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Introduction to Micro and Nano-Layering LLDPE with Cyclic Olefin Copolymers (COC)

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Outline

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- What is COC & Its Value Propositions?
- What is Micro & Nanolayer Extrusion?
- Experimental:
  - Film Structures & Materials
  - Capillary Rheology
  - AFM (Atomic Force Microscopy)
- 80/20 LLDPE-(A&B)/COC // 20/80 LLDPE-B/COC
  - AFM Image Analysis
  - Mechanical Property Analysis
- Conclusions

What is COC & Its Value Propositions?

Cyclic Olefin Copolymer: Synthesis & Structure

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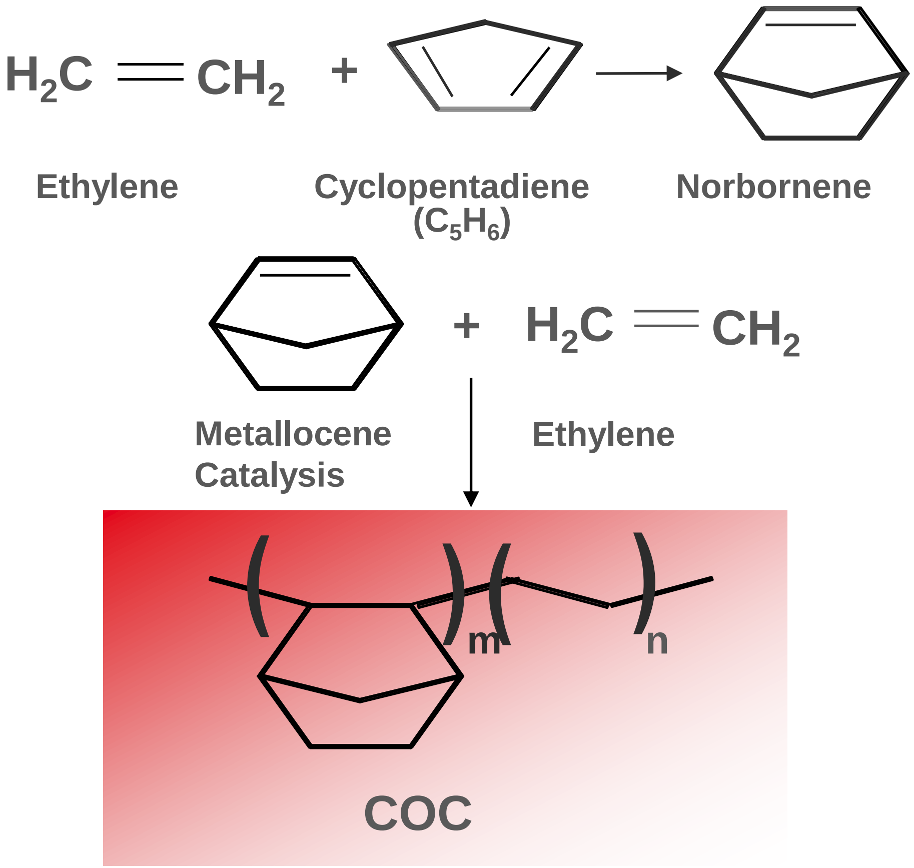

- Readily available raw materials
- Highly efficient catalyst
  - Low usage
  - Catalyst removed as part of process
  - High purity product
- Amorphous
- Crystal clear

COC Is Amorphous

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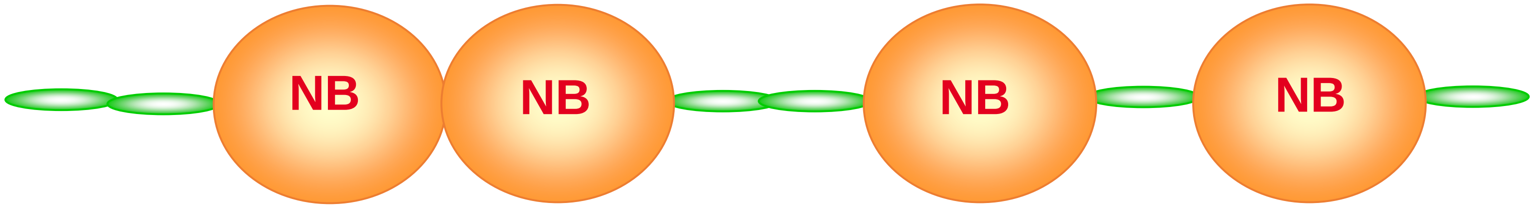
COC molecule is a chain of small CH_2-CH_2 links randomly interspersed with large bridged ring elements

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

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

Why Study COC Micro & Nano-Layering?

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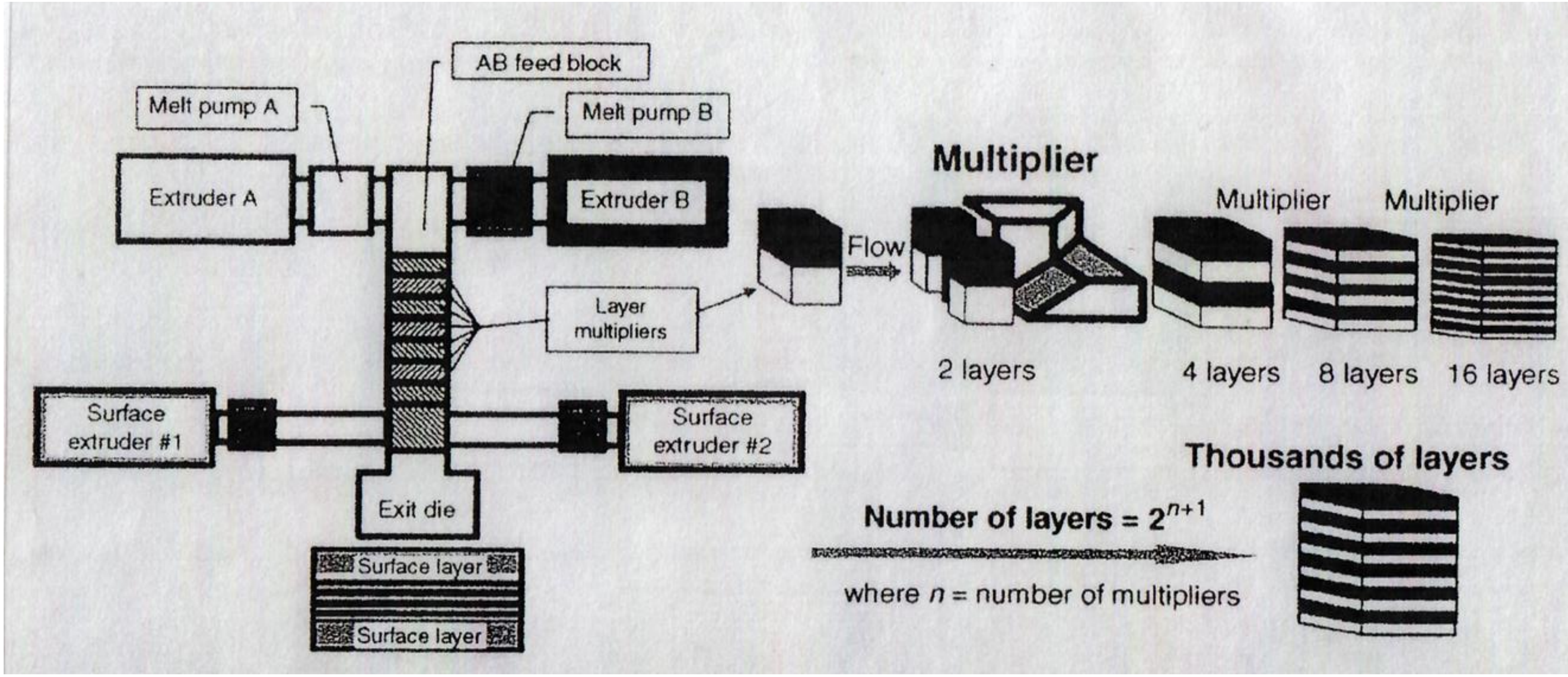
- COC has unique features and properties:
  - COC is amorphous
  - COC is a polyolefin, compatible with LLDPE, LDPE & HDPE
  - COC offers more heat resistance
- Enable more efficient use of COC:
  - Mechanical properties improve significantly
  - Monolayer blend → single discrete → 2 split layers → more?
  - Improve film economics
- Reduce low COC ductility influence in PE films
  - Enable stronger and tougher films
- Discover something new and unexpected

What is Micro- & Nanolayer Extrusion?

Micro & Nano-Layer Process Sketch



Source: Manufacturing and Novel Applications of Multilayer Polymer Films, D. Langhe and M. Pointing (PDL Handbook Series), p. 20.

Two extruded layers enter multiplier units.
Multiplier unit splits flow into two streams; recombining them into higher ordered multilayer structure.

Film Structures & Materials

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Film Structures LLDPE Rich	Total Layers	COC Layers {(Total Layers-1)/2}
LLDPE Controls	1	0
LLDPE-A/COC	3	1
LLDPE-B/COC	5	2
(80/20, v/v)	9	4
Thickness:	33	16
50-µm	129	64
	513	128
	2049	1014

Film Structures COC Rich	Total Layers	LLDPE Layers {(Total Layers-1)/2}
LLDPE-B Control	1	1
LLDPE-B/COC	3	1
(20/80, v/v)	5	2
	9	4
Thickness:	33	16
50-µm	129	64
	513	128
	2049	1014

LLDPE-A: 0.917 g/cc; 2.7 dg/min (190°C, 2.16 kg); hexene.

LLDPE-B: 0.935 g/cc; 2.5 dg/min (190°C, 2.16 kg); octene.

COC (Tg=78°C): 1.01 g/cc; 1.8 dg/min (190°C, 2.16 kg); norbornene.

Capillary Rheology: LLDPE-A & -B, COC

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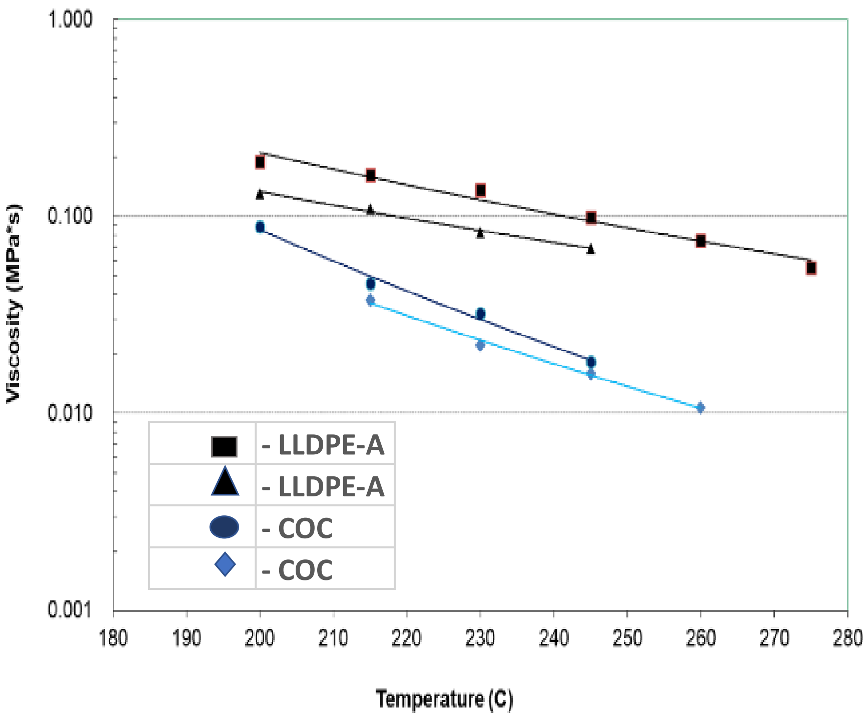

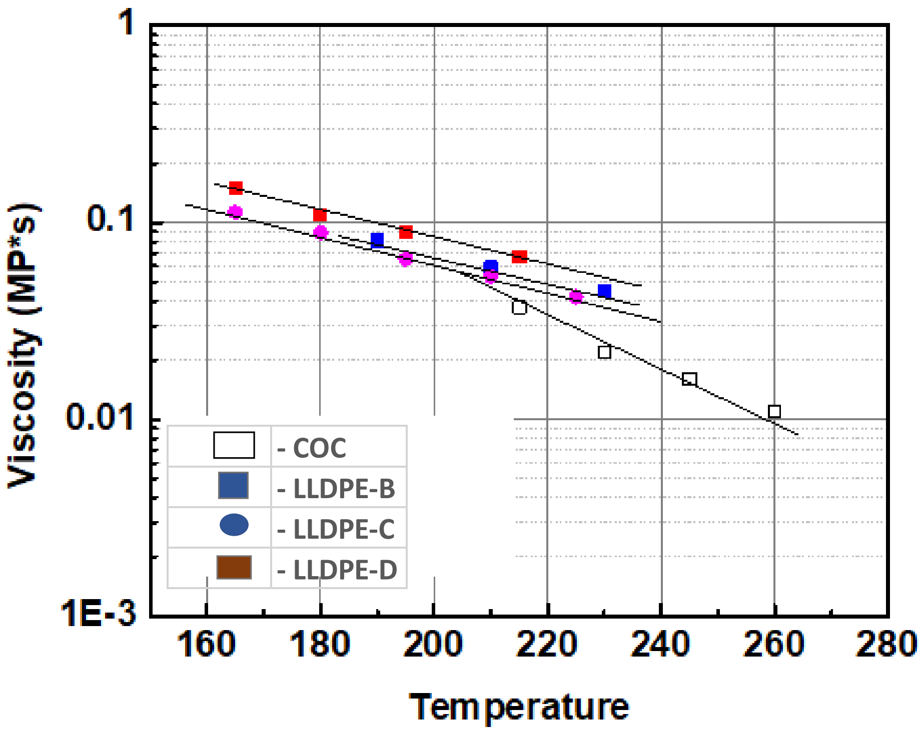

LLDPE-B shows closer viscosity match to COC than LLDPE-A.
Process temperatures in layer replicating units were 200 - 210°C.

Sample Preparation for AFM Imaging

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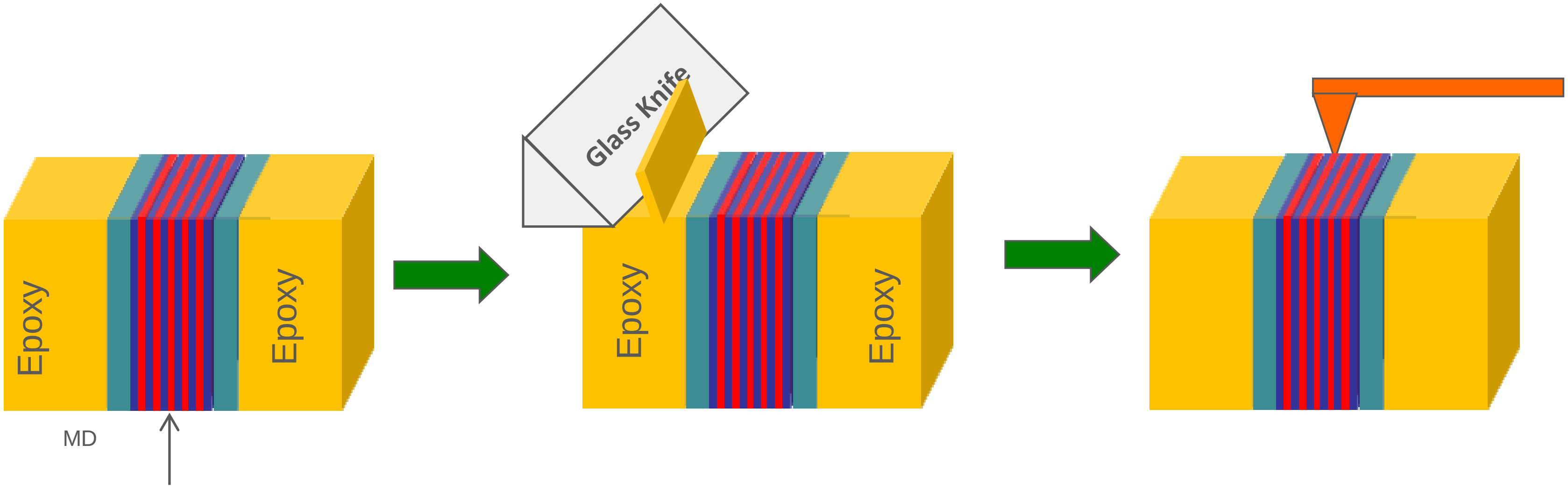


Sample Embedding

Cryo-Microtoming (-120 °C)

AFM Imaging (Tapping Mode)

Image Source: Polymer Plus, LLC

Cut sample from the center of the film.

View layer structure in MD direction.

Embed film in epoxy and microtome at -120 °C.

Microtomed sample section was imaged in tapping mode AFM.

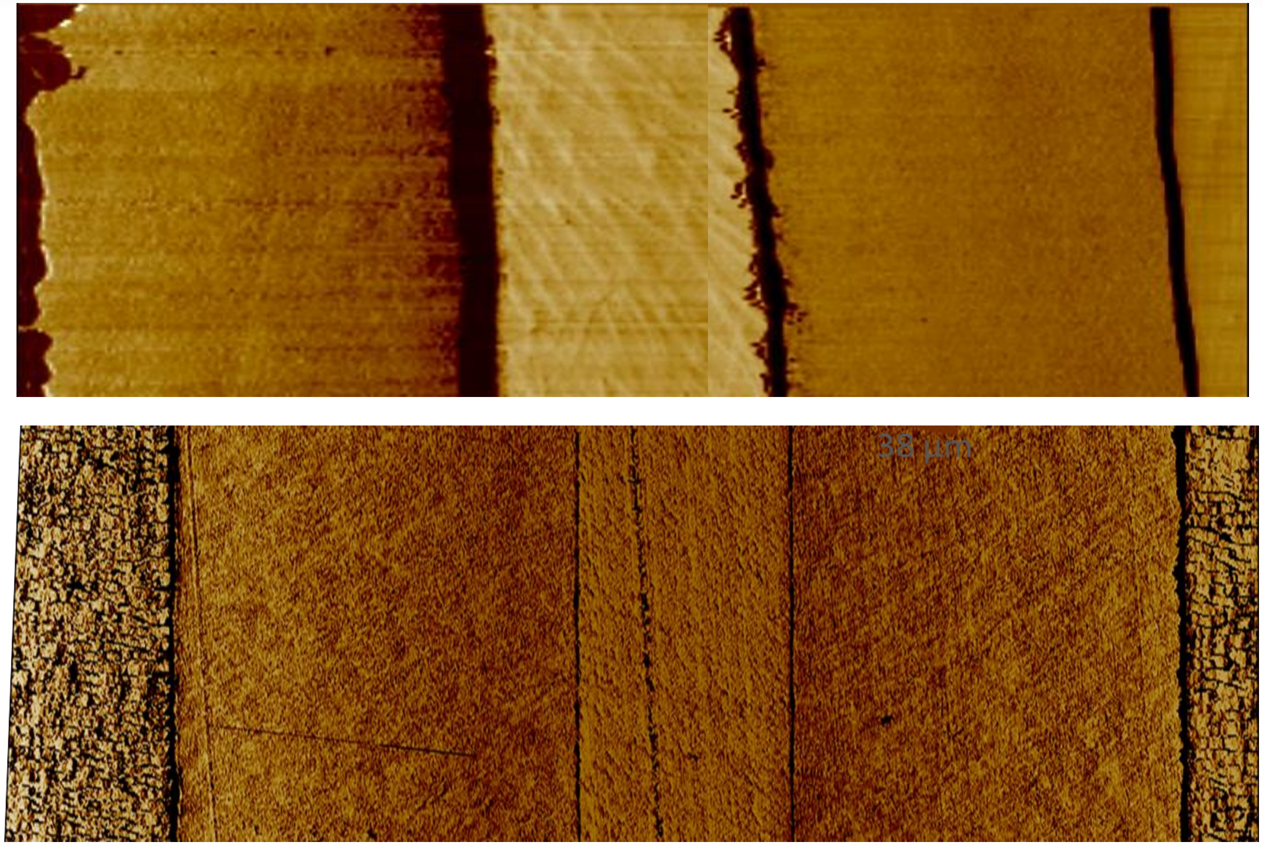
AFM Imaging & Analysis

- Multiple AFM images were taken to view entire film cross section.
- Several images, usually between 4 -10, are stitched together to form a composite image of the full cross-section.
- Determination of layer thickness and distribution:
  - For lower layer count structures thickness for up to 128 individual layers are measured.
  - For higher layer count structures thickness for groups of about 200 layers are measured.

80/20 LLDPE-A & -B/COC

AFM Images & Mechanical Properties

AFM: 3-Layer 80/20 LLDPE-A &-B/COC



LLDPE-A (µm)	
Target	Measured
20	15
COC (µm)	
Target	Measured
10	8

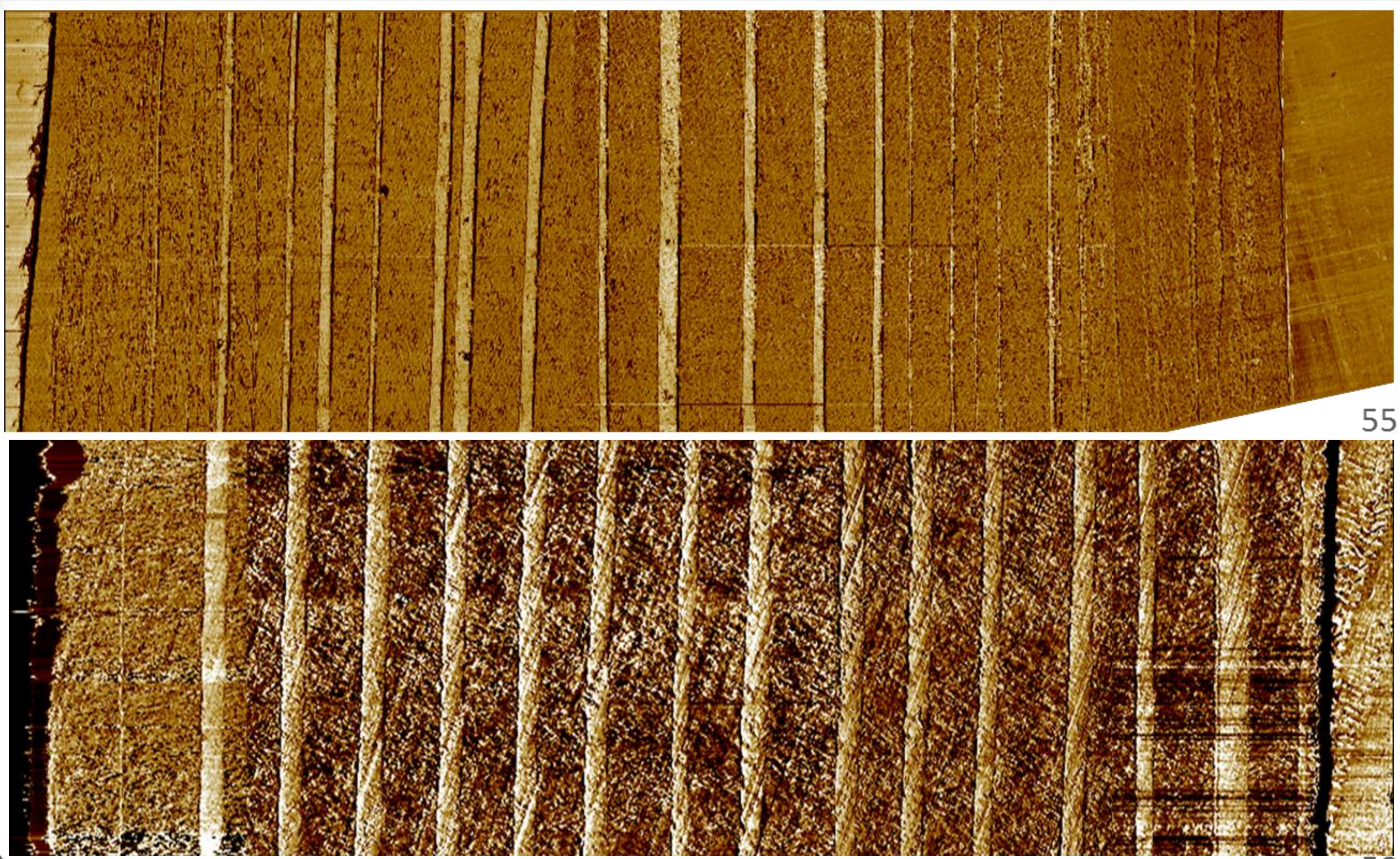
LLDPE-B (µm)	
Target	Measured
20	20.9
COC (µm)	
Target	Measured
10	11.3

LLDPE layers appear darker then COC layer.

Thickness of the imaged section LLDPE-A/COC & LLDPE-B/COC was 38 & 53 µm.

Measured ratio of LLDPE/COC was 79/21.

AFM: 33-Layer 80/20 LLDPE-A &-B/COC



LLDPE-A (nm)	
Target	Measured
2500	2500±1700
COC (nm)	
Target	Measured
625	380 ±210

LLDPE-B (nm)	
Target	Measured
2500	2300±600
COC (nm)	
Target	Measured
625	715±130

Rheological property difference between LLDPE-A & COC at processing temperatures led to layer thickness variation.
With exception of both outermost COC layers; considerably less layer thickness variation observed for LLDPE-B / COC.

AFM: 129-Layer 80/20 LLDPE-A &-B/COC

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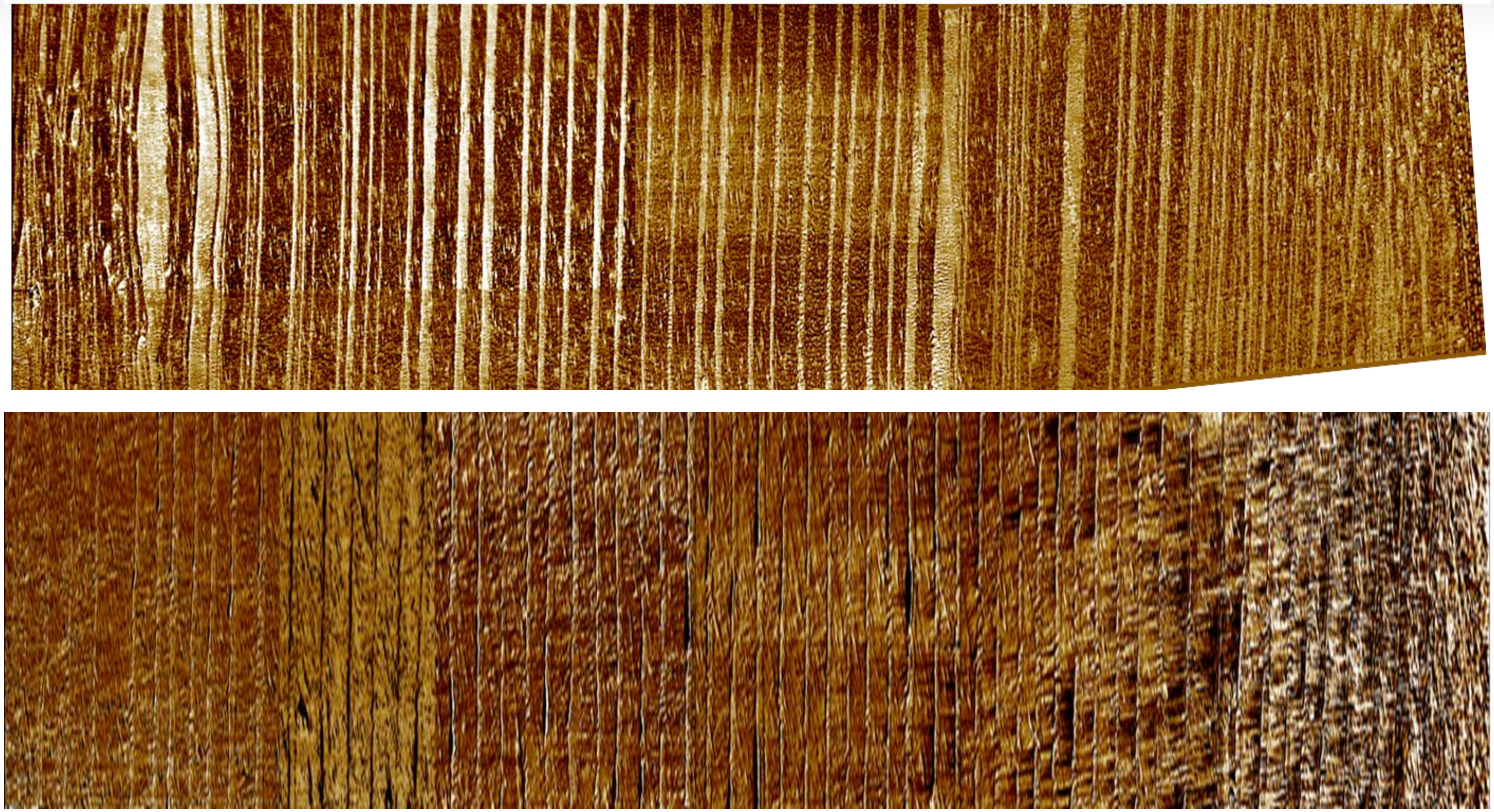

LLDPE-A (nm)	
Target	Measured
625	409±140
COC (nm)	
Target	Measured
155	160 ±110

LLDPE-B (nm)	
Target	Measured
625	620±110
COC (nm)	
Target	Measured
160	180 ±25

Top: 5 µm section on each side of the film was not imaged. 40+ distinct layers of COC and 40+ distinct layers of LLDPE could be seen in the imaged section. Layer integrity appears better in the middle layers.

Bottom: film showed good layer structure and low thickness variation. Measured composition from thicknesses was 77/23. Thinner layers are challenging to measure as the modulus difference becomes indistinguishable for AFM imaging.

AFM: 513-Layer 80/20 LLDPE-A &-B/COC

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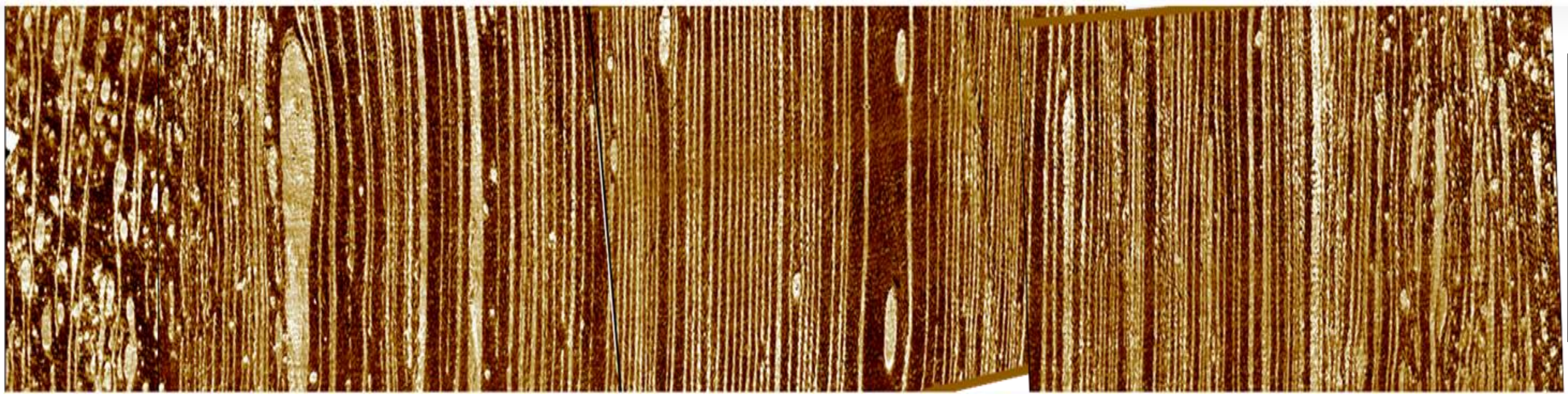
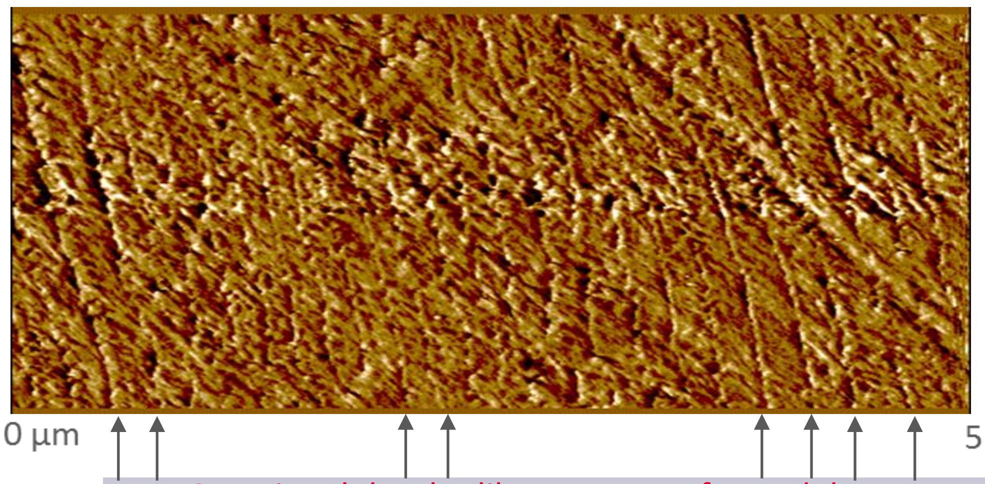


LLDPE-A (nm)	
Target	Measured
150	80-200
COC (nm)	
Target	Measured
40	30-70



LLDPE-B (nm)	
Target	Measured
160	150-200
COC (nm)	
Target	Measured
40	30-50

Top: Occasional droplet like structures formed due to partial layer break-up of very thin layers. Although there is significant viscosity mismatch, COC was coextruded down to few tens of nanometer.
Bottom: Layer differentiation was difficult due to low contrast between the layers. Film contained continuous layers, with possible partial layer break-up. Dark arrows represent COC layers.

2% Secant Modulus vs. Film Layers: 80/20 LLDPE-A & LLDPE-B/COC

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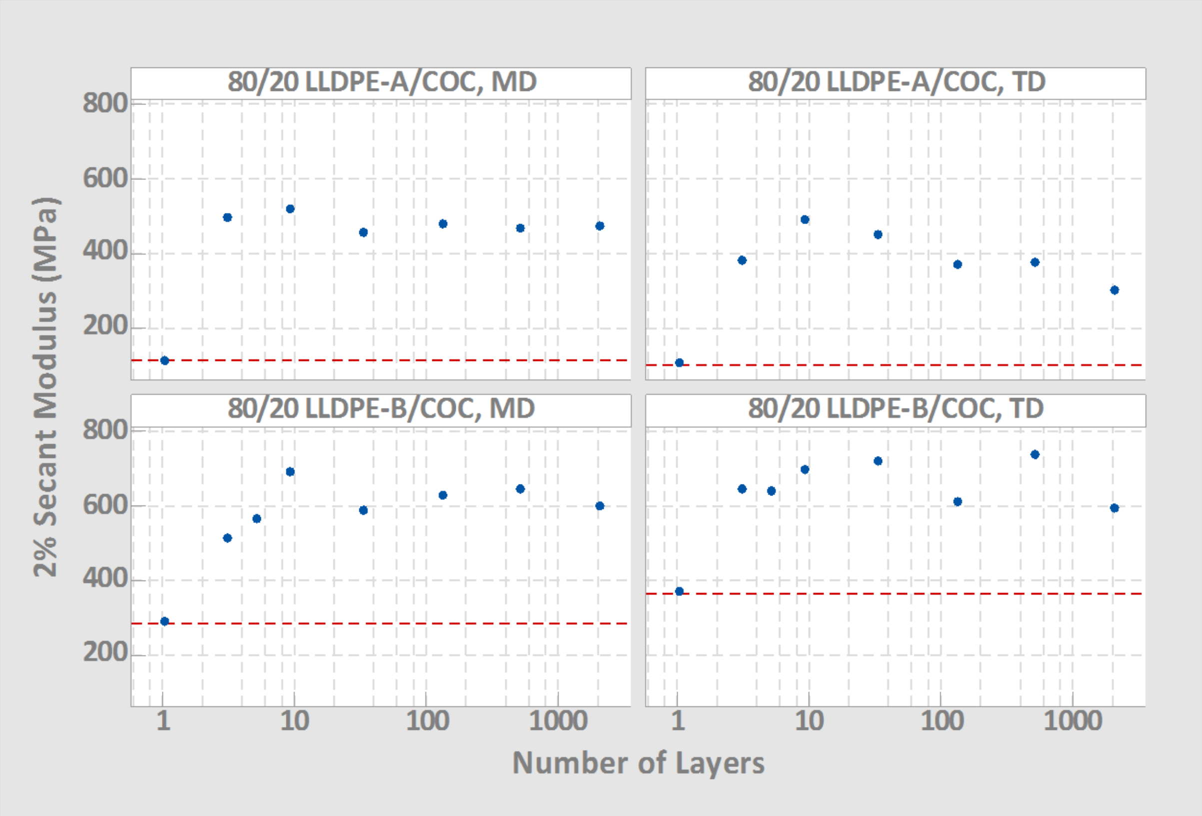

LLDPE-A:

- COC significantly improves stiffness.
- Splitting COC layers has minor positive influence on modulus.
- TD variation

LLDPE-B:

- Splitting COC layers has more influence on modulus vs. LLDPE-A.
- TD variation

Significant difference observed between LLDPE grades.
Splitting COC into multiple layers has modest positive influence on modulus.
Benefit retained across many layers.

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Stress at Yield vs. Film Layers: 80/20 LLDPE-A & LLDPE-B/COC

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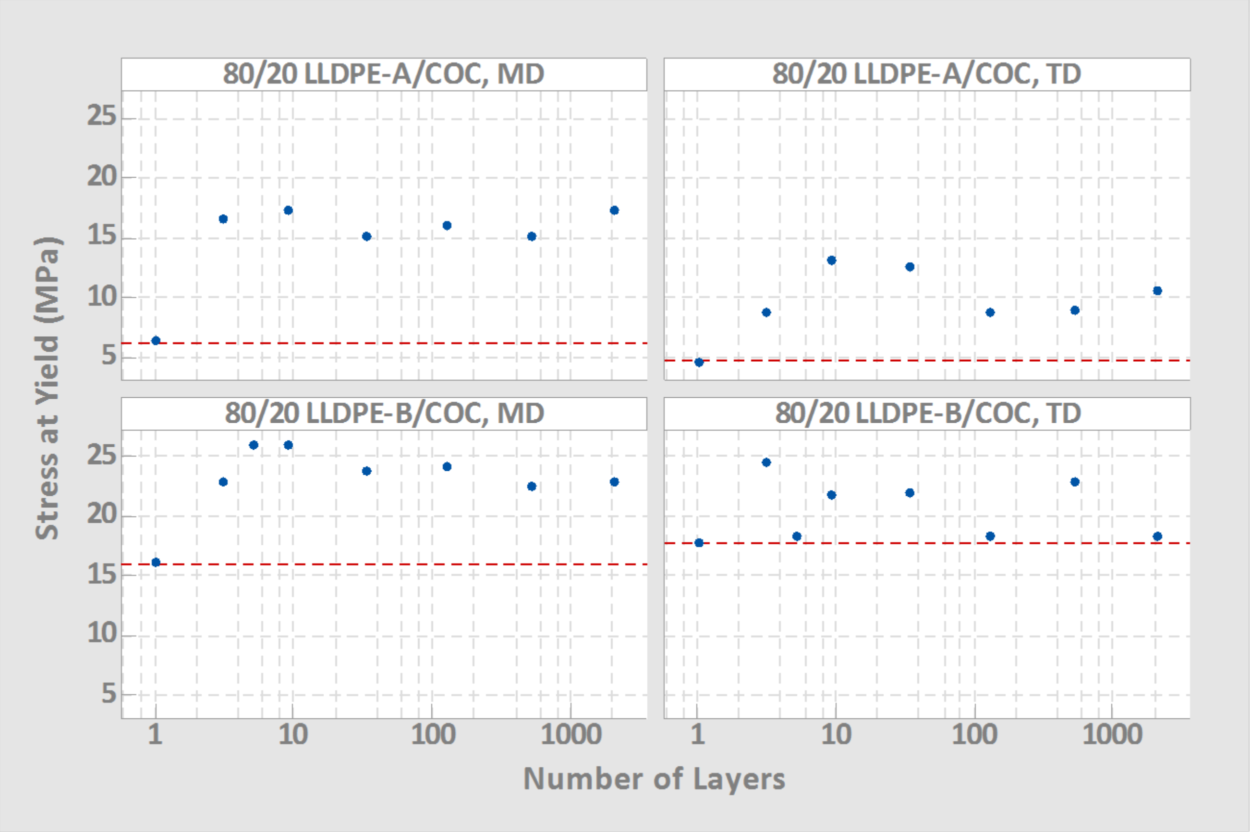

LLDPE-A:

- COC significantly improves stress at yield.
- Splitting COC layers has minimal influence on stress at yield.
- TD variation

LLDPE-B:

- Much higher stress at yield vs. LLDPE-A.
- TD variation

Significant difference observed between LLDPE grades.
Splitting COC into multiple layers has minimal influence on stress at yield.

Stress at Break vs. Film Layers: 80/20 LLDPE-A & LLDPE-B/COC

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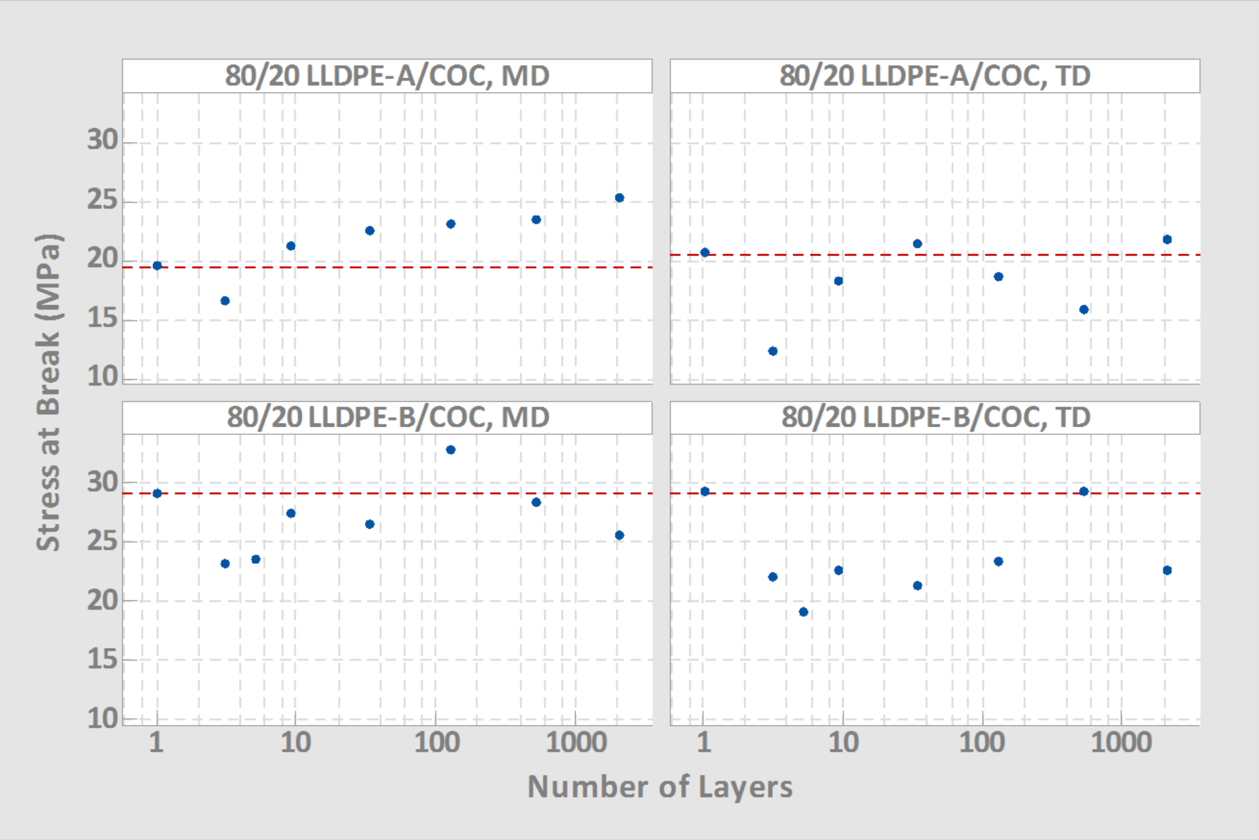

LLDPE-A:

- COC significantly improves stress at break.
- Splitting COC layers has strong positive influence on stress at stress
- TD variation

LLDPE-B:

- Splitting COC layers modestly improves stress at break.
- TD variation

Significant difference observed between LLDPE grades.

Splitting COC into multiple layers has strong positive influence on stress at break, enabled by more strain hardening.

Strain at Break vs. Film Layers: 80/20 LLDPE-A & LLDPE-B/COC

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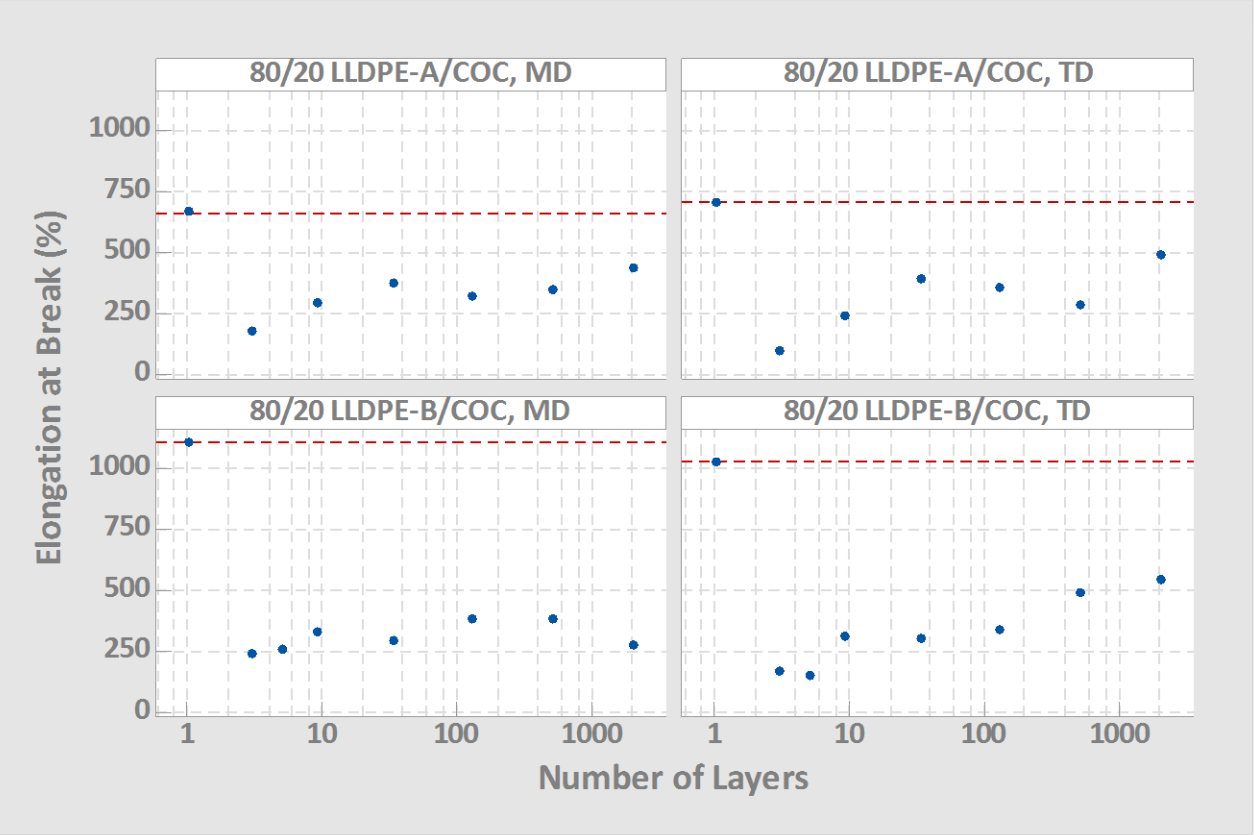

LLDPE-A:

- <10 layers, recovery in film ductility occurs from splitting COC layers.

LLDPE-B:

- Film ductility gradual recovers from splitting COC layers.
- Better viscosity match

Splitting COC layers helps restore film ductility.
Significant EOB difference observed between LLDPE grades.

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Tensile Energy (TE) Film Layers: 80/20 LLDPE-A & LLDPE-B/COC

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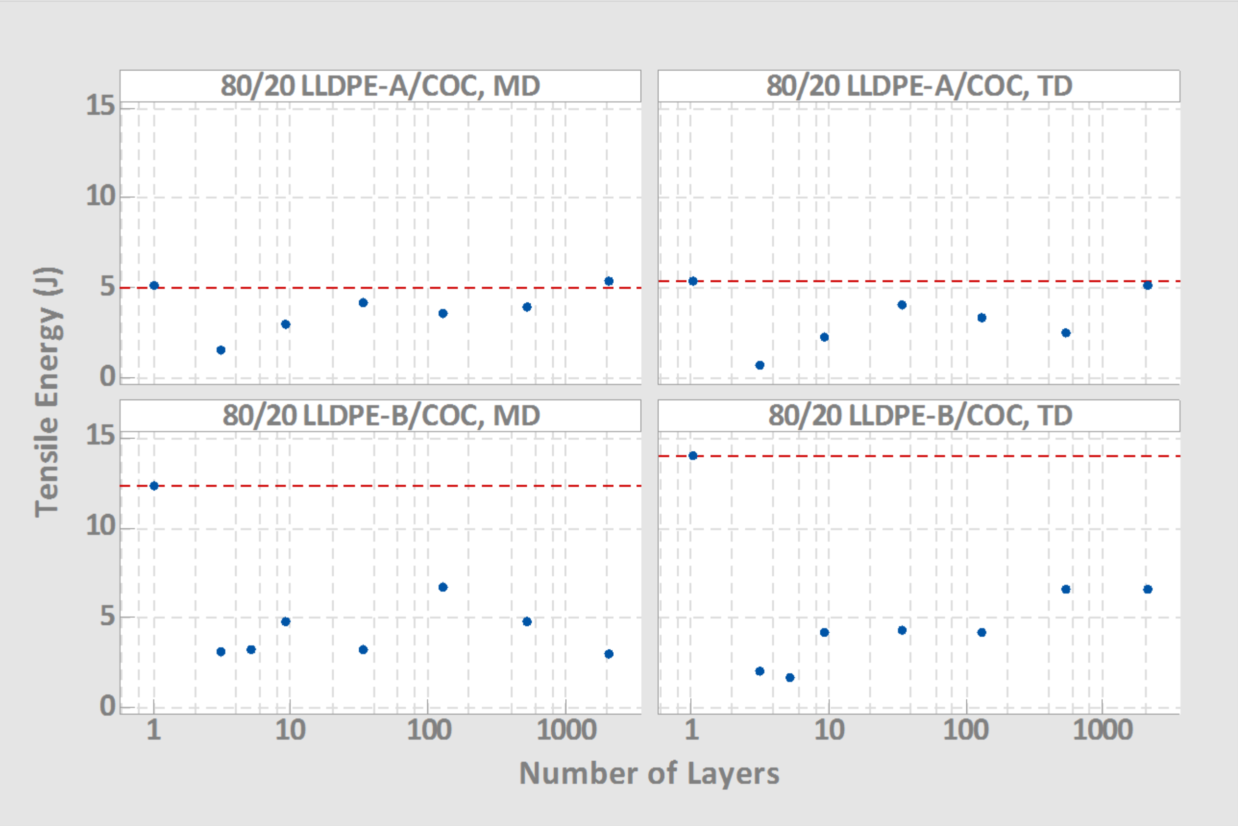

LLDPE-A:

- 10-100 layers: splitting COC layers "recovers" (TE) toward pure LLDPE-A

LLDPE-B:

- 10-100 layers: modest increase in (TE) occurs from splitting COC layers.

Significant difference observed between LLDPE grades.
Splitting COC into multiple layers enables better durability!

Total Haze vs. Film Layers:
80/20 LLDPE-A & LLDPE-B/COC

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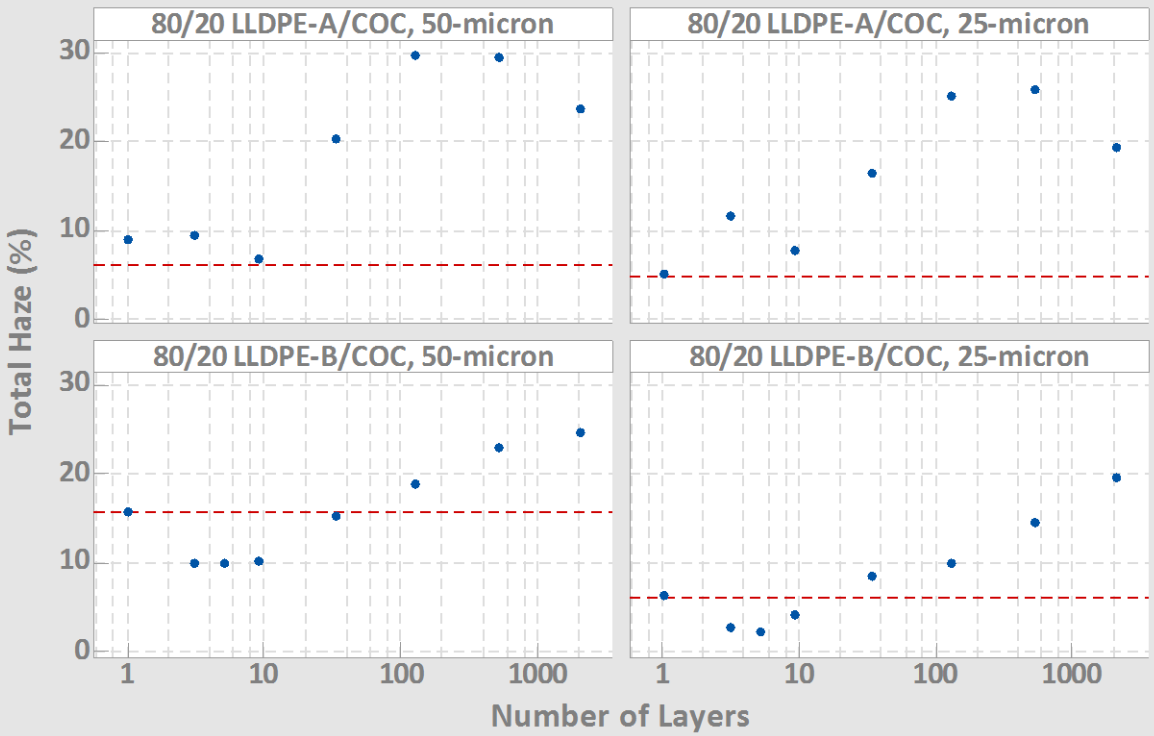

LLDPE-A:

- >10 layers, sharp increase in total haze occurs from splitting COC layers.

LLDPE-B:

- <10 layers, significant haze minimization occurs from splitting COC layers.
- Better viscosity match!

Viscosity match between LLDPE & COC in the replication die is essential to maintain layer distinction, especially above 100 layers.

Significant difference observed between LLDPE grades.

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80/20 & 20/80 LLDPE-B/COC
AFM Images & Mechanical Properties

AFM: 9-Layer 20/80 & 80/20 LLDPE-B/COC

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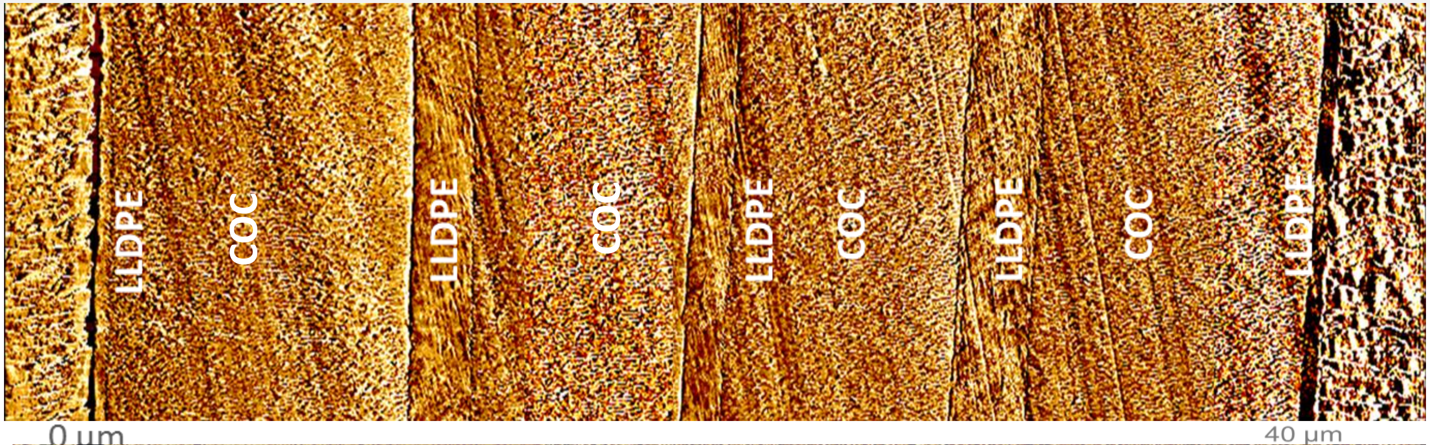
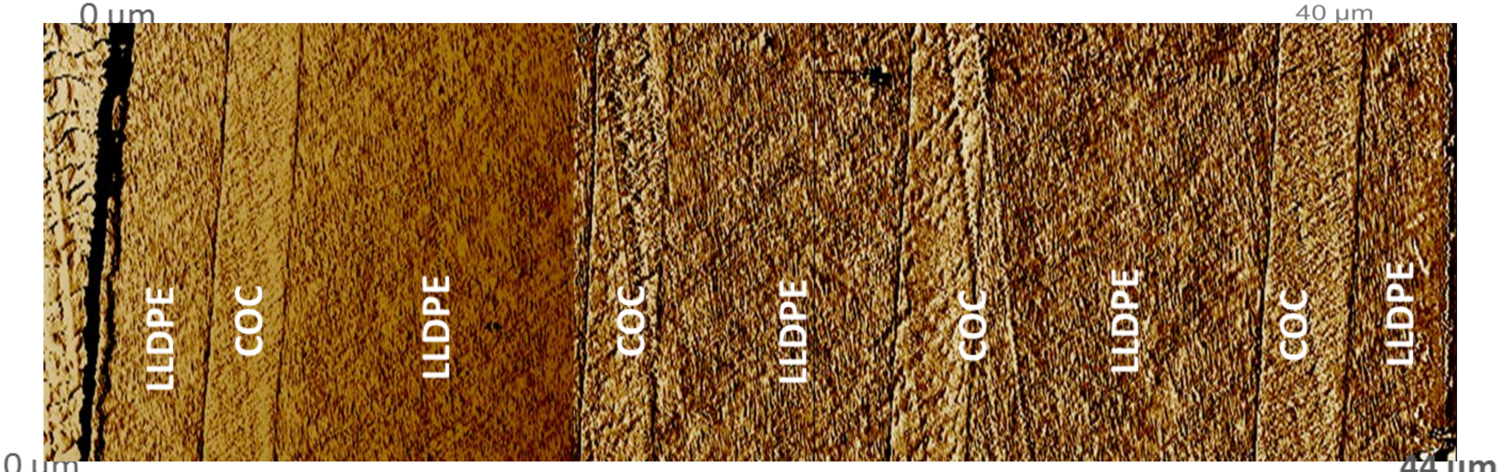


20/80 (µm)
COC Target: 10
COC Measured:
9.4, 7.6, 7.3, 8.3
LLDPE Target: ---
LLDPE Measured:
0.6, 2.0, 1.4, 2.3, 0.6



80/20 (µm)
COC Target: 2.5
COC Measured:
2.4, 2.3, 2.5, 2.7
LLDPE Target: ---
LLDPE Measured:
3.6, 9.5, 8.0, 9.5, 3.7

Both films have good layer stability and minimal layer thickness variation.
Measured layer ratios are 19/81 and 78/22 respectively, close to targets.

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AFM: 129-Layer 20/80 & 80/20 LLDPE-B/COC

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20/80 (nm)	
COC (nm)	
Target	Measured
625	550±60
LLDPE (nm)	
Target	Measured
160	140 ±25

80/20 (nm)	
COC (nm)	
Target	Measured
160	180 ±25
LLDPE (nm)	
Target	Measured
625	620±110

Top: 126+ layers were imaged. Leftmost layer could not be imaged due to significant delamination between epoxy-LLDPE interface. Overall, the film showed good layer structure and periodicity. No layer break-up was observed.

Bottom: film showed good layer structure and low thickness variation. Measured composition from thicknesses was 77/23. Thinner layers are challenging to measure as the modulus difference becomes indistinguishable for AFM imaging.

AFM: 513-Layer 20/80 & 80/20 LLDPE-B/COC

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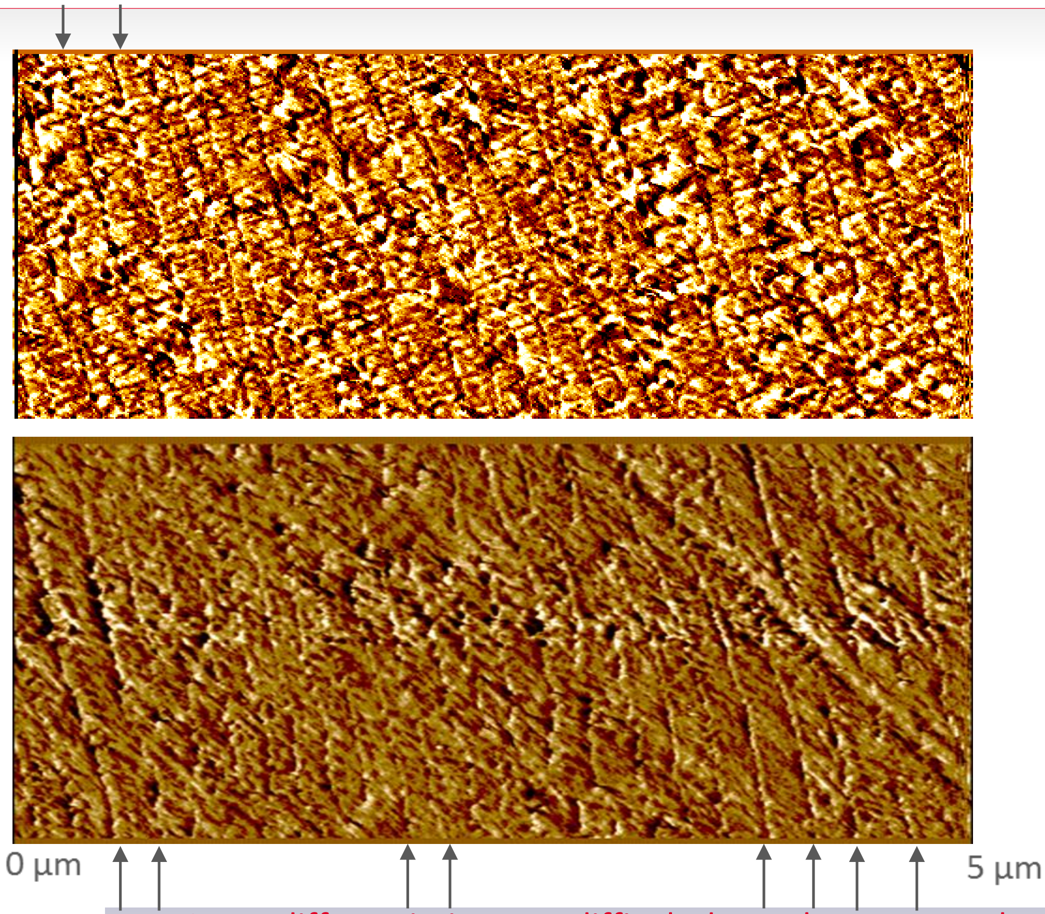

20/80 (nm)	
COC (nm)	
Target	Measured
160	150-200
LLDPE (nm)	
Target	Measured
40	30-50

80/20 (nm)	
COC (nm)	
Target	Measured
40	30-50
LLDPE (nm)	
Target	Measured
160	150-200

Top: Layer differentiation was difficult due to low contrast between the layers. Film contained continuous layer in the imaged section. Black arrows represent 30-50 nm LLDPE layers.
Bottom: Film contained continuous layers, with possible partial layer break-up. Dark arrows represent 30-50 nm COC layers.

2% Secant Modulus vs. Film Layers: 80/20 & 20/80 COC with LLDPE-B

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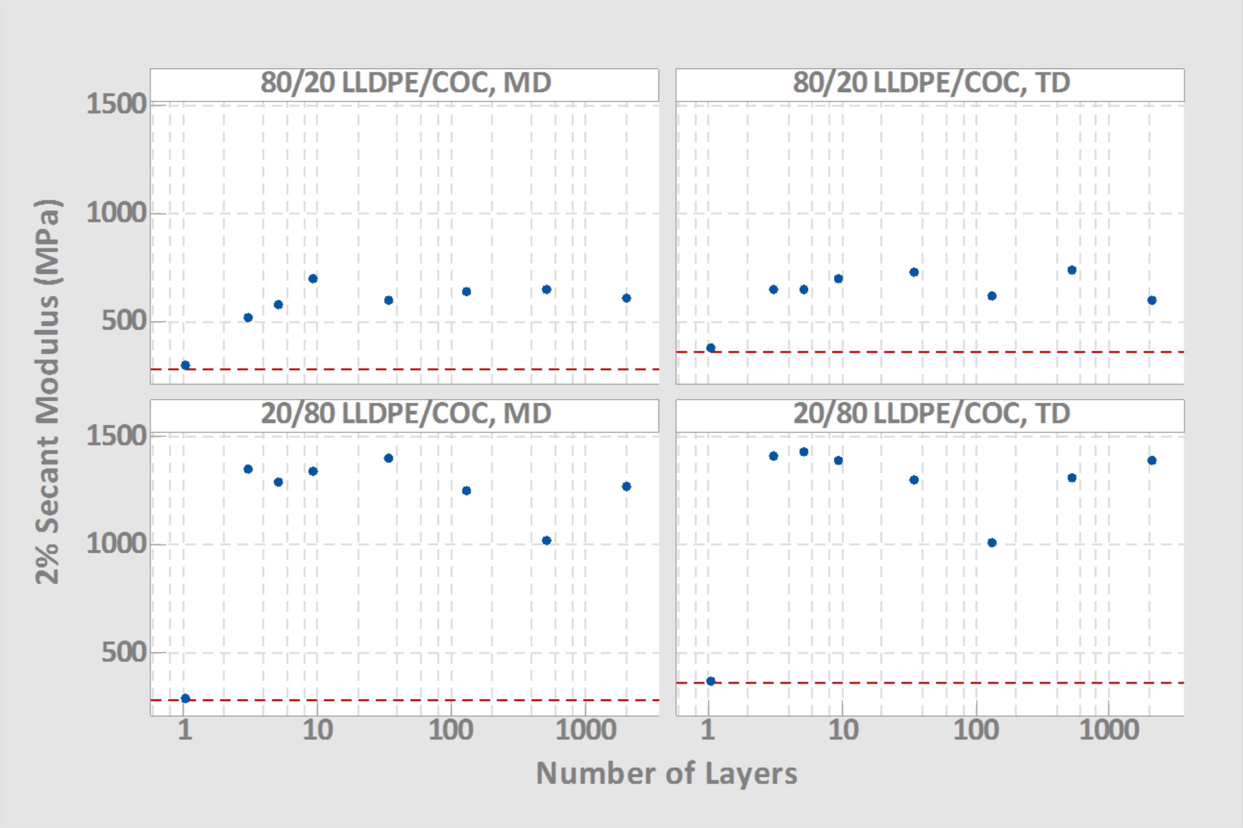

LLDPE Rich 80/20:

- COC improves stiffness of LLDPE.
- Modulus improves slightly by splitting into <100 layers.
- Layer splitting does not compromise modulus.

COC Rich 20/80:

- Very high modulus.
- More variation above >100 layers due to onset LLDPE layer break-up.

20% COC enhances LLDPE film stiffness by factor of 2-3 times.
<100 layers, splitting does not compromise modulus.

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Stress at Yield vs. Film Layers: 80/20 & 20/80 COC with LLDPE-B

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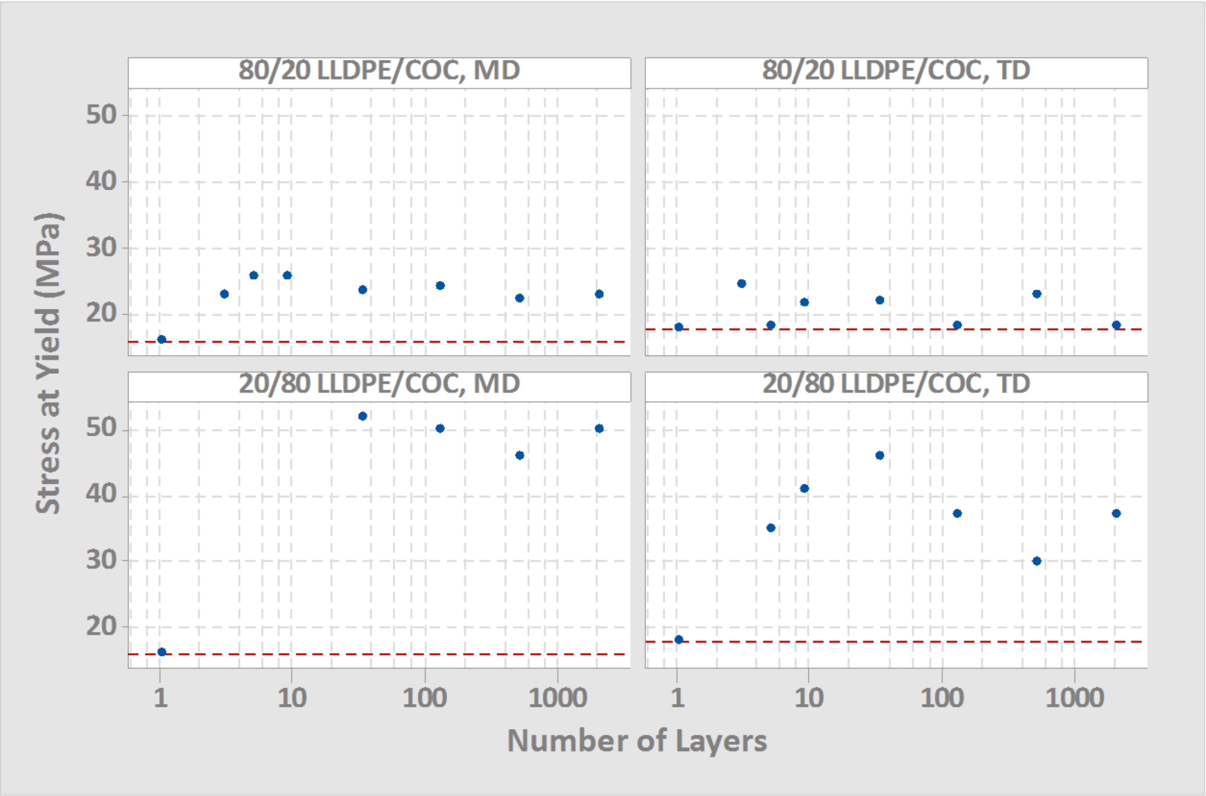

LLDPE Rich 80/20:

- COC improves yield stress for LLDPE.
- Modest improvement in MD from splitting COC layers.

COC Rich 20/80:

- Pure COC does not have yield point.
- LLDPE layer splitting enables measurable yield point.

20% COC enhances LLDPE film yield stress, but at the expense of yield strain.

20% LLDPE enables yield point in COC film, but by slightly improving elongation at yield.

Best results achieved by splitting into 129 layers.

Tensile Energy vs. Film Layers: 80/20 & 20/80 COC with LLDPE-B

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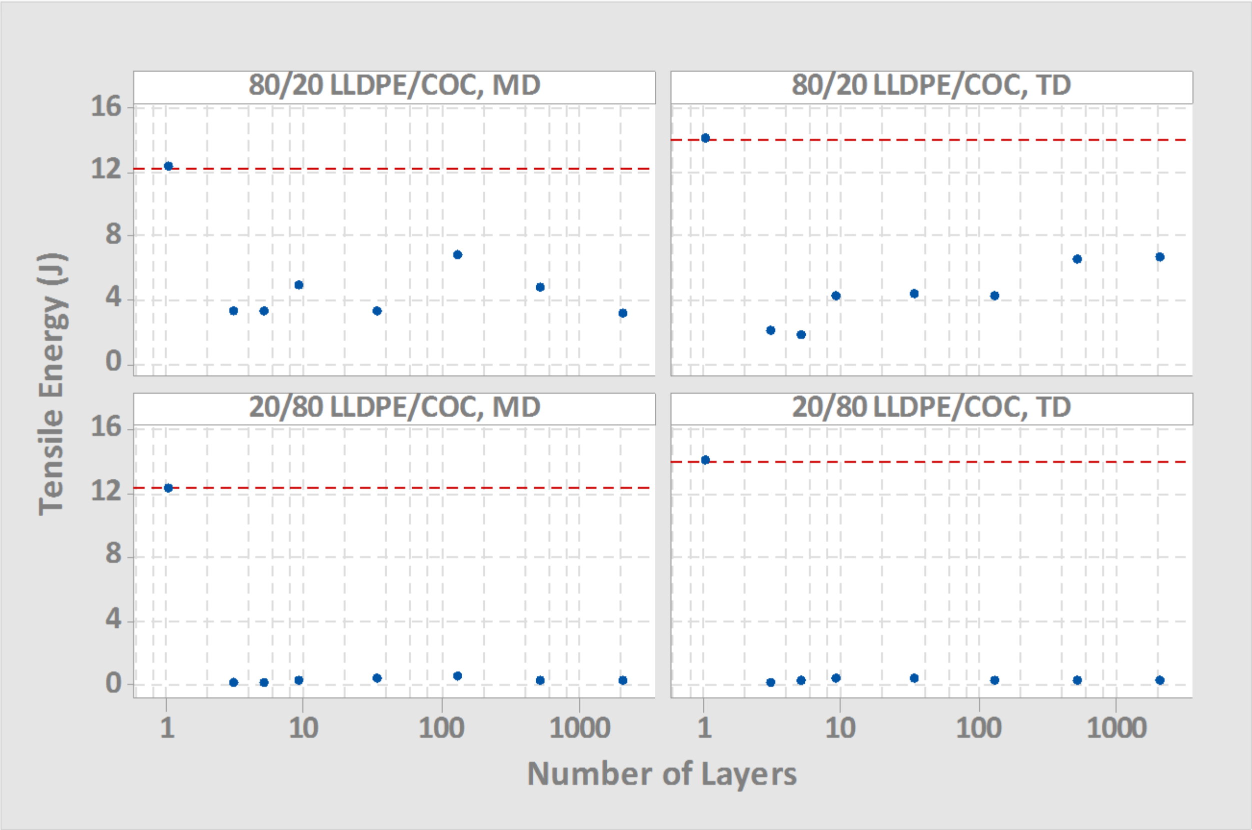

LLDPE Rich 80/20:

- Multiple split layers of COC "recovers" film durability, by reducing low ductility & brittleness of COC.

COC Rich 20/80:

- Discrete layers of LLDPE fail to improve durability of COC.

LLDPE films with 20% COC can minimize loss in tensile energy by splitting COC layers. COC films with 20% LLDPE failed to improve durability. More LLDPE needed.

Total Haze vs. Film Layers: 20/80 & 80/20 COC with LLDPE-B

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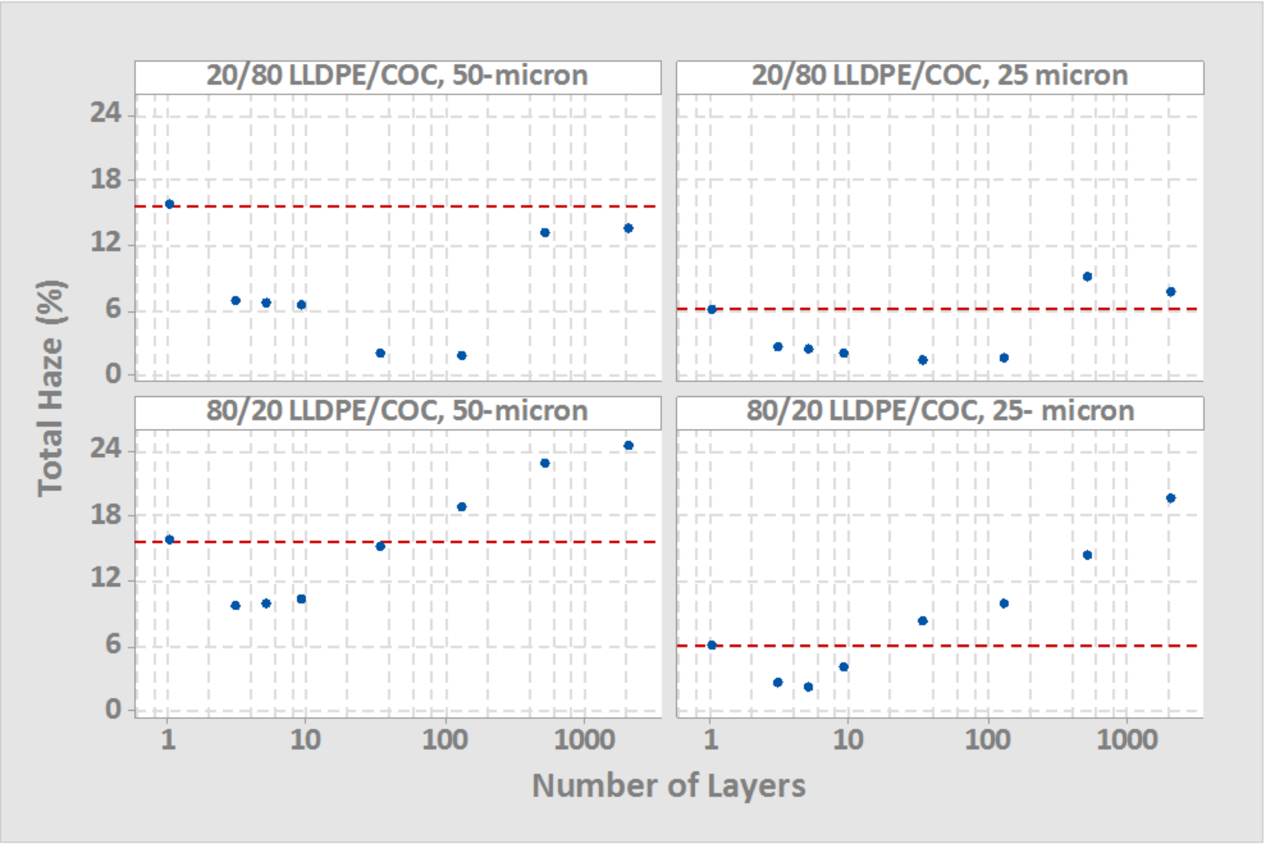

COC Rich 20/80:

- Very low haze at 33 & 133 layers.
- Small contribution from LLDPE-B.

LLDPE Rich 80/20:

- <10 layers, COC split layers reduces total haze of LLDPE films.
- >500 layers, onset of layer breakup.

Independent of COC/LLDPE-B ratio, total haze minimization occurs by splitting COC layers multiple times.

Gloss, 60° vs. Film Layers: 20/80 & 80/20 COC with LLDPE-B

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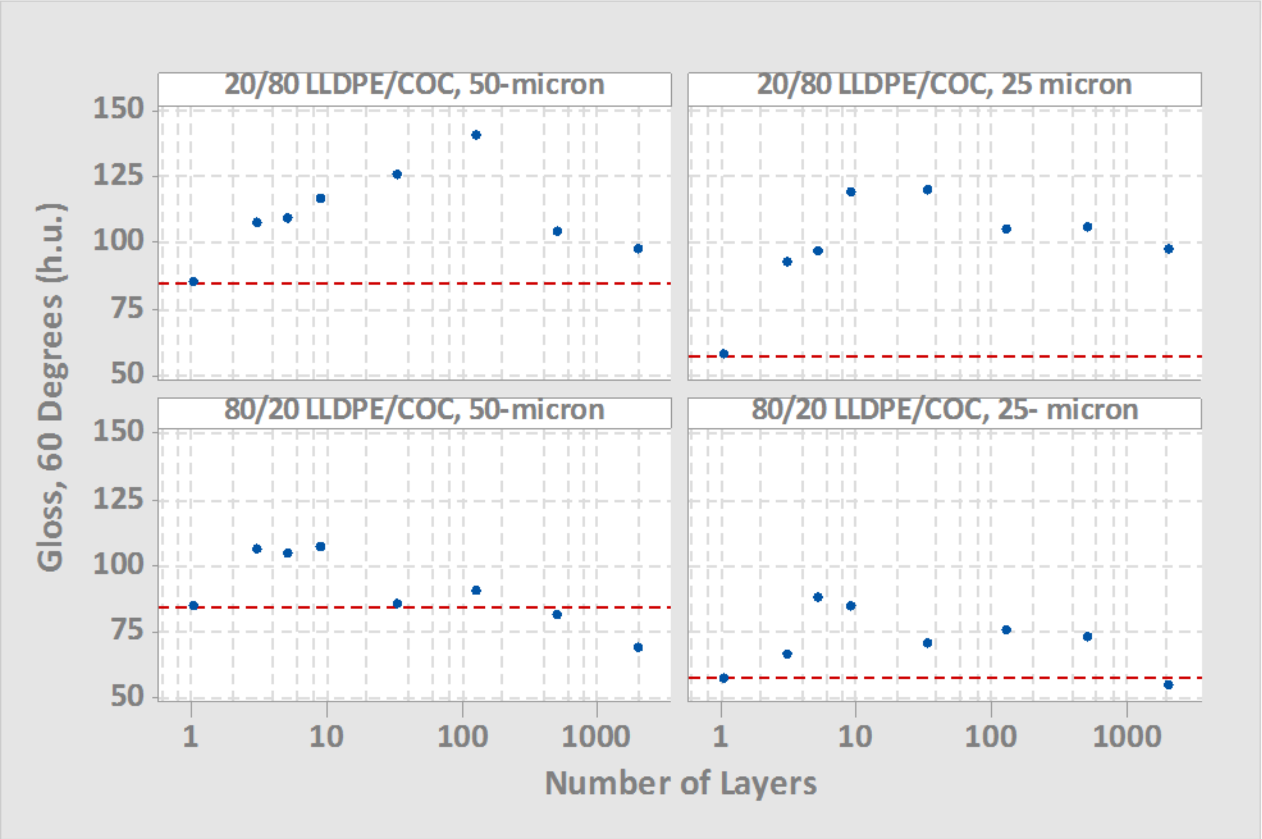

COC Rich 20/80:

- Very high gloss at 33 & 133 layers.
- Enhancement caused by multiple LLDPE layers.

LLDPE Rich 80/20:

- COC enhances gloss of LLDPE films.
- Higher gloss observed in 25 & 50-µm film from COC split layers.

Independent of COC/LLDPE-B ratio, gloss enhancement occurs by splitting COC layers multiple times.

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Conclusions

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Conclusions (1)

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- **Stiffness, strength, durability and optics of LLDPE films can be improved by using multiple COC layers.**
  - **Nearly all beneficial enhancements occur in films with <129 layers.**
  - **Practically speaking, most benefits occur in films with few split COC layers, which can be accomplished with commercially installed 7-11 layer blown & cast extrusion lines.**
- **Close LLDPE & COC viscosity matching is critical to maintain good layer stability and low layer thickness variation.**
  - **Poor viscosity matching contributes to layer non-uniformity & onset of layer breakup.**

Conclusions (2)

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- Splitting COC layers helps restore film ductility and durability.
- As shown in 513 layer films, COC can be extruded into discrete continuous layers with thickness of about 40 nm. (Technically unexpected)
- Multiple layers of LLDPE did not improve durability of 20/80 LLDPE-B/COC films. However, as many as few dozen LLDPE layers reduced total haze and increase gloss.

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TOPAS® COC Modifies Billions of Pounds of Polyethylene -- One Pound at a Time

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