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Cyclic Olefin Copolymer (COC) – Valuable Polymeric Modifier for Recyclable & Sustainable PE Packaging Applications

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Outline

- What is COC?
- COC Compatibility with PE
- Unmet Needs for Recyclable & Sustainable PE Packaging:
  - Stiffness Enhancement
  - Mechanical Stability at Elevated Temperatures
- Film Structure Guidelines
- Testing Recyclability:
  - Trex Criteria & Results
  - APR Recycling Study: COC-HDPE Films for Stand-Up Pouch (SUP)
- Conclusions

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What is COC?

COC Compatibility with PE

COC Is Amorphous

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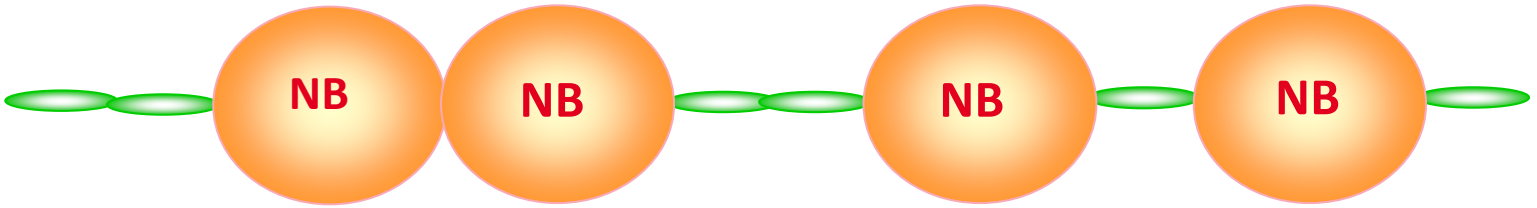
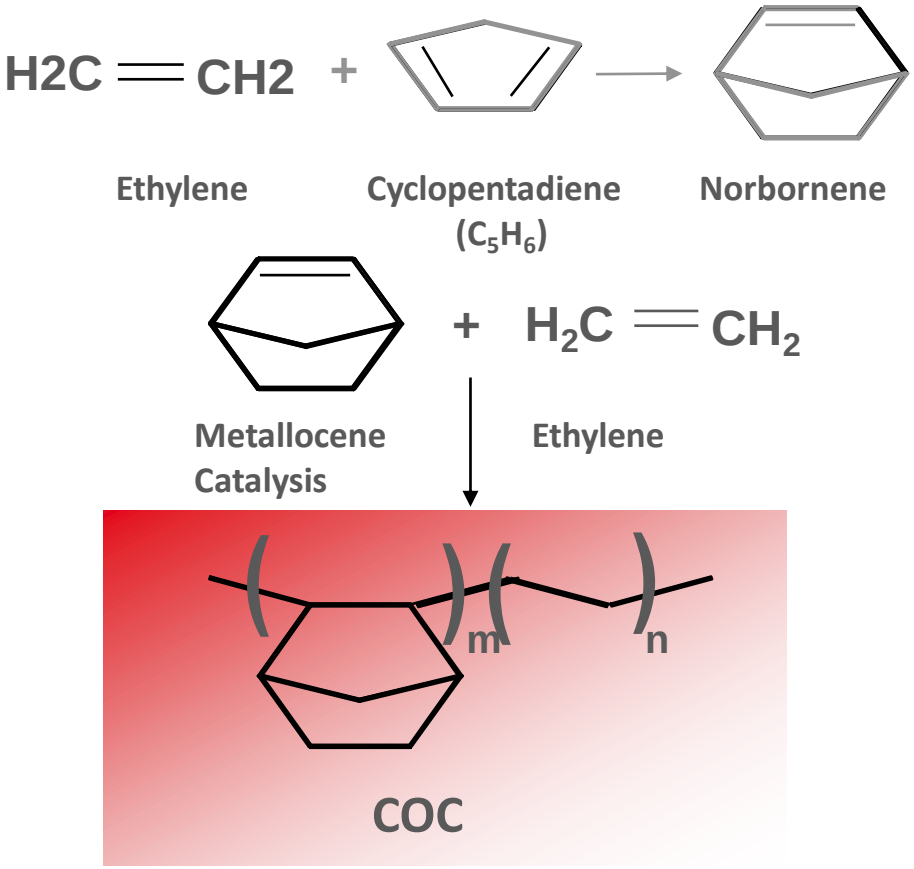
COC molecule is a chain of small CH_2-CH_2 links randomly interspersed with large bridged ring elements

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
- Transparent
  - Rigid bridged-ring structure prevents crystallization

COC Compatibility with PE

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	Cyclic Olefin Copolymer (COC)	Linear Low Density (LLDPE)
1st Co-monomer	Ethylene	Ethylene
2nd Co-monomer	Norbornene	Alpha Olefins (Butene, Hexene, Octene)
Co-monomer Structure	Cyclic	Linear
Polymer Structure	Linear	Linear
Morphology	Amorphous	Semi-crystalline
Catalysts	Metallocene	Metallocene, Single-Site, Ziegler-Natta
Thermal Transition:		
Glass Transition Temp. (^{o}C)	68 - 180	----
Melting Point (^{o}C)	----	120 - 127
Distortion Temperature:		
Vicat (^{o}C)	68 - 178	90 - 120
HDT (^{o}C; 66 psi, 0.46 MPa)	62 - 168	58 - 60
HDT (^{o}C; 264 psi, 1.8 MPa)	57 - 151	38 - 40

COC & LLDPE share similar chemical features.
Consequently, COC is compatible with PE!
COC molecular structure enables higher temperature resistance.

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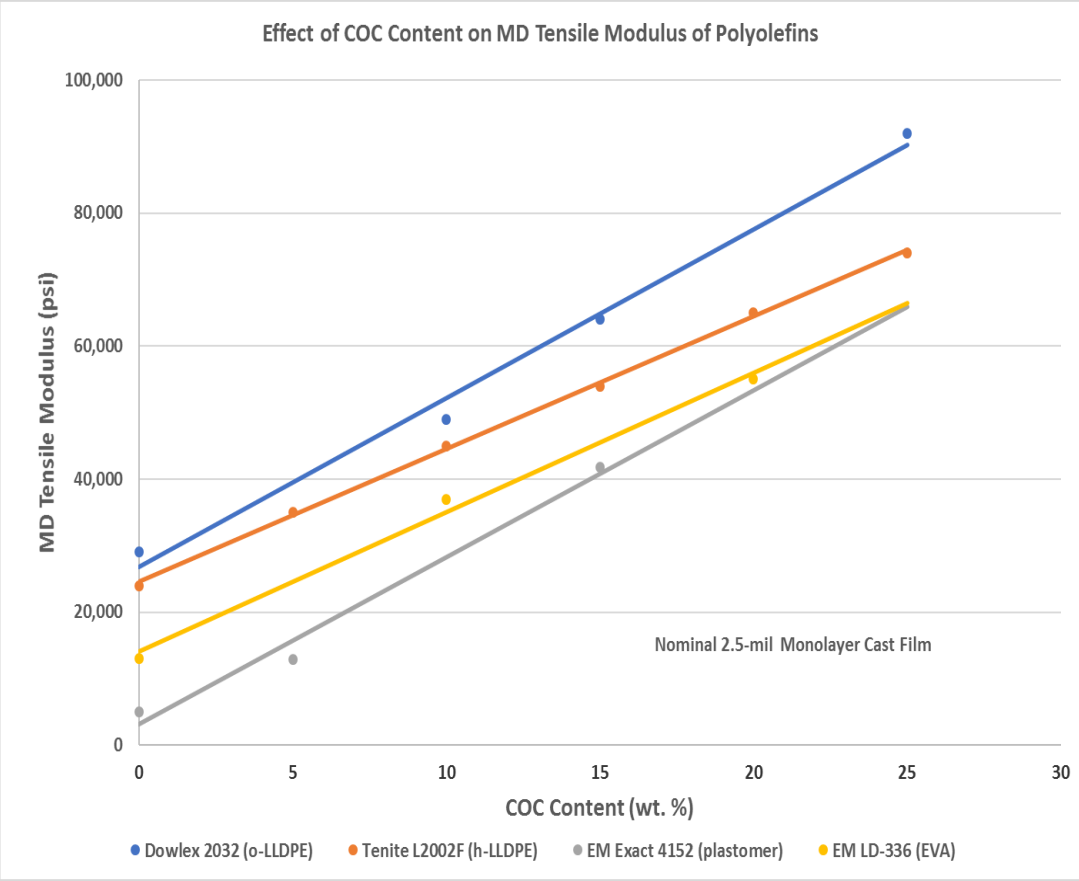
Unmet Needs for Recyclable & Sustainable PE Packaging:

Stiffness Enhancement

Stiffness Enhancement



Benefits for PE Packaging:

- Enable thinner films
- Reduce stretching & deformations
- Improve machine handling
- Enable faster converting speeds

MD Tensile Modulus:

- 5-10% COC increases stiffness significantly.
- Similar linear response among polyolefins
- Efficient and effective

Stiffness Enhancement Illustrated: Formed Cavities: COC & Octene LLDPE

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0 10 15 20 30 % COC

Incremental addition of TOPAS® 8007 into monolayer LLDPE clearly shows progressive improvement in cavity appearance.

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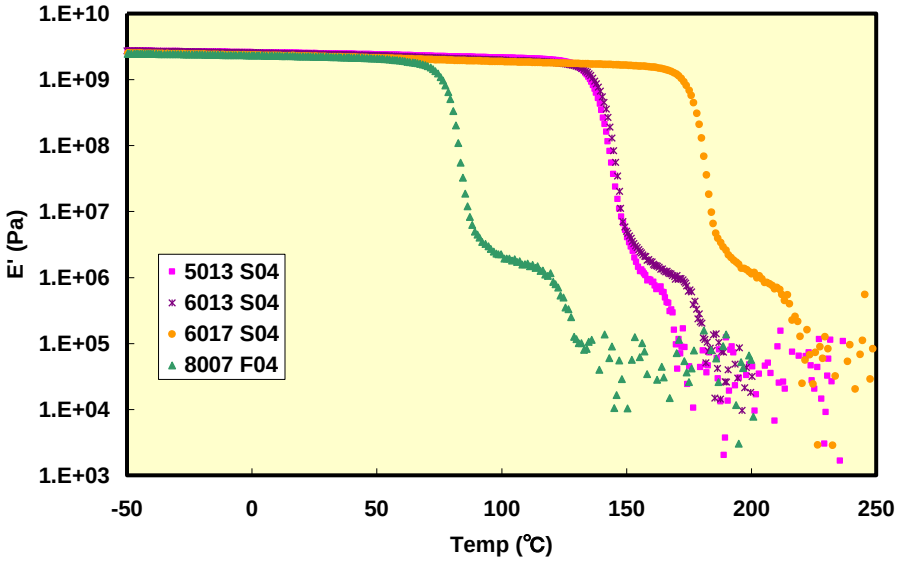
Unmet Needs for Recyclable & Sustainable PE Packaging:

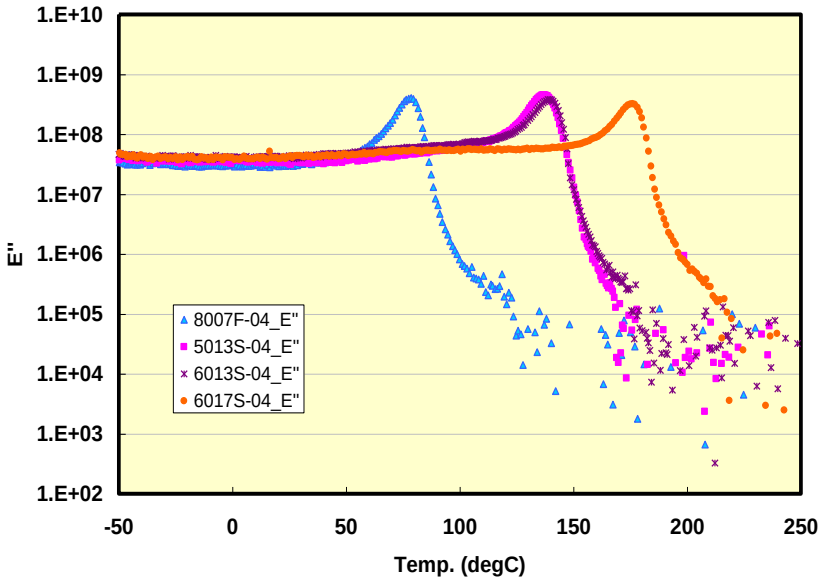
Mechanical Stability at Elevated Temperatures

TOPAS® COC – Viscoelasticity



storage elastic modulus

Mechanical properties stable up to within 10°C of glass transition temperature



loss elastic modulus

Mechanical and Thermal Property Comparison***

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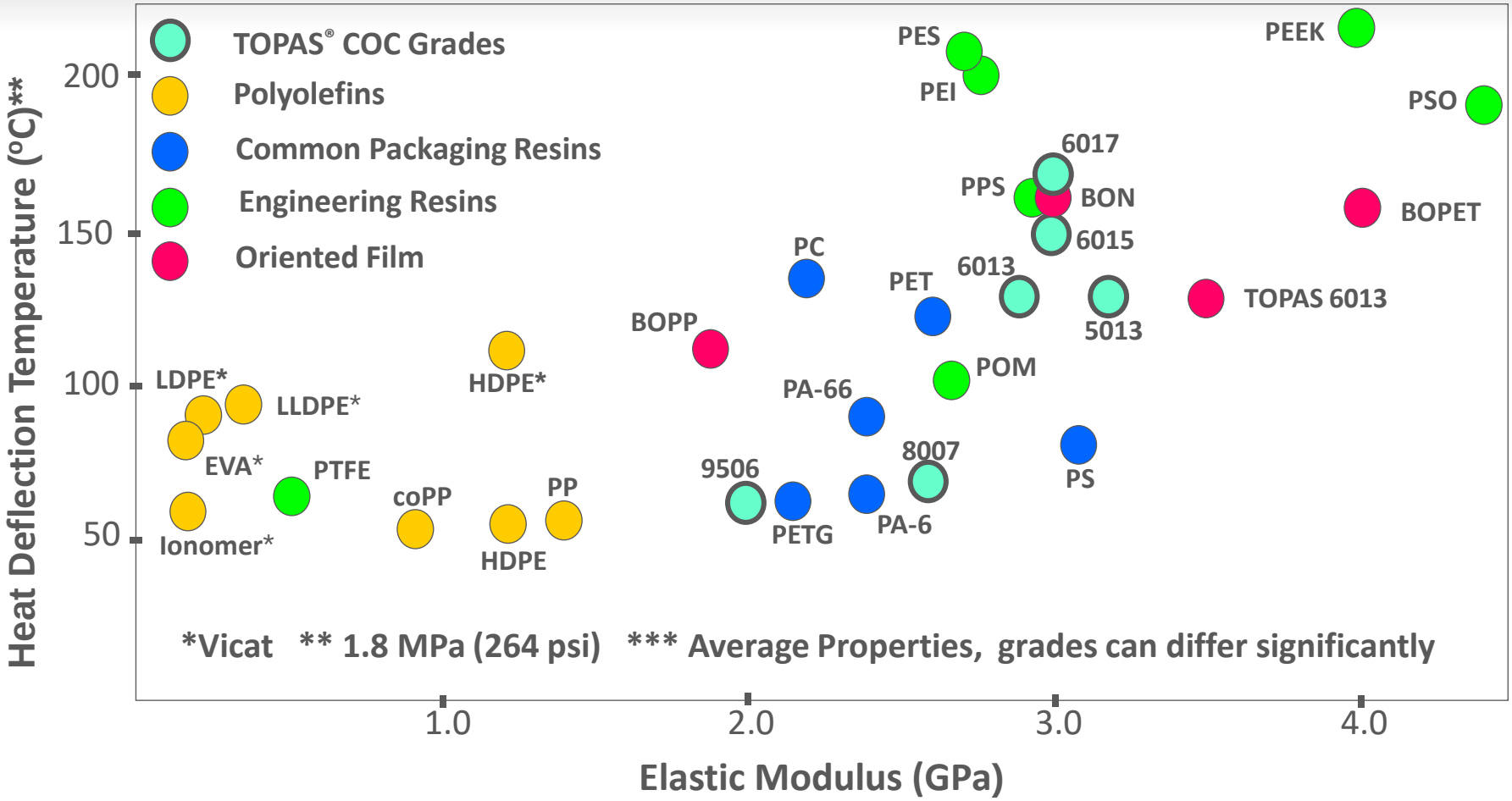

Unique among polyolefins, HDT and Modulus of COC performs like many temperature resistant engineering thermoplastics such as PA & PET.

TOPAS® COC

Thermal Distortion & Transitions Temperatures: COC & PE

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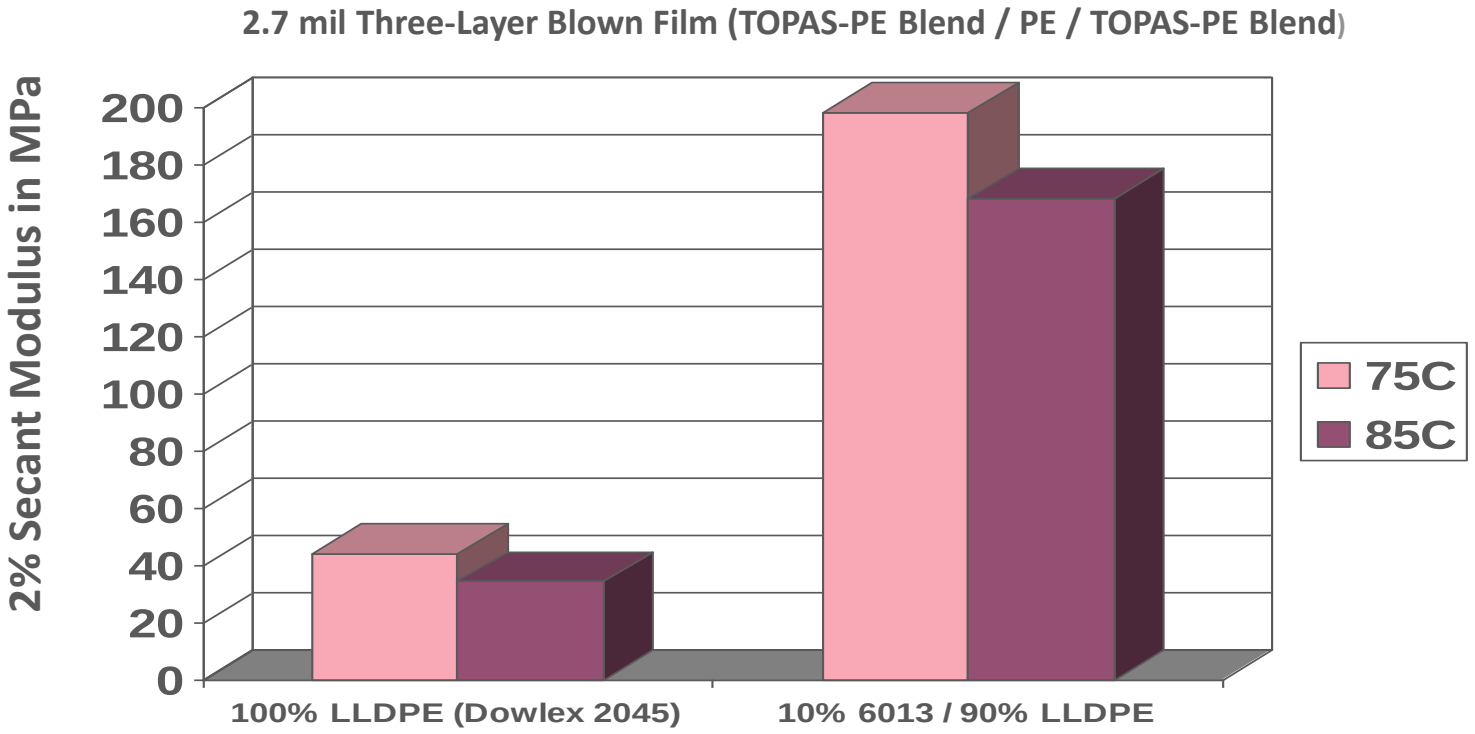
Polymer	Grade	Manufacture	Density (g/cc)	Melting Point (°C)	Tg (°C)	Vicat Softening Temp. (°C)	HDT (°C) [66 psi, 0.46 MPa]	HDT (°C) [264 psi, 1.8 MPa]
Test Method			ASTM D792 / D1505 ISO 1183	ISO 306/A ASTM D3418	ISO 11357	ASTM D1525 ISO 306	ASTM D648 ISO 75	ASTM D648 ISO 75
LLDPE	Dowlex 2045	Dow Chemical	0.920	122	---	108	---	---
LLDPE	Dowlex 2064G	Dow Chemical	0.935	125	---	119	---	---
LLDPE	Dowlex 2032	Dow Chemical	0.926	124	---	109	---	---
LLDPE	Petrothene GA635962	LyondellBasell	0.935	---	---	---	57	39
LDPE	Agility 1022	Dow Chemical	0.921	109	---	91	---	---
LDPE	LDPE 4010	Dow Chemical	0.917	105	---	89	---	---
HDPE	Alathon H4250	LyondellBasell	0.942	124	---	116	60	---
HDPE	Alathon H5618	LyondellBasell	0.956	130	---	125	73	---
HDPE	HD 6601.29	ExxonMobil	0.948	130	---	---	69	42
HDPE	HD 6719	ExxonMobil	0.952	131	---	---	73	46
COC	TOPAS 9506	Polyplastics	1.02	---	65	68	62	58
COC	TOPAS 8007	Polyplastics	1.02	---	78	79	72	66
COC	TOPAS 7010	Polyplastics	1.02	---	110	*108	*103	*92
COC	TOPAS 5013	Polyplastics	1.02	---	134	134	126	114
COC	TOPAS 6013	Polyplastics	1.02	---	138	135	130	117
COC	TOPAS 6015	Polyplastics	1.02	---	158	155	150	133
COC	TOPAS 6017	Polyplastics	1.02	---	178	178	170	151
Sources:	Company Datasheets & www.ulprospector.com; *estimated value							

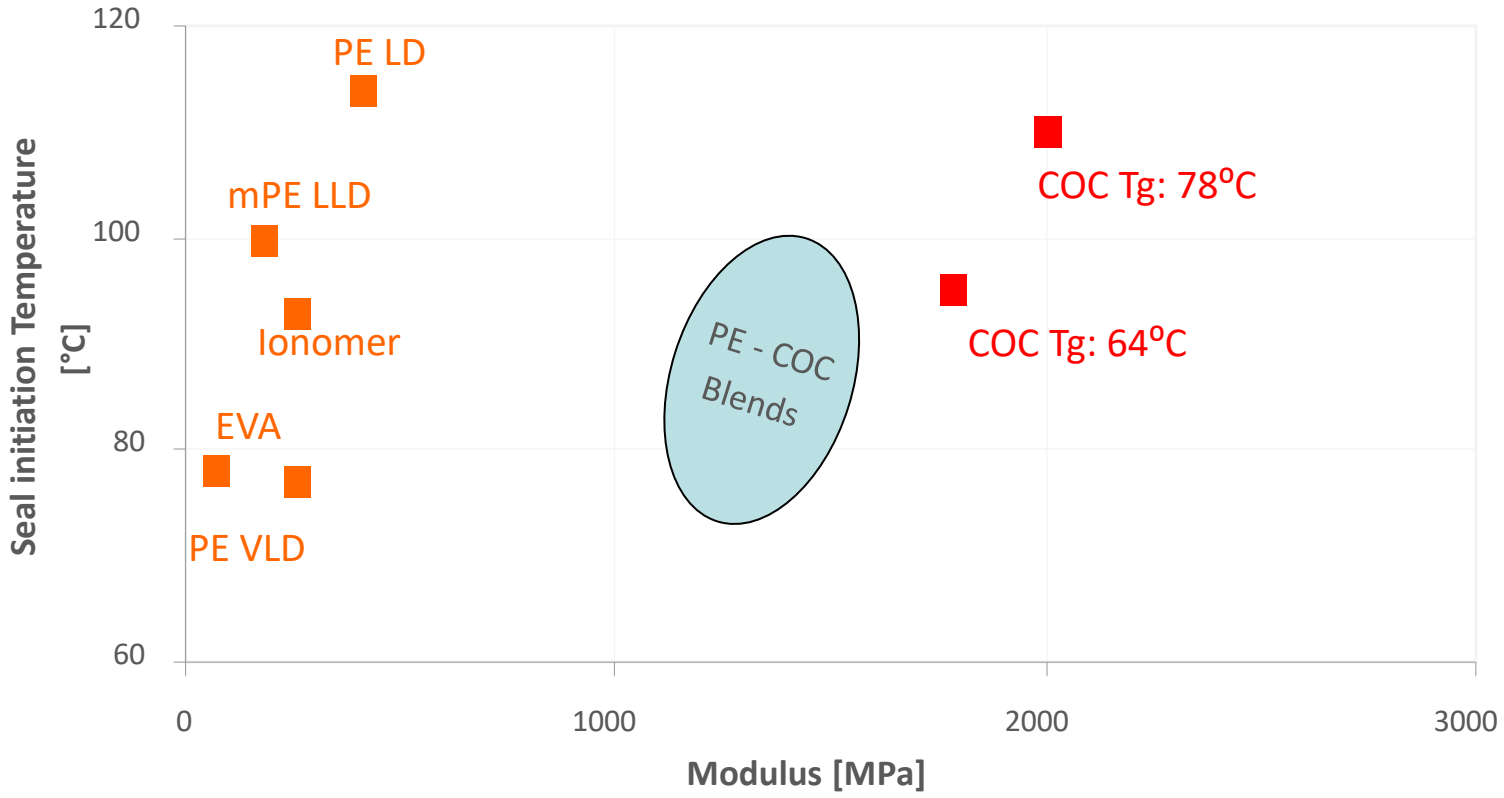
HDT measures resistance to deformation at elevated temperatures under load. COC can minimize distortion of PE exposed to thermal & mechanical stress!

TOPAS® COC - Modulus vs. Temperature



TOPAS 6013F-04 (T_g 138°C) dramatically increases PE modulus at hot fill temperatures

Seal Initiation vs. Modulus



COC significantly improves film modulus without compromising seal initiation temperature.

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Film Structure Guidelines

PE-COC Guideline Structures for Recyclable* ALL PE Films

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Polyolefin Materials

- COC, LLDPE (any comonomer), HDPE, LDPE (sparingly)

Monolayer

- 20-40% COC (inefficient, not recommended)
- Multiple layers enable efficient distribution of COC in the film, tailored mechanical properties, and lower material cost.

Three Layer: Ratio: 20-60-20 or 15-70-15

- A: 30-70% COC: outer skin layer, temperature resistance
- B: 0-20% COC: core layer, deformation stability, stiffness, reclaim
- C: 10-15% COC: sealant layer, seal strength

Five Layer: Ratio: 15-15-40-15-15 or 10-20-40-20-10

- A: 30-70% COC: outer skin layer, temperature resistance
- B: 0-20% COC: outer tie layer, deformation stability, stiffness, reclaim
- C: 0-30% COC: core layer, deformation stability, stiffness, reclaim
- D: 0-20% COC: inner tie layer, deformation stability, stiffness, reclaim
- E: 10-15% COC: sealant layer, seal strength

* These are all readily reprocessible in-house; as post-consumer 'recyclability' definitions and testing are continually evolving, please ensure any structure conforms to recycling regulations and guidelines for the region where product is to be sold and used

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Recycle Testing Results:
Trex
Association of Plastics Recyclers (APR)

Recycle: Trex Analysis

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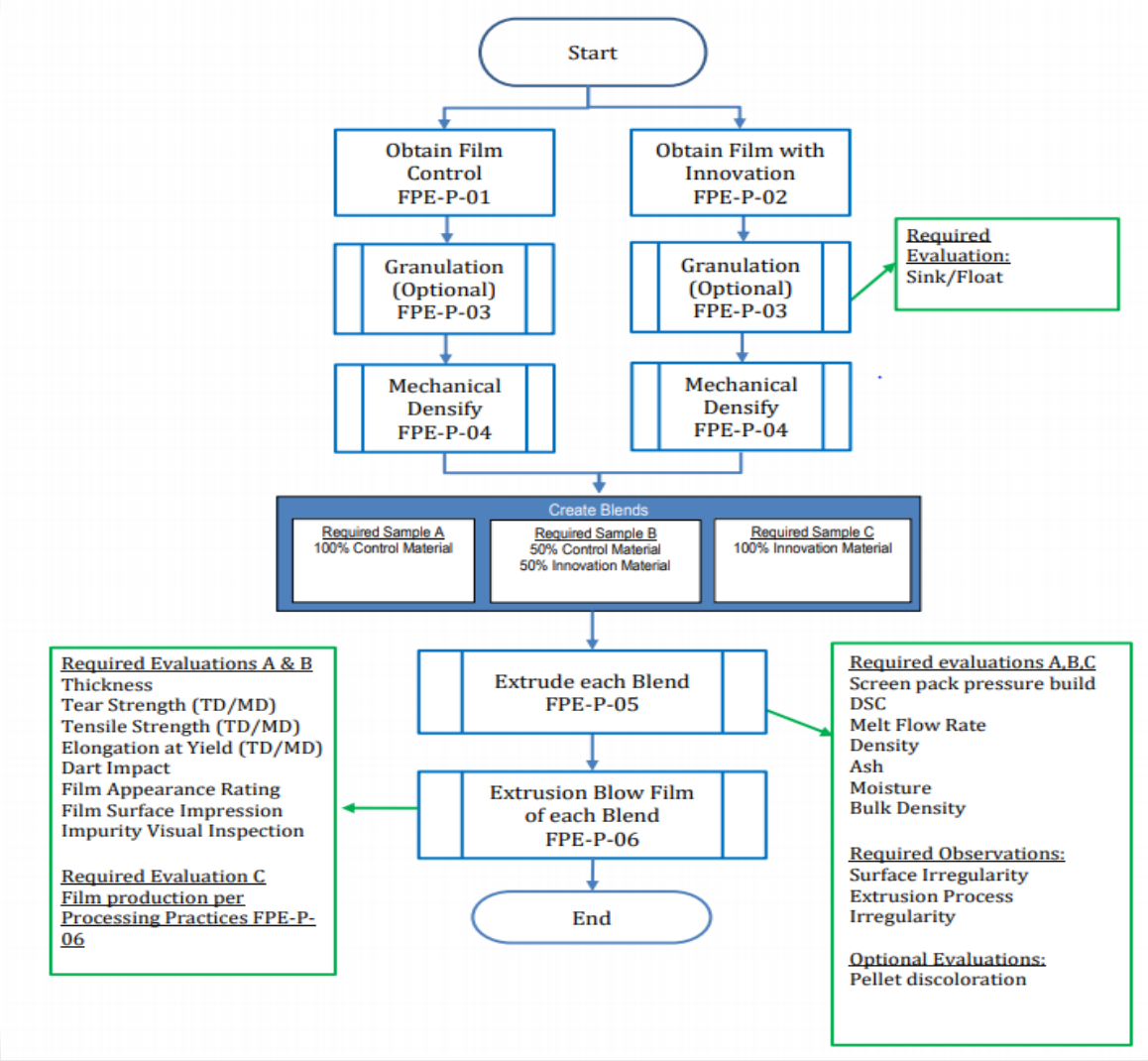
TOPAS Sample #	Description (monolayer)	PE MFR (dg/min) *(190°C; 2.16kg)	COC MFR (dg/min) (190°C; 2.16kg)	COC Tg (°C)	Trex Sample #	Melt Index (dg/min)	Ash (%)	DSC Peak Temperature (°C)	Indicative Structure	Acceptance
F06-35-1	Exxon HD7925 (HDPE)	2.5	---	---	19-0137	13.519	0.00	138	HDPE Blend	Yes
F06-35-2	HD7925 + 20% 8007F-400	2.5	1.8	78	19-0139	2.4405	0.0071	139	HDPE Blend	Yes
F06-49-1	Exceed 1018CA (LLDPE)	1.0	---	---	19-0140	0.9601	0.0008	121	LDPE/LLDPE Blend	Yes
F07-12-5	90% 1018 CA + 10% 8007 F04	1.0	1.8	78	19-0138	1.004	0.0031	121	LDPE/LLDPE Blend	Yes
F07-12-6	80% 1018CA + 20% 8007 F04	1.0	1.8	78	19-0141	1.0189	0.0021	120	LDPE/LLDPE Blend	Yes
F07-12-7	70% 1018CA + 30% 8007 F04	*1.0	1.8	78	19-0142	1.0718	0.0195	122	LDPE/LLDPE Blend	Yes
F12-52-20	95% FP120C + 5% 5013F-04	*1.0	<0.1	134	19-0143	0.9197	0.039	119	LDPE/LLDPE Blend	Yes
F12-52-21	90% FP120C + 10% 5013F-04	*1.0	<0.1	134	19-0144	0.8151	0.0009	124	LD/HDPE Blend	Yes
F12-52-22	80% FP120C + 20% 5013F-04	*1.0	<0.1	134	19-0145	0.7741	0.0005	123	LD/HDPE Blend	Yes

All COC containing film samples are recyclable according to Trex Protocols.
DSC clearly distinguished HDPE crystalline melting point from LLDPE, LDPE or PP.

APR PE Film Critical Guidance (FPE-CG-01)



Polyolefin Control & Innovation SUP Films

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5-Layer Polyolefin Control Film

Layer	Layer Thickness (%)	Material Percentage in Layer	Resin Type
A (Outer)	10	85	LLDPE
		15	LDPE
B (Outer Tie)	20	100	HDPE
C (Core)	40	85	LLDPE
		15	LDPE
D (Inner Tie)	20	100	HDPE
E (Sealant)	10	80	LLDPE
		20	LDPE
Total:	100		

5-Layer Polyolefin-COC Innovaton Film

Layer	Layer Thickness (%)	Material Percentage in Layer	Resin Type
A (Outer)	10	35	COC: Tg = 110°C
		35	COC: Tg = 138°C
		30	LLDPE
B (Outer Tie)	20	85	LLDPE
		15	COC: Tg = 78°C
C (Core)	40	100	HDPE
D (Inner Tie)	20	80	LLDPE
		20	COC: Tg = 78°C
E (Sealant)	10	85	LLDPE
		15	COC: Tg = 65°C
Total:	100		

Innovation SUP film uses total of 15.5% COC, distributed as: 3.5% Tg=138°C, 3.5% Tg=110°C, 7.0% Tg=78°C & 1.5% Tg=65°C.

APR Film Test Results: Bulk Density

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	Incoming Film	Densified Film
Control		
Test		

Pre-Extrusion Data

Variable	Control	Test
Initial Bulk Density (lb./ft^3)	5.50	12.83
Final Bulk Density (lb./ft^3)	5.89	13.71

No detrimental influence from COC on film bulk density.

APR Film Test Results: Extrusion & Pellets

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Extruded Pellet	
Control	
Test 50%	
Test 100%	

Extrusion/Pellet Data

Variable	Control	Test 50%	Test 100%
Melt Temperature (℃)	220	220	221
Screen Pack Pressure Build (%)	-5.00%	3.60%	-2.94%
Density (g/cm^3)	0.946	0.947	0.949
Melt Flow Rate (g/10min)	1.455	1.097	0.855
Volatiles/Moisture (%)	0.0041	0.0198	0.0145
Ash Content (%)	0.41%	0.31%	0.19%
Bulk Density (kg/m^3)	545	542	529
Primary Peak Temperature (℃)	128.63	128.16	127.35
Percent Polypropylene	<1.00%	<1.00%	<1.00%

All films exhibit similar extrusion behavior.

APR Film Test Results: Properties

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Blown Film

Control

Test 50%

Test 100%

Blown Film Data

Variable	Control	Test 50%	Test 100%
Process Stability	Yes	Yes	Yes
Thickness (mils)	2.0	2.0	2.1
MD Tear Strength (gf) (Delta%)	159.2	338.0 (112.37%)	624.6 (292.39%)
TD Tear Strength (gf) (Delta%)	248.8	521.1 (109.43%)	389.0 (56.40%)
MD Tensile Strength (psi) (Delta%)	3055	3421 (11.97%)	3253 (6.49%)
TD Tensile Strength (psi) (Delta%)	2481	3148 (26.90%)	3303 (33.11%)
MD Elongation at Yield (%) (Delta%)	40.798	41.645 (2.08%)	57.879 (41.87%)
TD Elongation at Yield (%) (Delta%)	8.057	44.450 (451.70%)	55.332 (586.76%)
Dart Impact Strength (g) (Delta%)	158	200 (26.84%)	698 (342.86%)
F.A.R	1	0	0

COC improved all mechanical properties!

Conclusions

Summary - Conclusions

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- Unique among polyolefins, HDT and Modulus of COC perform like temperature-resistant engineering thermoplastics such as PA & PET.
- HDT better explains how polyolefin materials respond to thermal deformation under load than Vicat.
- COC can minimize distortion of PE exposed to thermal & mechanical stress!
- COC demonstrated recyclable under Trex protocols.
- Stand-Up Pouch (SUP) film with 15% COC satisfied APR PE Film and Flexible Packaging protocols (FPE-CG-01).
  - Critical Guidance Recognition letter is in The APR Design® Guide for Plastics Recyclability.
- In Europe, COC has been certified as recyclable in both PE and PP films by Institut cyclos-HTP.
- Shrink sleeves with COC have passed bottle recycling protocols in US & EU.
- Further recyclability testing is underway in multiple regions.

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