**Concept of Barrier Properties of Packaging Materials**
**-- Its Impact in Food Packaging**

Jiajian Georgia Gu
MOCON, Inc., 7500 Boone Ave. N., Minneapolis, MN 55428, USA

# I. Barrier Materials and Permeation

Modern Packaging has the following basic functions:

- Containment
  It should have proper size and shape, be easy to use
- Protection
  It should provide proper barrier that product can meet the desired Shelf Life. Also it should have proper physical strength that can withstand any situation in transportation.
- Information
  Ingredient and nutrition of the product should printed on the package
- Marketing
  Designed to have special appearance to attract consumers

With the advancement of modern science and technologies, packaging materials have greatly evolved from traditional to modern time. Examples of traditional packaging materials are glass bottles, metal cans and paper bags. Examples of modern packaging materials are polymer bags or bottles and packages with multi-layered materials.

For traditional packaging materials, they are either non-permeable such as glass and metal, or highly permeable such as paper. For the non-permeable packages, the possible leak paths such as seams, closure interface are of the most concern. For modern packaging materials that are mainly polymer or composite materials, permeation of the material itself should be considered, in addition to possible leak paths of seams, closure interface, etc. Please remember that all plastics are permeable. It is impossible to study the barrier property of a packaging material without studying the permeation of the material.

Permeation is a process that is invisible but happens all the time. Look at the typical PET bottle that is filled with carbonated soft drink (Figure 1). Since the filled $CO_2$ (usually 4atm to start with) is higher than the ambient $CO_2$ pressure, the partial pressure difference makes $CO_2$ permeation happen from inside the bottle towards outside exterior environment. On the other hand, the ambient air (21% oxygen) permeates into the bottle.


Figure 1: $CO_2$ filled bottle

Permeation rates determine how much barrier or protection is provided from packaging materials. The lower the permeation, the better the barrier. Here, the protection means to prevent the failure of a product due to the quality change. In the Food industry, food products basically have the following failure modes:

• Rancidity
– Oxidation of unsaturated fats and oils
– UV induced oxidation
• Stale
– Moisture gain
• Dehydrate
– Moisture loss
• Flavor loss or off-flavor
– Scalping, migration

In order to protect the product from failure within the desired shelf life, proper barrier properties are required for different products:
• Gas Barrier
– Oxygen
– Carbon Dioxide
• Light Barrier
– Visible
– Ultraviolet
• Moisture Barrier
• Aroma and Flavor Barrier (chemical barrier)

## II. Permeation Basics

Permeation follows Solution-Diffusion Mechanism.
The gas absorbs at the entering face and dissolves within the material at the high-pressure side of the material, diffuses through the polymer phase, and desorbs or evaporates at the low-pressure side (Figure 2).

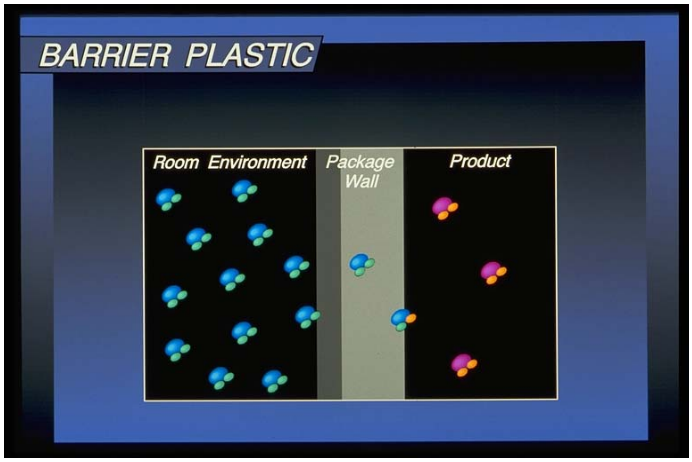


Figure 2: Solution-Diffusion Mechanism Diagram

Permeation can be expressed as:

Permeation rate:
cc(STP) * mil / (100in$^2$ * 24hr * atm)
cc(STP) * cm / (m$^2$ * 24hr * atm)
cc(STP) * cm / (cm$^2$ * sec * cmHg)

Transmission rate:
cc(STP) / (100in$^2$ * 24hr)
cc(STP) / (m$^2$ * 24hr)

The barrier property of a polymer material is impacted by the environment, such as temperature, relative humidity, etc. and fickian behavior of the material itself.

Permeation rates typically change 5-7% per degree C (Figure 3). Crucial errors can occur when testing at elevated temperatures close to the glass transition temperature (Tg) of the sample (Figure 4).

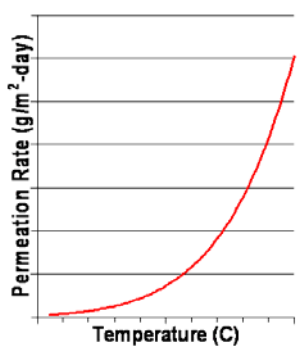


Figure 3: Permeation and Temperature

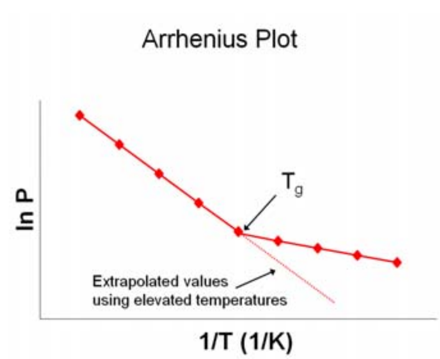


Figure 4: Tg on Arrhenius Plot

RH can greatly affect permeation for hydrophilic materials. Proper RH generation and measurement are necessary for accurate permeation results. Figure 5 shows how RH affects OTR of different materials.

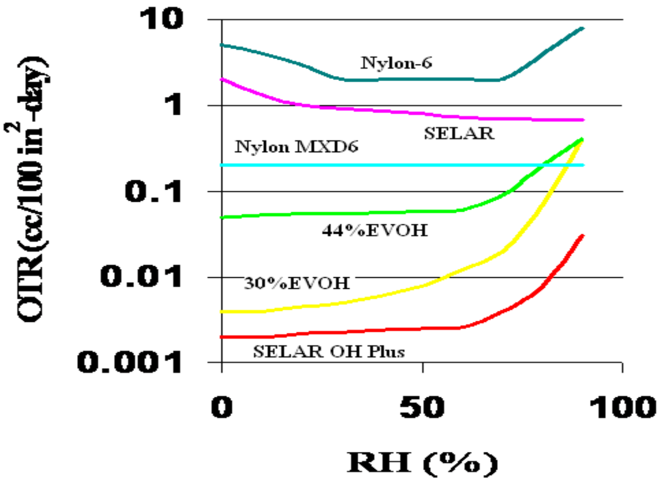



Figure 5: RH affects OTR of different materials

For Fickian materials (or those that obey Fick's Law), permeation is linear with concentration for all concentration ranges. Non-Fickian behavior means changes in materials due to polymer and permeant interactions (swelling, plasticizing, etc). Displayed graphically, Fickian and Non-Fickian materials would look like the following (Figure 6):

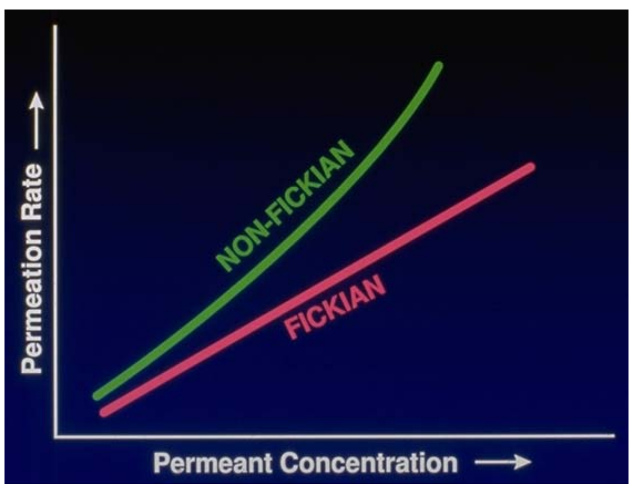



Figure 6: Fickian vs. Non- Fickian Behavior

## III. Case Studies - Food Packaging Application

### Case Study 1. Flat film versus finished package - Infant Formula Package

Most R&D work is completed on flat films. It is beneficial for development and excellent for comparison purposes. Many times the finished package is not evaluated.
The following case study illustrates why finished package evaluation is needed.

Here is an infant formula manufacture. The company wanted to switch from traditional can packaging to a multi-layer flexible pouch. Product is water sensitive (powder) and oxygen sensitive (oxidizable compounds) so that candidate materials (Table 1) must be evaluated for water vapor transmission rate (WVTR) and oxygen transmission rate (OTR) both as flat film and finished pouch. Since the destination market is in the tropical region, the test conditions were set as described in Table 2. All the tests were performed on MOCON permeation test instruments.

Table 1. Candidate Materials

| ID | Sample Structure |
|---|---|
| 1 | PET / Al / Nylon / LLDPE |
| 2 | PET / Al / PE |
| 3 | PET / Al / PETMET / PE |
| 4 | PET / Al / Nylon / PE |
| 5 | PET / PE (extruded)/ Al / PE(extruded)/PE |

Table 2. Test Conditions and Equipment

| **Test Item** | **Test Conditions** | **Test Instrument** |
|---|---|---|
| Pouch OTR (cc/pkg*day) | Temperature: 37C<br>Test gas: 100% $O_2$ with 90%RH<br>Carrier gas: Dry nitrogen | MOCON Ox-Tran 2/61 |
| Film OTR (cc/$m^2$-day) | Temperature: 37C<br>Test gas: 100% $O_2$ with 90%RH<br>Carrier gas: Dry nitrogen | MOCON Ox-Tran 2/21 |
| Pouch WVTR (gm/ pkg*day) | Temperature: 37C<br>Test gas: 100% RH water vapor<br>Carrier gas: Dry nitrogen | MOCON Permatran W 3/31 |
| Film WVTR (gm/$m^2$-day) | Temperature: 37C<br>Test gas: 100% RH water vapor<br>Carrier gas: Dry nitrogen | MOCON Permatran W 3/31 |

Table 3. Film Testing Results

| ID | **OTR (cc/ m$^2$-day)** | **WVTR (g/ m$^2$-day)** |
|---|---|---|
| 1 | <0.005 | <0.005 |
| 2 | <0.005 | <0.005 |
| 3 | <0.005 | <0.005 |
| 4 | <0.005 | <0.005 |
| 5 | <0.005 | <0.005 |

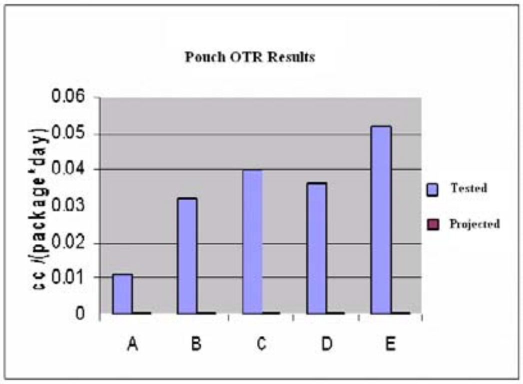
Table 4. Pouch Projected Results (using film data)

| ID | **OTR (cc/ pkg*day)** | **WVTR (g/ pkg*day)** |
|---|---|---|
| 1 | <0.0004 | <0.0004 |
| 2 | <0.0004 | <0.0004 |
| 3 | <0.0004 | <0.0004 |
| 4 | <0.0004 | <0.0004 |
| 5 | <0.0004 | <0.0004 |

Table 5. Actual Pouch Test Results

| ID | **OTR (cc/ pkg*day)** | **WVTR (g/ pkg*day)** |
|---|---|---|
| 1 | 0.011 | 0.0021 |
| 2 | 0.032 | 0.0010 |
| 3 | 0.040 | 0.0022 |
| 4 | 0.036 | 0.0034 |
| 5 | 0.052 | 0.0015 |

Results from Table 3 showed that all the film materials were very good barriers and all the OTR and WVTR values were below the detection limit of the instrument. Using these film results and the actual size of the pouches, the projected OTR and WVTR values of pouches were obtained (Table 4). When the actual tested pouch OTR and WVTR results (Table 5) were compared with projected results, it was found that none of these pouches was as good as the projected ones, especially the OTR were much worse.



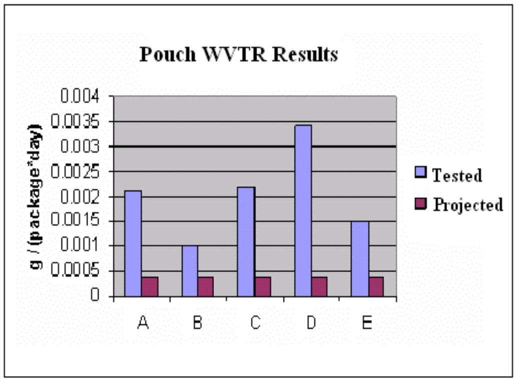




Figure 7: Comparison:
Projected results vs. Tested results

Additional studies found that there was defect along the crease of the package side wall. It could be one of the reasons that contributed to the higher than projected permeation results. Other possible reasons that worsen the barrier of a finished package could be seals, harsh handling during general processing such as filling / packing / labeling, shipping and distribution. This example indicated that evaluating only the package material is not enough. Final finished package should always be tested to ensure total packaging integrity.

**Case Study 2. Bottle vs. Closure - Antacid / Calcium Supplement Package**

The Antacid / Calcium Supplement product is packaged in polymer bottles with closure liners from different vendors. Permeation studies were conducted on

- bottles with induction seals closure
- bottles without closure, testing samples are mounted on metal plate

Figure 8: Test the bottle with closure

Figure 9: Test the bottle body only

Table 6 summarizes WVTR test results for bottles with and without closures.

Table 6. Bottle test results

| Sample Name | WVTR (g/package-day) |
|---|---|
| W-1 | 0.00081 |
| W-2 | 0.00089 |
| W-3 | 0.00099 |
| W-4 | 0.00092 |
| W-5 | 0.0107 |
| W-6 (without cap) | 0.0003 |

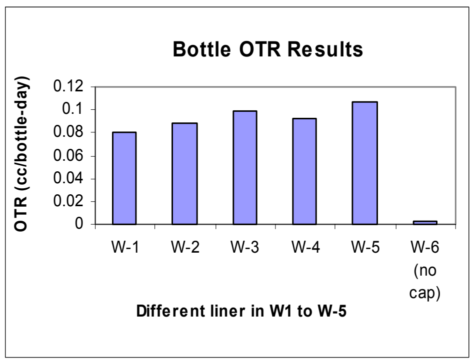



Figure 10: Bottle OTR results

From results shown, sample W-6 (without cap) demonstrated the lowest WVTR value, while the WVTR value of other samples (with closures) varied and were much higher than the bottle body by itself. The higher value of these capped bottles could result from permeation from different closure and liner materials. It could also result from micro-leakage through the cap/bottle opening interface due to physical design, improper sealing parameters.

The above two case studies demonstrate the importance of testing the finished package. After selecting the proper material, additional tests on the finished package should be conducted so that one can make sure that the barrier has not been worsened by the processing. This testing aids in determining whether process parameters should be modified or improved.

**Case Study 3. Select packaging materials wisely - Using destination environment conditions**

The ultimate goal of packaging is to provide the sufficient barrier that the product can maintain its quality within desired shelf life. On the other hand, one does not want the expense of over-packaging the product. In order to select packaging materials wisely, one should combine all his technical, geographical and economical knowledge.

The following is an example about how to select packaging material for a snack product using destination environment conditions. The company produces waffle products which are exported to three different global regions. Due to the different environmental condition in each region, different grades of packaging materials could be chosen to achieve the desired shelf life.
Three grades of film materials were tested at three test conditions that mimic the environment of these three regions.

Table 7. Candidate film testing conditions and results

| Ship To | Film A (Excellent) | Film B (Good) | Film C (Fair) | Testing Conditions |
|---|---|---|---|---|
| Northern Europe | PASS | PASS | PASS | 15C, 30%RH |
| Japan | PASS | PASS | FAIL | 23C, 50%RH |
| Vietnam | PASS | FAIL | FAIL | 30C, 85%RH |

Results in Table 7 showed that Film A is the only choice for Vietnam due to its tropical condition. For the other two regions, more than one film can be chosen. Now is the time to ask management people for input from the marketing and economy point of view, and then decide whether the highest barrier will be used or sufficient barrier will be used.

## IV. Introduction to MOCON Permeation Instrumentations

Now that we know the important of study the barrier properties when selecting packaging material. In order to evaluate the barrier properties of packaging materials, high quality permeation test instruments are required.

MOCON is the world leader in the category of dynamic permeation test instrumentation. We have been innovating with products and serving our customers for 40 years. Today, MOCON's product line is the most extensive, with over 35 permeation instruments offered. MOCON's instruments have the highest sensitivity of any permeation testers on the market, they are upgradeable to future designs and offerings, allow for trade-ins, and have the best local service. We have the largest customer base of any permeation test manufacturer in the world, with thousands of instruments installed around the globe. Specifically, MOCON permeation test instrumentation provides:

- Accurate measurements
- Better lab to lab reproducibility
- Precise controlled temperature and RH
- Testing films, and packages as well
- Modular design

MOCON is very proud to have ASTM and other standards that reference MOCON Instruments and related test methods.

## A. Test Methods and Standards Summary

### *1. Oxygen Test Methods*

**ASTM – D 3985 films** - Current MOCON OXTRAN® method. MOCON is the only company listed as a supplier.

**ASTM - F 1307 packages** - Current MOCON OXTRAN ® method. MOCON is the only company listed as a supplier.

**ASTM - F 1927 O2TR films with RH** - Current MOCON OXTRAN ® method. MOCON is the only company listed as a supplier.

**JIS - K-7126 (JAPAN) films** - Current method – MOCON OXTRAN ® is part of this method.

**DIN - 53380 (Germany) films** - Current method. MOCON OXTRAN ® is part of this method.

**ISO – 14663-2** - Determination of steady-state rate of transmission of oxygen gas through ethylene/vinyl alcohol copolymer in the form of film using a coulometric sensor.

### *2. Water Vapor Test Methods*

**ASTM - F1249 WVTR** - Current MOCON PERMATRAN®-W method. MOCON is the only company listed as a supplier.

**ASTM – D 6701 WVTR** - Current MOCON PERMATRAN ®-W Model 101K method. MOCON is the only company listed as a supplier.

**ASTM - E 398** - Current MOCON PERMATRAN ®-W Model 398 method. Test Method for Water Vapor Transmission Rate of Sheet Materials Using a Rapid Technique for Dynamic Measurement.

**JIS K-7129 WVTR** - Current MOCON PERMATRAN® -W method.

**ISO – 15106-2** - Plastics - Film and sheeting — Determination of water vapor transmission rate — Part 2: Infrared detection sensor method

**TAPPI T-557** - Water vapor transmission rate through plastic film and sheeting using a Modulated Infrared Sensor.

### *3. Carbon Dioxide Test Method*

**ASTM – F 2476 -** Current MOCON PERMATRAN ®-C Model 4/41 method.
Test Method for Determination of Carbon Dioxide Gas Transmission Rate ($CO_2$TR) Through Barrier Materials Using an Infrared Detector.

## B. Examples of MOCON Instruments with the Greatest Application in Packaging and Barrier Material Industries

**For oxygen barrier studies: OXTRAN® Model 2/21 and 2/61**

**For water vapor barrier studies: PERMATRAN-W® Model 3/33 and 3/61**

Figure 11: Appearance for both OTR and WVTR equipments

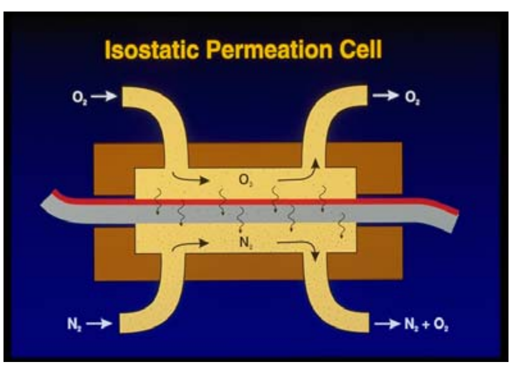



Figure 12: MOCON permeation concept

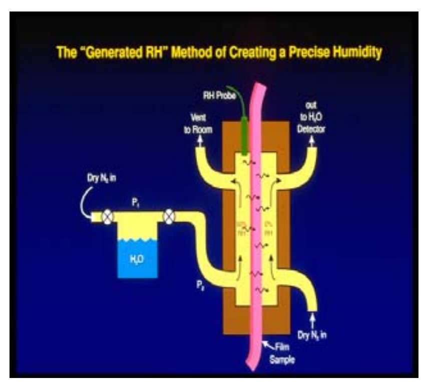



Figure 13: Generated RH

MOCON OXTRAN® uses our exclusive, propriety, COULOX sensor which is a sole source oxygen detector. It never needs calibration. MOCON's permeation test cell is designed for Isostatic method. During the test, one side of the film is challenged with test gas (shown oxygen in Figure 12) while the other side is swept with a nitrogen carrier gas. The flux is analyzed with a detector. All testing is conducted at precisely controlled temperature and atmospheric pressure. For tests requires relative humidity, NIST recommended Two Pressure Method is used for generating RH (Figure 13).


Figure 14: Two test stations instrument

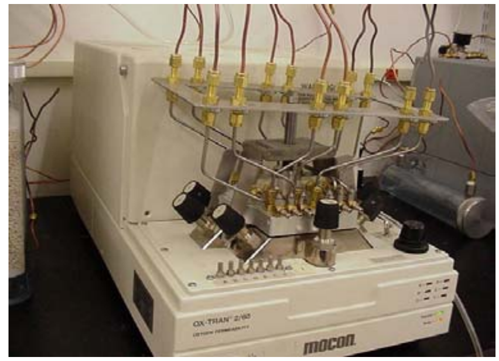



Figure 15: Six test stations instrument

The most common test instrument has two test cells or multiple test cells to meet customer's different applications (Figure 14 and 15).

More details regarding above instruments can be found from MOCON web site: http://www.mocon.com/permeation.info/index.shtml

## V. Most Recent Developed Instruments for Permeation and Packaging Integrity Testing

**Aquatran™ Model 1:**
AQUATRAN® Model 1 is a new (2006) water vapor transmission rate (WVTR) instrument for measuring the gas permeation rate of ultra-barrier films including those used in the manufacture of Organic Light Emitting Displays (OLED). With this new system it is now possible to measure water vapor transmission rates down to 0.0005 $g/m^2$-day under varying temperature conditions offering a method by which to accurately benchmark material development progress. Please see detailed information at the following MOCON web page: http://www.mocon.com/permeation.info/index.shtml

**Permatran-C ® Model 10:**
Non-destructive carbon dioxide transmission rate analyzer system for testing beverage bottles. It has the ability to test 500 different bottle sizes using different sized capture volumes. Please see detailed information at the following MOCON web page: http://www.mocon.com/permeation.info/index.shtml

**Ox-Tran® Model 2/10:**
The latest cost-effective system for oxygen transmission rate testing of flat films and finished packages. It utilizes a standard calibration-dependent, electrochemical (non-coulometric) oxygen sensor, reliably measures oxygen barrier in a range of 0.1 to 144,000 cc/($m^2$ -day) with precise temperatures and relative humidity. Read the details at: http://www.mocon.com/permeation.info/index.shtml

**Permatran-W® Model 398:**
This simple, low maintenance system conforms to the new ASTM Standard E-398 and produces the accurate and reliable data the industry has come to expect only from MOCON. The low-cost Model 398 is designed for medium to high barriers and allows for two films to be tested independently. Each test cell has its own sensor. Read details at: http://www.mocon.com/permeation.info/index.shtml

**Pac Check ® Model 333:**
It is a triple Gas Analyzer ($O_2$, $CO_2$, and CO) specifically designed for fresh meat packages or other modified atmosphere package. Please visit the following web page: http://www.mocon.com/in/pdf/9.26.05%20Mocon%20Pac%20Check%20333.final.pdf

**Pac Check ® Model 800 Series**
*Pac Check ® Model 840:*
It is the desktop "first of its kind" 3 in 1 to determines leak hole size, percent $0_2$ within the headspace and package volume.

*Pac Check ® Model 820:*
It is the portable "first of its kind" 3 in 1 to determines leak hole size, percent $0_2$ within the headspace and package volume.

For more information regarding Pac Check ® Model 840 and 820, visit the following web page:
http://www.mocon.com/pdf/PC820and%20840forwebsitesmall.pdf