Introduction of EVAL® EVOH for Geosynthetics 2011
Kuraray Company Limited
• Introduction of Kuraray Company

EVAL® EVOH resin
• Properties and Applications

Application Development
• Examples of non-food application development
Kuraray Company Limited

Founded in 1926, Kuraray is headquartered in Tokyo and Osaka. A specialty chemical company conducting business in 40 countries with 6800 employees.
Global EVAL® EVOH Production

35,000T
Pasadena, Texas

24,000T
Antwerp, Belgium

10,000T
Okayama, Japan

4,400T

EVAL Resin Plant

EVAL Film Plant

kuraray
EVAL® EVOH production in the USA

Pasadena, Texas

Manufacturing 35,000 MT of EVAL resins in America
Global EVAL R&D Group Capabilities

- 80 people devoted to development and support of EVAL and barrier technologies
  - Core competency polymer chemistry and polymer processing

EVAL Capabilities

- Analytical support
  - Permeation – Gases and hydrocarbons
  - Analytical Chemistry & Microscopy
  - Physical Characterization of polymers

- Pilot facilities
  - Coextrusion Cast Film & Sheet, Co-Injection, Blowmolding and Sheet manufacturing
  - Downstream converting, forming, sealing

- Training & Support
  - Timely support and troubleshooting of process/product issues
  - Training for manufacturing or development teams
What is EVOH?

A random co-polymer of …

Polyethylene (PE)

*Extrudes and orients easily*

\[ -(CH_2 \cdot CH_2)_m - \]

Polyvinyl Alcohol (PVA)

*Provides Gas Barrier*

\[ -(CH_2 \cdot CH)_n \quad | \quad OH \]

\[ -(CH_2 - CH_2)_m - (CH_2 - CH)_n \quad | \quad OH \]

Ethylene Vinyl Alcohol
Key properties of EVOH

**Gas Barrier** (O₂, CO₂, etc)

- Abuse resistance
- Extrudable
- Recyclability
- Oil resistance
- Solvent Barrier
- Hydrocarbon Barrier
- Odor Barrier

**EVOH PROPERTIES**
Effect of mol% on properties of EVOH

Better:
- Water vapour barrier
- Flexibility

EVOH is a random copolymer of Ethylene and Vinyl Alcohol

- Better O₂ barrier
- Better solvent barrier
Effect of mol% on oxygen barrier

OTR cc.mil/100 sq. in./day.atm

Mol% Ethylene

Barrier of EVOH at 1 mil  cc.mil /100 in.2 day.atm at 20°C and 65% RH
## Gas Barrier Property

### Oxygen Transmission Rate of Films

<table>
<thead>
<tr>
<th>Polyolefin</th>
<th>Oxygen Transmission at 20°C, 65%RH</th>
</tr>
</thead>
<tbody>
<tr>
<td>EVOH - 32 mol%</td>
<td>0.4</td>
</tr>
<tr>
<td>EVOH – 44 mol%</td>
<td>0.8</td>
</tr>
<tr>
<td>PVDC copolymer (Extrusion Grade)</td>
<td>2.6</td>
</tr>
<tr>
<td>Nylon</td>
<td>38.0</td>
</tr>
<tr>
<td>PET</td>
<td>54.0</td>
</tr>
<tr>
<td>HDPE</td>
<td>2300.0</td>
</tr>
<tr>
<td>C-PP</td>
<td>3000.0</td>
</tr>
<tr>
<td>PC</td>
<td>5000.0</td>
</tr>
<tr>
<td>LDPE</td>
<td>10000.0</td>
</tr>
<tr>
<td>EVA</td>
<td>18000.0</td>
</tr>
</tbody>
</table>

Unit: cc・20μm / m²・day・atm
EVOH oxygen barrier

Oxygen Transmission Rate of Films

Unit: cc·20μm / m²·day·atm
## EVOH vs. HDPE Gas Barrier Properties

<table>
<thead>
<tr>
<th>Gas</th>
<th>EVOH*</th>
<th>HDPE**</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td>0.019</td>
<td>190</td>
</tr>
<tr>
<td>Oxygen</td>
<td>0.25</td>
<td>2300</td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>0.6</td>
<td>17526</td>
</tr>
<tr>
<td>Sulfur Dioxide</td>
<td>0.3</td>
<td>21844</td>
</tr>
<tr>
<td>Methane</td>
<td>0.4</td>
<td>2845</td>
</tr>
</tbody>
</table>

Volumetric permeation rate in (cc.20µ/m².day.atm)
Conditions: 23°C – 0% RH (ASTM D1434T)
* ASTM D1434 at Kuraray lab – 32mol% EVOH
**Permeability Properties of Plastics and Elastomers, Massey, 2nd Edition
A common measure of solubility is the solubility parameter (a numerical value)
- It is derived from the cohesive energy density of the solvent which is in turn derived from the heat of vaporization

One of the simplest and most convenient relative measures of solubility is the Hildebrand solubility parameter.

The solubility parameter of a polymer is more difficult to predict but in many cases the combined Hildebrand parameter is used with success to predict the interaction of solvent and solute

The basic concept of solubility parameters is “like dissolves like” and that a comparison of solubility parameters can be used as a predictor of chemical resistance and barrier properties.
Solubility parameters – solvents vs polymers

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Solubility Parameter δ(SI) [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>dichloromethane</td>
<td>20.3</td>
</tr>
<tr>
<td>1,2 dichlorethane</td>
<td>20.0</td>
</tr>
<tr>
<td>trichloroethylene</td>
<td>19.0</td>
</tr>
<tr>
<td>benzene</td>
<td>18.7</td>
</tr>
<tr>
<td>toluene</td>
<td>18.2</td>
</tr>
<tr>
<td>ethyl benzene</td>
<td>18.0</td>
</tr>
<tr>
<td>m-xylene</td>
<td>18.0</td>
</tr>
<tr>
<td>water</td>
<td>47.9</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Solubility Parameter δ(SI) [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polypropylene</td>
<td>16.2</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>16.4</td>
</tr>
<tr>
<td>Polyvinylchloride</td>
<td>19.6</td>
</tr>
<tr>
<td>Polyurethane</td>
<td>20.5</td>
</tr>
<tr>
<td>Nylon 6</td>
<td>26.0</td>
</tr>
<tr>
<td>Nylon 66</td>
<td>27.8</td>
</tr>
<tr>
<td>EVOH (32mol%)</td>
<td>38.9</td>
</tr>
</tbody>
</table>

Solubility parameters predict that EVOH will have excellent resistance to majority of hydrocarbons and VOC solvents.

Moisture barrier of EVOH is lower than polyethylene due to affinity to water.
EVOH vs HDPE – solvent resistance

Diffusion coefficient $D_g$ of solvents in EVOH and HDPE

<table>
<thead>
<tr>
<th>Solvent</th>
<th>EVOH *</th>
<th>HDPE**</th>
</tr>
</thead>
<tbody>
<tr>
<td>trichloroethyelene</td>
<td>$3.1 \times 10^{-17}$</td>
<td>$4.0 \times 10^{-13}$</td>
</tr>
<tr>
<td>toluene</td>
<td>$3.1 \times 10^{-17}$</td>
<td>$3.0 \times 10^{-13}$</td>
</tr>
</tbody>
</table>

Diffusion coefficient $D_g$ in m²/s
*Kiwa NV report April 2008 for EVAL Europe N.V
** Sangam and Rowe, Migration of dilute aqueous organic pollutants through a HDPE geomembrane, Geotextiles and Geomembranes 19 (2001) 329-357

Wide ranging studies of solvent resistance (weight gain, retention of physical properties etc) established excellent performance of EVOH for automotive and ag-chemical applications
Example of EVOH solvent barrier...

Reference Fuel C is 50% toluene, 50% iso-octane

<table>
<thead>
<tr>
<th>Fuel Type</th>
<th>Permeation (gms/20μm/sq. m/day) at 40 deg C</th>
</tr>
</thead>
<tbody>
<tr>
<td>EVOH (32mol%)</td>
<td>3224</td>
</tr>
<tr>
<td>Nylon 6</td>
<td>0.23</td>
</tr>
<tr>
<td>HDPE</td>
<td>0.014</td>
</tr>
</tbody>
</table>

REF Fuel C
Applications

EVOH is typically used as a discrete layer in a coextrusion or composite. 5~10% of total thickness will be EVOH.
EVOH Application – Food Packaging

EVOH used in food packaging since 1986

Gas barrier properties of EVOH allow replacement of metal foil and glass with lightweight packaging, with shelf life of 30 days to 18 months.
EVOH Application – Nike Airsoles

Nike switched from SF6 to nitrogen in 2000

TPU/EVOH airsole was the only solution to meet barrier and physical performance requirements

Pressure retention of 20psi nitrogen for > 3 years
• One of the major applications for EVOH is in auto-motive fuel systems to control emissions of hydro-carbons from fuel lines and tanks.

• The use of EVOH in a coextrusion blowmolded tank with high molecular weight HDPE (HMWPE) originated in the United States in response to mandates of VOC emission reductions by the US Environmental Protection Agency (EPA) and the California Air Resources Board (CARB).

• The EVOH barrier PFT has now been in widespread use for fifteen years in more than 100 million vehicles with zero failures
  – Following adoption in the US, the same coextrusion technology spread geographically to Europe, Latin America and is now entering China and India.
**EVOH Application Automotive Plastic Fuel Tanks**

- Development started in 1989 in response to CARB and EPA mandates.

- Emissions regulations have progressively become tighter each decade.

- EVOH became barrier of choice due to VOC barrier properties:
  - Emissions through tank shell are <10mg/24hrs

<table>
<thead>
<tr>
<th>Regulation-Agency</th>
<th>Allowable Emissions*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tier 1 - EPA</td>
<td>2000mg/test 3 day diurnal</td>
</tr>
<tr>
<td>LEV 1 - CARB</td>
<td>2000mg/test 3 day diurnal</td>
</tr>
<tr>
<td>LEV 2 - CARB</td>
<td>500mg/test 3 day diurnal</td>
</tr>
<tr>
<td>PZEV - CARB</td>
<td>350mg/test 3 day diurnal</td>
</tr>
</tbody>
</table>

Allowable emissions from entire vehicle over service life (100,000 to 150,000 miles)
EVOH vs HDPE VOC barrier

Mass flux of solvent in gm.20 microns/m².day at 40° C and 65%RH
Pesticides and herbicides with xylene or toluene solvents are packaged in ag-chem bottles with EVOH inner layer to prevent HDPE from dissolving.

**Xylene Storage Test (50°C, 20 days)**

<table>
<thead>
<tr>
<th>Condition</th>
<th>Result (0.04%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monolayer</td>
<td>0.0%</td>
</tr>
<tr>
<td>Fluorination Level 1</td>
<td>1.3% 33X</td>
</tr>
<tr>
<td>Fluorination Level 3</td>
<td>0.8% 20X</td>
</tr>
<tr>
<td>Fluorination Level 5</td>
<td>0.4% 10X</td>
</tr>
<tr>
<td>Co-ex 4-layer</td>
<td>0.04%</td>
</tr>
</tbody>
</table>

Conditions: CFR 49.173.24 Appendix B, 1L bottles, HDPE/Regrind/Tie/EVAL F101(in), 100% Xylene, 50°C, n = 3, 20 day, explosion proof oven storage test.

EVOH in use in this application since 1987.
EVOH Application Underfloor heating pipe

EVOH in under floor and district heating pipe systems.

EVOH allows PEX pipe to comply with DIN4726 for \(<0.32\text{mg/m}^2\) at 40°C and replace metal piping.

Physical tests of pipe include ageing for 2000hrs in 100°C water, 200hrs in air oven before tensile testing.

EVAL EVOH certified for 50 year service life in EU at high temperature (up to 95°C water).
Drinking Water Pipe
HDPE/EVAL™ coextrusion for piping through VOC contaminated soil

Since the early 1980’s a growing number of permeation accidents have been reported in Europe. These were mostly caused by the permeation of VOC’s and organic solvents into the piping system. In particular, plastic pipes near gasoline stations, dry cleaners and industrial areas have proved to be a potential threat to drinking water quality.

This contamination risk can be minimized by the incorporation of an EVAL™ barrier layer into the drinking water piping system. Multilayer plastic drinking water pipes with a specific EVAL™ grade can be considered as CLASS I pipes for light polluted ground as validated by an accredited institute.”

EVOH piping is in test at Kiwa
Fumigants are used for the commercial production of fruits, vegetables, trees and flowers.

Methyl bromide (MB) is the most efficient fumigant – but MB is an ozone depleting substance and is being regulated out of use.

MB alternatives pose both acute and chronic health effects on field workers and are also regulated.
Benefit of EVAL in Fumigation Films

TIF = EVAL barrier film

85% Reduction

87 - 92%

Figure 2. Field trial design for measuring fumigant emission rates in strawberry fields. Sampling inside the fields as well as surrounding the fields will be identical for the four fields.
Target B&C Membrane applications

Heap leach mining liner

Land fill liners

Oil sand mining liner

Radon and vapor barrier and concrete liners

VaporBlock Plus is a trademark product of Raven Industries
Radon & vapor barrier liners

Radon Barrier
- Radioactive gas formed from decay of Radium 86
- Benefit of radon barrier
  - Health & safety
    - Reduce incidence of lung cancer (21,000 deaths per year)
  - Economic
    - Eliminate expensive remediation costs of remodeling or venting

Potential & Indoor detection
<table>
<thead>
<tr>
<th>Zone</th>
<th>High</th>
<th>&gt; 4 pCi/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zone 1</td>
<td>moderate</td>
<td>2 - 4 pCi/L</td>
</tr>
<tr>
<td>Zone 3</td>
<td>low</td>
<td>&lt; 2 pCi/L</td>
</tr>
</tbody>
</table>

EPA Map of Radon Zones
Radon and vapor intrusion

Vapor intrusion or VI is defined as the migration of volatile chemicals in building spaces from groundwater of soil. The chemicals of primary concern are benzene, ethyl benzene, toluene and xylene (BTEX) or chlorinated solvents such as trichloroethylene (TCE) or perchloroethylene (PERC).

Chronic effects of long term exposure to very low levels of these chemicals motivated the EPA to issue guidelines for limits on vapor intrusion in 2002 to 2005, which are now being acted upon by states, with California, Colorado, Wisconsin, New York and New Jersey being the most active.

Action level for remediation or mitigation based on VI is often very low, typically being the level of a volatile chemical with a one in a million chance of causing cancer over a 20 year period (translates to 1 μg/m3 for toluene in indoor air).

The ITRC is a coalition of state environmental regulators working with federal partners, industry, and stakeholders to advance innovative environmental decision making.
Addition of EVOH to geomembrane liner would improve VOC and hydrocarbon barrier of primary or secondary liner.
Use of barrier geomembranes with EVOH would improve barrier to hydrocarbons and reduce potential for ground water contamination.
Concept for coextrusion for select geomembrane applications

Polyethylene or other polyolefin

Adhesive

EVOH

Polyethylene or other polyolefin
Estimate of reduction in mass flux of toluene by including EVOH in geomembrane

Toluene concentration 2mg/L (2ppm). Service temperature 40°C

Model geomembrane 1500 μm (60 mil) with 3% EVOH (45 μm)
Conclusion

• Existing monolithic geomembranes comprised of polypropylene, polyethylene and polyvinylchloride are excellent hydraulic and heavy metal barriers.
  – These materials are NOT good barriers for volatile organic compounds migrating by diffusion

• The inclusion of EVOH by coextrusion into select geomembrane designs would significantly minimize diffusive migration of VOC’s
  – Offers a cost effective alternative to expensive remediation of contaminated sites

• A High Barrier Geomembrane (HBGM) with EVOH offers potential for significantly improved protection of soil and water quality.