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

embrittlement, lack of transparency, loss of additives, and formation of toxic compounds.[9]

The exposure of polymeric materials to different oxidizing agents under various conditions may affect overall material performance.[14] Shin et al.[7] reported changes in the mechanical properties of PS, nylon, and LDPE after exposure to ClO$_2$ gas at 20,000 ppmV or higher. Decreases in tensile strength (TS) and elongation and a slight increase in oxygen permeability of LDPE, LLDPE, oriented polypropylene, and biaxially oriented nylon after exposure of ClO$_2$ gas were reported by Ozen[6]; the observed effects were dependent on gas concentration, relative humidity, and testing temperature. However, when nylon was exposed to O$_3$, which is considered to be a stronger oxidizing agent than ClO$_2$, Ozen et al.[14] found an increase in tensile properties of the exposed material, regardless of the applied conditions, and the nylon's barrier to oxygen improved as the time of exposure increased.

Alterations in the mechanical, physical, and barrier properties of a packaging material, which result from the chemical changes caused by oxidative degradation may also reduce the shelf life of a product packaged in that material or affect the package integrity. Therefore, it is critical to assess how ClO$_2$ may impact polymeric materials. The objectives of this study were to evaluate the effects of exposure of gaseous ClO$_2$ on various chemical, physical, mechanical, and barrier properties of the selected polymeric materials.

MATERIALS AND METHODS

Polymeric packaging materials

The polymeric materials selected for this study were LDPE and LLDPE (Flexopack S.A., Attiki, Greece), HDPE (James River Corp. Flexible Packaging Group, Richmond, VA), BOPP (Cryovac, Duncan, SC), PS (TRYCITE^{TM} 8001, Dow Chemical Company, Midland, MI), PET (Mylar® A, DuPont, Wilmington, DE), PVC (BEMIS, Shirley, MA), nylon 66 (Dartek F-101, DuPont, Wilmington, DE), PLA (EVLON®, BI-AX International, Wingham, Ontario, Canada), and a multilayer EVA/EVOH/EVA (Cryovac, Duncan, SC).

Preparation of ClO$_2$ solution

A solution to provide 10 mg ClO$_2$/L of gas ($\sim$ 3600 ppmV) was prepared from a stock solution of 1000 mg/L ClO$_2$ using the same methodology as a previous mass transfer study.[8] Briefly, the stock solution was prepared by submerging a sachet containing the chemical precursors, that is, sufficient sulfuric acid (H$_2$SO$_4$) and sodium chlorite (NaClO$_2$) to generate

$\sim$ 2 × 10^{-3} kg of ClO$_2$ (z-series, ICA TriNova, Newnan, GA), in 2 L of deionized, distilled water for 48 h. The solution was titrated to determine the actual concentration using the titration procedure outlined by ICA Trinova.

Exposure of polymeric films to ClO$_2$

For each material type, the film samples were obtained from a roll of film by randomly cutting from the middle and edge area along the roll's width. All samples were preconditioned at 23°C and 50% RH for at least 24 h before ClO$_2$ exposure. The film samples were suspended in a glass container (two samples per container) and treated with 10 mg ClO$_2$/L of gas (3600 ppmV), released from 200 mL of ClO$_2$ solution at the bottom of the container. The exposed samples were removed from the container after 24, 168, and 336 h (Day 1, 7, and 14); exposed film samples were further conditioned at 23°C and 50% RH for at least 24 h. Unexposed films were also conditioned for at least 24 h under the same conditions.

Control or "Day 0" samples (unexposed + conditioned) and treated films (exposed + conditioned) were characterized for their chemical, physical, mechanical, and barrier properties as outlined in Figure 1. Samples were then discarded after each test.
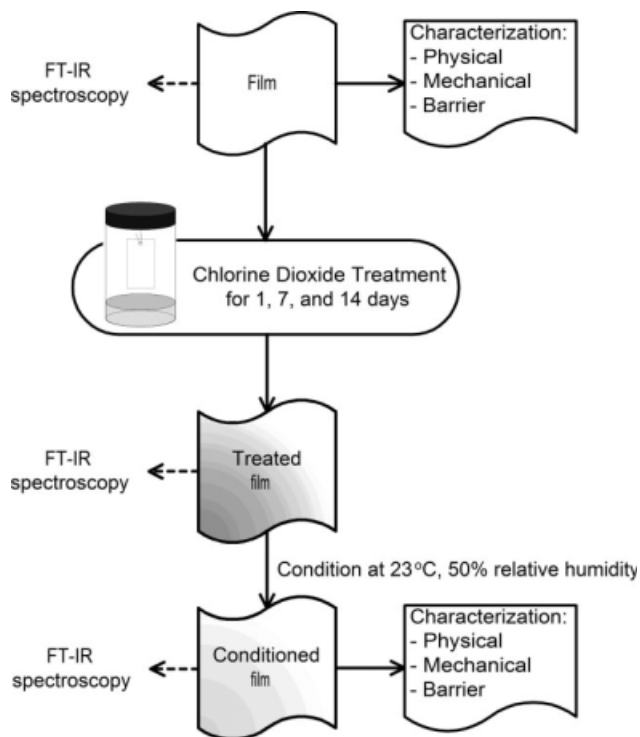

Figure 1 Flow diagram for the characterization and ClO$_2$ gas treatment of polymeric films. The film treatment consisted of exposure to 3600 ppmV of ClO$_2$ gas for four different exposure times.

Evaluation of chemical structure of polymeric materials

A Fourier transform infrared (FTIR) spectrophotometer, in transmission mode (Shimadzu IR Prestige-21, Shimadzu Scientific Instruments, Columbia, MD), was used to evaluate the polymeric materials before and after ClO_2 exposure to assess any chemical changes that occurred. IR spectra were collected for the control and all treated films to evaluate if the changes were transient or permanent. Four IR spectra were collected for each sample type.

Evaluation of physical properties

The glass transition (T_g) and melting (T_m) temperatures (°C), and enthalpy of fusion, ΔH_m (J/g), of the control and exposed polymeric films were determined using a differential scanning calorimeter (DSC Q-100, TA Instruments, New Castle, DE) according to ASTM D 3418-03.[15] The analyses were done using Universal Analysis Software (UAS Version 3.9A, TA Instruments, New Castle, DE). Four replicates of each sample were run.

Color measurement

The surface color of the film samples was measured from two random locations per piece of film (eight replicate samples for each film type) for L^*, a^*, and b^* values using a reflectometer (Integrating Reflectometer JY 9800, TMI Testing Machines, Ronkonkoma, NY). The overall color difference (ΔE) was calculated as:

$$\Delta E = \sqrt{\Delta L^2 + \Delta a^2 + \Delta b^2} \qquad (1)$$

where ΔL, Δa, and Δb are the differences between the L, a, and b values, respectively, of the control and corresponding exposed samples.

The data obtained were analyzed by analysis of variance (ANOVA) using Statistical Analysis System (SAS) software (SAS Institute, Cary, NC) at the confidence level of 95% (α = 0.05) with Tukey's adjustment in the comparison of means.

Evaluation of mechanical properties

TS (N m^{-2}) and modulus of elasticity, MoE (N m^{-2}), in both machine direction (MD) and transverse direction (TD) of the control and exposed polymeric films were measured using a universal tensile tester machine (Instron 5565, Instron, Canton, MA), according to ASTM D 882-02.[16] The TS for each polymer is either "at yield" or "at break," depending on which value is the maximum stress in the stress–strain curve; using the maximum TS approach was

considered acceptable because the comparison was done within the same polymer type and not across different types. The TS was considered at the yield point for HDPE, BOPP, PLA, PS, and EVA/EVOH/EVA, whereas the TS was considered at break point for LDPE, LLDPE, PET, PVC, and nylon.

The predetermined parameters for measuring TS and MoE of the samples as required by ASTM D 882 were as follows: films with <20% elongation (PS and PLA) used an initial grip separation of 1.25 × 10^{-1} m with a rate of grip separation of 2.08 × 10^{-4} m/s. Films with 20–100% elongation (BOPP, PVC, PET, and EVA/EVOH/EVA) used an initial grip separation of 1.00 × 10^{-1} m with a rate of grip separation of 8.33 × 10^{-4} m/s. And, films with >100% elongation (PEs and nylon) used an initial grip separation of 5.00 × 10^{-2} m with a rate of grip separation of 8.33 × 10^{-3} m/s. Testing was carried out on five replicate samples of each film.

The data obtained were analyzed by ANOVA using Statistical Analysis System (SAS) software (SAS Institute, Cary, NC) at the confidence level of 95% (α = 0.05) with Tukey's adjustment in the comparison of means.

Evaluation of barrier properties

The barrier characteristics of the control and exposed polymeric films were determined in accordance with ASTM D 1434-82(2003).[17] Water vapor transmission rates (WVTR) were evaluated using a water vapor permeability analyzer (Permatran-W® Model 3/11, Mocon, Minneapolis, MN). Carbon dioxide permeation rates (CO_2TR) were evaluated using a carbon dioxide permeability analyzer (Permatran-C™ Model 4/41, Mocon, Minneapolis, MN). Oxygen transmission rates (O_2TR) were measured using an oxygen permeability analyzer (O_2TR 8001, Illinois Instruments, Johnsburg, IL). The experimental conditions for each of the measurements were as follows:

- WVTR (kg m^{-2} s^{-1}): 100% relative humidity (RH) difference across the film, 23°C.
- CO_2TR (kg m^{-2} s^{-1}): 101,325 Pa partial pressure of CO_2 across the film, N_2 carrier gas, 23°C, and 0% RH.
- O_2TR (kg m^{-2} s^{-1}): 21278.25 Pa partial pressure of O_2 across the film, N_2 carrier gas, 23°C, and 0% RH.

The test areas of each sample were between 7.90 × 10^{-5} and 5.00 × 10^{-3} m^2, depending on the barrier characteristics of each film. The WVTR, CO_2TR, and O_2TR values obtained were then used to calculate the permeability coefficient P_{H_2O}, P_{CO_2}, and P_{O_2}, respectively, of the film samples by multiplying the
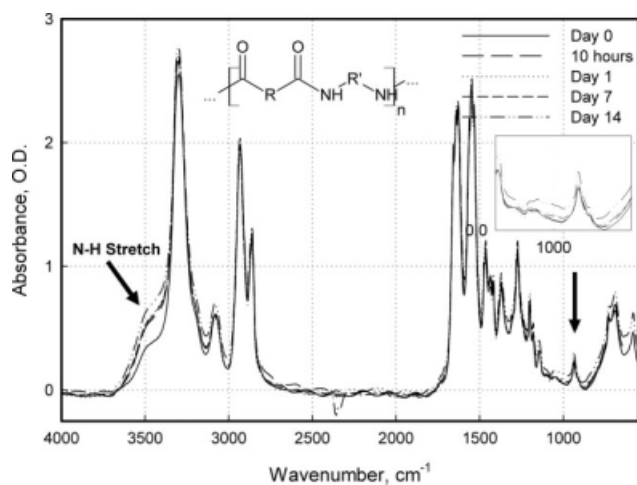
Figure 2 FTIR spectra of nylon before and after exposure to ClO$_2$ gas: Day 0 control (——); 10 h (———); Day 1 (········); Day 7 (----); and Day 14 (— ·· —).

thickness of the samples and dividing by the partial pressure gradient. The final values were expressed as kg m m^{-2} s^{-1} Pa^{-1}.

Four replicate samples were subjected to each test. The data obtained were analyzed by ANOVA using Statistical Analysis System (SAS) software (SAS Institute, Cary, NC) at the confidence level of 95% ($\alpha = 0.05$) with Tukey's adjustment in the comparison of means.

RESULTS AND DISCUSSION

The chemical, physical, and mechanical properties of the films in this study were evaluated as a function of short- or long-term exposure to ClO$_2$. The ClO$_2$ concentration used and the exposure times for the polymeric films were selected to meet the typical shelf-life requirements for fresh produce.[7,18] The 1-day exposure was considered short-term exposure,
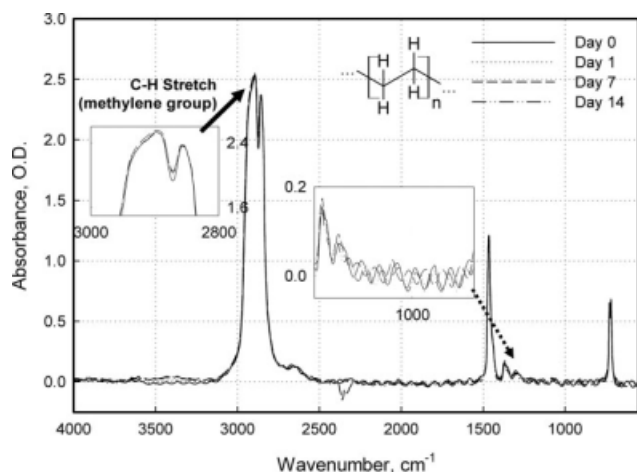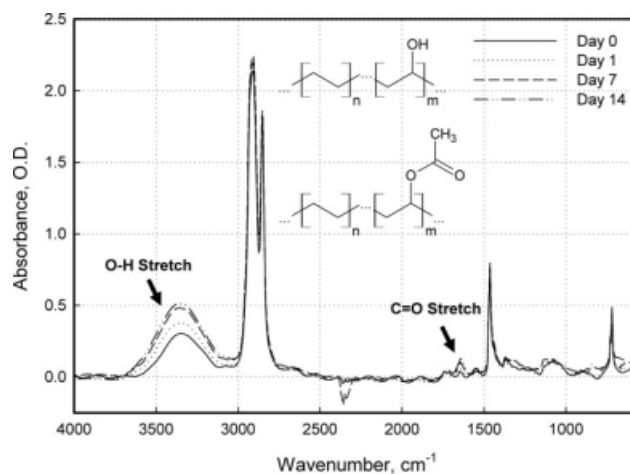

Figure 4 FTIR spectra of EVA/EVOH/EVA before and after exposure to ClO$_2$ gas: Day 0 control (——); Day 1 (········); Day 7 (----); and Day 14 (— ·· —).

where the mass transfer of ClO$_2$ at a concentration of 3600 ppmV is at steady state in all the polymeric materials tested, with the exception of multilayer EVA/EVOH/EVA.[19] The 7- and 14-day exposures were regarded as long-term exposure, which is referred to as "persistent gas exposure" (PGE). A PGE could be encountered, for example, when a sustained-release device is included in a packaging system. According to this scenario, ClO$_2$ gas would be present at specific concentration within the package atmosphere up to the end of the product's shelf life.

Chemical structure characterization of polymeric materials

Changes were observed in the intensities of the IR spectra of exposed polymeric films (Figs. 2–5 and Tables I–IV), which were attributed to possible interactions between ClO$_2$ gas and the films. In

Figure 3 FTIR spectra of LLDPE before and after exposure to ClO$_2$ gas: Day 0 control (——); Day 1 (········); Day 7 (----); and Day 14 (— ·· —).
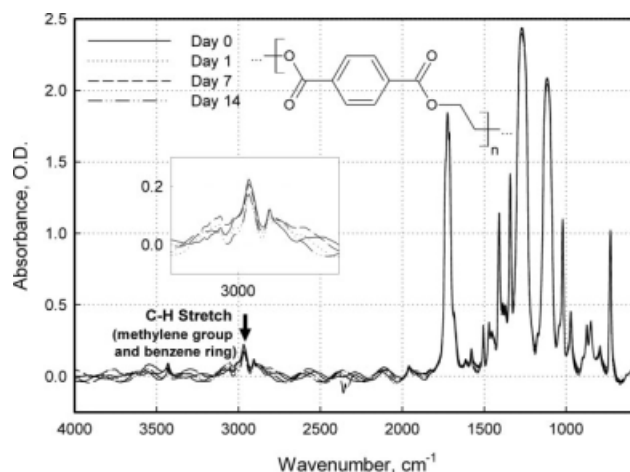

Figure 5 FTIR spectra of PET exposed to ClO$_2$ gas: Day 0 control (——); Day 1 (········); Day 7 (----); and Day 14 (— ·· —).

TABLE I
Absorbance Intensities of Specific Peaks from FTIR
Spectra of Nylon as a Function of ClO_2 Exposure Time

Wavenumber (cm^{-1})	Exposure to ClO_2 (days)	Absorbance intensity
3439.09	0	0.404 ± 0.000
	1	0.642 ± 0.002
	7	0.736 ± 0.008
	14	0.626 ± 0.006
3300.2	0	2.554 ± 0.069
	1	2.711 ± 0.016
	7	2.774 ± 0.008
	14	2.685 ± 0.007
935.48	0	0.223 ± 0.003
	1	0.226 ± 0.002
	7	0.309 ± 0.001
	14	0.245 ± 0.003

general, the types of changes observed from the persistent (long-term) exposure study were in agreement with those from the short-term exposure to ClO_2. The degree of change also increased as a function of exposure time.

The IR spectra of the exposed and conditioned samples were collected and compared to those without conditioning to help determine if chemical changes were transient or permanent. Generally, the changes in the absorbance intensities observed for most of the short-term exposed samples were only temporary, because the absorbance intensities of the exposed samples after conditioning were equivalent to those of the respective control samples. However, after long-term exposure, most of the changes tended to be permanent; the absorbance intensities of the exposed and conditioned film samples were different than those of the controls. Changes observed in the various peaks are a result of the changes in the chemical characteristics of the film due to the interaction with the ClO_2 gas and not just a ClO_2 residual because the main absorption peak of ClO_2 is located within 450 cm^{-1}.[20]

The most notable results were observed in the exposed nylon sample (Fig. 2 and Table I). An additional IR spectrum of the nylon sample was obtained

TABLE II
Absorbance Intensities of Specific Peaks from FTIR
Spectra of LLDPE as a Function of ClO_2 Exposure Time

Wavenumber (cm^{-1})	Exposure to ClO_2 (days)	Absorbance intensity
2899.01	0	2.530 ± 0.001
	1	2.523 ± 0.000
	7	2.549 ± 0.001
	14	2.516 ± 0.009
2856.58	0	2.355 ± 0.002
	1	2.357 ± 0.001
	7	2.374 ± 0.002
	14	2.359 ± 0.001

TABLE III
Absorbance Intensities of Specific Peaks from FTIR
Spectra of EVA/EVOH/EVA as a Function of ClO_2
Exposure Time

Wavenumber (cm^{-1})	Exposure to ClO_2 (days)	Absorbance intensity
3352.28	0	0.304 ± 0.004
	1	0.377 ± 0.014
	7	0.486 ± 0.010
	14	0.511 ± 0.009
1643.35	0	0.040 ± 0.001
	1	0.061 ± 0.001
	7	0.103 ± 0.005
	14	0.130 ± 0.002

after 10 h of exposure, which was the time taken for ClO_2 to reach a steady state of permeation.[19] Changes in the IR spectrum after 10 h of exposure were equivalent to those observed at 1 and 7 days when compared with the spectrum of the control (Day 0) sample.

Generally, for film samples affected by ClO_2, changes in the peak intensities after 14 days exposure were the most dramatic, followed by those after 7 days, and then those after short-term exposure. However, peak intensity changes seem to occur at a slower rate with longer exposure times. This slower rate of change could be attributed to less availability of the functional groups that ClO_2 can react with, as oxidative degradation is normally a surface phenomenon.[12,13]

The similar IR spectra of HDPE, LDPE (not shown), and LLDPE (Fig. 3 and Table II) showed minor changes in the intensities of the peaks in the 2700–3000 cm^{-1} region after exposure, which indicates possible changes in the C—H bonds of the methyl or methylene group. The IR spectra of exposed PVC and BOPP (not shown) revealed only slight changes in absorbance intensities. In exposed PEs and PS (not shown), the shifts of the peaks in the fingerprint area, the 750–1400 cm^{-1} region, to higher wavenumbers indicate the possible presence of a C—Cl bond in the exposed samples.[21] The increase in methyl group signal in the ClO_2-treated PE spectra and the possible chlorination of all exposed PE indicates degradation of the polymer's main chain and the formation of polar groups,

TABLE IV
Absorbance Intensities of Specific Peaks from FTIR
Spectra of PET as a Function of ClO_2 Exposure Time

Wavenumber (cm^{-1})	Exposure to ClO_2 (days)	Absorbance intensity
3053.32	0	0.057 ± 0.000
	1	0.069 ± 0.001
	7	0.098 ± 0.001
	14	0.046 ± 0.000

TABLE V
Physical Properties of Selected Polymeric Films Exposed to ClO₂ Gas

Sample	Exposure to ClO$_2$ (days)	T_g (°C)	T_m (°C)	Heat of fusion (J/g)
LDPE	0	n/d*	112.6 ± 0.09	64.2 ± 7.20
	14	n/d	112.3 ± 0.19	66.0 ± 1.90
PS	0	92.6 ± 0.16[†]	n/a[‡]	n/a
	14	91.6 ± 0.42	n/a	n/a
PLA	0	69.1 ± 0.22	167.2 ± 0.51	29.2 ± 0.42
	14	69.5 ± 1.16	166.6 ± 0.32	28.1 ± 0.42
PET	0	81.6 ± 0.42	249.0 ± 0.55	31.3 ± 1.56
	14	80.4 ± 0.18	248.4 ± 0.15	34.0 ± 2.64
Nylon	0	n/d	261.4 ± 0.12	56.0 ± 0.86
	14	n/d	259.8 ± 0.25	62.9 ± 1.48
EVA/EVOH/EVA:				
EVA	0	n/d	123.7 ± 1.00	50.5 ± 8.76
	14	n/d	122.8 ± 0.56	52.5 ± 5.83
EVOH	0	n/d	159.3 ± 0.40	3.70 ± 0.27
	14	n/d	147.7 ± 0.90	2.55 ± 0.40

* n/d = not determined because of equipment limitations.
[†] Within columns, means (±S.D.) sharing the same superscript letter are not significantly different ($P > 0.05$; $n = 4$).
[‡] n/a = not available because of the absence of a particular attribute.

which is in agreement with the results from other studies that exposed nonpolar polymeric compounds, such as polyolefin, to oxidative agents.[11,14]

The increases in absorbance intensities in the fingerprint area of the exposed nylon (Fig. 2 and Table I) and EVA/EVOH/EVA films (Fig. 4 and Table III) also suggest partial chlorination[21] of the exposed samples. This alteration would increase the polymers' polarity and may lead to an increase in their barrier to gases and other organic compounds if the degree of chlorination is sufficiently high.[22,23]

An increase in the intensity of the peaks within 3000–3700 cm^{-1} region of the exposed multilayer EVA/EVOH/EVA film (Fig. 4) indicates a change of the hydroxyl group in the EVOH layer. A minor increase in absorbance of the peak in the 1600–1700 cm^{-1} region could be due to the formation of a carbonyl group (Table III).

The increases in absorbance intensities of the exposed PLA (not shown) and nylon (Fig. 2 and Table I) samples in the 3300–3700 cm^{-1} region were similar to changes in the hydroxyl groups and N—H bonds, respectively. It should be noted that absorbance in this region for the nylon sample is higher at Day 14 compared with control, but is lower than that of the Day 7 sample. The increase in absorbance intensities of the exposed nylon in the 1100–1200 cm^{-1} region indicates changes in the C—N bonds.[14,21]

In the spectra for PET shown in Figure 5, the slight changes in the peak intensities in the 2800–3100 cm^{-1} region of the exposed film samples might represent changes in the C—H bonds of the methylene group and/or benzene ring (Table IV). Such changes were not observed in the exposed PS samples (not shown) because the absorbance signals at that particular region were at the noise level. Gener-

ally, the surface oxidation of PET is reported to be complex and, in some cases, leads to the formation of many functional groups, such as carboxylic acid, terminal vinyl groups, and phenols[11]; however, there was no significant formation of such groups in the ClO₂-exposed samples under these testing conditions, and therefore there would not be any adverse impact on the safety of the food product.

Physical properties characterization

A major increase ($P < 0.05$) in the heat of fusion was observed in exposed nylon, indicating an increase in crystallinity of the exposed sample (Table V). The shift in T_m and the increase in crystallinity of the nylon film could be the result of an increase in molecular ordering, which has also been observed upon exposure of nylon to other strong oxidizing compounds.[14]

Color of the polymeric material

The overall lightness (L^*) of the exposed LDPE, PVC, PS, PET, and nylon films increased when compared with those of the unexposed samples (Table VI). The changes in the b^* values of the exposed PEs, PVC, PS, PET, and nylon films indicated that the films became more yellow in color after 1 and 7 days of exposure; however, after 14 days of exposure, the color shifted toward being more blue. Significant overall color differences (ΔE^*) were found in exposed PVC and PS samples.

Visual observations on discoloration of the exposed samples indicated that most film samples changed from opaque white or transparent to a dull yellowish and became darker in color by 14 days

TABLE VI
Color Properties of Selected Polymeric Packaging Materials Exposed to ClO_2 Gas

Sample	Exposure to ClO_2 (days)	L^*	a^*	b^*	ΔE^*
LDPE	0	38.34 ± 0.98*	−2.69 ± 0.28	−6.06 ± 0.22	
	1	39.24 ± 0.72	−2.67 ± 0.26	−5.91 ± 0.24	0.91 ± 0.85
	7	39.02 ± 1.04	−3.09 ± 0.31	−5.68 ± 0.18	0.88 ± 0.80
	14	39.44 ± 0.38	−2.75 ± 0.18	−6.53 ± 0.20	1.20 ± 0.69
PVC	0	28.27 ± 0.57	−2.82 ± 0.17	−2.10 ± 0.19	
	1	29.28 ± 1.54	−2.37 ± 0.21	−2.48 ± 0.51	1.17 ± 1.01
	7	28.95 ± 1.12	−2.53 ± 0.84	−2.03 ± 0.35	0.83 ± 0.81
	14	32.87 ± 0.54	−2.37 ± 0.28	−3.79 ± 0.30	4.92 ± 0.53
PS	0	25.96 ± 0.83	−2.29 ± 0.51	−1.90 ± 0.29	
	1	34.55 ± 1.23	−3.14 ± 0.83	−1.06 ± 0.63	8.67 ± 1.04
	7	35.74 ± 1.81	−3.28 ± 0.87	−1.01 ± 0.19	9.87 ± 1.40
	14	38.05 ± 2.18	−3.59 ± 0.43	−2.16 ± 0.24	12.2 ± 1.64
PET	0	34.91 ± 1.37	−3.13 ± 0.64	−3.27 ± 0.16	
	1	33.12 ± 1.52	−2.96 ± 0.61	−2.95 ± 0.31	1.83 ± 1.42
	7	33.71 ± 0.81	−2.96 ± 0.54	−2.93 ± 0.22	1.26 ± 1.08
	14	36.38 ± 0.97	−2.59 ± 0.49	−3.98 ± 0.28	1.72 ± 1.03
Nylon	0	33.68 ± 0.79	−2.82 ± 0.59	−6.06 ± 0.25	
	1	38.01 ± 2.77	−2.67 ± 0.74	−4.97 ± 0.87	4.47 ± 1.98
	7	37.50 ± 0.77	−2.72 ± 0.62	−4.91 ± 0.32	3.99 ± 0.75
	14	37.42 ± 2.25	−2.61 ± 0.39	−5.75 ± 0.62	3.76 ± 1.68

* Within columns, means (±S.D.) sharing the same superscript letter are not significantly different ($P > 0.05$; $n = 8$).

exposure. The development of color in oxidized polymers is a consequence of several possible degradation reactions, such as the formation of conjugated double bonds, and the oxidation of additives. Color changes have been reported previously for some polymeric materials when exposed to oxidizing agents.[11,12,24]

Mechanical properties characterization

Exposure of PEs to ClO_2 resulted in a significant decrease ($P < 0.05$) in the TS and MoE of the films (Table VII) due to the oxidative degradation of the polymer chains, as confirmed earlier by the increase in the methyl group signal of the IR spectra (Fig. 3 and Table II).[14] Such degradation can reduce the structure's rigidity, thereby altering the tensile characteristics of the oxidized polymers.[22]

The mechanical performance of the other polymer films remained unchanged after exposure, even though the formation of polar groups was observed in most of the IR spectra. Theoretically, an increase in polarity should improve the intermolecular forces between the polymer chains, limiting the mobility of the chains and leading to an increase in TS and a decrease in elongation at break.[22]

Barrier properties characterization

One potential application of ClO_2 gas is in a modified atmosphere packaging (MAP) system in combination with other gases, such as O_2 and CO_2, so the

TABLE VII
Tensile Properties of Selected Polymeric Packaging Materials Exposed to ClO_2 Gas

Sample	Exposure to ClO_2 (days)	Tensile strength × 10^7 (N/m^2)		Modulus of elasticity (secant) × 10^8 (N/m^2)	
		MD	TD	MD	TD
HDPE	0	4.15 ± 0.12*	2.71 ± 0.06	6.09 ± 0.14	6.68 ± 0.28
	14	3.45 ± 0.38	2.24 ± 0.52	5.29 ± 0.21	6.45 ± 0.51
LDPE	0	3.08 ± 0.12	1.99 ± 0.03	0.89 ± 0.06	0.84 ± 0.06
	14	2.85 ± 0.12	1.87 ± 0.09	0.83 ± 0.02	0.76 ± 0.04
PET	0	19.2 ± 1.36	21.5 ± 0.41	43.2 ± 1.92	47.2 ± 1.03
	14	18.8 ± 0.95	21.4 ± 0.68	43.8 ± 0.33	44.4 ± 0.67
Nylon	0	6.86 ± 0.38	6.80 ± 0.53	9.69 ± 0.42	10.1 ± 0.55
	14	6.43 ± 0.52	5.84 ± 1.06	9.50 ± 0.21	9.78 ± 0.44
EVA/EVOH/EVA	0	11.2 ± 0.34	9.53 ± 0.39	5.51 ± 0.15	4.92 ± 0.75
	14	10.0 ± 2.31	8.59 ± 0.69	6.14 ± 0.93	5.96 ± 0.63

* Within columns, means (±S.D.) sharing the same superscript letter are not significantly different ($P > 0.05$; $n = 5$).

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, non-reactive 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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