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Surface modification of low density polyethylene films by homogeneous catalytic ozonation

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ABSTRACT

Low density polyethylene films were treated by ozone to generate peroxides on the surfaces. The peroxides generated are capable of initiating radical graft polymerization of hydrophilic vinyl monomers onto the polymers, resulting in hydrophilic surfaces. Results of ozonation revealed that molecular ozone instead of hydroxyl radicals was the main oxidant for peroxide generation. A novel approach, aqueous ozonation with the addition of a soluble transitional metal salt, $FeCl_3$, as a homogeneous catalyst, was proposed and proved to be successful in this study. The addition of $FeCl_3$ could increase peroxide generation by 22.7%, compared to its non-catalyzed counterpart. An optimum catalyst concentration, 0.04 g/L, was determined. Also, the effects of pH, ozonation time and applied ozone dose on peroxide generation were investigated. The loss in tensile strength of the films would be 15% or less if the applied ozone dose was not over 2 wt.%. The functional groups generated on the film surfaces were characterized by FTIR, the contact angle and surface roughness of the film were also examined before and after ozonation.

Keywords: Catalytic ozonation; Polyethylene film; Surface modification; Peroxide generation; Hydrophilicity enhancement

1. Introduction

Polymers have been used extensively for membranes, biosensors, and biomaterials. For these applications, excellent surface hydrophicility is highly desirable in order to prevent membrane fouling and protein adsorption (Mao et al., 2004; Desai and Singh, 2004; Guo et al., 2008). However, most polymer surfaces are naturally inert and hydrophobic, to date, the hydrophilicity problem of polymer materials has not been completely solved.

The hydrophilicity of polymer surfaces can be improved by techniques such as plasma treatment, corona discharge, irradiation with gamma-rays, ozonation, etc. (Mao et al., 2004; Desai and Singh, 2004; Dasgupta, 1990; Robin, 2004). These treatments generate peroxide groups on the polymer surfaces (Ikada, 1992; Fujimoto et al., 1993). The peroxides generated are capable of initiating radical graft polymerization of hydrophilic vinyl monomers onto the polymers, resulting in hydrophilic surfaces. Among these techniques, ozonation has the advantage of uniformly introducing peroxides on the polymer surfaces even with complicated shapes. Moreover, ozonation is an easy-to-handle and inexpensive method (Mao et al., 2004; Robin, 2004; Tu et al., 2005; Zhou et al., 2010).

Ozonation can be conducted in either gaseous phase or aqueous phase. When ozone is dissolved in water, the molecular ozone self-decomposes to form hydroxyl radicals, which are stronger oxidants than molecular ozone itself. Oxidation by molecular ozone is defined as direct oxidation, while oxidation by radicals is defined as indirect oxidation (Hoigne and Bader, 1976). Therefore, in gaseous phase ozonation, only direct oxidation occurs, but in aqueous phase, since molecular ozone and hydroxyl radicals are both present, the direct and indirect oxidations occur at the same time. To date, researches on ozone modification of polymers have been conducted mainly in gas phase. In fact, in addition to the presence of hydroxyl radicals, aqueous ozonation also has the advantage of enabling convenient introduction of catalysts into the system, regardless of whether the catalyst is a liquid, a gas or

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a solid. The use of catalysts not only enhances the efficiency of ozone oxidation, but also reduces the length of ozonation to excuse the bulk polymers from oxidative degradation. However, until now there has been no report on the use of catalyst for ozone modification of polymer surfaces.

In this study, a conventional polymer film, LDPE/LLDPE, which is the blend of low density polyethylene (LDPE) and linear low density polyethylene (LLDPE), was treated by ozone to generate peroxides on the surfaces. This polymer was chosen because it has excellent chemical and physical properties, is inexpensive and largely available (Desai and Singh, 2004; Shan et al., 2006). The main objective of this study was to explore the effect of catalyst on peroxide generation for aqueous ozonation of the chosen polymer film. At the same time, the oxidation pathways were investigated, the polymer surfaces were characterized. Also, the mechanical strength of the films and the stability of the peroxides generated were examined.

2. Experimental

2.1. Materials

Commercial LDPE/LLDPE films with a thickness of 60 μm were obtained from Exopack Company Ltd. (Newmarket, Ontario). The films have neither coatings nor additives. The catalyst, $FeCl_3$, was purchased from Sigma–Aldrich Canada (Oakville, Ontario). All other chemicals used in this study were reagent grade and were supplied by Sigma–Aldrich Canada (Oakville, Ontario) or VWR Canlab (Mississauga, Ontario).

2.2. Apparatus and procedure of ozonation

Ozone was generated from pure oxygen in a Model-GL-1 ozone generator (PCI-WEDECO Environmental Technologies, Charlotte, NC). The weight percentage of ozone in the output gas of the ozone generator was measured by an ozone monitor (Model HC-400) from the same company. The applied ozone dose was readily adjustable by varying ozone weight percentage and/or gas flowrate. In this study it was adjusted by varying ozone weight percentage only while keeping the gas flowrate and pressure constant. The gas flowrate was 9 L/min and the gas pressure was 96.5 kPa (14 psi). All experimental runs were duplicated.

The reactor was a plexiglass cylindrical column equipped with a porous ceramic gas diffuser (Refractron Technologies Corp., Newark, NY). The mean pore size of the diffuser was 30 μm. 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 the ozone-containing gas continuously. Two circular stainless steel frames were installed at the top and the bottom of the reactor, respectively, 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 (Yong et al., 2005; Gu et al., 2009).

The LDPE/LLDPE films were cut into strips of 1.5 in. × 10 in. and were held individually by Nylon strips onto the stainless steel frames inside the reactor to avoid overlapping. The strips were cleaned with distilled water in ultrasonic cleaner before use.

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. Polymer films were taken out at appropriate time intervals for analysis and were degassed under vacuum for several hours to remove absorbed ozone before analytical measurements.

2.3. Analytical methods

The amount of peroxide groups generated by ozonation was determined by the iodometric method (Kokatnur and Jelling, 1941). Briefly, 50 mL of isopropanol were added to the ozonated and degassed HDPE film sample, followed by 2 mL of saturated potassium iodide and 2 mL of glacial acetic acid. The mixture was heated to near boiling condition, kept at incipient boiling for 2–5 min with occasional swirling, then without cooling, titrated with standard sodium thiosulfate solution to the disappearance of the yellow color (Gu et al., 2009; Xu et al., 2003; Zhou et al., 2005).

The contact angle of the film surface was measured by a goniometer (Model p/n 250-F1, 400-30, rame-hart Instrument Co., Netcong, NJ) with a sessile drop method.

The polymer surfaces were characterized for their functional groups by the Fourier transform infrared (FTIR) spectrometer (Spectrum One, Perkin Elmer, Woodbridge, ON, Canada).

The tensile strength of the films was measured by a Model 3367 Instron machine (Grove City, PA, USA). The film samples were prepared according to ASTM D882-10 standard (ASTM, 2011), and the tensile strength of the samples was measured at a cross-head speed of 10 in/min. Each tensile strength data was the average of 10 measurements with 5 measurements in the machine direction (MD) and another 5 in traverse direction (TD).

The roughness of the film surface was measured by a BioScope Atomic Force Microscope (AFM) (Digital Instruments, Santa Barbara, CA, USA). The images were obtained in the Tapping mode. Characterization of the surface roughness was conducted by silicon cantilever with a theoretical spring force constant of 10–130 N/m and resonance frequency of 287 kHz.

3. Results and discussion

3.1. Ozonation of LDPE/LLDPE films in the absence of catalyst(s)

3.1.1. Comparison of gaseous and aqueous ozonation

To increase hydrophilicity of polymer surface by ozone, peroxide groups should be generated on the surface by ozonation first. The peroxides can then initiate graft polymerization of hydrophilic monomers onto the polymer surfaces, resulting in more hydrophilic polymer surfaces (Mao et al., 2004; Fujimoto et al., 1993; Tu et al., 2005; Kulik et al., 1997; Wang et al., 2000). Therefore, generation of peroxides is the essential step.

Ozonation was conducted in gaseous and aqueous phases, respectively, in the absence of catalysts. The applied ozone dose was 1.0 wt.% and the gas flowrate was 9 L/min under the pressure of 96.5 kPa (14 psig). The efficiency of gaseous and aqueous ozonation in terms of peroxide generation was compared. By comparing results of oxidation conducted in the two media, the contribution of direct or indirect reaction to the generation of peroxides would be revealed.