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

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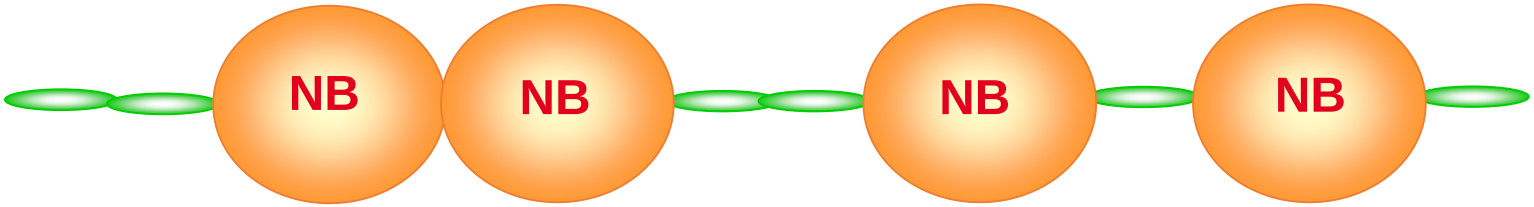
- ***What is COC, Value Propositions & Applications?***
- **Design of Experiments (DOE)**
- **Main Effects Plots – Properties**
- **Discrete vs. Split Layer**
- **Conclusions**

COC Is Amorphous

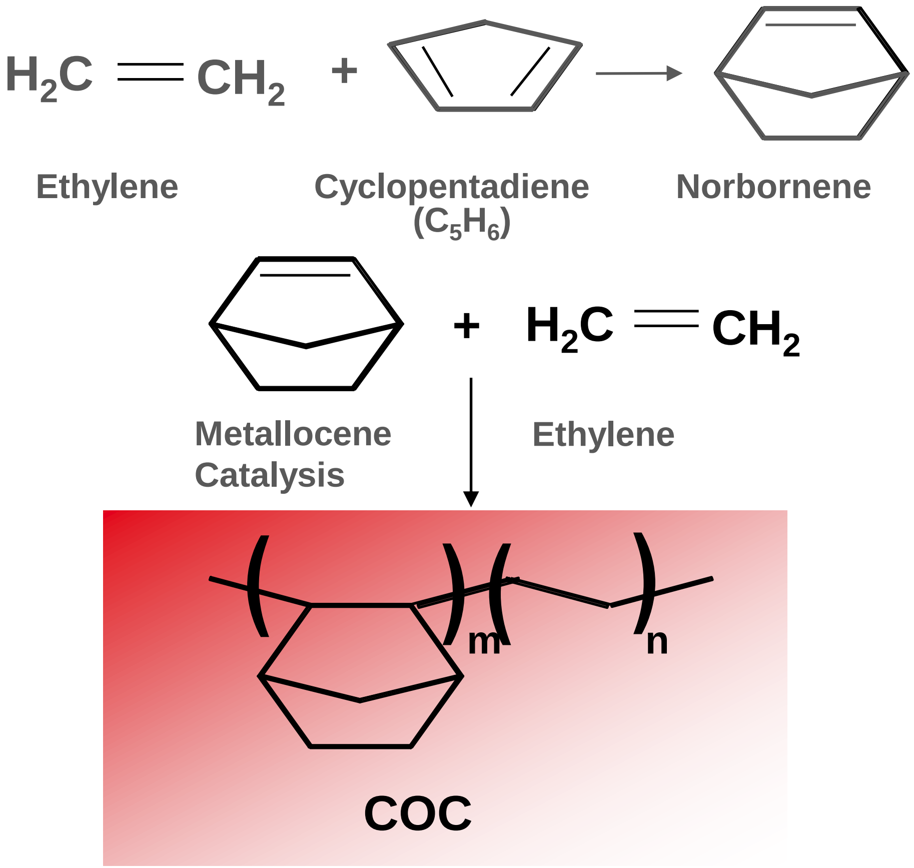
COC molecule is a chain of small CH_2-CH_2 links randomly interspersed with large bridged ring elements

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

COC - New Solution for Film & Packaging Markets

Value Propositions

- Stiffness & Strength
- Thermoformability
- Transparency & Gloss
- Temperature Resistance
- Barrier – WVTR, Alcohol
- Chemical Resistance
- Sustainability
- Low Adsorption
- N_2 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?
- *Design of Experiments (DOE)*
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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 & 110ºC**
    - **BUR: 2.0:1, 2.5:1 & 3.0:1**
    - **COC Modification: none, 30% LLDPE & 30% E-140**

DOE Matrix & Non-COC Control Films

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Experiment Number	Variable I COC Grade	Variable II BUR	Variable III COC Modification
1	9506F-500	2:1	100% 9506F-500
2	9506F-500	2:1	70% 9506F-500 / 30% LLDPE
3	9506F-500	2:1	70% 9506F-500 / 30% E-140
4	9506F-500	2.5:1	100% 9506F-500
5	9506F-500	2.5:1	70% 9506F-500 / 30% LLDPE
6	9506F-500	2.5:1	70% 9506F-500 / 30% E-140
7	9506F-500	3:1	100% 9506F-500
8	9506F-500	3:1	70% 9506F-500 / 30% LLDPE
9	9506F-500	3:1	70% 9506F-500 / 30% E-140
10	8007F-600	2:1	100% 8007F-600
11	8007F-600	2:1	70% 8007F-600 / 30% LLDPE
12	8007F-600	2:1	70% 8007F-600 / 30% E-140
13	8007F-600	2.5:1	100% 8007F-600
14	8007F-600	2.5:1	70% 8007F-600 / 30% LLDPE
15	8007F-600	2.5:1	70% 8007F-600 / 30% E-140
16	8007F-600	3:1	100% 8007F-600
17	8007F-600	3:1	70% 8007F-600 / 30% LLDPE
18	8007F-600	3:1	70% 8007F-600 / 30% E-140

Experiment Number	Variable I COC Grade	Variable II BUR	Variable III COC Modification
19	7010F-600	2:1	100% 7010F-600
20	7010F-600	2:1	70% 7010F-600 / 30% LLDPE
21	7010F-600	2:1	70% 7010F-600 / 30% E-140
22	7010F-600	2.5:1	100% 7010F-600
23	7010F-600	2.5:1	70% 7010F-600 / 30% LLDPE
24	7010F-600	2.5:1	70% 7010F-600 / 30% E-140
25	7010F-600	3:1	100% 7010F-600
26	7010F-600	3:1	70% 7010F-600 / 30% LLDPE
27	7010F-600	3:1	70% 7010F-600 / 30% E-140
28	80% LDPE / 20% LLDPE	2:1	No Modification
29	80% LDPE / 20% LLDPE	2.5:1	No Modification
30	80% LDPE / 20% LLDPE	3:1	No Modification
34	93% m-h-LLDPE + 7% LDPE	2:1	No Modification
35	93% m-h-LLDPE + 7% LDPE	2.5:1	No Modification
36	93% m-h-LLDPE + 7% LDPE	3:1	No Modification

DOE Structures & Materials

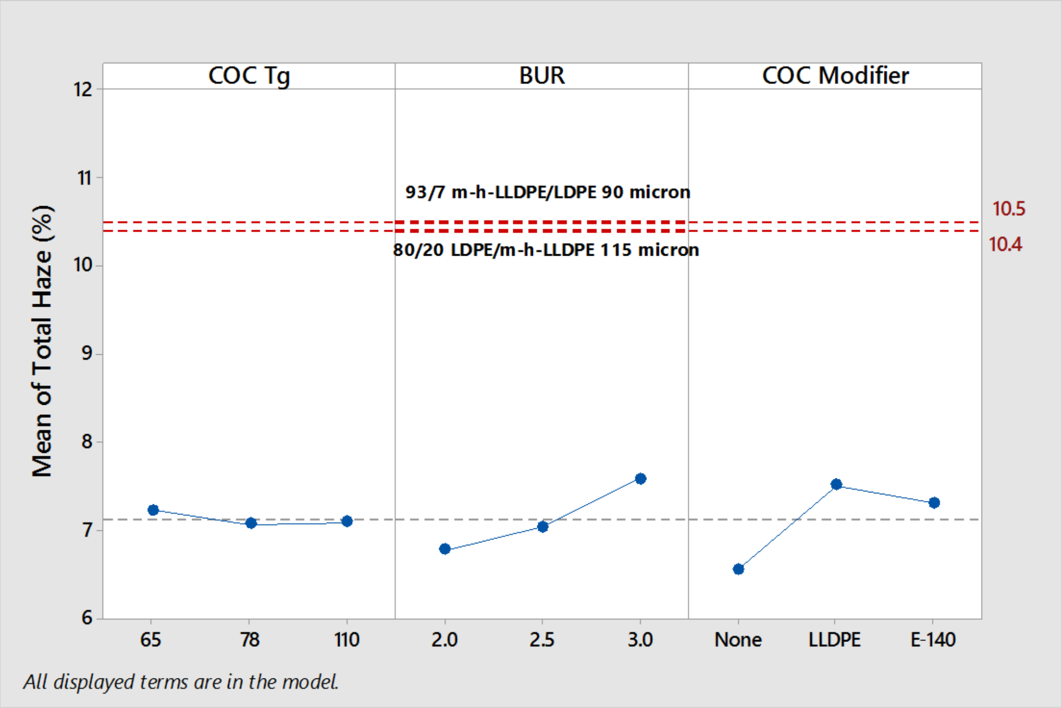
- Film structure:
  - 90-micron (3.6-mil)
  - Three layer A-B-A
  - Layer ratio:
    - 40/20/40 ≈ 36/18/36 micron
- COC film composition:
  - A-Layer: 93/7 LLDPE/LDPE
  - B-Layer: COC specified per trial
- Non-COC film composition:
  - Control (90-micron)
    - All layers: 93/7 LLDPE/LDPE
  - Generic (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

DOE Process Conditions

- 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: 180ºC
  - B-Layer: zones 1-3: 210, 200, & 190ºC
- 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

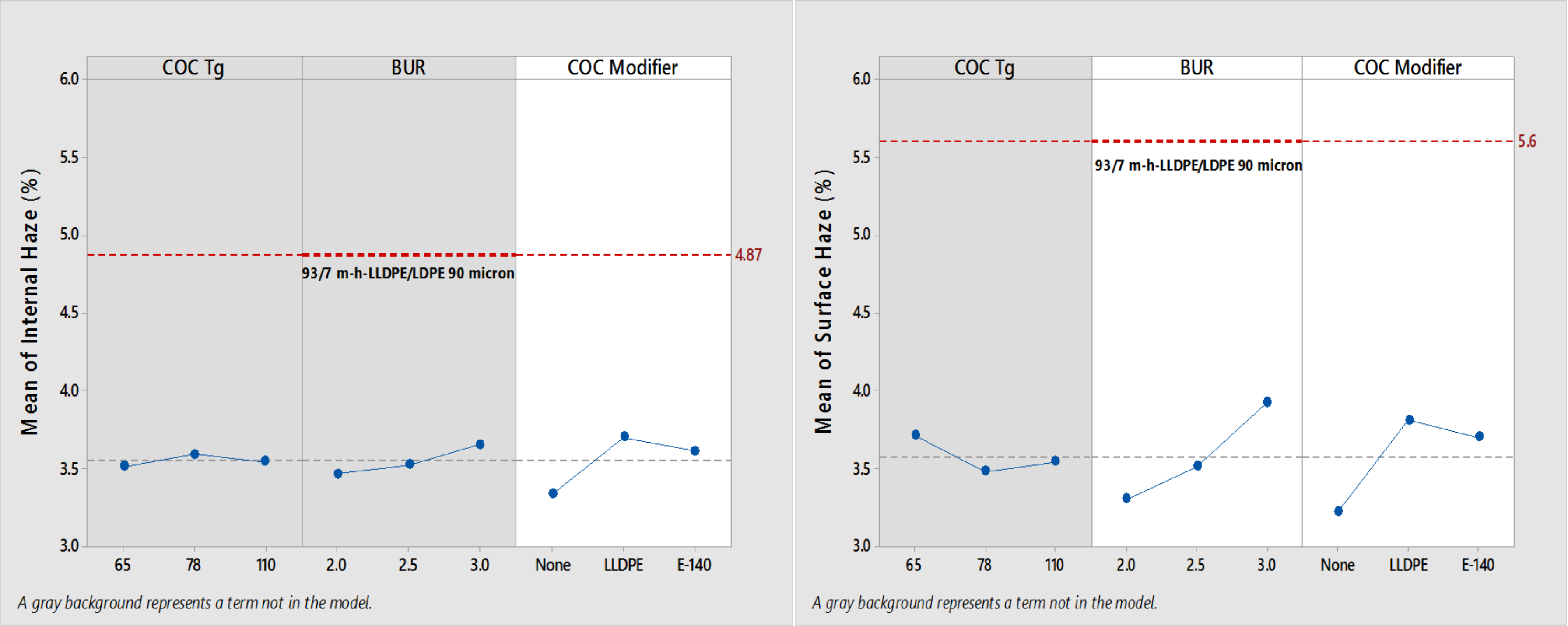
Main Effects Plot for Total Haze



- Plot features:
  - Three main effects
  - Three levels
  - Two non-COC films
  - Stepwise linear regression
  - Fitted means:
    - DOE (27)
    - Data points (9)
  - Two continuous variables
  - One discrete variable

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.

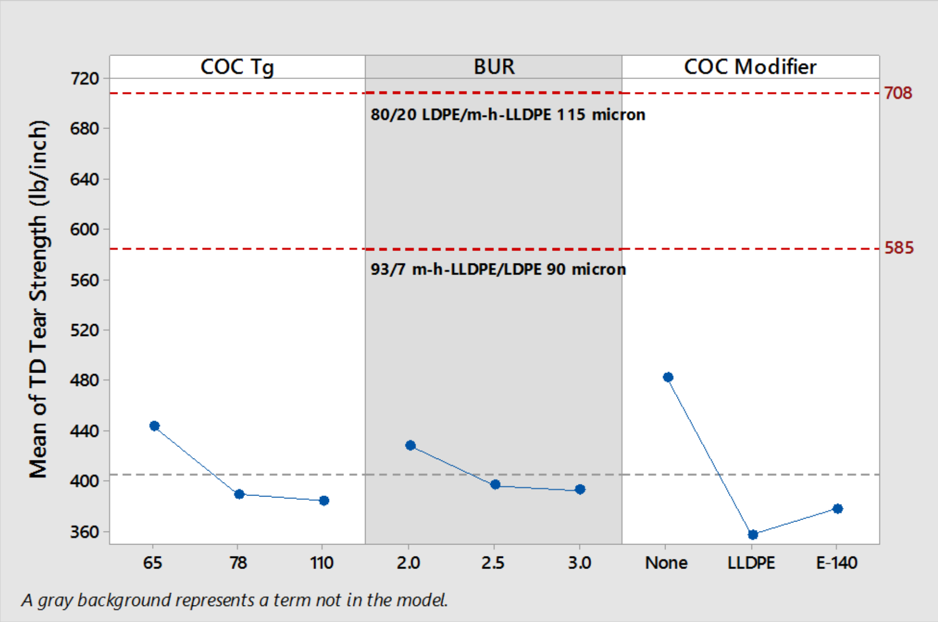
Main Effects Plots for Internal & Surface Haze

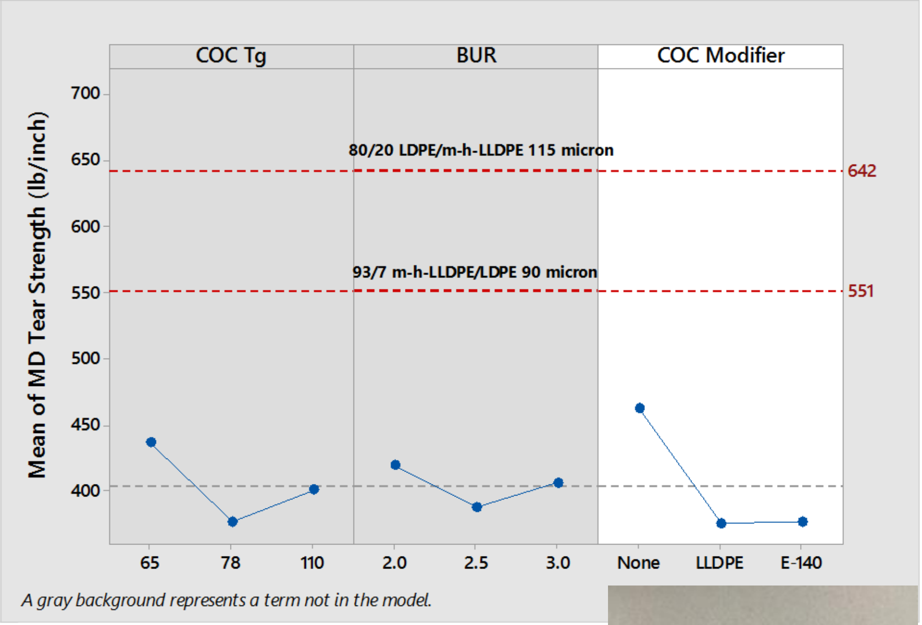


COC Modification influences internal and surface haze.

Discrete layer of COC in LLDPE film significantly reduces internal and surface haze.

Main Effects Plot for TD/MD Tear Strength



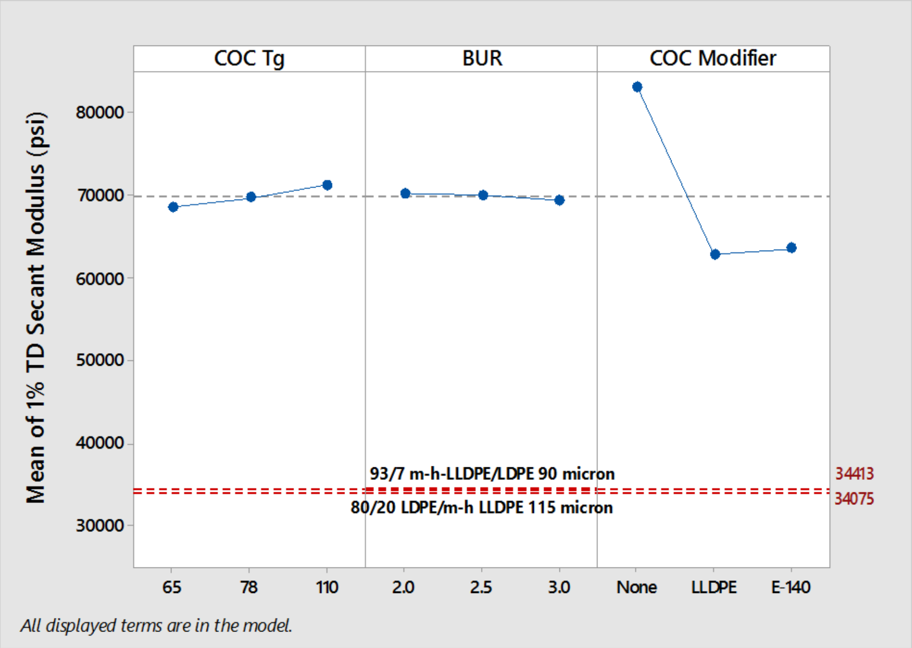


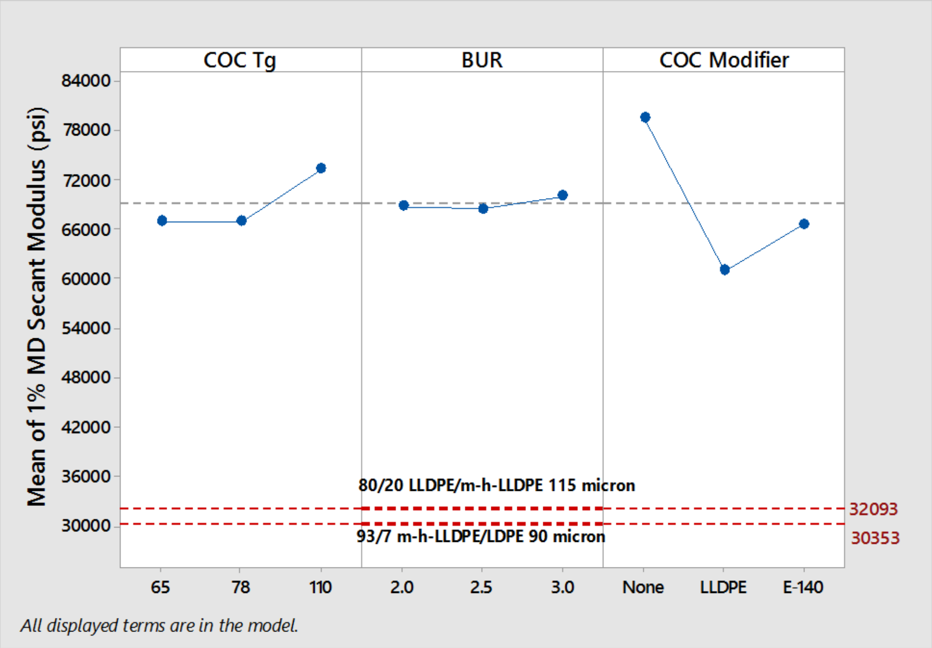
Single 18-micron COC layer reduces TD/MD Tear Strength.

COC modification reduces TD/MD Tear Strength.

Unmodified 65°C Tg COC provides highest TD/MD Tear Strength.

Main Effects Plot for TD/MD Secant Modulus





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.

Main Effects Plot for Impact Resistance

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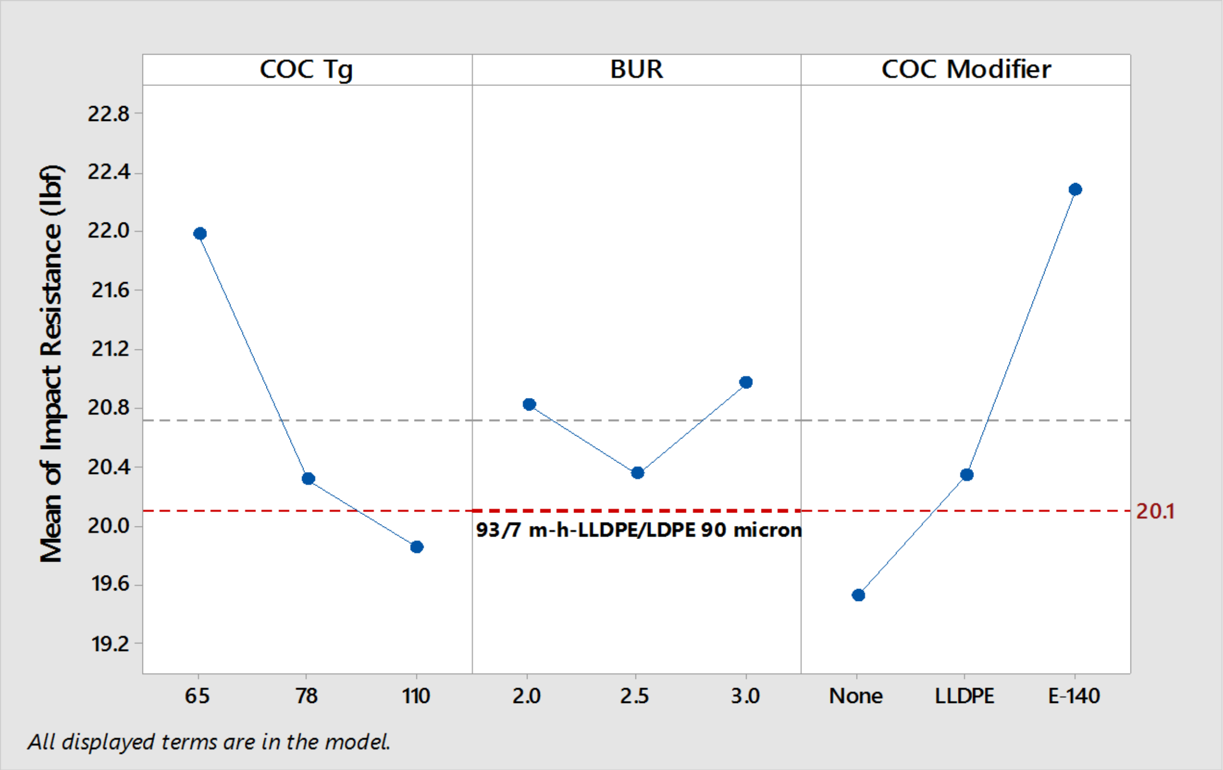
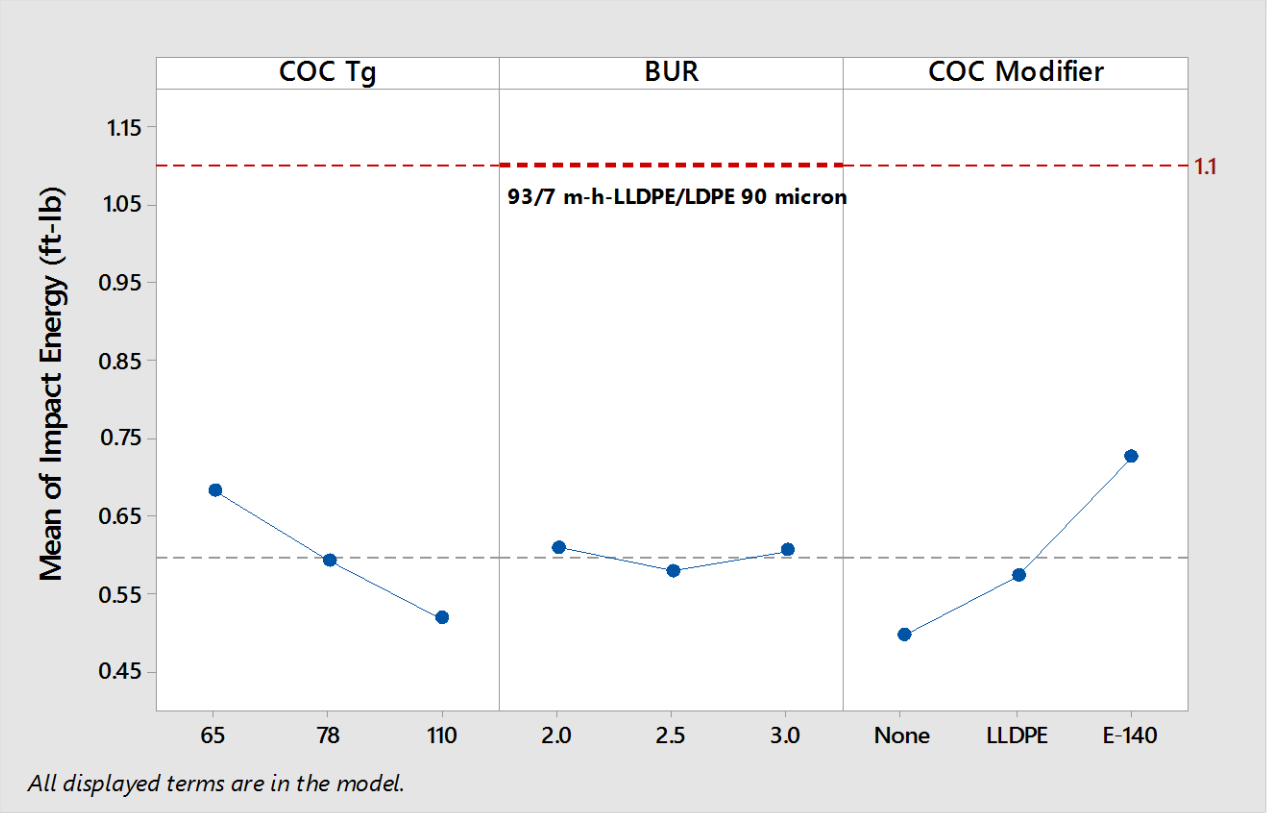


COC layer into blended LLDPE film improves impact resistance.

COC Modifier and Tg strongly influence impact resistance.

Impact resistant films can be made with low Tg COC modified with E-140.

Main Effects Plot for Impact Energy

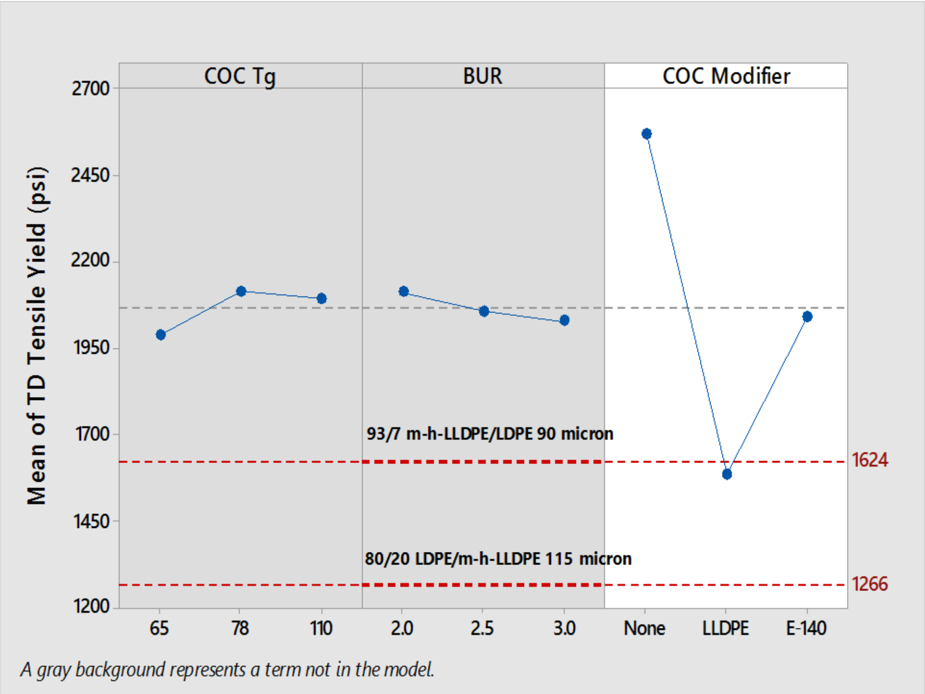


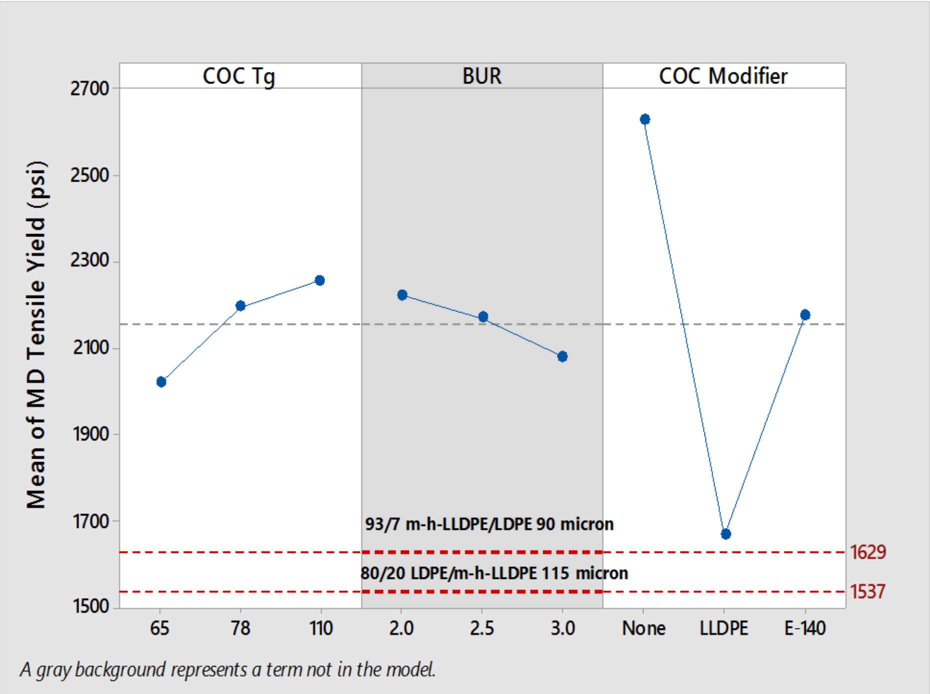
COC layer into blended LLDPE film reduces impact energy.

COC Modifier and Tg strongly influence impact energy.

Film toughness can be improved with low Tg COC modified with E-140.

Main Effects Plot for TD/MD Tensile Yield

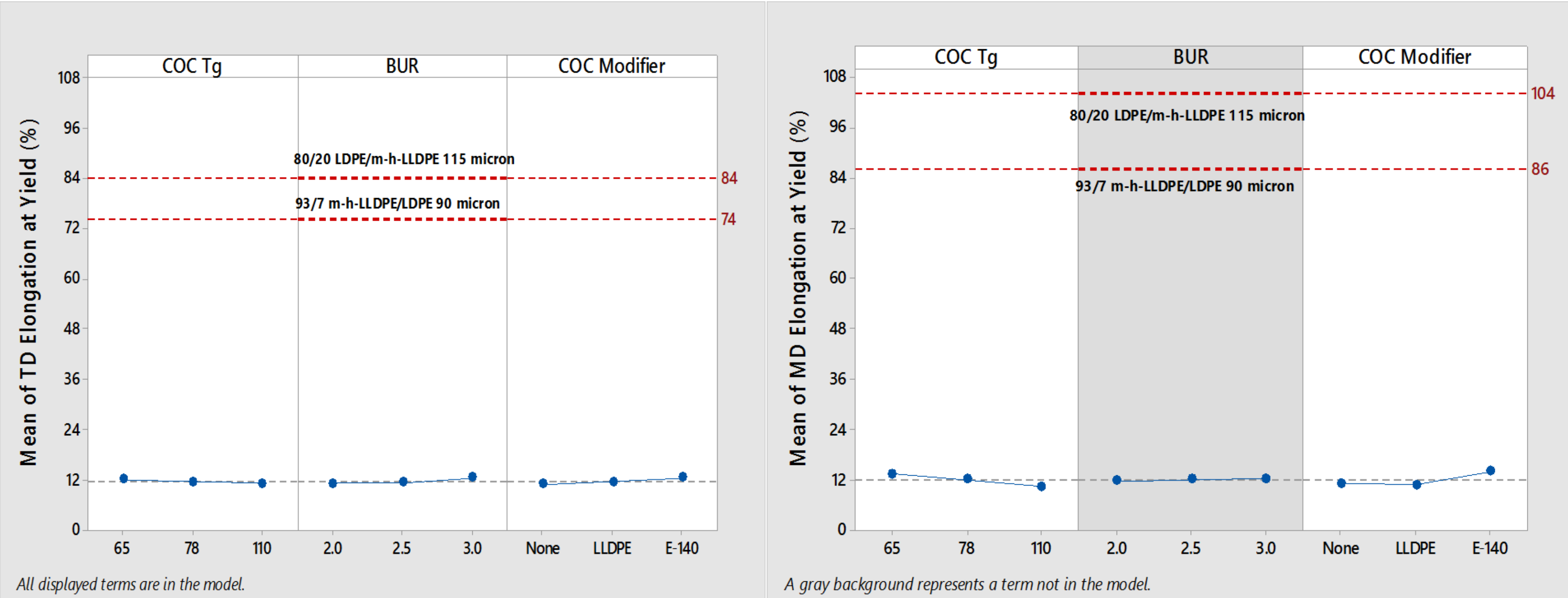




COC layer into blended LLDPE film significantly improves TD & MD tensile strength.

COC Modifier type and quantity can dilute COC benefit.

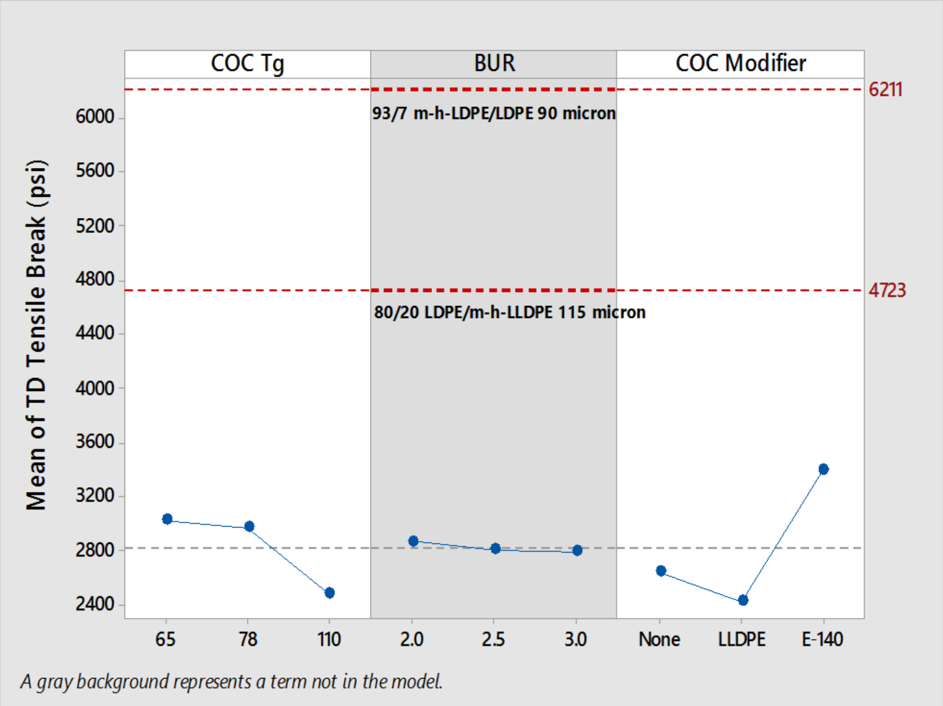
Main Effects Plot for TD/MD Elongation @ Yield

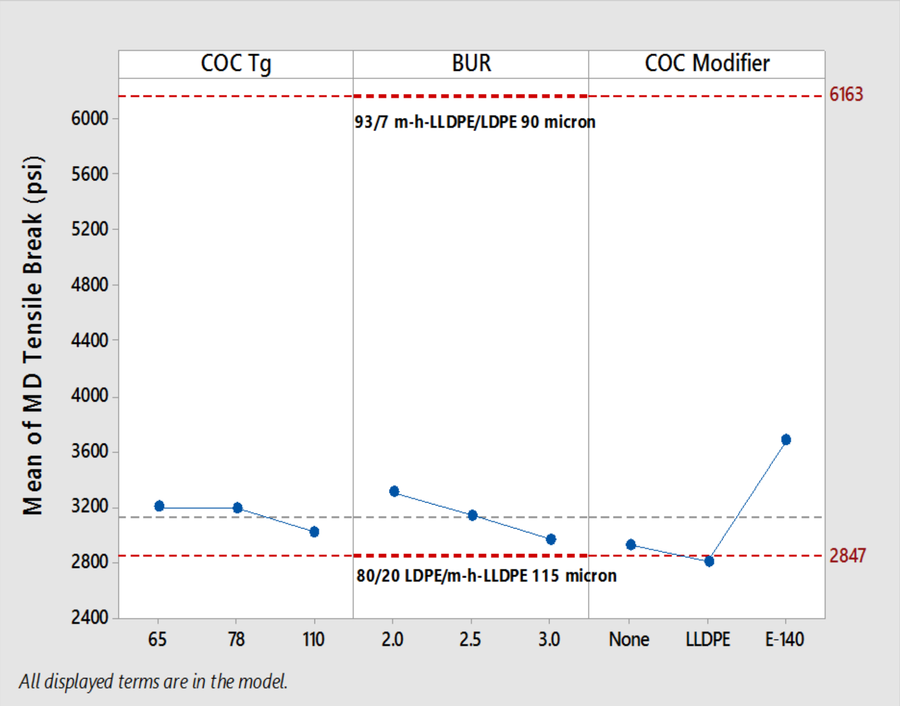


COC layer into blended LLDPE film significantly reduces TD & MD elongation at yield.

COC Modifier, Tg and BUR had minimal effect.

Main Effects Plot for TD/MD Tensile Break

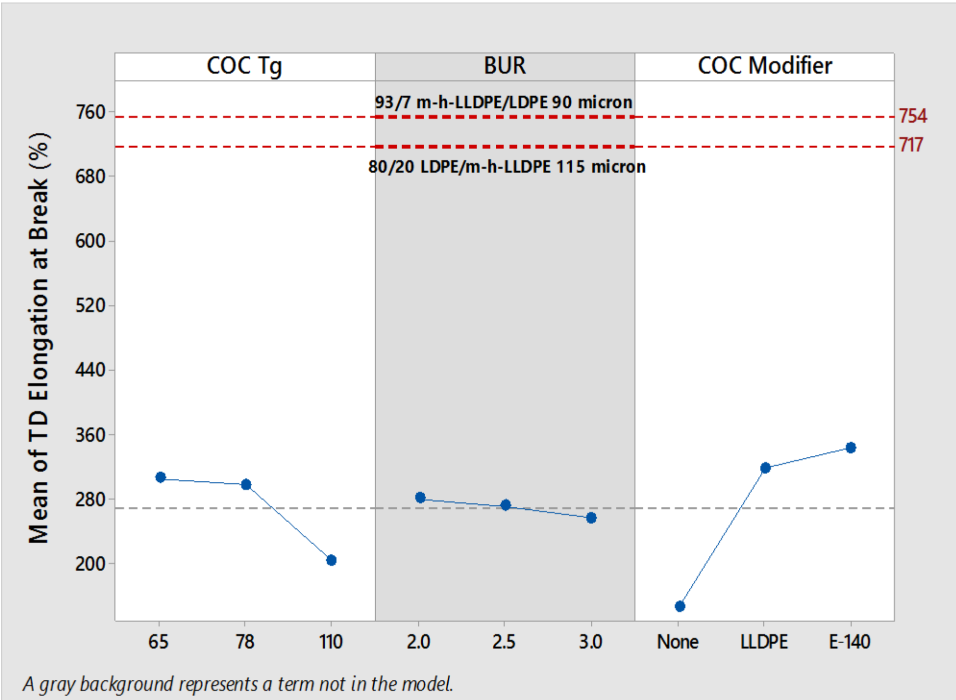


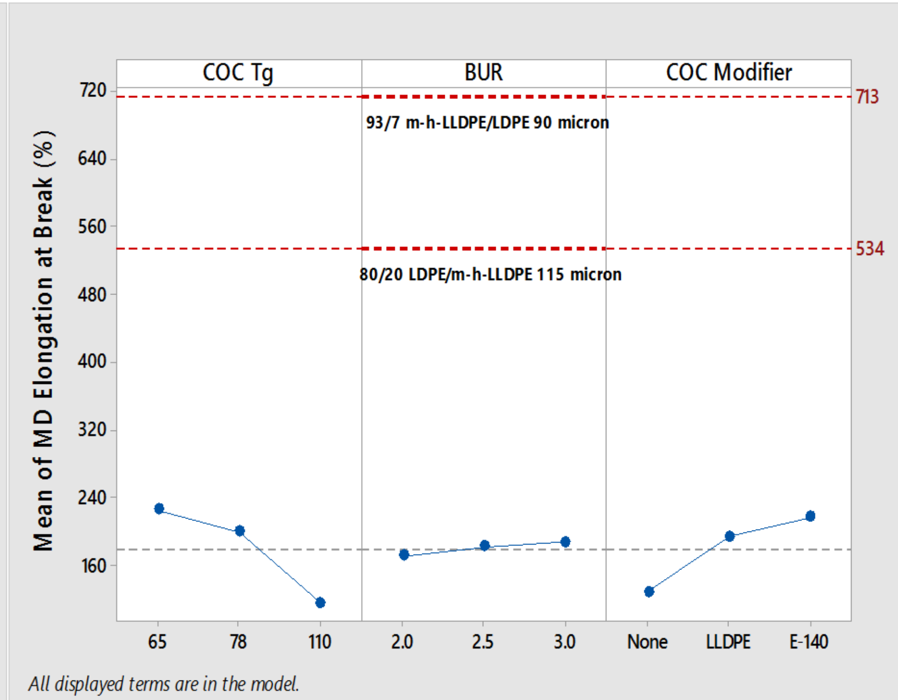


COC layer into blended LLDPE film significantly reduces TD & MD tensile at break by limiting LLDPE strain hardening.

COC Modifier and Tg show minor influence.

Main Effects Plot for TD/MD Elongation @ Break





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

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6-mil Cast Extrusion Property	Unit	1 COC Layer 40% m-h-LLDPE 20% COC 40% m-h-LLDPE	2 COC Layers 31% m-h-LLDPE 10% COC 18% m-h-LLDPE 10% COC 31% m-h-LLDPE
Fast Puncture Force	lbf	35.1	34.4
Fast Puncture Energy	ft-lb	1.1	1.0
MD Tensile Yield	psi	2,490	2,510
TD Tensile Yield	psi	2,590	2,480
MD Elong. @ Yield	%	8	8
TD Elong. @ Yield	%	8	8
MD Tensile Break	psi	2,930	3,370
TD Tensile Break	psi	3,030	3,530
MD Elong. @ Break	%	330	410
TD Elong. @ Break	%	330	430
TD Tensile Modulus	psi	140,000	134,000
MD Tensile Modulus	psi	138,000	139,000
Total Haze	%	38	19

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.

Single vs. Split Layers: Modified COC

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6-mil Cast Extrusion Property	Unit	1 COC Layer 40% m-h-LLDPE 20% COC 40% m-h-LLDPE	2 COC Layers 31% m-h-LLDPE 10% COC 18% m-h-LLDPE 10% COC 31% m-h-LLDPE
Fast Puncture Force	lbf	34.4	40.9
Fast Puncture Energy	ft-lb	1.3	1.9
MD Tensile Yield	psi	2,010	1,990
TD Tensile Yield	psi	1,970	1,880
MD Elong. @ Yield	%	9	9
TD Elong. @ Yield	%	12	13
MD Tensile Break	psi	3,220	3,550
TD Tensile Break	psi	3,400	3,680
MD Elong. @ Break	%	450	500
TD Elong. @ Break	%	480	540
TD Tensile Modulus	psi	106,000	62,300
MD Tensile Modulus	psi	95,200	51,100
Total Haze	%	16	16

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.

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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!

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TOPAS® Cyclic Olefin Copolymer (COC)

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