POLYOLEFINS IN FILM APPLICATIONS

2017 International Conference on Polyolefins
Tutorial Session

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Polyolefin in Film Applications

OUTLINE

- Polyolefin Processes
- Polyolefin Resin Characterization
- Polyolefin Material
- Blown Film Process Parameters
- Blown Film Equipment Overview
- Advances in Blown Film

Polyolefin in Film Applications

Polyolefin Resins

- LDPE
- LDPE Copolymers
- LLDPE
- HDPE
- m-LLDPE

Polyolefin Processes

FREE RADICAL AUTOCLAVE

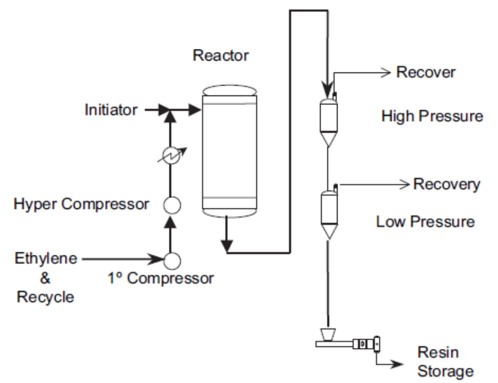


Fig. 2-14 Autoclave reactor (simplified).

FREE RADICAL TUBULAR

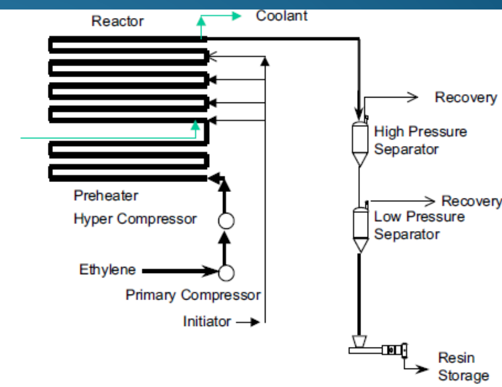


Fig. 2-15 Tube reactor (simplified).

SOLUTION

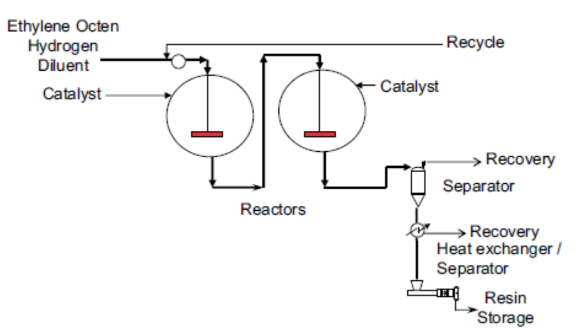


Fig. 2-26 Solution process (simplified).

GAS PHASE

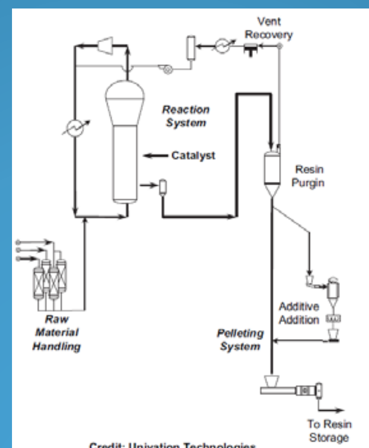


Fig. 2-24 Gas phase process (simplified).

SLURRY LOOP

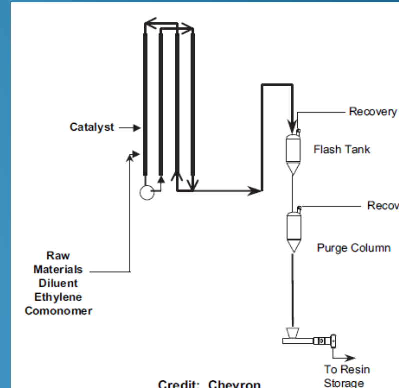
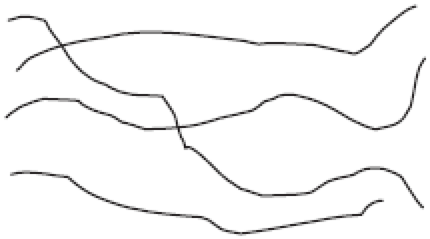


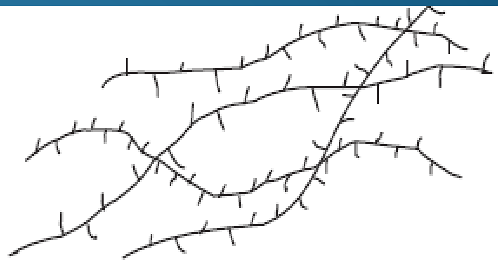
Fig. 2-27 Slurry loop process (simplified).

Polyolefin Resin Characterization

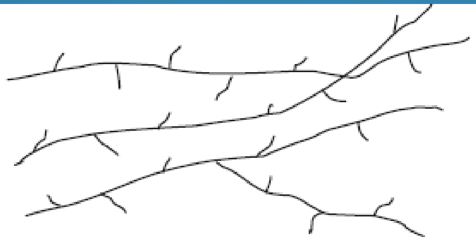
5 Common PE Molecular Structures



Linear Polymer

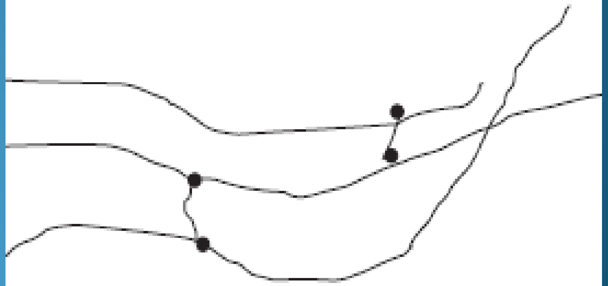


Short- Chained Branched



Short- Chained Branched with Controlled Levels of Long-Chain Branching

Short and Long-Chained Branched



Polymer with cross links

Polyolefin in Blown Film

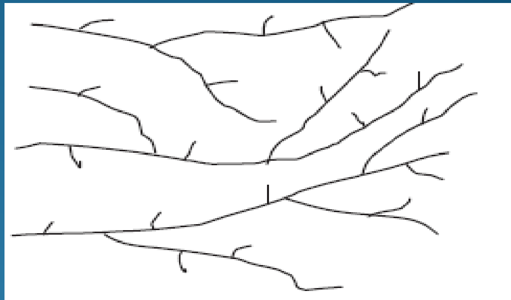
Film Properties are determined by a combination of:

Resin Characterization	**Equipment**	**Process Conditions**
MW MWD Branching Crystallinity Functionality	Screw Design Mixing Die Design Die Gap Cooling	Blow-Up Ratio (BUR) Drawn Down Ratio Frost Line Height Specific Output

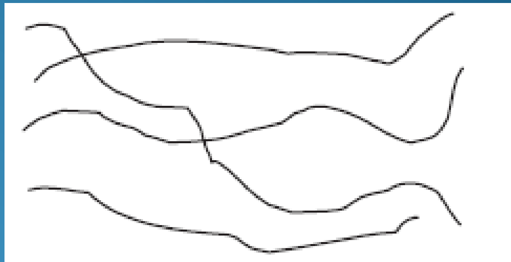
Film Properties

HDPE in Blown Film

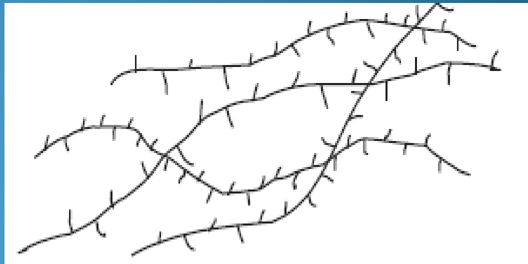
- Polyethylene Formation and Structure
  - Ethylene $CH_2=CH_2$: building block
  - When initiator (peroxide) is used a free radical reaction occurs producing polymer chain with branched structure (LDPE)
  - When catalyst is used the reaction will occur at the active catalyst site to form a linear polymer chain (HDPE)
  - If a comonomer (butene, hexane, or octane) is included in the process, a linear polymer chain with side branches is formed (LLDPE)



Short and Long-Chained Branched



Linear Polymer



Short- Chained Branched

Polyolefin Resin Characterization

- Key Resin Characterization Include:

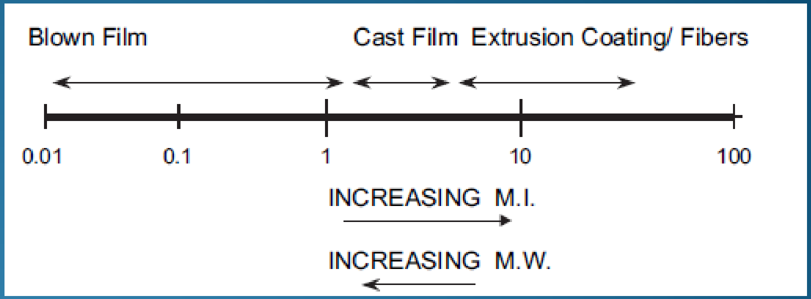
▪ MW (MFR)	Melt Index
▪ MWD	GPC, I/10/I2
▪ Density	Density Column
▪ Branching	FTIR,TREF
▪ Melt point	DSC

HDPE in Blown Film

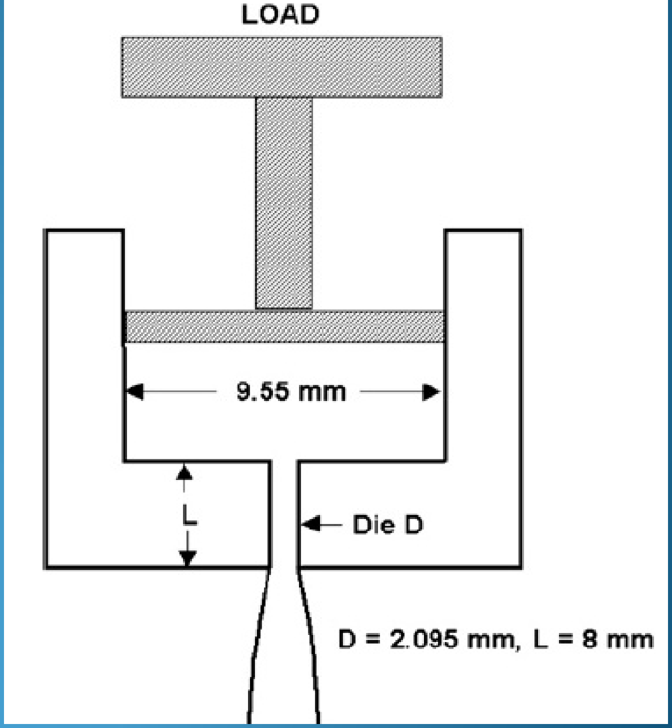
- Polymer Properties
  - Molecular Weight:
    - MW is a measure of the size of the polymer chain
    - The longer the polymer chain, the higher the molecular weight
    - Melt Index (MI) is used as a measure of MW
      - MI is inversely proportional to MW
  - Molecular Weight Distribution:
    - MWD is a statistical measure of the distribution of the molecular weight within the polymer sample
    - NMWD: all of the molecules in a sample have similar chain length
    - BMWD: all of the molecules in a sample have significant difference in chain length

Polyolefin Resin Characterization

- Melt index (MI) or (MFI)
  - ASTM D-1238
  - Units: g/10 minutes
  - Condition E - for PE
    - 2.16 kg piston load
    - 190 C



- Blown film PE grades typically range from 0.01 to about 3 grams/10 min



Polyolefin Resin Characterization

- MWD (Polydispersity)
  - MWD= Mw/Mn
    - Mw= Weight-average Molecular Weight
    - Mn= Number-average Molecular Weight
  - Measured by GPC (Gel permeation chromatography)
    - The polymer molecules are dissolved in a solvent and processed through columns packed with gel particles that separate the molecules, which are detected as they emerge from the column

$$M_n = \frac{\sum n_i M_i}{\sum n_i}$$

$$M_w = \frac{\sum n_i M_i M_i}{\sum n_i M_i} = \sum w_i M_i$$

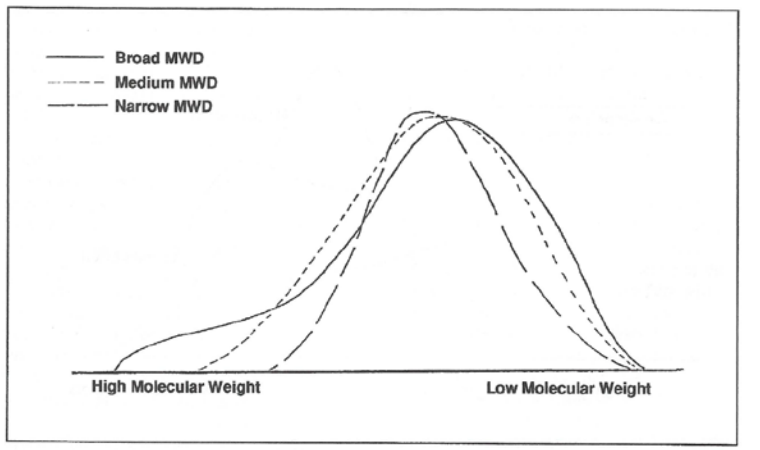
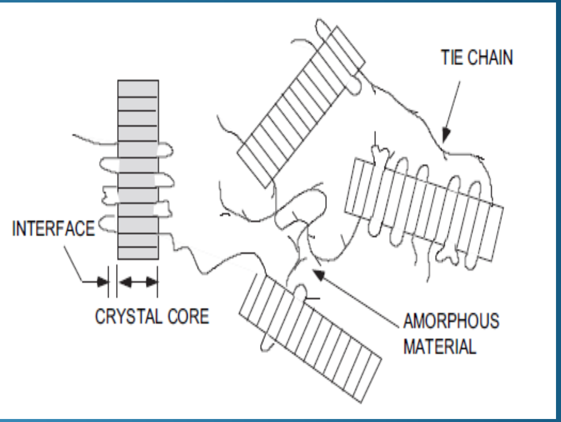


Figure 3. Comparison of a Polyethylenes of the Same Molecular Weight with Different Molecular Weight Distributions.

Polyolefin Resin Characterization

- Polymer properties (cont'd)
  - Density/Crystallinity:
    - Density/crystallinity of a polymer is a function of the comonomer content
    - Homopolymer HDPE (no comonomer) resin is highly crystalline: density of about 0.960 gm/cc
    - As comonomer content increase, both density and crystallinity decrease.
    - LLDPE will have a density below 0.935 gm/cc
    - Density is measured in the lab using a gradient density tube



Polyolefin Blown Film Resin Types

PE Type	Density Range
VLDPE	0.88-0.915
LDPE	0.910-0.925
LLDPE	0.915-0.925
MDPE	0.0926-0.940
HDPE	>0.941

Polyolefin Film Properties

- Resins are selected based on end-use product performance requirements
  - Dart Impact
  - Puncture
  - Tear
  - Tensile
  - Elongation
  - Secant Modulus
  - COF
  - Sealability

Polyolefin Film Properties

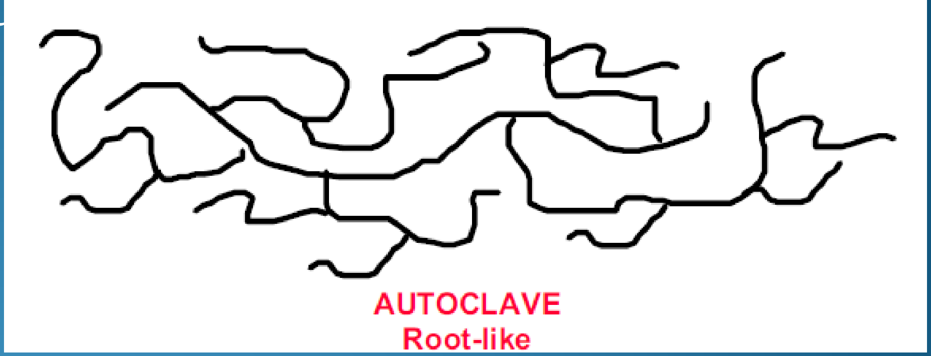
- Barrier Properties
  - MVTR
  - OTR
- Optical Properties
  - Transparency
  - Gloss
  - Haze
  - COF
  - Sealability

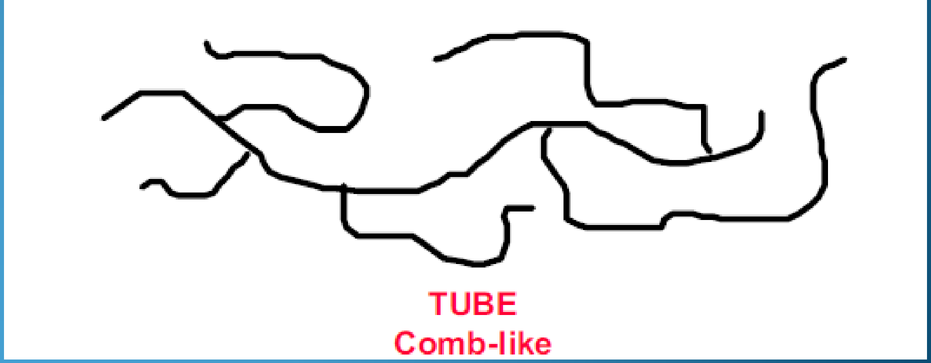
Effects of Resin Characteristics on Film Properties

Resin Design Parameters	As Density Increases	As MW increases	As MWD increases
Stiffness	↑		
Tensile Strength	↑		↓
Dart Impact Strength	↑	↑	↓
Tear Strength	↓		↓
MVTR	↓		
Melt Viscosity		↑	
Melt Strength		↑	↑
Toughness		↑	↓
Abrasion		↑	
Processability			↑
Bubble Stability			↑
Downgauge Ability			↑
Optics	↓	↓	
Heat-Seal Strength		↑	
Permeability	↑		
Melting Point	↓		
Stress Crack			↑

LDPE IN Blown Film

- Free Radical Process
  - High Pressures > 10,000 to 50,000 psi
  - High Temperatures >175 to 315ºC
- Homopolymer: LDPE
- Copolymers:
  - EVA
  - EMA
  - EAA
  - EMAA
  - EBA
- Properties which make LDPE attractive for film
  - Light weight
  - Economical
  - Flexibility
  - Toughness
  - Chemical Resistance
  - Ease of Sealability





LDPE- Typical Properties

- Typical LDPE Resin Properties

Melt Index, g/10 min	2.0
Density, g/cc	0.920
Melting Point, C	107

- Typical Film Properties

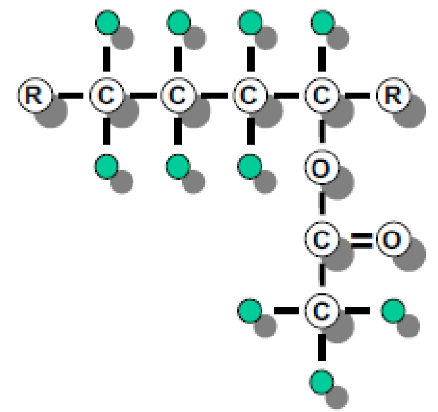
Melt Index, g/10 min	2.0
Resin Density, g/cc	0.922
Film Thickness, mil	1.5
Melt Temp, F	375
Film Density, g/cc	0.9181
Dart Impact, g	100
Elmendorf Tear, g MD/TD	400/200
Ultimate Tensile, PSI, MD/TD	3300/2700
Tensile Yield, PSI, MD/TD	1600/1550
Elongation, %, MD/TD	325/575
60 Gloss, %	55
Haze %	6.5

LDPE- Typical End Uses

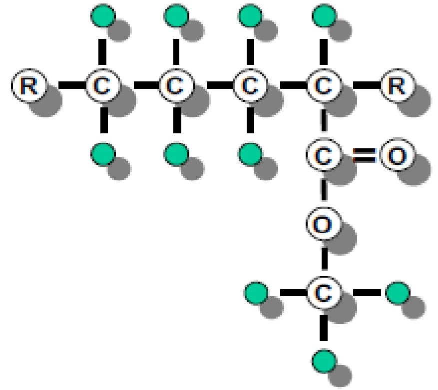
- Largest Market for LDPE
  - Bags and Liners
    - Trash Bags
    - Shopping Bags
    - Produce Bags
    - Bread and Bakery
    - Grocery Sacks
    - Shipping bags
    - Liners
    - Garmet Bags
  - Shrink Bundling
  - Pallet Stretch-Cling
  - Construction and Agricultural film
    - Mulch film
    - Greenhouse coverings
  - Lamination applications requiring good salability

LDPE - Copolymers

- EVA and EMA Copolymers:
  - The (VA) and (MA) are randomly distributed
  - EVA and EMA exhibit:
    - Polar functionality
    - Low crystallinity
    - Adhesive characteristics
    - Low seal initiation temperatures
  - As VA/MA levels increase, density increases but crystallinity decreases



Ethylene – Vinyl Acetate



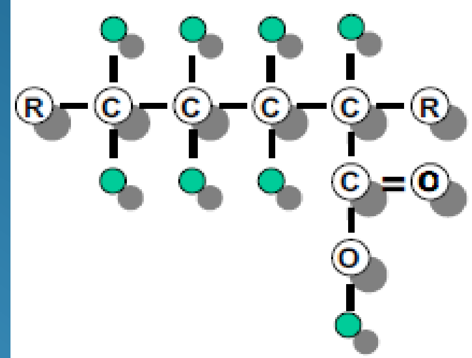
Ethylene – Methyl Acrylate

LDPE - Copolymers

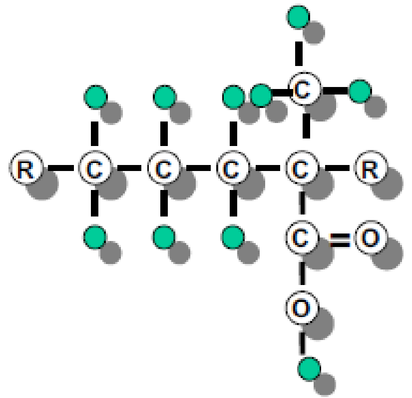
- The acrylic acids, (EAA) and (EMAA) use acids as a copolymers

- EAA and EMAA exhibit:
    - Polar functionality
    - Low crystallinity
    - Adhesive characteristics
        - Hydrogen bonding capability
    - Low seal initiation temperatures
  - Good adhesive polymers for metals and polyamides

- The crystallinity decreases as comonomer levels increase.



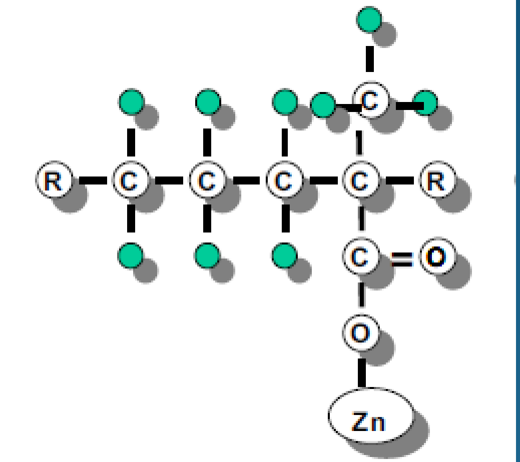
Ethylene - Acrylic Acid



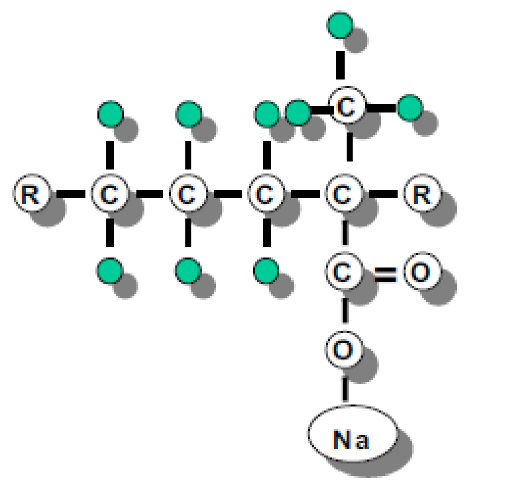
Ethylene – Methyl Acrylic Acid

LDPE - Copolymers

- Ionomers are produced from
  - Acid copolymers
  - Acid functionality is neutralized using bases:
    - Sodium
    - Zinc
- The neutralization creates ionic clusters that act like cross-linked networks



Zinc Ionomer

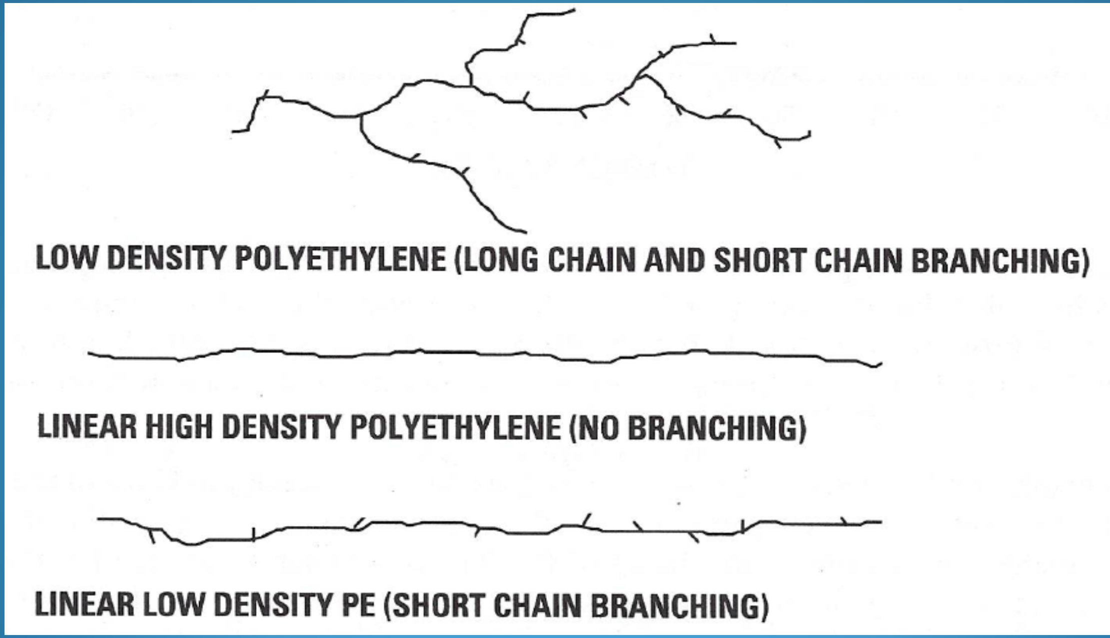


Sodium Ionomer

LLDPE in Blown Film

Linear Low Density Polyethylene characterization

- Key distinction between LLDPE and LDPE
  - LLDPE has no LCB
  - Narrow MWD



LLDPE in Blown Film

Linear Low Density Polyethylene characterization

- Branch length is determined by monomer type:

  Butene Hexene Octene

TABLE 28-1. Comonomer Type and Short Chain Branch Length.

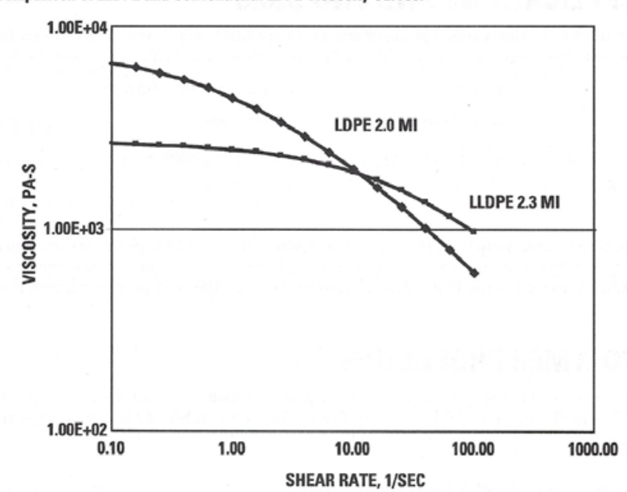
BUTENE	HEXENE	OCTENE
C	C	C
C	C	C
C	C	C
C-C-C	C-C-C-C-C	C-C-C-C-C-C
C	C	C
C	C	C
C	C	C

LLDPE in Blown Film

Linear Low Density Polyethylene characterization

- The difference in molecular architecture of LLDPE's result in significant improvements in Physical Properties relative to LDPE:
  - Tear strength
  - Puncture resistance
  - Tensile Strength
  - Stiffness
- LLDPE exhibit higher viscosity in shear flow than LDPE
  - LLDPE doesn't shear thin as much as LDPE
  - LLDPE requires more
    - Torques (power)
    - Higher Amps
    - Higher melt temps
    - Higher pressures

FIGURE 28-3. Comparison of LLDPE and Conventional LDPE Viscosity Curves.

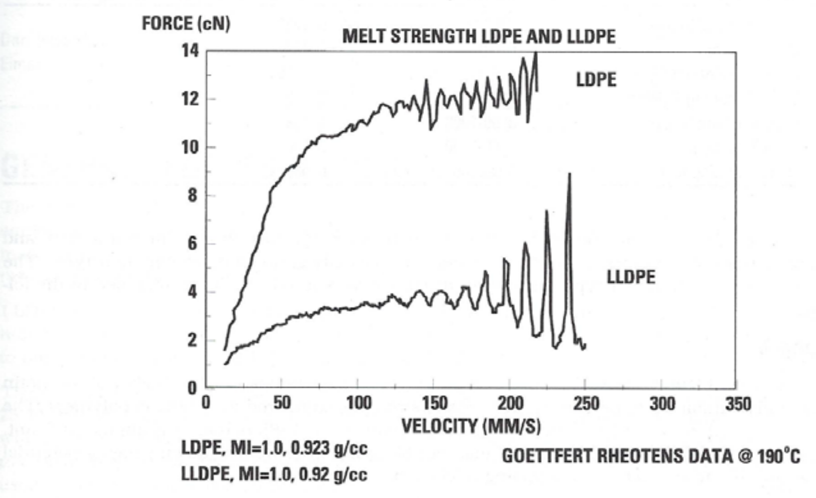


LLDPE in Blown Film

Linear Low Density Polyethylene

- The extensional viscosity of LDPE increases as the deformation rate is increased due to strain hardening
- Strain hardening of the LDPE melt provides good bubble stability
- LLDPE exhibit little stain hardening
  - Drawdown is very good
  - Bubble stability is not as good as LDPE
  - Modification of air rings are required

FIGURE 28-4. Melt Strength Differences Between LLDPE Polymers and LDPE.



LLDPE- Typical End Uses

Typical Applications

- Trash Bags
- Stretch Cling
- Frozen Food
- Grocery Sacks
- Heavy Duty Shipping
- Ice Bags
- Milk Bags
- Bag-in-Box
- Produce
- Liners
- Shrink Wrap

LLDPE- Film Properties

LLDPE Film Properties

Table 3. LLDPE Film Properties.

Film Property	Butene LLDPE	Octene LLDPE	LDPE
MELT INDEX, g/10 min	1.0	1.0	0.25
DENSITY, g/cc	0.920	0.920	0.920
THICKNESS, mils	1.5	1.5	1.5
ULTIMATE TENSILE, psi MD	5880	6590	4780
	4660	5115	3180
ULTIMATE ELONGATION, % MD	620	630	215
	760	810	645
DART IMPACT, g	145	240	170
ELMENDORF TEAR, g MD	180	371	110
	510	816	205

Table 4. Film Properties of LLDPE and LDPE Blends.

% LLDPE (1.0 MI, 0.920)	100	90	80	70	50	30
% LDPE (2.0 MI, 0.922)	0	10	20	30	50	70
SPECIFIC OUTPUT, lb/hr/in	9.7	10.7	11.4	12.8	14.6	16.0
THICKNESS, mils	1.65	1.75	1.5	1.5	1.8	1.8
TENSILE, psi MD	8130	7165	6830	6835	5255	5395
	4920	4892	4225	4234	4035	3575
YIELD, psi MD	1690	1570	1515	1585	1700	1965
	1765	1575	1555	1605	1745	1710
ELONGATION, % MD	595	660	675	675	460	215
	775	780	652	691	588	275
ELMENDORF TEAR, g MD	360	268	147	121	96	172
	771	780	652	691	588	275
HAZE, %	17.9	10.0	7.5	4.6	7.4	8.6
20° GLOSS, %	22.2	53.9	78.5	68.5	30.1	31.4

ULDPE in Blown Film

Ultra Linear Low Density Polyethylene (ULDPE, VLDPE)

- Linear copolymers with densities below 0.915 g/cc
- Technology is limited to 0.88 or 0.89 g/cc
- ULDPE provides a combination of the strength of LLDPE polymers with improved:
  - Impact
  - Flexibility
- Comonomers:
  - Octene
  - Hexene
  - Butene
  - Methylpentene
  - Propylene

ULDPE in Blown Film

ULDPE Characterization:

- MW and MWD similar to LLDPE
- High levels of comonomer contribute to the additional improvement in:
  - Impact
  - Puncture
  - Increase flexibility
  - Improved Optics

TABLE 29-1. Modulus of Polyethylenes.

POLYMER	DENSITY G/CC	SECANT MODULUS PSI
HDPE	0.94-0.97	80,000-175,000
LLDPE	0.935-0.915	30,000-50,000
LDPE	0.915-0.93	20,000-30.000
ULDPE	0.89-0.915	5,000-20,000
EPR*	0.879	5,000-10,000

ULDPE in Blown Film

Typical Applications

- Meat
- Poultry
- Cheese Packaging
- Stretch Cling
- Bag-in-box
- Shrink Film
- Heavy-Duty Shipping Sacks
- Frozen Food Packaging

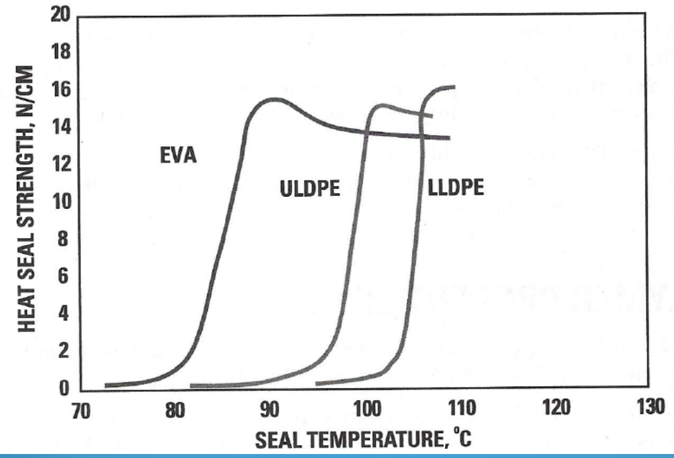
ULDPE in Blown Film

Typical Properties of ULDPE

TABLE 29-4. Typical ULDPE Film Properties.

PROPERTY	VLDPE	ULDPE	EVA
Comonomer	Butene	Octene	12% VA
Melt Index g/10 min	0.9	1.0	0.4
Density, g/cc	0.906	0.912	0.933
Film Thickness, mils	1.0	1.0	1.0
Dart Impact, g	200	750	480
Elmendorf Tear (avg.), g	275	475	130
Ultimate Tensile (avg.), psi	6,000	8,300	4,700
2% Secant Modulus (avg.), psi	14,000	18,000	12,000
Haze, %	6.0	5.0	4.0
45° Gloss, %	55	55	55

FIGURE 29-4. Heat-seal Strength LLDPE, ULDPE, and EVA.



HDPE in Blown Film

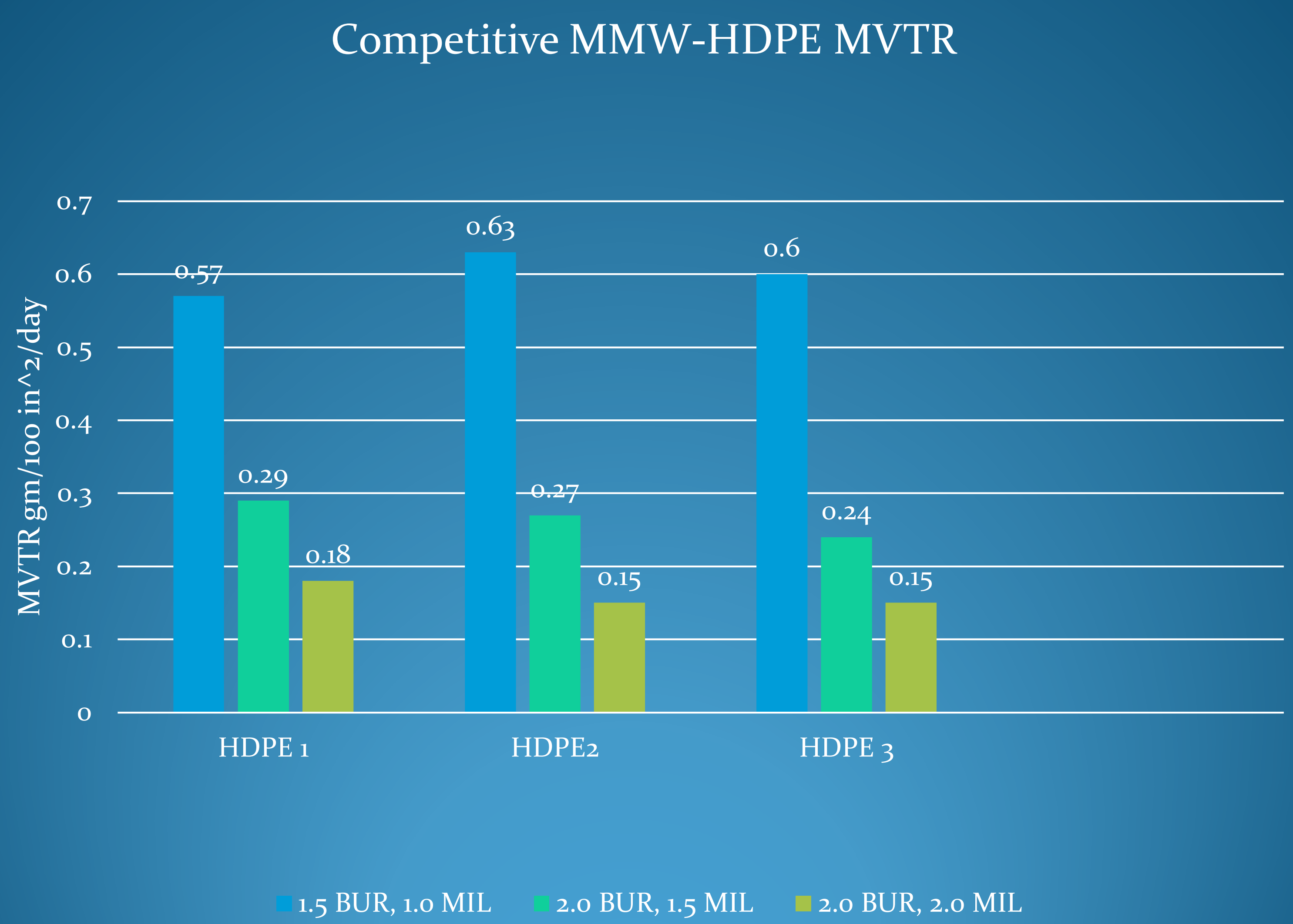
- HDPE is manufactured by following Processes:
  - Solution
  - Gas Phase
  - Slurry
- HDPE is characterize by its:
  - Opacity
  - Chemical Resistance
  - High moisture barrier resistance
  - Toughness

HDPE in Blown Film

- HDPE Molecular Weight Range

MW Group	MW Range	MI	Application
Very Low MW	Below 1000	Above 100	Greases, Waxes
Low MW	1000-100,000	10-100	Injection Molding
Medium MW	100,000-150,000	0.6-10	Injection & BM and Film
High MW	250,000-750,000	0.15-0.6	BM, Film
Very High MW	750,000-2 MM	<0.1	BM, Film
Ultra High MW	Above 2MM	<0.01	Forging

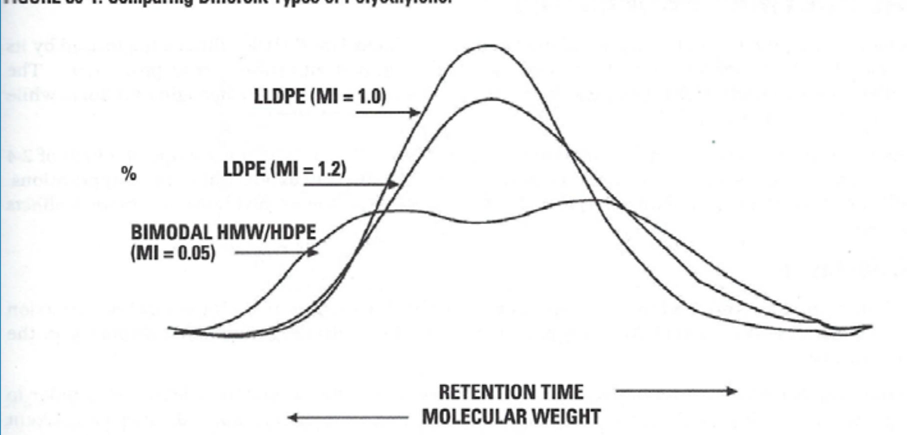
MMW-HDPE in Blown Film



HMW-HDPE in Blown Film

- Bi-modal HMW-HDPE resins are manufactured using 2 reactors in series
  - First reactor makes high molecular weight portion
  - Second reactor makes low molecular weight portion
- HMW-HDPE - linear structure with few side branches
  - Densities range from 0.941 to 0.965 gm/cc

FIGURE 30-1. Comparing Different Types of Polyethylene.



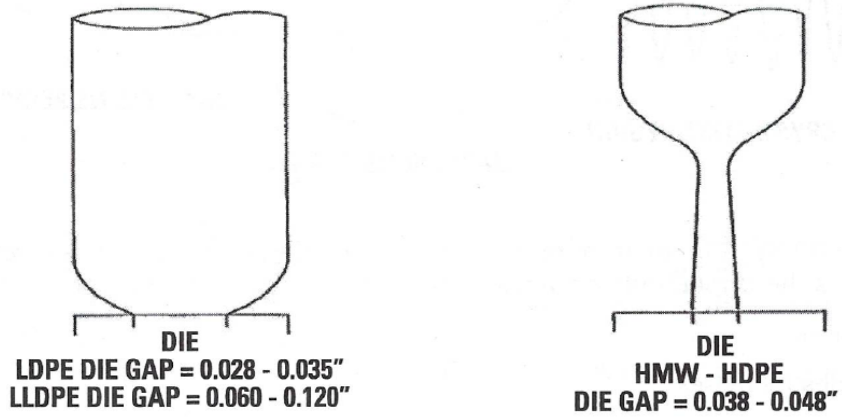
HMW-HDPE in Blown Film

- Typical Polymer Properties
  - HMW-HDPE film Characterized by:
    - Opacity
    - Excellent dart impact
    - High tensile strength
    - Stiffness
    - High moisture barrier
  - Film gauges range from:
    - Deli overwrap 0.25 mils
    - Heavy duty shipping sacks 2-4 mils

HMW-HDPE in Blown Film

- HMW-HDPE film properties are optimized by controlling the bubble geometry
  - Long neck height allows the molecules to relax
  - High BUR is required to balance orientation– MD/TD
  - HMW-HDPE bubble geometry looks quite different than conventional LDPE or LLDPE

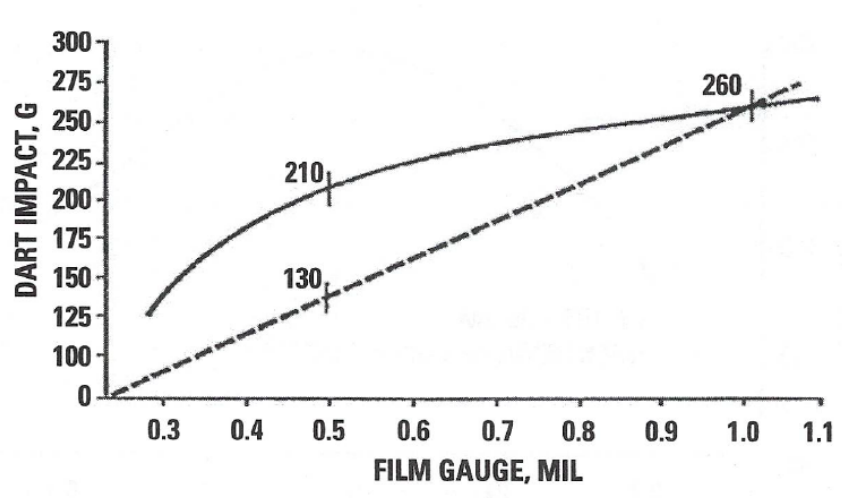
FIGURE 30-3. HMW vs. LDPE Bubble Geometry.



HMW-HDPE in Blown Film

- HMW-HDPE high melt strength provides advantages in downgauging
  - HMW film: drawn down to thin gauges/high rates
  - As HMW film is downgauged from 1.0 mil to 0.5 mil, the dart impact is almost the same as 1.0 mil
  - More balanced orientation between neck and FL as film downgauged

Influence of Biaxial Orientation on Downgauging.



HMW-HDPE in Blown Film

- BUR and Neck Height
  - 4:1 BUR is ideal for most applications
  - Lower BUR may sacrifice film impact strength but some applications may require higher TD tear: Grocery sacks
  - Trash bags requires more balanced tear properties

FIGURE 30-6. Influence of BUR on Dart Impact.

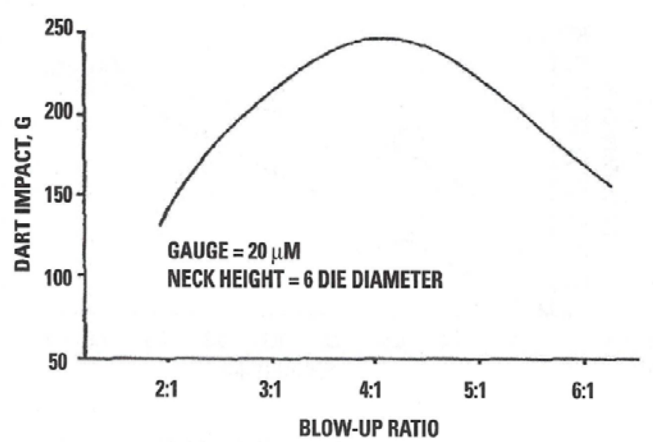
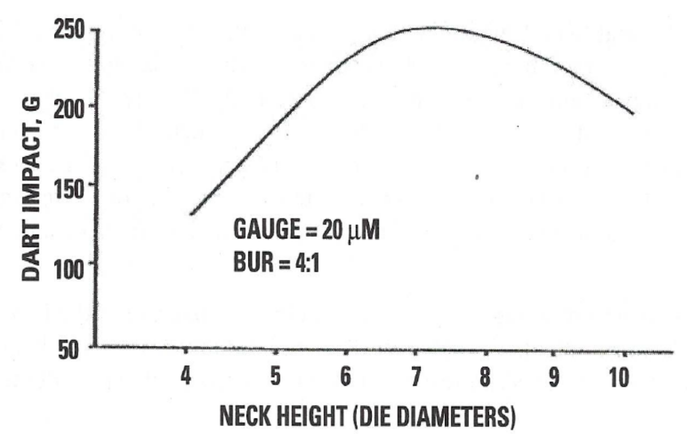


FIGURE 30-7. Influence of Neck Height on Dart Impact.



HMW-HDPE in Blown Film

- HMW-HDPE General Processing Guidelines
  - Requires intensively cooled grooved feed extruder designed specifically for this type of resin
  - L/D ratio of 21:1 to 30:1
  - Melt temp recommendation: 390 to 420 F
  - Extruder back pressure range from 7000 to 11000 PSI
  - Recommended Die Gap: 32 to 60 mils

HMW-HDPE in Blown Film

- Typical HMW-HDPE Film Applications
  - Grocery Sacks
  - Trash Can Liners
  - Heavy duty shipping sacks
  - Deli
  - Tissue overwrap
  - Merhandise Bags
  - Multi-wall liner

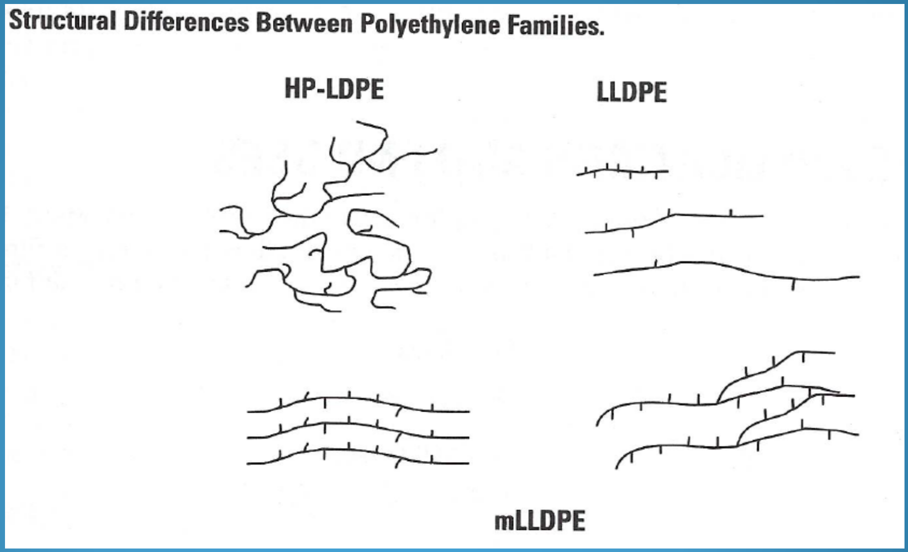
m-LLDPE in Blown Film

- m-LLDPE resins are manufactured by polymerizing:
  - Ethylene
  - Alpha-olefin Comonomer
  - Metallocene catalyst

- Low pressure metallocene processes
  - Gas-phase fluidized bed
  - Gas-phase stirred bed
  - Liquid-phase slurry
  - Liquid-phase solution

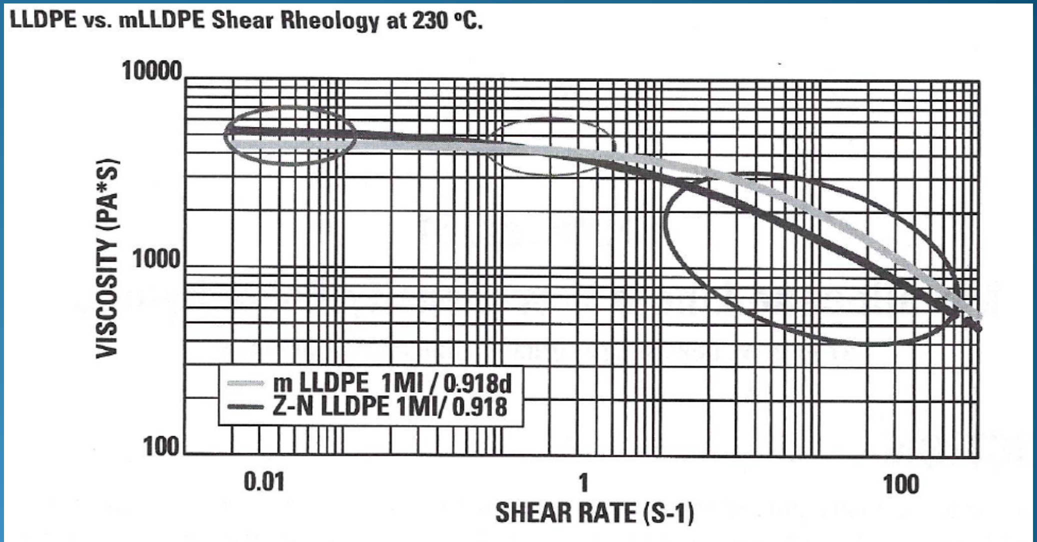
m-LLDPE in Blown Film

- m-LLDPE Characterization:
  - SCB, no LCB
  - Narrow MWD
  - Uniform Comonomer Distribution (CD)
  - Most common Comonomer: Hexene, Octene



m-LLDPE in Blown Film

- Physical Property Improvements:
  - Seal Initiation Temp
  - Puncture Resistance
  - Tensile Strength
  - Dart Impact
  - Optics
- Sacrificed processability
  - m-LLDPE exhibit higher viscosity in shear flow than same MI conventional LLDPE



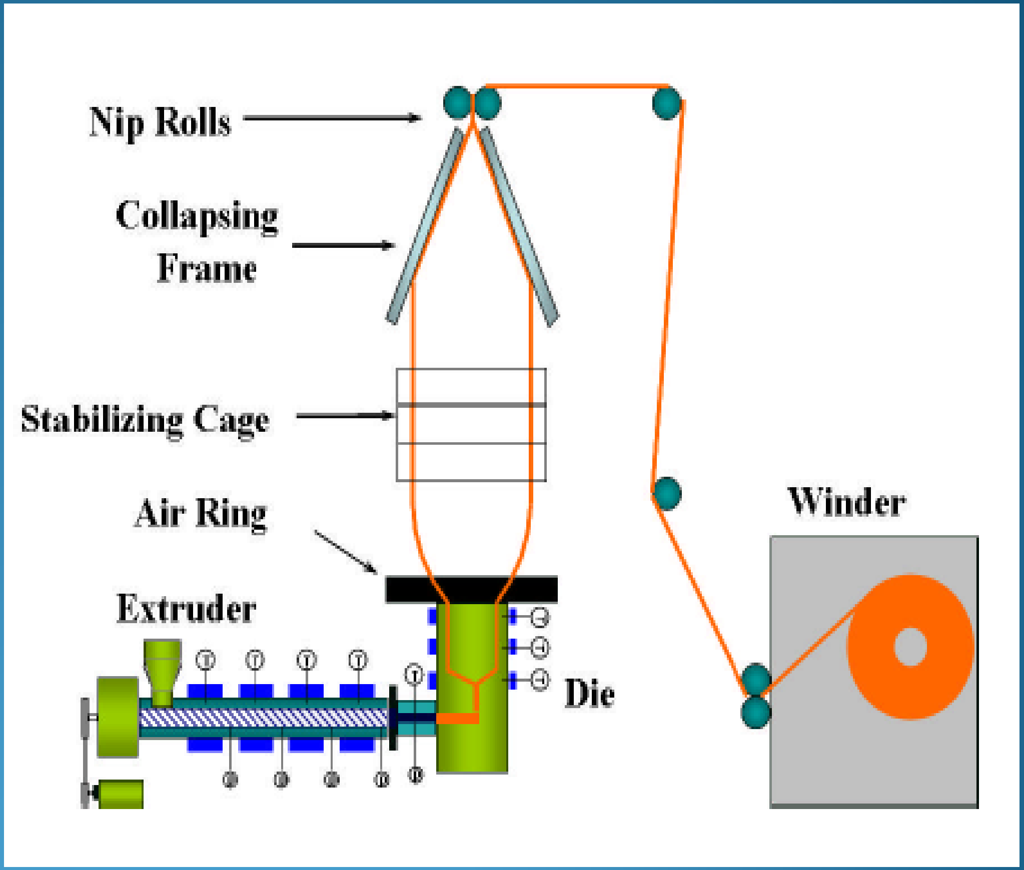
m-LLDPE in Blown Film

- Typical Polymer Properties Improvements:
  - Seal Initiation Temp
  - Puncture Resistance
  - Tensile Strength: 15 - 40% higher than LLDPE
  - Dart Impact 2 - 10 times higher than LLDPE
  - Optics
  - Note: Tear strength: slightly lower than LLDPE

Blown Film Process Overview

Blown Film Equipment

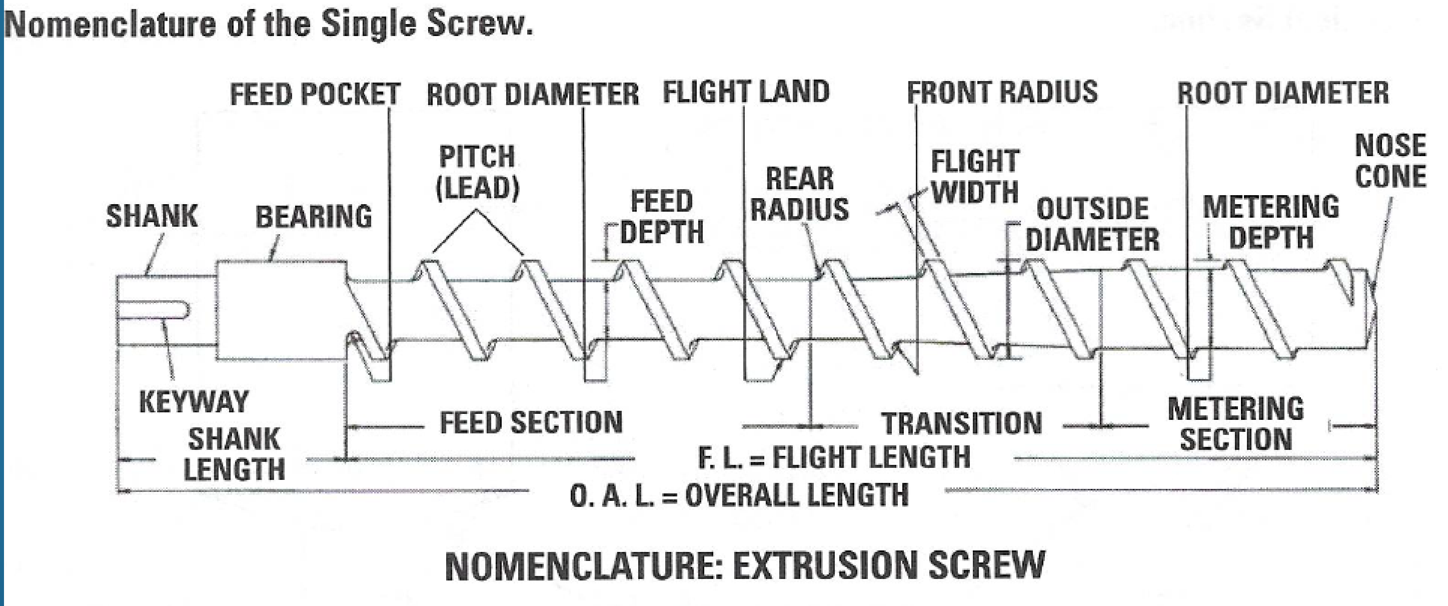
- Extruder
- Screw
- Die
- Air Ring
- Collapsing Frame



Blown Film Process Overview

Single Screw Design

- Feed Section
- Transition Section
- Metering Section



Blown Film Process Overview

Die Designs

- Spiral Die
- Stacked Die

FIGURE 11-2. Conventional Coextrusion Die Consisting of 5 Nested Cylinders.

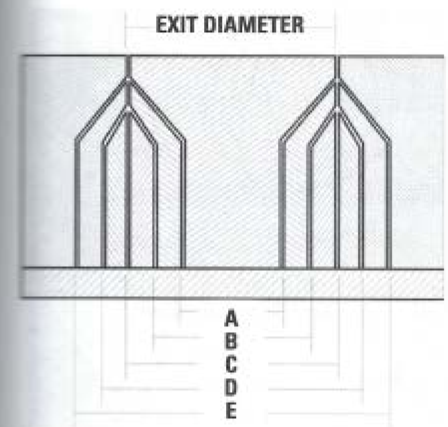


FIGURE 11-3. Conventional Cylindrical Spiral Mandrel Distribution System.

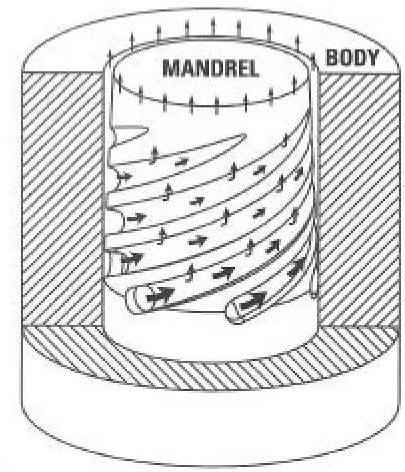


FIGURE 11-4. Stacked Type of Coextrusion Die.

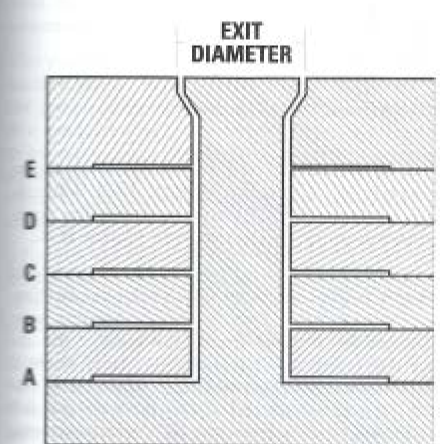
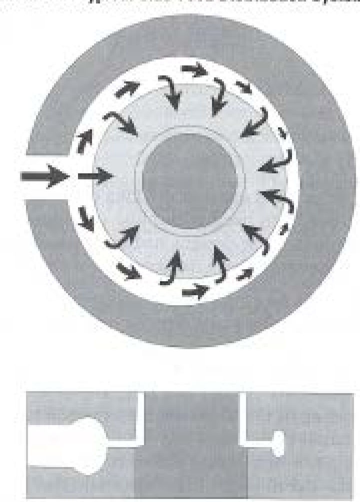
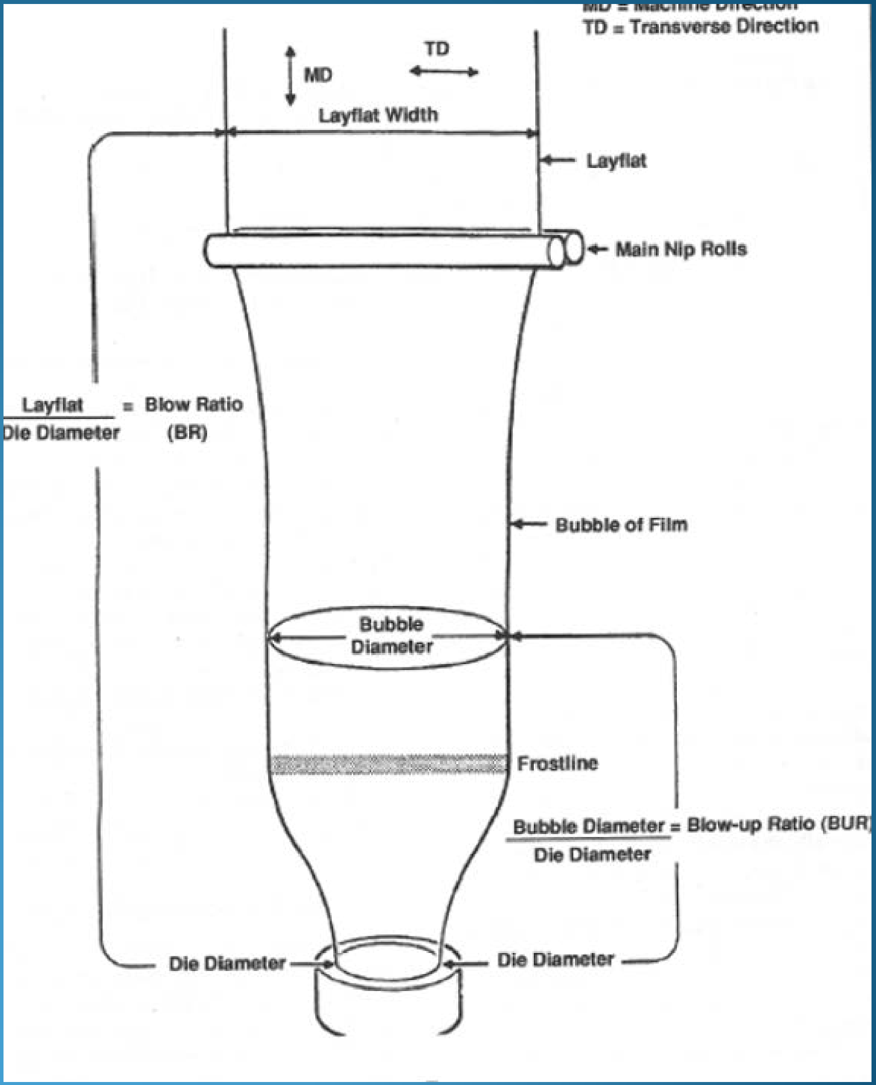


FIGURE 11-5. A Typical Side-Feed Distribution System.



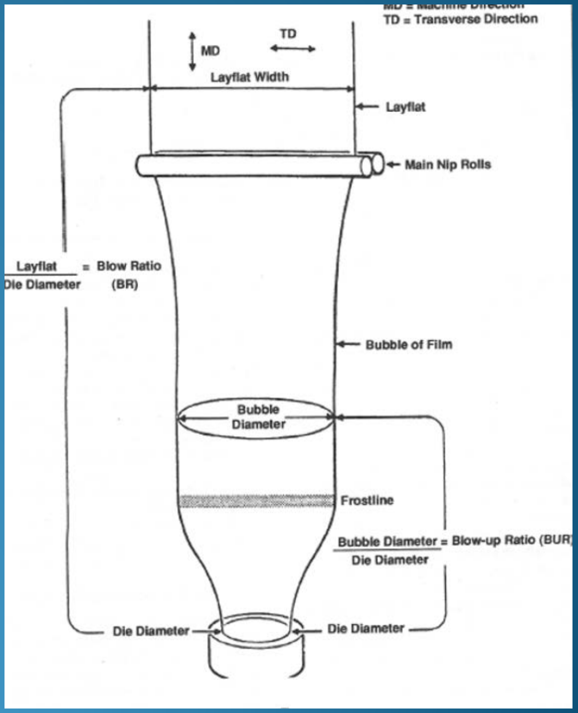
Polyolefin Blown Film Parameters

- Critical Blown Film Parameters
  - Melt Temp
  - Blow-Up Ratio (BUR)
    - Bubble Dia./Die Dia.
  - Die Gap & Film Thickness
    - Drawdown Ratio (DDR)
    - Die Gap/(Film Gauge x BUR)
  - Specific Output Rate
    - LB/HR/(Die Dia. X 3.14)
  - Frostline Height
    - Distance from top of die to bubble freeze line
  - Quench Rate



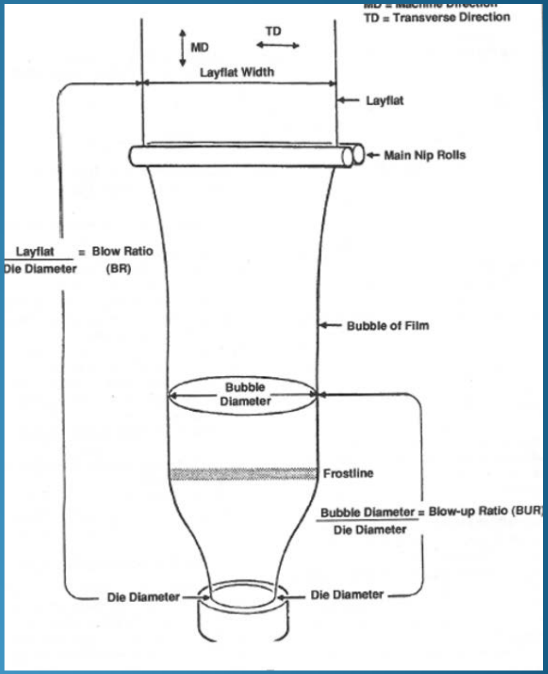
Polyolefin Blown Film Parameters

- Effect of Blown Film Parameters on Film Properties
  - Melt Temp– Increasing
    - Increases optical properties– improves surface defects
  - Quench Rate Increased
    - Film crystallinity is reduced, improving optical properties and impact strength
  - Blow-Up Ratio (BUR) – Increasing
    - Increases cross-direction orientation, which improves:
      - Impact strength
      - CD tensile
      - MD elongation
      - MD tear



Polyolefin Blown Film Parameters

- Effect of Blown Film Parameters on Film Properties
  - Die Gap – Increasing :Increases MD orientation which results in:
    - Lower MD tear
    - Lower MD Elongation
    - Improved CD tear
    - Improved MD Tensile
  - Output – Increasing: Higher MD orientation
    - Higher MD tensile
    - Increased impact
    - Improved optics
  - Frostline Height – Increasing: Decrease MD orientation with slower quenching rate
    - Optics will reach an optimum and then decrease



Advance in Blown Film Technology
Annular Nanolayer Film Extrusion

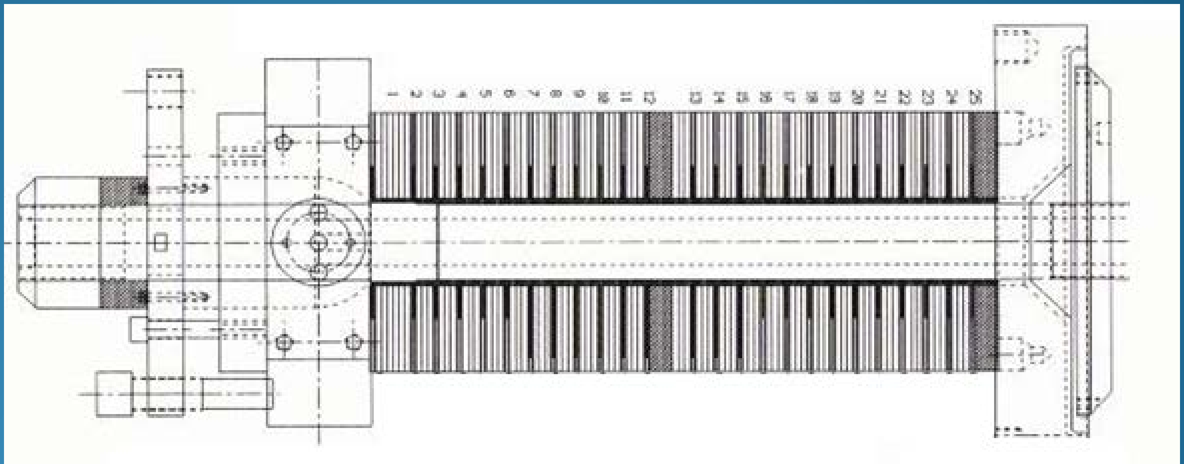
- Base
  - Melt entrance
- Adjustable inner mandrel
  - Pivot adjustment
- Melt Exit
  - Disc stack clamp & die lip assembly
- Modular Disc assemblies

Cross Section / Side View

Base

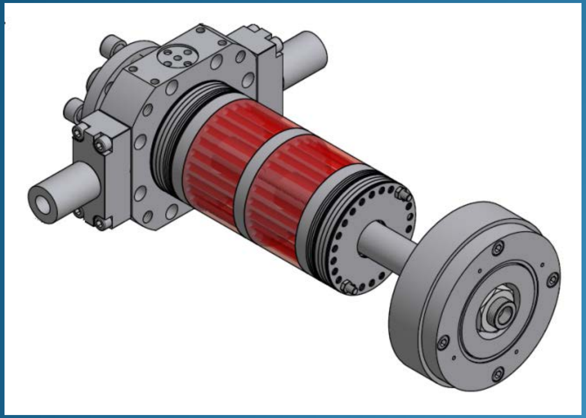
Melt Exit Assembly

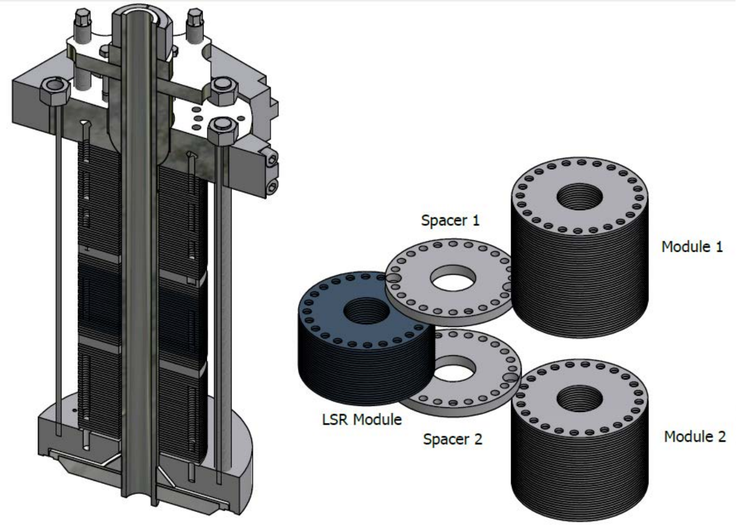
Adjustable Inner Mandrel

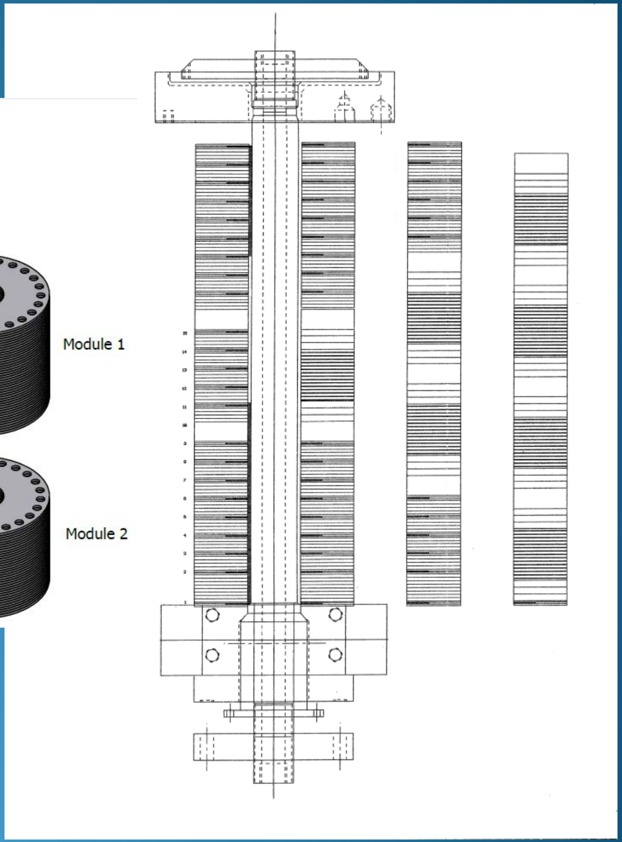


Disc Stack Assemblies

Die Assembly Configurations



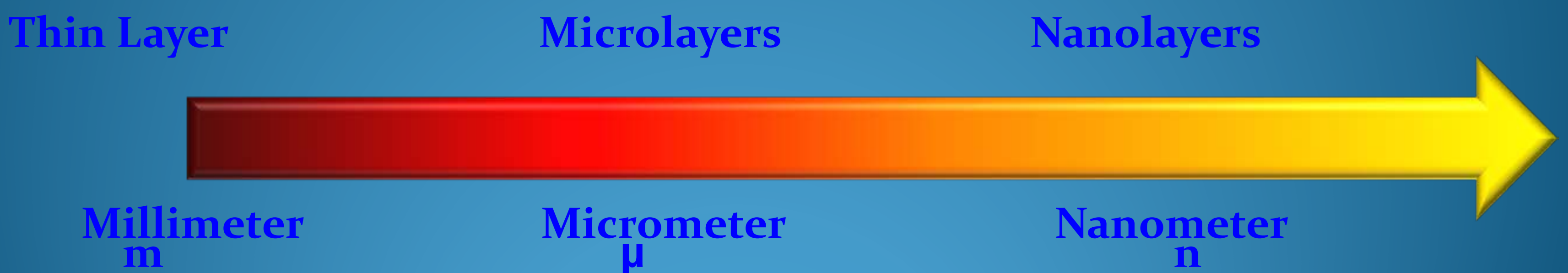




Virtually limitless in possibilities

Nanolayer

The physical scale of a Nanolayer has a defined value, but as it applies to film properties that value varies according to the effect and interaction



A Nanolayer may well be defined as:

"The thickness where unique physical characteristics to the polymeric film occurs imparting special properties not observed in that polymeric film as a thicker structure"

Summary

- Declarative Statements*
  - No loss in throughput, potential for highest throughput as compared to any existing technology
  - Potential to utilize more commodity raw materials
  - Potential to reduce overall gauge maintaining current properties
  - Potential to have properties not existing with any materials or process
  - Potential to produce more products on existing/new equipment
  - Potential to expand capabilities with incremental upgrades
- There is typically a minimum of 25% cost benefit available in this approach*

* Dependent on film formulation and application

Thank You

Questions