Aluminum oxide barrier coatings on polymeric substrates

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Peter Kelly, Chris Liauw

‘Barrier Technologies’ – CCR NIChe Workshop
Outline

- Introduction
- Objective
- Results
  - Barrier performance
  - Surface topography (DIC, SEM, AFM)
  - Coating thickness (TEM)
  - Coating to substrate adhesion
  - Surface energy of AlO$_x$ coating
- Summary and conclusions
AIO$_x$ coating process – Reactive thermal evaporation

Industrial ‘boat type’ R2R metallizer

- Standard high speed coating equipment
- Modified for AIO$_x$ deposition by oxygen injection
- Production of AIO$_x$ barrier coatings at low cost
$\text{AlO}_x$ coating process

- Evaporator Temperature: 1450°C
- Wire Feed System
- Oxygen Injection
- Gas Bar
- Clear Barrier
- OD Beam
Why ceramic clear barrier coatings?

Advantages over polymer based transparent barrier films (PVdC, EVOH)
- No barrier loss at high RH (e.g. for EVOH)
- Thickness in nm-range (PVdC/EVOH µm-range)
- Economical benefits (raw material consumption & cost)
- Recyclable as single layer material

Advantages over metallized polymer films
- Product visibility
- Microwaveability, Retortability
- Suitable for metal detectors
Objective

- Food packaging application of AlO$_x$ coated polymer films

- Aims:
  - Barrier performance of AlO$_x$ coated films comparable to metallized films
  - Replacement of traditional clear barrier films (polymer based with PVdC & EVOH)

<table>
<thead>
<tr>
<th>Film, description</th>
<th>Film, description</th>
<th>OTR* cm$^3$/m$^2$ d</th>
<th>WVTR** g/(m$^2$ d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BOPP, 20 µm</td>
<td>Plain</td>
<td>2000 – 2500</td>
<td>4 – 7</td>
</tr>
<tr>
<td>EVOH coextruded barrier film$^1$ (29 µm)</td>
<td>1 – 1.5</td>
<td>4.5</td>
<td></td>
</tr>
<tr>
<td>PVdC coated$^1$ (26 µm)</td>
<td>20</td>
<td>4.2</td>
<td></td>
</tr>
<tr>
<td>Metallized 2.2 OD</td>
<td>≤ 100</td>
<td>≤ 1</td>
<td></td>
</tr>
<tr>
<td>PET, 12 µm</td>
<td>Plain</td>
<td>100 – 150</td>
<td>40 – 50</td>
</tr>
<tr>
<td>Metallized 2.2 OD</td>
<td>≤ 2</td>
<td>≤ 1</td>
<td></td>
</tr>
</tbody>
</table>

$^1$ ‘Development of new BOPP Barrier Films by Coextrusion and Simultaneous Biaxial Orientation’
Brueckner Maschinenbau GmbH, Siegsdorf, Germany, Dr. M. Wolf, Dr. J. Breil, Dipl.-Ing. R. Lund

*OTR 23 °C, 50 % RH
**WVTR 37.8 °C, 90 % RH
### Barrier performance of $\text{AlO}_x$ coated films

- **$\text{AlO}_x$ on PET** ➔ Reliable barrier properties: OTR $< 1 \text{ cm}^3/(\text{m}^2 \text{ d})$
  
  WVTR $< 1 \text{ g/(m}^2 \text{ d)}$

- **$\text{AlO}_x$ on BOPP** ➔ Variation of barrier properties depending on substrate

<table>
<thead>
<tr>
<th>BOPP film</th>
<th>Plain</th>
<th>$\text{AlO}_x$ coated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>OTR*</td>
<td>WVTR**</td>
</tr>
<tr>
<td></td>
<td>cm$^3/(\text{m}^2 \text{ d})$</td>
<td>g/(m$^2$ d)</td>
</tr>
<tr>
<td>BOPP A, 30 µm</td>
<td>$\approx 1600$</td>
<td>$\approx 4.0$</td>
</tr>
<tr>
<td>BOPP B, 15 µm</td>
<td>$\approx 2700$</td>
<td>$\approx 7.0$</td>
</tr>
<tr>
<td>BOPP C, 20 µm</td>
<td>$\approx 2400$</td>
<td>$\approx 6.0$</td>
</tr>
<tr>
<td>BOPP D*, 18 µm</td>
<td>$\approx 500$</td>
<td>$\approx 4.5$</td>
</tr>
</tbody>
</table>

*Film supplied by Brückner Maschinenbau GmbH & Co.KG, Siegsdorf, Germany

*OTR 23 °C, 50 % RH
**WVTR 37.8 °C, 90 % RH
### Barrier performance – Effect of plasma treatment (BOPP C)

- Standard packaging grade BOPP film
- Corona treated
- 20 µm thickness
- 3 layer structure

**Corona treated skin layer**
- Heatsealable skin layer
- Homopolymer core

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<table>
<thead>
<tr>
<th>Trial</th>
<th>Plasma treatment</th>
<th>OTR* cm³/(m² d)</th>
<th>BIF</th>
<th>WVTR** g/(m² d)</th>
<th>BIF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plain film</td>
<td>-</td>
<td>≈ 2400</td>
<td>-</td>
<td>≈ 6</td>
<td>-</td>
</tr>
<tr>
<td>1</td>
<td>No</td>
<td>47.00 ± 5.35</td>
<td>51</td>
<td>5.89 ± 0.23</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>PRE</td>
<td>35.33 ± 3.05</td>
<td>68</td>
<td>6.08 ± 0.17</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>PRE + POST</td>
<td>25.35 ± 1.38</td>
<td>95</td>
<td>4.73 ± 0.07</td>
<td>1.3</td>
</tr>
</tbody>
</table>

*COTR 23 °C, 50 % RH **WVTR 37.8 °C, 90 % RH

→ Clear improvement of OTR with pre- and post-treatment
Barrier performance – Effect of plasma treatment (BOPP D)

- Special skin layer
- 18 µm thickness
- 5 layer structure

### Film supplied by Brückner Maschinenbau GmbH & Co.KG, Siegsdorf, Germany

### Table: Barrier performance

<table>
<thead>
<tr>
<th>Trial</th>
<th>Plasma treatment</th>
<th>OTR* cm³/(m² d)</th>
<th>WVTR** g/(m² d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plain film</td>
<td>-</td>
<td>≈ 500</td>
<td>≈ 4.5</td>
</tr>
<tr>
<td>1</td>
<td>No</td>
<td>0.89 ± 0.01</td>
<td>2.18 ± 0.07</td>
</tr>
<tr>
<td>2</td>
<td>PRE</td>
<td>0.83 ± 0.30</td>
<td>0.62 ± 0.07</td>
</tr>
<tr>
<td>3</td>
<td>PRE + POST</td>
<td>0.60 ± 0.14</td>
<td>0.55 ± 0.25</td>
</tr>
</tbody>
</table>

*OTR 23 °C, 50 % RH **WVTR 37.8 °C, 90 % RH

Clear improvement of WVTR with pre-treatment

Image supplied by Brückner Maschinenbau GmbH & Co.KG, Siegsdorf, Germany
DIC analysis of plain BOPP films

- Differential interference contrast light microscopy
- 3D presentation of surface topography
- Antiblock (AB) particle size and distribution density in film surface

**BOPP A**
- Many small ABs, fewer large ABs

**BOPP B**
- Many small ABs, fewer large ABs

**BOPP C**
- Substantially larger ABs

**BOPP D**
- No ABs

*Film supplied by Brückner Maschinenbau GmbH & Co.KG, Siegsdorf, Germany*
SEM analysis of BOPP films

- Scanning electron microscopy
- No conductive layer applied to avoid masking of surface details
- Low acceleration voltage of 0.4/0.5 kV
- ‘Grainy’ surface structure for BOPP (‘orange-peel’)

BOPP A

BOPP B

BOPP C

→ Surface defects ‘dimples’ on BOPP A
SEM analysis of AlO$_x$ coated BOPP films

- AlO$_x$ coating reproduces plain film surface topography

- AlO$_x$ coating on BOPP A shows pores and growth/thickness irregularities

- Assumption: Pores in AlO$_x$ on BOPP A cause high OTR
AFM analysis of plain and AlO$_x$ coated films

- Atomic force microscopy
- Confirms SEM results
- AlO$_x$ coating reproduces plain film surface topography
- 5 x 5 µm$^2$ scans for plain BOPP films

**BOPP A**
RMS 4.1

**BOPP B**
RMS 5.7

**BOPP C**
RMS 4.1

**BOPP D**
RMS 2.8

→ Surface defects on BOPP A

*Film supplied by Brückner Maschinenbau GmbH & Co.KG, Siegsdorf, Germany*
## AFM analysis – Roughness data

<table>
<thead>
<tr>
<th>Film</th>
<th>Plasma treatment</th>
<th>Root mean square nm</th>
<th>Roughness average nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>BOPP A</td>
<td>Plain film</td>
<td>4.1 ± 0.7</td>
<td>3.3 ± 0.5</td>
</tr>
<tr>
<td>OTR 150 - 200</td>
<td>PRE</td>
<td>3.8 ± 0.5</td>
<td>3.0 ± 0.4</td>
</tr>
<tr>
<td>BOPP B</td>
<td>Plain film</td>
<td>5.7 ± 1.8</td>
<td>4.5 ± 1.5</td>
</tr>
<tr>
<td>OTR ≤ 100</td>
<td>PRE</td>
<td>5.8 ± 0.9</td>
<td>4.6 ± 0.7</td>
</tr>
<tr>
<td></td>
<td>PRE + POST</td>
<td>6.0 ± 0.7</td>
<td>4.8 ± 0.6</td>
</tr>
<tr>
<td>BOPP C</td>
<td>Plain film</td>
<td>4.1 ± 0.3</td>
<td>3.2 ± 0.2</td>
</tr>
<tr>
<td>OTR ≤ 50</td>
<td>PRE</td>
<td>4.6 ± 0.2</td>
<td>3.6 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>PRE + POST</td>
<td>4.3 ± 0.3</td>
<td>3.4 ± 0.2</td>
</tr>
<tr>
<td>BOPP D*</td>
<td>Plain film</td>
<td>2.8 ± 0.2</td>
<td>2.2 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>PRE</td>
<td>2.9 ± 0.2</td>
<td>2.3 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>PRE + POST</td>
<td>3.0 ± 0.2</td>
<td>2.4 ± 0.1</td>
</tr>
<tr>
<td>PET</td>
<td>Plain film</td>
<td>1.6 ± 0.2</td>
<td>1.2 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>PRE + POST</td>
<td>1.8 ± 0.3</td>
<td>1.4 ± 0.3</td>
</tr>
</tbody>
</table>

- **Tapping mode and pulsed force mode AFM**
- **Calculated from 5 x 5 µm² scans**

→ Plain and AlOₓ coated films show similar surface roughness

*Film supplied by Brückner Maschinenbau GmbH & Co.KG, Siegsdorf, Germany*
TEM analysis – $\text{AlO}_x$ coating thickness

- Transmission electron microscopy
- Analysis of various $\text{AlO}_x$ coated film samples
- TEM clearly reveals the common three layer structure of BOPP film
- $\text{AlO}_x$ thickness in the range of 9 to 11 nm
**ALO$_x$ adhesion – Peel test**

- ‘EAA peel test for metal adhesion’ on ALO$_x$ coated BOPP
- Peel tests possible as coating removal visible

<table>
<thead>
<tr>
<th>Film</th>
<th>Plasma treatment</th>
<th>Peel force (N/(15 mm), g/inch)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BOPP A</td>
<td>PRE A</td>
<td>3.88 ± 0.09, 669 ± 15</td>
</tr>
<tr>
<td>OTR 150 – 200</td>
<td>PRE B</td>
<td>3.68 ± 0.14, 635 ± 24</td>
</tr>
<tr>
<td>BOPP B</td>
<td>No</td>
<td>3.46 ± 0.08, 597 ± 14</td>
</tr>
<tr>
<td>OTR ≤ 100</td>
<td>PRE</td>
<td>3.51 ± 0.10, 606 ± 18</td>
</tr>
<tr>
<td></td>
<td>PRE + POST</td>
<td>3.50 ± 0.16, 604 ± 27</td>
</tr>
<tr>
<td>BOPP C</td>
<td>No</td>
<td>5.05 ± 0.17, 871 ± 29</td>
</tr>
<tr>
<td>OTR ≤ 50</td>
<td>PRE</td>
<td>5.07 ± 0.12, 875 ± 22</td>
</tr>
<tr>
<td></td>
<td>PRE + POST</td>
<td>5.04 ± 0.14, 869 ± 23</td>
</tr>
<tr>
<td><strong>Metallized, PRE</strong></td>
<td></td>
<td><strong>1.09 ± 0.11, 189 ± 19</strong></td>
</tr>
</tbody>
</table>

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**Diagram**

- EAA-film
- Coated film
- Metal plate
- Peel direction
- Peel-off angle 180°
- Coating layer on EAA-film
- Double-sided adhesive tape
- EMA (European Metallizers Association) test procedure for metal adhesion (seal test)
**AIOₓ adhesion – Peel test**

- Very high peel forces obtained (a lot higher than for metallized BOPP)
- Peel force independent of pre-treatment
- Material peeled outside sealed area

→ Analysis of peeled EAA via infra red spectroscopy (ATR FTIR) to identify polymer

→ IR spectrum shows EAA and PP peaks
→ Parts of BOPP film (skin layer) peeled off
AlO$_x$ surface energy – Change with storage time

- Drop of surface energy with storage time
- Drop of polar part of surface energy
- Drop due to contact of AlO$_x$ with low surface energy BOPP (reverse side of film)
- Transfer of polymeric material

*Film supplied by Brückner Maschinenbau GmbH & Co.KG, Siegsdorf, Germany
Barrier performance - Acrylate top coat

- Flash evaporation of monomer liquid
- Condensing liquid film conceals surface features of substrate
- Crosslinking via curing (electron beam radiation) → solid film
- Approx. 1 µm acrylate thickness
- Off-line top coat

<table>
<thead>
<tr>
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<th>WVTR** g/(m² d)</th>
<th>BIF</th>
</tr>
</thead>
<tbody>
<tr>
<td>BOPP B</td>
<td>plain</td>
<td>≈ 2700</td>
<td>-</td>
<td>≈ 7</td>
</tr>
<tr>
<td></td>
<td>AIOₓ</td>
<td>85.56 ± 16.80</td>
<td>5.89 ± 0.18</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>AIOₓ + acrylate</td>
<td>2.05 ± 0.44</td>
<td>3.88 ± 0.16</td>
<td>1.8</td>
</tr>
<tr>
<td>BOPP C</td>
<td>plain</td>
<td>≈ 2400</td>
<td>-</td>
<td>≈ 6</td>
</tr>
<tr>
<td></td>
<td>AIOₓ</td>
<td>25.35 ± 1.38</td>
<td>4.73 ± 0.07</td>
<td>1.3</td>
</tr>
<tr>
<td></td>
<td>AIOₓ + acrylate</td>
<td>1.89 ± 0.31</td>
<td>0.40 ± 0.01</td>
<td>15</td>
</tr>
</tbody>
</table>

*OTR 23 °C, 50 % RH  **WVTR 37.8 °C, 90% RH

Acrylate coating conducted by Sigma Technologies Int'l, LLC, Tuscon AZ, USA
Summary and conclusions

- Approx. 10 nm thin $\text{AlO}_x$ barrier coating deposited onto film substrates
- While film surface defects affect barrier, roughness appears to have less impact
- $\text{AlO}_x$ adhesion to the BOPP film is stronger than the intrinsic strength of the BOPP film
- $\text{AlO}_x$ coated BOPP like metallized BOPP has a high dyne level which diminishes over time
- Special polymer skin layers and acrylate top coats significantly improve barrier properties of $\text{AlO}_x$ coated BOPP films
Acknowledgements

- Brückner Maschinenbau GmbH & Co.KG, Siegsdorf, Germany (film supply)

- Innovia Films, Wigton, United Kingdom (access to analytical equipment)

- Fraunhofer Institute for Process Engineering and Packaging IVV, Freising, Germany (access to AFM)

- Sigma Technologies Int'l, LLC, Tuscon AZ, USA (acrylate coating)

- Dr. Charles A. Bishop, CAB Consulting Ltd.
Thank You

Any questions?