The effect of barrier materials on salmon quality and retort pouch properties stored under elevated conditions

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ABSTRACT

The effects of retort pouch barrier material on salmon quality and pouch properties were investigated. Four different retort pouch structures were used; AlO_x-coated PET/Nylon/CPP (ALOX), PET/ SiO_x-coated Nylon/CPP (SIOX), PET/Al-foil/CPP (FOIL), cast polypropylene (CPP). Oxygen permeability of SIOX increased significantly after retorting. Conversely, oxygen permeability of the FOIL pouches did not change significantly and oxygen permeability of ALOX pouch increased slightly after retorting. Salmon in the SIOX pouches had higher thiobarbituric acid reactive substances (TBARS) values when compared to salmon in the FOIL pouches after a storage time of 7 weeks. An untrained sensory panel determined that salmon packaged in SIOX pouches had less acceptability than salmon in FOIL pouches after 8 weeks storage time. Salmon packaged in ALOX pouches had similar sensory and TBARS values when compared to salmon packaged in FOIL pouches. ALOX provided adequate barrier for maximum shelf life compared to traditional foil-barrier pouches.

KEYWORDS: Retort pouch, Thin metal oxide coating, Accelerated storage condition, Sensory analysis, Oxygen permeability

INTRODUCTION

Historically, thermal processing has been a common food preservation technique. It typically involves the heating of foods to eliminate pathogenic microorganisms and enzymes that deteriorate the food during storage.

Aluminum foil has traditionally been the functional barrier material used in retort pouches. However, it is not suitable for microwave heating. Several non-foil barrier materials are available to food processors desiring a microwaveable retort pouch.

Currently, polymer films with thin metal oxide coatings, such as silicon oxide (SiO_x) and aluminum oxide (Al_xO_y), are used in retort pouch industry as non-foil barrier materials. SiOx or Al_xO_y coated films offer several advantages such as; high gas barrier, microwaveable, colorless, light weight, complex shape and design freedom, and transparency *(1).*

There has been little work done in comparing the effect of barrier materials, especially barrier materials with thin metal oxide coatings, on the shelf life of shelf stable food products.

Fresh, frozen salmon were used for as the food product for this project. Thermal sterilization of food always requires a compromise between the beneficial and destructive influences of heat on the food. Color and flavor are important factors used to determine fish quality *(2, 3).*

Depending on the food products nature, various properties or quality indices must be experimentally followed as a function of time in order to evaluate degradation of food product quality through the use of shelf life tests. However, real time shelf life tests for shelf stable food products can be very time-consuming. In an effort to speed up this process and to fully account for all the degradation criteria, accelerated shelf life testing methods have been adopted *(4).*

The objective of this study was to measure the effect of functional barrier materials on salmon quality and retort pouch properties stored under elevated conditions following thermal processing.

MATERIALS AND METHODS

Barrier materials

Four different retort pouches structures were used. The foil barrier pouch material consisted of 48 ga PET/60 ga Al-foil/ 3 mil CPP (FOIL). The non-foil barrier materials consisted of 48 ga AlO_x-coated PET/ 60 ga Nylon/70 µm CPP (ALOX) and 48 ga PET/ 60 ga SiO_x-coated Nylon/ 3 mil CPP (SIOX). A non-barrier material, 80 µm cast polypropylene (CPP), was used as a control.

Food simulant

Frozen, raw salmon was purchased as skinless and boneless fillets at a local a local Wal-Mart store in Anderson, S.C. The frozen salmon all originated from the Pacific Ocean. The salmon was stored in a freezer until thawing and thawed for 24 hrs at 4 °C. The thawed fillets were processed within 24 hrs. The thawed salmon fillets were cut into 60 g portions of similar size and thickness. Following the reference *(5),* portion of sample was used for different purpose.

Thermal factor analysis

Retort pouches (4’ x 5’) were filled with 60 g of salmon and vacuum sealed with a Koch vacuum sealer. Prior to sealing, Ecklund thermocouples were inserted into the pouches through a packing gland and the thermocouple tip was immobilized in the geometric center of a salmon portion. Filled pouches were processed in a Surdry Model APR-95 Pilot retort (Spain) operating in the still, water-spray mode. Heat penetration data was collected for 12 pouches and a thermal process was calculated from the data using modified Ball formula method in Cal Soft 32, version 2.0 software (Technical Inc., Kenner, Louisiana, USA).

Water Spray Retort

A pilot-scale rotary, single cage, water spray retort in static mode was employed in this research. Salmon was thermally processed for 23 min at 250 °F, 30 psi to reach F_0 values of 6 using Surdry Model APR-95 Rotary Pilot Retort (Stock America, Cary, North Carolina, USA)

Accelerated storage conditions

All retorted pouches were stored at 90 °F (± 2), 90% RH (± 2) in an environmental chamber throughout the test period.

Oxygen transmission rate

Oxygen transmission rate (OTR) of the films was measured using OX-Tran 2/60 transmission tester (Mocon Control Inc. Minneapolis, MN, USA). Samples were exposed to 0% relative humidity (RH) and tested at 23 ℃. The system was operated according to ASTM standard method D 3985.

Lipid oxidation (TBARS)

The extent of lipid oxidation in retort salmon was determined according to the thiobarbituric acid reactive substances (TBARS) method. Five grams of salmon was mixed with 10 mL trichloroacetic acid (TCA, 10% w/v) and 0.1 mL butylated hydroxyanisole (BHA, 1% w/v). The pre-mixture was homogenized at 3000 rpm for 90 second. The homogenate was centrifuged at 2000 rpm for 20 minute. The supernatant was filtered through Whatman No. 1

filter paper. Five milliliters of filtrate was transferred to test tube followed by 5 mL of 2-thiobarbituric acid (TBA). Test tube were subsequently incubated for 20 min in a water bath at 97 ^{o}C and cooled to room temperature. The absorbance was measured at 531 nm. TBARS were expressed as milli extinction unit per gram of salmon (mE/g).

Sensory analysis

A multiple comparisons test was used to evaluate the sensory characteristics of retorted salmon *(6)*. In multiple comparison tests, a known reference or standard sample is labeled R and presented to the panelist with several coded samples. The panelist is asked to compare each coded sample with the reference sample (R) on the basis of some specified characteristic. Sensory evaluation for color, aroma, and overall acceptance were carried out with 8-13 trained panelists. Panelists rated the sensory attributes from weaker than R (1) to stronger than R (9) for aroma, from less acceptable than R (1) to more acceptable than R (9) for acceptability. F values were used to determine if there was any significant difference between the samples using Tukey's Test.

Statistical analysis

Data was analyzed by ANOVA using SAS (version 9.1, SAS Institute Inc., Cary, NC, USA) and differences among mean values were processed by the Student-Newman-Keul multiple range test. Significance was defined at $P < 0.05$.

RESULTS AND DISCUSSION

Oxygen transmission rate

Gas transport through materials can take place by two mechanisms; Diffusive flow via solubility-diffusion or flow through defects in the material such as pinholes, porosities, microchannels, and microcracks. Oxygen permeation through high barrier coatings is dominated by flow through defects in the coating *(7)*.

The principal mechanism of oxygen transport through SiO_x coated-barrier occurs through nano-scale defects in the SiO_x coating *(8)*.

The oxygen transmission rate (OTR) of ALOX slightly increased during storage time, but the OTR of FOIL did not changed significantly during storage time except immediately after retorting and the 5 week interval. Even as the OTR of ALOX increased slightly during storage, it still had a good gas barrier property. CPP does not typically have good oxygen barrier properties so it exhibited a higher OTR value than the other films during the storage period. Finally, the OTR of SIOX increased considerably during the storage time. The largest increase in the OTR of SIOX, more than 10 times the pre-retort value, was measured right after retorting (Table 4).

This increase reflects a combination of physically constrained H_2O molecules and chemically interacting water molecules via hydrogen bonding to the SiO_x surface *(8)*.

Changes in the intrinsic stress in SiO_x films upon long-term exposure of to an ambient atmosphere leads to cracks. Moisture plays a key role in such phenomena, as it diffuses into the film and reacts with strained Si-O bonds and reconstructs them into a minimum energy configuration *(9)*.

During thermal processing and accelerated storage time, water diffused into the film and reacted with strained Si-O bonds and increasing cracks in the SiO_x-coated Nylon. This phenomenon affected the increase of oxygen transmission rate in SiO_x-coated Nylon.

Lipid oxidation (TBARS)

Lipid oxidation of salmon was measured using TBARS (Figure 2). TBARS numbers of salmon in CPP had the highest value during storage time. This dramatic increase in oxidation can be attributed to the high oxygen transmission rate of CPP. Until week 6, TBARS number of salmon in ALOX, SIOX, and FOIL were not significantly different from each other. However, the TBARS number of salmon in SIOX was higher than ALOX and FOIL after week 8 due to the increase in the oxygen transmission rate of SIOX. The TBARS number of salmon in ALOX was higher than FOIL after week 10 which correlates with the OTR results (Table 4).

Sensory analysis

Aroma and acceptability were evaluated by sensory analysis (Table 2-3). After week 10, Salmon in CPP was not measured for sensory analysis due to the sample being unacceptable.

There were no significant differences in aroma evaluation at week 1 and 2. At week 5, salmon in CPP had the highest aroma value (strongest aroma). At week 10, salmon in CPP (6.50^a) and SIOX (6.13^a) had higher value than salmon in ALOX (4.88^b) and FOIL (4.63^b). At week 11, salmon in SIOX (6.88^a) had higher value than salmon in ALOX (5.38^b) and FOIL (5.25^b). After week 8, salmon in SIOX had strong aroma than salmon in ALOX and FOIL.

Salmon in SIOX (6.20^a) had most acceptable value and followed ALOX (5.40^b), FOIL (4.90^c), and CPP (4.30^d) at week 2 and 5. However, salmon in SIOX was less acceptable than salmon in Foil and CPP after week 8.

Due to the high oxygen transmission rate, SIOX had higher TBARS numbers than FOIL after week 7 and had less acceptability than FOIL after week 8. SIOX did not provide adequate barrier for maximum shelf life when compared to both ALOX and FOIL barrier materials.

However, ALOX had similar results compared to FOIL in sensory analysis and TBARS test. ALOX film was more transparent and flexible after retorting relative to the other flims. ALOX provided adequate barrier for maximum shelf life compared to Foil-barrier pouches

LITERATURE CITED

(1) Leterrier, Y. Durability of nanosized oxygen-barrier coatings on polymers. *Progress in Material Science.* **2003**, 48, 1-55.

(2) Durance, T.D.; Collins, L.S. Quality enhancement of Sexually Mature Chum Salmon *Oncorhynchus keta* in Retort Pouches. *Journal of Food Science* **1991**, 56, 1282-1286.

(3) Ramaswamy, H.S.; Grabowski, S. Thermal Processing of Pacific Salmon in steam/air and water-immersion still retorts: Influence of container type/shape on heating behavior. *Lebensm.-Wiss.u.-Technol.* **1999**, 32, 12-28.

(4) Charlotte, A.; Wadso, L.; Sjoholm, I. Accelerated storage and isothermal microcalorimetry as methods of predicting carrot juice shelf-life. *Journal of the Science of Food and Agriculture*. **2005**, 85, 281-285.

(5) Rora, A. M. B.; Kvale, A.; Morkore, T.; Rorvik, K. A.; Steien, S. H.; Thomassen, M. S. Process yield, color and sensory quality of smoked Atlantic salmon in relation to raw material characteristics. *Food Research International.* **1998**, 31(8), 601-609.

(6) Canada Department of Agriculture. Methods for sensory testing. *Laboratory methods for sensory evaluation of Food*, Kromar Printing Ltd.: Ottawa, Canada, **1977**; 19-37.

(7) Chatham, H. Oxygen diffusion barrier properties of transparent oxide coatings on polymeric substrates. *Surface and Coatings Technology*. **1996**, 78, 1-9.

(8) Erlat, A. G.; Spontak, R. J. SiO_x gas barrier coatings on polymer substrates: morphology and gas transport considerations. *J. Phys. Chem. B.* **1999**, 103, 6047 -6055.

(9) Song, Y.; Sakurai, T.; Kishimoto, K.; Maruta, K.; Matsumoto, S.; Kikuchi, K. Syntheses and optical properties of low-temperature SiOx and TiOx thin films prepared by plasma enhanced CVD. *Vacuum.* **1998**, 51, 525-530.

TABLES AND FIGURES

Table 1. Description of thermal factor and thermal processing for sample

Retort temperature	250°F
J_h	1.67 min
J_{Tc}	1.67 min
F_h	10.19 min
F_z	5.60 min
X_{bh}	17.40 min

Table 2. Sensory analysis (Aroma) of salmon in four different retort pouches at accelerated storage times.

	1	*2*	*5*	*6*	*7*	*8*	*9*	*10*	*11*	*12*
ALOX	4.69	5.00	4.91[b]	5.00	3.73	5.22[c]	5.00	4.88[b]	5.38[b]	4.50
CPP	5.23	5.10	6.45[a]	4.70	4.09	7.56[a]	5.56	6.50[a]		
FOIL	4.92	4.30	4.73[b]	4.90	4.18	5.00[c]	5.56	4.63[b]	5.25[b]	5.00
SIOX	5.08	4.50	4.82[b]	4.50	4.00	6.33[b]	5.22	6.13[a]	6.88[a]	5.63

[a] Reference = 5.0, Stronger than R= 6 to 9, Weaker than R = 1 to 4.

[b] a-d: The different letters within same column differ significantly ($p < 0.05$).

Table 3. Sensory analysis (Acceptability) of salmon in four different retort pouches at accelerated storage times.

	1	*2*	*5*	*6*	*7*	*8*	*9*	*10*	*11*	*12*
ALOX	4.46	5.40[b]	4.64[b]	4.80	4.55	5.00[b]	4.78	5.13[a]	4.25[b]	4.75[a]
CPP	4.38	4.30[d]	3.45[c]	4.30	4.91	3.56[d]	3.56	4.00[b]		
FOIL	4.31	4.90[c]	4.55[b]	5.10	4.91	5.44[a]	4.56	5.38a	4.75[a]	4.63[a]
SIOX	5.08	6.20[a]	6.64[a]	5.20	3.82	4.11[c]	4.33	4.00[b]	3.25[c]	3.50[b]

[a] Reference = 5.0, More acceptable than R= 6 to 9, Less acceptable than R = 1 to 4.

[b] a-d: The different letters within same column differ significantly ($p < 0.05$).

Table 4. Oxygen transmission rate (10^{-18} Lm/m^2sPa) of four different retort pouches at accelerated storage times.

	Control	*Retort*	*5 week*	*8 week*	*12 week*
ALOX	2.9[d]	4.5[c]	5.5[bc]	6.0[b]	8.1[a]
CPP	17751[a]	11007[ab]	14711[b]	11405[b]	
FOIL	6.3[ab]	6.5[a]	5.6[b]	5.8[ab]	5.8[ab]
SIOX	10.1[c]	121.4[a]	126.0[a]	137.4[a]	102.6[b]

[a] a-d: The different letters within same row differ significantly ($p < 0.05$).

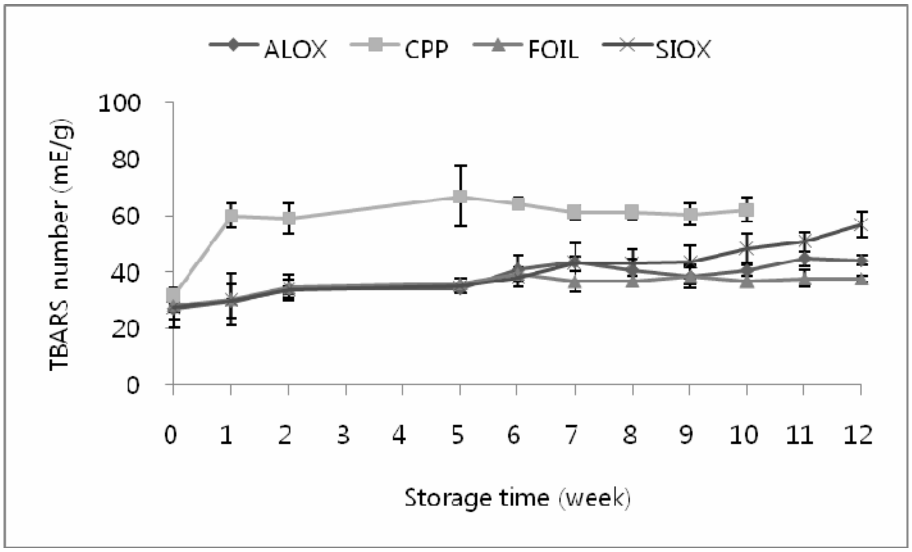

Figure 1. TBARS number of salmon in four different packaging materials at accelerated storage times.

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The effect of barrier materials on salmon quality and retort pouch properties stored under accelerated storage conditions.

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Background

- Aluminum foil has traditionally been the functional barrier material used in retort pouches.
- Aluminum foil is not suitable for microwave heating.
- Several non-foil barrier materials are available to food processors desiring a microwaveable package.

Thin metal oxide coatings on polymers

- Thin oxide film deposited on polymer substrates by vapor deposition techniques; evaporation and plasma-enhanced chemical vapor evaporation (PECVD)

- Reactant gases at room temperature enter the reaction chamber. The gas mixture is heated as it approaches the deposition surface

- Light weight, transparent, excellent barrier properties, and cost-effective.

Thin metal oxide coatings on polymers

Polymer	Coating	Permeability ($10^{16} cm^3(STP)*cm/cm^2/s/Pa$)
LDPE	-	2500
HDPE	-	500
PP	-	530-1700
Polyamide	-	5-25
PET	-	10-30
Polyethylene	SiOx	85
PP	SiOx	50
Polyamide	SiOx	0.07
PET	SiOx	0.04-0.15

*Reference: Y.Leterrier(2003) Progress in materials science 48.1-55

Objectives

Measure the effect of functional barrier materials on salmon quality and retort pouch properties stored under elevated conditions following thermal processing

Materials

- Foil barrier materials
  - 48ga PET/60ga Al-foil/ 3mil CPP (Foil)
- Non Foil barrier materials
  - 48ga AlOx-coated PET/ 60ga Nylon/70μm CPP (AlOx)
  - 48ga PET/ 60ga SiOx -coated Nylon/3 mil CPP (SiOx)
- 80μm CPP
- Food simulant: Salmon

Overall Procedure

1. Prepare retort pouches (4.5x4 inch)
2. 60g salmon
3. Vacuum packaging
4. Retort at 250°F, 23min
5. Stored at 90±2°F, 90±2 % RH
6. Measure TBARS and Oxygen Transmission Rate.
   Sensory analysis at retort, 1 to 2 weeks, and 5 to 12 weeks

TBARS for lipid oxidation analysis

1. 5g salmon + 10ml TCA (w/v 10%) + 0.1ml BHA (w/v 1%)
2. Homogenization (90s, 3000rpm)
3. Centrifuge (20min, 2000rpm)
4. Supernatants were filtered (whatman No1.)
5. 5ml filtrate + 5ml TBA (w/v 3%)
6. Water bath 97℃, 20min
7. Cooling at ambient temperature
8. Measure OD at 531nm

Sensory Analysis

- Laboratory Methods for Sensory Evaluation of food, Agriculture Canada

- Multiple comparison test
  - Aroma: stronger than R(9), equal to R(5), weaker than R(1)
  - Acceptability: More acceptable than R(9), equal to R(5), Less acceptable than R(1)

- Difference was determined using Tukey's Test

* Oxygen Transmission Rate

  : Ox-Tran 2/20 , ASTM D-3985, 0% RH, 23℃

* Statistical analysis

  : SAS 9.1

Sensory Analysis (Aroma)

	1 week	2 week	5 week	6 week	7 week	8 week	9 week	10 week	11 week	12 week
Alox	4.69	5.00	4.91^{b}	5.00	3.73	5.22^{c}	5.00	4.88^{b}	5.38^{b}	4.50
CPP	5.23	5.10	6.45^{a}	4.70	4.09	7.56^{a}	5.56	6.50^{a}		
Foil	4.92	4.30	4.73^{b}	4.90	4.18	5.00^{c}	5.56	4.63^{b}	5.25^{b}	5.00
Siox	5.08	4.50	4.82^{b}	4.50	4.00	6.33^{b}	5.22	6.13^{a}	6.88^{a}	5.63

Reference = 5.0, Stronger than R= 6 to 9, Weaker than R= 1 to 4

a-c: The different letters within same column differ significantly ($p < 0.05$)

Sensory Analysis (Acceptability)

	1 week	2 week	5 week	6 week	7 week	8 week	9 week	10 week	11 week	12 week
Alox	4.46	5.40^{b}	4.64^{b}	4.80	4.55	5.00^{b}	4.78	5.13^{a}	4.25^{b}	4.75^{a}
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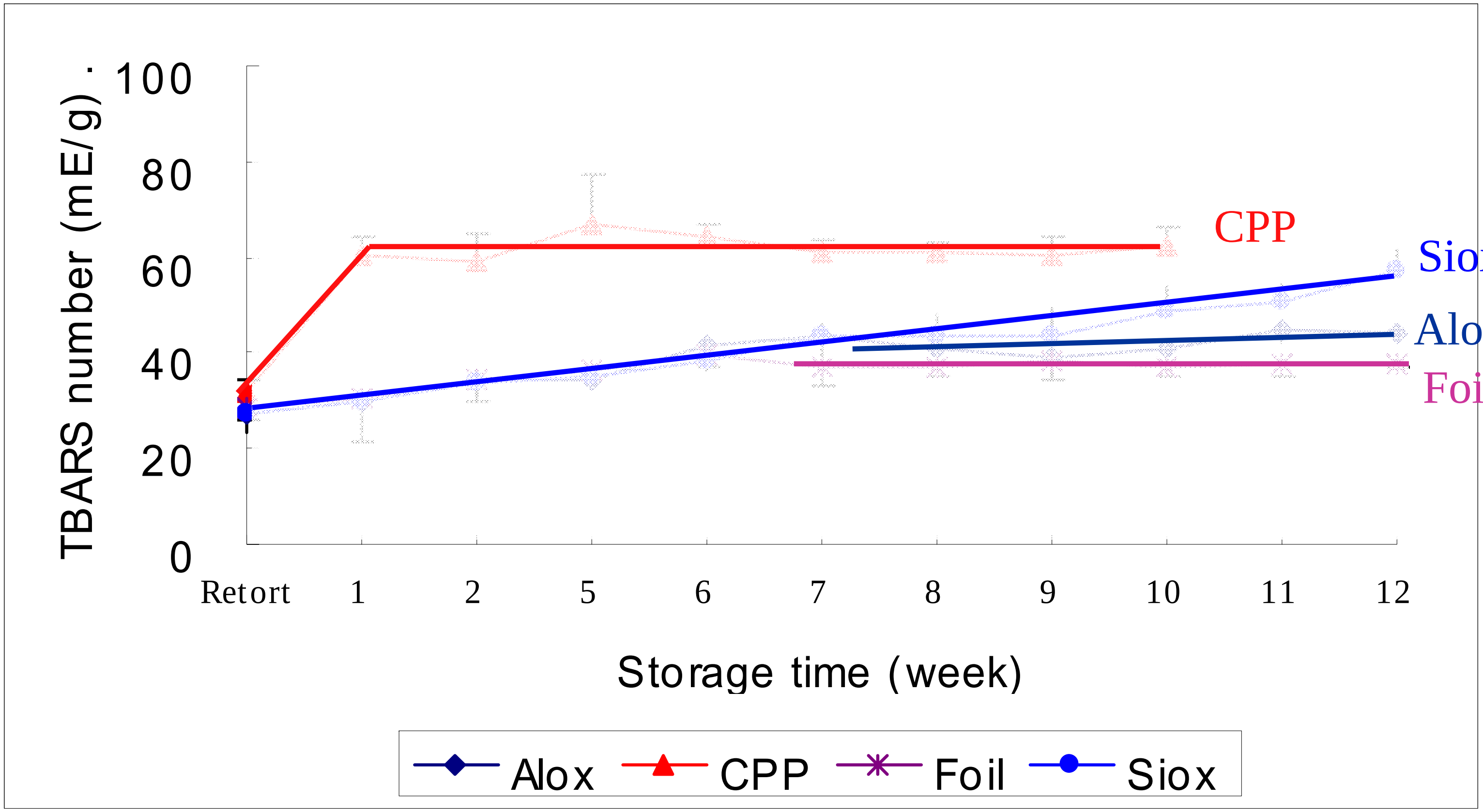
TBARS



TBARS Number were exhibited as milli extinction unit/ gram of salmon (mE/g)

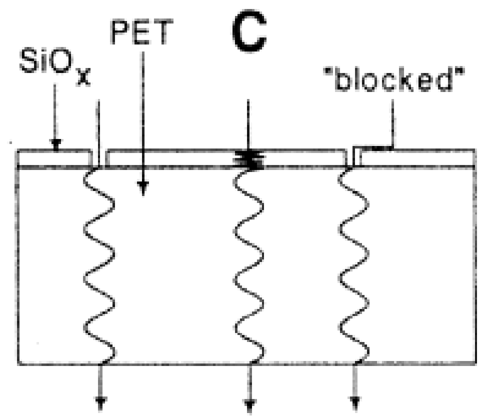
Discussion

- Gas transport through materials can take place by two mechanisms

  - Diffusive flow via solubility-diffusion
  - Flow through defects in the material
    (inhomogeneities, such as pinholes,
    porosities, microchannels, and microcracks.)

Flow through defects in the material

- Oxygen permeation through high barrier coatings is dominated by flow through defects in the coating



*Reference: Hood Chatham (1996) Surface and coatings technology 78.1-9

Aging phenomena in the oxide thin film

- Internal stress state of the coated polymer changes with time.
  - the time-dependent nature of polymers
  - aging phenomena in the oxide thin film
  - particularly those resulting from interactions with moisture.

*Reference: Robic JY (1996) Thin solid films. 291.34-39

Moisture plays a key role

- Changes in intrinsic stress in SiOx films upon long-term exposure of to an ambient atmosphere leads to cracks.
- Moisture plays a key role in such phenomena, as it diffuses into the film and reacts with strained Si-O bonds and reconstructs them into a minimum energy configuration.

*Reference: Song Y(1998) Vacuum 51.525-530

Conclusion

- In sensory test, SiOx had less acceptability than Foil after 8 week storage time.
- SiOx had higher TBARS numbers than Foil after 7 week storage time.
- During storage, moisture diffuses into the film and reacts with strained Si-O bonds and leads to cracks.

- SiOx did not provide adequate barrier for maximum shelf life when compared to both AlOx and Foil barrier materials.

Conclusion

- In sensory and TBARS test, AlOx had similar result to Foil.
- AlOx was more transparent and flexible than others, and microwaveable.

- AlOx provided adequate barrier for maximum shelf life compare to Foil barrier pouches.

Thank You

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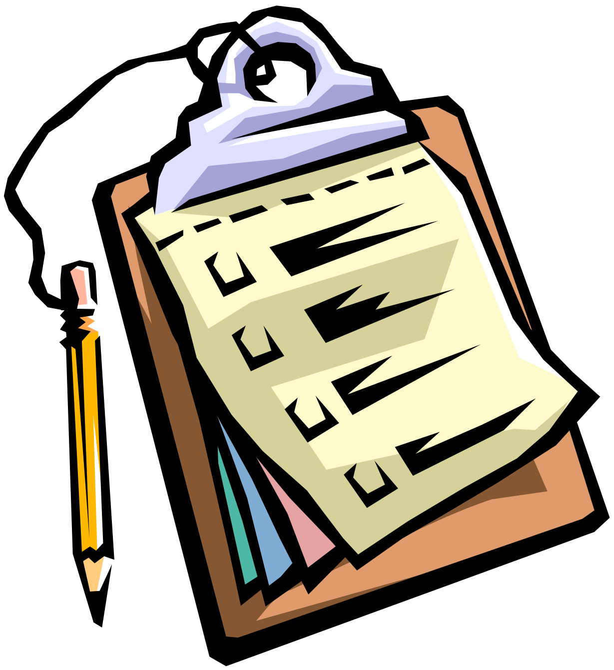

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