Effect of Chlorine Dioxide Gas on Polymeric Packaging Materials

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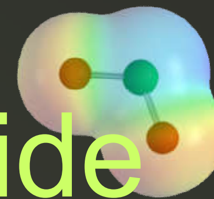
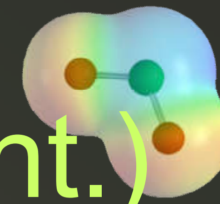


Chlorine Dioxide

- High oxidizing capacity and broad disinfecting property

(USEPA, 1999)

Chlorine Dioxide (cont.)



- Inactivating capacity against:
  - *Escherichia coli* O157:H7
  - *Salmonella* spp.
  - yeasts and molds
  - etc.

(Sy *et al*, 2005a and 2005b; USEPA, 1999)

Chlorine Dioxide (cont.)

- Used, both in gaseous and liquid forms:
  - Fresh produces
  - Drinking- and waste water production
  - Food-contact surface
  - Pharmaceutical and factory tools
  - etc.

(Sy *et al*, 2005a and 2005b; USEPA, 1999)

Chlorine Dioxide (cont.)

- Vapor phase decontamination
  - Antimicrobial gas
  - Application
    - Sanitizing steps in production line
    - Product/packaging system
      - MAP, Active packaging, etc.

Chlorine Dioxide (cont.)

- Its effects on pkg material ?
  - Mass transfer phenomenon
  - Oxidative degradation
    - Undesirable changes in pkg properties and performances

(Ozen, 2000; Ozen, 2002; Walzak *et al*, 1995)

Objectives

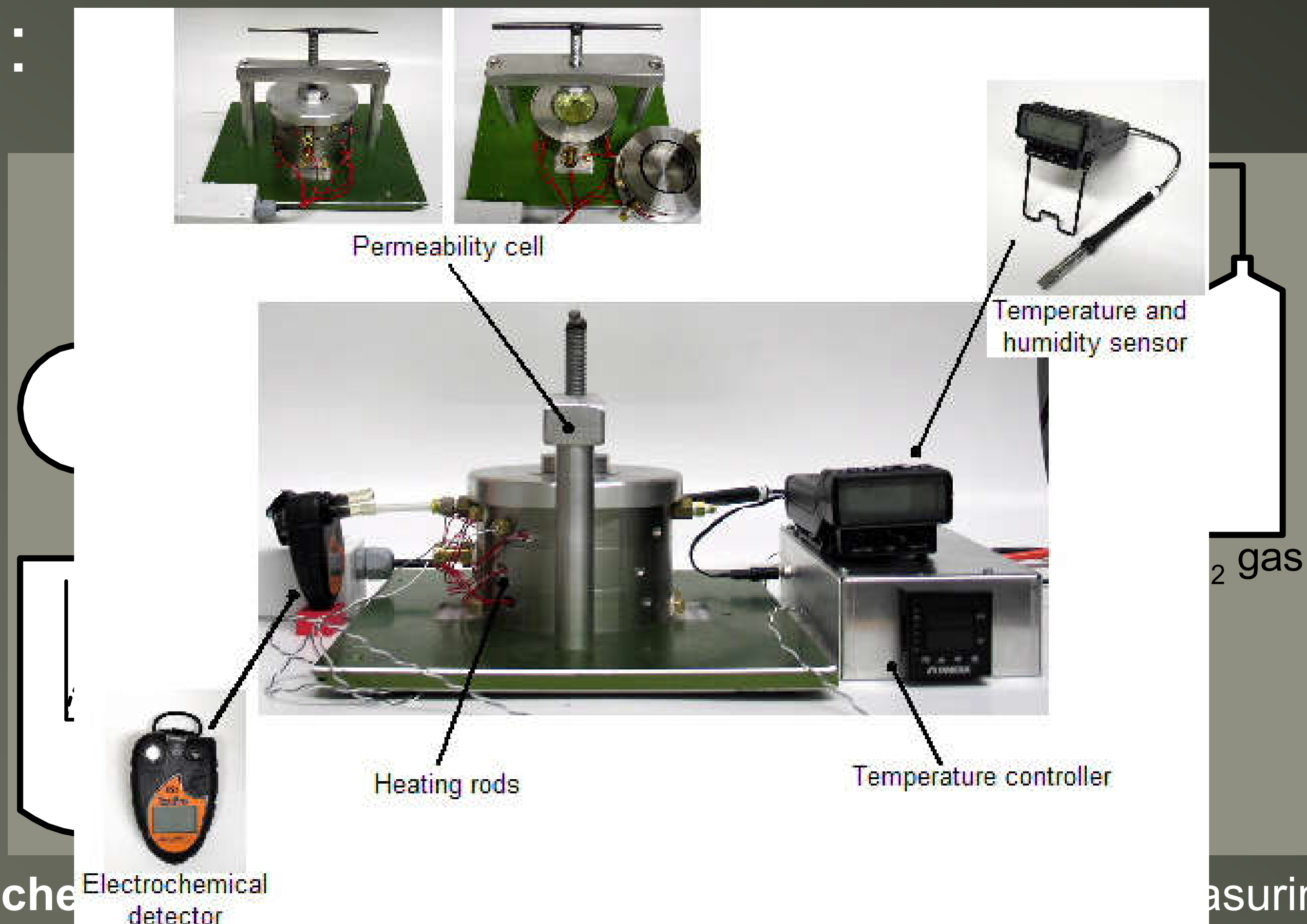
- To develop a continuous detection method for mass transfer measurement of ClO_2
- To assess the mass transfer profile of ClO_2 through different polymeric packaging materials

Objectives (cont.)

- To determine the impact of ClO_2 gas on the chemical, physical, mechanical, and barrier properties of selected polymeric packaging materials

Materials & Methods

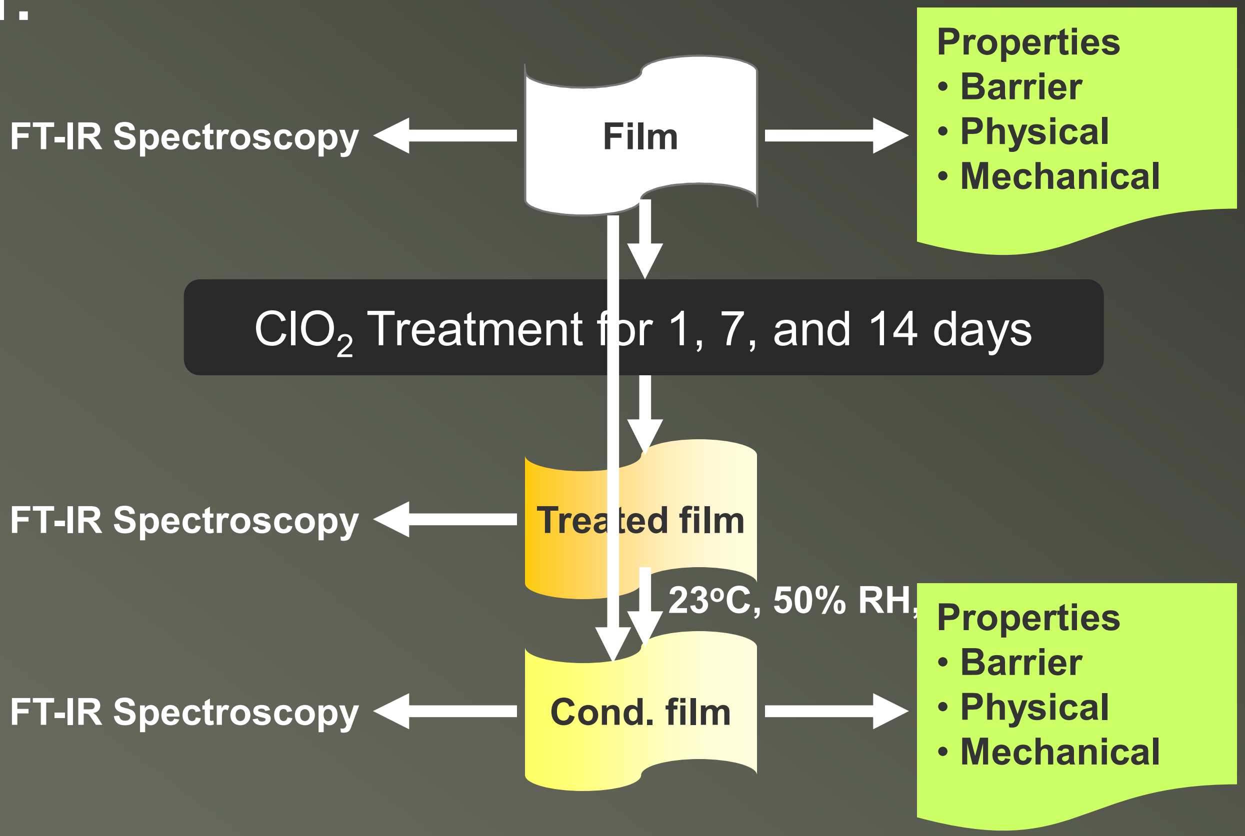
Part I:



Sche asuring
ClO_2 mass transfer

Materials & Methods (cont.)

Part II:



Scheme 2. Flow Diagram of Chlorine Dioxide Treatment of Packaging Materials

Materials & Methods (cont.)

- Polymeric packaging materials
  - Normally used in packaging systems for perishable and non-perishable food products
    - LDPE, LLDPE, HDPE, PP, PS, PET, PVC, nylon, PLA, and multilayer structure of EVA/EVOH/EVA

Materials & Methods (cont.)

- ClO_2 solution
  - Prepared from precursors (z-series, ICA TriNova, Newnan, GA)
  - Final solution provide 10 mg ClO_2/L of gas (approximately, 3600 ppmV) in the headspace

Results & Discussions

Part I: Mass Transfer Study

Results & Discussions (cont.)

Part I:

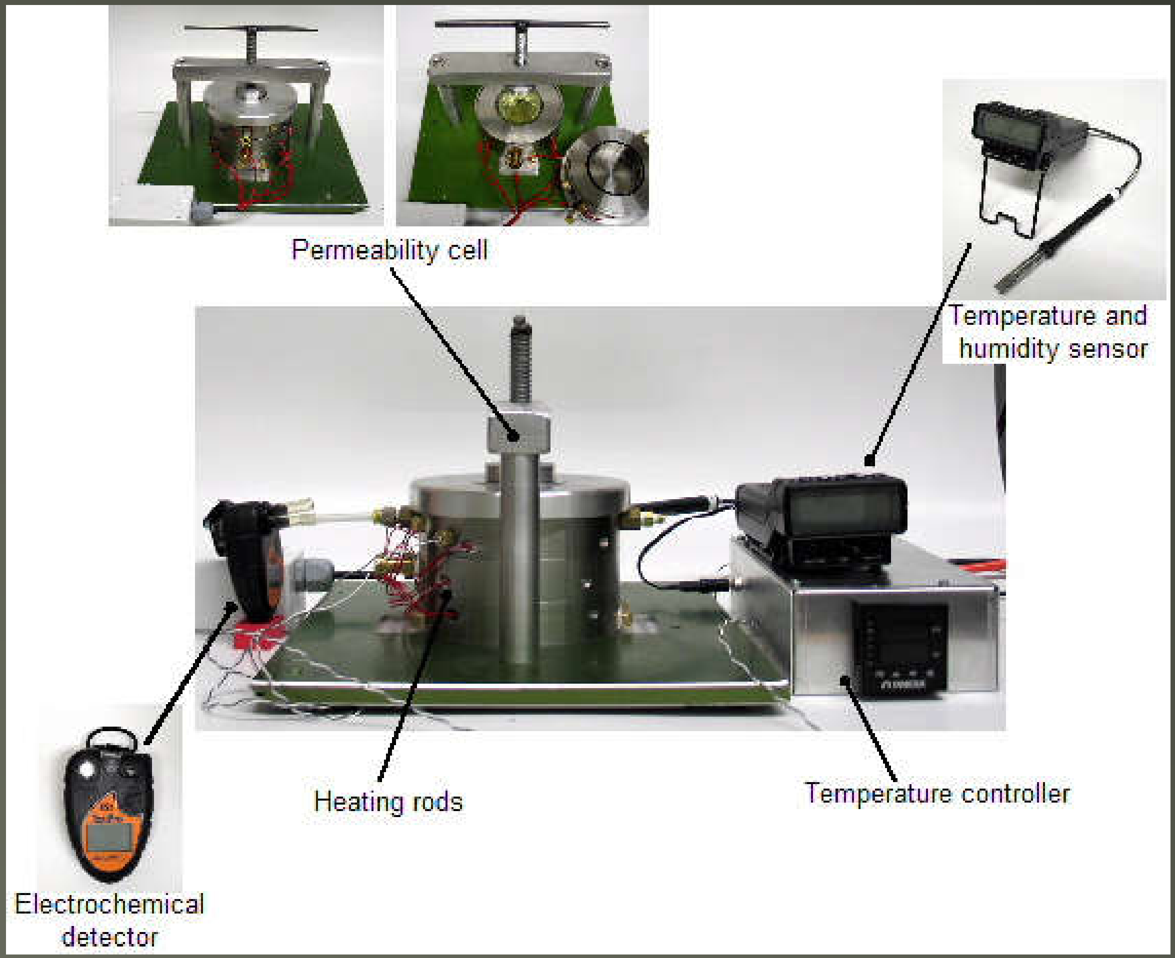


Figure 1. Setup of Continuous System for Measuring ClO_2 mass transfer

Results & Discussions (cont.)

Part I:

- Determined permeability, solubility and diffusion coefficients (P, D, and S, respectively) of ClO_2 on different materials
- Isostatic method
- electrochemical sensor

Results & Discussions (cont.)

Part I:

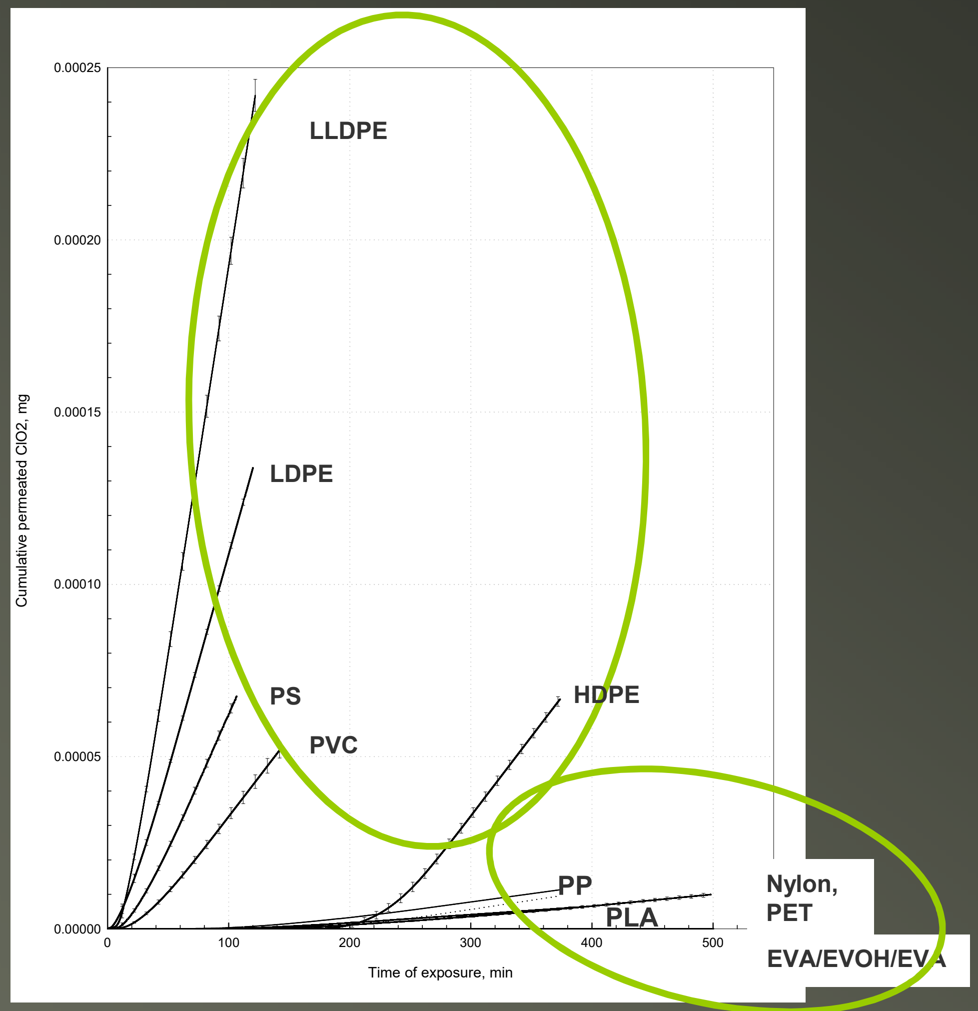


Figure 2. Mass transfer of 10 mg ClO_2/L ClO_2 gas through polymeric packaging material

Results & Discussions (cont.)

Part I:

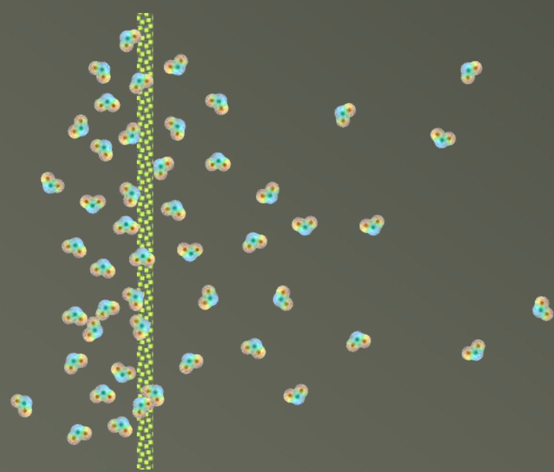
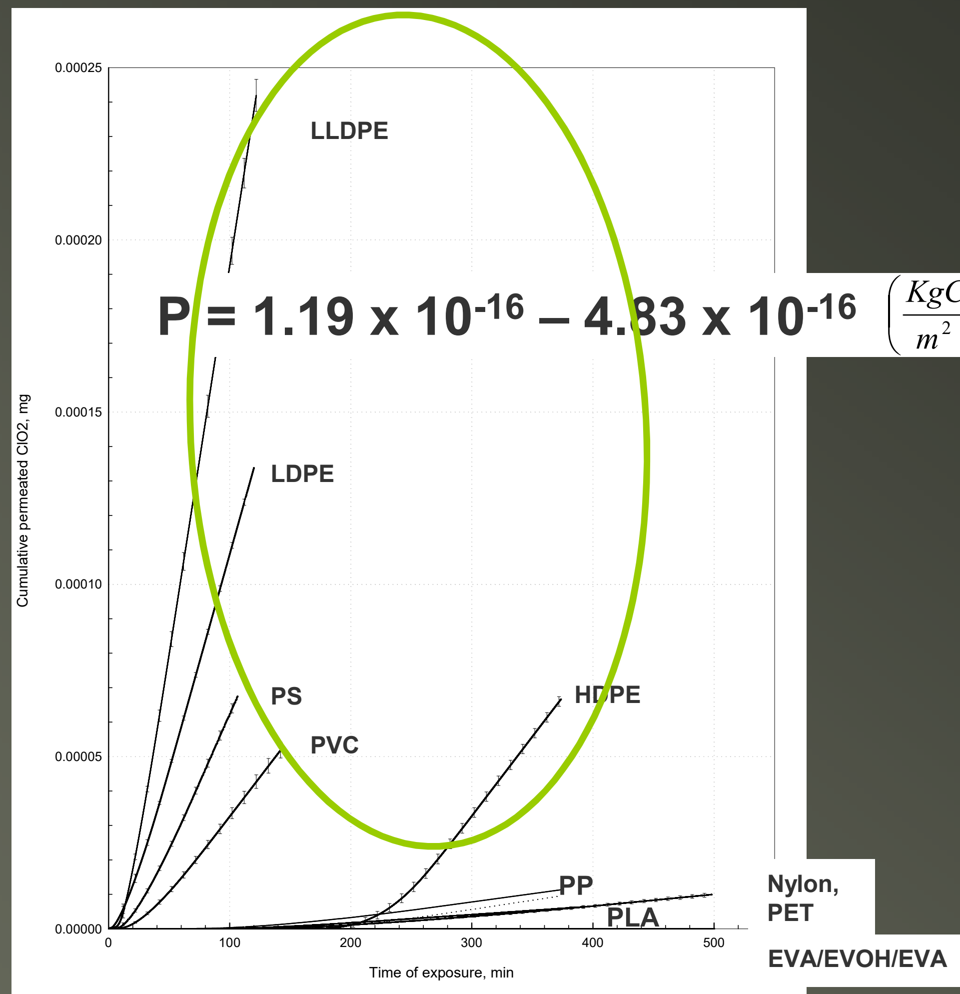


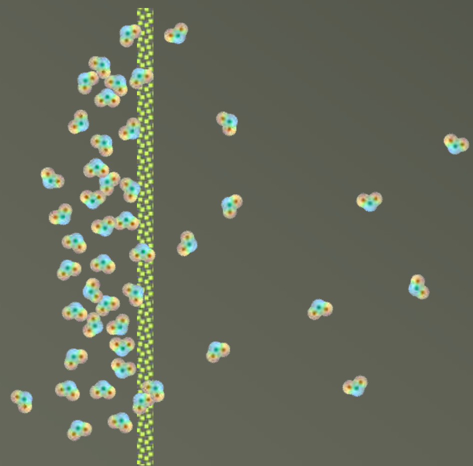
Figure 2. Mass transfer of 10 mg ClO_2/L ClO_2 gas through polymeric packaging material

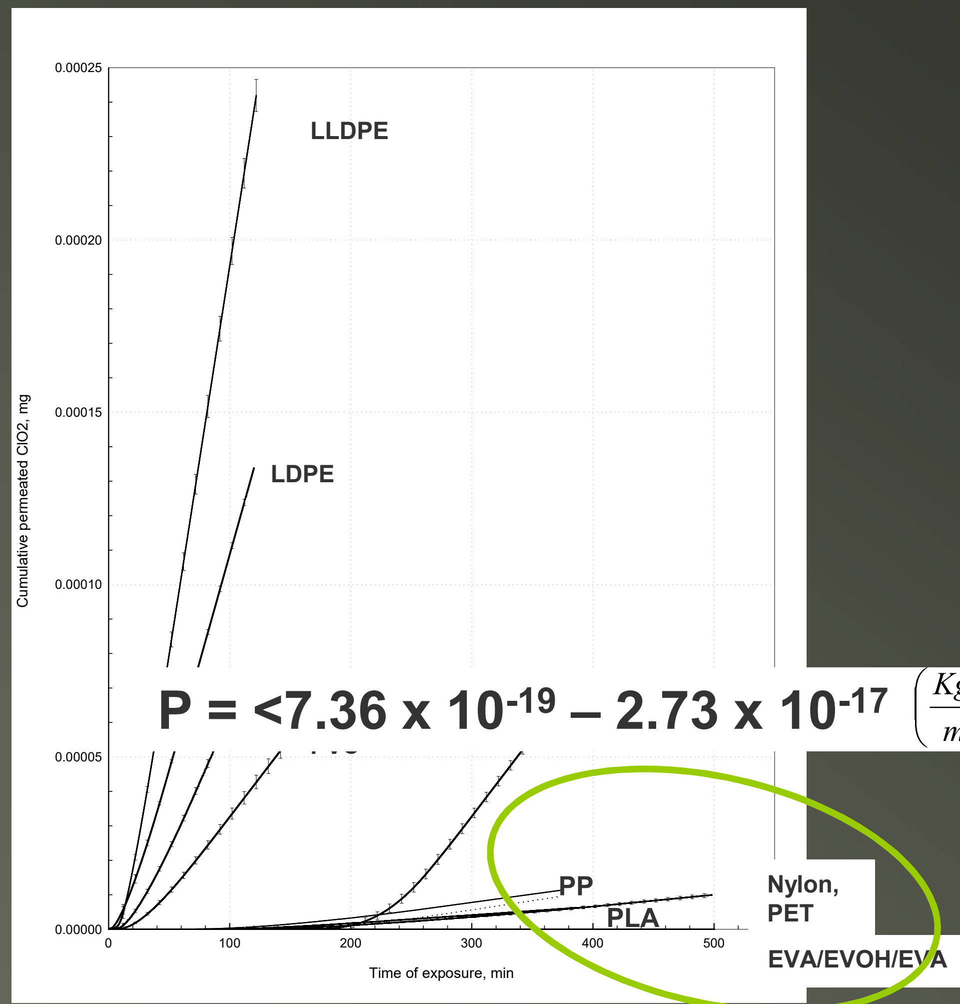


$$P = 1.19 \times 10^{-16} - 4.83 \times 10^{-16} \left(\frac{KgClO_2 \cdot m}{m^2 \cdot s \cdot Pa}\right)$$

Results & Discussions (cont.)

Part I:





$$P = <7.36 \times 10^{-19} - 2.73 \times 10^{-17} \left(\frac{KgClO_2 \cdot m}{m^2 \cdot s \cdot Pa} \right)$$

Figure 2. Mass transfer of 10 mg ClO_2/L ClO_2 gas through polymeric packaging material

Results & Discussions (cont.)

Part I:

Table 1. Physical properties of Nylon exposed to gaseous ClO_2

Polymer	P, $\left(\frac{KgClO_2 \cdot m}{m^2 \cdot s \cdot Pa}\right)$	D, $\left(\frac{m^2}{s}\right)$	S, $\left(\frac{Kg}{m^3 \cdot Pa}\right)$
HDPE	$1.20 \times 10^{-16} \pm 0.02 \times 10^{-16,\ a}$	$3.79 \times 10^{-14} \pm 0.06 \times 10^{-14,\ a}$	$3.17 \times 10^{-3} \pm 0.10 \times 10^{-3,\ a}$
LDPE	$3.27 \times 10^{-16} \pm 0.03 \times 10^{-16,\ b}$	$1.64 \times 10^{-13} \pm 0.03 \times 10^{-13,\ b}$	$1.99 \times 10^{-3} \pm 0.02 \times 10^{-3,\ b}$
LLDPE	$4.83 \times 10^{-16} \pm 0.08 \times 10^{-16,\ c}$	$4.27 \times 10^{-13} \pm 0.11 \times 10^{-13,\ c}$	$1.13 \times 10^{-3} \pm 0.05 \times 10^{-3,\ c}$
PP	$1.44 \times 10^{-17} \pm 0.07 \times 10^{-17,\ c}$	$3.76 \times 10^{-15} \pm 0.30 \times 10^{-15,\ d}$	$3.84 \times 10^{-3} \pm 0.10 \times 10^{-3,\ d}$
PS	$2.08 \times 10^{-16} \pm 0.04 \times 10^{-16,\ e}$	$8.12 \times 10^{-14} \pm 0.09 \times 10^{-14,\ d}$	$2.56 \times 10^{-3} \pm 0.06 \times 10^{-3,\ f}$
PVC	$1.19 \times 10^{-16} \pm 0.05 \times 10^{-16,\ a}$	$7.77 \times 10^{-14} \pm 0.33 \times 10^{-14,\ d}$	$1.53 \times 10^{-3} \pm 0.11 \times 10^{-3,\ d}$
PET	$6.25 \times 10^{-18} \pm 0.07 \times 10^{-18,\ d}$	$3.55 \times 10^{-15} \pm 0.04 \times 10^{-15,\ e}$	$1.76 \times 10^{-3} \pm 0.03 \times 10^{-3,\ e}$
PLA	$2.73 \times 10^{-17} \pm 0.00 \times 10^{-17,\ d}$	$2.96 \times 10^{-14} \pm 0.48 \times 10^{-14,\ d}$	$9.37 \times 10^{-4} \pm 1.40 \times 10^{-4,\ d}$
Nylon	$8.95 \times 10^{-18} \pm 0.42 \times 10^{-18,\ d}$	$5.53 \times 10^{-15} \pm 0.05 \times 10^{-15,\ e}$	$1.62 \times 10^{-3} \pm 0.07 \times 10^{-3,\ d}$
EVA/EVOH/EVA	Permeability is less than 7.36 x 10-19 (24 hour of exposure)		

* Different superscript letters indicates statistically differences between means at α of 0.05

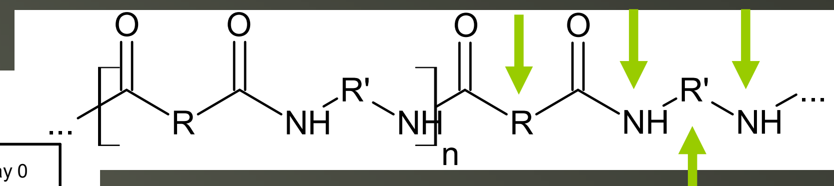
Results & Discussions (cont.)

Part II: Effects on Chemical, Barrier, Mechanical, & Physical Properties

Results & Discussions (cont.)

Part II:

- Chemical properties: IR Spectra
  - Nylon



N-H bond

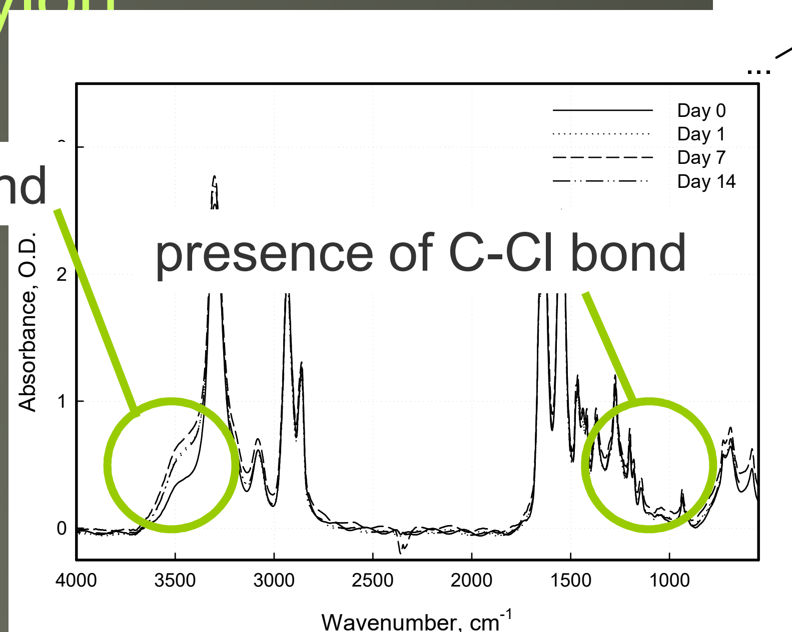


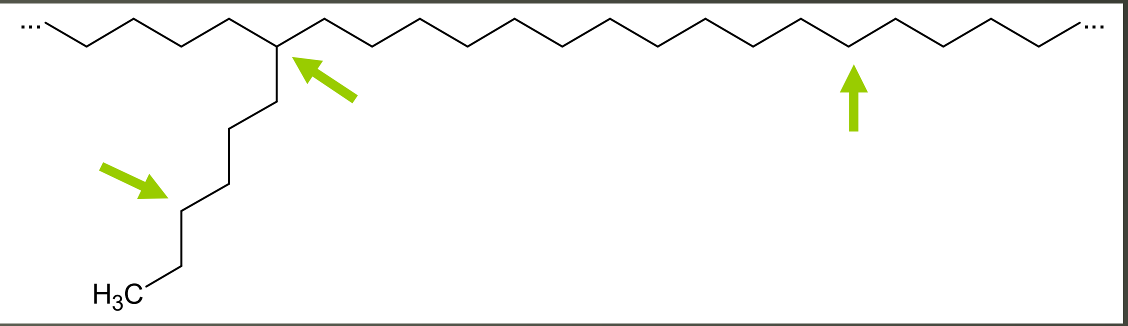
Figure 3. FT-IR spectra of nylon

(Ozen, 2000; Ozen 2002; Walzak *et al*, 1995)

Results & Discussions (cont.)

Part II:

- Chemical properties: IR Spectra
  - PEs

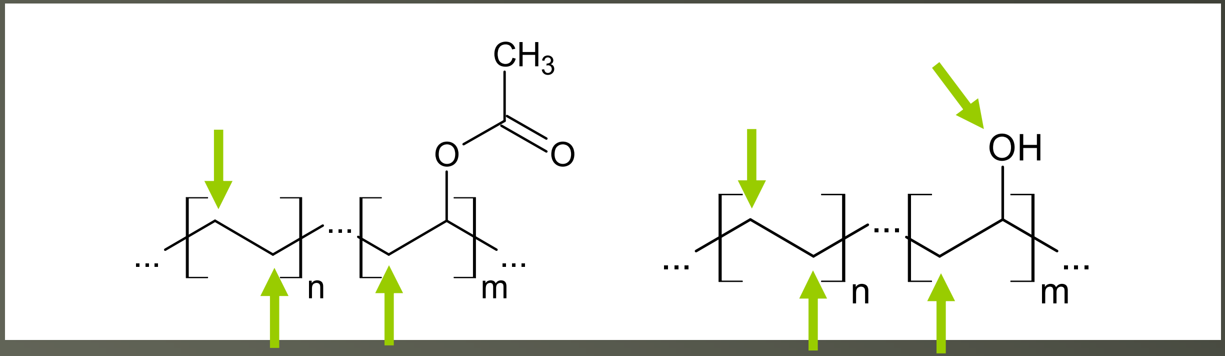


- Main-chain scission
- Possible presence of the C-Cl bond
  - Partial chlorination
  - ~ PS

Results & Discussions (cont.)

Part II:

- Chemical properties: IR Spectra
  - EVA/EVOH/EVA



- Change in hydroxyl gr. (EVOH layer)
- Formation of carbonyl gr.

Results & Discussions (cont.)

Part II:

- Barrier to moisture: WVTR

Table 2. WVTR of polymeric materials exposed to gaseous ClO2

Material	WVTR* (cc•m-2•day-1)*		% Change
	Day 0	Day 14	
PET	[illegible]	[illegible]	⬆ 23.18%
PP	4.11 ± 0.02[a]	4.57 ± 0.03[b]	⬆ 11.25%
PE (HDPE)	2.82 ± 0.05[a]	2.78 ± 0.12[a]	-
PS	135.04 ± 9.58[a]	126.71 ± 13.62[a]	-
PVC	84.42 ± 3.07[a]	87.07 ± 0.09[b]	⬆ 3.14%
PLA	241.88 ± 10.15[a]	230.81 ± 13.36[a]	-
Nylon	n/a		
EVA/EVOH/EVA	7.43 ± 0.37[a]	7.55 ± 0.95[a]	-

* Different superscript letters indicates statistically differences between means at α of 0.05

Results & Discussions (cont.)

Part II:

- Mechanical properties

Table 3. Tensile properties of PEs film exposed to gaseous ClO2

Sample	Time of Exposure (day)	Tensile strength (ksi)		Modulus (secant) (ksi)	
		MD	TD	MD	TD
Nylon	0	9.95 ± 0.55a	9.86 ± 0.77a	140.48 ± 6.14a	146.77 ± 8.00a
	14	9.32 ±0.76a	8.46 ± 1.54a	137.82 ± 3.06a	141.84 ± 6.34a
EVA/EVOH/EVA	0	16.24 ± 0.5a	13.82 ± 0.56a	79.92 ± 2.13a	71.36 ± 10.83a
	14	14.56 ± 3.35a	12.46 ± 1.00a	89.01 ± 13.44a	86.51 ± 9.11a
PE (HDPE)	0	**6.02 ± 0.18[a]**	[illegible]	**88.32 ± 1.96[a]**	[illegible]
	14	**5.00 ± 0.55[b]**	[illegible]	**76.65 ± 3.05[b]**	[illegible]

↓ 16.94%

↓ 13.21%

* Different superscript letters indicates statistically differences between means at α of 0.05

Results & Discussions (cont.)

Part II:

- Physical properties
  - Minor ⬇ in Tg and Tm
  - Nylon

Table 4. Physical properties of Nylon exposed to gaseous ClO2

Sample	Tg (°C)		Tm (°C)		Heat of Fusion (J/g)	
	Day 0	Day 14	Day 0	Day 14	Day 0	Day 14
PE (HDPE)	n/a	n/a	133.55 ± 0.26[a]	133.86 ± 0.82[a]	111.27 ± 8.96[a]	111.10 ± 10.41[a]
PET	**81.66 ± 0.50[a]**	**80.37 ± 0.22[b]**	248.93 ± 0.67[a]	248.38 ± 0.18[a]	31.33 ± 1.91[a]	33.99 ± 3.23[a]
Nylon	n/a	n/a	**261.35** ⬇ 1.54°C	**± 0.30[b]**	**56.01** ⬆ 12.92%	**1.81[b]**

* Different superscript letters indicates statistically differences between means at α of 0.05

Conclusions

Part I: Mass transfer study

- Developed the continuous system for measuring permeation of ClO_2, utilizing permeability cell & electrochemical sensor through Isostatic approach

Conclusions (cont.)

Part I: Mass transfer study

- P, D, and S of ClO_2
- High barrier
  - PET, PLA, PP, nylon, and multilayer EVA/EVOH/EVA
- Low barrier
  - PS LLDPE, LDPE, HDPE, and PVC

Conclusions (cont.)

Part II: Effects on important properties

- Possible changes from ClO_2 exposure
  - At 10 mg ClO_2/L of gas (~ 3600 ppmV)
  - Main-chain scission
    - PEs
  - Partial C-Cl bonding
    - PEs, PS, and nylon
  - Change or Formation of oxygen-containing, or other functional groups
    - Nylon, PLA, and EVA/EVOH/EVA

Conclusions (cont.)

Part II: Effects on important properties

- Barrier to moisture: WVTR
  - ⬇ in barrier characteristic in general
    - PET
      - ⬆ WVTR ~ 23.18%, after 2 weeks
    - ~ PP and PVC

Conclusions (cont.)

Part II: Effects on important properties

- Mechanical properties
  - ⬇ TS and MoE in PEs
- Physical properties
  - Minor ⬇ in Tg and Tm
  - ⬆ ~13% crystallinity in exposed Nylon

Acknowledgement

- ICA TriNova LLC (Newnan, GA) for the supply of ClO_2 precursors

- Families, Committee members, & Friends @ School of Packaging

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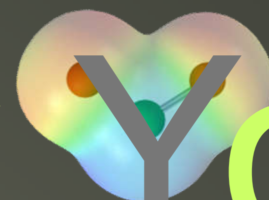
Thank You



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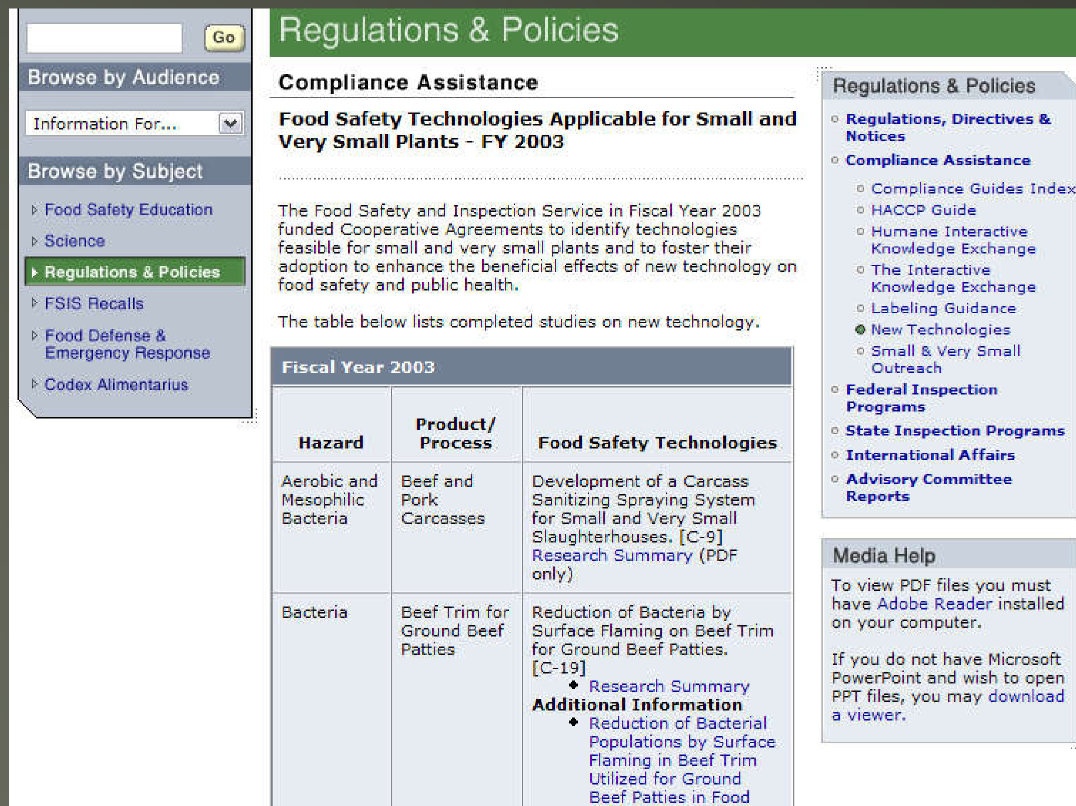
Food Safety

- Several foodborne outbreaks have been reported to be linked to food products, especially, fresh produce

Foodborne outbreak

Technology for Food Safety



Oxidative degradation

- Typical changes:
  - Main-chain scission
  - Depolymerization
  - Cross-linking
  - Changes in functional groups

⬇

May impact the polymer characteristic, properties, and performances

(Ozen, 2000; Ozen, 2002; Walzak *et al*, 1995)

Oxidative degradation (cont.)

- EVA/EVOH/EVA
  - + Carbonyl group
    - Two-fold effect
    - ⬆ susceptibility to photodegradation
      - good UV absorbers

(Ozen 2002)

Oxidative degradation (cont.)

- PET
  - Its surface oxidations are reported to be complex
    - Formation of many functional groups, e.g. carboxylic acid, terminal vinyl groups, and phenols

(Walzak, *et al*, 1995)

Oxidative degradation (cont.)

- PEs / Polyolefin
  - Formation of polar gr.
    - ⬆ hydroplilicity and intermolecular forces
  - Main-chain scission
  - ⬇ Tm
  - If exposed longer…
    - ⬆ molecular ordering
    - ⬆ crystallinity and MoE
  - Simultaneous degradation & rebuilding of macromolecules

Ozen 2002)

Oxidative degradation (cont.)

- Nylon
  - Molecular-reordering
    - ⇧ TS
    - ⇧ barrier properties

(Ozen 2002; Walzak, *et al*, 1995)

Chlorine Dioxide

- Stability
  - Decompose in sunlight
  - Exists in two isomeric forms:
    - Symmetric OClO
    - Asymmetric ClOO
      - Thermodynamically more stable
      - Very reactive in the gas phase
  - Remains in solution as dissolved gas
    - OClO form is kinetically more stable
    - Reaction rate is 7-10 times slower than that of the hydrolysis of Cl2

Dunn, R. C. a. S., J. D., Excited-State Photoreactions of Chlorine Dioxide in Water. *Journal of the American Chemical Society* **1992,** 114, 4856 - 4860.
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Chlorine Dioxide (cont.)

- > or = disinfecting capacity as compared to Cl_2
- pH has less effect on biocidal prop.
- Does not produce carcinogenic by-products
- Less organoleptic problem

- ⬇ efficiency as temp. ⬇
  - = Cl_2

(USEPA, 1999)

Chlorine Dioxide (cont.)

- Costs associated with training, sampling & lab. Testing are high
- Explosive at conc. > 10% vol. in air
  - Has to be made on-site

(USEPA, 1999)

Chlorine Dioxide (cont.)

- Oxidation reduction potential (ORP) of atm. medium affects metabolism of MO
  - Disinfect by oxidation
  - Mechanism is not well understood, but appear to vary by MO type
    - Disrupt protein synthesis
    - Disrupt permeability of outer membrane

(USEPA, 1999)

Chlorine Dioxide (cont.)

- MO:
  - *Listeria monocytogenes*
  - *Bacillus anthracoides, Bacillus subtilis*
  - *Shigella dysenteriae*
  - *Staphylococcus aureus*
  - *Pseudomonas aeruginosa*
  - *Salmonella paratyphi*
  - etc.

(Sy *et al*, 2005a and 2005b; USEPA, 1999)

Chlorine Dioxide (cont.)

- Food products:
  - Raw chicken
  - Seafood
  - Fresh & fresh-cut fruits
  - Blueberries, strawberries & raspberries
  - etc.

(Sy *et al*, 2005a and 2005b; USEPA, 1999)

Materials & Methods

- Precursor
  - Sulfuric acid (H_2SO_4)
  - Sodium chlorite ($NaClO_2$)
- Henry's Law
- [ClO_2]
  - High dose range for food application

Chlorine Oxygen Acids and Salts, Chlorous Acid, Chlorites, and Chlorine Dioxide. John Wiley & Sons, Inc.: 2001; Vol. 4.
Ishi, G., Solubility of chlorine dioxide. *Chemical engineering (Japan)* **1958,** 22, 153 - 154.

Materials & Methods (cont.)

- Isostatic approach
  - Concentration increase method
  - A partial pressure difference is maintained by sweeping continuously with an inert gas
  - Method of measuring [gas] can be specific to that gas
    - O_2 (Ox-tran) = Coulometric detector
    - CO_2 (Permatran-C) = IR detector

Materials & Methods (cont.)

- Isostatic approach (cont.)
  - Calculating P, at a steady-state
    - Concentration gradient of the permeant, across the film, remain constant
  - D is calculated from the mass transfer profile in the transient region
  - S, calculated using the ‘solution-diffusion’ model

$$P = D \cdot S$$

Materials & Methods (cont.)

- Isostatic approach (cont.)
  - Diffusion process is assumed to follow Fickian diffusion
    - i.e. independent of [permeant], and polymer relaxation
    - Non-organic gases, and for particular organic vapors at low concentration

Materials & Methods (cont.)

- Quasi-isostatic approach
  - Concentration increase method
  - Aliquot of the permeant gas are removed at predetermined time intervals for analysis

Materials & Methods (cont.)

- Permeated ClO2 at time t (mg/min)

$$= \frac{\text{Permeated } ClO_2\ (\mu L/L) \bullet 67.5\ g/mol \bullet 1000\ mg/g \bullet N_2 \text{ gas flow rate } (mL/min)}{1000000\ \mu L/L \bullet \text{one mol of ideal gas at particular temperature } (L/mol) \bullet 1000\ mL}$$

- P = $F_{ss} \cdot \frac{\ell}{A \cdot \Delta p}$

- D = $\frac{\ell^2}{7.2 t_{1/2}}$

Materials & Methods (cont.)

- Electrochemical sensor
  - For toxic and combustible gases in confined space
  - Operating condition for ToxiPro® detectors
    - -20oC to +50oC
    - < 95%RH with no condensation

Materials & Methods (cont.)

- Electrochemical sensor (cont.)
  - Quantitatively determine gas by generating an electrical signal through the reactions with the gas
    - $ClO_2 + 4H^+ + 5e^- \rightarrow Cl^- + 2H_2O$
    - Produces the electric current, proportional to the gas concentration
      - Sensing (or working) electrode = react diffused gas
      - Counter electrode = supply/receive the electrons
      - Reference electrode = maintain the stable constant potential

Materials & Methods (cont.)

- Electrochemical sensor (cont.)
  - The EC detector, ToxiPro®
    - Calibrated every two weeks
      - Zero calibration, 0.00 ppm of ClO2
      - 1.00 ppm of ClO2 (EC gas generator, Cal 2000, ACD, Tucson, AZ)
      - Bump test
        - » Exposing the detector to known concentration of ClO2
        - » 1.00, 2.50, 3.00, 4.00, 4.50 ppm

Materials & Methods (cont.)

- FT-IR Spectroscopy
  - Shimadzu IR Prestige-21 (Shimadzu Scientific Instruments, Columbia, MD)
  - ‘Day 0’, ‘Day 1’, ‘Day 7’, ‘Day 14’, and ‘after treatment and conditioning’

Materials & Method (cont.)

- Physical properties
  - Tg, Tm, and △Hm
  - DSC Q-100 (TA Instruments, New Castle, DE)
  - ASTM D3418-03
  - Universal Analysis Software (UAS, Version 3.9A)

Materials & Method (cont.)

- Barrier properties
  - WVTR
    - Water Permeability
    - Analyzer 100, (VTI, Florida, USA)
    - ASTM D1434-82 (2003)

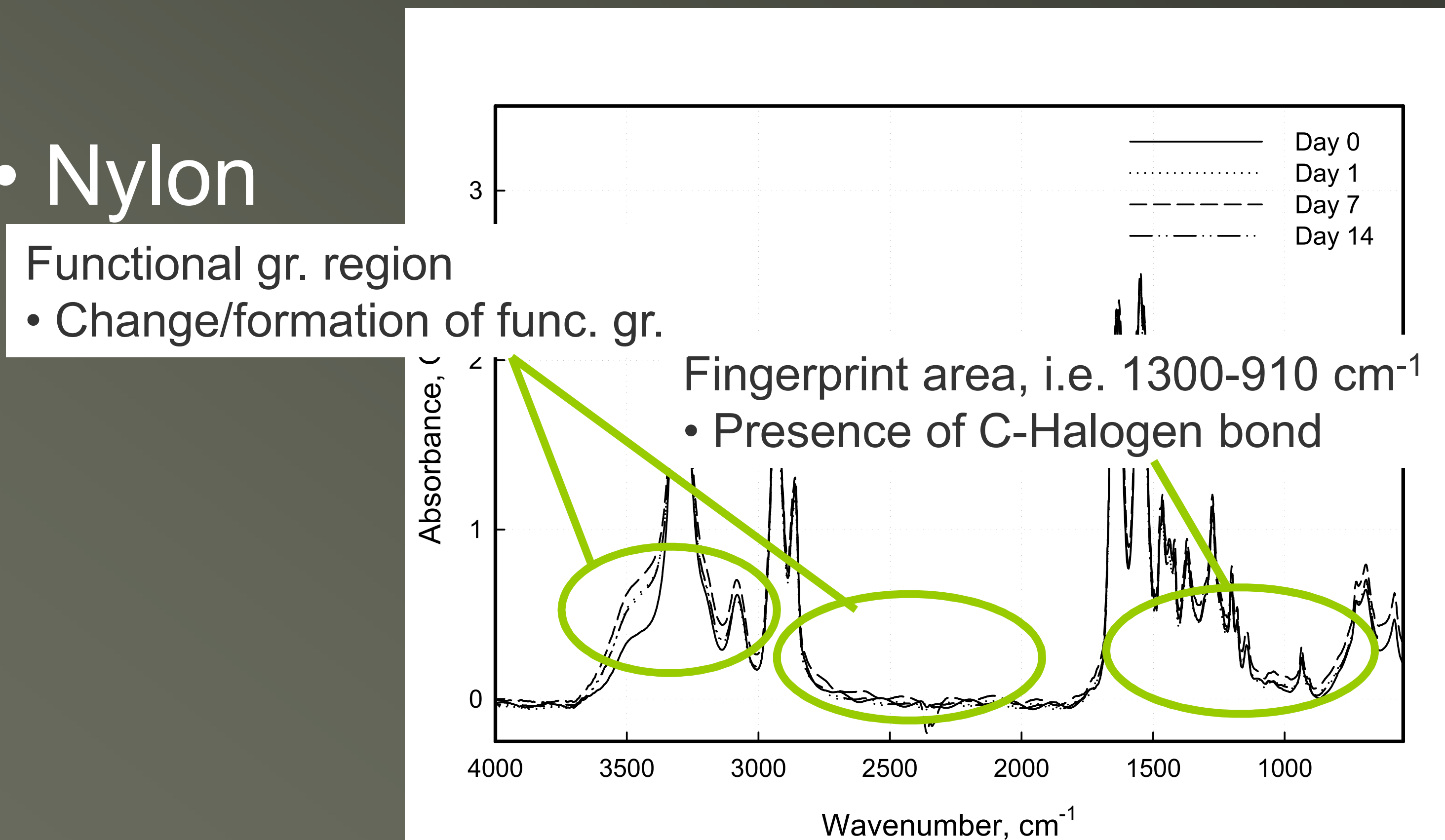
Materials & Method (cont.)

- Mechanical properties
  - Tensile strength and elongation at break
  - Instron Tensile Tester 5565 (Instron, Canton, MA)
  - ASTM D882-97

Results & Discussions (cont.)

Part II:

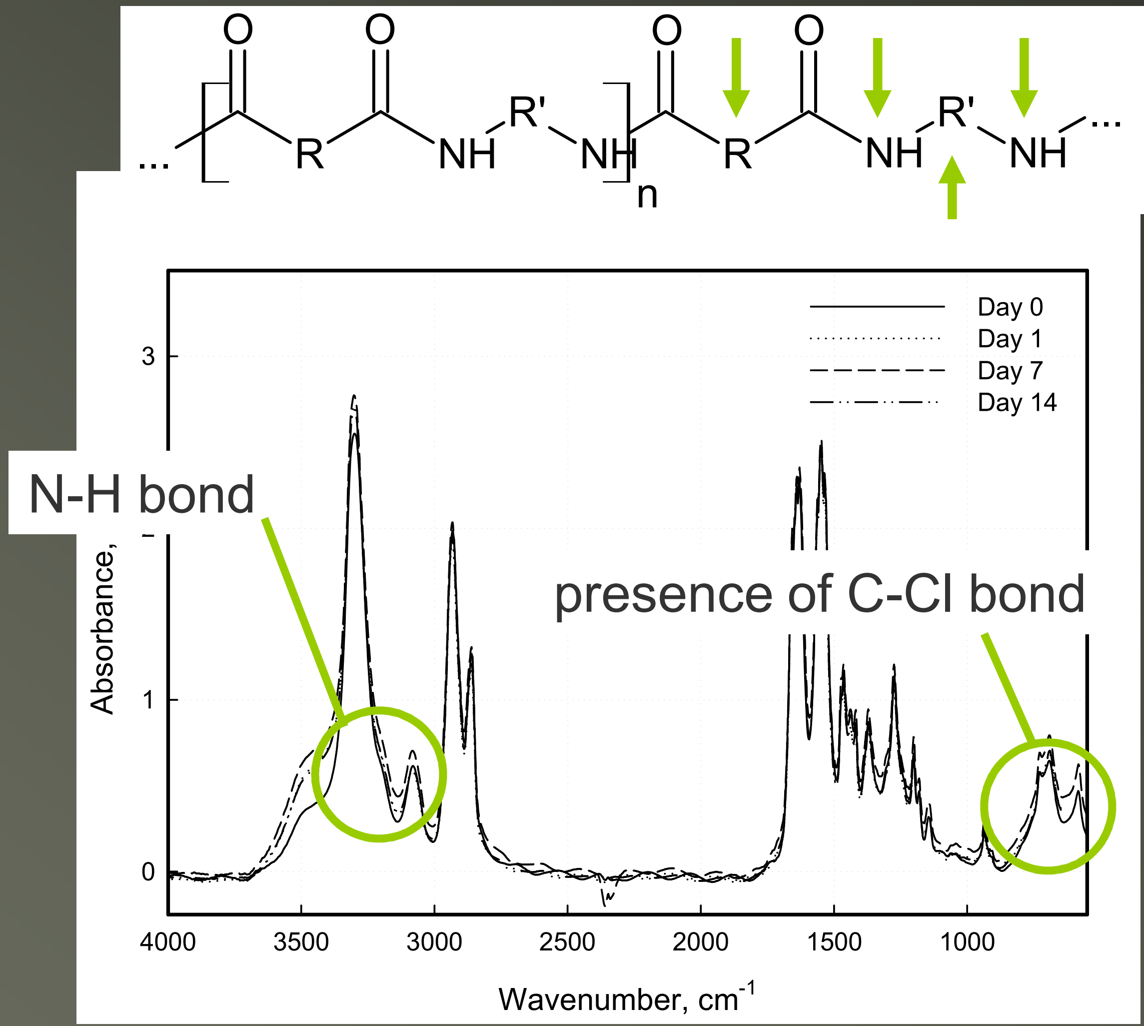
- Nylon



Results & Discussions (cont.)

Part II:

- Nylon

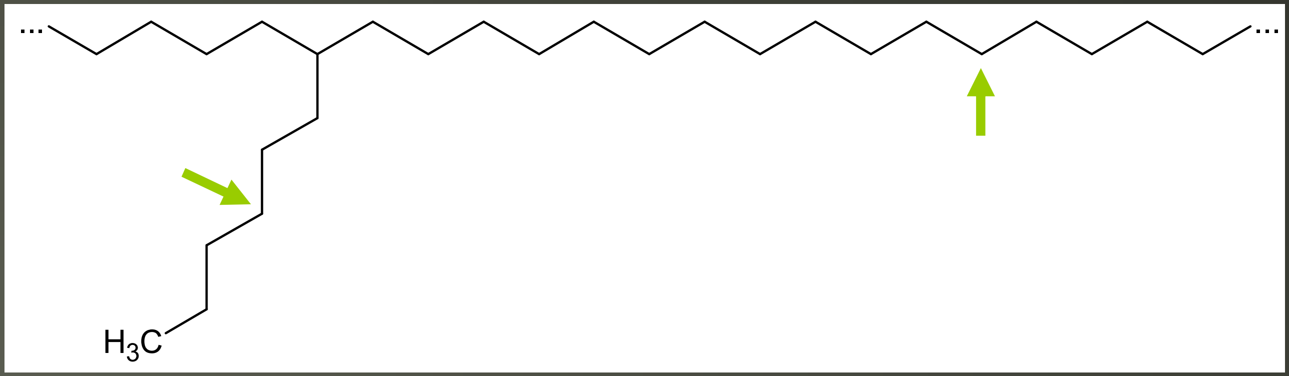


(Ozen, 2000; Ozen 2002; Walzak *et al*, 1995)

Results & Discussions (cont.)

Part II:

- PEs



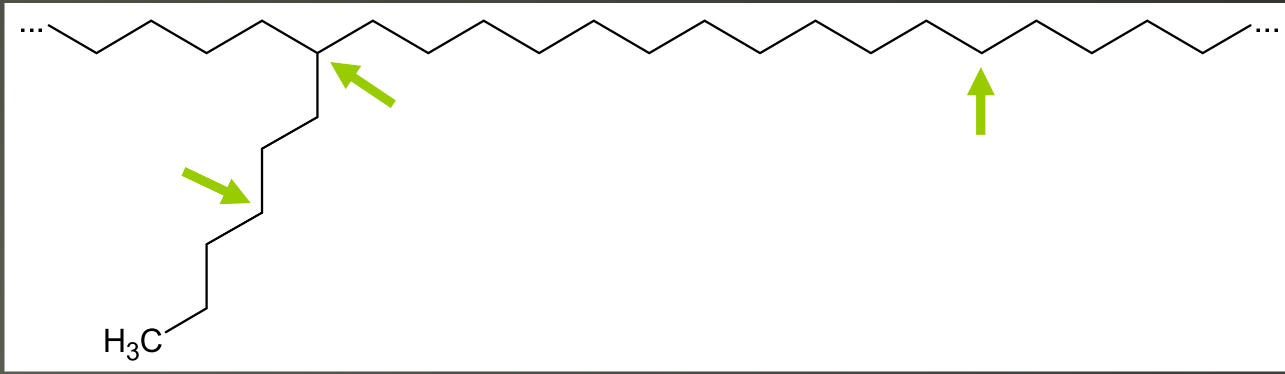
  - ⬆ Absorbance intensities in the 3000- 2700 cm-1 region
    - Change in C-H bond in methyl or methylene gr.
    - Main-chain scission

(Ozen, 2000; Ozen 2002; Walzak *et al*, 1995)

Results & Discussions (cont.)

Part II:

- PEs



  - Shift to higher wavenumbers in fingerprint area (1300-910 cm-1 region)
    - ~ PS
    - Possible presence of the C-Cl bond
    - Partial chlorination

(Ozen, 2000; Ozen 2002; Walzak *et al*, 1995)

Results & Discussions (cont.)

Part II:

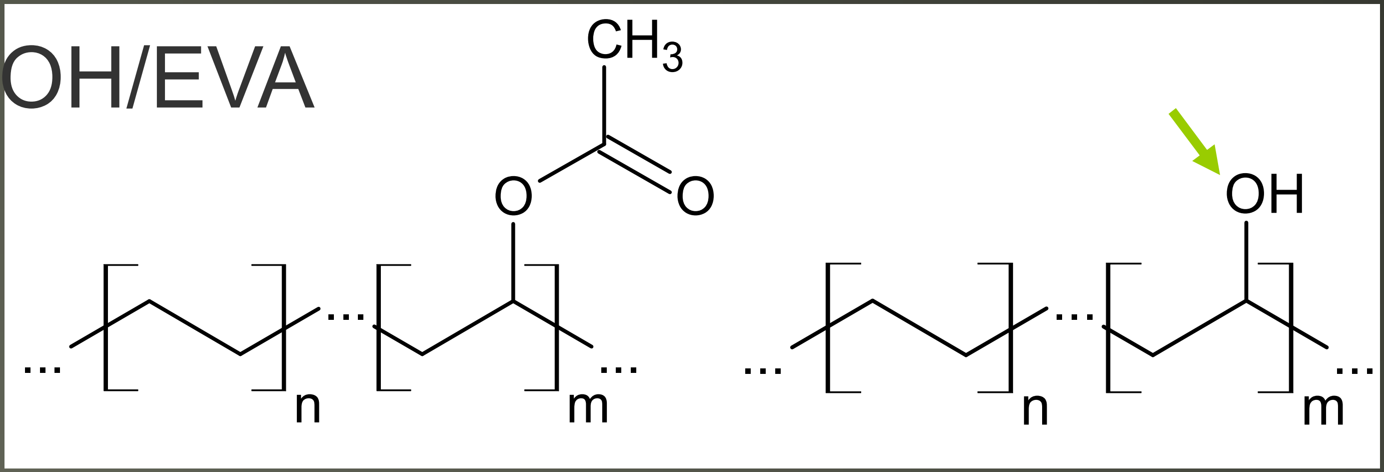
- PLA
  - ⬆ Absorbance intensities in the 3700-3300 cm-1 region
    - Change in hydroxyl gr.

(Ozen, 2000; Ozen 2002; Walzak *et al*, 1995)

Results & Discussions (cont.)

Part II:

- EVA/EVOH/EVA



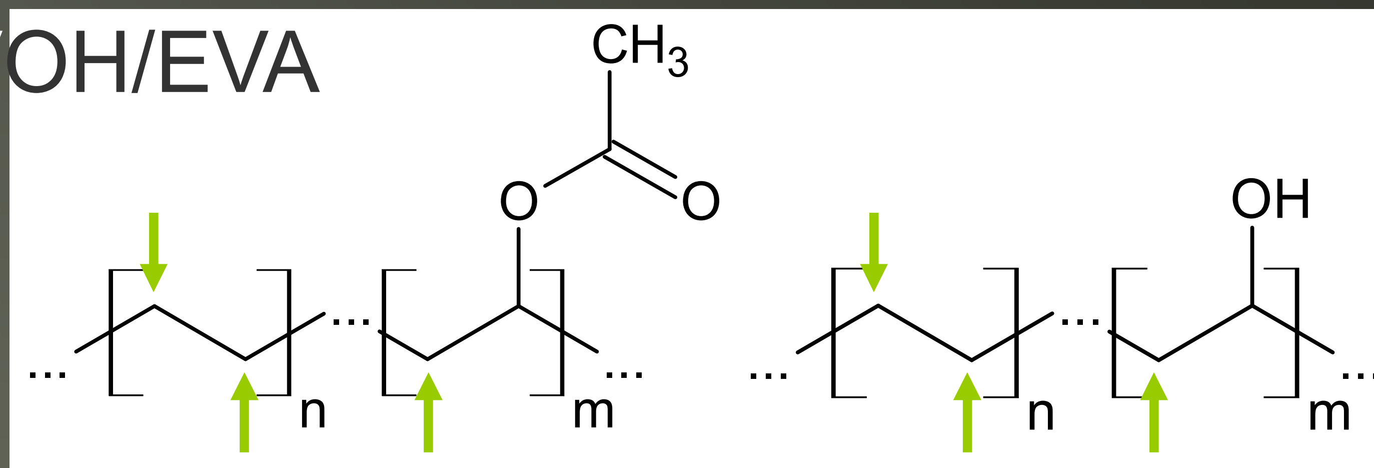
  - Absorbance intensities in 3700-3000 cm-1 region
    - Change of hydroxyl gr. (EVOH layer)

(Ozen 2002)

Results & Discussions (cont.)

Part II:

- EVA/EVOH/EVA



  - Minor ⬆ in absorbance intensities in 1700-1600 cm-1 region
    - Formation of carbonyl gr.

(Ozen 2002)

Conclusions

Part II: Effects on important properties

- Overall performances depend on the dominant reaction, e.g.
  - PEs: ⬇ tensile properties
    - Main-chain degradation

Future Study

- Additional tests, e.g.
  - O_2TR, CO_2TR
    - ⬆ crystallinity, ⬆ barrier properties
    - etc.