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Effect of Chlorine Dioxide Gas on Physical, Thermal, Mechanical, and Barrier Properties of Polymeric Packaging Materials

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ABSTRACT: The effects of gaseous chlorine dioxide (ClO_2) on properties and performance of 10 selected polymeric packaging materials, including polyethylene (PE), biaxially oriented poly(propylene), polystyrene, poly(vinyl chloride), poly(ethylene terephthalate) (PET), poly(lactic acid), nylon, and a multilayer structure of ethylene vinyl acetate (EVA)/ethylene vinyl alcohol (EVOH), were evaluated. Physical, mechanical, barrier, and color properties as well as infrared (IR) spectra were assessed before and after polymer samples were exposed to 3600 ppmV ClO_2 gas at 23°C for 24, 168, and 336 h. The IR spectra of the ClO_2-treated samples revealed many changes in their chemical characteristics, such as the formation of polar groups in the polyolefin, changes in functional groups, main chain scission degradation, and possible chlorination of several materials. The ClO_2-treated PE samples showed a decrease in tensile properties compared with the untreated (control) films. Decreases in moisture, oxygen, and/or carbon dioxide barrier properties were observed in the treated PE, PET, and multilayer EVA/EVOH/EVA samples. A significant increase ($P < 0.05$) in the barrier to O_2 was observed in the ClO_2-treated nylon, possibly the result of molecular reordering, which was found through an increase in the crystallinity of the material. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 1742–1750, 2010

Key words: degradation; barrier; FTIR; thermal properties; mechanical properties

INTRODUCTION

The use of antimicrobial gases in the package headspace has become a novel complementary approach to improve the safety of packaged fresh produce.[1] Chlorine dioxide (ClO_2), approved by FDA to be incorporated in food packaging films and used as packaging material for meats, poultry, and seafood,[2] is considered by many researchers to have potential as an antimicrobial headspace gas because of its high oxidizing capacity and broad disinfecting property.[1,3–5] However, current knowledge regarding compatibility of ClO_2 gas with polymeric packaging materials for food products is very limited.[6,7]

In a previous study in our laboratory,[8] the permeability, solubility, and diffusion coefficients (P, S, and D, respectively) of ClO_2 for 10 polymeric materials were determined through an isostatic method using an electrochemical sensor. This study showed that poly(ethylene terephthalate) (PET), poly(lactic acid) (PLA), biaxially oriented poly(propylene) (BOPP), nylon, and multilayer structure of ethylene vinyl acetate (EVA) and ethylene vinyl alcohol (EVOH) (EVA/EVOH/EVA) are good barriers to ClO_2, whereas polystyrene (PS), linear low-density polyethylene (LLDPE), low-density polyethylene (LDPE), high-density polyethylene (HDPE), and poly(vinyl chloride) (PVC) are poor barriers to ClO_2. Such information is useful in selecting an appropriate material for membrane applications, such as in packaging design.

When polymeric materials are exposed to strong oxidizing agents, such as ozone (O_3) and ClO_2, oxidative degradation can occur. Such degradation is usually "selective," either by reacting specifically with certain functional groups or taking place exclusively in the amorphous region of a semicrystalline polymer.[9–11] In most cases, the maximum interactions and changes occur on the surface of a polymer. The typical changes caused by oxidative degradation are main chain scission, depolymerization, crosslinking, and the formation of conjugated double bonds, carbonyl groups, etc.[12,13] These changes in polymer characteristics may, in turn, affect mechanical properties and result in

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TABLE VIII
Barrier Properties of Selected Polymeric Packaging Materials Exposed to ClO_2 Gas

Sample	Exposure to ClO_2 (days)	$P_{H_2O} \times 10^{-18}$ (kg m m^{-2} s^{-1} Pa^{-1})	$P_{CO_2} \times 10^{-18}$ (kg m m^{-2} s^{-1} Pa^{-1})	$P_{O_2} \times 10^{-18}$ (kg m m^{-2} s^{-1} Pa^{-1})	P_{CO_2}/P_{O_2}	% Change
HDPE	0	0.49 ± 0.00*	58.3 ± 8.08	9.26 ± 1.24	6.30 ± 1.21	
	14	0.48 ± 0.00	77.6 ± 0.40	8.40 ± 0.29	9.24 ± 0.32	+46.8
PS	0	10.5 ± 0.74	111 ± 6.63	16.8 ± 0.57	6.59 ± 0.45	
	14	9.84 ± 1.06	123 ± 6.37	15.8 ± 0.64	7.77 ± 0.51	+17.9
BOPP	0	10.5 ± 0.74	18.3 ± 0.61	3.86 ± 0.20	4.75 ± 0.29	
	14	9.84 ± 1.06	19.2 ± 0.47	3.91 ± 0.18	4.90 ± 0.26	+3.15
PLA	0	28.2 ± 1.18	37.3 ± 17.2	21.2 ± 2.66	1.76 ± 0.84	
	14	26.9 ± 1.56	43.4 ± 13.9	30.8 ± 10.0	1.41 ± 0.63	−20.0
PET	0	1.64 ± 0.01	1.54 ± 0.04	0.22 ± 0.01	6.87 ± 0.35	
	14	1.94 ± 0.03	1.53 ± 0.04	0.26 ± 0.04	5.79 ± 0.83	−15.8
Nylon	0	n/a	1.23 ± 0.01	0.24 ± 0.01	5.07 ± 0.11	
	14	n/a	1.21 ± 0.03	0.22 ± 0.00	5.63 ± 0.17	+10.9
EVA/EVOH/EVA	0	0.40 ± 0.01	0.35 ± 0.04	0.09 ± 0.01	3.86 ± 0.56	
	14	0.41 ± 0.01	0.71 ± 0.04	0.13 ± 0.01	5.28 ± 0.64	+36.7

* Within columns and polymer materials, means (±S.D.) sharing the same superscript letter are not significantly different ($P > 0.05$; $n = 4$).

impact of ClO_2 gas on the barrier properties of polymeric materials to O_2, CO_2, and moisture is of great concern. Barrier properties of polymeric materials are critically important to the performance of packaging systems for many food applications, especially for fresh produce where respiration is still taking place during the postharvest period.[18,25] The concentrations of O_2 and CO_2 accumulated in the package headspace affect the deterioration rate of fresh produce. Once the packaging material is selected for a particular commodity, it is crucial that its permeaselectivity ratio (P_{CO_2}/P_{O_2}) be maintained throughout the shelf life of the product, as in the case of MAP where a stable gaseous ratio in the package headspace is necessary.[18,22,25]

In this study, comparisons of P_{H_2O}, P_{CO_2}, and P_{O_2} between the control and ClO_2 exposed film samples indicated that significant changes occurred in the barrier characteristics of some polymeric materials tested (Table VIII).

Moisture

The moisture barrier of PET film significantly decreased ($P < 0.05$) after ClO_2 treatment. No changes were observed in the P_{H_2O} of other polymer materials tested.

It is important to note the shift to lower T_g in the exposed PET samples (Table V) implying the oxidative degradation of the material after ClO_2 exposure could lead to the increase in the polymer's chain mobility and the decrease in its intermolecular forces. This plays an important role in the significant increase in P_{H_2O} of the material, because it will accelerate the diffusion process.[14]

The IR spectra of the exposed PLA sample showed an increase in its hydroxyl group, indicating an increase in polarity of the film, which could increase the intermolecular forces between polymeric chains and promote rigidity in the structure. The hydroxyl groups will also favor the interaction between the polymer and moisture.[11,14,22,26] These antagonistic interactions likely resulted in no changes in the barrier of PLA after exposure.

Oxygen and carbon dioxide

Based on the results of P_{O_2}, only the nylon film samples showed an increase in the barrier to O_2 after exposure to ClO_2 (Table VIII). This increase could be due to the increase in crystallinity (Table V), as this implied that the exposed material has lower available amorphous region in which permeation can take place.[9,10,26] We expected an increase of the O_2 barrier in the exposed materials because of a partial chlorination that would promote polarity within the polymer matrix. Barrier to CO_2 of HDPE, PS, and EVA/EVOH/EVA films decreased after ClO_2 exposure. The main chain scission of ClO_2-treated PE samples (as demonstrated by the IR spectra) could be the dominant degradation reaction in all three materials, as this would increase the chain mobility and facilitate gas transfer throughout the polymer structure (Fig. 3 and Table II). The same explanation can reasonably be given to the increase in P_{O_2} of the treated EVA/EVOH/EVA samples.

The P_{CO_2} of a polymeric material is usually higher than the P_{O_2} of the same material, and because both gases are of the same penetrant type, that is, nonreactive gas,[22,26,27] a similar trend would be expected

with the exposed polymeric films. However, the degree of changes varied (Table VIII), depending on the particular polymer/penetrant pair[26,27] and resulted in an alteration of the P_{CO_2}/P_{O_2} ratio of the materials after exposure to ClO_2. A comparison of the modified P_{CO_2}/P_{O_2} ratios with the original values showed that after 14 days of persistent exposure, the P_{CO_2}/P_{O_2} ratio of several materials significantly changed, with changes ranging from 0 to 47%. The most notable change occurred in the exposed HDPE sample.

The ASTM testing conditions used for the barrier measurements were not at the typical environments encountered during storage and distribution of perishable food products. Nevertheless, the current findings could be served as a basic guideline when designing a MAP system for fresh produce that incorporates ClO_2 and where the ratio of CO_2 and O_2 within the packaging atmosphere will impact the shelf life of the product.

CONCLUSIONS

The effects of gaseous ClO_2 on properties and functionalities of HDPE, LDPE, LLDPE, BOPP, PS, PVC, PET, PLA, nylon, and the multilayer structure of EVA/EVOH/EVA were studied after exposing the samples to 3600 ppmV ClO_2 for 24, 168, and 336 h. Changes in the peak intensities of the IR spectra of different exposed polymeric films indicated: (i) possible main chain scissions in polyolefin; (ii) formation of the polar groups in some exposed polyolefin; (iii) changes in the polar groups in PLA, multilayer EVA/EVOH/EVA, and nylon; and (iv) possible chlorination of polyolefin, PS, nylon, and EVA/EVOH/EVA.

Minor changes in physical and mechanical properties were observed in many exposed materials. The comparisons to control films showed significant decreases in barrier properties (or increases in permeation) of several exposed polymers, with the exception of the increase of barrier to O_2 of nylon film.

Future studies on effects of different treatment conditions, such as ClO_2 concentration, relative humidity, and temperature, on polymeric materials' integrities and performance should be conducted to further determine the potential use of ClO_2 gas as an antimicrobial headspace gas.

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