

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

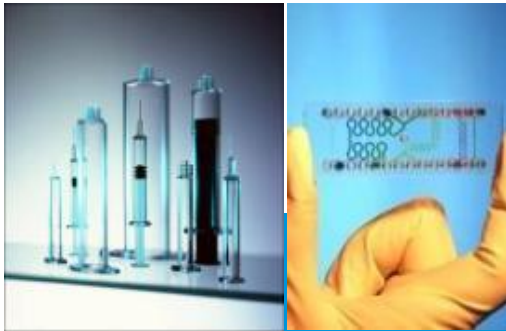
The Basics



TOPAS[®] COC – Market Segments

Healthcare & Diagnostic

Cartridges, syringes, vials, drug delivery devices, microplates, microfluidic devices, cuvettes, bio-chips, PCR



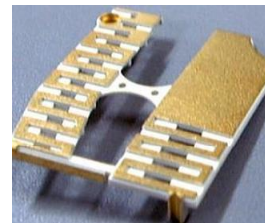
Consumer Electronics

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

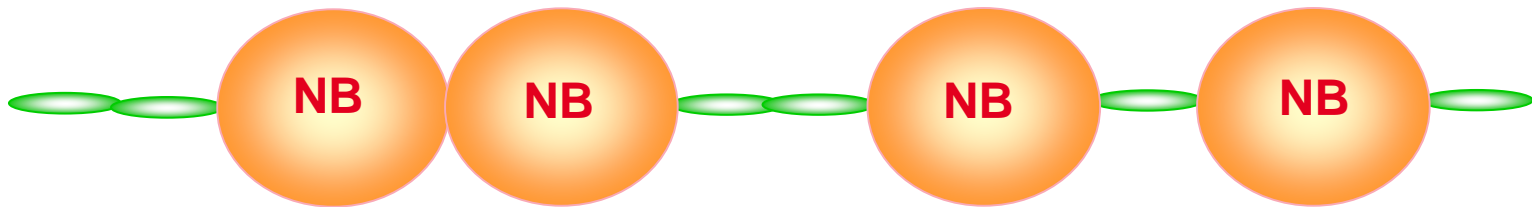
- Stiffness & Strength
- Thermoformability
- Transparency & Gloss
- Temperature Resistance
- Barrier – Water, Alcohol, Acid, Nitrogen, Helium
- Chemical Resistance
- Sustainability
- Low Adsorption
- Low Orientation Stress
- Heat Sealing



COC Is Amorphous

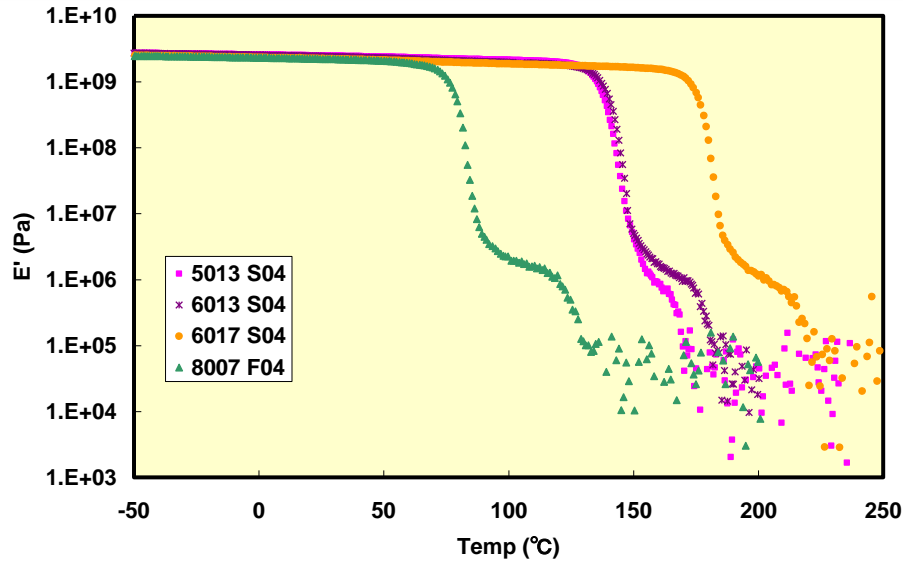
COC molecule is a chain of small $\text{CH}_2\text{-CH}_2$ links randomly interspersed with large bridged ring elements

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



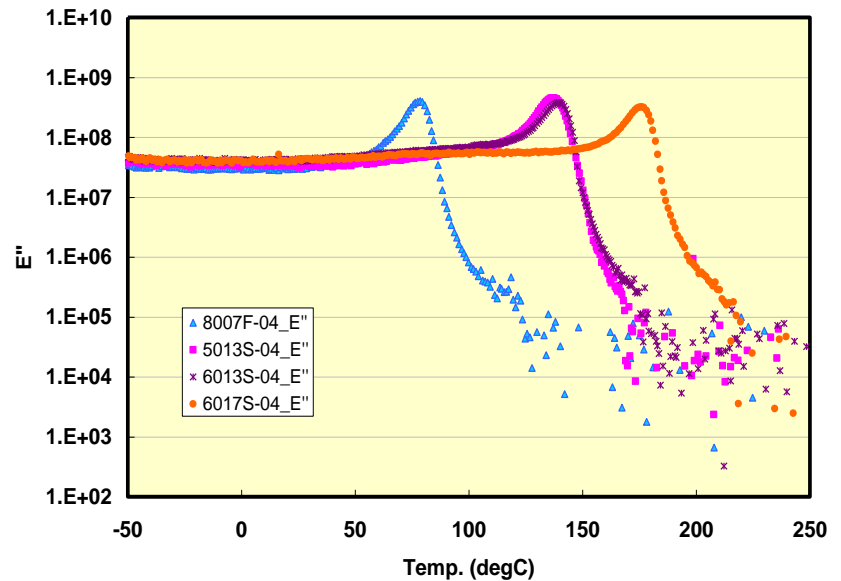
COC has no crystalline melting point, but only a glass transition temperature, T_g , at which the polymer goes from “glassy” to “rubbery” behavior

TOPAS[®] COC – Viscoelasticity























storage elastic modulus




Mechanical properties stable up to glass transition temperature



loss elastic modulus

TOPAS[®] COC - Chemical Resistance

pH < 7 (acidic / aqueous)	pH = 7 (neutral / aqueous)	pH > 7 (basic / aqueous)
hydrochloric acid 36 % 	Water 	sodium hydroxide 50 % 
sulfuric acid 40 % 	Aqueous solution of soap 	ammonia (aq. sol.) 35 % 
nitric acid 65 % 	saline solution 	
acetic acid > 94 % 		
Polar organic solvents	Aromatic solvents	Non-polar organic solvents
ethanol, methanol, butanol, isopropanol, (short chain alcohols) 	Benzaldehyde 	Pentane, hexane, heptane etc. (alkanes) 
Acetone, butanone (short chain ketones) 	Toluene 	Gasoline (petrol ether) 
	Benzene 	Norbornene 
	Chlorinated Solvents 	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

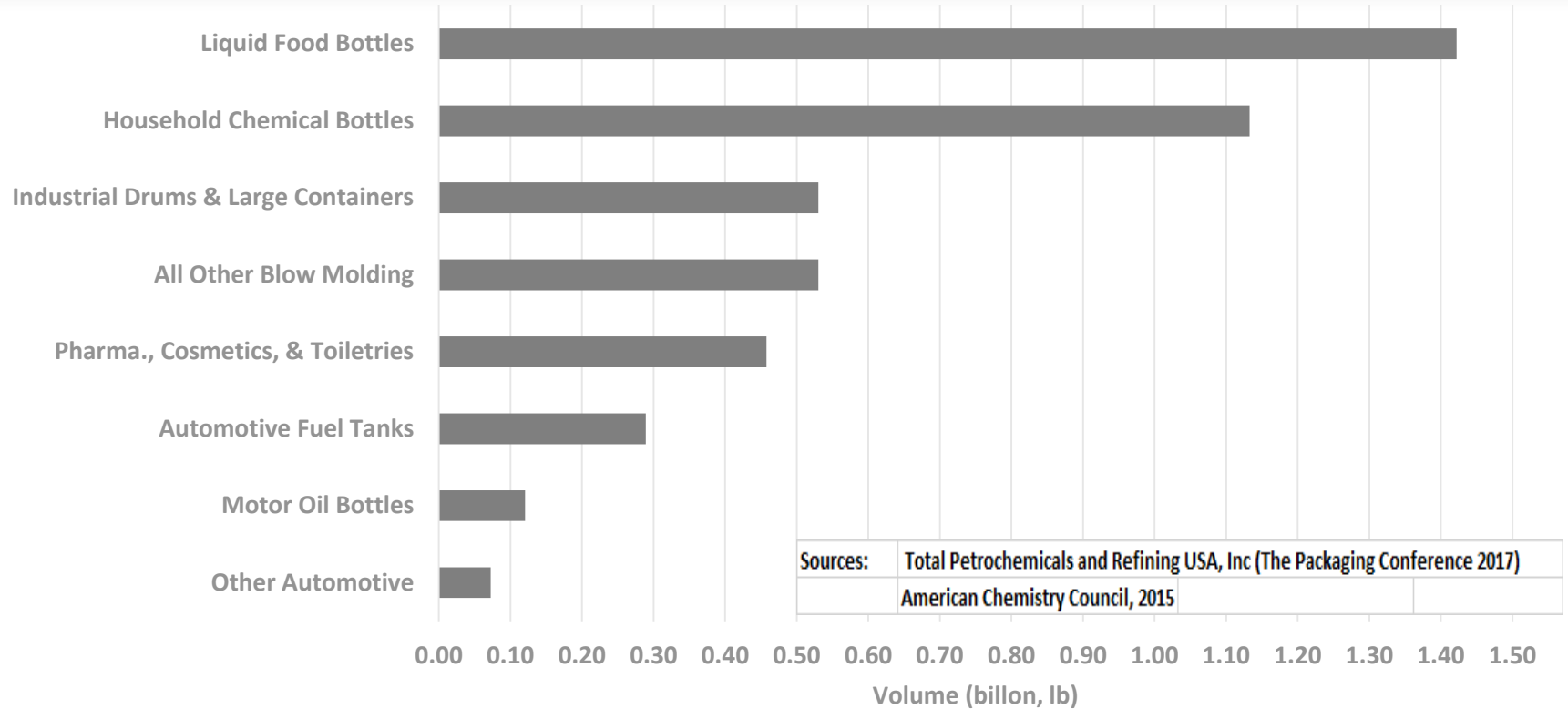
Reheat Injection Stretch Blow Molding (ISBM)



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

Segmentation: NA HDPE Blow Molding Market



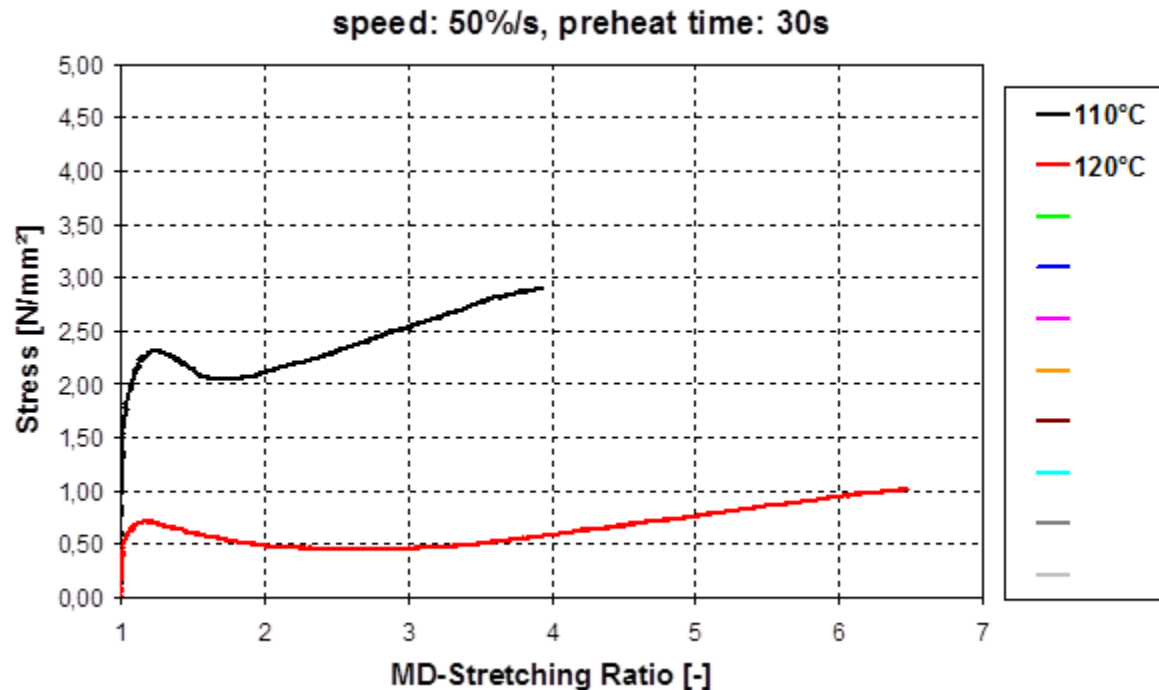
Annual Sales (2014): 4.6 billion lb.
EBM Bottle Estimate (TAPI): 1.9-2.4 billion lb.
Large untapped market for HDPE reheat ISBM!

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



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_f) at 1.0-inch Deflection

HDPE	HDPE / 10% COC-1	HDPE / 15% COC-1	HDPE / 15% COC-2
29.4	23.5	18.3	35.6

Bruceton Staircase Drop Impact Test

Mean Failure Height (inch)

Drop Temperature & Orientation	HDPE	HDPE / 15% COC-2	HDPE / 17% COC-2
23°C Vertical	>96	>96	>96
4°C Vertical	>96	>96	>96
4°C Horizontal	57	60	51

Material Distribution

Wall Thickness (mil)

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

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

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!

Conclusions:

- 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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