Polyethylene

by

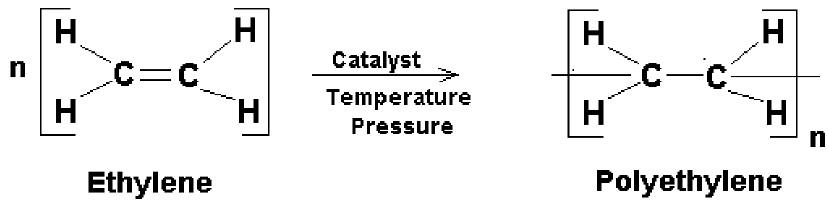
Dr. Yatish B. Vasudeo

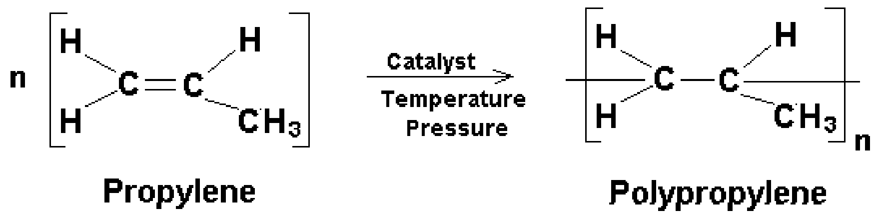
Innovation Consultant

Polyolefins: Success Factors

- Ethylene and Propylene - Cheapest building blocks known to man
- Easily accessible raw materials
- Non polluting process
- Easy processability
- Broad product portfolio; diverse applications
- Ability to tailor make products
- Easy to recycle

Polymerisation





Polyethylene…..

- Global demand for polyethylene (PE) has grown quickly since its early days.

- Primary reasons for this sustained growth are

❖ PE is well established plastic resin with broad application range.
Its use has grown faster than overall economic growth.

❖ It continues to have the potential to replace traditional materials like glass, wood, paper and metal.

- Today, the family of polyethylene resins represents the largest single group of plastic materials produced and consumed in the world.

Early Days

- In 1933, Polyethylene was accidentally discovered in the ICI laboratories in the UK that ethylene, in the presence of adventitious oxygen. This discovery, a by-product of the study of chemical reactions at high pressure.

- The first so-called linear PE was made at Du-Pont by free radical polymerization at 50 -80^{o}C and 707 MPa (7000 atm),

Polyethylene – Stages in Development

- 1930's – Development of high pressure process to arrive at branched PE – LDPE
- 1950's – Development of co-ordination catalysts – Chromium Oxide & Ziegler-Natta catalysts for linear PE – HDPE. Development of slurry processes for HDPE.
- 1970's - Development of low pressure gas phase technology for HDPE & LLDPE (Swing). Development of other processes also began – mainly in 80's
- 1990's – Development of single site catalyst (metallocene) for m-LLDPE.

Supply & Consumption

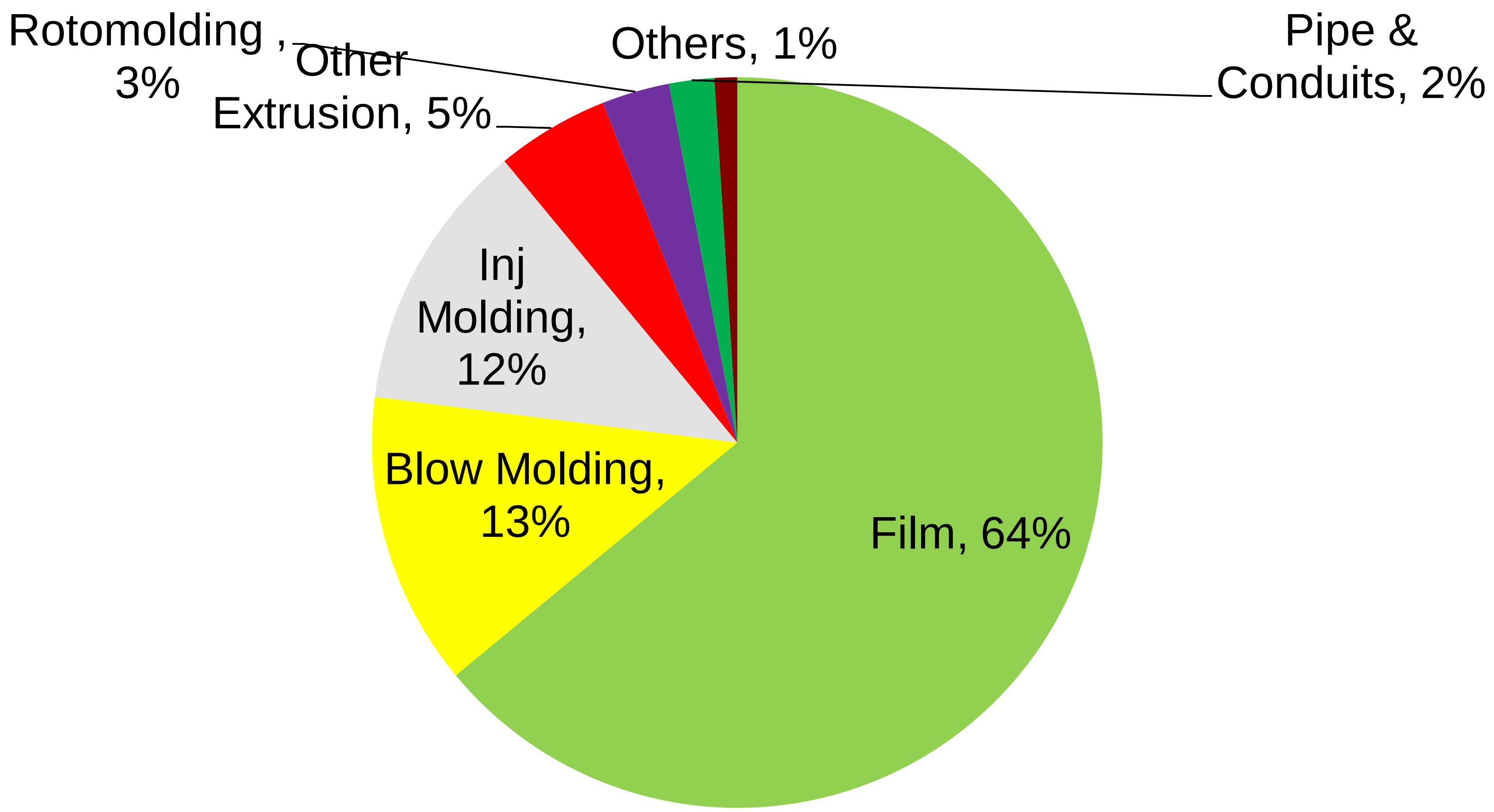
Supply

- According to latest statistics, the polyethylene production capacities in the GCC will increase to 21.5 MMT by the year 2015.
- The production of polypropylene will also increase to 9.5 MMT by 2015
- This will bring the combined production capacities of the two major polyolefin resins to over 31 MMT by 2015.

Consumption

- GCC countries total consumption would be 5.5 MMT by 2015.

Polyethylene Consumption



Types of Polyethylene

Classification by Density

- Low Density Polyethylene (LDPE)

  Density - 0.918 gm/cc - 0.930 gm/cc

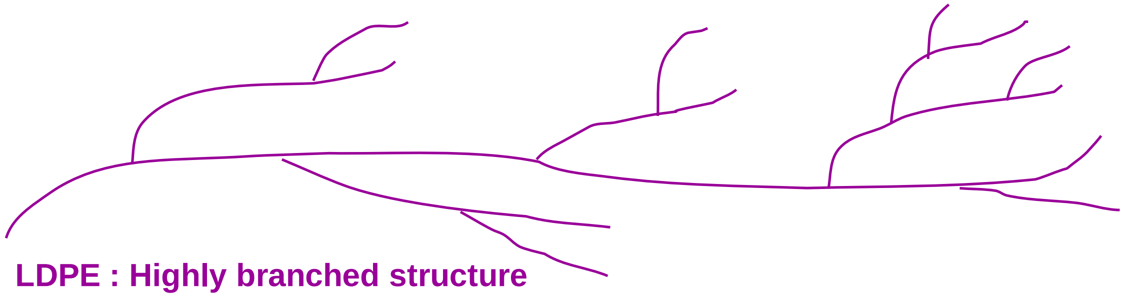
- Linear Low Density Polyethylene (LLDPE)

  Density - 0.918 gm/cc - 0.935 gm/cc

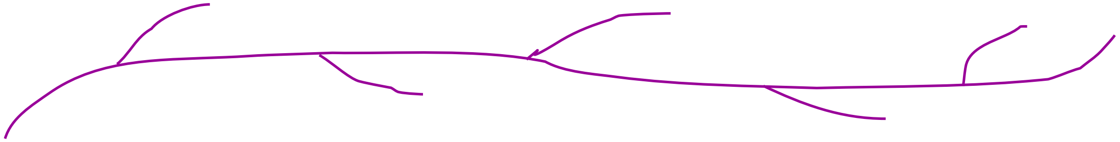
- High Density Polyethylene (HDPE)

  Density - 0.940 gm/cc - 0.960 gm/cc

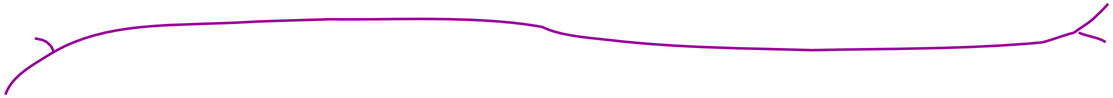
Molecular Chains



LDPE : Highly branched structure

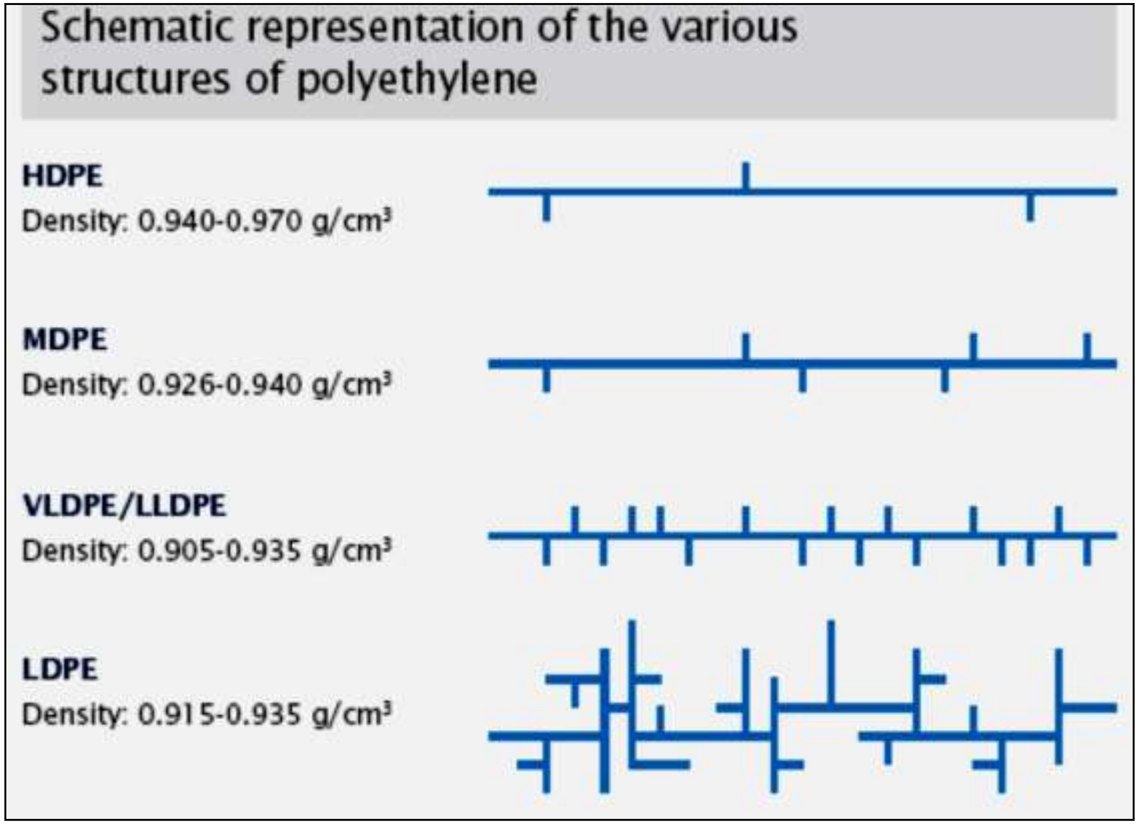


LLDPE : Short branching



HDPE : Linear structure

Various Structure of LDPE



High pressure polymerization (LDPE) - Manufacturing

- **Autoclave process**- ICI, Dupont,CDF Chimie(now Enichem)
- **Tubular process**- BASF (now Basell),DSM, Enichem

High pressure polymerization (LDPE) - Product Properties

Density : 0.918 gm/cc - 0.935 gm/cc

Controlled by varying - Reactor pressure

Reactor temperature

MFI, g/10 mins : 0.2 - 50

Controlled by varying pressure - Reactor pressure

Reactor temperature

Concentration of modifiers

Structure : Short ethyl branches

Long branches; PE chains

Low Density Polyethylene (LDPE)

Characteristics

- ✷ Products offer excellent processability
  - ⇒ Low motor loads
  - ⇒ Excellent bubble stability (films)
  - ⇒ Very low neck-in and excellent adhesion (extrusion coating)
  - ⇒ very good opticals
- ✷ Moderate product properties
  - ⇒ Mechanical properties
  - ⇒ Dart Impact strength
  - ⇒ Tear strength

Low Density Polyethylene (LDPE)

Characteristics

- ✸ Severe process conditions
  - ⇒ Very high pressure
  - ⇒ High temperature
- ✸ High capital cost
  - ⇒ Sizing of equipment for high pressures
- ✸ Higher operating cost
  - ⇒ To run high capacity compressor
- ✸ Relatively lower capacity plants

Low Pressure Polymerization

LLDPE

HDPE

Mechanisms and catalysts for various Types

Type of PE	Mechanism of Polymerization	Catalysts
LDPE	Radical	Oxygen &/or peroxides
LLDPE & HDPE	Co-ordination	Supported Chromium oxide
		Ziegler Natta
		Metallocene

Catalyst types for Polyolefins

Catalyst systems

✷ **Ziegler Natta**

- ⇒ Based on Titanium
- ⇒ Trialkylaluminium cocatalyst
- ⇒ Magnesium support

Work horse catalyst used by 90% of polymerisation plants in the world

Catalyst types for Polyolefins

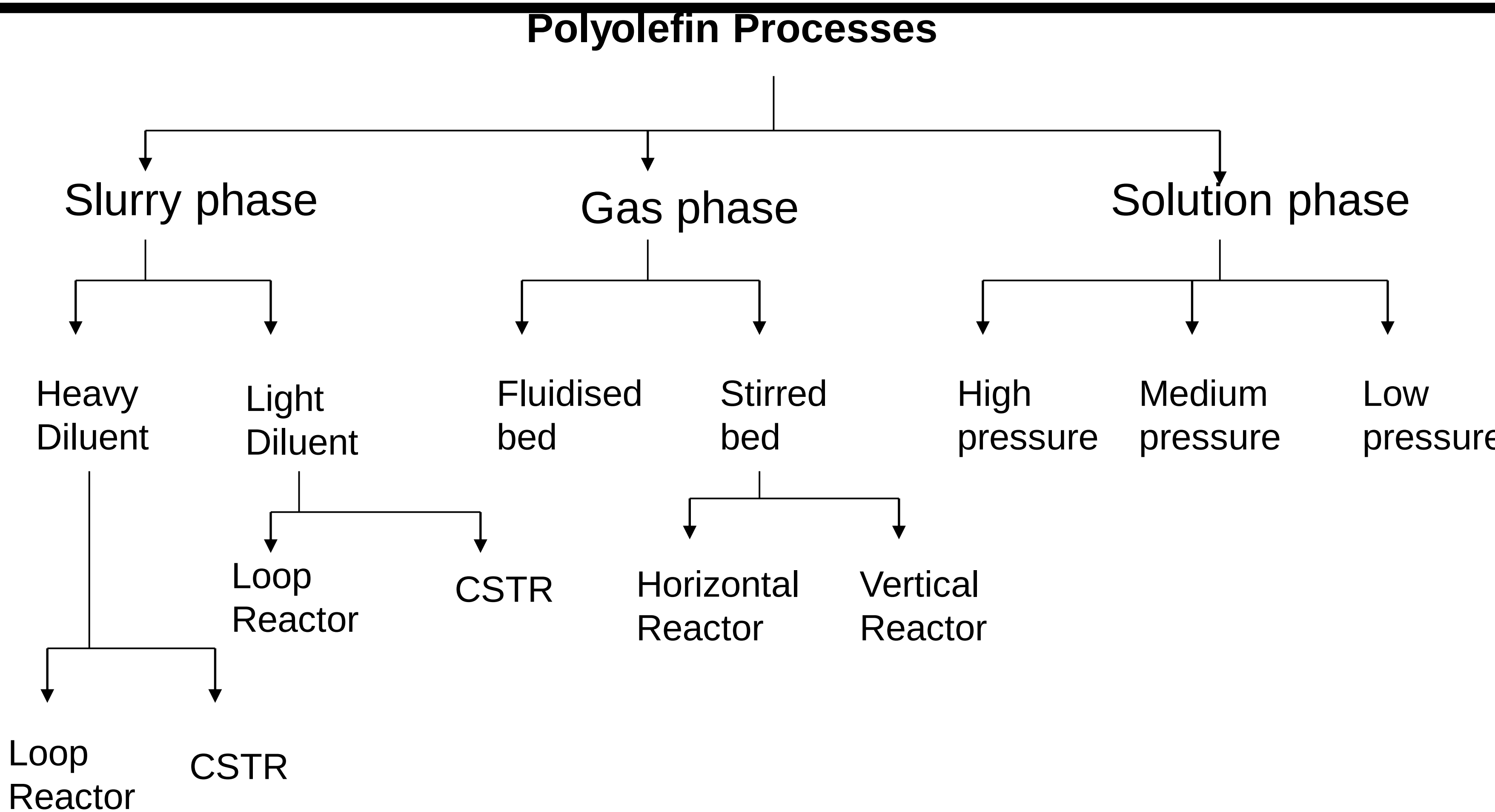
✷ Phillips catalyst

- ⇒ Based on chromium oxide
- ⇒ Yield broad MWD products
- ⇒ Widely used for HDPE and HMHDPE

✷ Metallocene catalysts

- ⇒ Homogenous type

Manufacturing Processes for various types…



Slurry polymerisation (CSTR), Polyethylene

Best known example

- Hostalen process(Basell)
- Mitsui CX process
- Equistar- Maruzen bimodal process
- Nippon-Nisseki process

Slurry Polymerization (Loop), Polyethylene

Best known examples

- Chevron Phillips process
- Borstar Slurry loop-Gas phase process (Borealis)
- Solvay process

Solution Polymerization, Polyethylene

Best known examples

- Sclairtech process (Nova chemicals)
- Dowlex process
- DSM process

Gas phase, Fluidised bed process

Best known examples

- Unipol process(UCC-Univation)
- Lupotech process(BASF-Basell)
- Innovene process (BP Amoco)
- Spherilene process (Montell-basell)
- Evolue process (Mitsui)
- Unipol-II process (UCC-Univation)

Comonomer species (α-olefin) and physical properties

- In order to improve the quality of LLDPE, a comonomer is generally selected and added for the modification of strength.

- It is general practice to copolymerize PE with a comonomer having high molecular weight to improve mechanical strength. As the molecular weight of the comonomer becomes higher, the strength of PE goes up.

Co-Monomers

-C-C-C-C-C-C-C-C-

C-C

C4 Butene-1

-C-C-C-C-C-C-C-C-

C

C-C-C

C6 Octene-1

-C-C-C-C-C-C-C-

C-C-C-C

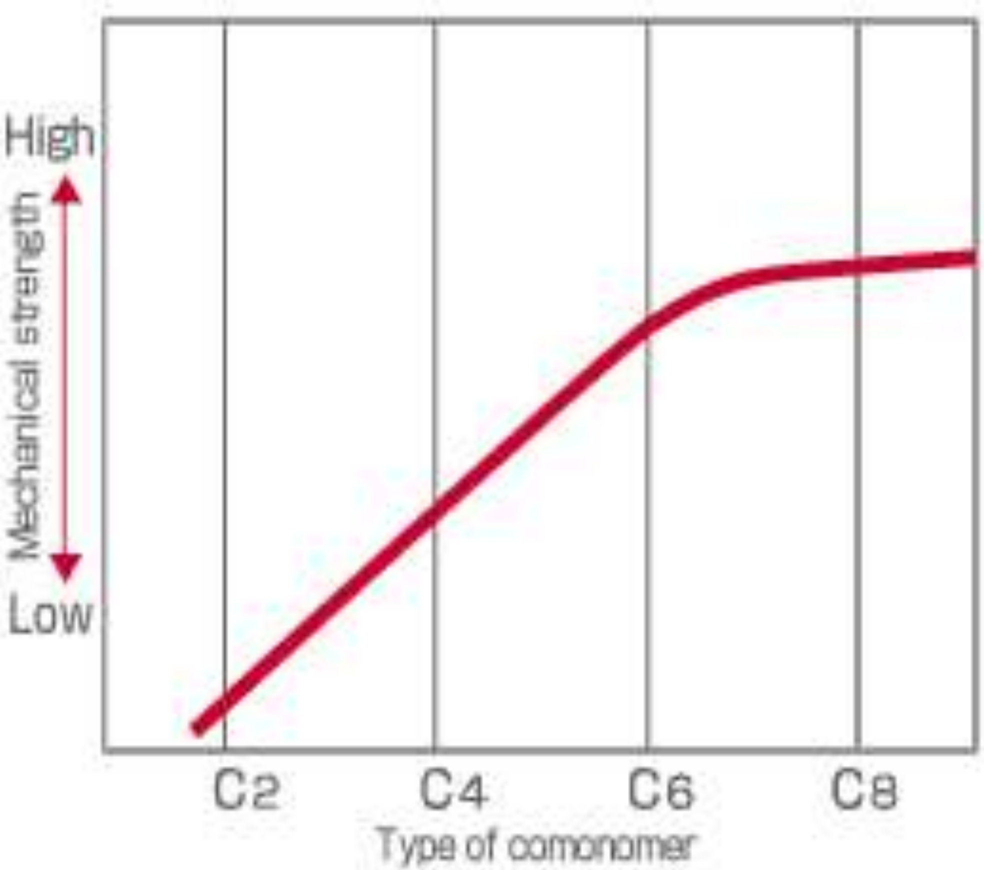
C6 Hexene-1

-C-C-C-C-C-C-C-

C-C-C-C-C-C

C8 Octene-1

Influence of Co-monomer on Properties



C4 Butene-1

C6 Hexene-1 / 4methyl pentene

C8 Octene-1

Physical Properties of LLDPE

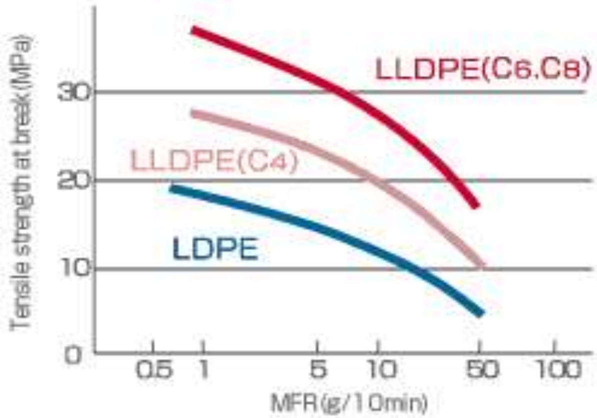
Linear low-density PE (LLDPE)

LLDPE has bulky molecules because side chains are introduced into PE. Because of this, LLDPE is not dense and has lower density than that of HDPE.

The physical properties of LLDPE vary as shown in the figures (next slides), depending on the levels of the molecular weight (MFR) and density. As the side chains introduced become longer, strength and low-temperature resistance become higher.

Tensile strength and MFR

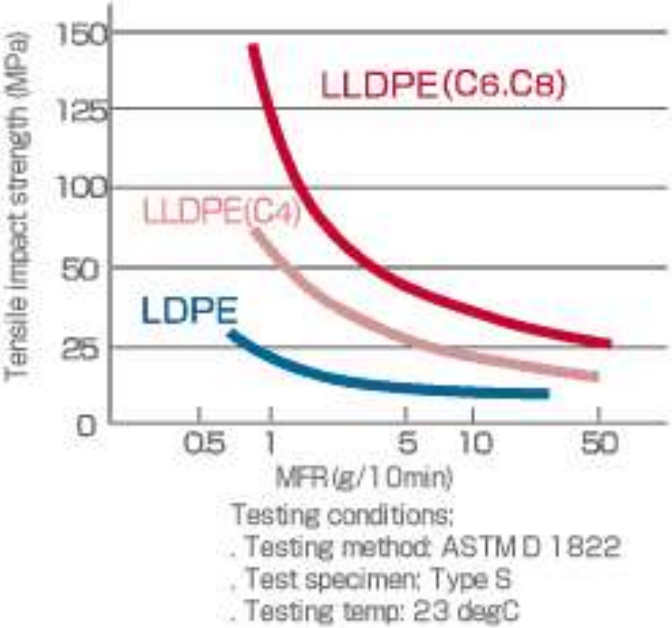
As the side chains become longer, strength increases. Furthermore, as MFR decreases (higher molecular weight), tensile strength becomes higher. LLDPE has higher tensile strength at the same MFR than that of LDPE.



Testing conditions;
. Testing method: JIS K 7113
. Test specimen: No.2 dumbbell
. Testing temp: 23 degC
. Pulling rate: 200mm/min

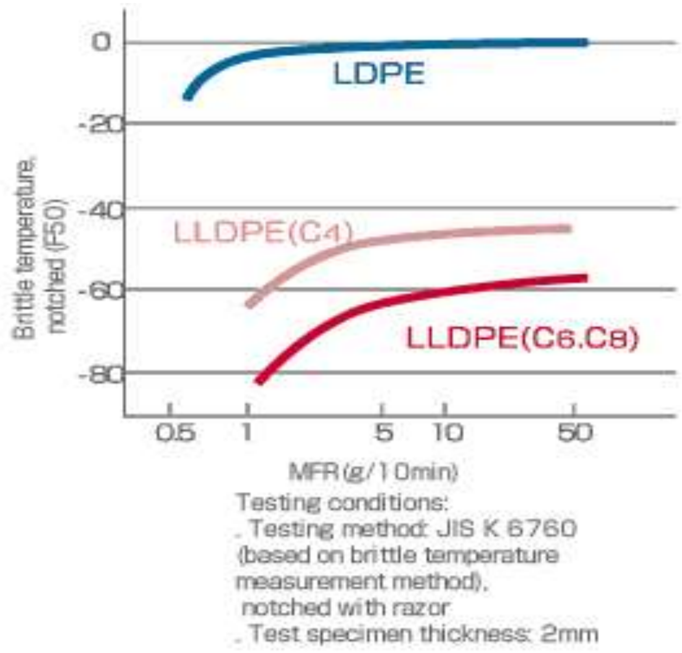
Tensile impact strength and MFR

- As MFR decreases (higher molecular weight), tensile impact strength increases. LLDPE has higher impact strength at the same MFR than that of LDPE.

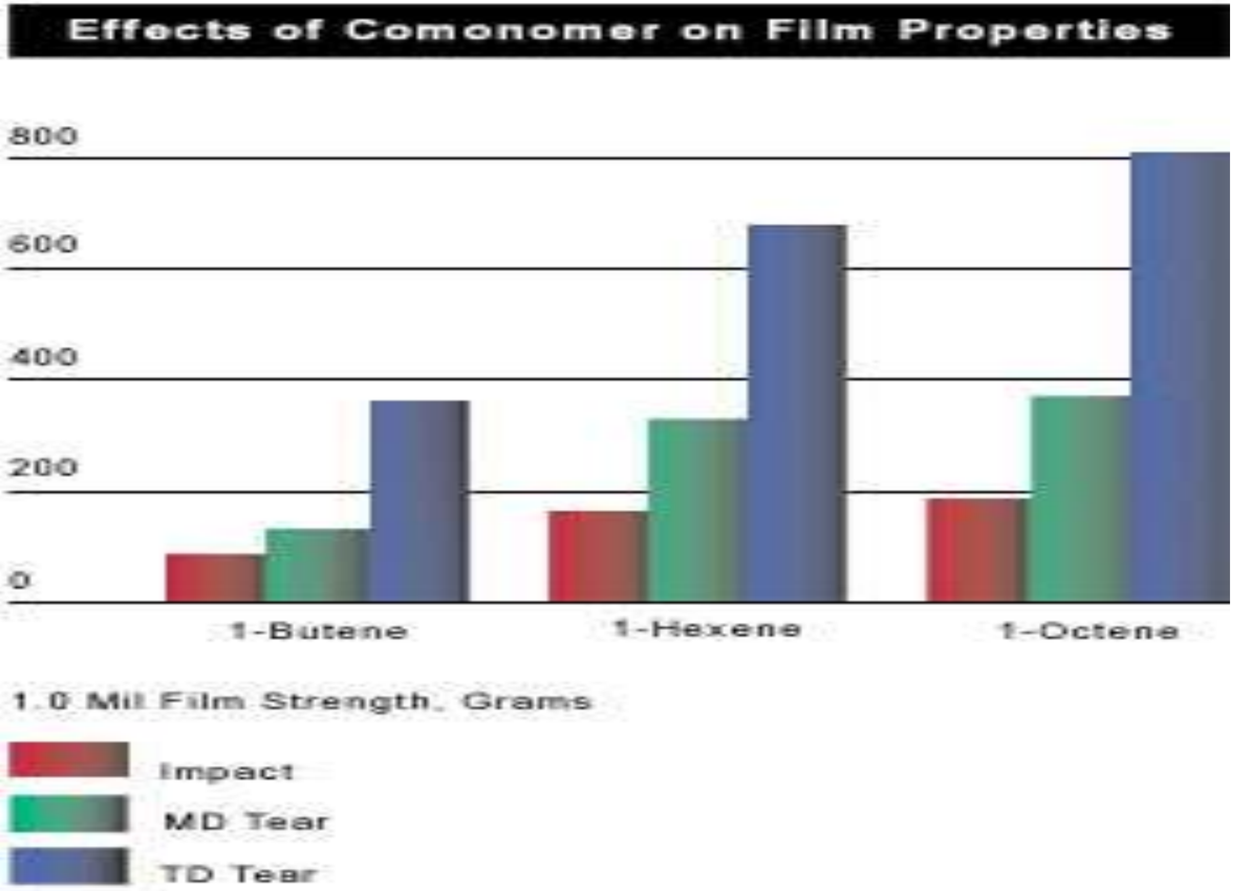


Brittle temperature and MFR

- As MFR decreases (higher molecular weight), brittle temperature decreases. LLDPE is lower in brittle temperature at the same MFR than LDPE.



Effect of Comonomer on Film Propertiues



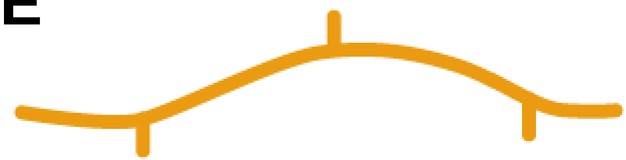
Physical properties of HDPE

Basic properties of high-density PE

- Among the factors controlling the physical properties of HDPE are MFR, density, molecular weight, molecular weight distribution, crystallinity, double bonds, branched species, etc. But the three basic physical properties (factors) that regulate physical properties are molecular weight, molecular weight distribution, MFR and density.
- Various grades are manufactured by controlling these physical properties.

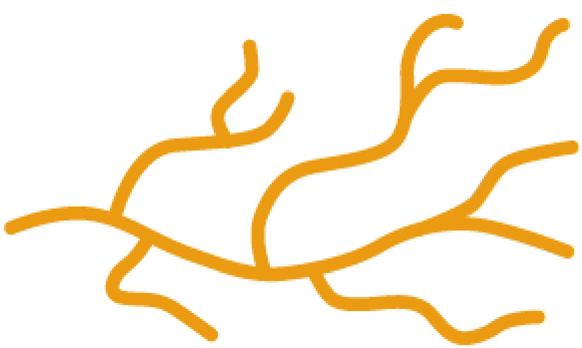
Molecular Configuration

HDPE



Side chains are short and small in number.

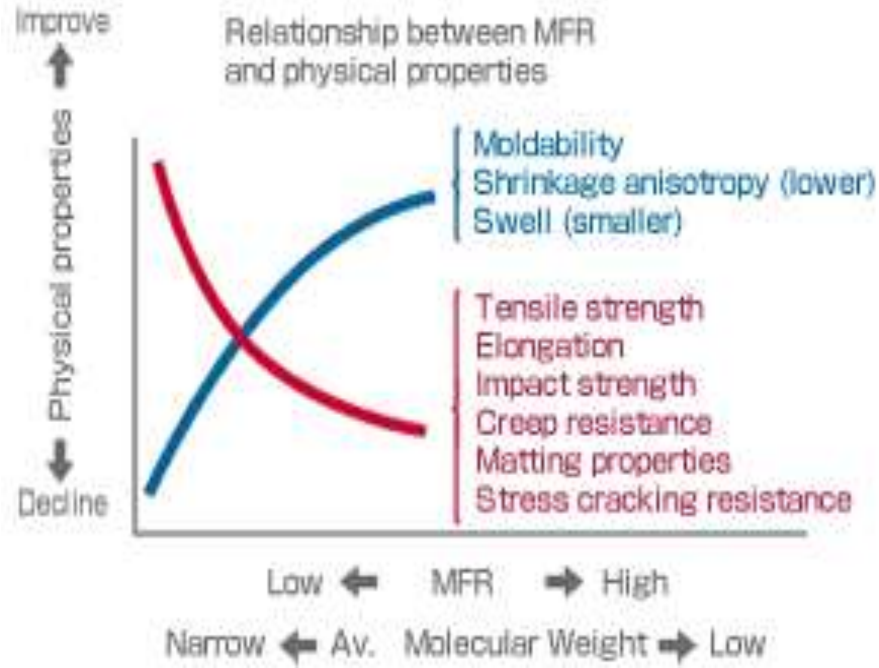
LDPE



There are many irregular side chains.

Molecular weight of HDPE

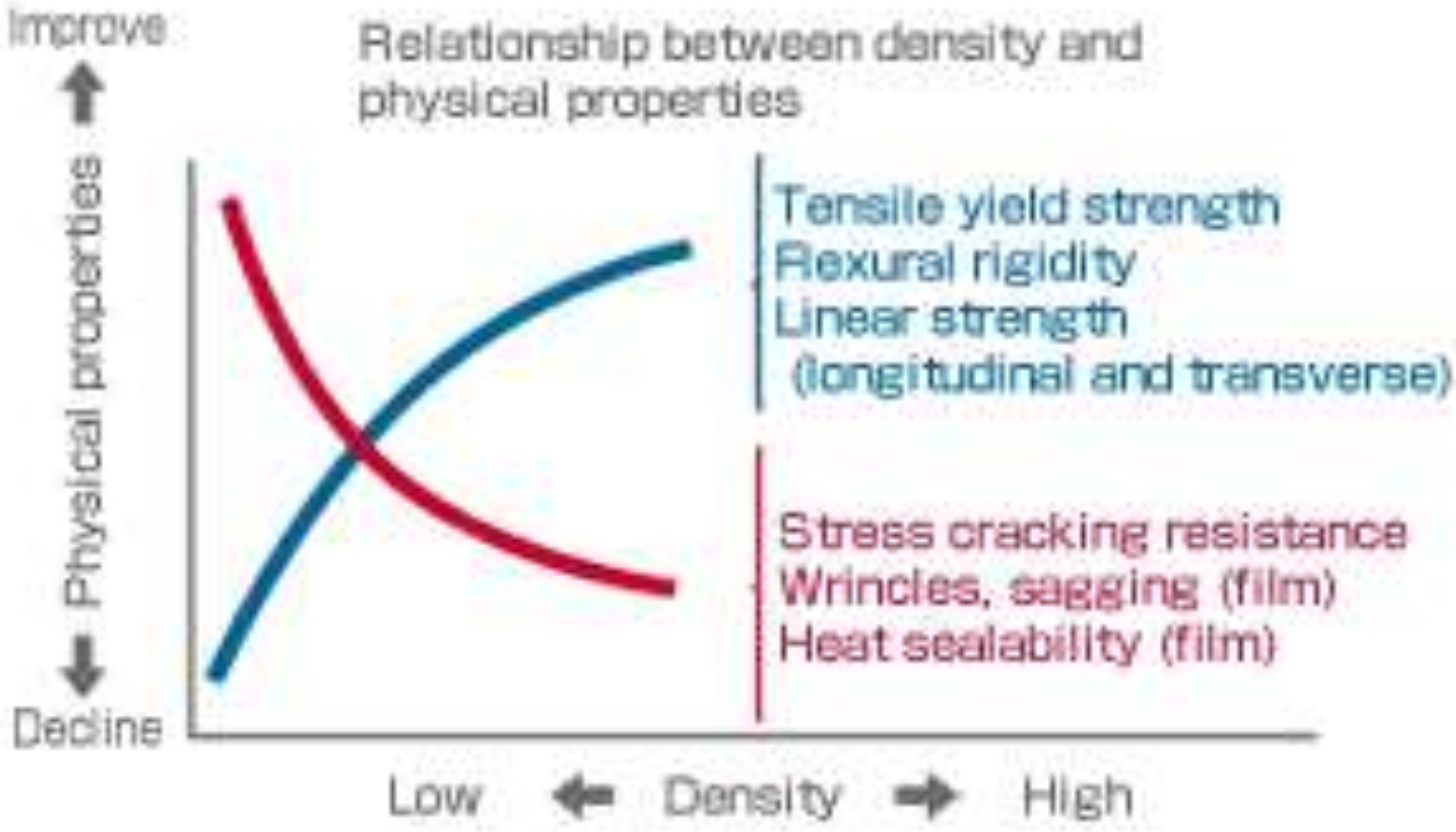
As molecular weight increases (lower MFR), mechanical strength generally increases, but on the other hand, melt viscosity increases, making flowability (moldability) lower.



Molecular weight distribution of HDPE

Molecular weight distribution affects the flowability and mechanical properties of the polymer significantly. As molecular weight distribution becomes wider, improvement in flowability (moldability). Further, as the distribution becomes narrower, mechanical properties such as tensile strength and impact resistance become better.

Molecular weight distribution of HDPE



Density

As density increases, tensile strength and rigidity, among other things, increases, but impact strength, transparency, stress cracking resistance, etc. decline

Relationship between molecular structure and physical properties

The general physical properties of HDPE trend in accordance with a fall in molecular weight, an expansion of molecular weight distribution and a rise in density.

Bimodal polyethylene

Products with unique combination of

- Processability
- Mechanical properties

Speciality grades

- Blow Moulding
- Film
- Wire and Cable
- Pressure pipe

Bimodal polyethylene - BORSTAR

- The fundamental feature of the Borstar technology is its dual reactor operation which allows us to produce materials for film extrusion in a wider range of densities and MFR, with a broad (bimodal) molecular weight distribution and tailored comonomer distribution.

- Borstar technology is suited to a very wide range of PE product properties and applications, and offers new materials with enhanced performance.

Metallocene LLDPE Benefits & Applications

- Metallocene LLDPE resins are well recognized for their excellent dart impact and puncture resistance, superior organoleptics, brilliant clarity and outstanding hot tack and heat seal benefits.
- Metallocene LLDPE resins ideally suited for high-performance film applications such as food and medical packaging, shrink wrap, heavy duty sacks, medical packaging, other non-food packaging, retail bags and sacks, agriculture film and other non-packaging applications.

LLDPE/LDPE/Metallocene Blends

Film Properties: LLDPE with 20% blend of LD1005FY20				
Properties	Unit	O19010	Surpass FP117D	Elite 5401
Tear Strength, MD	gm/ mic	6	5.6	5.3
TD		28	28	29
Dart Impact	gm/ mic	4.4	7	10.3
Thickness	micron	49	48	50
Haze	%	15	16	19
Gloss @ 60°	-	70	61	58
SIT	°C	109	103	105
Hot Tack Strength	gm/25mm	155 @ 112°C	140 @ 106°C	190 @ 109°C
Heat Seal Strength	gm/25mm	> 1500	> 1300	> 1200

Blends with Metallocene

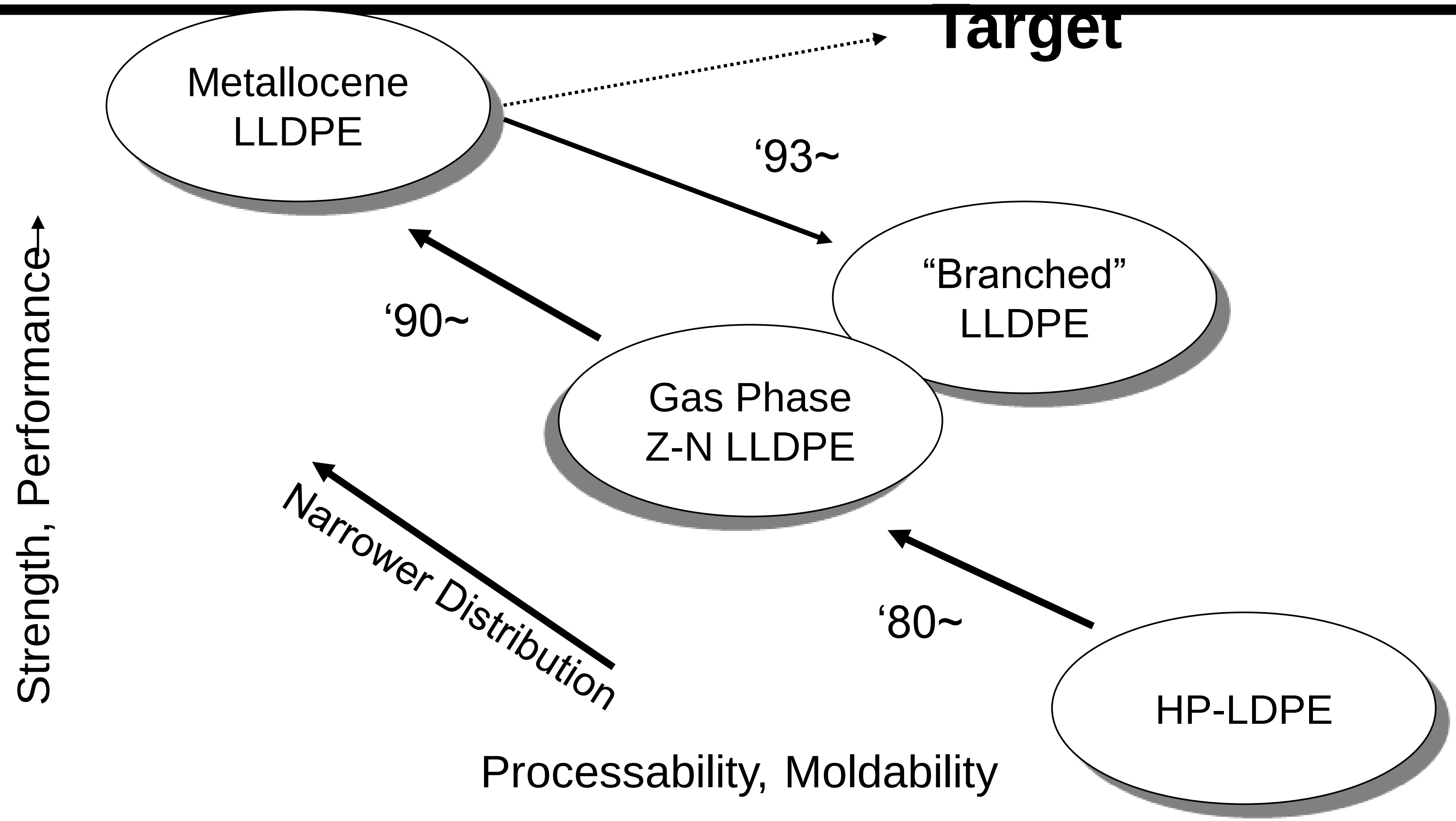
Film Properties (2.25 BUR, 25 microns)				
Properties	Units	Sample 1	Sample 2	Sample 3
Motor loads	*ampere*	11	11	10.5
Output	*kg/ hr*	19.8	19.8	19.6
Dart Impact	*gm/ mic*	9.5	12	13.9
Tear - MD	*gm/ mic*	15	16.4	20
- TD		19	20	23
COF, Static	-	0.19	0.2	0.22
Kinetic	-	0.16	0.17	0.17
Haze	%	29.4	28.3	28.1
Gloss @ 60°	-	58	60	58

Sample 1: *O19010*

Sample 2: *O19010 + 2.5% Engage*

Sample 3: *O19010 + 5% Engage*

Polyethylene Evolution



Metallocene LLDPE
High Clarity

Metallocene LLDPE

LLDPE

Polyethylene Films

Thank You

….To Polypropylene