Polyethylene for Blown and Cast Film

Mike Rutkowske

Senior TS&D Specialist

The Dow Chemical Company

Original Author: Wes Hobson

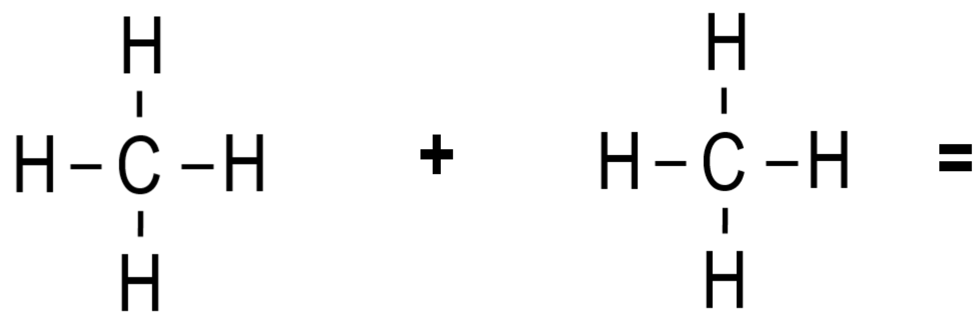
DOW

Seek Together

Agenda

- Chemistry Review
- Types of Polyethylene
- Defining Polyethylene
- Properties of Polyethylene
- Comonomer Choices
- Plastomers and Elastomers
- Quiz

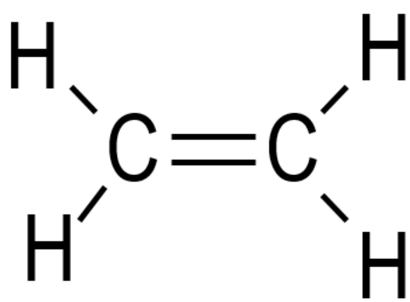
Hippie Chemistry



Methane Methane

Bonus Points – why is it Hippie?

Ethylene (Technically Ethene)



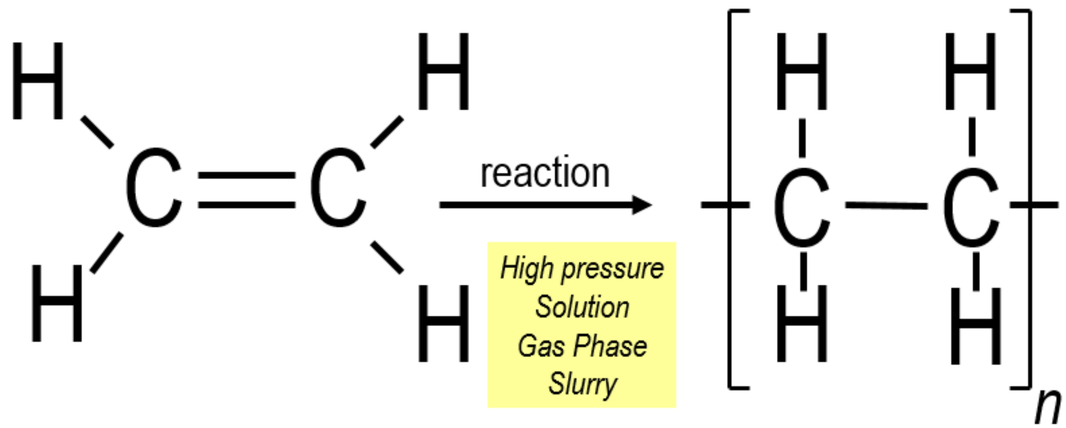
Ethene

Bonus Points – Organic Alphabet

C
C2
C3
C4
C5
C6
C7
C8
C9
C10
……..

Extra Bonus Points - Why not Ethane?

Polyethylene



Root Word (Poly) = Many
"n" can be hundreds
or thousands…

How many kinds of polyethylene are there?

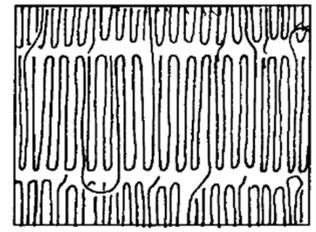
……….Thousands?

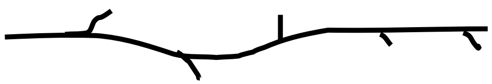
……………………..Millions?

Fortunately, we can segment broadly with one variable….

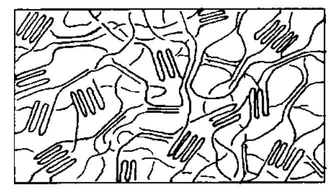
3 Types of PE – Defined by Branching

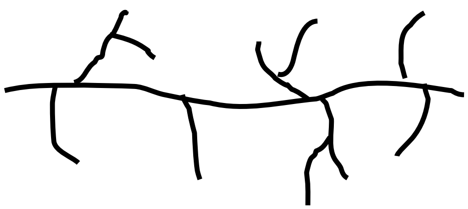
HDPE





LLDPE



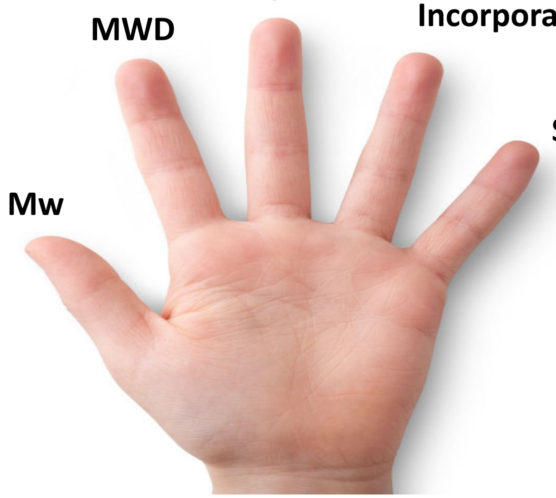


LDPE

Branching lowers the density of the polymer by preventing it from being able to fold up into a crystal.

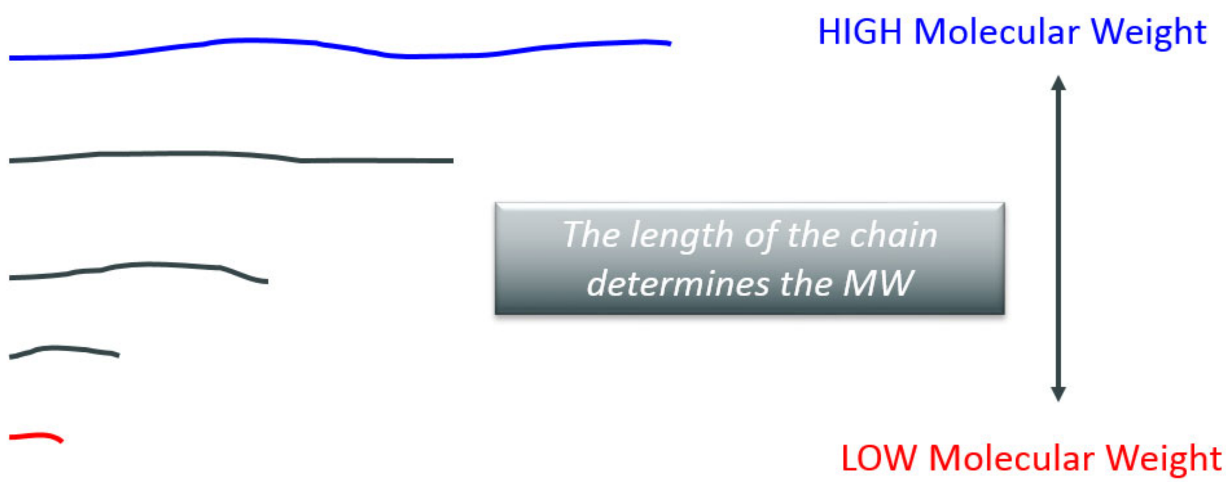
5 Things Determine ALL Polyethylene

- There are only 5 variables that completely define ANY polyethylene.
- Let's quickly learn them!



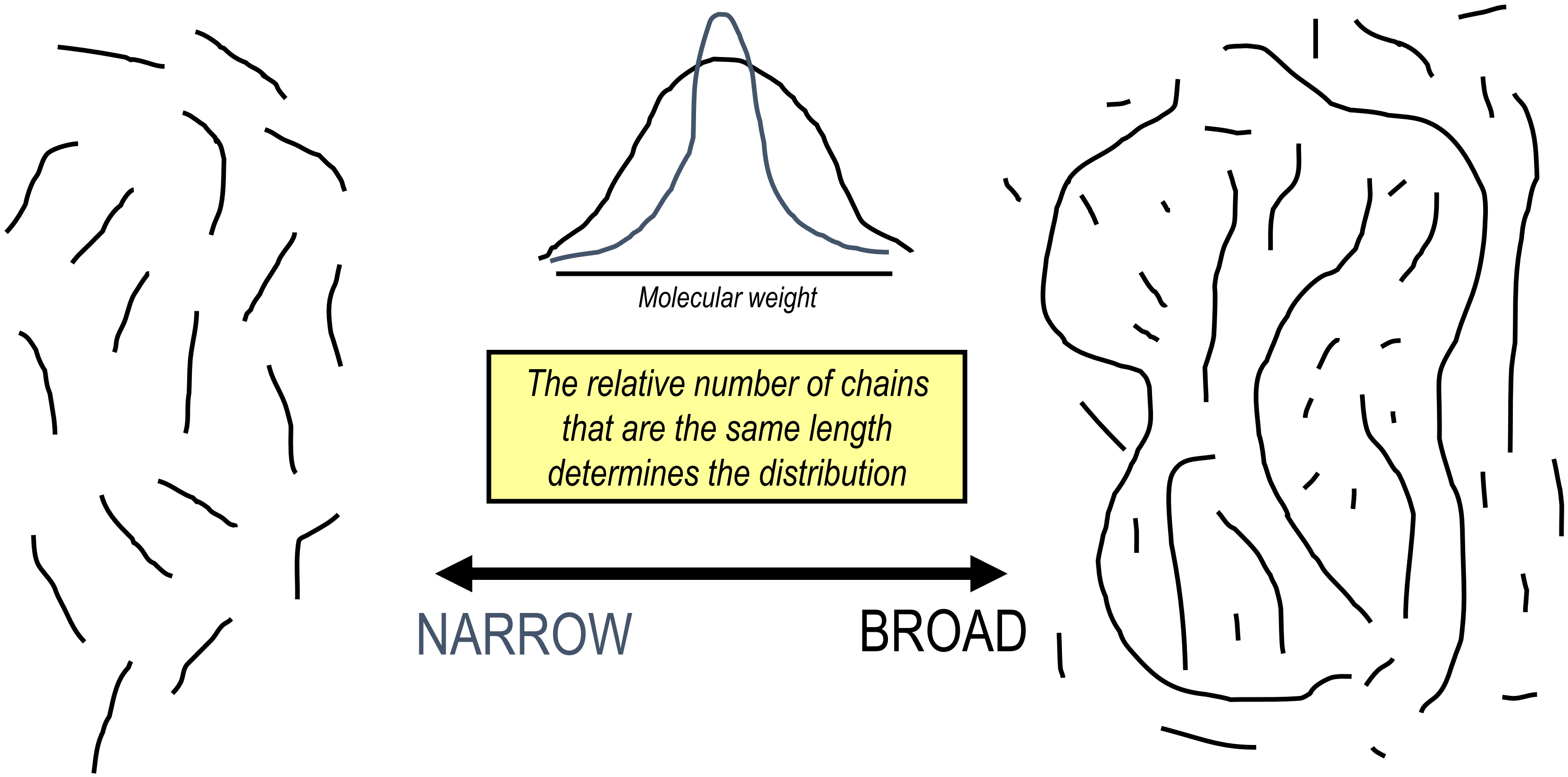
Mw = ***Molecular Weight***
MWD = ***Molecular Weight Distribution***
LCB = ***Long Chain Branching***
SCB = ***Short Chain Branching***
SCBD = ***Short Chain Branching Distribution***

1. Molecular Weight (MW)

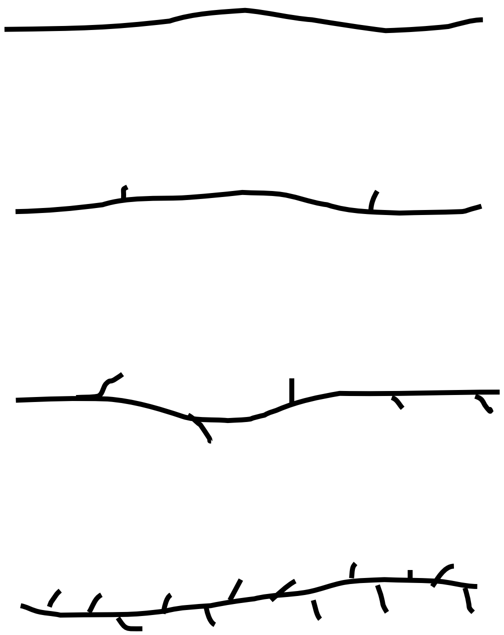


Melt **Index measurement gives an indication of Molecular Weight** (Higher Melt Index indicates Lower Molecular Weight**)**

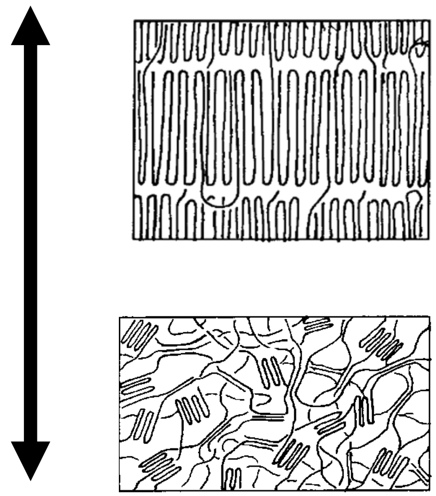
2. Molecular Weight Distribution (MWD)



3. Short Chain Branching (SCB)



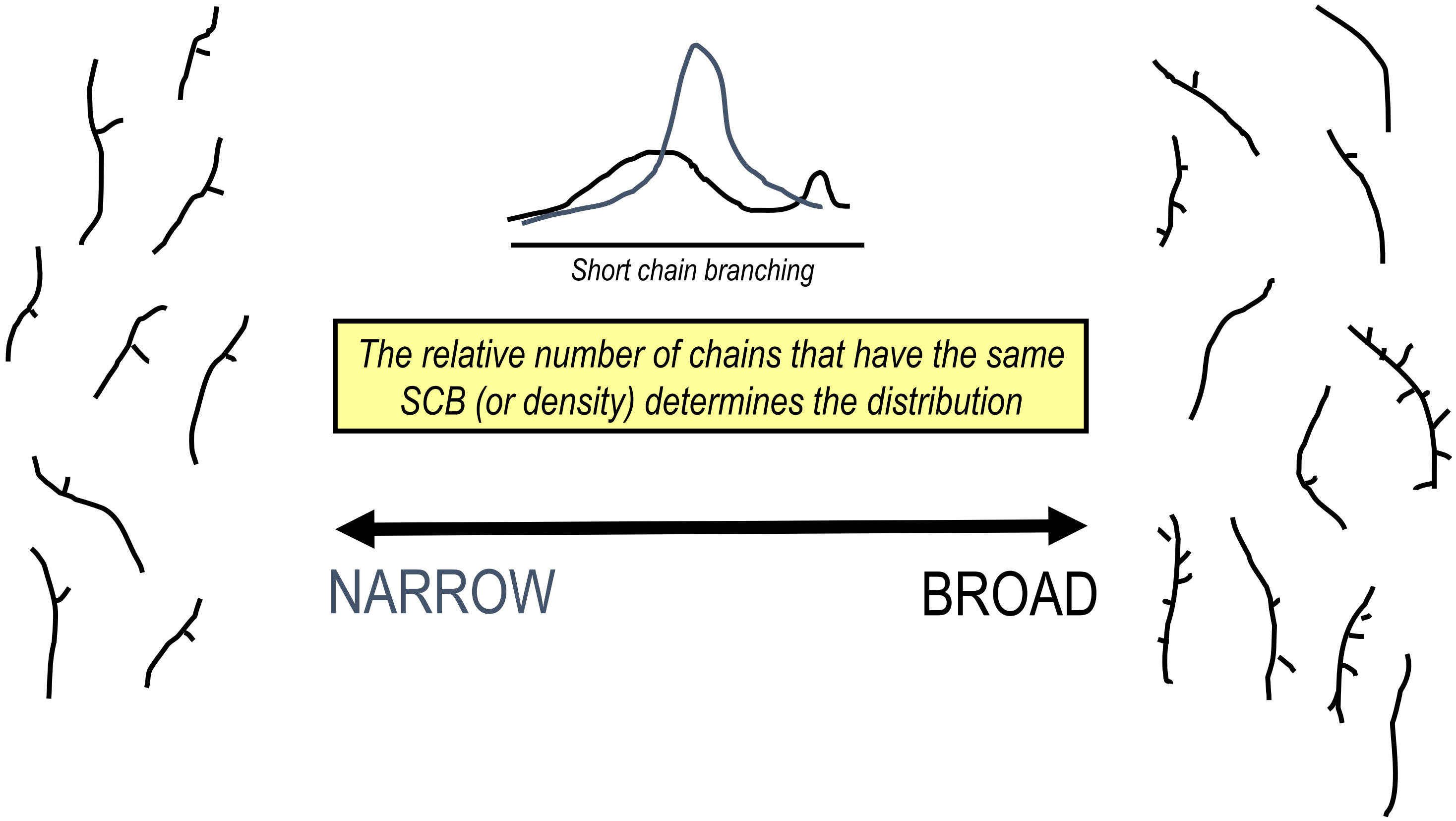
LOW Branching – HIGH Density



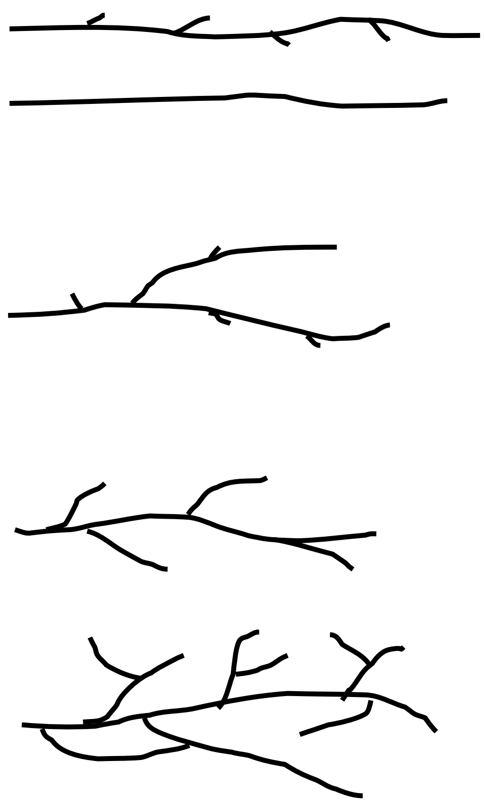
The number of branches on the chain determines the density.

HIGH Short Chain Branching – LOW Density

4. Short Chain Branching Distribution (SCDB)



5. Long Chain Branching (LCB)



NO Long Chain Branching

↕

HIGH Long Chain Branching

The number of major branches determines the long chain branching

SCB DOES NOT EQUAL LCB

5 Things Determine ALL Polyethylene

Mw	Molecular weight
MWD	Molecular weight distribution
SCB	Short chain branching
SCBD	Short chain branching distribution
LCB	Long chain branching

So what?

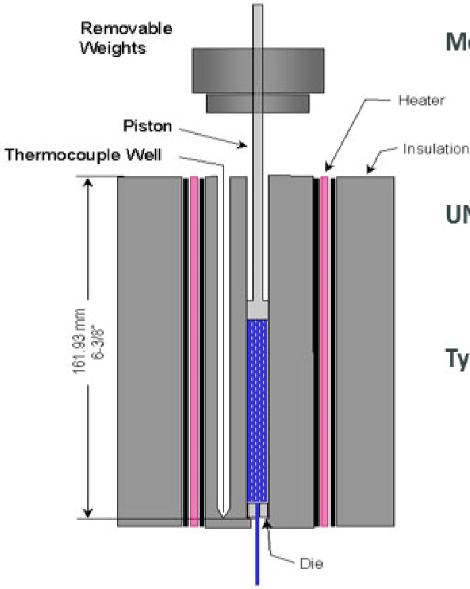
- Those 5 properties affect the final properties of the polymer.
- <u>Some</u> of those 5 properties affect processing.

- If you understand “even just a little” of it, you can understand the relative physical properties of different polymers and how to process them.

So How Do We Measure?

M_w	~ Melt Index (I_2) (↑M_w, ↓MI)
MWD	~ I_{10} / I_2 (↑MWD, ↑I_{10}/I_2)
SCB	~ Density (↑SCB, ↓Density)
SCBD	*No quick measure*
LCB	~ Melt Strength (↑LCB, ↑MS/MT)
	Or Melt Tension

Properties – Melt Index and I_{10}/I_2 [Mw & MWD]



Method A: Manual Method

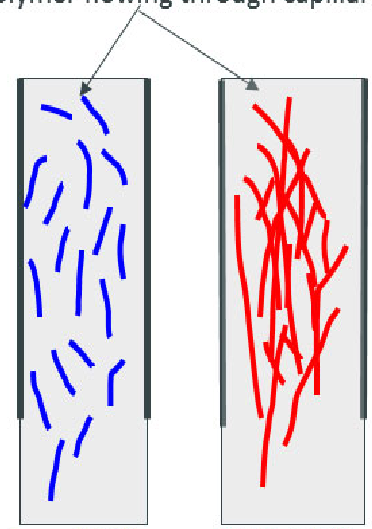
At a fixed load polymer is extruded through capillary and collected over a timed period and weighed.

UNIT OF MEASUREMENT:

grams/10 minutes at constant temp. (190°C for PE and 230°C for PP)

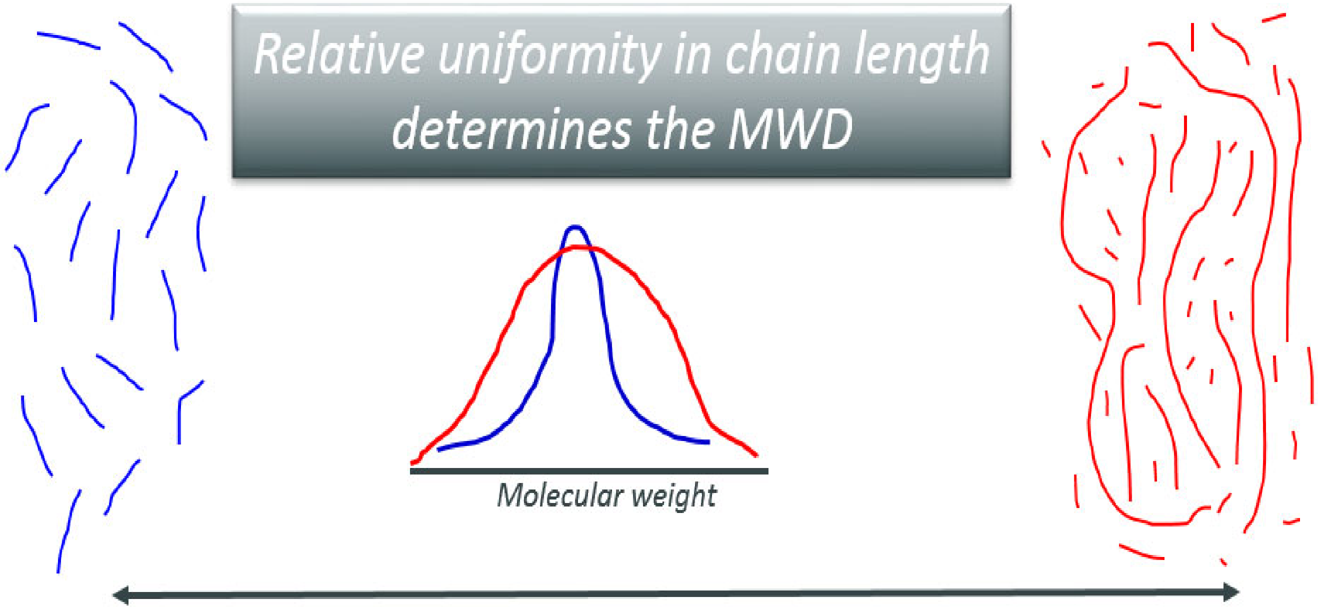
Typical Load Weights:

- **I_2 2.16 Kg = 44 psi**
- I_5 5 Kg = 100 psi
- **I_{10} 10 Kg = 200 psi**
- **I_{21} 21.6 Kg = 440 psi**



Bonus Points: Why is this important for extrusion?

Molecular Weight Distribution (MWD)



NARROW MWD

BROAD MWD (Uni-modal or Bi-modal)

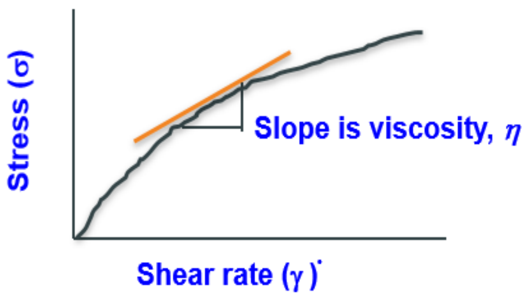
Polymer Melt Rheology

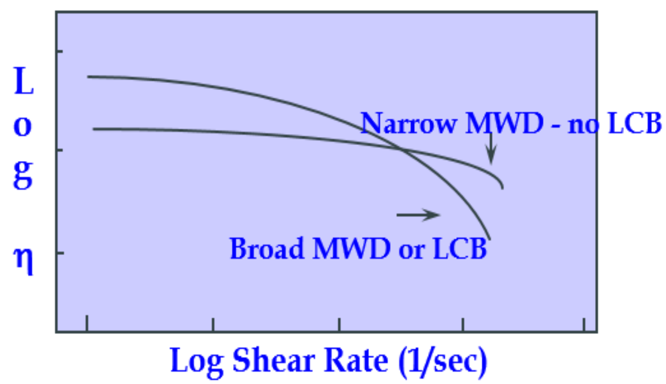
- Non-Newtonian "shear thinning"

  -"Rules":

    a) Broad Mol. Wt. Distribution increases shear thinning

    b) Long Chain Branching increases shear thinning.





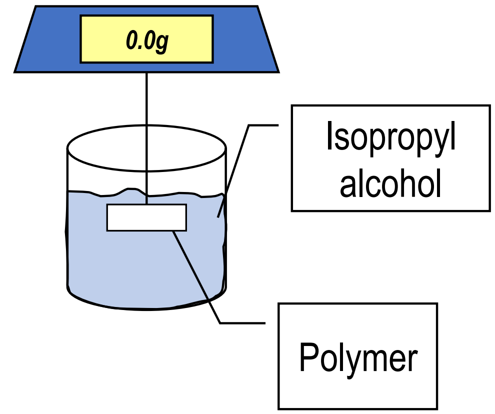
Bonus Points: Why is this important for extrusion?

Properties – Density [SCB]

1. Make a solid chunk of plastic
2. Tie a string to it
3. Tie the other end to a scale
4. Weigh it in air
5. Submerge the plastic in a bath of isopropyl alcohol
6. Weigh it again
7. Calculate the density from:

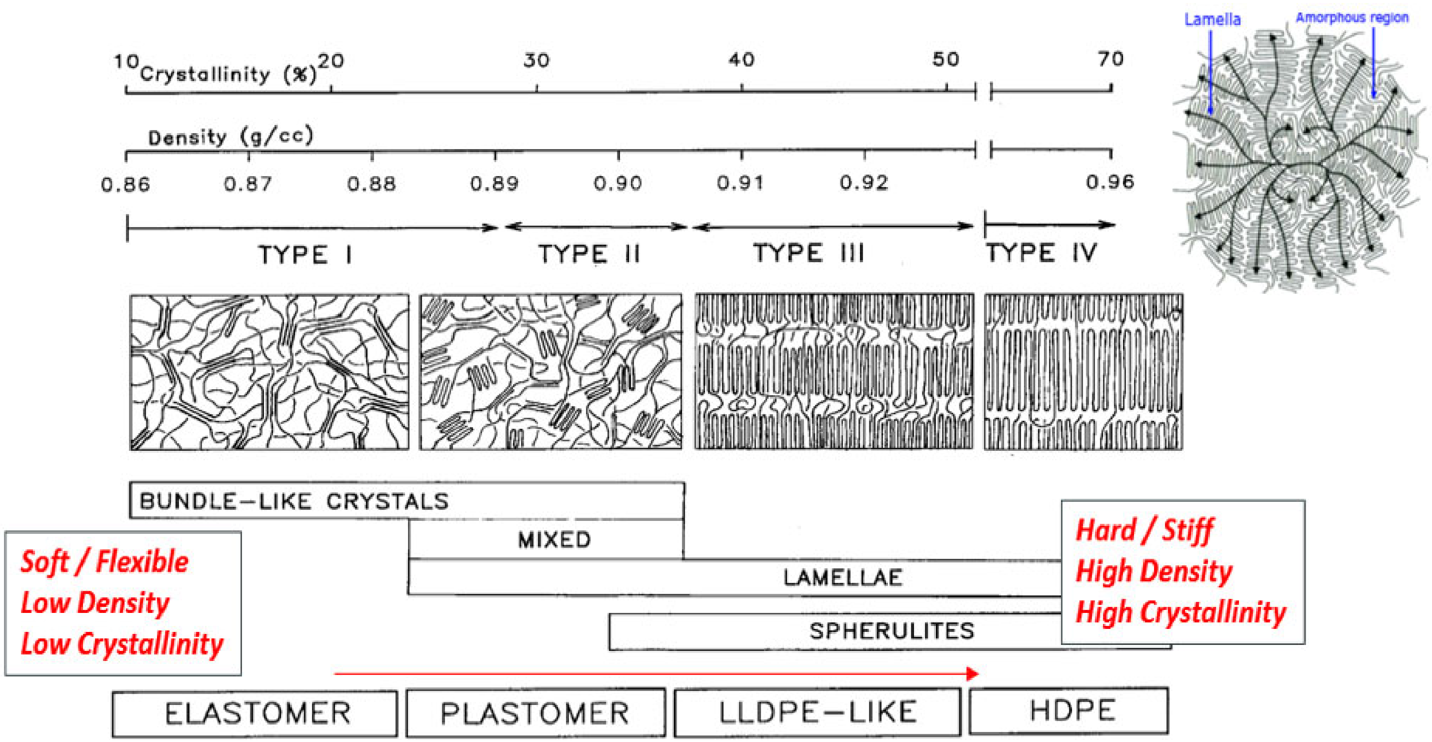
$$PolymerDensity = IsoAlcoholDensity * \frac{Weight_{Air}}{Weight_{Air} - Weight_{IsoAlcohol}}$$

Archimedes Principle – Principle of Buoyancy



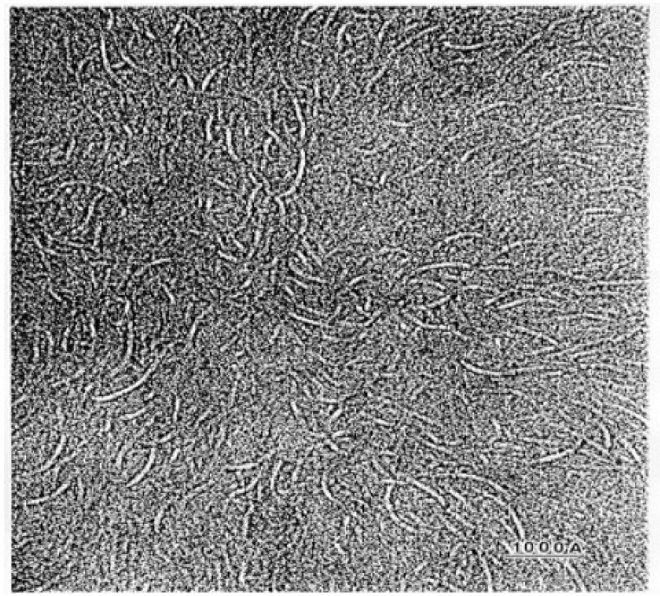
LDPE: .915 - .930
HDPE: .946 - .967
MDPE: .927 - .945
LLDPE: .912 - .926
ULDPE: .900 - .912
Elastomers: .858 - .900

Morphology Model for Polyethylene



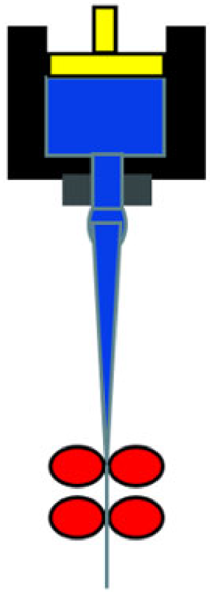
Bonus Points: Why 10 – 70 % Crystallinity?

Microstructure of PE – Electron Microscope

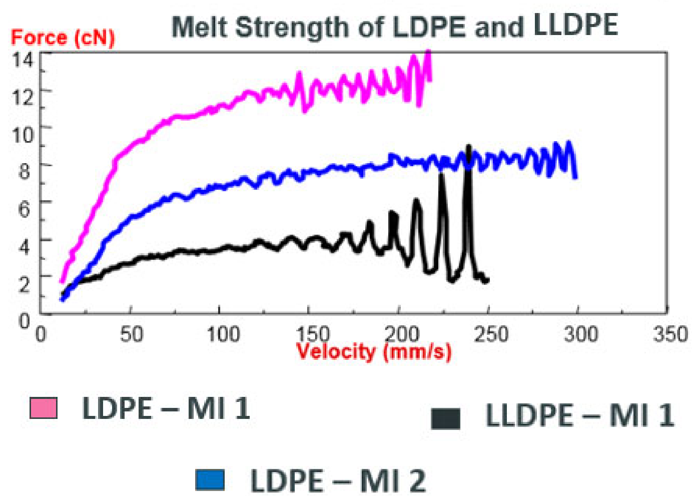


TEM micrograph of a 0.920 g/cc ethylene/octene copolymer made by single site catalyst (SSC) technology

Measurement of LCB content – Melt Strength [LCB*]

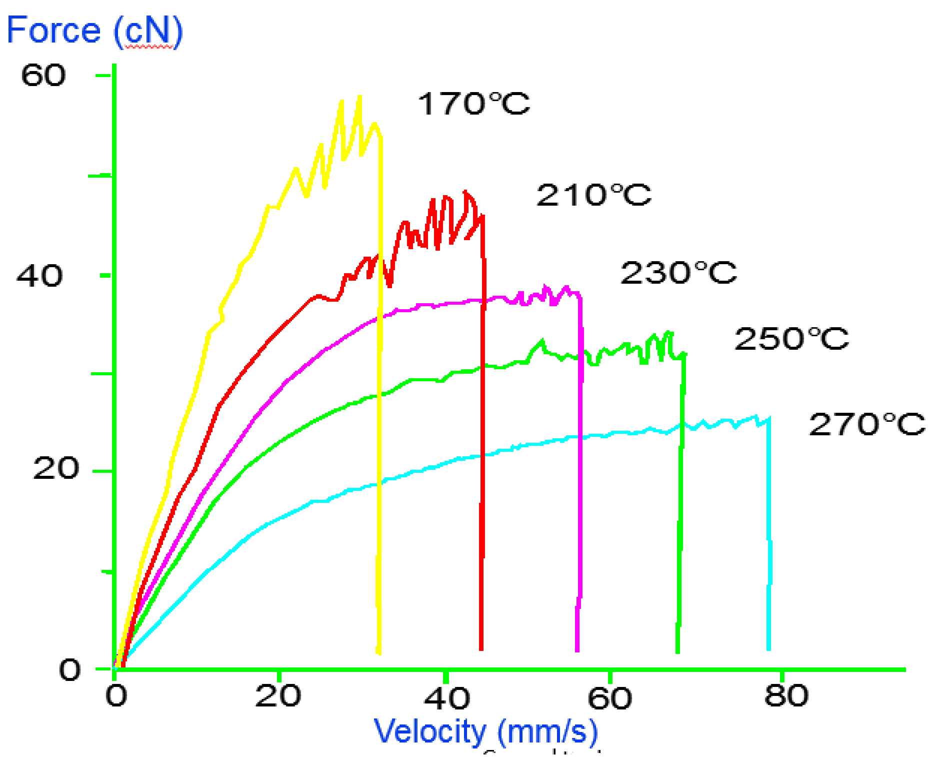


- Capillary Rheometer supplies melt at constant rate
- Wheels rotate drawing melt away from die
- Load cell at wheels measure force (resistance to extension) measured in cN



LDPE >> Linear polymers

Effect of Temperature on Melt Strength (LDPE)

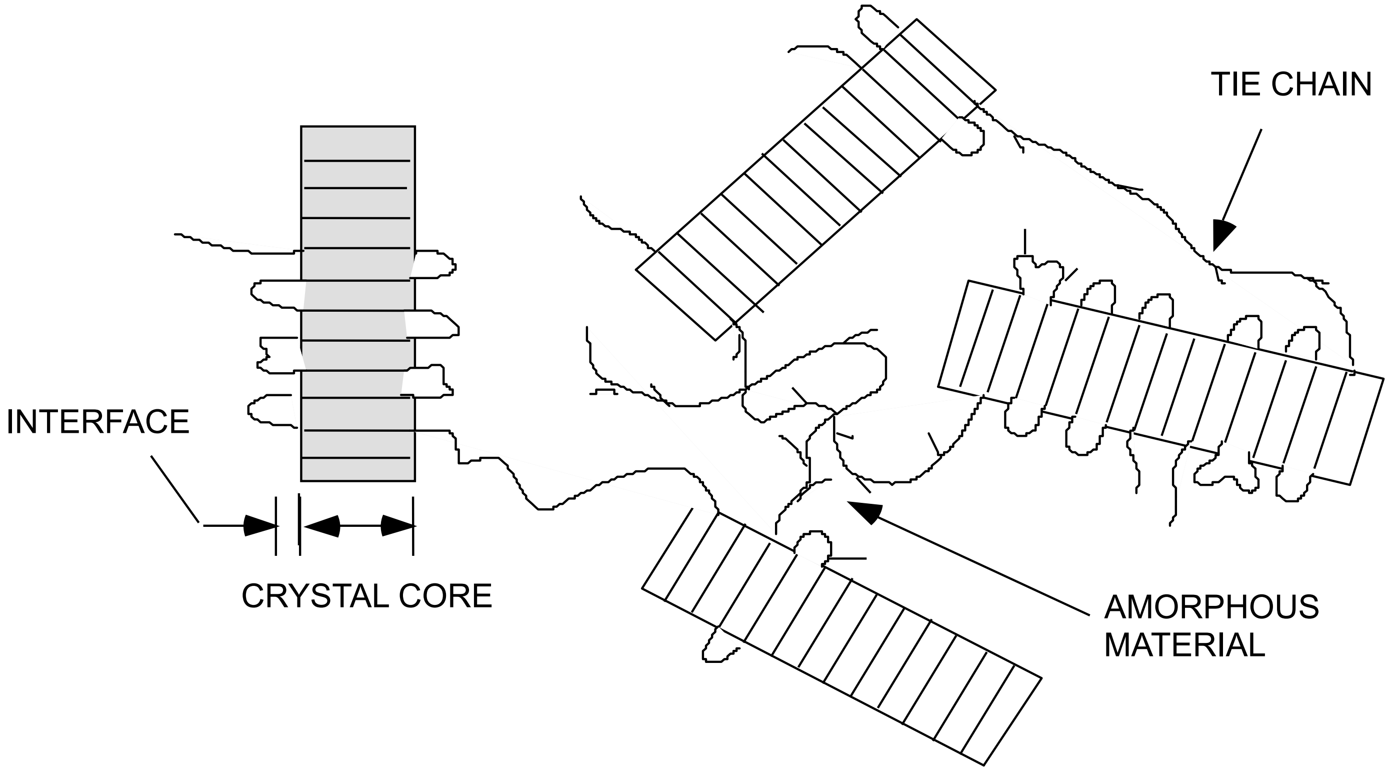


Polyethylene

- Polymers are either amorphous (zero crystallinity) or semi-crystalline (~1-75% crystallinity).
- ***Polyethylene is a semi-crystalline polymer.***
- All polyethylene consists of an amorphous <u>rubbery</u> phase and a crystalline phase.
- Molecules in the amorphous phase have random packing (no order). Molecules in crystalline phase have regular and close packing (3-D order).

Semi-Crystalline Morphology

Since Short Chain Branching (SCB) disrupts crystallinity, more branching means fewer and smaller crystals. Conventional LLDPE is a mixture of small and large crystals while mLLDPE has uniform crystal size distribution



PE is Semicrystalline…so it can Melt!

- ✓ Polyethylene must be melted (at least once) and processed (extrusion blown / cast, blow / injection / roto-molded, profile extruded…) before it reaches the shape desired by the final user (film, fiber, pipe, container, coating…)

The polymer structure (density/crystallinity) will determine how a particular polyethylene will melt (melt temperature)however,

Melt Properties depend on COMPOSITION

Molecular Weight, Molecular Weight Distribution, Long Chain Branching

Melt Properties: Flow (Processability), Melt Strength,
Die Swell, Melt Fracture, Draw-Down

But…we usually see <u>solid</u> polyethylene!

The final consumer always uses polyethylene in its solid state:

<u>Solid state properties depend on….</u>
Composition AND MORPHOLOGY

Solid State Properties: Toughness (impact, puncture, tear), modulus, abrasion, optics, sealability*…)

Solid State Properties

<u>Determined by:</u>

Percent Crystallinity (Density)

- Amount of Short Chain Branching

Tie-chain Concentration (Toughness)

- Short Chain Branching Distribution
- Molecular Weight

Orientation

- Molecular Weight Distribution
- Long Chain Branching
- Processing

Properties – Two Kinds

Solid

- What the consumer cares about.
- Properties of the final article.

Molten

- What the converter cares about.
- Properties during fabrication of the article.

Properties – Two Kinds

Solid

Dart

Puncture

Tear

Tensile Strength

Optics (Haze, Gloss)

Modulus (Stiffness)

Sealability

Molten

Processibility

Extensibility

Melt Strength

Molten Properties

Processability

- Extruder amps: How hard it is to drive the extruder?
- Bubble Stability: How fast can you run the blown film line before the bubble starts shaking uncontrollably?
  - **Melt Strength**

Extensibility

- Draw down: How thin can the film be made before it breaks?

Bonus Points: Does density matter in extrusion?

Property Tradeoffs

As much as we would like, we can't get something for free…

Resin design always involves tradeoffs

"There's no such thing as free lunch"

-Milton Friedman

Properties vs Melt Index (MW)

As you increase Melt Index	***The property goes:***
Dart	Down (worse)
Puncture	Down (worse)
Tear	Down (worse)
Tensile Strength	Down (worse)
Haze	Down (better)
Gloss	Up (better)
Modulus (Stiffness)	Doesn't change much
Sealability	Up (better)
Processibility	Up (better) (less amps)
Bubble stability	Down (worse)

Properties vs Melt Index (MW)

Or put more simply…

If you go DOWN in melt index, the resin gets TOUGHER, makes a more STABLE BUBBLE, doesn't LOOK as good, and processes like ROCKS.

Properties vs Density (SCB)

As you increase Density	***The property goes:***
• Dart	Down (worse)
• Puncture	Down (worse)
• Tear	Down (worse)
• Tensile Strength	Down (worse)
• Haze	Up (worse)
• Gloss	Down (worse)
• Modulus (Stiffness)	Up - Stiffer (better)
• Sealability	Down (worse)
• Processibility	No effect
• Bubble stability	No effect

Properties vs Density (SCB)

Or put more simply…

If you go DOWN in Density, the resin gets TOUGHER, LOOKS better, SEALS better, but gets FLIMSY.

Properties vs I_{10}/I_2 (MWD)

As you increase I_{10}/I_2	***The property goes:***
Dart	Down (worse)
Puncture	Down (worse)
Tear	Down (worse)
Tensile Strength	Down (worse)
Haze	Up (worse)
Gloss	Down (worse)
Modulus (Stiffness)	Up - Stiffer (better…minor effect)
Sealability	No effect
Processibility	Up (better) (less amps)
Bubble stability	Up (better)

Properties vs I_{10}/I_2 (MWD)

Or put more simply…

If you go DOWN in I_{10}/I_2, the resin gets TOUGHER, LOOKS better, but gets HARDER to process.

Properties vs Long Chain Branching (LCB)

LCB in broad terms:

As LCB increases ↑

- Toughness decreases ↓
  - ✓Dart, Tear, Puncture
- Processibility increases ↑
  - ✓ Amp draw goes down
  - ✓ Bubble stability goes up

❖ ***One of the BIGGEST reasons why LDPE is still in use today.***

Properties vs Short Chain Branching Distribution (SCBD)

SCBD in broad terms:

As SCBD increases...

Toughness decreases

Two Questions Left

- What is... Octene? Hexene? Butene?
- What's a metallocene? What's it good for?

Comonomers

In LDPE, branching comes from branches of ethylene during the reaction.

In LLDPE, Short Chain Branches are added by feeding something else with the ethylene into the reactors - **Comonomers.**

- Butene (C4)
- Hexene (C6)
- Octene (C8)

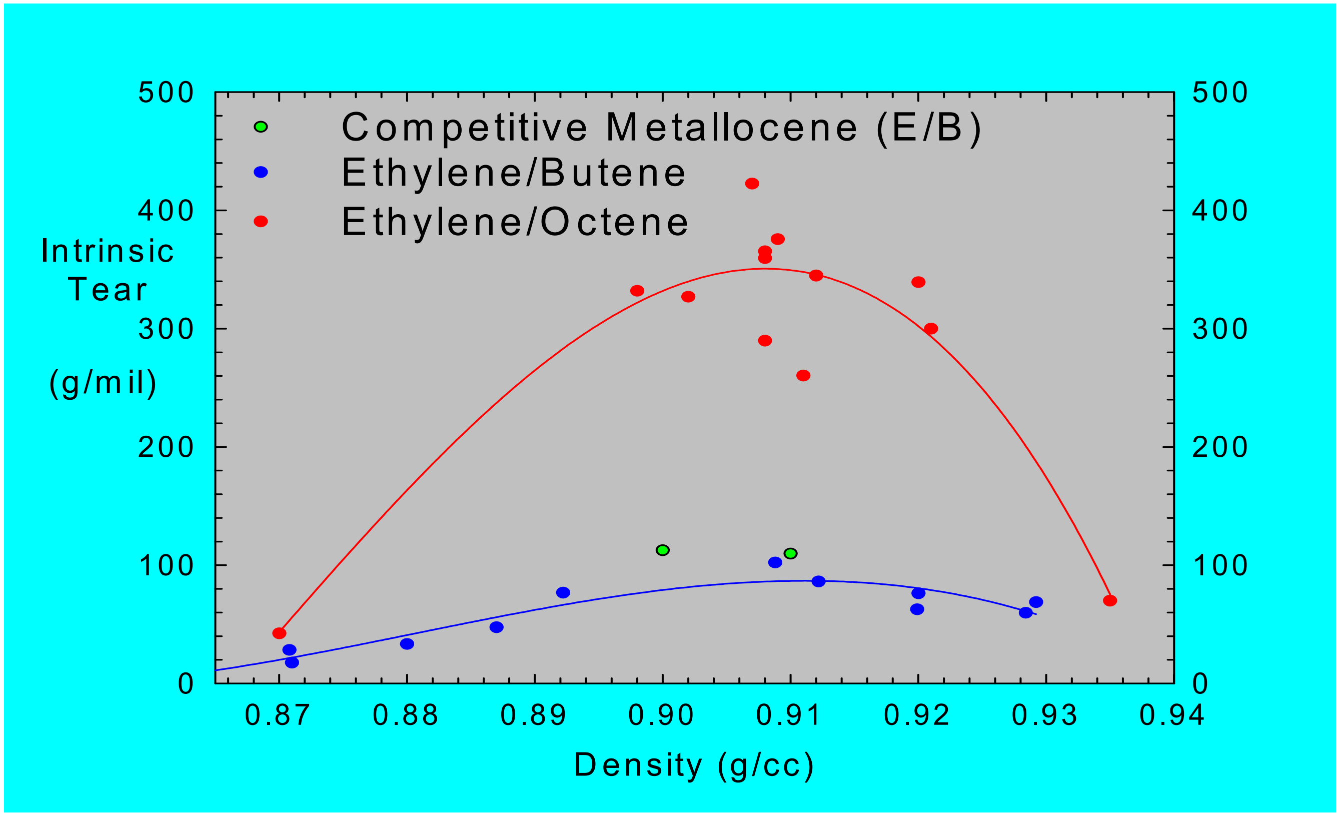
Comonomer is added to control the polymer density

Comonomers

There IS a performance difference

Octene > Hexene >>> Butene

Intrinsic Tear Comparison



Chain Length Matters

- Z-N/Chrome/Single-site catalyzed ethylene/α-olefin copolymers

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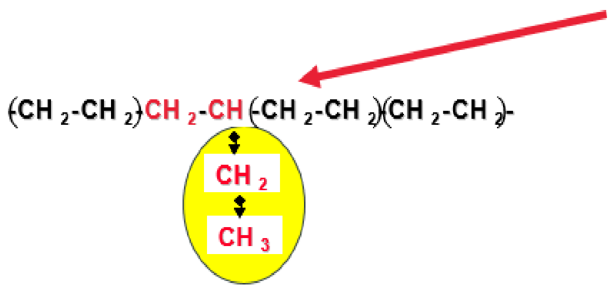
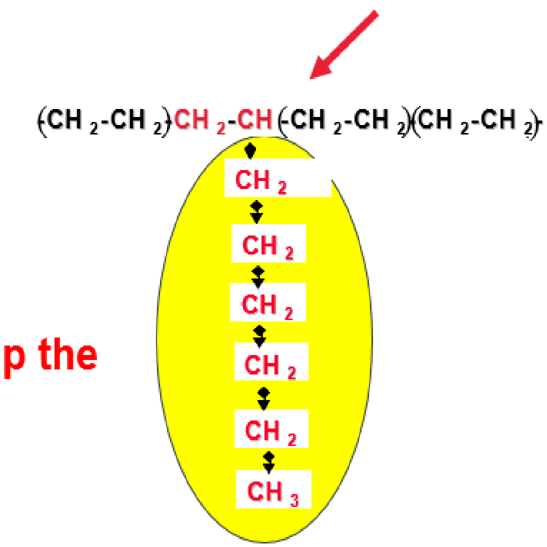
Commonly used α-olefins are 1-butene, 1-hexene and 1-octene



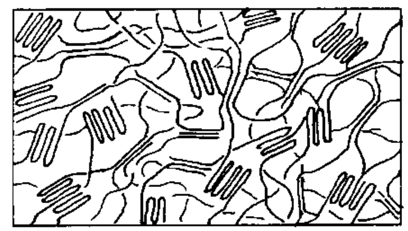


Short side chains break up the polymer crystallinity

Comonomers

- WHY IS there a performance difference?

  - For toughness, need the “Crystals” to look like this:



To form something called Tie Chains…

- ***Butene tends to be too small (C4) when incorporated to form tie chains.***

- ***Octene forms tie chains very easily.***

Two Questions Left

✓ What is... Octene? Hexene? Butene?

- What's a metallocene? What's it good for?

Metallocene (mLLDPE)

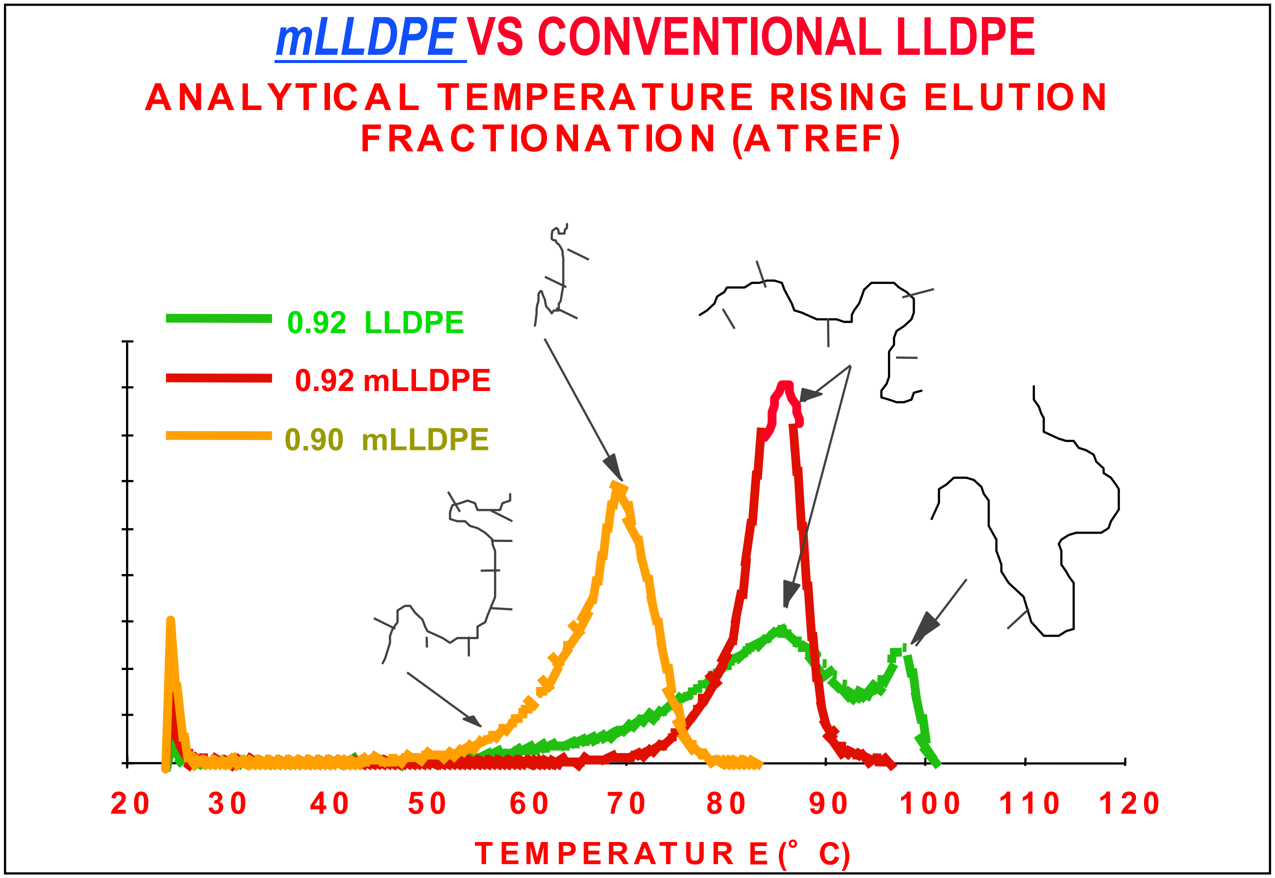
Metallocene, or Single-Site Catalysts

- Make Narrow Molecular Weight Distribution
- Make Narrow Short Chain Branching Distribution
- Think “clean” polymers…makes the same stuff

What does it do to properties?

- MUCH Tougher
- Optics look better
- Harder to run (amps)
- Bubble stability worse

Metallocene - Short Chain Branching Distribution (SCBD)



Resin Selection in Fabrication

Governed by Melt Index: *(general guide)*

2 to 8 Melt Index

- Cast Film

10 to 100 Melt Index

- Coating / Lamination

0.003 to 4 Melt Index

- Blown film
  - Higher MI possible in co-ex conventional, downward bubble, or water quench processes

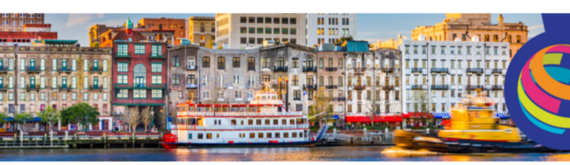
Types of Polyethylene

Polyethylene is composed of only carbon and hydrogen (with some exceptions), which can be combined in a number of ways to make many different polyethylenes. These can generally be grouped into 3 major types (commercial):

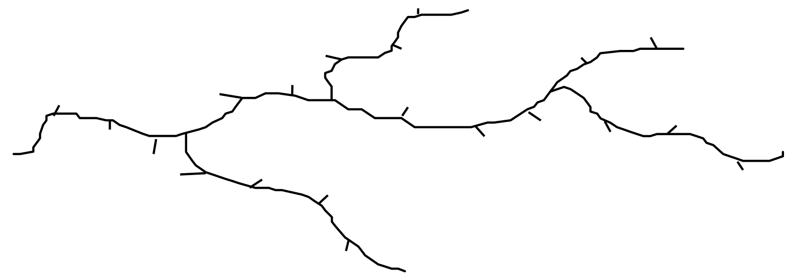
- LDPE, Low Density Polyethylene
- HDPE, High Density Polyethylene
- LLDPE, Linear Low Density Polyethylene
  - *mLLDPE or Single-site Polyethylene*

Subcategories:

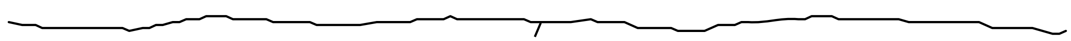
- ULDPE, Ultra Low Density Polyethylene (Plastomers)
- VLDPE, Very Low Density Polyethylene (Elastomers)



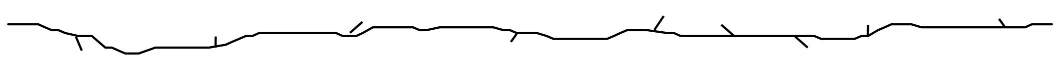
Polyethylene Chain Structures - Review



Low Density Polyethylene (long chain and short chain branching)

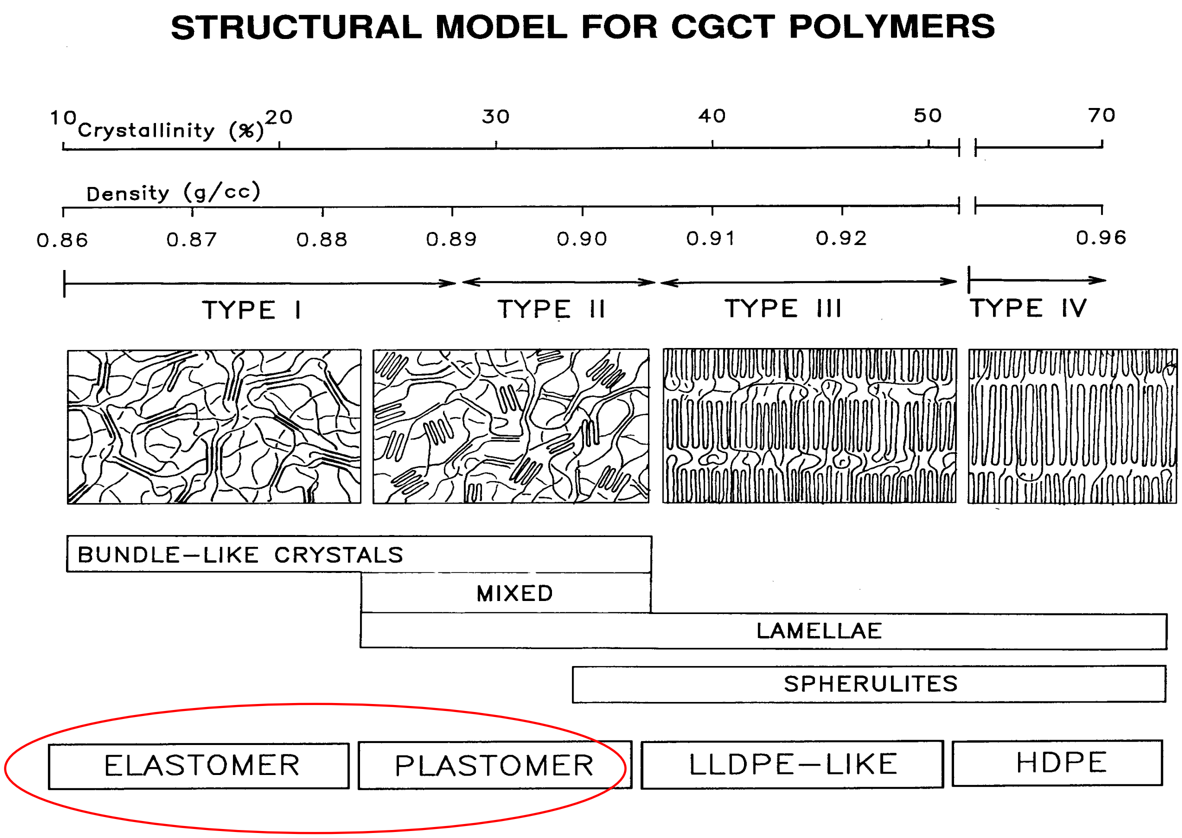


High Density Polyethylene (little or no short chain branching)



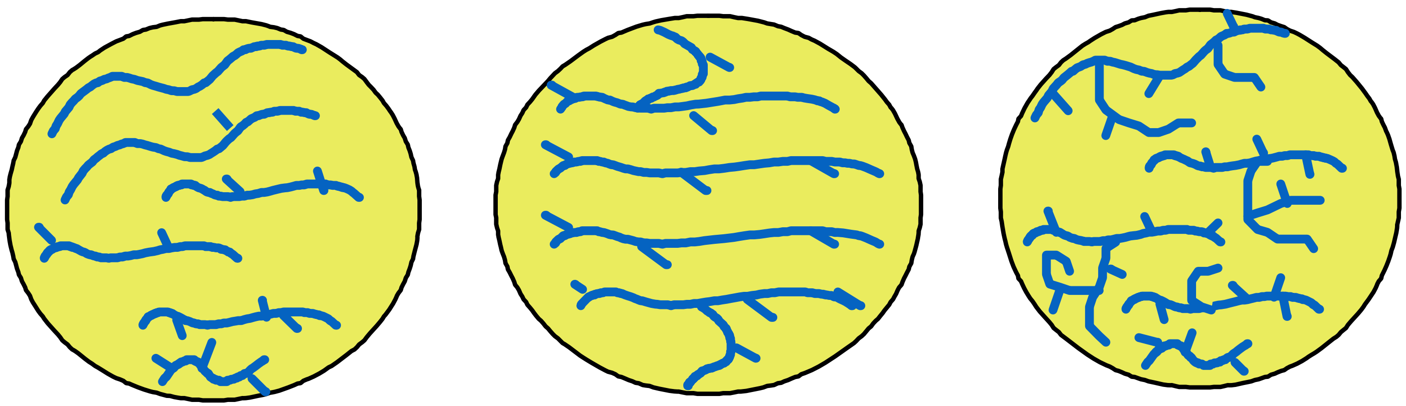
Linear Low Density PE (SCB length = comonomer length - 2)

Morphology Evolution of LLDPE



Conventional LLDPE cannot go much below 0.900 g/cc

Polyethylene Chain Structures



LLDPE/VLDPE	mLLDPE/ULDPE	LDPE/EVA
Broad MWD	Narrow MWD	Broad MWD
Heterogeneous SCBD	Homogeneous SCBD	Homogenous SCBD
No LCB	Low Levels of LCB	High levels of LCB
Ziegler-Natta Catalyst	Constrained Geometry Catalyst	Free-radical, High Press.

Polyethylene Technology Evolution

Type	Density	Melting Point (°C)	% Crystallinity	Year
LDPE	0.915 - 0.93	106 - 120	40 - 60	1935
EVA	0.93 - 0.95*	40 - 105	5 - 40	1955
HDPE	0.94 - 0.965	125 -135	65 - 80	1955
LLDPE	0.91 - 0.94	120 - 125	40 - 60	1975
VLDPE	0.89 - 0.91	118 -122	25 - 40	1983
mLLDPE	0.86 - 0.965	40 - 135	5 - 80	1991

***   Density of EVA is higher due to bulky vinyl acetate group. Hence, EVA density can not be compared to polyethylenes when considering properties.***

Seek Together

Decreasing the Crystallinity (Density)

Is accomplished by...

- Increasing the amount of short chain branching by adding **comonomer**

And results in...

- Decreasing the modulus (stiffness)
- Decreasing the yield strength
- Improving optics (haze, gloss, clarity)
- Increasing cost
- **Lowering the melting & softening points**

Plastomers & Elastomers- What Do We Know?

Plastomers and Elastomers are:

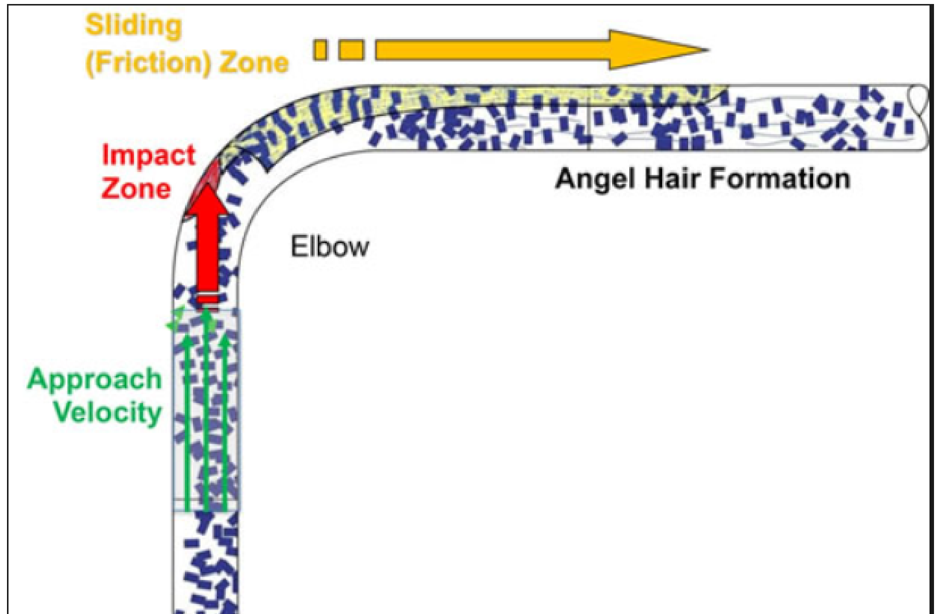
- ✓ Sub-family of LLDPE Polyethylene
- ✓ Catalyzed either ZN or mLLDPE
- ✓ Highly Branched (SCB/SCBD)
- ✓ Co-polymers
- ✓ Low Crystallinity and Density
- ✓ Low Melting Point

So... What does that mean?

Some Process Challenges and Unique Properties

Plastomers and Elastomers:

- Material handling
- Extrusion
- Post die concerns



*ptonline.com

Material Handling

Because of their low density ***Plastomer pellets are soft, spherical, and have a high surface COF*** and can have blocking issues.

Plastomers can cause dusting, angel hair, and streamers when handling systems are not designed to handle these densities.

Slower transfer velocity with long radius bends along with shot peening of transfer pipes can help to mitigate the effects of the very low density.

Recommended velocities:

- Pickup ~ 20m/s
- End of the line < 30m/s (step the line if necessary)
- Screens, traps, & filtration systems are recommended.

Material Handling

Once in the hopper we can still have issues

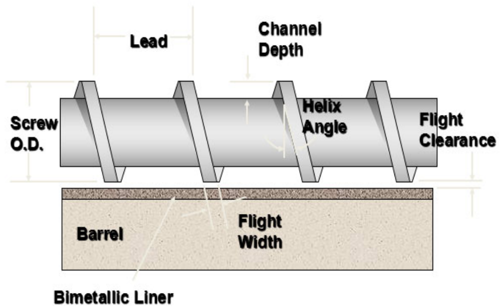
- **A high surface COF can cause bridging issues and segregation problems when blending.**
- **Feed hopper angles should be designed to provide a "mass flow" (right) rather than a "funnel flow".**
- **Plastomer pellets can be sticky** which could cause material to hang up in blenders and transfer lines resulting in longer transition times and possible contamination issues.

Extrusion – Screw Recommendations

Plastomers melt quickly!

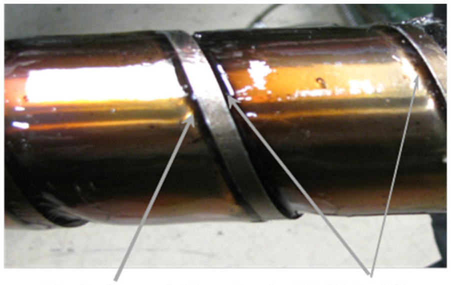
Some suggestions relating to screw designs.

- ❖ Single flight screws should have a smaller compression ratio (2:6 -2:8)
- ❖ 70mm (2.75”) or larger should preferably have a barrier screw design.
- ❖ Barrier undercut in the range of 0.5 - 0.7% of screw diameter
- ❖ Depth of Metering section in the range of 4-7% of screw diameter
- ❖ Spiral mixer with lead angle of 60º is typical.
- ❖ Root radii = long angle (1.5% of local depth)
- ❖ If you process plastomers, please discuss with your screw designer so they know!



CR = Compression Ratio

$$CR = \frac{\text{Feed Channel Depth}}{\text{Meter Channel Depth}}$$



Resin degradation due to Moffat eddies.

Extrusion – Continued

Plastomers melt quickly!

- Care should be taken when setting up the temperature profile to avoid pre-melting of material. **Feed zone temps critical.**
- Pre-melting can cause bridging, surging, or complete loss of flow.

Smooth bore:

- Feed throat cooling zone = < 100ºF (37ºC)

Groove Feed:

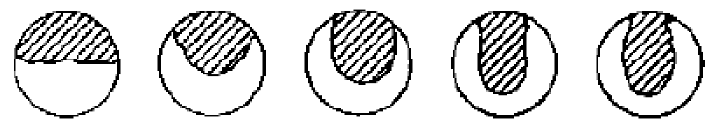
- Feed Temp (water/oil) 70 – 100ºF (21-49ºC)

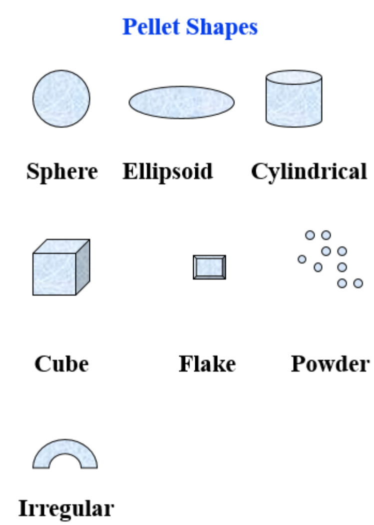
Melting Challenges with Blends

- Plastomer’s low melting point can cause viscoelastic encapsulation issues when blending resulting in un-melt gels.

- Low head pressure will increase the probability of encapsulation when blending.

- Pellet geometry differences will add to the likelihood of gels, especially when melt temperatures are significantly different.





Processing – Formulating with Plastomers

Formulating with Plastomers can be challenging.

- When used in co-ex formulations rheology differences could result in interlayer instability.

- When rheology can't be matched layer stability might be achieved through balancing velocity (i.e., layer thickness vs. die cut).

- Plastomers, which are tacky, can have challenges in web handling when on the film surface layer if blown or cast film. Surface modification additives may be necessary.

- Watch for issues with **rotating nips.**
  - ❖ *On blown film lines turning bars with large orifices to allow for high air velocity will help keep film from sticking when using the oscillation feature.*

Processing Plastomers – Additives

To prevent / avoid blocking when winding.

- Slip (*erucamide, stearamide, oleamide*)
- Antiblock (*talc, SiO2, CaCO3*)

High COF of plastomers can cause melt fracture (especially when on the outside of the formulation).

- Polymer process aid (PPA).

Ensure that additives don't negatively effect performance.

- Example: Stretch cling

Plastomers - Properties

The molecular design of plastomers provides unique properties.

- *Good optics*
- *Toughness*
- *Elasticity*
- *Cling*
- *COF (high)*
- *Soft / flexible*
- *Low seal initiation with high hot tack*

Lightning Round

Tell me which is the better resin and why!

Lightning Round – Octene vs. Butene

1. 1 MI, 0.920 Density, Octene

2. 1 MI, 0.920 Density, Butene

(1) Octene provides better properties

Lightning Round – Which is tougher?

1. 0.8 MI, 0.920 Density, Octene

2. 1.0 MI, 0.920 Density, Octene

(1) Lower MI is tougher

Lightning Round – Which is tougher?

1. 1 MI, 0.920 Density, Octene

2. 1 MI, 0.917 Density, Octene

(2) Lower Density is tougher

Lightning Round – Which is stiffer?

1. 1 MI, 0.920 Density, Octene

2. 1 MI, 0.925 Density, Octene

(2) Higher Density is STIFFER

Lightning Round – Which is tougher?

1. 1 MI, 0.920 Density, 8.0 I10/I2 Octene

2. 1 MI, 0.920 Density, 7.7 I10/I2 Octene

(2) Lower I10/I2 is tougher

Lightning Round – Which is tougher?

1. 1 MI, 0.920 Density, Hexene

2. 1 MI, 0.920 Density, Butene, Metallocene

(1) Hexene is tougher…metallocene can't fix butene

DOW
Seek Together

Lightning Round – Which has better processability?

1. 1 MI, 0.920 Density, LDPE

2. 1 MI, 0.920 Density, Octene

(1) LDPE has higher Long Chain Branching

Summary

- ✓ 3 Types of Polyethylene – HDPE, LDPE, LLDPE
- ✓ 5 Governing Properties – Mw, MWD, LCB, SCB, SCBD
- ✓ 3 key Properties for Extrusion
  - molecular weight, molecular weight distribution, long chain branching
- ✓ Final Properties Determined by:
  - Formulation (blends, layers, additives)
  - Morphology (orientation - processing)
- ✓ *Plastomers/Elastomers: Sub-categories of LLDPE*
  - Defined by density
  - Unique challenges

Thank You

Mike Rutkowske
Sr. TS&D Specialist
mcrutkowske@dow.com