

Mass Transfer Study of Chlorine Dioxide Gas Through Polymeric Packaging Materials

Siriyupa Netramai,¹ Maria Rubino,¹ Rafael Auras,¹ Bassam A. Annous²

¹School of Packaging, Michigan State University, East Lansing, Michigan 48824-1223

²Eastern Regional Research Center-ARS-USDA, Wyndmoor, Pennsylvania 19038-8598

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ABSTRACT: The mass transfer profile (permeability, diffusion, and solubility coefficients) of chlorine dioxide (ClO₂), a strong oxidizing agent that is used in food and pharmaceutical packaging, was determined through various common polymeric packaging materials. A continuous system for measuring permeation of ClO₂, using an electrochemical detector, was developed. It was observed that biaxially-oriented poly(propylene), poly(ethylene terephthalate), poly(lactic acid), nylon, and a multilayer structure of ethylene vinyl acetate and ethyl-

ene vinyl alcohol were better barriers for gaseous ClO₂, as compared to polyethylene, poly(vinyl chloride), and polystyrene. The activation energies of permeation for ClO₂ through poly(ethylene terephthalate) and poly(lactic acid) were determined to be 51.05 ± 4.35 and 129.03 ± 2.82 kJ/mol, respectively. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 2929–2936, 2009

Key words: activation energy; diffusion; films; gas permeation; chlorine dioxide

INTRODUCTION

Chlorine dioxide (ClO₂) is a strong oxidizing agent and an effective surface disinfectant that was used initially to treat water, as it causes less organoleptic problems than chlorine (Cl₂).¹ ClO₂ is soluble in water and has equal, if not higher, disinfecting capacity than that of Cl₂, but is less effective than ozone (O₃).¹ Generally, chlorine dioxide exists in two isomeric forms, i.e., a symmetric OClO and an asymmetric ClOO form. In a diluted water solution, the OClO form is kinetically more stable at room temperature, and demonstrates no thermal dissociation over many days.² Eventually, the excitation of ClO₂ gas in the near-UV region leads to its photochemical dissociation into ClO + O, or its isomerization to form the unstable ClOO, which will further dissociate into atomic Cl + O₂.^{2,3} The reactive nature of ClO₂ makes it difficult to find a suitable detection method to accurately measure its concentration.

Because of its bacteriocidal effects, ClO₂ gas is gaining significant interest in the food and pharmaceutical industries.^{4,5} One of the most recent applications of ClO₂ is as a headspace gas in packaging

systems where it acts in vapor-phase decontamination to extend the shelf-life of perishable food products.^{4,6,7} The introduction of gaseous ClO₂ within food packaging systems is often by means of a sachet, either slow- or fast-release.^{8,9} Also, in 2001, the U.S. Food and Drug Administration (FDA) approved the incorporation of ClO₂ precursors in food packaging films used for uncooked meats, such as poultry and seafood.¹⁰

If a package is to be considered as a strategy for the release and application of ClO₂ gas, then the mass transfer properties of ClO₂ must be determined since this will impact the selection of material(s) with an appropriate barrier to the gas.

Ozen (2000) studied the mass transfer of gaseous ClO₂ through polymeric materials, using a quasi-isostatic method, by exposing 100 mg/L ClO₂ to the film sample in a three-compartment permeability cell, and utilizing an amperometric titration method as a detection technique. The reported permeability (*P*) values of ClO₂ gas, at 20°C, for linear low-density polyethylene (LLDPE), oriented poly(propylene) (OPP), and biaxially-oriented nylon (BON) were 7.62 × 10⁻¹⁶, 6.21 × 10⁻¹⁷, and 2.34 × 10⁻¹⁷ kgClO₂ m/m² s Pa, respectively. However, steady state of permeation was reached in less than 50 min in LLDPE, and there was a delayed response in the detection system used, which prevented the assessment of the unsteady region for the calculation of the diffusion coefficient.¹¹ To obtain a complete mass transfer profile of ClO₂ through packaging membranes, it is critical to

Correspondence to: M. Rubino (mariar@msu.edu).

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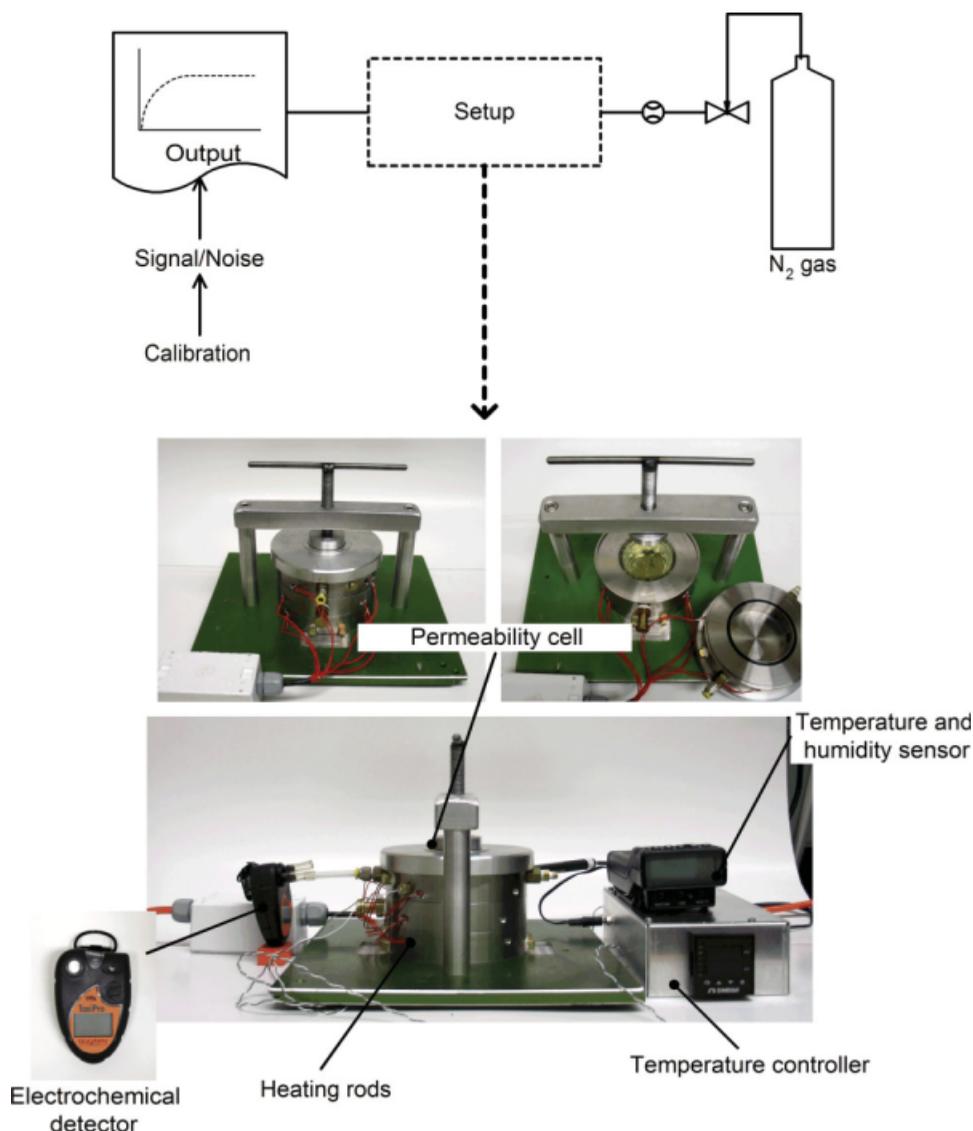


Figure 1 Flow diagram of mass transfer study showing permeation system set up. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

develop a continuous detection technique that can provide information of the unsteady-state.

The objectives of this study were (i) to develop a continuous detection method for mass transfer measurement of ClO_2 , and (ii) to assess the mass transfer of ClO_2 through various polymeric packaging materials by determining their permeability, diffusion, and solubility coefficients (P , D , and S , respectively).

MATERIALS AND METHODS

Part I: Development and calibration of continuous detection system

The flow diagram and set up of the permeation system developed in our laboratory is shown in Figure 1. The system consisted of a nitrogen supply,

a flow meter/controller, a permeability cell, and an electrochemical (EC) detector. Nitrogen gas from the generator picks up gaseous ClO_2 that permeates through the film sample installed in the permeability cell, and carries the ClO_2 to the EC detector. The detector records the output of concentration of the permeated ClO_2 (in ppm or ppmV) every 30 s.

Permeability cell

The permeability cell (Fig. 2) is made of grade 316 stainless-steel, which has excellent overall corrosion resistance properties. The two half-cells are sealed together using a Viton[®] O-ring made from fluoroelastomers which did not interact with ClO_2 gas at the testing concentrations.

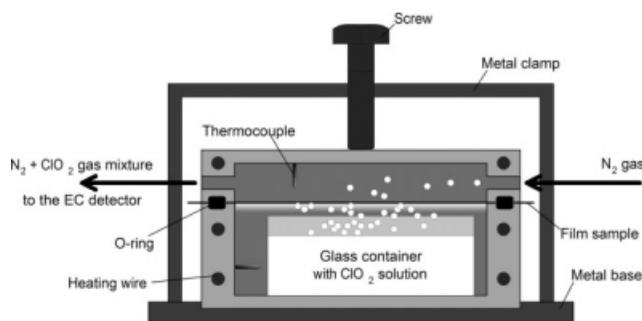


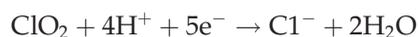
Figure 2 Schematic of ClO_2 permeation through polymer film in the permeability cell.

The film sample is placed between the upper and lower chambers that have volumes of $8.7 \times 10^{-5} \text{ m}^3$ and $20.3 \times 10^{-5} \text{ m}^3$, respectively. The permeated ClO_2 collects in the upper chamber. A temperature control device, which consists of six heating wires fitted in the metal wall (two wires for the upper chamber, and four wires for the lower chamber), heats the permeability cell to the desired temperature. Temperature is monitored by two thermocouples located at the top and bottom of the unit, and data is transferred to the temperature controller. The temperature fluctuation inside the chamber varied $\pm 0.50^\circ\text{C}$ from the testing condition. A relative humidity (RH) sensor installed in the upper chamber monitored %RH of the chamber throughout the experiment.

Electrochemical detector

The detector used in this study was a ToxiPro[®] EC detector (Biosystems, Plano, TX) for ClO_2 . The detector is able to quantitatively determine the concentration of a particular gas by generating an electrical signal that correlates the reaction of the electrode with the target gas. A typical EC sensor (two-electrode type), main component of EC detector, consists of the following components: (a) a hydrophobic membrane that protects and controls the amount of gas reaching the electrode; (b) a sensing (or working) electrode, which the diffused gas reacts with; (c) a counter electrode that supplies or receives the electrons for the sensing electrode; and (d) an electrolyte that facilitates the reaction and enables the ionic flow. The system produces an electric current proportional to the gas concentration. A three-electrode type EC sensor also has a third electrode, a reference electrode, to stabilize the sensing electrode.¹²

The reaction that takes place in the sensor for ClO_2 is¹²:



For the ToxiPro[®] detector, the operating temperature and humidity ranges are from -20 to 50°C , and

up to 95% RH, respectively, with no condensation (according to the manufacturer's specifications).¹²

The unit displayed on the detector is ppm (or ppmV), i.e., μL of ClO_2 gas per 1 L of sampled gas mixture. The concentration in ppmV of ClO_2 can also be converted to mg of ClO_2/L of gas (mg/L), which is one of the common units used to describe the concentration of gaseous ClO_2 .^{13,14}

Calibration of EC detector

The EC detector was calibrated every 2 weeks by exposing the detector to air (zero calibration, 0.00 ppmV of ClO_2) and 1.00 ppmV of ClO_2 gas generated by an EC gas generator (Cal 2000, ACD, Tucson, AZ). A bump test to monitor the response of the detector, i.e., exposing the detector to a known concentration of ClO_2 at 0.00, 1.00, 2.50, 3.00, and 4.00 ppmV, was also performed every month by the local Office of Radiation, Chemical & Biological Safety (ORCBS) (East Lansing, MI). The detector gave a linear response with a correlation factor (R^2) of 0.9995.

Determination of noise and signal to noise ratio of EC detector

The background noise of the EC detector was determined by collecting mass transfer data in the absence of ClO_2 solution in the lower chamber of the permeability cell over 24 h for all temperature conditions used in this study. The test was repeated four times at each temperature. The data obtained were then used to calculate the amplitude of noise as $3s$, where s is the square root of the mean squared error (MSE).¹⁵ The calculated amplitude of noise and the response of the detector obtained from the bump test (mentioned previously) were then used to calculate the signal to noise (S/N) ratio of the EC detector at various concentrations of gaseous ClO_2 .

Preparation of ClO_2 solutions

A solution to provide 10 mg ClO_2/L of gas (~ 3600 ppmV) was prepared from a stock solution of 1000 mg ClO_2 per liter, which was obtained by submerging a sachet containing the chemical precursors, i.e., sufficient sulfuric acid (H_2SO_4) and sodium chlorite (NaClO_2) to generate $\sim 2 \times 10^{-3} \text{ kg}$ 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.¹³ The stock solution was diluted, as required, right before use. The final concentration was determined by titration and, according to the Henry's constant of gaseous ClO_2 reported in the literature,^{7,14} gave a concentration of 10 mg ClO_2/L of gas (~ 3600 ppmV) in the

headspace. That concentration was selected for this study because it provides a high dose range of gaseous ClO₂ that is considered most suitable for food applications yet does not significantly affect the organoleptic properties and/or other important attributes of tested food products.^{4,7}

Part II: Mass transfer study

Polymeric packaging materials

The polymeric materials selected for this study were low-density polyethylene (LDPE) and linear low-density polyethylene (LLDPE) (Flexopack S.A., Attiki, Greece), high-density polyethylene (HDPE) (James River Corp., Flexible Packaging Group, Richmond, VA), biaxially-oriented poly(propylene) (BOPP) (Cryovac, Duncan, SC), polystyrene (PS) (TRYCITE™ 8001, Dow Chemical Company, Midland, MI), poly(ethylene terephthalate) (PET) (Mylar® A, DuPont, Wilmington, DE), poly(vinyl chloride) (PVC) (BEMIS, Shirley, MA), nylon 66 (Dartek F-101, DuPont, Wilmington, DE), poly(lactic acid) (PLA) (EVLON®, BI-AX International, Wingham, ON, Canada), and a multilayer structure of ethylene vinyl acetate (EVA) and ethylene vinyl alcohol (EVOH) (EVA/EVOH/EVA; Cryovac, Duncan, SC). These materials are normally used in packaging systems for perishable food products and various non-perishable and pharmaceutical goods. Samples of each film were taken from the same lot and were conditioned at 23°C and 50% RH for at least 24 h before starting any experiment.

Polymer characterization

The density, ρ , in kg/m³ of the polymer film samples was measured using the flotation method at 23°C. A mixture of methanol and water, or a solution of calcium nitrate [Ca(NO₃)₂], were used as the flotation media for the films with $\rho < 1$ or $\rho > 1$, respectively.^{7,16}

The glass transition temperature, T_g (°C), and enthalpy of fusion, ΔH_m (kJ/kg), of the polymeric films were determined using a Q-100 differential scanning calorimeter (DSC) (TA Instruments, New Castle, DE)

according to the ASTM D3418-03 method.¹⁷ At least 5×10^{-6} kg of sample was used in each run, which consisted of two cycles (heat/cool/heat) with heating and cooling rates of 10°C/min. The experiment was repeated five times for each type of material. The ΔH_m and T_g data were collected from the first and second heating, respectively, and data analyzes were done using Universal Analysis Software (UAS Version 3.9A, TA Instruments, New Castle, DE). The crystallinity of the film samples was calculated by:

$$\% \text{ Crystallinity} = \frac{\Delta H_m}{\Delta H_m^0} \times 100 \quad (1)$$

where ΔH_m is the heat of fusion of the sample obtained by DSC, and ΔH_m^0 is the heat of melting of 100% crystalline material; kJ/kg values used were 288 (PE), 79 (BOPP), 138 (PET), 93.6 (PLA), 301 (nylon), 293 (EVA), and 163 (EVOH).^{18,19}

Determination of ClO₂ mass transfer parameters

Permeability, diffusion, and solubility coefficients of ClO₂ for the various polymeric packaging materials were determined using a permeation approach that follows an isostatic method. The diffusion process of gaseous ClO₂ through the materials was assumed to be independent of the permeant's concentration and the polymer relaxation, which is known as Fickian diffusion.^{20,21} The diffusion coefficient was calculated from the mass transfer profile in the transient region that leads to the steady-state of the mass transfer, where the concentration gradient of the permeant across the film remain constant. The S values were calculated using the "solution-diffusion" model²⁰:

$$P = D \times S \quad (2)$$

As described earlier, the gaseous ClO₂ was released from the prepared ClO₂ solution at a constant rate, and exposed to the film sample located between two halves of the permeability cell (Fig. 2). The experiment was repeated four times for each type of material. The amount of ClO₂ gas permeated per second was calculated as follows:

$$\begin{aligned} & \text{Permeated ClO}_2 \text{ measured at time } t(\text{kg/s}) \\ &= \frac{\text{permeated ClO}_2 (\mu\text{L/L}) \times 67.5 \text{ g/mol} \times \text{N}_2 \text{ gas flow rate (L/s)}}{10^6 \mu\text{L/L} \times 1 \text{ mol of ideal gas at particular temperature (L/mol)} \times 10^3 \text{g/kg}} \end{aligned} \quad (3)$$

where 67.5 g/mol is the molecular weight of ClO₂. The N₂ gas flow rate is equal to 4.81×10^{-3} L/s and represents the volume of N₂ gas that flows through the upper chamber of the permeability cell in 1 s and carries the permeated ClO₂ gas to the detector.

The volume of 1 mol of ideal gas at 23, 30, and 40°C is 24.3, 24.9, and 25.7 L/mol, respectively.

The quantity of permeated ClO₂ gas (kg) at time t (s) was then plotted to obtain the permeation curve. The P value was calculated from the flow rate of the

permeated ClO₂ gas at steady-state, F_{SS} (kg/s). In this study, the steady-state was reached when the concentration of the permeated ClO₂ detected did not increase over time and did not fluctuate more than ± 0.01 ppmV for the remainder of the experiment. The experiment was successfully terminated when steady-state was reached and held for four-fold the lag time of the particular material.

The diffusion coefficient, D , was obtained by the following calculations:

$$P = F_{SS} \times \frac{\ell}{A \cdot \Delta p} \quad (4)$$

$$\Delta p = p_2 - p_1 \quad (5)$$

$$D = \frac{\ell^2}{7.2t_{1/2}} \quad (6)$$

where ℓ is the film thickness (m), A is the surface area of the film sample (m²), and Δp is the partial pressure gradient of ClO₂ between the lower half (p_2) and upper half (p_1) of the permeability cell. Since there is a constant removal of permeated ClO₂ from the upper chamber, p_1 is equal to 0.00 Pa. The partial pressure of gaseous ClO₂ over the solution placed in the lower chamber was calculated from Henry's solubility coefficient (obtained from the literature) and is equal to 3.65×10^2 Pa.¹⁴ The $t_{1/2}$ is the time taken to reach a flow rate equivalent to half of F_{SS} .

Determination of activation energy for permeation

The temperature-dependence of the mass transfer phenomenon commonly follows an Arrhenius relationship. The activation energy of permeation (E_p) can be calculated by:

$$P = P_0 e^{\frac{E_p}{RT}} \quad (7)$$

where P_0 is the proportionality constant (pre-exponential term), R is the gas constant (8.314472×10^{-3} kJ/Kmol), and T is temperature in kelvins (K).

The E_p (kJ/mol) of ClO₂ for PET and PLA were determined by running permeation tests at 23, 30, and 40°C and plotting the P data obtained on a graph of $\ln P$ versus $1/T$. E_p values were calculated from the slope which is equal to $-\frac{E_p}{R}$.^{19–22}

Statistical analysis

The data obtained from four replicates of each sample were statistically analyzed by two-way analysis of variance (ANOVA) using the 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 study of permeation of gaseous ClO₂ through polymeric materials becomes a crucial issue when ClO₂ is included in the package headspace. The data obtained in this study could lead to an improved packaging system that is able to deliver and maintain specific amounts of ClO₂ to sanitize the product within the package, without compromising package integrity.

Continuous permeation system

The amplitudes of the background noise of the permeation system at 23, 30, and 40°C, as shown in Table I, increased with increasing temperature. At 23°C, the S/N ratio of the system improved significantly as the concentration of ClO₂ increased. In this study, the concentration of permeated ClO₂ at the steady state varied, depending on the type of polymeric material being studied, and ranged from ~ 0.10 to 3.00 ppmV. The noise level was very low as compared to the signal; e.g., noise was only 1.29% at the signal of 0.10 ppmV. The permeation system developed for this study could be considered reliable and consistent for the measurements. This

TABLE I
Permeation System Mean Square Error and Amplitude of Noise at 0.00 ppmV, and Signal to Noise (S/N) Ratio at Various Concentrations of ClO₂

Temperature (°C)	ClO ₂ (ppmV)	MSE $\times 10^{-7}$ (s ²)	Amplitude $\times 10^{-3}$ (3s)	S/N $\times 10^2$
23	0.00	1.95 \pm 1.09 ^{a1}	1.29 \pm 0.36 ^a	–
	1.00	–	–	7.82 \pm 0.17 ^a
	2.50	–	–	19.7 \pm 0.31 ^b
	3.00	–	–	23.4 \pm 0.22 ^c
	4.00	–	–	30.7 \pm 0.24 ^d
30	0.00	3.30 \pm 0.74 ^a	1.71 \pm 0.19 ^a	–
40	0.00	5.06 \pm 0.35 ^b	2.13 \pm 0.07 ^b	–

¹ Within columns, means sharing the same superscript letter are not significantly different ($P > 0.05$; $n = 4$).

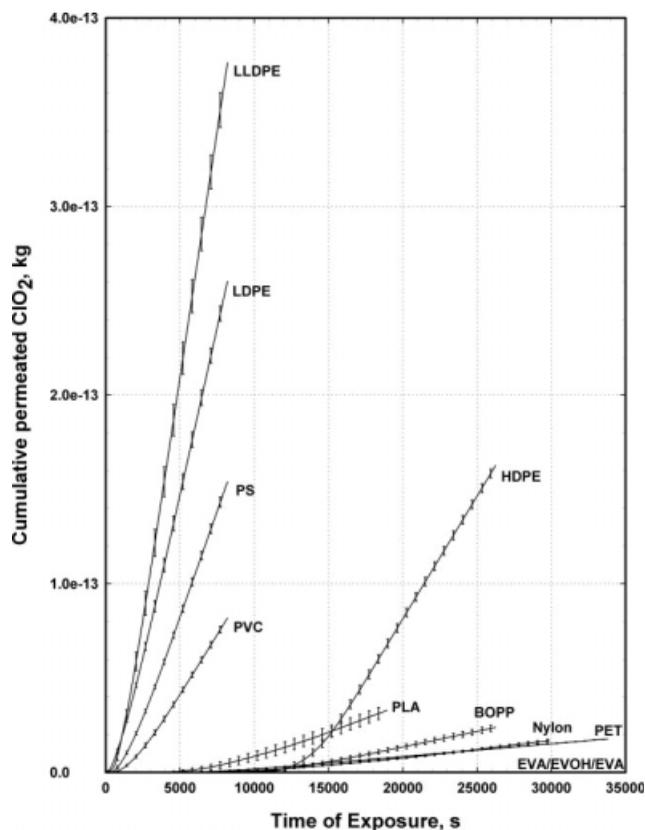


Figure 3 Mass transfer of 10 mg ClO₂/L ClO₂ gas (3600 ppmV) through polymeric materials. Film thicknesses: LDPE (4.57×10^{-5} m), LLDPE (2.79×10^{-5} m), HDPE (5.59×10^{-5} m), BOPP (1.78×10^{-5} m), PS (2.54×10^{-5} m), PET (1.27×10^{-5} m), PVC (2.79×10^{-5} m), PLA (3.81×10^{-5} m), nylon (2.03×10^{-5} m), and EVA/EVOH/EVA (1.78×10^{-5} m).

continuous system is also easy to set up and operate, as well as being space- and cost-effective.

Mass transfer of ClO₂ in polymeric films

The mass transfer profiles of 10 mg ClO₂/L of gas (3600 ppmV) through various polymeric materials are shown in Figure 3. These permeation profiles represent the cumulative permeated gaseous ClO₂ (kg) of each material versus time (s).²³ The corresponding *P*, *D*, and *S* values of the materials as determined at 23°C are listed in Table II.

The *P* value of gaseous ClO₂ for LLDPE was 96.8×10^{-17} kgClO₂ m/m² s Pa, which is similar to the value previously reported by Ozen.¹¹ Since the response of the particular EC detector is typically within 90 s,¹² the lag time of the mass transfer phenomenon could be recorded, thus the *D* and *S* values were determined in this work. For an isostatic technique, such an immediate response of the detector also leads to the more precise identification of the time to reach steady state flow rate, *F*_{SS}.

Permeabilities of gaseous ClO₂ through PET, nylon, BOPP, PLA, and multilayer EVA/EVOH/EVA were at least one order of magnitude lower than those through PE, PVC, and PS, indicating that the former materials are better barriers for ClO₂ gas.

No permeability (at detection limit of 7.32×10^{-19} kgClO₂ m/m² s Pa) was observed in EVA/EVOH/EVA multilayer film samples exposed to ClO₂ for 24 h. Among all the selected materials under consideration, this material seemed to have the highest barrier against gaseous ClO₂; the strong intermolecular forces from polar groups and hydrogen bonds may lower the chain mobility of the polymer and limit the available free volume as the molecules are held close together.²⁰

The diffusion mechanism plays an important role in the mass transfer of ClO₂ in PE films (Table II). While the *S* values of PE films are in the same range, the *D* values of LDPE and LLDPE are ~8 and 13 times higher, respectively, than that of HDPE. As diffusion coefficients are particularly affected by the polymer's *T*_g and free volume properties,²⁰ the differences in mass transfer profiles of ClO₂ through different types of PE were probably due mainly to the differences in their free volumes, i.e., the unoccupied spaces between molecules in the polymers' structures.^{21,22}

The material characteristics, density, glass transition temperature (*T*_g), and crystallinity of the 10 different packaging materials considered in this work are reported in Table III. As mentioned earlier, the crystallinity and *T*_g influence the mass transfer parameters.

BOPP was also tested above its *T*_g, but its low *P* value could be due to the decreased mobility of the oriented material²⁴ and the highly crystalline nature

TABLE II
Permeability (*P*), Diffusion (*D*), and Solubility (*S*)
Coefficients of 10 Mg ClO₂/L ClO₂ Gas (3600 ppmV) for
Selected Polymers at 23°C

Polymer	$P \times 10^{-17}$ ($\frac{\text{kgClO}_2 \cdot \text{m}}{\text{m}^2 \cdot \text{s} \cdot \text{Pa}}$)	$D \times 10^{-14}$ ($\frac{\text{m}^2}{\text{s}}$)	$S \times 10^{-3}$ ($\frac{\text{kg}}{\text{m}^3 \cdot \text{Pa}}$)
HDPE	24.1 ± 0.42 ^{a1}	3.14 ± 0.06 ^{a,e}	7.68 ± 0.27 ^a
LDPE	66.0 ± 1.09 ^b	26.2 ± 5.11 ^b	2.59 ± 0.46 ^{b,g}
LLDPE	96.8 ± 1.34 ^c	40.4 ± 2.40 ^c	2.40 ± 0.17 ^{c,g}
BOPP	3.04 ± 0.16 ^d	0.39 ± 0.02 ^a	7.84 ± 0.17 ^a
PS	41.8 ± 0.82 ^e	9.15 ± 0.47 ^d	4.57 ± 0.02 ^d
PVC	23.5 ± 0.46 ^a	7.65 ± 0.96 ^{d,e}	3.11 ± 0.38 ^{b,f}
PET	1.26 ± 0.03 ^f	0.32 ± 0.02 ^a	3.92 ± 0.19 ^e
PLA	5.40 ± 0.13 ^g	2.86 ± 0.18 ^a	1.90 ± 0.15 ^c
Nylon	1.80 ± 0.07 ^{d,f}	0.53 ± 0.02 ^a	3.43 ± 0.18 ^{e,f}
EVA/ EVOH/ EVA	Permeability is less than 0.07 ($\frac{\text{kgClO}_2 \cdot \text{m}}{\text{m}^2 \cdot \text{s} \cdot \text{Pa}}$) (24 h of exposure)		

¹ Within columns, means (±SD) sharing the same superscript letter are not significantly different (*P* > 0.05; *n* = 4).

TABLE III
Polymer Film Characteristics Including Thickness, Density (ρ), Crystallinity, and Glass Transition Temperature (T_g)

Polymer	Thickness $\times 10^{-5}$ (m)	$\rho \times 10^3$ ($\frac{\text{kg}}{\text{m}^3}$)	Crystallinity (%)	T_g ($^{\circ}\text{C}$)
HDPE	5.59	0.931	38.63 ± 3.11	nd ^a
LDPE	2.79	0.924	23.04 ± 3.31	nd
LLDPE	4.57	0.917	24.13 ± 1.52	nd
BOPP	1.78	0.917	33.08 ± 2.01	3.00 ± 1.36
PS	2.54	1.03	na ^b	92.65 ± 0.20
PVC	2.79	1.30	na	57.96 ± 0.49
PET	1.27	1.39	22.38 ± 1.36	81.66 ± 0.50
PLA	3.81	1.21	31.44 ± 0.55	69.07 ± 0.27
Nylon	2.03	1.13	24.35 ± 0.46	nd
EVA/EVOH/EVA:EVA	1.78	na	17.25 ± 3.66	nd
EVOH			2.25 ± 0.20	

^a nd, not determined due to equipment limitations.

^b na, not available due to absence of a particular attribute, or test not performed.

of the isotactic PP, which reduces the availability of free volume in its structure.²¹ The tightly packed polymer chains create a tortuous path for the permeant to move through, thus limiting the diffusion of ClO₂ gas and resulting in its low permeability.

PS had a high permeability value due to high D and fairly high S values. This result, similar to the case of PE films, was due to the abundant free volume created by the bulkiness of the benzene ring side group and the chain stiffness of the PS molecule.²⁰ Also, the PS commonly used for packaging purposes is atactic, having a noncrystalline structure.²¹

For PVC, its high D value resulted in a rather high permeability of ClO₂. As most PVC available for packaging purposes is usually highly plasticized to improve processability,²¹ its poor barrier to ClO₂ could be due to the presence of plasticizers that act as lubricants, reducing the intermolecular forces between polymer molecules, increasing the chain mobility, and facilitating the movement of ClO₂ molecules through the polymer's matrix.²⁰

The incompatibility of nylon and PET to ClO₂ was possibly due to their high intermolecular forces, gen-

erating a rigid compact structure to ClO₂. For PLA film, the weaker secondary forces and therefore less compact polymer structure make the polymer have lower barrier to ClO₂ as compared to PET, even though the barrier properties to gases and vapors of the two polymers are normally comparable.^{19,20}

Activation energy of ClO₂

The E_p data of ClO₂ for PET and PLA films obtained from plotting P data obtained at various temperatures ($\ln P$ vs. $1/T$) are shown in Table IV. The E_p value for PET is significantly lower than that for PLA indicating that the permeation of ClO₂ through PLA is less temperature dependent, which could be considered beneficial in a packaging system that is occasionally subjected to temperature abuse during transportation or distribution.

CONCLUSION

A continuous system for measuring the mass transfer of ClO₂ through different polymeric materials was developed utilizing an electrochemical detector.

TABLE IV
Permeability Coefficients (P) at Various Temperatures and Activation Energy for Permeation (E_p) of ClO₂ for Pet and PLA Films

Temperature ($^{\circ}\text{C}$)	PET		PLA	
	$P \times 10^{-17}$ ($\frac{\text{kgClO}_2 \cdot \text{m}}{\text{m}^2 \cdot \text{s} \cdot \text{Pa}}$)	E_p (kJ/mol)	$P \times 10^{-17}$ ($\frac{\text{kgClO}_2 \cdot \text{m}}{\text{m}^2 \cdot \text{s} \cdot \text{Pa}}$)	E_p (kJ/mol)
23	$1.26 \pm 0.00^{\text{a1}}$	51.05 ± 4.35	$5.40 \pm 0.13^{\text{a}}$	129.03 ± 2.82
30	$2.67 \pm 0.04^{\text{b}}$		$21.5 \pm 0.74^{\text{b}}$	
40	$3.98 \pm 0.05^{\text{c}}$		$94.4 \pm 0.52^{\text{c}}$	

¹ Within columns, means (\pm SD) sharing the same superscript letter are not significantly different ($P > 0.05$; $n = 4$).

The permeability, diffusion, and solubility coefficients (P , D and S , respectively) of 10 mg ClO_2/L of gas (3600 ppmV) ClO_2 for 10 types of selected polymeric materials were determined by an isostatic method. The results ranged from a permeability value below $0.07 \times 10^{-17} \text{ kgClO}_2 \text{ m/m}^2 \text{ s Pa}$ for multilayer EVA/EVOH/EVA to $96.8 \times 10^{-17} \text{ kgClO}_2 \text{ m/m}^2 \text{ s Pa}$ for LLDPE, BOPP, PET, PLA, nylon, and the multilayer EVA/EVOH/EVA are good barriers for gaseous ClO_2 as compared to PE, PVC, and PS, which have higher permeability coefficients than the former group. The activation energy of permeation, in the temperature range of 23–40°C, for ClO_2 gas for PET and PLA were found to be 51.05 and 129.03 kJ/mol, respectively.

Especially in food packaging applications, ClO_2 exposure must not significantly affect the polymeric material or the gas permeability of the packaging system. Since it is a strong oxidizing agent, ClO_2 could impact the packaging system's characteristics, and consequently, the package integrity and its performance in terms of mass transfer of gases, such as oxygen or carbon dioxide, and vapors, such as moisture.^{11,24} Thus, additional studies are being conducted in our laboratory to assess and determine the effects of gaseous ClO_2 exposure on the integrity and performance of polymeric materials.

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