Introduction to Commodity Plastics

Polypropylene

by

Dr. Yatish B. Vasudeo

Innovation Consultant

Polypropylene - History

PP was first synthesized in 1954 by Natta in Italy using a modification of the catalyst system originally developed by Ziegler for the polymerization of ethylene.

The stereospecific polymerization process of Natta was commercialized within three years of

invention.

Polypropylene - History

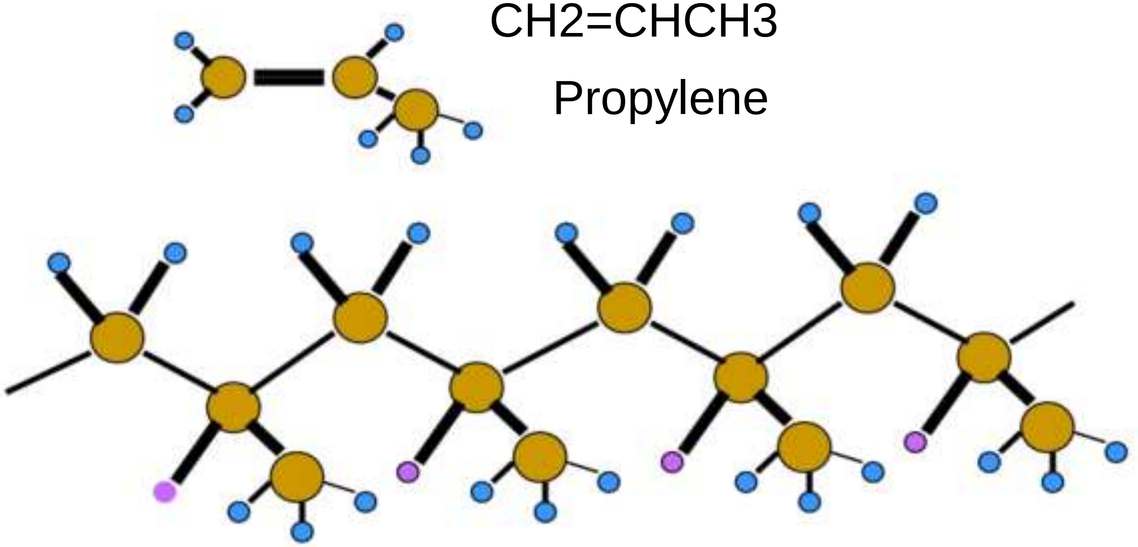
Commercial exploitation was very rapid, with isotactic polypropylene being marketed by Montecatini as Moplen as early as 1957.

The expiry of the basic patents led to a surge in production capacity in the 1970s which so exceeded demand that the material became available at abnormally low prices, which in turn stimulated more growth in usage.

Polypropylene developments milestones

- First crystalline polypropylene prepared - 1954
- First polypropylene manufacturing plant (Ferrara, Italy) -1957
- First impact copolymer produced - 1968
- High yield catalyst used for polypropylene - 1975
- Metallocene catalyst for polypropylene commercialized -1995
- 5 th generation Ziegler-Natta catalyst used -2000

Polypropylene



CH2=CHCH3

Propylene

-CH2-CHCH3-CH2-CHCH3-

● Carbon atom

● Hydrogen atom

● Labile H atom making PP Vulnerable to oxidation and UV degradation

Polypropylene

- Lightest self supporting plastics material in unmodified form - density 0.9 g/cc.
- Prepared from a monomer available by separation during basic petroleum refining process (FCC) and basic petrochemical process (Hydro-cracking of naphtha & gas) No separate monomer manufacture plant required.
- Will be available till petroleum refining and petrochemical process.
- **Low cost & weight, versatility, modification friendliness**

Polypropylene

- **A commodity plastics material..**
- Lower in strength as compared to engineering plastics

- Strength can be enhanced by compounding with fillers & reinforcements

- **Plastics material prone to degradation by UV.**

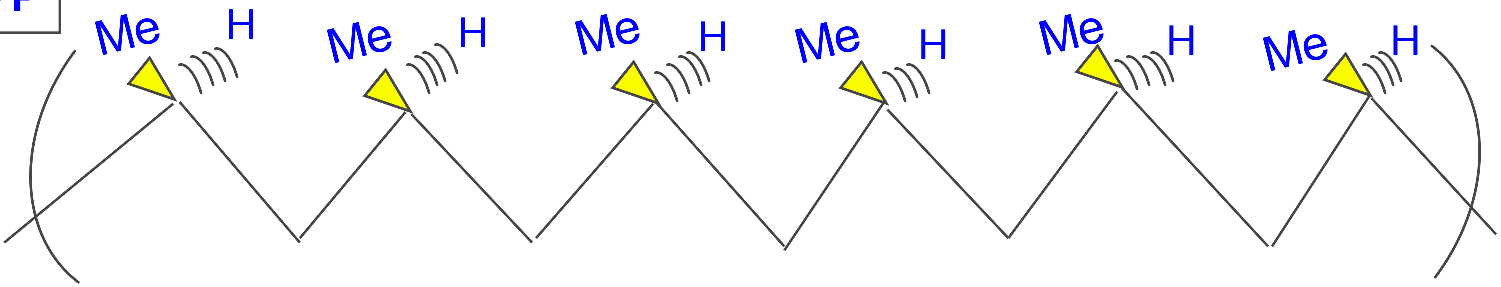
UV resistance for desired life can be extended by additives

Polypropylene - Stereo specificity in PP

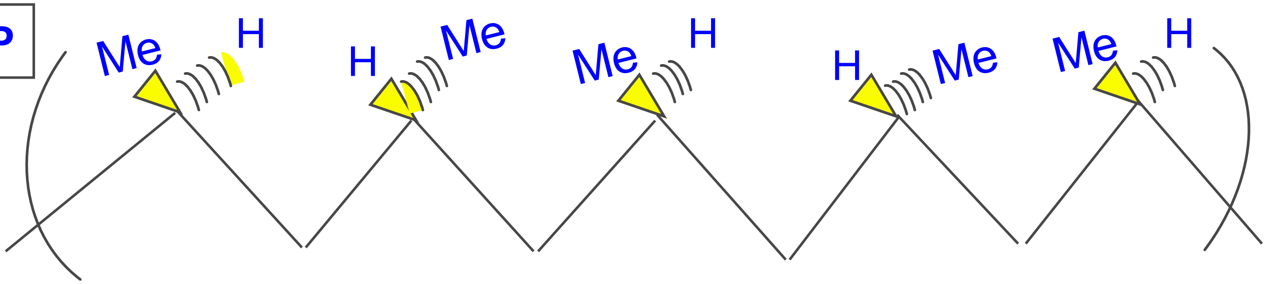
- **Stereospecificity** :Placement of pendant Methyl group in the linear chain
- **Tacticity**
  - Isotactic :Methyl group on one side of polymer chain
  - Syndiotactic : Methyl group alternate
  - Atactic : Arrangement of Methyl group random

Polypropylene - Stereo specificity in PP

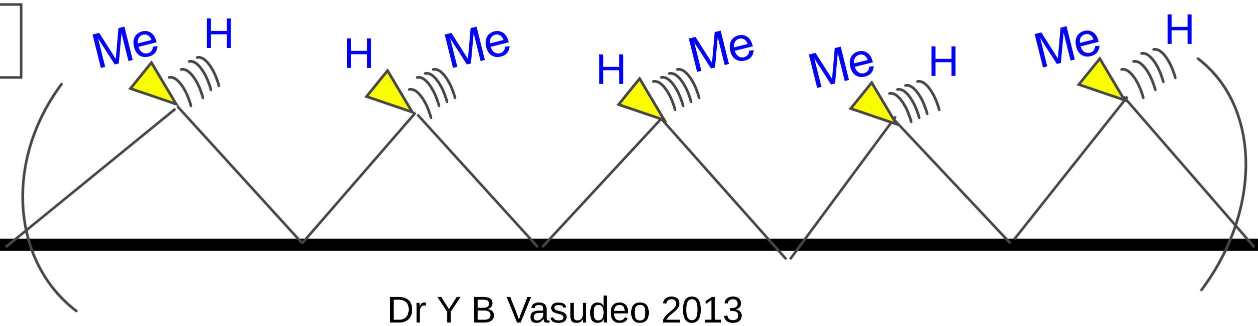
☞ **i-PP**



☞ **S-PP**



☞ **a-PP**



Polypropylene

Types of Commercial Polypropylene

- Commercial PP is available as
  - **Homopolymer** - PPPPPPP
  - **Random copolymer** - PPPEPPPEPPEPPE
  - **Impact copolymer** - PPPP + EPEPEPEP +

    PPPPPP + EPEPEP

P : Propylene

E : Ethylene

Polypropylene - Homopolymer

Product Characteristics:

- High stiffness
- High solvent resistance
- High crystallinity
- High melting point
- Low impact strength

Polypropylene - Homopolymer

- Homopolymers consist of only propylene molecules. Melt flow and xylene solubles (which is a measure of the atactic fraction) are the distinguishing performance parameters for homopolymers. Both of these properties are tailored to give optimum performance in end use applications.
- The lower melt flow grades are mainly used for applications requiring high melt strength such as extrusion and thermoforming. At intermediate melt flows, the film, stretched tapes and injection molding applications predominate. The highest melt flows are generally associated with fibre grade.
-

Polypropylene - Copolymer

Impact copolymer

Not a true copolymer but an intimate mixture of Homopolymer and Ethylene Propylene Rubber

Produced in Sequential Reactor stage

- High impact strength
- Higher level of toughness
- Low stiffness
- Low tensile strength
- More opaque
- Low Hardness

Polypropylene - Copolymer

- **Impact copolymers** are not true copolymers. They are an intimate molecular scale mixture of homopolymer and ethylene-propylene rubber produced in sequential reaction stages. In this process propylene is homopolymerised as a first step and amorphous ethylene-propylene rubber is produced on the homopolymerized polypropylene matrix in a separate reactor. Impact copolymers retain the high melting temperature of the homopolymer, are translucent, show good low temperature impact strength and reduced stiffness and hardness.

Polypropylene - Copolymer

- Depending on the rubber content, impact copolymers are classified into various grades. When the rubber content goes up, stiffness decreases. Therefore, grade selection is a trade-off between stiffness and impact strength. Generally, low melt flow grades have better toughness at a given rubber content. Higher melt flow grades are used in intricateto-fill moulds. They allow fast cycle times in injection moulding.

Polypropylene - Copolymer

Random copolymer

A true copolymer containing ethylene or other Alpha Olefin Comonomer groups directly inserted into the growing polymer chain

Made in a single reactor

- High clarity
- Low melting point
- Reduced crystallinity
- Reduced stiffness
- Better impact
- Enhanced clarity
- Lower heat sealing temperature

Polypropylene - Copolymer

- **Random copolymers** are true copolymers containing ethylene or other alpha olefin comonomer directly inserted into the growing polymer chain and are made in a single reactor

Polypropylene - Copolymer

- The low ethylene content grades (0.5-4%) are used for making oriented films, for blow moulding and injection moulding.
- The very low ethylene grades compete with homopolymers in film applications where improved processability is the major advantage. These products are referred to as ethylene enhanced homopolymers.

- The grades containing more than 4% ethylene are heat seal grades. They have a broad softening range and improved heat seal performance.

Polypropylene - Copolymer

Random Copolymers

- Random copolymers also have good chemical resistance and low permeability to water vapour.

- Melt flow and ethylene content are the distinguishing features of random copolymers..

Comparison of end-use property for different Polypropylenes

- **Rigidity : HP>RCP>PPCP**
- **Clarity : RCP>HP>PPCP**
- **Impact Strength : PPCP>RCP>HP**

Properties of Polypropylene

Property	**Units**	**Homopolymer**	**RCP**	**ICP**
Specific Gravity	-	0.9	0.9	0.9
Tensile St. at yield	Mpa	32-36	25-28	19-28
Elongation at yield	%	8-11	10-12	7-10
Notched Izod Impact	J/m	25-48	60-80	50->500
Flexural Modulus	Mpa	1400-1700	900-1300	800-1300
HDT (455kPa)	oC	~5	~(-5)	(-52 to-42) Rubber
Cryst Melting Point	oC	160 to175	145 to 150	160 to 170

Properties of Polypropylene

Properties are influenced by

- ☐ MFI, isotacticity, ethylene content in Random Copolymers,
- ☐ Rubber Content and additives in Impact Copolymers.

Polypropylene Manufacturing Technologies

- The process technology for PP manufacture has kept pace with catalyst advances and the development of new product applications and markets. In particular, the relationship between process and catalyst technology was clearly symbiotic and that of a partnership.

Polypropylene Manufacturing Technologies

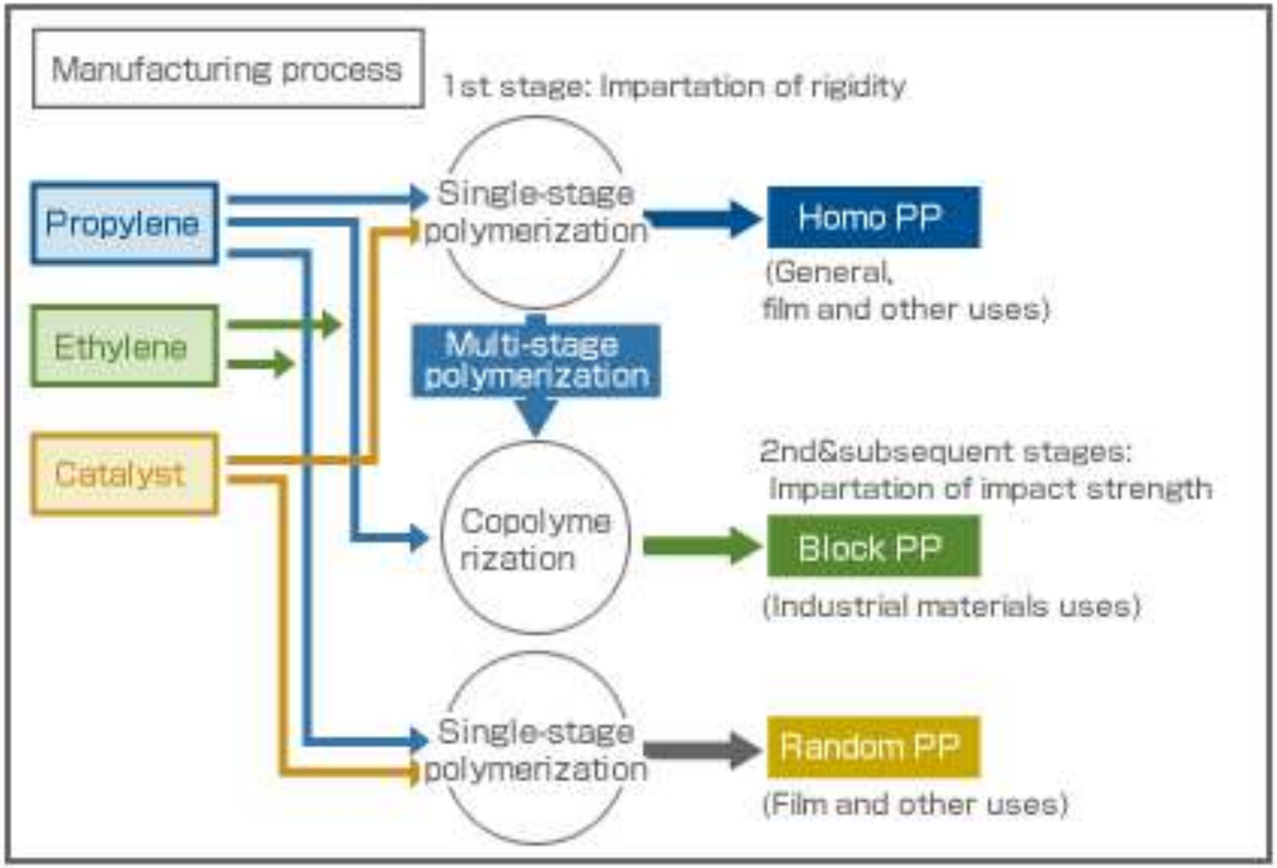
- Advances in one technology had always exerted a strong push-pull effect on the other to improve its performance. The progress in process technology has resulted in process simplification, investment cost and manufacturing cost reductions, improvement in plant constructability, operability, and broader process capabilities to produce a wider product mix.

Polypropylene – Manufacturing Technologies

- There are three main types of generic industrial processes for the production of polypropylene

- **Slurry process** :
- **Bulk** : Basell (SPHERIPOL), Mitsui (HYPOL II)
- **Gas phase** : BP (INNOVENE), Chisso, Sumitomo, Novolen Technology Holdings (NOVOLEN), Union Carbide (UNIPOL)
- **Bulk / Gas phase** : Borealis (BORSTAR)

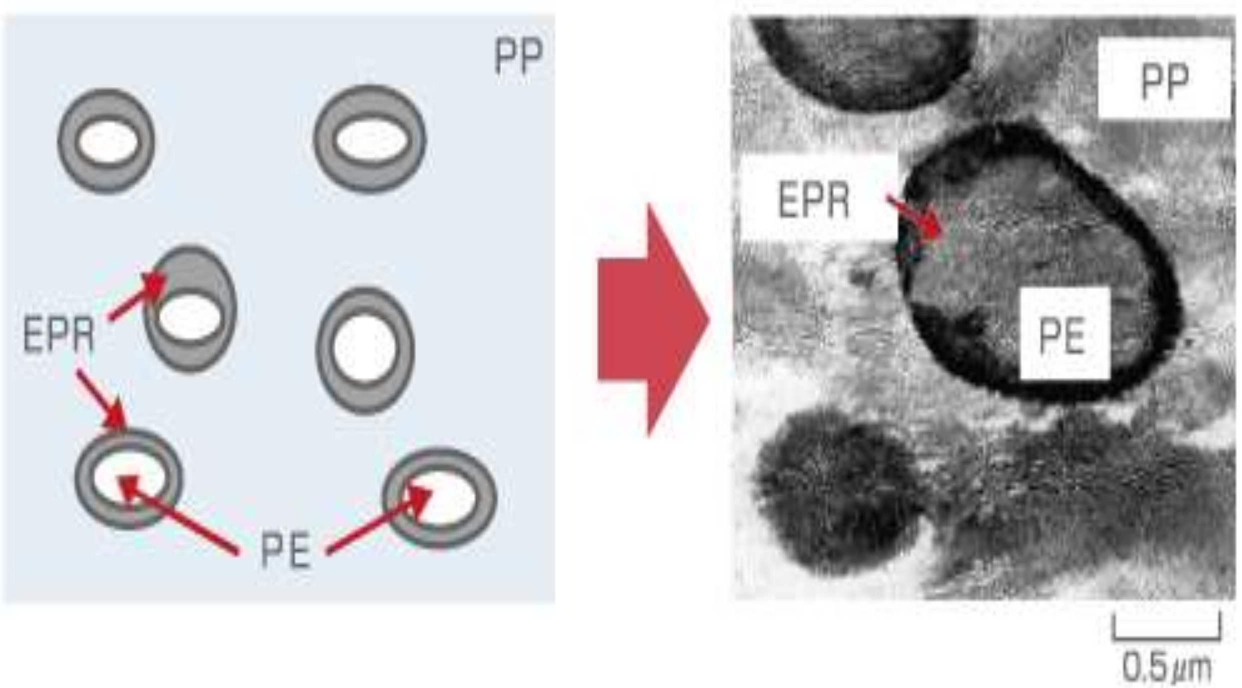
Manufacturing Process



Structure of Block /Impact PP

- Block PP contains PE dispersed in it as shown in the illustration below. There is the EPR phase (rubber phase) around the PE. Because of this structure, the impact strength of block PP is higher than that of homo PP. If homo PP is compared to the sea, PE / EPR looks as if they are islands. For this reason, this structure is sometimes called “island structure”.
- It is said that the reason why block copolymer shows higher impact strength than homo polymer is that it is due to the “island structure” of PE / EPR.

Structure of Block /Impact PP



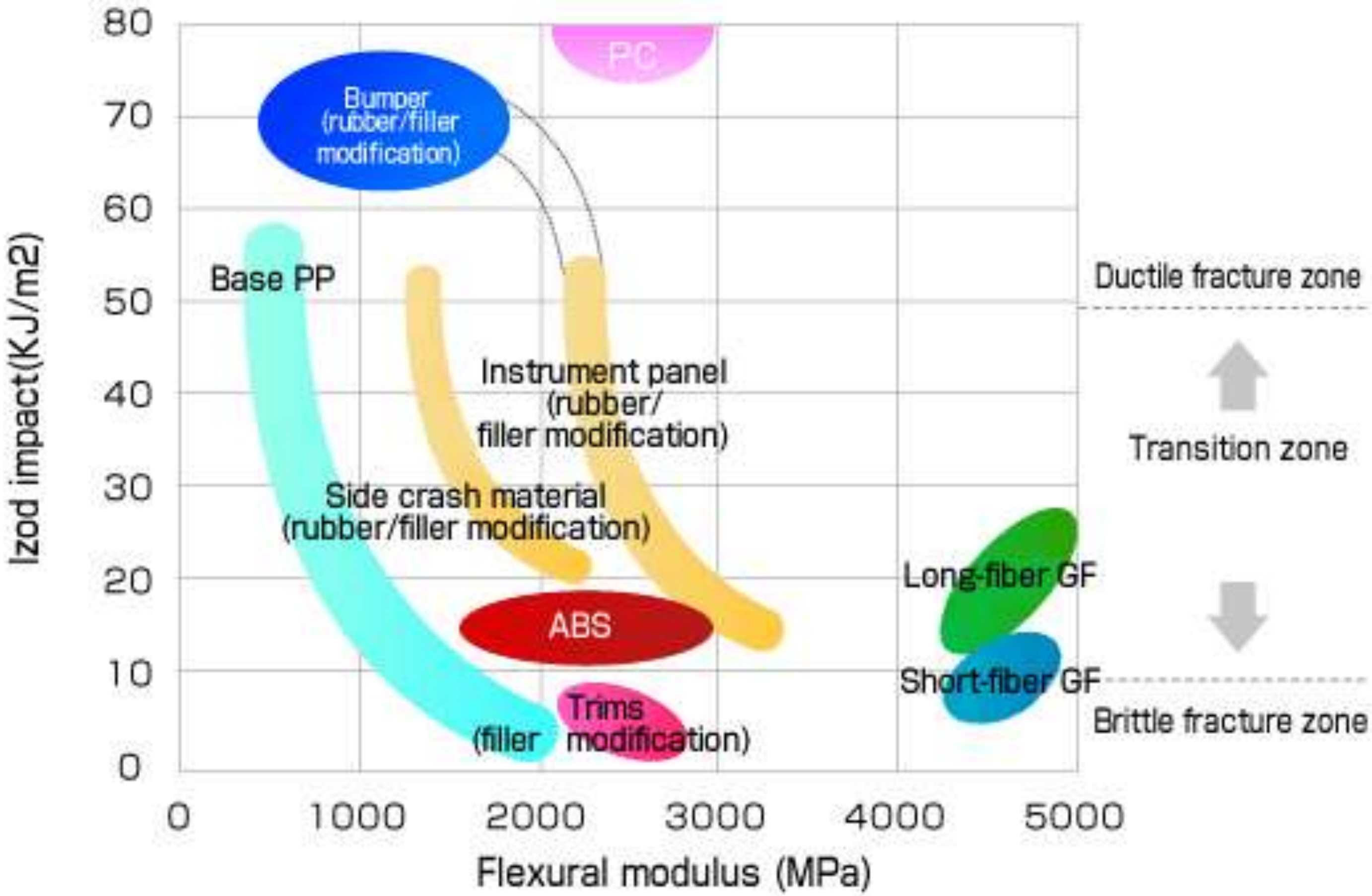
Conceptual diagram of block PP

Electron microscope photograph of block PP
(press-molded article)

Positioning

PP allows subsidiary materials such as talc and glass fiber (GF) to be added in a large amount. It is possible to give PP those properties which cannot be attained by PP alone. We have successfully developed materials having controlled rigidity and impact properties by our own materials design technology. These materials are used in many industrial areas such as automotive parts.

Positioning



Polypropylene - Applications

- Injection Molding
- Blow Molding
- Sheets & Thermoforming
- Films – TQPP, CPP, BOPP
- Rafia & Monofilaments
- Extrusion Coating
- Fibers

Polypropylene - Films

- TQPP
- Cast & BOPP

Comparative Properties Of Flexible Packaging Film

Property	**Unit**	**TQPP**	**BOPP**	**CPP**	**HDPE**	**LDPE**	**LLDPE**
Density	g/cc	0.90	0.90	0.90	0.94 – 0.97	0.91-0.925	0.918-
Yield	m2/kg 25 micron	45	45	45	41	43	42
Haze	%	3-4	2	4-5	75	10-15	18
Gloss	-	Good	Excellent	Good	Poor	Good	Good

Comparative Properties Of Flexible Packaging Film

Property	Unit	TQPP	BOPP	CPP	HDPE	LDPE	LLDPE
UTS							
MD	MPa	56.0	150	65	45	18	52
TD		38.0	300	30	42	20	48
Elongation	%						
MD		650	130	600	600	215	720
TD		750	50	550	650	645	800
Tear	g/micron						
MD		3	8	25	0.7	2.75	15
TD		4	15	25	16	12	28
WVTR	g.mil/100in2.d	0.9	0.3	0.9	0.7	1.5	1.5

Crystallinity in Polymers

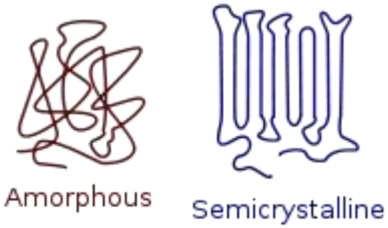
- Most people are familiar with crystals only because of salt and perhaps growing crystals aspart of a school science project. Therefore, talking about crystals and plastics together is a new concept to many people. In reality, polymers are not like salt, which is totally crystalline, but are semi-crystalline. Unlike crystals like salt, polymers have only short-range order and a much looser organization.

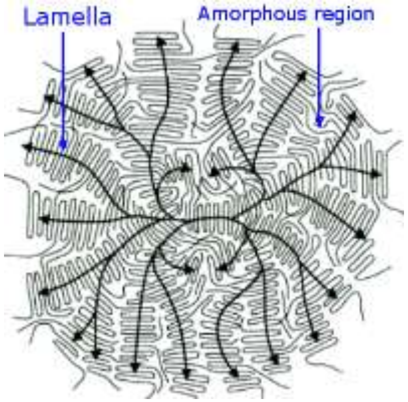
Crystallinity in Polymers

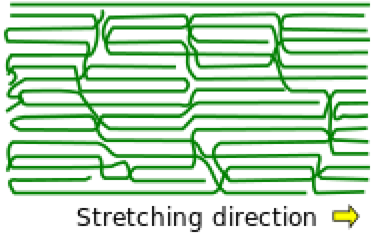
- **Crystallinity is one of the great divisions of the complete family of plastics. Amorphous polymers (those with no significant degree of crystallization) behave very differently than crystalline polymers (those with a significant degree of crystallization). Understanding crystallization and the effect it has on the properties of polymers can make understanding the behavior of polymer families much easier.**

Structure Property Relationship in Polypropylene

- Polypropylene is composed of long molecular chains which form irregular, entangled coils in the melt. Polypropylene chains rearrange upon cooling and form partly ordered regions. Therefore, within the ordered regions, the polypropylene chains are both aligned and folded. Those regions are therefore neither crystalline nor amorphous and are classified as semicrystalline.
- **Polypropylene is semicrystalline polymer and properties depend on how this structure develops in the final application/product.**







Thank You