Introduction to Micro and Nano-Layering LLDPE with Cyclic Olefin Copolymers (COC)

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Outline

- What is COC & Its Value Propositions?
- What is Micro & Nanolayer Extrusion?

Experimental:
- Film Structures & Materials
- Capillary Rheology
- AFM (Atomic Force Microscopy)

- 80/20 LLDPE-(A&B)/COC // 20/80 LLDPE-B/COC
  - AFM Image Analysis
  - Mechanical Property Analysis

- Conclusions
What is COC & Its Value Propositions?
Cyclic Olefin Copolymer: Synthesis & Structure

- Readily available raw materials
- Highly efficient catalyst
  - Low usage
  - Catalyst removed as part of process
  - High purity product
- Amorphous
- Crystal clear

\[
\text{Ethylene} + \text{Cyclopentadiene (C}_5\text{H}_6) + \text{Norbornene} \rightarrow \text{Cyclic Olefin Copolymer (COC)}
\]
COC molecule is a chain of small CH$_2$-CH$_2$ links randomly interspersed with large bridged ring elements.

It cannot fold up to make a regular structure, i.e., a crystallite.

COC has no crystalline melting point, but only a glass transition temperature, $T_g$, at which the polymer goes from “glassy” to “rubbery” behavior.
Packaging with Cyclic Olefin Copolymers (COC)

Value Propositions

- Stiffness & Strength
- Thermoformability
- Transparency & Gloss
- Temperature Resistance
- Barrier – Water, Alcohol, Acid, Nitrogen, Helium

- Chemical Resistance
- Sustainability
- Low Adsorption
- Low Orientation Stress
- Heat Sealing
Why Study COC Micro & Nano-Layering?

- COC has unique features and properties:
  - COC is amorphous
  - COC is a polyolefin, compatible with LLDPE, LDPE & HDPE
  - COC offers more heat resistance

- Enable more efficient use of COC:
  - Mechanical properties improve significantly
  - Monolayer blend → single discrete → 2 split layers → more?
  - Improve film economics

- Reduce low COC ductility influence in PE films
  - Enable stronger and tougher films

- Discover something new and unexpected
What is Micro- & Nanolayer Extrusion?
Micro & Nano-Layer Process Sketch

Two extruded layers enter multiplier units. Multiplier unit splits flow into two streams; recombining them into higher ordered multilayer structure.

# Film Structures & Materials

**LLDPE**
- **A**: 0.917 g/cc; 2.7 dg/min (190°C, 2.16 kg); hexene.
- **B**: 0.935 g/cc; 2.5 dg/min (190°C, 2.16 kg); octene.

**COC** (Tg=78°C): 1.01 g/cc; 1.8 dg/min (190°C, 2.16 kg); norbornene.

<table>
<thead>
<tr>
<th>Film Structures</th>
<th>LLDPE Rich</th>
<th>Total Layers</th>
<th>COC Layers ({(Total Layers-1)/2})</th>
<th>LLDPE Layers</th>
<th>Total Layers</th>
<th>{(Total Layers-1)/2}</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>LLDPE Controls</strong></td>
<td>1</td>
<td>0</td>
<td></td>
<td></td>
<td>1</td>
<td>1</td>
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<tr>
<td><strong>LLDPE-A/COC</strong></td>
<td>3</td>
<td>1</td>
<td>1</td>
<td></td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td><strong>LLDPE-B/COC</strong></td>
<td>5</td>
<td>2</td>
<td>2</td>
<td></td>
<td>5</td>
<td>2</td>
</tr>
<tr>
<td><strong>(80/20, v/v)</strong></td>
<td>9</td>
<td>4</td>
<td>4</td>
<td></td>
<td>9</td>
<td>4</td>
</tr>
<tr>
<td><strong>Thickness: 50-µm</strong></td>
<td>33</td>
<td>16</td>
<td>16</td>
<td></td>
<td>33</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>129</td>
<td>64</td>
<td>64</td>
<td></td>
<td>129</td>
<td>64</td>
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<tr>
<td></td>
<td>513</td>
<td>128</td>
<td>128</td>
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<td>513</td>
<td>128</td>
</tr>
<tr>
<td></td>
<td>2049</td>
<td>1014</td>
<td>1014</td>
<td></td>
<td>2049</td>
<td>1014</td>
</tr>
</tbody>
</table>

**Notes:**
- LLDPE-A: 0.917 g/cc; 2.7 dg/min (190°C, 2.16 kg); hexene.
- LLDPE-B: 0.935 g/cc; 2.5 dg/min (190°C, 2.16 kg); octene.
- COC (Tg=78°C): 1.01 g/cc; 1.8 dg/min (190°C, 2.16 kg); norbornene.
LLDPE-B shows closer viscosity match to COC than LLDPE-A. Process temperatures in layer replicating units were 200 - 210°C.
Sample Preparation for AFM Imaging

Cut sample from the center of the film.
View layer structure in MD direction.
Embed film in epoxy and microtome at -120 °C.
Microtommed sample section was imaged in tapping mode AFM.
Multiple AFM images were taken to view entire film cross-section.

Several images, usually between 4-10, are stitched together to form a composite image of the full cross-section.

Determination of layer thickness and distribution:
- For lower layer count structures thickness for up to 128 individual layers are measured.
- For higher layer count structures thickness for groups of about 200 layers are measured.
80/20 LLDPE-A & -B/COC

AFM Images & Mechanical Properties
AFM: 3-Layer 80/20 LLDPE-A &-B/COC

LLDPE layers appear darker than COC layer.
Thickness of the imaged section LLDPE-A/COC & LLDPE-B/COC was 38 & 53 µm.
Measured ratio of LLDPE/COC was 79/21.
Rheological property difference between LLDPE-A & COC at processing temperatures led to layer thickness variation. With exception of both outermost COC layers; considerably less layer thickness variation observed for LLDPE-B / COC.
Top: 5 µm section on each side of the film was not imaged. 40+ distinct layers of COC and 40+ distinct layers of LLDPE could be seen in the imaged section. Layer integrity appears better in the middle layers.

Bottom: film showed good layer structure and low thickness variation. Measured composition from thicknesses was 77/23. Thinner layers are challenging to measure as the modulus difference becomes indistinguishable for AFM imaging.
**AFM: 513-Layer 80/20 LLDPE-A & B/COC**

**Top:** Occasional droplet like structures formed due to partial layer break-up of very thin layers. Although there is significant viscosity mismatch, COC was coextruded down to few tens of nanometer.

**Bottom:** Layer differentiation was difficult due to low contrast between the layers. Film contained continuous layers, with possible partial layer break-up. Dark arrows represent COC layers.

<table>
<thead>
<tr>
<th></th>
<th>Target</th>
<th>Measured</th>
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<tbody>
<tr>
<td>LLDPE-A (nm)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>150</td>
<td>80-200</td>
<td></td>
</tr>
<tr>
<td>COC (nm)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>30-70</td>
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<thead>
<tr>
<th></th>
<th>Target</th>
<th>Measured</th>
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</thead>
<tbody>
<tr>
<td>LLDPE-B (nm)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>160</td>
<td>150-200</td>
<td></td>
</tr>
<tr>
<td>COC (nm)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>30-50</td>
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</tbody>
</table>
2% Secant Modulus vs. Film Layers: 80/20 LLDPE-A & LLDPE-B/COC

Significant difference observed between LLDPE grades.
Splitting COC into multiple layers has modest positive influence on modulus.
Benefit retained across many layers.

LLDPE-A:
- COC significantly improves stiffness.
- Splitting COC layers has minor positive influence on modulus.
- TD variation

LLDPE-B:
- Splitting COC layers has more influence on modulus vs. LLDPE-A.
- TD variation
Stress at Yield vs. Film Layers: 80/20 LLDPE-A & LLDPE-B/COC

Significant difference observed between LLDPE grades.
Splitting COC into multiple layers has minimal influence on stress at yield.

LLDPE-A:
- COC significantly improves stress at yield.
- Splitting COC layers has minimal influence on stress at yield.
- TD variation

LLDPE-B:
- Much higher stress at yield vs. LLDPE-A.
- TD variation
Stress at Break vs. Film Layers:
80/20 LLDPE-A & LLDPE-B/COC

Significant difference observed between LLDPE grades. Splitting COC into multiple layers has strong positive influence on stress at break, enabled by more strain hardening.

LLDPE-A:
- COC significantly improves stress at break.
- Splitting COC layers has strong positive influence on stress at break.
- TD variation

LLDPE-B:
- Splitting COC layers modestly improves stress at break.
- TD variation
Splitting COC layers helps restore film ductility. Significant EOB difference observed between LLDPE grades.

**LLDPE-A:**
- <10 layers, recovery in film ductility occurs from splitting COC layers.

**LLDPE-B:**
- Film ductility gradual recovers from splitting COC layers.
- Better viscosity match
Tensile Energy (TE) Film Layers: 80/20 LLDPE-A & LLDPE-B/COC

**LLDPE-A:**
- 10-100 layers: splitting COC layers “recovers” (TE) toward pure LLDPE-A

**LLDPE-B:**
- 10-100 layers: modest increase in (TE) occurs from splitting COC layers.

Significant difference observed between LLDPE grades. Splitting COC into multiple layers enables better durability!
Total Haze vs. Film Layers: 80/20 LLDPE-A & LLDPE-B/COC

**LLDPE-A:**
- >10 layers, sharp increase in total haze occurs from splitting COC layers.
- Better viscosity match!

**LLDPE-B:**
- <10 layers, significant haze minimization occurs from splitting COC layers.

Viscosity match between LLDPE & COC in the replication die is essential to maintain layer distinction, especially above 100 layers. Significant difference observed between LLDPE grades.
80/20 & 20/80 LLDPE-B/COC
AFM Images & Mechanical Properties
Both films have good layer stability and minimal layer thickness variation. Measured layer ratios are 19/81 and 78/22 respectively, close to targets.
**Top:** 126+ layers were imaged. Leftmost layer could not be imaged due to significant delamination between epoxy-LLDPE interface. Overall, the film showed good layer structure and periodicity. No layer break-up was observed.

**Bottom:** film showed good layer structure and low thickness variation. Measured composition from thicknesses was 77/23. Thinner layers are challenging to measure as the modulus difference becomes indistinguishable for AFM imaging.

**Table:**

<table>
<thead>
<tr>
<th>Layer</th>
<th>Target (nm)</th>
<th>Measured (nm)</th>
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<tbody>
<tr>
<td>20/80</td>
<td>625</td>
<td>550±60</td>
</tr>
<tr>
<td>COC</td>
<td>160</td>
<td>140±25</td>
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<tr>
<td>LLDPE</td>
<td></td>
<td></td>
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<tr>
<td>COC</td>
<td>625</td>
<td>620±110</td>
</tr>
<tr>
<td>LLDPE</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
**AFM: 513-Layer 20/80 & 80/20 LLDPE-B/COC**

**Top:** Layer differentiation was difficult due to low contrast between the layers. Film contained continuous layer in the imaged section. Black arrows represent 30-50 nm LLDPE layers.

**Bottom:** Film contained continuous layers, with possible partial layer break-up. Dark arrows represent 30-50 nm COC layers.

<table>
<thead>
<tr>
<th>Layer</th>
<th>COC (nm)</th>
<th>LLDPE (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>20/80</strong></td>
<td>Target: 160, Measured: 150-200</td>
<td></td>
</tr>
<tr>
<td><strong>80/20</strong></td>
<td>Target: 40, Measured: 30-50</td>
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</tr>
</tbody>
</table>
2% Secant Modulus vs. Film Layers: 80/20 & 20/80 COC with LLDPE-B

LLDPE Rich 80/20:
- COC improves stiffness of LLDPE.
- Modulus improves slightly by splitting into <100 layers.
- Layer splitting does not compromise modulus.

COC Rich 20/80:
- Very high modulus.
- More variation above >100 layers due to onset LLDPE layer break-up.

20% COC enhances LLDPE film stiffness by factor of 2-3 times. <100 layers, splitting does not compromise modulus.
Stress at Yield vs. Film Layers:
80/20 & 20/80 COC with LLDPE-B

20% COC enhances LLDPE film yield stress, but at the expense of yield strain.
20% LLDPE enables yield point in COC film, but by slightly improving elongation at yield.
Best results achieved by splitting into 129 layers.

LLDPE Rich 80/20:
- COC improves yield stress for LLDPE.
- Modest improvement in MD from splitting COC layers.

COC Rich 20/80:
- Pure COC does not have yield point.
- LLDPE layer splitting enables measurable yield point.
Tensile Energy vs. Film Layers: 80/20 & 20/80 COC with LLDPE-B

LLDPE Rich 80/20:
- Multiple split layers of COC “recovers” film durability, by reducing low ductility & brittleness of COC.

COC Rich 20/80:
- Discrete layers of LLDPE fail to improve durability of COC.

LLDPE films with 20% COC can minimize loss in tensile energy by splitting COC layers.
COC films with 20% LLDPE failed to improve durability. More LLDPE needed.
Total Haze vs. Film Layers: 20/80 & 80/20 COC with LLDPE-B

- Independent of COC/LLDPE-B ratio, total haze minimization occurs by splitting COC layers multiple times.

**COC Rich 20/80:**
- Very low haze at 33 & 133 layers.
- Small contribution from LLDPE-B.

**LLDPE Rich 80/20:**
- <10 layers, COC split layers reduces total haze of LLDPE films.
- >500 layers, onset of layer breakup.
Gloss, 60° vs. Film Layers:
20/80 & 80/20 COC with LLDPE-B

Independent of COC/LLDPE-B ratio, gloss enhancement occurs by splitting COC layers multiple times.

COC Rich 20/80:
- Very high gloss at 33 & 133 layers.
- Enhancement caused by multiple LLDPE layers.

LLDPE Rich 80/20:
- COC enhances gloss of LLDPE films.
- Higher gloss observed in 25 & 50-µm film from COC split layers.
Conclusions
Conclusions (1)

- Stiffness, strength, durability and optics of LLDPE films can be improved by using multiple COC layers.
  - Nearly all beneficial enhancements occur in films with <129 layers.
  - Practically speaking, most benefits occur in films with few split COC layers, which can be accomplished with commercially installed 7-11 layer blown & cast extrusion lines.
- Close LLDPE & COC viscosity matching is critical to maintain good layer stability and low layer thickness variation.
  - Poor viscosity matching contributes to layer non-uniformity & onset of layer breakup.
Conclusions (2)

- Splitting COC layers helps restore film ductility and durability.
- As shown in 513 layer films, COC can be extruded into discrete continuous layers with thickness of about 40 nm. (Technically unexpected)
- Multiple layers of LLDPE did not improve durability of 20/80 LLDPE-B/COC films. However, as many as few dozen LLDPE layers reduced total haze and increase gloss.
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Tim Kneale

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