Enhancement of Appearance, Stiffness, and Toughness of Olefinic Blown Films with Cyclic Olefin Copolymers

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What is COC, Value Propositions & Applications?

- Design of Experiments (DOE)
- Main Effects Plots – Properties
- Discrete vs. Split Layer
- Conclusions
COC Is Amorphous

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.
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

\[
\begin{align*}
\text{H}_2\text{C} & \quad \text{CH}_2 \\
\text{Ethylene} & \quad \text{Cyclopentadiene} & \quad \text{Norbornene} \\
\end{align*}
\]

Metalocene Catalysis

\[
\begin{align*}
\text{H}_2\text{C} & \quad \text{CH}_2 \\
\text{Ethylene} & \quad \text{Cyclopentadiene} & \quad \text{Norbornene} \\
\end{align*}
\]

\[
\text{COC}
\]
### Value Propositions
- Stiffness & Strength
- Thermoformability
- Transparency & Gloss
- Temperature Resistance
- Barrier – WVTR, Alcohol
- Chemical Resistance
- Sustainability
- Low Adsorption
- N₂ Gas Barrier
- Low Orientation Stress
- Heat Sealing

### Applications
- Forming Film & Sheet
- TD & MD Shrink Labels
- Soft Shrink Film
- Heat Sealing Films
- Twist Wrap
- Protective Packaging
- Blister Packaging
- PAN Replacement Film
- Easy Tear
- And More
What is COC, Value Propositions & Applications?

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Design of Experiments (DOE)

- **Study Questions:**
  - How does COC influence blown film properties?
  - How does discrete COC layer influence multilayer film properties?
  - Does COC Tg influence film properties?
  - Does Blow-Up Ratio (BUR) influence film properties?
  - Does diluting COC with PE compromise benefits of using COC?
  - Any benefits to splitting COC into more than one layer?

- **Design Matrix:**
  - 3 x 3 full factorial
  - Three independent variables, three levels:
    - COC Tg: 65, 78 & 110°C
    - BUR: 2.0:1, 2.5:1 & 3.0:1
    - COC Modification: none, 30% LLDPE & 30% E-140
## DOE Matrix & Non-COC Control Films

<table>
<thead>
<tr>
<th>Experiment Number</th>
<th>COC Grade</th>
<th>BUR</th>
<th>COC Modification</th>
<th>Experiment Number</th>
<th>COC Grade</th>
<th>BUR</th>
<th>COC Modification</th>
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<tr>
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<td>2:1</td>
<td>100% 9506F-500</td>
<td>19</td>
<td>7010F-600</td>
<td>2:1</td>
<td>100% 7010F-600</td>
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<tr>
<td>2</td>
<td>9506F-500</td>
<td>2:1</td>
<td>70% 9506F-500 / 30% LLDPE</td>
<td>20</td>
<td>7010F-600</td>
<td>2:1</td>
<td>70% 7010F-600 / 30% E-140</td>
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<td>9506F-500</td>
<td>2:1</td>
<td>70% 9506F-500 / 30% E-140</td>
<td>21</td>
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<td>2:1</td>
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<td>4</td>
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<td>2.5:1</td>
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<td>9506F-500</td>
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<td>3:1</td>
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<td>8007F-600</td>
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<td>100% 8007F-600</td>
<td>28</td>
<td>80% LDPE / 20% LLDPE</td>
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<td>No Modification</td>
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<td>12</td>
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<td>30</td>
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<td>2.5:1</td>
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<td>93% m-h-LLDPE + 7% LDPE</td>
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<td>No Modification</td>
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<td>14</td>
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<td>35</td>
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<td>No Modification</td>
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<td>2.5:1</td>
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<td>36</td>
<td>93% m-h-LLDPE + 7% LDPE</td>
<td>3:1</td>
<td>No Modification</td>
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<td>16</td>
<td>8007F-600</td>
<td>3:1</td>
<td>100% 8007F-600</td>
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<td></td>
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<td>17</td>
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<td>70% 8007F-600 / 30% LLDPE</td>
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<td></td>
<td></td>
<td></td>
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<tr>
<td>18</td>
<td>8007F-600</td>
<td>3:1</td>
<td>70% 8007F-600 / 30% E-140</td>
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<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
• Film structure:
  • 90-micron (3.6-mil)
  • Three layer A-B-A
  • Layer ratio:
    • 40/20/40 ≈ 36/18/36 micron
• COC film composition:
  • A-Layer: 93/7 LLDPE/LDPE
  • B-Layer: COC specified per trial
• Non-COC film composition:
  • Control (90-micron)
    • All layers: 93/7 LLDPE/LDPE
  • Generic (115-micon)
    • All layers: 80/20 LDPE/LLDPE
• Materials (good for appearance)
  • LLDPE: EM Exceed 2018KB
    • C6; 0.918 g/cc; 2.0 dg/min
  • LDPE: Thai PPT 2426H
    • Tubular; 0.924 g/cc; 1.9 dg/min
Extrusion:
- Tomi Machinery Co., Ltd. (Japan)
- Three extruders:
  - 40-mm (1.6-inch) screw diameter
  - 26:1 L/D

Fabrication:
- 106-mm (4.2-inch) die diameter
- 2.5-mm (0.1-inch) die gap
- 25 cm (10-inch) frost line height

Barrel Temperatures:
- A-Layer: zones 1-3: 180°C
- B-Layer: zones 1-3: 210, 200, & 190°C

Total Rate & Specific Output:
- 2.0:1 BUR: 60 lb./hr.; 4.6 lb./hr. die inch
- 2.5:1 BUR: 77 lb./hr.; 5.9 lb./hr. die inch
- 3.0:1 BUR: 91 lb./hr.; 7.0 lb/hr. die inch
What is COC, Value Propositions & Applications?
Design of Experiments (DOE)
*Main Effects Plots – Properties*
Discrete vs. Split Layer
Conclusions
Sandwiching 18-micron discrete COC layer in between two blended LLDPE layers lowers total haze from 10.5 to 7.1 percent, or more than 30 percent reduction in LLDPE film haze.
COC Modification influences internal and surface haze. Discrete layer of COC in LLDPE film significantly reduces internal and surface haze.
Single 18-micron COC layer reduces TD/MD Tear Strength.

COC modification reduces TD/MD Tear Strength.

Unmodified 65°C Tg COC provides highest TD/MD Tear Strength.
COC layer into blended LLDPE film more than doubles TD & MD secant modulus.
COC Modifier modestly reduces TD & MD secant modulus.
Tg and BUR had minimal effect.
COC layer into blended LLDPE film improves impact resistance. COC Modifier and Tg strongly influence impact resistance. Impact resistant films can be made with low Tg COC modified with E-140.
COC layer into blended LLDPE film reduces impact energy. COC Modifier and Tg strongly influence impact energy. Film toughness can be improved with low Tg COC modified with E-140.
COC layer into blended LLDPE film significantly improves TD & MD tensile strength. COC Modifier type and quantity can dilute COC benefit.
COC layer into blended LLDPE film significantly reduces TD & MD elongation at yield.
COC Modifier, Tg and BUR had minimal effect.
COC layer into blended LLDPE film significantly reduces TD & MD tensile at break by limiting LLDPE strain hardening.

COC Modifier and Tg show minor influence.
COC layer into blended LLDPE film significantly reduces TD & MD elongation at break by limiting LLDPE strain hardening. COC Modifier and Tg show minor influence.
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## Single vs. Split Layers: Unmodified COC

### 6-mil Cast Extrusion

<table>
<thead>
<tr>
<th>Property</th>
<th>Unit</th>
<th>1 COC Layer</th>
<th>2 COC Layers</th>
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</thead>
<tbody>
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<td></td>
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<td>40% m-h-LLDPE</td>
<td>31% m-h-LLDPE</td>
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<tr>
<td>Fast Puncture Force</td>
<td>lbf</td>
<td>35.1</td>
<td>34.4</td>
</tr>
<tr>
<td>Fast Puncture Energy</td>
<td>ft-lb</td>
<td>1.1</td>
<td>1.0</td>
</tr>
<tr>
<td>MD Tensile Yield</td>
<td>psi</td>
<td>2,490</td>
<td>2,510</td>
</tr>
<tr>
<td>TD Tensile Yield</td>
<td>psi</td>
<td>2,590</td>
<td>2,480</td>
</tr>
<tr>
<td>MD Elong. @ Yield</td>
<td>%</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>TD Elong. @ Yield</td>
<td>%</td>
<td>8</td>
<td>8</td>
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<tr>
<td>MD Tensile Break</td>
<td>psi</td>
<td>2,930</td>
<td>3,370</td>
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<tr>
<td>TD Tensile Break</td>
<td>psi</td>
<td>3,030</td>
<td>3,530</td>
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<tr>
<td>MD Elong. @ Break</td>
<td>%</td>
<td>330</td>
<td>410</td>
</tr>
<tr>
<td>TD Elong. @ Break</td>
<td>%</td>
<td>330</td>
<td>430</td>
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<tr>
<td>TD Tensile Modulus</td>
<td>psi</td>
<td>140,000</td>
<td>134,000</td>
</tr>
<tr>
<td>MD Tensile Modulus</td>
<td>psi</td>
<td>138,000</td>
<td>139,000</td>
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<tr>
<td>Total Haze</td>
<td>%</td>
<td>38</td>
<td>19</td>
</tr>
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</table>

**COC:** TOPAS 800F-600  
**m-h-LLDPE:** Exceed 3512CB

Splitting 1.2 mil (30.5 µ) COC layer into two 0.6 mil (15.2 µ) layers improves tensile properties, especially ductility, and lowers total haze.

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### Single vs. Split Layers: Modified COC

<table>
<thead>
<tr>
<th>Property</th>
<th>Unit</th>
<th>1 COC Layer</th>
<th>2 COC Layers</th>
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<tr>
<td>Fast Puncture Force</td>
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<td>Fast Puncture Energy</td>
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<td>1,880</td>
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<td>TD Elong. @ Yield</td>
<td>%</td>
<td>12</td>
<td>13</td>
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<tr>
<td>MD Tensile Break</td>
<td>psi</td>
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<td>3,550</td>
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<td>500</td>
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<tr>
<td>TD Elong. @ Break</td>
<td>%</td>
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<td>Total Haze</td>
<td>%</td>
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</table>

COC: TOPAS 70% 9506F-04 + 30% E-140  
m-h-LLDPE: Exceed 3512CB

Splitting 1.2 mil (30.5 µ) COC layer into two 0.6 mil (15.2 µ) layers enables more strain hardening thereby improving tensile break properties and impact resistance.
What is COC, Value Propositions & Applications?
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Conclusions
Conclusions:

- Addition of one or more unmodified discrete COC layers to LLDPE films:
  - Reduces total, surface and internal haze
  - More than doubles secant modulus
  - Modestly improves impact resistance
  - Reduces tear resistance
  - Reduces tensile properties

- Addition of one or more discrete modified COC layers to LLDPE films: (Depends on modifier type, COC Tg & amount)
  - Reduces total, surface and internal haze
  - Reduces tear resistance
  - Increases stiffness
  - Increases impact resistance
    - Can exceed LLDPE!
  - Reduces tensile properties
Conclusions:

- Most mechanical properties were insensitive to changes in BUR between 2:1 and 3:1:
  - Suggests larger BUR are possible
  - Enables bubble stability at larger BUR

- COC Tg
  - Influences film ductility and impact resistance
  - Reduces tear strength

- Splitting COC into at least two discrete layers, unmodified or modified, allows more strain hardening LLDPE, enabling reduction in loss of elongation at break, tensile strength and impact energy.
  - Splitting COC into more than two discrete layers is expected to further reduce these losses!
Acknowledgements

Polyplastics R&D (Japan)
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Adam Barton
Tim Kneale

TOPAS® Cyclic Olefin Copolymer (COC)
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