

Machine	LLOYD LR 5K		Speed	10 in/min
1 in(w) x 1 in(L) sample gap of the clamps				
BOPP samples 1.0hr vacuum degassed and dried after ozone oxidization				
Ozone flow rate	10 l/min		Reactor volume (gaseous medium)	12.5 l
Material:	BOPP 20		Ozone pressure:	13 psi

tensile strength	raw mat kgf/ in	1 hr 3.7% Ozone kgf/ in	1.7 hr 3.7% Ozone kgf/ in	2.5 hr 3.7% Ozone kgf/ in	2.7 hr 3.7% Ozone kgf/ in	3.5 hr 3.7% Ozone kgf/ in
	8.83	4.39	4.30	3.61	3.10	3.48
	8.66	4.36	4.33	3.66	3.37	3.22
	10.17	4.62	4.33	3.71	3.76	3.51
	11.13	4.71	4.18	3.74	3.65	3.58
		4.81			3.74	
					3.80	
Avg.	9.70	4.58	4.29	3.68	3.57	3.45
Mpa (MN/m^2)	187.03	88.25	82.67	71.02	68.81	66.46

Appendix VII

Experimental Data Tables of BOPP reaction with ozone

Table VII-5 Elongation data table of BOPP in aqueous medium

Machine	LLOYD LR 5K		Speed	10 in/min
1 in(w) x 1 in(L) sample gap of the clamps				
BOPP samples 1.0hr vacuum degassed and dried after ozone oxidization				
Ozone flow rate	10 l/min		Distilled water (gaseous medium)	10.5 l
Material:	BOPP 20		Ozone pressure:	13 psi

Elongation	raw mat mm	0.5 hr 3.7% Ozone mm	1.0hr 3.7% Ozone mm	2.5 hr 3.7% Ozone mm	3.0 hr 3.7% Ozone mm	4 hr 3.7% Ozone mm	5 hr 3.7% Ozone mm
	38.37	31.18	26.87	11.64	14.56	9.88	15.04
	36.03	31.06	28.16	19.02	17.55	16.67	11.79
	44.70	29.77	24.84	20.40	17.48	16.09	3.89
		31.00	26.93	18.95	19.08	14.98	3.27
				19.08	3.05	14.23	2.69
Avg.	39.70	30.75	26.70	17.82	14.34	14.37	7.34
%	156.26	121.04	105.09	70.13	56.46	56.56	28.88

Appendix VII

Experimental Data Tables of BOPP reaction with ozone

Table VII-6 Elongation data table of BOPP in gas mixture

Machine	LLOYD LR 5K		Speed		10 in/min	
1 in(w) x 1 in(L) sample gap of the clamps						
BOPP samples 1.0hr vacuum degassed and dried after ozone oxidization						
Ozone flow rate	10 l/min		Reactor volume (gaseous medium)		12.5 l	
Material:	BOPP 20		Ozone pressure:		13 psi	

Elongation	raw mat mm	1 hr 3.7% Ozone mm	1.7 hr 3.7% Ozone mm	2.5 hr 3.7% Ozone mm	2.7 hr 3.7% Ozone mm	3.5 hr 3.7% Ozone mm
	38.37	21.21	21.44	12.66	9.83	14.29
	36.03	19.75	20.10	12.90	9.93	10.38
	44.70	20.62	21.16	13.91	15.07	14.63
		23.63	18.97	15.82	13.96	15.20
		23.76			15.39	
		21.79			17.95	
Avg.	39.70	21.79	20.42	13.82	13.69	13.63
%	156.26	85.78	80.36	54.40	53.87	53.63

Appendix VIII

Experimental Data Tables of PET reaction with ozone

Table VIII-1 Peroxide data table of PET in aqueous medium

Ozone treated:	Sample pieces fixed in reactor, ozone diffused through the diffuser		
Solution:	50 ml(Isopropanol : Glacial Acetic Acid = 25 : 1 + Potassium Iodide saturated in solution)		
Treated:	3 pieces of 1.5 in x 10 in of ozone oxidized films soaked in solution, heated nearly to boiling, stirred and kept 2-5 min		
Titration:	0.001 N Na₂S₂O₃ solution		
Material:	PET 12	Distilled water (AQUEOUS PHASE)	10.5 liter
Ozone flow rate:	10 l/min	Ozone pressure:	13 psi
PET samples 1.0hr vacuum degassed and dried after ozone oxidization			

Ozone %wt	Time hr	0.001N Na₂S₂O₃ Titration consumption ml	Repeatable experiments	Molality of peroxide mmol	Area of samples m²	mmol/m²
3.7	0.5 hr	2.4	2.15	0.001175	0.058064	0.020
3.7	1.0 hr	3.1		0.00155	0.058064	0.027
3.7	1.5 hr			0	0.058064	0.000
3.7	2 hr	3.4	3.50	0.0017	0.058064	0.029
3.7	2.5 hr		4.50	0	0.058064	0.000
3.7	3 hr	3.9		0.00195	0.058064	0.034
3.7	3.5 hr	4.7		0.002325	0.058064	0.040
3.7	4 hr	4.5		0.00225	0.058064	0.039
3.7	5 hr	4.1		0.002025	0.058064	0.035

Appendix VIII

Experimental Data Tables of PET reaction with ozone

Table VIII-2 Peroxide data table of PET in gas mixture

Ozone treated:	Sample pieces fixed in reactor, ozone diffused through the diffuser		
Solution:	50 ml(Isopropanol : Glacial Acetic Acid = 25 : 1 + Potassium Iodide saturated in solution)		
Treated:	3 pieces of 1.5 in x 10 in of ozone oxidized films soaked in solution, heated nearly to boiling, stirred and kept 2-5 min		
Titration:	0.001 N Na$_2$S$_2$O$_3$ solution		
Material:	PET 12	Reactor volume (AQUEOUS PHASE)	12.5 liter
Ozone flow rate:	10 l/min	Ozone pressure:	13 psi
PET samples 1.0hr vacuum degassed and dried after ozone oxidization			

Ozone %wt	Time hr	0.001N Na$_2$S$_2$O$_3$ Titration consumption ml	Repeatable experiments	Molality of peroxide mmol	Area of samples m^2	mmol/ m^2
3.7	0.5			0	0.058064	
3.7	1.0	3.1	3.16	0.00155	0.058064	0.027
3.7	1.7	5.2		0.0026	0.058064	0.045
3.7	2.0			0	0.058064	
3.7	2.5	6.4	5.80	0.0032	0.058064	0.055
3.7	2.7	5.1		0.002525	0.058064	0.043
3.7	3.5			0	0.058064	
3.7	4.0	6.4		0.0032	0.058064	0.055

Appendix VIII

Experimental Data Tables of PET reaction with ozone

Table VIII-3 Tensile strength data table of PET in aqueous medium

Machine	LLOYD LR 5K		Speed		10 in/min			
1 in(w) x 1 in(L) sample gap of the clamps								
PET samples 1.0hr vacuum degassed and dried after ozone oxidization								
Ozone flow rate	10 1/min		Distilled water (AQUEOUS PHASE)		10.5 1			
Material:	PET 12		Ozone pressure:		13 psi			

tensile strength	raw mat kgf/ in	0.5 hr 4.0% Ozone kgf/in	1 hr 3.7% Ozone kgf/in	2 hr 3.7% Ozone kgf/in	3 hr 3.7% Ozone kgf/in	3.5 hr 3.7% Ozone kgf/in	4 hr 3.7% Ozone kgf/in	5 hr 3.7% Ozone kgf/in
	6.69	6.44	6.88	6.17	5.38		5.52	5.31
	6.09	6.89	4.34	5.53	4.79	4.63	4.46	4.62
	6.66	5.40	6.86	5.29	5.87	4.83	6.18	5.75
		6.95		5.97		5.37	6.32	5.05
						5.32	6.10	5.55
Avg.	6.48	6.42	6.03	5.74	5.35	5.04	5.72	5.26
Mpa(MN/m²)	208.26	206.29	193.75	184.47	171.88	161.90	183.73	168.92

Appendix VIII

Experimental Data Tables of PET reaction with ozone

Table VII-4 Tensile strength data table of BOPP in gas mixture

Machine	LLOYD LR 5K		Speed		10 in/min
1 in(w) x 1 in(L) sample gap of the clamps					
PET samples 1.0hr vacuum degassed and dried after ozone oxidization					
Ozone flow rate	10 l/min		Reactor volume (GASEOUS PHASE)		12.5 l
Material:	PET 12		Ozone pressure:		13 psi

tensile strength	raw mat kgf/ in	1 hr 3.7% Ozone kgf/ in	1.7 hr 3.7% Ozone kgf/ in	2.5 hr 3.7% Ozone kgf/ in	2.7 hr 3.7% Ozone kgf/ in	4.0 hr 3.7% Ozone kgf/ in
	6.69	4.96	6.24	3.81	4.13	3.70
	6.09	4.66	6.19	5.07	6.24	5.04
	6.66	4.83	6.10	4.31	6.13	5.28
		5.09	5.37	4.36	5.04	
			6.44	5.76	5.34	
				4.78		
Avg.	6.48	4.89	6.07	4.68	5.38	4.68
Mpa (MN/m^2)	208.26	157.02	195.10	150.43	172.84	150.28

Appendix VIII

Experimental Data Tables of PET reaction with ozone

Table VIII-5 Elongation data table of PET in aqueous medium

Machine	LLOYD LR 5K		Speed	10 in/min
1 in(w) x 1 in(L) sample gap of the clamps				
PET samples 1.0hr vacuum degassed and dried after ozone oxidization				
Ozone flow rate	10 l/min		Distilled water (AQUEOUS PHASE)	10.5 1
Material:	PET 12		Ozone pressure:	13 psi

Elongation	raw mat mm	0.5 hr 3.7% Ozone mm	1 hr 3.7% Ozone mm	2.0 hr 3.7% Ozone mm	3.5 hr 3.7% Ozone mm	4 hr 3.7% Ozone mm	5 hr 3.7% Ozone mm
	31.87			30.61	14.58	27.71	24.18
	31.76	32.62	37.27	23.33	18.22	14.36	14.86
		39.89	9.23	20.79	26.07	34.39	31.04
		21.10	38.61	31.82	27.25	35.15	23.12
		39.40				32.52	29.14
		33.25	28.37		21.53	28.83	24.47
Avg.	31.82	33.25	28.37	26.64	21.53	28.83	24.47
%	125.22	130.88	111.66	104.84	84.74	113.46	96.30

Appendix VIII

Experimental Data Tables of PET reaction with ozone

Table VIII-6 Elongation data table of PET in gas mixture

Machine	LLOYD LR 5K		Speed		10 in/min
1 in(w) x 1 in(L) sample gap of the clamps					
PET samples 1.0hr vacuum degassed and dried after ozone oxidization					
Ozone flow rate	10 l/min		Reactor volume (GASEOUS PHASE)		12.5 1
Material:	PET 12		Ozone pressure:		13 psi

Elongation	raw mat mm	1 hr 3.7% Ozone mm	1.7 hr 3.7% Ozone mm	2.5 hr 3.7% Ozone mm	2.7 hr 3.7% Ozone mm	4 hr 3.7% Ozone mm
	31.87	16.00	34.06	7.48	11.04	3.95
	31.76	12.90	32.76	17.02	28.21	18.32
		14.05	31.37	9.56	35.48	23.53
		17.97	21.43	9.86	20.80	
			36.68	26.16	26.16	
		15.23		13.99		
Avg.	31.82	15.23	31.26	14.01	24.34	15.27
%	125.22	59.94	123.04	55.15	95.79	60.09

Appendix IX

Experimental Data Tables of HDPE reacting conditions studies---different ozone applied doses effect

Table IX-1 Peroxide data table of HDPE in aqueous medium with different ozone applied doses and one hour treating time

Ozone treated:	Sample pieces fixed in reactor, ozone diffused through the diffuser		
Solution:	50 ml (Isopropanol : Glacial Acetic Acid = 25 : 1 + Potassium Iodide saturated in solution)		
Treated:	3 pieces of 1.5 in x 10 in of ozone oxidized films soaked in solution, heated nearly to boiling, stirred and kept 2-5 min		
Titration:	0.001 N Na$_2$S$_2$O$_3$ solution		
Material:	HDPE 15	Distilled water (AQUEOUS PHASE)	10.5 liter
Ozone flow rate:	10 1/min	Ozone pressure:	13 psi
HDPE samples 1.0hr vacuum degassed and dried after ozone oxidization			

Ozone %wt	Time hr	0.001N Na$_2$S$_2$O$_3$ Titration consumption ml	Repeatable experiments	Molality of peroxide mmol	Area of samples m^2	mmol/ m^2
1.0	1.0 hr	2.9		0.00143	0.05806	0.0245
2.0	1.0 hr	2.9	2.5	0.00145	0.05806	0.0250
3.0	1.0 hr	3.4	3.5	0.00171	0.05806	0.0294
3.7	1.0 hr	3.6		0.0018	0.05806	0.0310
4.0	1.0 hr	4.2		0.0021	0.05806	0.0362

Appendix IX

Experimental Data Tables of HDPE reacting parameter studies---different ozone applied doses effect

Table IX-2 Peroxide data table of HDPE in gas phase with different ozone concentration and one hour treating time

Ozone treated:	Sample pieces fixed in reactor, ozone diffused through the diffuser		
Solution:	50 ml (Isopropanol : Glacial Acetic Acid = 25 : 1 + Potassium Iodide saturated in solution)		
Treated:	3 pieces of 1.5 in x 10 in of ozone oxidized films soaked in solution, heated nearly to boiling, stirred and kept 2-5 min		
Titration:	0.001 N $Na_2S_2O_3$ solution		
Material:	HDPE 15	Reactor volume (GASEOUS PHASE)	12.5 liter
Ozone flow rate:	10 l/min	Ozone pressure:	13 psi
HDPE samples 1.0hr vacuum degassed and dried after ozone oxidization			

Ozone %wt	Time hr	0.001N $Na_2S_2O_3$ Titration consumption ml	Repeatable experiments	Molality of peroxide mmol	Area of samples m^2	mmol/m^2
1.0	1.0 hr	2.6		0.0013	0.05806	0.0224
2.0	1.0 hr	2.9	2.70	0.00145	0.05806	0.0250
3.0	1.0 hr	3.4		0.0017	0.05806	0.0293
3.7	1.0 hr	3.4	3.60	0.0017	0.05806	0.0293
4.0	1.0 hr	3.6		0.00178	0.05806	0.0306

Appendix IX

Experimental Data Tables of HDPE reacting parameter studies---different ozone applied doses effect

Table IX-3 Tensile strength data table of HDPE in aqueous medium with different ozone applied doses and one hour treating time

Machine	LLOYD LR 5K		Speed	10 in/min
1 in(w) x 1 in(L) sample gap of the clamps				
HDPE samples 1.0hr vacuum degassed and dried after ozone oxidization				
Ozone flow rate	10 l/min		Distilled water (AQUEOUS PHASE)	10.5 1
Material:	HDPE 15		Ozone pressure:	13 psi

tensile strength	raw mat kgf/ in	1.0 hr 1.0%wt Ozone kgf/ in	1 hr 2.0% wt Gas Ozone kgf/ in	1.0 hr 3.0% wt Ozone kgf/ in	1.0hr 3.7% wt Ozone kgf/ in	1.0hr 4.0%wt Ozone kgf/ in
	2.89	1.93	1.67	1.18	1.10	1.17
	2.78	1.99	1.59	1.20	1.09	1.19
	2.69	2.14	1.54	1.27	1.13	1.18
	2.68	2.18	1.69	1.31	1.11	1.11
		1.95	1.75	1.36		1.11
		1.90	1.78	1.45		1.12
		1.90		1.52		1.14
		1.93		1.53		
				1.13		
Avg.	2.76	1.99	1.67	1.33	1.11	1.14
Mpa (MN/m^2)	70.95	51.16	42.91	34.11	28.55	29.39

Appendix IX

Experimental Data Tables of HDPE reacting parameter studies---different ozone applied doses effect

Table IX-4 Tensile strength data table of HDPE in gas phase with different ozone concentration and one hour treating time

Machine	LLOYD LR 5K		Speed		10 in/min	
1 in(w) x 1 in(L) sample gap of the clamps						
HDPE samples 1.0hr vacuum degassed and dried after ozone oxidization						
Ozone flow rate	10 1/min		Reactor volume (GASEOUS PHASE)		12.5 1	
Material:	HDPE 15		Ozone pressure:		13 psi	

tensile strength	raw mat kgf/ in	1.0 hr 1.0%wt Ozone kgf/ in	1 hr 2.0% wt Gas Ozone kgf/ in	1.0 hr 3.0% wt Ozone kgf/ in	1.0hr 3.7% wt Ozone kgf/ in	1.0hr 4.0%wt Ozone kgf/ in
	2.89	1.77	1.39	1.05	1.12	1.07
	2.78	1.77	1.30	1.06	1.18	1.03
	2.69	1.69	1.22	1.06	1.15	1.03
	2.68	1.59	1.16	1.04	1.14	1.08
		1.70	1.10	1.06	1.16	1.25
		1.75	1.18	1.14		1.24
		1.74	1.15	1.15		1.21
			1.08	1.20		
Avg.	2.76	1.72	1.20	1.10	1.15	1.13
Mpa(MN/m^2)	70.95	44.12	30.77	28.17	29.63	29.04

Appendix IX

Experimental Data Tables of HDPE reacting parameter studies---different ozone applied doses effect

Table IX-5 Elongation data table of HDPE in aqueous medium with different ozone concentration and one hour treating time

Machine	LLOYD LR 5K		Speed	10 in/min
1 in(w) x 1 in(L) sample gap of the clamps				
HDPE samples 1.0hr vacuum degassed and dried after ozone oxidization				
Ozone flow rate	10 l/min		Distilled water (AQUEOUS PHASE)	10.5 1
Material:	HDPE 15		Ozone pressure:	13 psi

Elongation	raw mat mm	1.0 hr 1.0% Ozone mm	1 hr 2.0% Ozone mm	1.0 hr 3.0% Ozone mm	1.0 hr 3.7% Ozone mm	1.0 hr 4.0% Ozone mm
	115.60	99.13	82.98	59.20	34.63	27.77
	81.24	90.35	79.94	67.51	36.41	45.82
	107.10	97.85	81.10	77.81	47.34	41.76
	112.00	105.20	89.22	66.93		29.94
		101.30	96.13	63.07		7.10
		92.25	99.62	63.94		
		102.30		67.66		
		116.00		75.58		
Avg.	103.99	100.55	88.17	67.71	39.46	30.48
%	409.39	395.86	347.11	266.58	155.35	119.99

Appendix IX

Experimental Data Tables of HDPE reacting parameter studies---different ozone applied doses effect

Table IX-6 Elongation data table of HDPE in gas phase with different ozone applied doses and one hour treating time

Machine	LLOYD LR 5K	Speed	10 in/min
1 in(w) x 1 in(L) sample gap of the clamps			
HDPE samples 1.0hr vacuum degassed and dried after ozone oxidization			
Ozone flow rate	10 1/min	Reactor volume (GASEOUS PHASE)	12.5 1
Material:	HDPE 15	Ozone pressure:	13 psi

Elongation	raw mat mm	1.0 hr 1.0% Ozone mm	1 hr 2.0% Ozone mm	1.0 hr 3.0% Ozone mm	1.0 hr 3.7% Ozone mm	1.0 hr 4.0% Ozone mm
	115.60	111.80	69.55	41.08	34.63	4.53
	81.24	110.90	62.79	40.58	36.41	3.83
	107.10	104.10	57.15	38.34	47.34	4.95
	112.00	97.43	52.34	22.64		8.56
		99.13	49.07	34.89		
		92.47	63.94	34.51		
		98.37	67.92	45.76		
			54.02	44.42		
Avg.	103.99	102.03	59.60	37.78	39.46	5.47
%	409.39	401.69	234.64	148.73	155.35	21.53

Appendix X

Experimental Data Tables of HDPE reacting parameter studies---1.0%wt ozone applied dose and different treating time effect

Table X-1 Peroxide data table of HDPE in aqueous medium with different treating time and 1.0 wt% applied ozone dose

Ozone treated:	Sample pieces fixed in reactor, ozone diffused through the diffuser				
Solution:	50 ml(Isopropanol : Glacial Acetic Acid = 25 : 1 + Potassium Iodide saturated in solution)				
Treated:	3 pieces of 1.5 in x 10 in of ozone oxidized films soaked in solution, heated nearly to boiling, stirred and kept 2-5 min				
Titration:	0.001 N Na$_2$S$_2$O$_3$ solution				
Material:	HDPE 15		Distilled water (AQUEOUS PHASE)		10.5 liter
Ozone flow rate:	10 1/min		Ozone pressure:		13 psi
HDPE samples 1.0hr vacuum degassed and dried after ozone oxidization					

Ozone %wt	Time hr	0.001N Na$_2$S$_2$O$_3$ Titration consumption ml	Molality of peroxide mmol	Area of samples m^2	mmol/m^2
1.0	0.5	2.9	0.00145	0.05806	0.025
1.0	1.0	3.0	0.0015	0.05806	0.026
1.0	1.5	3.5	0.00175	0.05806	0.030
1.0	2.0	3.6	0.0018	0.05806	0.031
1.0	2.5	4.0	0.002	0.05806	0.034

Appendix X

Experimental Data Tables of HDPE reacting parameter studies---1.0wt% ozone applied dose and different treating time effect

Table X-2 Tensile strength data table of HDPE in aqueous medium with different treating time and 1.0%wt ozone concentration

Machine	LLOYD LR 5K		Speed		10 in/min	
1 in(w) x 1 in(L) sample gap of the clamps						
HDPE samples 1.0hr vacuum degassed and dried after ozone oxidization						
Ozone flow rate	10 1/min		Distilled water (AQUEOUS PHASE)		10.5 1	
Material:	HDPE 15		Ozone pressure:		13 psi	

tensile strength	raw mat kgf/ in	0.5 hr 1.0%wt Ozone kgf/ in	1 hr 1.0% wt Ozone kgf/ in	1.5 hr 1.0% wt Ozone kgf/ in	2.0hr 1.0% wt Ozone kgf/ in	2.5hr 1.0%wt Ozone kgf/ in
	2.89	1.96	1.95	1.78	1.29	1.26
	2.78	2.07	1.77	1.77	1.23	1.31
	2.69	2.23	1.89	1.79	1.27	1.21
	2.68	2.30	1.81	1.71	1.35	1.26
		2.30	1.70		1.39	1.31
Avg.	2.76	2.17	1.82	1.76	1.31	1.27
Mpa(MN/m²)	70.95	55.90	46.83	45.25	33.60	32.61

Appendix X

Experimental Data Tables of HDPE reacting parameter studies---1.0wt% ozone applied dose and different treating time effect

Table X-3 Elongation data table of HDPE in aqueous medium with different treating time and 1.0wt% applied ozone dose

Machine	LLOYD LR 5K		Speed		10 in/min	
1 in(w) x 1 in(L) sample gap of the clamps						
HDPE samples 1.0hr vacuum degassed and dried after ozone oxidization						
Ozone flow rate	10 1/min		Distilled water (AQUEOUS PHASE)		10.5 1	
Material:	HDPE 15		Ozone pressure:		13 psi	

Elongation	raw mat mm	0.5 hr 1.0% Ozone mm	1 hr 1.0% Ozone mm	1.5 hr 1.0% Ozone mm	2.0 hr 1.0% Ozone mm	2.5hr 1.0% Ozone mm
	115.60	94.86	112.50	98.99	78.95	62.73
	81.24	99.86	90.13	94.34	74.08	74.56
	107.10	111.60	109.40	93.58	75.23	52.94
	112.00	114.00	99.45	87.03	74.48	64.27
		120.50	87.81		76.23	69.88
Avg.	103.99	108.16	99.86	93.49	75.79	64.88
%	409.39	425.84	393.14	368.05	298.40	255.42

Appendix XI

Experimental Data Tables of HDPE reacting parameter studies---PH value effects with 1.0%wt ozone concentration and 1.0 hour treating time

Table XI-1 Peroxide data table of HDPE in aqueous medium ---PH value effects with 1.0%wt ozone concentration and 1.0 hour treating time

Ozone treated:	Sample pieces fixed in reactor, ozone diffused through the diffuser		
Solution:	50 ml(Isopropanol : Glacial Acetic Acid = 25 : 1 + Potassium Iodide saturated in solution)		
Treated:	3 pieces of 1.5 in x 10 in of ozone oxidized films soaked in solution, heated nearly to boiling, stirred and kept 2-5 min		
Titration:	0.001 N Na$_2$S$_2$O$_3$ solution		
Material:	HDPE 15	Distilled water (AQUEOUS PHASE)	10.5 liter
Ozone flow rate:	10 l/min	Ozone pressure:	13 psi
HDPE samples 1.0hr vacuum degassed and dried after ozone oxidization			

Ozone %wt	Time hr	PH value	0.001N Na$_2$S$_2$O$_3$ Titration consumption ml	Normality of peroxide	Area of samples	mmol/m2
1.0	1.0	10.6	2.9	0.00145	0.05806	0.0250
1.0	1.0	9.7	2.7	0.00133	0.05806	0.0228
1.0	1.0	7.5	3.1	0.00153	0.05806	0.0263
1.0	1.0	6.6	3.2	0.0016	0.05806	0.0276
1.0	1.0	4.4	3.2	0.00165	0.05806	0.0284
1.0	1.0	2.4	3.3	0.00165	0.05806	0.0284

Appendix XI

Experimental Data Tables of HDPE reacting parameter studies---PH value effects with 1.0%wt ozone concentration and 1.0 hour treating time

Table XI-2 Tensile strength table of HDPE in aqueous medium ---PH value effects with 1.0%wt ozone concentration and 1.0 hour treating time

Machine	LLOYD LR 5K		Speed	10 in/min
1 in(w) x 1 in(L) sample gap of the clamps				
HDPE samples 1.0hr vacuum degassed and dried after ozone oxidization				
Ozone flow rate	10 l/min		Distilled water (AQUEOUS PHASE)	10.5 l
Material:	HDPE 15		Ozone pressure:	13 psi

tensile strength	raw mat kgf/ in	1.0 hr 1.0%wt PH2.488 kgf/ in	1.0 hr 1.0%wt PH4.446 kgf/ in	1.0 hr 1.0%wt PH6.623 kgf/ in	1.0 hr 1.0%wt PH7.493 kgf/ in	1.0 hr 1.0%wt PH9.746 kgf/ in	1.0 hr 1.0%wt PH10.620 kgf/ in
	2.89	1.52	1.48	1.74	1.57	1.97	2.16
	2.78	1.59	1.54	1.86	1.84	2.17	1.74
	2.69	1.63	1.56	1.84	1.56	2.16	2.06
	2.68	1.60	1.62	1.79	1.52	2.37	2.44
		1.61		1.81	1.62	2.20	2.01
Avg.	2.76	1.59	1.55	1.81	1.62	2.17	2.08
Mpa (MN/m^2)	70.95	40.89	39.84	46.49	41.66	55.83	53.54

Appendix XII

Experimental Data Tables of contact angle of virgin, ozonated and AAm grafted HDPE

Table XII-1 Contact angle of virgin, ozonated and AAm grafted HDPE films

Super pure distilled water				3.0 µl	Room temp.		static contact angle			
FILM	one side					other side				Avg
	point 1	point 2	point 3	point 4	point 1	point 2	point 3	point 4		
Virgin HDPE	70.4	78.95	71.4		82.25	83.5	64.5	73.45		74.92
1.0%wt 1.0h O_3 oxidized HDPE	73.6	72.15	71.35	69.75	69	71.8	67.3			70.71
3.7%wt 1.0h O_3 oxidized HDPE	62.15	65.95	73		77.5	73.4	66.25			69.71
1.0%wt 1.0h O_3 oxidized and AAm grafted HDPE	41.75	31.8	35.7		42.95	40.55				38.55

Appendix XIII

BEER' LAW (http://en.wikipedia.org/wiki/Beer-Lambert_law)

There are several ways in which the law can be expressed,

$$A = \alpha \, l \, c$$

$$T = \frac{I_1}{I_0} = 10^{-A} = 10^{-\alpha l c}$$

where,

$$A = \log_{10}\left(\frac{I_0}{I_1}\right)$$

$$\alpha = \frac{4\pi k}{\lambda}$$

- A is the absorbance of the sample
- I_0 is the intensity of the incident light
- I_1 is the intensity after passing through the material
- l is the distance that the light travels through the material (the path length)
- c is the concentration of absorbing species in the material
- α is the absorption coefficient or the molar absorptivity of the absorber
- λ is the wavelength of the light
- k is the extinction coefficient
- T is the transmittance

In spectroscopy and spectrophotometry, the law is almost always defined in terms of common logarithm. In optics, the law is often defined in an alternate exponential form,

$$\frac{I_1}{I_0} = e^{-\alpha' l c},$$