Ethylene vinyl alcohol copolymer (EVOH) as a functional barrier against surrogate components migrating from recycled paperboard packaging

Presented by:
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EVAL Europe nv - Kuraray
Hasselt University

Overview

- Mineral oil migration
- How can we prevent mineral oil migration?
- Experimental evaluation of mineral oil barriers
- Conclusions
Overview

- Mineral oil migration
  - What are mineral oils?
  - Sources of mineral oil contamination
  - Regulation
- How can we prevent mineral oil migration?
- Experimental evaluation of mineral oil barriers
- Conclusions

What are mineral oils?

“Mineral oils” or “Mineral oil products”
Crude oil fraction: C\textsubscript{10} – C\textsubscript{50}

- MOSH
  - n-alkanes
  - branched alkanes
  - Bio-accumulate
  + micro-granulomas in liver, spleen nodes and other tissues

- MOAH
  - containing a benzene ring
  - Potentially mutagenic and carcinogenic

EFSA Panel on Contaminants in the Food Chain (CONTAM), 2012, EFSA Journal, vol. 10, no. 6
Weber et al., 2018, Analytical Chemistry Insights, vol. 13, pp. 1-16
Sources of mineral oil contamination

- Recycled paper
- Additives
- Machine oils
- Pesticides
- Environment
- Naturally occurring

Recycled paperboard = Major source of contamination

EFSA Panel on Contaminants in the Food Chain (CONTAM), 2012, EFSA Journal, vol. 10, no. 6
Sources of mineral oil contamination

- Highest migration potential: \( \text{C}_{16} - \text{C}_{24} \)
- At ambient temperature migration substantial \(<\text{C}_{24}\)
  and noticeable \(<\text{C}_{28}\)
- 60-80\% of \(<\text{C}_{24}\) fraction transferred into food
- 10-20\% of this fraction = MOAH
- Migration >>> ADI = 0.01 mg/kg body weight per day → 0.6 mg/kg food

Lorenzini et al., 2010, Food Additives & Contaminants: Part A, vol. 27, no. 12, pp. 1765-1774
Vollmer et al., 2010, European Food Research & Technology, vol. 232, no. 1, pp. 175-182

Recommendation: “Foods packed into recycled paperboard should be protected by a functional barrier.”

No EU Regulation yet

“Bedarfsgegenständeverordnung”: Recycled paper- & cardboard not in contact with food unless appropriate measures are taken. For instance by means of a barrier layer.

4th Draft Ordinance: Functional barrier mandatory for recycled paper- & cardboard. Focus only on MOAH: SML ≤ 0.5 mg/kg food
Overview

- Mineral oil migration
- How can we prevent mineral oil migration?
  - Functional barriers
  - EVOH as a solution
- Experimental evaluation of mineral oil barriers
- Conclusions

How can we prevent migration of mineral oils?

Migration into food over time

- Specific migration limit (SML)
- Maximum migration in food

Integrate functional barrier!

Max. migration < SML

Shelf life < Breakthrough time

Time
Integrate functional barrier into the primary packaging

EVAL™ EVOH is a functional barrier

Random copolymer, combining the strengths of

- More ethylene
- Thermoplastic
- Hydrophobic
- Flexible

- Less ethylene
- Higher barrier
- More RH sensitive

• Already widely used for paper based and full plastic consumer packaging
  • Resistance to flex-crack and pinholes in folding, processing and transport
  • Oxygen barrier (extended shelf life)
  • Aroma barrier
  • Grease barrier
Overview

- Mineral oil migration
- How can we prevent mineral oil migration?
- Experimental evaluation of mineral oil barriers
  - Dynamic Accumulation Method (Donor-Receptor)
  - Online Permeation Method (GC)
- Conclusions

Methods

**Dynamic Accumulation Method**
Developed by Kantonales Labor Zürich
Switzerland

- Donor
- EVOH
- Receptor

> Concentration changes over time

In cooperation with
Hasselt University & SQTS

**Online Permeation Method**
Developed by Fraunhofer IVV
Germany

- Donor
- EVOH
- Sweep gas

Permeation continuously monitored

References:
Principle of Dynamic Accumulation Method

1. Prepare testpack: donor – barrier – receptor
2. Analyse receptor at periodic intervals
3. Breakthrough in receptor < 1% of initial concentration = good barrier
4. Prepare donor: spike paperboard with known components & concentration
5. Analyse donor for initial concentration

OVEN at 50°C → Accelerate test

“Schweizerisches Verpackungsinstitut SVI Guideline 05_2015_Internal bags”

Test Packs

Receptor is completely sealed inside of barrier film

## Surrogate components

<table>
<thead>
<tr>
<th>Name</th>
<th>Abbrev.</th>
<th>Structure</th>
<th>Simulant for</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-methyl benzophenone (1)</td>
<td>MBP</td>
<td><img src="image1.png" alt="MBP" /></td>
<td>Photo-initiator</td>
</tr>
<tr>
<td>di-n-propyl phthalate (1)</td>
<td>DPP</td>
<td><img src="image2.png" alt="DPP" /></td>
<td>Plasticiser</td>
</tr>
<tr>
<td>n-heptadecane (1)</td>
<td>C17</td>
<td><img src="image3.png" alt="C17" /></td>
<td>MOSH</td>
</tr>
<tr>
<td>perylene (2)</td>
<td>PER</td>
<td><img src="image4.png" alt="PER" /></td>
<td>MOAH</td>
</tr>
<tr>
<td>anthracene (2)</td>
<td>ANT</td>
<td><img src="image5.png" alt="ANT" /></td>
<td>MOAH</td>
</tr>
</tbody>
</table>

(2) Schweizerisches Verpackungsinstitut SVI Guideline 01.2015 Internal bags
(2) Additional components added for this study

## Samples

<table>
<thead>
<tr>
<th>Barrier</th>
<th>Mol-% ethylene</th>
<th>Average layer distribution [µm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>EVAL™ L171B</td>
<td>27</td>
<td>22/5/3/5/21</td>
</tr>
<tr>
<td>EVAL™ F171B</td>
<td>32</td>
<td>21/5/3/5/20</td>
</tr>
<tr>
<td>EVAL™ F171B</td>
<td>32</td>
<td>21/4/5/5/20</td>
</tr>
<tr>
<td>PA6/6.6</td>
<td>/</td>
<td>20/5/3/4/18</td>
</tr>
<tr>
<td>PET</td>
<td>/</td>
<td>12</td>
</tr>
</tbody>
</table>

Films extruded on Dr. Collin 5-layer blown film pilot line
Layer distribution determined by microscopic analysis
O₂GTR determined on MOCON OXTRAN® 2/21 (ASTM F1927)
### Samples

<table>
<thead>
<tr>
<th>Barrier</th>
<th>Mol-% ethylene</th>
<th>Average layer distribution LDPE/tie/Barrier/tie/LDPE [µm]</th>
<th>O₂GTR @ 20°C, 65% RH [cm³/(m².day.atm)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>EVAL™ L171B</td>
<td>27</td>
<td>22/5/3/5/21</td>
<td>0.7</td>
</tr>
<tr>
<td>EVAL™ F171B</td>
<td>32</td>
<td>21/5/3/5/20</td>
<td>1.7</td>
</tr>
<tr>
<td>EVAL™ F171B</td>
<td>32</td>
<td>21/4/5/5/20</td>
<td>0.7</td>
</tr>
<tr>
<td>PA6/6.6</td>
<td>/</td>
<td>20/5/3/4/18</td>
<td>479</td>
</tr>
<tr>
<td>OPET</td>
<td>/</td>
<td>/</td>
<td>91</td>
</tr>
</tbody>
</table>

Films extruded on Dr. Collin 5-layer blown film pilot line
Layer distribution determined by microscopic analysis
O₂GTR determined on MOCON OXTRAN® 2/21 (ASTM F1927)

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### Breakthrough at 50°C – Hasselt University

- **Functional barrier**: if <1% at end of shelf life
- **Shelf life of 2 years at 25°C**

- **Breakthrough after 2 months at 50°C**

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19 Caroline Maes, EVAL Europe nv – Kuraray & Hasselt University – Functional Barrier against Mineral Oils- 17th TAPPI European PLACE Conference 2019 Porto - Session 11 - Paper 1

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Breakthrough at 50°C – SQTS independent lab

Breakthrough after 2 months at 50°C

Shell life of 2 years at 25°C

Conclusion of Dynamic Accumulation Method

Discrepancy between tests

Nevertheless, it can be concluded that EVOH is a good barrier in both tests
**Methods**

**Dynamic Accumulation Method**  
Developed by Kantonales Labor Zürich  
Switzerland

- Donor  
- EVOH  
- Receptor  

Concentration changes over time

**Online Permeation Method**  
Developed by Fraunhofer IVV  
Germany

- Donor  
- EVOH  
- Sweep gas  

Permeation continuously monitored

*In cooperation with Fraunhofer IVV*

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**Principle of the Online Permeation Method**

1. **OVEN at 40°C** → Accelerate test
2. **Spike paperboard** with known components & concentration
3. **Place donor in cell compartment with EVOH on top**
4. **Permeation curve as a function of time**
5. **Pre-trap + Enrichment unit**
6. **GC-FID**
7. **N₂ sweeps** top compartment

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Caroline Maes. EVAL Europe nv – Kuraray & Hasselt University – Functional Barrier against Mineral Oils- 17th TAPPI European PLACE Conference 2019 Porto - Session 11 - Paper 1
Surrogate components and Samples

- Photo-initiators
- MOAH

Processing aid

- MOSH
- EVOH32 (5µm)
- EVOH27 (3µm)
- OPET (12µm)
- EVOH32 (3µm)
- PA6/6.6 (3µm)

- DL < 0.002 µg/dm²·day
- DL < 0.003 µg/dm²·day (processing aid)

Permeation of components – EVOH32 (5 µm)

- Photo-initiators
- ≤ 0.004

Processing aid

- MOAH
- Below DL

- MOSH
- EVOH32 (5µm)
- EVOH27 (3µm)
- OPET (12µm)
- EVOH32 (3µm)
- PA6/6.6 (3µm)

- 0.006-0.007
- 0.005-0.006

- DL < 0.002 µg/dm²·day
- DL < 0.003 µg/dm²·day (processing aid)
Permeation of components – EVOH32 (3 µm)

Photo-initiators

0.002-0.004

MOSH

0.006

0.005-0.006

All below DL

MOAH

Processing aid

Below DL

EVOH32 (5µm) EVOH27 (3µm) OPET (12µm)

EVOH32 (3µm) PA6/6.6 (3µm)

DL < 0.002 µg/dm²·day
DL < 0.003 µg/dm²·day (processing aid)

Permeation of components – EVOH27 (3 µm)

Photo-initiators

≤ 0.003

MOSH

0.007-0.008

0.006

≤ 0.003

≤ 0.003

Below DL

MOAH

Processing aid

Below DL

EVOH32 (5µm) EVOH27 (3µm) OPET (12µm)

EVOH32 (3µm) PA6/6.6 (3µm)

DL < 0.002 µg/dm²·day
DL < 0.003 µg/dm²·day (processing aid)
### Permeation of components – PA6/6.6 (3 µm)

<table>
<thead>
<tr>
<th>Component</th>
<th>Value (µg/dm²·day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photo-initiators</td>
<td>0.002-0.004</td>
</tr>
<tr>
<td>MOAH</td>
<td>0.055-0.098</td>
</tr>
<tr>
<td>Processing aid</td>
<td>Below DL</td>
</tr>
</tbody>
</table>

### Permeation of components – OPET (12 µm)

<table>
<thead>
<tr>
<th>Component</th>
<th>Value (µg/dm²·day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photo-initiators</td>
<td>All below DL</td>
</tr>
<tr>
<td>MOAH</td>
<td>All below DL</td>
</tr>
<tr>
<td>Processing aid</td>
<td>Below DL</td>
</tr>
</tbody>
</table>

**DL values:**
- DL < 0.002 µg/dm²·day
- DL < 0.003 µg/dm²·day (processing aid)
### Comparative data of laminated PET (7.6 µm) - Fraunhofer

<table>
<thead>
<tr>
<th>Photo-initiators</th>
<th>MOSH</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Photo-initiators" /></td>
<td><img src="image2" alt="MOSH" /></td>
</tr>
</tbody>
</table>

PET 7.6 µm/laminating adhesive 9.0 µm/
HDPE co-extruded film 18.0 µm, 8.2 µm, 8.8 µm/
sealing wax 6.6 µm


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### Overview

- **Mineral oil migration**
  - What are mineral oils?
  - Sources of mineral oil contamination
  - Regulation
- **How can we prevent mineral oil migration?**
  - Functional barriers
  - EVOH as a solution
- **Experimental evaluation of mineral oil barriers**
- **Conclusions**
Conclusions

EVOH = Multifunctional solution
for protecting food products which need additional barrier functions
(e.g. oxygen sensitive, fatty or aromatic foods)

And this study also proves
EVOH = an excellent barrier against mineral oils
and other contaminants

Thank you for your attention!

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