Bottle and Container Enhancements Using Cyclic Olefin Copolymers

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TOPAS® Cyclic Olefin Copolymer (COC)
Your Clear Advantage
Outline

- Introduction to TOPAS® COC – The Basics
  - Market Segments
  - What is COC?
  - Viscoelastic Properties
  - Chemical Resistance
- Multilayer Extrusion Blow Molding (EBM) with COC
- Reheat ISBM: HDPE-COC
- Conclusions
TOPAS® COC – Market Segments

**Healthcare & Diagnostic**
Cartridges, syringes, vials, drug delivery devices, microplates, microfluidic devices, cuvettes, bio-chips, PCR

**Consumer Electronics**
Mobile light guides, windows, touch screens; lenses, sensors, flat panel displays; antennas

**Packaging and Films**
Food, healthcare, protective and optical films; containers and closures in personal care and consumer markets
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
COC is Amorphous

COC molecule is a chain of small CH₂-CH₂ 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.
Cyclopentadiene (C₅H₆) and norbornene are reacted with ethylene (H₂C = CH₂) under the influence of a metallocene catalyst to form cyclic olefin copolymer (COC). The process uses readily available raw materials, a highly efficient catalyst with low usage, and ensures high purity in the product. The resulting material is amorphous and crystal clear.
TOPAS® COC – Viscoelasticity

Mechanical properties stable up to glass transition temperature

storage elastic modulus

loss elastic modulus
### TOPAS® COC - Chemical Resistance

**Polar organic solvents**
- Ethanol, methanol, butanol, isopropanol, (short chain alcohols)
- Acetone, butanone (short chain ketones)

**Aromatic solvents**
- Benzaldehyde
- Toluene
- Benzene
- Chlorinated Solvents

**Non-polar organic solvents**
- Pentane, hexane, heptane etc. (alkanes)
- Gasoline (petrol ether)
- Norbornene
- Mineral Oil

**Other**
- Oleic Acid

Resistant:
- Increase of weight < 3% or loss of weight < 0.5%, elongation at break not substantially altered

Limited resistance:
- Increase of weight 3-8% or loss of weight 0.5-5%, elongation at break reduced by < 50%

Not resistant:
- Increase of weight > 8% or loss of weight > 5%, elongation at break reduced by > 50%

**TOPAS® COC is resistant to acids, alcohols, bases and polar solvents**
Multilayer Extrusion
Blow Molding (EBM)
Multilayer High Gloss EBM Bottle

Description:
- High shine in cost effective process

Value Proposition:
- Optimize shine
- Structures:
  - 20/ 80 COC / HDPE
  - COC/ HDPE + regrind/ HDPE
- Processing ease
- Environmentally & recycle friendly

TOPAS® Grade:
- 8007F-600

Color depth perception due to high shine
Chemical Resistance for Hair Dye Bottles

- **Description:**
  - Enhance chemical resistance to sustain shelf life

- **Value Proposition:**
  - Chemical Resistance
    - Alcohols & acetone
    - Ammonia, hydrogen peroxide
  - Optimal moisture barrier to extend shelf life
  - No paneling - stiff walls
  - Environmentally & recycle friendly
  - Eliminate post-fluorination

- **TOPAS® Grade:**
  - 8007F-600

Chemical resistance for sustained product life
Keys to Successful EBM with TOPAS® COC

- Preference for Multilayer vs. Monolayer Blends
  - Maintain melt strength
  - Maintain impact strength of HDPE
  - Structures:
    - COC/HDPE; COC/HDPE/COC; COC/HDPE+ recycle/COC

- COC Extrusion Process Guidelines to Eliminate Unmelts
  - Proper screw design is essential:
    - Barrier screw with mixing section
    - > 28:1 L/D
    - > 60 mm diameter
  - Reverse temperature profile (add heat early)
    - Pre-heat COC pellets in dryer
  - Blend COC with 10 – 20 % TOPAS® E-140
  - Lab scale extruders can make COC look bad
  - Polish Bottle Mold if High Gloss is Desired
HDPE-COC
Reheat Injection Stretch Blow Molding (ISBM)
Benefits of HDPE Reheat ISBM vs. HDPE EBM

- Light Weighting
  - Orientation and ordered molecular alignment provides stiffness
  - Reduce container weight by 20 – 40 percent
- Superior Bottle Finish
  - Improve consistency of thread dimensions
  - Improve surface detail
- Improve Aesthetics
  - Reduce haze
  - Increase gloss
- Reduce Waste
  - Less purge & shorter start-up times
  - No flash trim
- Improve Container Performance
  - Eliminate weld lines
  - Reduce pinhole leaks and drop impact failures
- Potential for Very Fast Production Rates
  - > 6X increase in bottles/hour/machine
Annual Sales (2014): 4.6 billion lb.
EBM Bottle Estimate (TAPI): 1.9-2.4 billion lb.
Large untapped market for HDPE reheat ISBM!
Limitations of HDPE for Reheat ISBM

- Deficiency of HDPE in Reheat ISBM Process
  - HDPE *DOES NOT* strain harden
  - Reheat ISBM HDPE bottles are difficult to manufacture, requiring precise temperature control
    - Stretching temperature process window 1–3°C
    - Slower rates and poor yield compromises process economics
  - Good & bad bottles can be made independent of process conditions

[Images of plastic bottles with labels]
PE-COC Strain Hardening – Illustrative Example

Five-Layer (290 µ): PE/COC-78/PE/COC-78/PE (LLDPE)
Layer Ratio: 4/14/64/14/4
Biaxially stretched at 4 x 4 & 6.5 x 6.5 (Bruckner-Karo)
Strain Hardening: Gradual increase in stress during stretching
Why Add COC to HDPE for Reheat ISBM?

- HDPE w/COC **DOES** strain harden
- Strain hardening enables uniform stretching over broad temperatures.
- Improve ISBM process for HDPE bottles w/ COC (“flip a switch”):
  - Broaden stretching temperature process window > 10°C
  - Substantial increase to productivity and yield
### Container Properties

#### Top Load

**Force (lb) at 1.0-inch Deflection**

<table>
<thead>
<tr>
<th></th>
<th>HDPE</th>
<th>HDPE / 10% COC-1</th>
<th>HDPE / 15% COC-1</th>
<th>HDPE / 15% COC-2</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>29.4</strong></td>
<td>23.5</td>
<td>18.3</td>
<td>35.6</td>
<td></td>
</tr>
</tbody>
</table>

#### Material Distribution

**Wall Thickness (mil)**

<table>
<thead>
<tr>
<th>Bottle Height (in)</th>
<th>HDPE</th>
<th>HDPE / 15% COC-2</th>
<th>HDPE / 17% COC-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.00</td>
<td>11</td>
<td>13</td>
<td>15</td>
</tr>
<tr>
<td>6.90</td>
<td>10</td>
<td>13</td>
<td>12</td>
</tr>
<tr>
<td>5.00</td>
<td>13</td>
<td>23</td>
<td>18</td>
</tr>
<tr>
<td>4.10</td>
<td>16</td>
<td>23</td>
<td>21</td>
</tr>
<tr>
<td>2.60</td>
<td>36</td>
<td>18</td>
<td>21</td>
</tr>
<tr>
<td>1.60</td>
<td>22</td>
<td>17</td>
<td>17</td>
</tr>
<tr>
<td>1.00</td>
<td>18</td>
<td>17</td>
<td>15</td>
</tr>
<tr>
<td>0.40</td>
<td>22</td>
<td>21</td>
<td>16</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td>18.5</td>
<td>18.1</td>
<td>16.9</td>
</tr>
<tr>
<td><strong>Standard Deviation</strong></td>
<td>8.4</td>
<td>4.0</td>
<td>3.1</td>
</tr>
</tbody>
</table>

- **COC content & Tg has positive effect on top load & drop impact performance**
- **COC reduces wall thickness variation**

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**Bruceton Staircase Drop Impact Test**

**Mean Failure Height (inch)**

<table>
<thead>
<tr>
<th>Drop Temperature &amp; Orientation</th>
<th>HDPE</th>
<th>HDPE / 10% COC-1</th>
<th>HDPE / 15% COC-1</th>
<th>HDPE / 17% COC-1</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>23ºC Vertical</strong></td>
<td>&gt;96</td>
<td>&gt;96</td>
<td>&gt;96</td>
<td></td>
</tr>
<tr>
<td><strong>4ºC Vertical</strong></td>
<td>&gt;96</td>
<td>&gt;96</td>
<td>&gt;96</td>
<td></td>
</tr>
<tr>
<td><strong>4ºC Horizontal</strong></td>
<td>57</td>
<td>60</td>
<td>51</td>
<td></td>
</tr>
</tbody>
</table>
HDPE-COC Reheat ISBM

- Study Benchmarks
  - Sidel SB01 Blow Molding Machine
  - Rate: 300 – 400 BPH
  - 1-litre, 31-gram container
  - Defects:
    - HDPE ~60%
    - HDPE-COC ~20%

- Further Optimization:
  - Pre-form molding conditions
    - Warmer is preferred
  - Pre-form design
    - Axial and hoop stretch ratios
  - IR heating optimized for PET, not HDPE
  - HDPE responds differently than PET!
Unique properties of COC improves processing and performance of HDPE in blow molding:
- Amorphous
- Heat resistance
- Strength & stiffness
- Low haze & high gloss
- Strain hardening

COC-HDPE for EBM
- High gloss & improved aesthetics
- Chemical resistance

ISBM HDPE w/ COC containers offers four compelling advantages:
- Light weighting (>25% reduction)
- 4X – 6X faster production rates versus EBM
- Improvement in mechanical properties
- Chemical resistance
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