

An Investigation Into Surface Modification of Polyethylene Films for Hydrophilicity Enhancement by Catalytic Ozonation

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ABSTRACT: For a conventional polyethylene film, ozonation was conducted to increase its surface hydrophilicity. Copper sulfate was found effective as a catalyst in aqueous ozonation to increase the generation of surface peroxides significantly, which is the essential step for hydrophilicity enhancement. The percentage increase in peroxide generation could range from 41% to 58% by aqueous catalytic ozonation over its noncatalyzed gaseous counterpart. The optimum concentration of copper sulfate was found to be 0.05 g/L. After adding the catalyst, the length of ozonation could be significantly reduced so that the bulk mechanical strength of the films, represented by tensile strength, could be well preserved after ozonation. A novel kinetic model for the aqueous ozonation was proposed. This model was developed by combing the reaction mechanism of gaseous ozonation of polyethylene films with that of ozone self-decomposition in water. The peroxide generation also increased with the applied ozone dose. The surface morphology and contact angle of the film were all examined before and after ozonation. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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INTRODUCTION

Polyethylene (PE) is the most widely used plastic in the world. Generally, PE is of low cost, excellent chemical resistance, and good mechanical properties. However, the hydrophobic nature of its surfaces limited its applications as membranes and biomaterials, which all require excellent surface hydrophilicity.^{1–4} Consequently, surface modifications to enhance hydrophilicity of PE are often performed. Ozone-induced graft polymerization is one of several methods used for this purpose.^{1,5} Exposure of PE to ozone results in generation of active peroxide groups on the PE surfaces. The peroxide groups can then initiate radical graft polymerization of vinyl monomers with hydrophilic groups, resulting in hydrophilic surfaces.^{1,5,6} Comparing with other surface modification techniques such as plasma treatment, UV-radiation, etc., ozonation is relatively inexpensive and it can introduce peroxide groups uniformly on the surfaces of different PE products even with complicated shapes.^{1,7,8}

Ozonation can be conducted in either gaseous or aqueous phases. Aqueous phase ozonation enables easy addition of homogeneous catalysts. Moreover, when dissolved in water, ozone self-decomposes to form hydroxyl radicals, which are even stronger oxidants than molecular ozone itself. Generally, oxidation by molecular ozone is defined as direct ozonation, while oxidation by hydroxyl radicals is defined as indirect ozonation.⁹

Many studies have been conducted on the ozone modification of polymer surfaces in the last decade.^{8,10–19} However, most of these studies were conducted in gaseous phase, only a few explored ozonation of polymers in distilled water, as well as in aqueous solutions of iso-propanol and ammonia.^{16–19} Nevertheless, the use of homogeneous catalysts for surface peroxide generation is an area barely touched.

The objectives of this study were to find effective homogeneous catalysts for aqueous ozonation of PE films, to investigate the ozonation mechanism, and to evaluate the effects of operating parameters on ozonation efficiency. A conventional polymer film, LDPE/LLDPE, which is the blend of low density polyethylene (LDPE) and linear low density polyethylene (LLDPE), was selected as a model polymer. This polymer was selected because it has excellent chemical and physical properties, is inexpensive and is largely available.^{5,15} To increase the surface hydrophilicity of polymers, generation of peroxides is the essential step. Therefore, the efficiency of ozonation was evaluated in terms of peroxide generation.

EXPERIMENTAL

Materials

Commercial LDPE/LLDPE films with neither coatings nor additives were provided by Exopack Company (Newmarket, Ontario, Canada). The thickness of the films was 51 μm and the weight

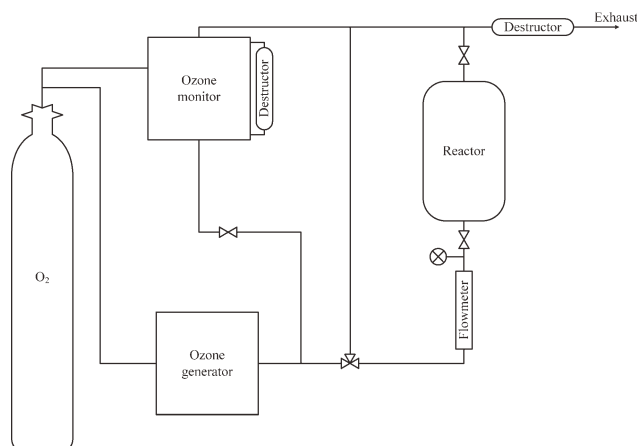


Figure 1. Schematic diagram of the ozonation system.

ratio of LDPE to LLDPE of the films was 60 to 40. Metal salts used in this study include copper sulfate, ferric chloride, silver acetate, and zinc sulfate. Other chemicals used were iso-propanol (IPA), potassium iodide, sodium thiosulfate, glacial acetic acid, tert-butyl alcohol (TBA), etc. All chemicals used were reagent grade and were supplied either by Sigma-Aldrich Canada (Oakville, Ontario) or VWR Canlab (Mississauga, Ontario).

Apparatus and Procedures

Figure 1 shows the schematic diagram of the ozonation system. Ozone was generated by feeding pure oxygen through a model GL-1 ozone generator (PCI-Wedeco Environmental Technologies, Charlotte, NC, NJ). The concentration of ozone exiting the generator was measured by an ozone monitor (OzoMeter TM, OzoCAN Corporation, Scarborough, Ontario, Canada). The applied ozone dose could be readily adjusted by varying the ozone weight percentage and/or the gas flow rate. In this study, the gas flow rate and gas pressure were kept constant. The gas flow rate was 9 L/min and the gas pressure was 25 kPa.

The reactor was a plexiglass cylindrical column equipped with a porous ceramic gas diffuser with a mean pore size 30 μm . The diffuser was obtained from Refractron Technologies (Newark, NY, USA). The diameters of the column and the diffuser were eight and seven inches, respectively. The volume of the reactor was 11 L and the reactor was operated by feeding ozone-containing gas continuously. Two circular stainless steel frames were installed at the top and the bottom of the reactor to hold the films. Excess ozone leaving the reactor was destroyed by a catalytic ozone-destruct unit filled with Carulite catalyst (Carus Chemical Company, Peru, IL). More details of the experimental setup were described elsewhere.^{16,20}

Ozonation of the LDPE/LLDPE films was conducted in gaseous and aqueous phases, respectively, several soluble metal salts were tested in aqueous phase to find if they could catalyze the ozone generation of peroxides.

The LDPE/LLDPE films were cut into strips of 3.81 cm \times 25.4 cm (1.5 \times 10 inches). In each run, six polymer films were first cleaned by submerging them in distilled water for 30 minutes, the films then further cleaned with distilled water in ultrasonic cleaner for three minutes before use. In gaseous ozonation, the

polymer films were vacuum dried for 60 minutes before the ozonation to remove the water. The six films were held individually by Nylon strips onto the stainless steel frames inside the reactor to avoid overlapping.

The ozonation process started when the ozone-oxygen mixture from the ozone generator was sparged continuously into the reactor. For liquid phase ozonation, the reactor was filled with 11 L of distilled water. All ozonation runs were conducted around 21°C. Films were taken out at appropriate time intervals for analysis. They were degassed under vacuum for several hours to remove absorbed ozone before analytical measurements.

Analytical Methods

The amount of peroxide groups on the films was determined by the standard iodometric method.^{18,21} Briefly, 50 mL IPA were added to the ozonated and degassed LDPE/LLDPE films, followed by adding 2 mL saturated potassium iodide and 2 mL glacial acetic acid. The mixture was heated to near boiling condition, kept at incipient boiling for 8 min with occasional swirling, then without cooling, titrated with standard sodium thiosulfate solution to the disappearance of the yellow color.

The water contact angle of the polymer film was measured by a goniometer (Model p/n 250-F1, 400-30; Rame-Hart Instrument Co., Netcong, NJ) with the static sessile drop method.^{11,16} The contact angle reported for each sample was an average of six measurements.

The polymer surfaces were characterized for their functional groups by a FTIR spectrometer (Spectrum One, Perkin Elmer, Woodbridge, Ontario, Canada).

The changes in surface morphology of the polymer films were examined by a scanning electronic microscopy (SEM; Model JSM-35 JEOL, Japan). The SEM image was taken at 10 kV. Samples were dried and precoated with gold at 0.2 Torr before the SEM analysis.

The tensile strength of the polymer film was measured by a model 4442 Instron Universal Testing Machine (Norwood). Film samples were prepared according to ASTM D882-09 standard.²² The testing speed was 20.0 cm/min. It was confirmed by our tests that the films were isotropic, therefore, the tensile strength measurements were taken in the transverse direction, and the reported tensile strength was an average of five measurements.

RESULTS AND DISCUSSION

Selection of Catalysts

To examine if a metal salt could serve as a catalyst to enhance the generation of peroxides, ozonation of the LDPE/LLDPE films was conducted in the absence and presence of several soluble metal salts in aqueous phase, respectively. The length of ozonation was 30 min with 1.0 wt % of applied ozone dose. Metal salts tested were ferric chloride, copper sulfate, zinc sulfate, and silver acetate. The metal salts were added at the same anhydrous amount of 0.2 g/L. The gaseous ozonation of the films was also conducted under the same operating conditions for comparison. Results are shown in Figure 2.

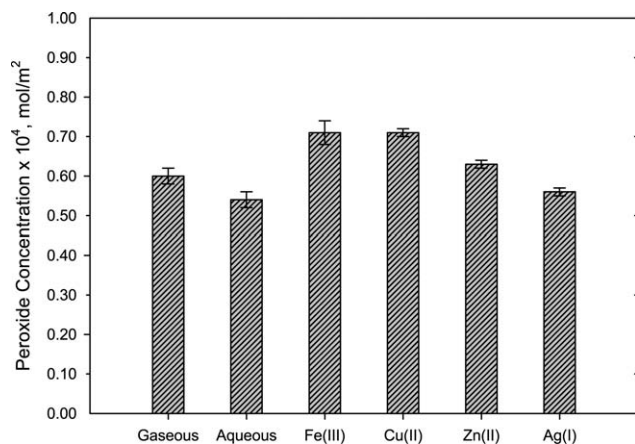


Figure 2. Effect of some metal salts on peroxide generation. applied ozone dose = 1.0 wt %; ozonation time = 30 min; anhydrous salt concentration (where applicable) = 0.2 g/L.

It can be observed from Figure 2 that aqueous ozonation in the absence of metal salts yielded a slightly lower peroxide concentration than gaseous ozonation. However, when some soluble metal salts were added to aqueous phase, the presence of Cu(II), Fe(III), and Zn(II) enhanced peroxide generation. The concentration of peroxides generated by gaseous ozonation was 0.60×10^{-4} mol/m², whereas 0.71×10^{-4} mol/m² peroxides were generated when 0.2 g/L of either copper (II) sulfate or iron (III) chloride was added, indicating 18.3% increase in the amount of peroxide. In this study, copper sulfate instead of iron (III) chloride was selected arbitrarily as the catalyst for further investigation.

Effect of Catalyst Concentration on Peroxide Generation

The optimum catalyst concentration was also explored. The LDPE/LLDPE films were ozonated in distilled water with the addition of different amount of copper sulfate. The applied ozone dose was 1.5 wt % and the ozonation time was 60 min. Results are shown in Figure 3. It is observed from Figure 3 that the generation of peroxides increased with the catalyst concen-

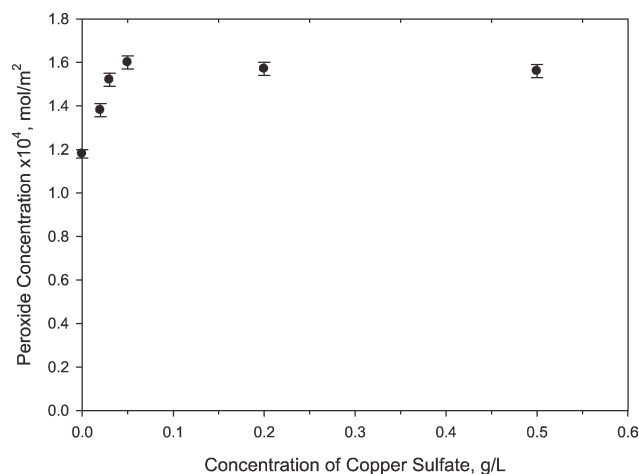


Figure 3. Effect of catalyst concentration on peroxide generation. applied ozone dose = 1.5 wt %; ozonation time = 60 min.

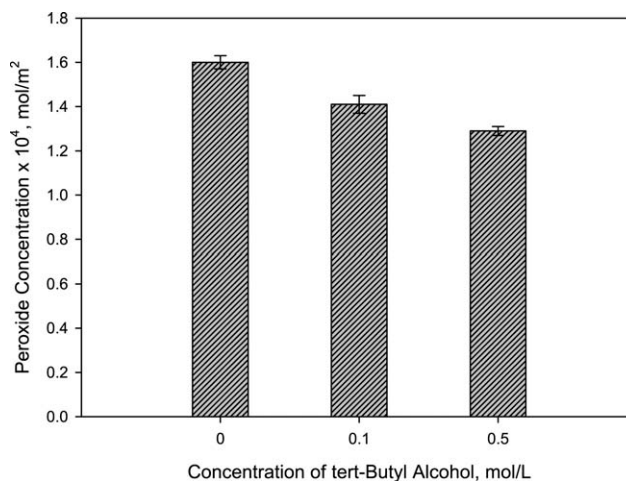


Figure 4. Peroxide generation in the presence and absence of a radical scavenger, TBA. applied ozone dose = 1.5 wt %; copper sulfate concentration = 0.05 g/L; ozonation time = 60 min.

tration until the catalyst concentration reached 0.05 g/L. Increase in catalyst concentration beyond this point could not improve the peroxide generation further. Results of ozonation conducted with higher applied ozone doses (2.0 and 3.0 wt %) also showed the same results (data not shown). Therefore, 0.05 g/L of copper sulfate was considered as the optimum catalyst concentration under the experimental conditions and used in subsequent study.

Effect of Radical Scavenger on Peroxide Generation

To explore the contribution of indirect ozonation on peroxide generation, aqueous catalytic ozonation runs were conducted in the presence of a known hydroxyl radical scavenger, TBA. Two different concentrations, 0.1 mol/L and 0.5 mol/L, of TBA were added and the results are shown in Figure 4.

It is observed from Figure 4 that addition of TBA did reduce the peroxide generation. The peroxides generated were 1.60×10^{-4} mol/m² when no TBA was added. However, after 0.1 mol/L of TBA were added, the peroxides generated were reduced to 1.41×10^{-4} mol/m². Addition of more TBA at 0.5 mol/L reduced the generation of peroxides further to 1.29×10^{-4} mol/m². The reductions in peroxide generation were 11.8% and 19.4%, respectively. Further experiments revealed that the reduction in peroxide generation was always around 19% even more TBA was added (data not shown). Therefore, it can be concluded that both direct and indirect ozonation contributed to the generation of peroxides but the indirect ozonation contributed much less than its direct counterpart.

Characterization of Film Surfaces by FTIR

The functional groups on the film surfaces before and after ozonation were characterized by the FTIR spectrometer. Figure 5 shows the results. It is observed that after ozonation a new peak occurred at the wavenumber of 1750 cm^{-1} . This peak may correspond to aliphatic aldehydes, carboxylic acids and aliphatic ketones.^{19,23} As reported by Razumovskii and coworkers,²⁴ when saturated hydrocarbon chains such as PE react with ozone, peroxy-radicals will form first, then the peroxy-radicals

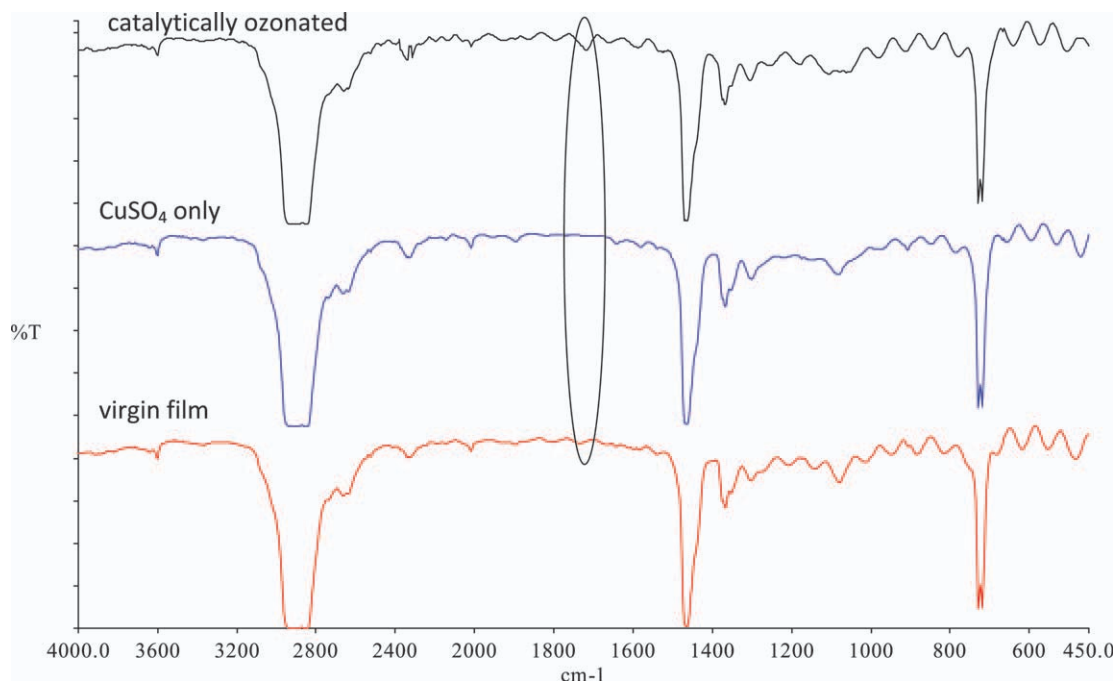


Figure 5. FTIR spectra of LDPE+LLDPE film before and after 60 min ozonation with 1.5 wt % of applied ozone dose and 0.05 g/L of copper sulfate. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

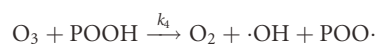
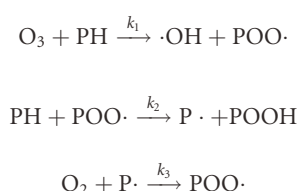
convert to peroxides, ketones, aldehydes, acids, etc. The peroxides were generated in ratio with carbonyl and carboxyl groups. Due to the O—O symmetric bond, the peroxide groups cannot be measured directly by FTIR spectroscopy.²⁵ Instead, the presence of the peroxides can be confirmed by carbonyl and carboxyl groups. Therefore, the peak at 1750 cm^{-1} indirectly confirmed the generation of peroxides by ozone.

For comparison purpose, a PE film was also put in a solution of 0.05 g/L copper sulfate for 60 min in the absence of ozone. The spectra of this film are the same as that of the virgin film. Therefore, the polymer film was inert to the presence of copper sulfate.

It is also observed that for the ozonated films no new peaks were detected in the wavenumber range of $3200\text{--}3700\text{ cm}^{-1}$. The absence of new peaks in this wavenumber range indicates either very low concentration or absence of alcohol functional groups in the ozonation products.⁶

Kinetic Study of Peroxide Generation

For gaseous ozonation of PE, with PH, P·, POO·, POOH, and ·OH representing PE, polyethylene alkyl radical, polyethylene peroxy radical, polyethylene peroxide, and hydroxyl radical, respectively, Kefeli et al. proposed the following mechanism:⁶



By considering all reaction steps above elementary, the rate law for peroxide generation by gaseous ozonation was derived as:⁶

$$[\text{POOH}] = \frac{k_1 k_2 [\text{PH}]^2 [\text{O}_3]}{\alpha k_5} (1 - e^{-\alpha t}) \quad (1)$$

where $\alpha = k_4 [\text{O}_3] \left(1 - \frac{k_2 [\text{PH}]}{k_5}\right)$

In eq. (1), [POOH] is the peroxide concentration, [O₃] is the concentration of ozone and k_1 to k_5 are all rate constants, which are functions of temperature only.²⁶

The proposed rate law, eq. (1), is for gaseous ozonation of PE, which involves the direct ozonation of PE. For aqueous catalytic ozonation, both molecular ozone and hydroxyl radicals are involved as oxidants. Therefore, it is necessary to explore if the participation of hydroxyl radicals would result in any change in reaction kinetics.

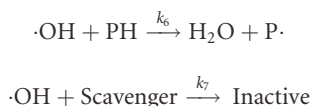
In this study, a kinetic model for aqueous ozonation of PE was proposed by combining the mechanism of gaseous ozonation of PE with that of ozone decomposition in water. It has been proved that decomposition of ozone in water is of first-order with respect to ozone:^{27,28}

$$\text{Rate of ozone self-decomposition} = k_d [\text{O}_3]$$

It is also known that two moles of hydroxyl radical are formed from the decomposition of three moles of ozone:²⁸

Rate of hydroxyl radical production from ozone self – decomposition = $2/3 k_d [O_3]$

The reaction steps for the indirect ozonation of PE are:²⁹



The following assumptions were made to derive the rate law:

1. All reaction steps are elementary.
2. Pseudo-Steady-State Hypothesis (PSSH)²⁶ is applicable to all radicals. Therefore, $r_{\text{POO}\cdot} = 0$, $r_{\text{P}\cdot} = 0$ and $r_{\text{OH}\cdot} = 0$.
3. Constant concentration of dissolved ozone.
4. Reactions between peroxide group and hydroxyl radicals are negligible, because the main role of hydroxyl radicals is to abstract hydrogen from alkyl groups.²⁹
5. Reactions between alkyl radicals and hydroxyl radicals are negligible, because products of reactions between alkyl radicals and hydroxyl radicals are alcohols; however, as shown in Figure 5, after aqueous catalytic ozonation, no new peaks occurred between 3200 cm^{-1} and 3700 cm^{-1} , indicating that there are no alcohol groups formed.³⁰

It should be noted that in aqueous catalytic ozonation, the ozone concentration, $[O_3]$, is the dissolved ozone concentration, whereas in gaseous ozonation, $[O_3]$ represents the gas phase ozone concentration. It is reasonable to assume $[O_3]$ is a constant in both media because of the constant feeding rate of the ozone containing gas to the reactor.

Applying the PSSH, i.e., $r_{\text{P}\cdot} = 0$, $r_{\text{POO}\cdot} = 0$, and $r_{\text{OH}\cdot} = 0$ yields:

$$[\text{POO}\cdot] = \frac{[O_3]}{k_5} \left\{ k_1[\text{PH}] + k_4[\text{POOH}] + \frac{k_6[\text{PH}]}{k_6[\text{PH}] + k_7[\text{S}]} \left(\frac{2}{3} k_d + k_1[\text{PH}] + k_4[\text{POOH}] \right) \right\} \quad (2)$$

According to the proposed mechanism, the rate of peroxide generation is:

$$\frac{d[\text{POOH}]}{dt} = k_2[\text{POO}\cdot][\text{PH}] - k_4[O_3][\text{POOH}] \quad (3)$$

Substituting eq. (2) into (3) and rearranging:

$$\begin{aligned} \frac{d[\text{POOH}]}{dt} = [O_3] \left\{ \frac{k_2[\text{PH}]^2}{k_5} \left(k_1 + \frac{k_6}{k_6[\text{PH}] + k_7[\text{S}]} \left(\frac{2}{3} k_d + k_1[\text{PH}] \right) \right) \right. \\ \left. - k_4 \left[\text{POOH} \right] \left(1 - \frac{k_2[\text{PH}]}{k_5} \left(1 + \frac{k_6[\text{PH}]}{k_6[\text{PH}] + k_7[\text{S}]} \right) \right) \right\} \quad (4) \end{aligned}$$

Integration of eq. (4) with zero initial value for $[\text{POOH}]$ gives:

$$[\text{POOH}] = \frac{k_2[\text{PH}]^2[O_3]}{\beta k_5} \times \left\{ k_1 + \frac{k_6}{k_6[\text{PH}] + k_7[\text{S}]} \left(\frac{2}{3} k_d + k_1[\text{PH}] \right) \right\} (1 - e^{-\beta t}) \quad (5)$$

where

$$\beta = k_4[O_3] \left\{ 1 - \frac{k_2[\text{PH}]}{k_5} \left(1 + \frac{k_6[\text{PH}]}{k_6[\text{PH}] + k_7[\text{S}]} \right) \right\}$$

To examine if the proposed kinetic model is applicable for aqueous catalytic ozonation, experiments were conducted at 21°C with an applied ozone dose of 1.5 wt % and with 0.05 g/L of copper sulfate added. Results are shown in Figure 6. Figure 6 also shows results of the noncatalyzed gaseous ozonation conducted at the same temperature and applied ozone dose. Obviously, all experimental data fit the exponential models [eq. (1) and (5)] very well, only the aqueous catalytic ozonation generated peroxides faster on the film surfaces than its noncatalyzed gaseous counterpart. For aqueous catalytic ozonation:

$$[\text{POOH}] = 2.488 \times 10^{-4} (1 - e^{-0.0189t}) \quad (6)$$

and for noncatalyzed gaseous ozonation:

$$[\text{POOH}] = 1.807 \times 10^{-4} (1 - e^{-0.0158t}) \quad (7)$$

The fact that aqueous catalytic ozonation had similar trend to its gaseous counterpart indicates that participation of hydroxyl radicals and the catalyst in the oxidation of PE made no significant differences in the kinetics. The reason might be as follows. Generally, the transitional metal catalyst works by binding to the intermediates of a reaction, and the metal atoms stabilize the intermediates, thereby increasing the concentration of the key intermediates. The stabilization speeds up reaction rates.³¹

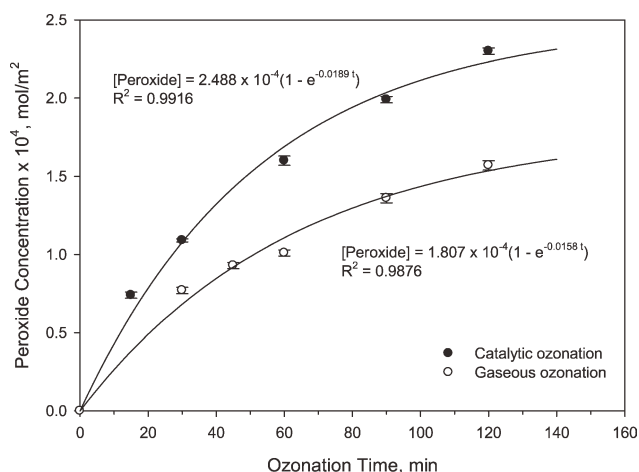


Figure 6. Peroxide generation versus ozonation time for aqueous catalytic ozonation and gaseous ozonation. Applied ozone dose = 1.5 wt %; copper sulfate concentration = 0.05 g/L (where applicable).

Table I. Comparison of Peroxide Generation using Different Ozonation Modes

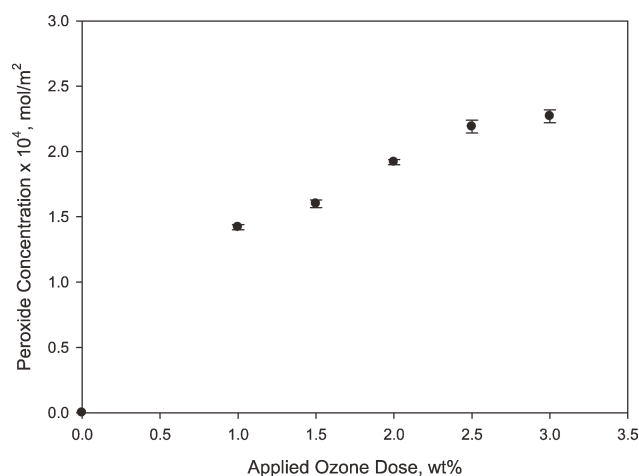
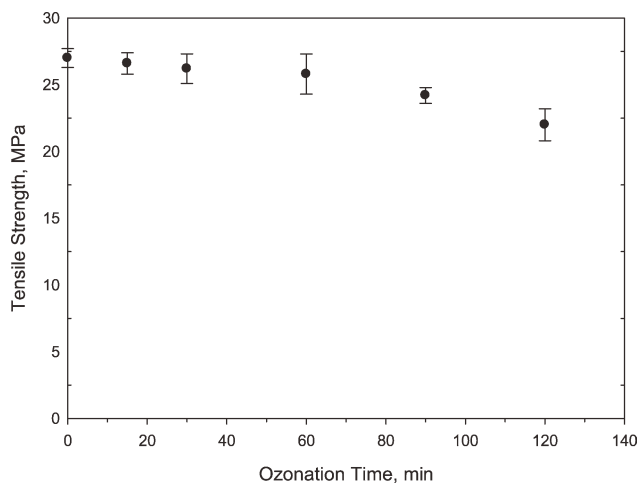
Ozonation time (min)	Peroxides generated by gaseous ozonation ^a [POOH] × 10 ⁴ (mol/m ²)	Peroxides generated by aqueous catalytic ozonation ^b [POOH] × 10 ⁴ (mol/m ²)	Increase in peroxide generation by catalytic ozonation (%)
30	0.77	1.09	41.6
60	1.01	1.60	58.4
90	1.36	1.99	46.3
120	1.57	2.30	46.5

^aApplied ozone dose = 1.5 wt %.

^bApplied ozone dose = 1.5 wt % and concentration of copper sulfate = 0.05 g/L.

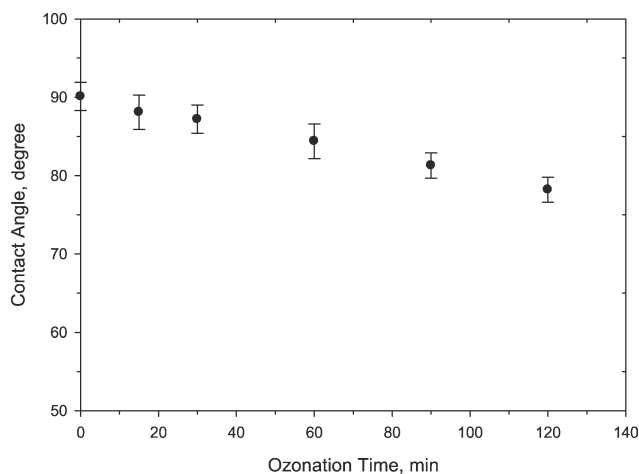
For aqueous catalytic ozonation of PE, the hydroxyl radicals produced by ozone self-decomposition should be the intermediates being stabilized. However, as discussed in the section: Effect of radical scavenger on peroxide generation, for the ozonation of PE, the contribution of indirect reaction by radicals was not as significant as that of direct reaction by molecular ozone. Consequently, although the indirect radical oxidation was enhanced by copper sulfate, because the amount of radicals are not dominant in the system, the rate of reaction was enhanced but the trend of kinetics was not altered.

For both aqueous catalytic and noncatalyzed gaseous ozonation, the generation of peroxides initially increased very rapidly, then the generation slowed down and would eventually reach a horizontal plateau at prolonged ozonation time as shown in Figure 6. It could be explained as follows. Ozone reacts with PE to form peroxy-radicals, which then convert to peroxides, ketones, aldehydes, acids, etc. simultaneously. At the same time, the peroxides formed also react with ozone to convert back to peroxy-radicals.^{6,23,24} When reaction proceeds, peroxide concentration

**Figure 7.** Effect of applied ozone dose on peroxide generation. copper sulfate concentration = 0.05 g/L; ozonation time = 60 min.**Figure 8.** Effect of ozonation time on tensile strength of LDPE+LLDPE films. Applied ozone dose = 1.5 wt %; copper sulfate concentration = 0.05 g/L.

increases, correspondingly, the rate of backward reaction, i.e., peroxides convert back to peroxy-radicals increases. Consequently, the increase in overall peroxide concentration slows down at longer ozonation time as shown in Figure 6.

It is observed from Figure 6 that addition of copper sulfate enhanced peroxide generation significantly. The values of percentage increase are listed in Table I. With 1.5 wt % applied ozone dose and 0.05 g/L of copper sulfate added, the percentage increase in peroxide generation by aqueous catalytic ozonation over its noncatalyzed gaseous counterpart ranged from 41% to 58%. In other words, to generate the same amount of peroxides, time required by the catalytic ozonation was significantly less than what its gaseous counterpart needed. For example, 60 min noncatalytic gaseous ozonation generated 1.01×10^{-4} mol/m² peroxides, which would be generated by less than 30 min catalytic ozonation (Figure 6). Also, peroxides generated by 120 min gaseous ozonation would be generated by approximately 50 min catalytic ozonation (Figure 6).

**Figure 9.** Effect of ozonation time on contact angle of LDPE+LLDPE films. applied ozone dose = 1.5 wt %; copper sulfate concentration = 0.05 g/L.

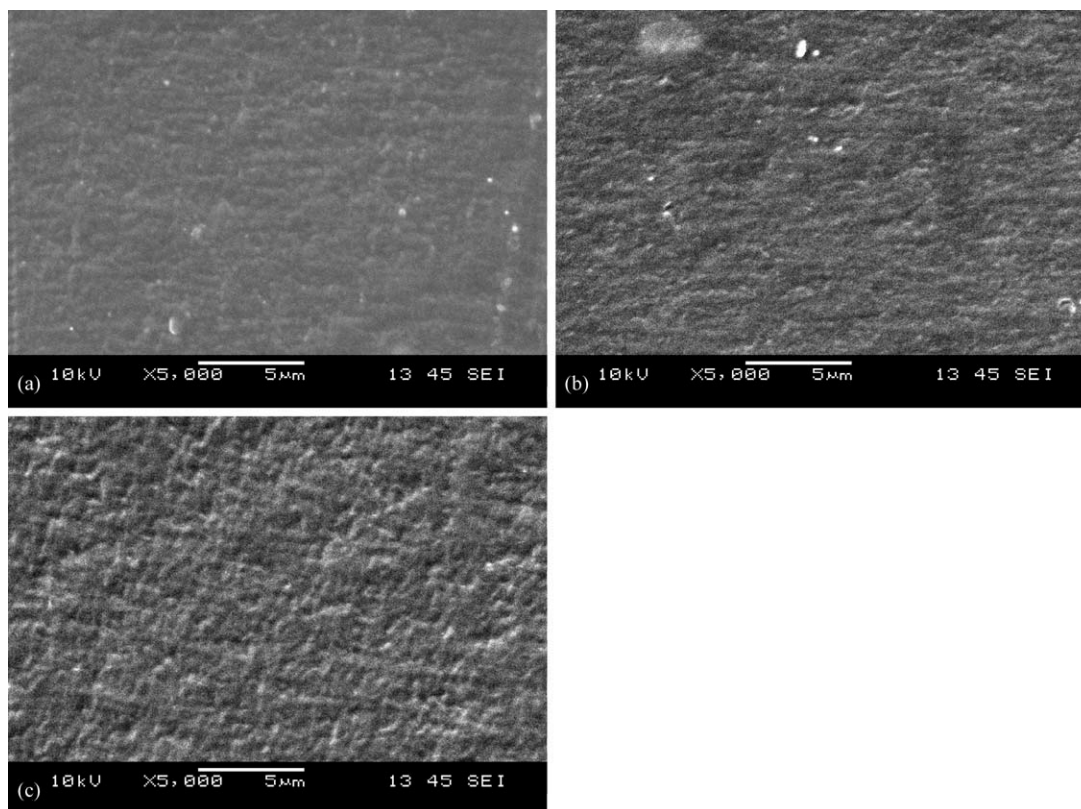


Figure 10. SEM images of LDPE+LLDPE films before and after ozonation: (a) before ozonation, (b) after 15 min ozonation, (c) after 90 min ozonation. applied ozone dose = 1.5 wt %; copper sulfate concentration = 0.05 g/L.

Effect of Applied Ozone Dose on Peroxide Generation

Experiments were also conducted to examine the effect of applied ozone dose on peroxide generation. The length of ozonation was 60 min, the ozone dose applied was from 1.0 to 3.0 wt % and copper sulfate concentration was 0.05 g/L. Results are shown in Figure 7. It is obvious that generation of peroxides increased with the applied ozone dose.

Tensile Strength of the Films

As previously mentioned, ozonation might reduce the bulk strength of polymers by attacking the backbone of the polymers. To examine the degree of deterioration in mechanical strength of the films after ozonation, tensile strength of the PE films was measured before and after ozonation. Results are shown in Figure 8. The applied ozone dose was 1.5 wt % and the concentration of copper sulfate was 0.05 g/L.

It is observed from Figure 8 that the tensile strength of the virgin film was 27.0 MPa, then it decreased to 26.2 MPa, 25.8 MPa, and 22.0 MPa after 30, 60 and 120 min aqueous catalytic ozonation, respectively, which corresponded to 3.0, 4.4, and 18.5% of reduction. It is important to point out that the aqueous catalytic ozonation already reduced ozonation time significantly as shown in Figure 6 and as discussed in Section: Kinetic study of peroxide generation. For example, the amount of peroxides generated by 60 min catalytic ozonation would be more than that generated by 120 min gaseous ozonation and at this point, the loss in tensile strength was only 4.4%. Therefore, it is

safe to conclude that mechanical strength of the films was well protected by the application of the catalyst due to the reduction in ozonation time.

Effect of Catalytic Ozonation on Contact Angle of the Films

Contact angle is a quantitative measure of the wetting of a solid by a liquid. It is defined geometrically as the angle formed by a liquid at the three phase boundary where a liquid, gas, and solid intersect. Low values of contact angle indicate that the liquid wets well, while high values indicate poor wetting.³² Figure 9 shows the contact angle change with ozonation time. Ozonation did not reduce the contact angle significantly. For example, when the virgin film had a contact angle of 90.1°, the contact angles after 60 and 120 min ozonation were 80.4° and 75.3°, respectively. This observation is reasonable, because ozonation in fact only serves as a pretreatment which produces peroxides for subsequent graft polymerization of hydrophilic monomers.

Surface Morphology

The surface morphology of the PE films before and after ozone treatment was examined by SEM. Results are shown in Figure 10. It is observed that the morphology of the film surfaces changed after ozonation. The ozonated PE surfaces were rougher than that of the virgin PE, and the longer the ozonation time, the rougher the surfaces. It is well known that ozone attacks strongly the double bonds of PE to form unstable ozonides, the decomposition of the ozonides then produces peroxides, carbonyl groups, and carboxyl groups.¹² The changes in

surface morphology of the PE film could be due to the breaking down of the double bonds by ozone oxidation, as well as the formation of ketones, aldehydes, and acids on the surfaces.

CONCLUSIONS

Copper sulfate was found in this study as an effective homogeneous catalyst for the aqueous ozone surface modification of a conventional PE film, LDPE/LLDPE. The optimum concentration of copper sulfate was found to be 0.05 g/L. Addition of this catalyst could achieve the percentage increase in peroxide generation from 41% to 58% over the noncatalyzed gaseous ozonation. Equivalently, to generate the same amount of peroxides, time required by the aqueous catalytic ozonation was significantly reduced. The reduction in ozonation time well protected the bulk mechanical strength of the LDPE/LLDPE films.

For the aqueous ozonation of the PE films, both direct and indirect ozonation occurred. However, the molecular ozone in direct ozonation was the main oxidant.

A novel kinetic model was developed for the aqueous ozonation of the PE films. This model was derived by combining mechanisms of gaseous ozonation and of ozone self-decomposition in water. The proposed model was verified by experimental results.

The peroxide generation increased with both the applied ozone dose and the length of ozonation. The contact angle was found to decrease slightly after ozonation. The morphology of the film surfaces also changed after ozonation.

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