An Oxygen Indicator for Assessment of Barrier Packaging

Roger L Kaas; Kaas Consulting Group, LLC and ISO Poly Films
and
Duncan Darby; Department of Packaging Science, Clemson University

Abstract
An oxygen indicator dye formulation utilizing methylene blue has been developed based on various literature references. The formulation has been used to qualitatively demonstrate the oxygen barrier levels of four side sealed pouches made with various barrier laminations before and after retort processing. The method can be used to assess the barrier of the entire package and demonstrate areas of localized damage to the barrier. While all the materials showed good barrier before retorting some barriers were adversely affected by the retort process. EVOH coextrusions and SiOx coatings were the most adversely affected by retorting. Areas of defects in the adhesive lamination were detected that would not have been evident in conventional permeation testing. Permeation through the edge of the heat seal was also demonstrated by a fine line of colored dye just inside the seal area. The work to date has been on the qualitative observation of barrier levels but there is the potential for quantitative permeation measurement using colorimetric methods.

Introduction
A number of barrier coatings and films are available; however, there are concerns about the reliability of the barrier levels they provide. Inorganic oxide coatings can be damaged by flex cracking, humidity and moisture can affect barrier levels especially after retorting, stretching on printing presses and laminators can cause defects in the barrier layers and heat or mechanical stresses during heat sealing can affect barrier.

A quick and efficient means of assessing the barrier levels of completed packages is needed. Typical barrier tests are conducted on flat sheet in a Mocon or other permeation test instrument. These tests do not provide information on the integrity of the barrier for the final package. Whole package tests are possible on permeation test instruments but this would require dedication of the instrument to test each individual package. This technique would only determine the overall oxygen ingress to the package and would not provide information about localized damage due to handling, processing, heat sealing and distribution. The qualitative indication of the barrier level using an oxygen indicating dye meets these needs.

A number of suppliers have shown results obtained using an oxygen indicating dye based on methylene blue. They have either been unable or unwilling to provide the detailed information on the dye formulation. Therefore, we have developed our own formulation based on literature references (1-4).

The formulation is based on methylene blue and glucose dissolved in water adjusted to a pH of 11 – 12 with NaOH. Natural agar is added to gel the system and immobilize the indicator. Glucose acts as a reducing agent and in the absence of oxygen methylene blue is colorless. It
turns blue in the presence of oxygen. The blue color persists if the oxygen ingress is more rapid than the glucose reduction reaction or if the glucose is consumed. After some preliminary tests with non-barrier polyethylene and low barrier nylon/PE pouches showed that the formulation was working as expected its use was extended to the evaluation of a number of barrier laminations.

A broad barrier lamination study is underway at the Packaging Science Department at Clemson University. The goal of the work is to evaluate different types of barrier materials in a typical retort pouch lamination. The target structure of the laminations is the high performance 4-ply PET/Barrier/nylon/cast PP used for the Army MRE pouches and some retail applications. A control structure having a double layer of nylon instead of the barrier is also included in the study. Barrier materials included in the study include polyacrylic acid coated PET, EVOH coexes, oriented EVOH film, PVdC film, SiOx coated PET, AlOx coated PET, a developmental barrier nylon, and nanocomposite coated PET.

Pouches were made from the laminations, filled with the oxygen indicator and sealed without retorting. Other pouches were filled with water and retorted for one hour at 250°F. They were then cut open, emptied and refilled with the oxygen indicator before resealing. Unfortunately, the oxygen indicator cannot be retorted in place because the high pH causes caramelization of the agar and glucose.

**Results and Discussion**

All of the unretorted barrier laminations showed excellent initial barrier. The double nylon control showed significant oxygen ingress very early during storage aging. Gradual color changes occurred over time indicating differences in the barrier level.

Retort processing caused distortion and changes in the stiffness of the pouches which caused some difficulties in resealing of the pouches after filling with the oxygen indicator. While some post-retort pouches had unacceptably seals we were able to retain representative samples of all variables. As expected laminations based on EVOH coexes are not acceptable because of whitening of the barrier and rapid post retort oxygen ingress. SiOx coatings appear to be more sensitive to the retort process than AlOx coatings. Polyacrylic acid coatings, the developmental nylon and nanocomposite coating are showing excellent barrier after retort. The lamination based on PVdC film is showing a low level of oxygen ingress.

The oxygen indicator has demonstrated the existence of defects in the pouches that are allowing oxygen ingress.

1. It has been reported (5-6) that permeation can occur through the edge of the heat seal. We have demonstrated that this does, in fact, occur. A very fine blue line is observed at the edge of the heat seals of pouches made with all of the barrier laminations. This indicates that oxygen is coming through the edge of the heat seal.
2. The blue dye indicates damage to the barrier material due to scratches, folds and creases in the film.
3. A skip in the lamination adhesive was observed by delamination in one of the barrier laminations. This resulted in high oxygen ingress along the delamination lines indicated by the blue color along those lines.
4. A non-uniform barrier coating was demonstrated by blue streaks in pouches made with that lamination.
The gradual color changes over time observed with the non-retorted pouches suggest the potential to quantify the rate on oxygen ingress with the color of the indicator. After the aging test was underway color measurements were conducted on the non-retorted pouches using a Minolta colorimeter. L, a, b parameters were measured and the $\Delta E$ was calculated relative to the polyacrylic acid coating which had the lowest color formation. There was a good correlation with the observed color and a generally increasing $\Delta E$ with time indicating oxygen ingress.

The correlation of $\Delta E$ with the OTR measured on a Mocon instrument was poor with a lot of scatter in the data. Most of the color change is in the b value which is the blue-yellow axis. When the OTR ranking of the lamination was compared with b value ranking considerably better correlation was obtained. A correlation coefficient $R^2$ value of 0.7227 was observed.

These results show the potential for quantitative determination of oxygen permeation using the oxygen indicator and colorimetric measurements. The poor correlations observed are due to inconsistencies in the OTR measurements and conducting color measurements on translucent materials with thickness variation in the pouches. Suggested future work to improve the correlation would include repeating OTR measurements to assure accuracy and consistency, establishing a well defined initial reference point for color, and using standardized pouch thicknesses.

References

4. US Patent 6,561,008
Barrier Assessment with an Oxygen Indicator Dye

Roger L. Kaas
Kaas Consulting Group, LLC & ISO Poly Films
and
Duncan Darby
Clemson University
A variety of different barrier coated films are available:
- Inorganic oxide coatings based on SiOx and AlOx
- Organic polymer coatings
- Nanocomposite coatings
- Coextruded films

Concerns about the reliability of the barrier levels, especially after handling and retort:
- Flex cracking of inorganic oxides
- Humidity effects on barrier related to retorting
- Handling effects due to stretching on printing presses and laminators
- Heat and mechanical stresses on pouch making and final sealing
Barrier Assessment with Oxygen Indicator Dye

- Typical barrier tests conducted on flat sheet in Mocon or other test instrument
- Difficulty in assessing the barrier of the final package
  - Need whole pouch testing to assess package integrity.
  - Need to determine if localized damage has occurred near heat seals
  - Damage due to handling, processing and distribution
  - Desire to conduct these tests without long term commitment of Mocon instruments
- Qualitative indication of barrier level using oxygen indicating dye meets these needs
Barrier Assessment with Oxygen Indicator Dye

- A number of suppliers have shown results using dye based on methylene blue dye
- Suppliers unwilling or unable to provide information on dye formulation
- Developed our own formulation based on literature references
- Guelph University has a patent on the use of indigo-carmine dye (U.S. Patent 6,561,008)
- Use methylene blue to avoid this patent
Oxygen Indicator Dye Formulation

- Methylene blue
- Glucose
- Agar
- Dissolved in water
- pH adjusted to 11-12 with NaOH
Barrier Assessment with Oxygen Indicator Dye

- Glucose acts as a reducing agent
- In its reduced form methylene blue is colorless
- Turns blue in oxidized form
  - Consumption of the glucose
  - Ingress more rapid than glucose reduction reaction
- Agar is used to gel the formulation
  - Immobilize to prevent mixing
  - Determine if localized damage has occurred to the oxygen barrier
- May be light sensitive
  - Recommend storing test samples in dark
- Initial blue color disappears if the package has sufficient barrier
Oxygen Indicator Dye in Polyethylene Pouch

3 Hours
Oxygen Indicator Dye in Nylon/PE Pouch

Initial

6 Hours

22 Hours

29 Hours

5 Days

12 Days

19 Days
A barrier lamination study is underway at Clemson. The goal is to evaluate a number of different barrier materials in a typical laminated structure.

- Four ply retort pouch model
- PET/Barrier/Nylon/CPP

Used the oxygen indicator to evaluate these laminations.

- Unretorted
- After retort
  - Filled pouches with water
  - Retorted one hour at 250°F
  - Emptied and refilled with indicator dye
  - Some difficulties resealing retorted pouches
### Barrier Lamination Variables

<table>
<thead>
<tr>
<th>Variable #</th>
<th>Post Retort Pouch Appearance</th>
<th>Barrier Description</th>
<th>Post Retort Dye Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Good appearance Clarity similar to 16</td>
<td>Polyacrylic acid coated PET</td>
<td>Good</td>
</tr>
<tr>
<td>2</td>
<td>Worming and whitening</td>
<td>Symmetrical COC/EVOH coex</td>
<td>Blue</td>
</tr>
<tr>
<td>3</td>
<td>Worming and whitening</td>
<td>Unbalanced COC/EVOH coex</td>
<td>Blue</td>
</tr>
<tr>
<td>4</td>
<td>Worming and whitening</td>
<td>LLDPE/EVOH coex</td>
<td>Blue</td>
</tr>
<tr>
<td>5</td>
<td>Yellow</td>
<td>PVdC Film</td>
<td>Very slight blue</td>
</tr>
<tr>
<td>6</td>
<td>Not run for dye study</td>
<td>4 ply foil</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Clear stripes clarity comparable to 16</td>
<td>SiOx coated PET #1</td>
<td>Slight blue</td>
</tr>
<tr>
<td>8</td>
<td>Not run for dye study</td>
<td>3 ply foil</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>Good appearance - no whitening - Clarity similar to 16, dimples not as visible as 16</td>
<td>Oriented EVOH film</td>
<td>Slight blue</td>
</tr>
<tr>
<td>10</td>
<td>Good appearance Clarity similar to 16</td>
<td>Developmental barrier nylon</td>
<td>Good</td>
</tr>
<tr>
<td>11</td>
<td>Good appearance slightly clearer than 16</td>
<td>SiOx coated PET #2</td>
<td>Slight blue</td>
</tr>
<tr>
<td>12</td>
<td>Good appearance slightly clearer than 16</td>
<td>May be duplicate of Variable #14</td>
<td>Blue</td>
</tr>
<tr>
<td>13</td>
<td>Clear stripes hazier than 16</td>
<td>AlOx coated PET #1</td>
<td>Good</td>
</tr>
<tr>
<td>14</td>
<td>Good appearance Clarity similar to 16</td>
<td>SiOx coated nylon</td>
<td>Blue</td>
</tr>
<tr>
<td>15</td>
<td>Good appearance slightly clearer than 16</td>
<td>AlOx coated PET #2</td>
<td>Good</td>
</tr>
<tr>
<td>16</td>
<td>Good appearance reference clarity</td>
<td>Double nylon control</td>
<td>Blue</td>
</tr>
<tr>
<td>17</td>
<td>Good appearance Clarity similar to 16</td>
<td>Nanocomposite coated PET</td>
<td>Good</td>
</tr>
</tbody>
</table>
All the barrier laminations showed excellent initial barrier

Double nylon control showed significant oxygen ingress

Some defects in coating or adhesive application were observed in the SiOx #1 samples

Gradual color changes over time indicating barrier differences
Unretorted Barrier Laminations

35 Days

64 Days

106 Days

141 Days
Some difficulty resealing retorted pouches
- Distortion and stiffening of material
- Able to retain samples of all the variables

Laminations based on EVOH are not acceptable for retort applications

SiOx coatings appear to be more sensitive to the retort process than AlOx coatings

Polyacrylic acid, developmental nylon, and nanocomposite coating are showing excellent barrier after retort

The lamination based on PVdC film is also showing a low level of oxygen ingress
Retorted Barrier Laminations

35 Days

64 Days

106 Days
Nanocomposite Barrier Coating Pouches

Non-retort 27 Days

Non-retort 55 Days

Retort 27 Days

Retort 55 Days
Permeation Through Heat Seal

- A very fine blue line observed at the edge of the heat seals
- Present in all of the barrier lamination pouches
- Presumably oxygen ingress is occurring though the seal edge
Damage to Barrier
Lamination Defects
Non-Uniform Barrier Coating
Aluminum Foil Pouch

- Foil pouch opened after 49 days
  - No indication of damage
  - Blue line observed at heat seal
Color Measurements

- Color measurements conducted on non-retorted pouches
- Did not start color measurements until well into the aging test
  - Measured L, a, b with Minolta colorimeter
  - Calculated ΔE relative to polyacrylic acid coating
- Good correlation with observed color
  - Generally increasing ΔE with time indicating oxygen ingress
Color Measurements Non-Retorted Pouches

$\Delta E$ Relative to Polyacrylic Acid Coating

Days

ΔE

0.00
10.00
20.00
30.00
40.00

LLDPE/EVOH coex
PV4C Film
Oriented EVOH film
Developmental barrier nylon
May be duplicate of SIOx nylon
AIOX coated PET #1
SIOx coated PET #2
AIOX coated PET #2
Double BON control

Symmetrical COC/EVOH coex
Unbalanced COC/EVOH coex
SIOx coated PET #1
AIOX coated PET #2

92
106
119
141
### ΔE Correlation Non-Retorted Pouches

<table>
<thead>
<tr>
<th>Ref.</th>
<th>18.28</th>
<th>10.11</th>
<th>11.61</th>
<th>12.09</th>
<th>6.38</th>
<th>18.51</th>
<th>5.78</th>
<th>13.01</th>
<th>27.44</th>
<th>2.35</th>
<th>27.34</th>
<th>5.07</th>
<th>35.64</th>
</tr>
</thead>
</table>

141 Days
Correlation of $\Delta E$ with OTR

Poor Correlation with OTR
Correlation of OTR with b value

- b value is the yellow – blue axis
- Most of measured color change is in b
  - Some a value shift toward green because of initial yellow color
- Compare OTR ranking with b value ranking
- Considerably better correlation

Correlation of OTR with Color Ranking

![Graph showing correlation with R² = 0.7227](image)
In principle, color change should be related to the oxygen ingress. Poor correlation because of errors:
- OTR measurements showed inconsistencies
- Color measurements on translucent material and thickness variation of pouches

Suggested future work:
- Redo OTR measurements to assure accuracy
- Refine color measurement technique
  - Use standardized thickness fixture and no agar to gel the indicator
  - Establish better initial reference points
  - Perhaps use visible light spectrum at specific wavelengths to quantify color
Acknowledgments

- US Army Natick Soldier Research Development and Engineering Center for funding of the project and permission to present this information
- Jerry Stoner and Pat Marcondes for many helpful suggestions and assistance in filling pouches and conducting tests
- Dr. Kay Cooksey for suggestions on color measurements
- Derrick Jordan for video photography
Thank you

Presented by:
Roger L. Kaas, Kaas Consulting Group, LLC
and ISO Poly Films
rlkaas@new.rr.com
and Duncan Darby
Clemson University
ddarby@clemson.edu

Please remember to turn in your evaluation sheet...