Plastics 101
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Plastics (Polymers)

The word plastics is from the Greek word *Plastikos*, meaning “able to be shaped and molded.”
Why Plastics?

- Light weight, high weight to strength ratio, particularly when reinforced
- Relatively low cost compared to metals and composite
- Corrosion resistance
- Low electrical and thermal conductivity, insulator
- Easily formed into complex shapes, can be formed, casted and joined.
- Wide choice of appearance, colors and transparencies
Disadvantages of Plastics

- Low strength
- Low useful temperature range (up to 600 °F)
- Less dimensional stability over period of time (creep effect)
- Aging effect, hardens and become brittle over time
- Sensitive to environment, moisture and chemicals
- Poor machinability
Polymers

- The earliest synthetic polymer was developed in 1906, called Bakelite.
- The development of modern plastics started in 1920s using raw material extracted from coal and petroleum products (Ethylene). Ethylene is called a building block.
- Polymers are long-chain molecules and are formed by polymerization process, linking and cross linking a particular building block (monomer, a unit cell).
- The term polymer means many units repeated many times in a chainlike structure.
- Most monomers are organic materials, atoms are joined in covalent bonds (electron-sharing) with other atoms such as oxygen, nitrogen, hydrogen, sulfur, chlorine,....
Classification of Polymers

There are two major classifications of polymers

**Thermoplastics**

As the temperature is raised above the melting point, the secondary bonds weaken, making it easier to form the plastic into any desired shape. When polymer is cooled, it returns to its original strength and hardness. **The process is reversible.** Polymers that show this behavior are known as *thermoplastics.*

**Thermosetting Plastics (thermosets)**

Thermosetting plastics are cured into permanent shape. Cannot be re-melted to the flowable state that existed before curing, continued heating for a long time leads to degradation or decomposition. **This curing (cross-linked) reaction is irreversible.** Thermosets generally have better mechanical, thermal and chemical properties. They also have better electrical resistance and dimensional stability than do thermoplastics.
Amorphous Vs. Crystalline Polymers

Amorphous polymers:
- Soften over a wide range of temperatures
  - Lower specific gravity
  - Lower tensile strength and tensile modulus
  - Higher ductility and impact strength
  - Lower creep resistance

Crystalline polymers:
- Distinct and sharp melting point
  - Higher specific gravity due to better packing
  - Higher tensile strength and tensile modulus
  - Lower ductility and impact strength
Polymers Worldwide

2012 World Polymer Demand 211 Million Metric Tons

- PVC, 18%
- PET, 9%
- LDPE, 9%
- LLDPE, 11%
- HDPE, 17%
- PC, 2%
- PP, 25%
- PS, 5%
- ABS, 4%
Polyethylene (PE) Basics
Basic Definitions...

• **Comonomer** - another small molecule which is added to modify the properties of the **Polymer**.

• **Homopolymer** - a **Polymer** made from one **Monomer** type only.

• **Copolymer** - a **Polymer** from more than one **Monomer** type.
Polyethylene (PE) resins are a general class of thermoplastics produced from ethylene gas (a). Ethylene gas is derived from the cracking of natural gas feedstocks or petroleum by-products. Under broad ranges of pressures, temperatures and catalysts (depending PE type), ethylene generally polymerizes to form very long polymer chains.

A polymer made from the monomer **ETHYLENE** or a copolymer of ethylene and a comonomer.
Types of Copolymers

- **Butene** - A four carbon long molecule.
  Formula: \( \text{C}_4\text{H}_8 \quad \text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{CH}_3 \)
  A gas at room temperature.

- **Hexene** - A six carbon long molecule.
  Formula: \( \text{C}_6\text{H}_{12} \quad \text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3 \)
  Liquid at room temperature.

- **Octene** - An eight carbon long molecule.
  Formula: \( \text{C}_8\text{H}_{16} \quad \text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3 \)
  A liquid at room temperature.
Types of Polymerization

There are 2 main polymerization processes for making Polyethylene:

1. Free Radical Polymerization
2. Catalytic Polymerization

<table>
<thead>
<tr>
<th>High Pressure Operation</th>
<th>Low Pressure Operation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HDPE</td>
</tr>
<tr>
<td></td>
<td>LDPE</td>
</tr>
</tbody>
</table>
Free Radical Polymerization

- Produces LDPE
- Mature technology (1937). Discovered by accident!
- Uses organic peroxide initiators to “assemble” the polymer
- \(~\text{CH}_2-\text{CH}_2\cdot + \text{CH}_2=\text{CH}_2 \rightarrow \text{~CH}_2-\text{CH}_2-\text{CH}-\text{CH}_2\cdot~\)
- Very high pressures (>40,000 psi)
- High Temperatures (up to 330° C)
- Reactors can be:
  - tubular (long pipe) - BASF
  - autoclave (pot/agitator) - ICI
Autoclave LDPE Process
Tubular LDPE Process
Catalytic Polymerization

- Produces **LLDPE** and **HDPE**
- Still evolving technology (1950’s)
- Ziegler and Natta co-discoverers. (Nobel Prize 1963)
- Uses active metal catalysts to grow the polymer by “insertion” (Ti, Zr, V, Cr, Al)

\[ \text{\sim CH}_2\text{-CH}_2\text{-}\{\text{Cat}\} + \text{CH=CH}_2 \]
\[ \text{\sim CH}_2\text{-CH}_2\text{-CH}-\text{CH}_2 \text{-}\{\text{Cat}\} \]

- **Metallocenes** are simply specific type of active metal catalyst.
- Much lower pressures (300-1,500 psi) and temperatures (100 –250° C) than LDPE processes
- Reactors types are mainly: Fluidized bed – gaseous (UCC/BP)
UNIPOL Gas Phase Process (LLDPE/HDPE)
SCLAIR Solution (LLDPE/HDPE)
SCLAIR Solution (LLDPE/HDPE)
## Summary

<table>
<thead>
<tr>
<th>Process Value</th>
<th>Comonomer Value</th>
<th>End Use</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Gas Phase LLDPE Butene</strong></td>
<td>Gas Phase tends to have higher gels and black specks</td>
<td>lowest in melt strength and properties</td>
</tr>
<tr>
<td><strong>Gas Phase LLDPE Hexene</strong></td>
<td>Gas Phase tends to have higher gels and black specks</td>
<td>In the middle, better than butene, but not as good as Octene</td>
</tr>
<tr>
<td><strong>Solution LLDPE Octene</strong></td>
<td>Solution products are lower gel and better organoleptics</td>
<td>Best melt strength, and physical properties especially in hot tack and sealing</td>
</tr>
</tbody>
</table>
**PE Molecular Structure**

<table>
<thead>
<tr>
<th>Type</th>
<th>Structure</th>
<th>Properties</th>
</tr>
</thead>
</table>
| LDPE   | ![LDPE Diagram](image) | - Multiple long branches  
          - Easier and cheaper to make |
| LLDPE  | ![LLDPE Diagram](image) | - Short Branches |
| HDPE   | ![HDPE Diagram](image) | - No/few branches  
          - Stronger than LDPE |
PE Defined By

- Melt Index
- Density
- Molecular Weight Distribution
Melt flow index or MFI is a measure of the ease of flow of the melt of a thermoplastic polymer. It is defined as the mass of polymer, in grams, flowing in ten minutes through a capillary of a specific diameter and length by a pressure applied via prescribed alternative gravimetric weights for alternative prescribed temperatures. The melt index provides a general indication of a product’s molecular weight (MW) and processability.
Melt Flow Index

• Measure of how fluid the resin is when molten.
• It is a measure of the polymer’s viscosity at a controlled set of conditions (190°C and 2.16 Kg) and is reported as the weight, in grams, extruded from a standard die in 10 minutes.
• The units are grams/10 minutes.
• Melt Index is an indicator of the average chain length or average Molecular Weight of a polymer.
• A resin with a LOW MI has a HIGH Molecular Weight and requires more energy to process because it has HIGH Viscosity.
• A resin with a HIGH MI has a LOW Molecular Weight and is easier to process because it has LOW Viscosity.
• It is also a rough indicator of a resin’s processability.
Melt Flow Index

The following Table shows typical ranges for some common polymer processes.

<table>
<thead>
<tr>
<th>Process</th>
<th>MI Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Injection Molding</td>
<td>5 - 150</td>
</tr>
<tr>
<td>Rotational Molding</td>
<td>2 - 20</td>
</tr>
<tr>
<td>Film Extrusion</td>
<td>0.5 - 6</td>
</tr>
<tr>
<td>Blow Molding</td>
<td>0.1 - 10</td>
</tr>
<tr>
<td>Profile Extrusion</td>
<td>0.1 - 1</td>
</tr>
</tbody>
</table>
Density is calculated by dividing the mass of the material by the volume and is normally expressed in g/cm³. Density measures crystallinity. As density and crystallinity increase, stiffness increases and impact decreases.
Density

**Crystallization of polymers** is a process associated with partial alignment of their molecular chains. Crystallization affects optical, mechanical, thermal and chemical properties of the polymer.

<table>
<thead>
<tr>
<th>Density Range for PE (gm/cc)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>LLDPE – Very Low</td>
<td>.880 - .915</td>
</tr>
<tr>
<td>LDPE</td>
<td>.910 - .925</td>
</tr>
<tr>
<td>LLDPE</td>
<td>.918 - .930</td>
</tr>
<tr>
<td>HDPE - Medium</td>
<td>.926 - .940</td>
</tr>
<tr>
<td>HDPE - High</td>
<td>.941 - .969</td>
</tr>
</tbody>
</table>
Molecular Weight Distribution

The molecular weight distribution in a polymer describes the relationship between the number of moles of each polymer species ($N_i$) and the molar mass ($M_i$) of that species.

Fluency
Extrudability
Resistance to Scratch
Resistance to Cracking
Resistance to the environment
Melted Takedown
Clarity
Brightness

Independent:
- Tensor Resistance
- Rigidity
- Resistance to Chemicals
- Heat Resistance
- Permeability

Molecular Weight Distribution
Molecular Weight Distribution

Ranges for PE (pm)

<table>
<thead>
<tr>
<th>Category</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDPE</td>
<td>50,000-200,000</td>
</tr>
<tr>
<td>HDPE - High</td>
<td>200,000-500,000</td>
</tr>
<tr>
<td></td>
<td>MI = .05-.1 gm/10min</td>
</tr>
<tr>
<td>HDPE – Ultra High</td>
<td>3,000,000 – 6,000,000</td>
</tr>
<tr>
<td></td>
<td>MI = 21&lt;.1 gm/10min</td>
</tr>
</tbody>
</table>
Differences between LDPE & LLDPE

RESINAS CON INDICE DE FLUIDEZ SIMILAR

VISCOSIDAD (LB-SEC/PC)

10^1

10^0

LINEAL

BAJA DENSIDAD

INDICE DE FLUIDEZ

RANGO DE EXTRUSION

RANGO

PASO DE DESLIZE (1/SEC)

VISCOSIDAD LOGARITMICA

10^1

10^0

BAJA DENSIDAD

LINEAL

DEFORMACION O EXTENSION
## PE Characteristics

<table>
<thead>
<tr>
<th>LDPE</th>
<th>LLDPE</th>
<th>HDPE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Easiest to process</td>
<td>Harder to process than LDPE</td>
<td>Hardest to process</td>
</tr>
<tr>
<td>High Clarity</td>
<td>More rigid compared to LDPE</td>
<td>Most rigid</td>
</tr>
<tr>
<td>Low Sealing Temperatures</td>
<td>High Penetration Resistance</td>
<td>High resistance to chemicals</td>
</tr>
<tr>
<td>Low permeability properties</td>
<td>High Torn Resistance</td>
<td>High permeability</td>
</tr>
<tr>
<td></td>
<td>High Elongation Resistance</td>
<td>High resistance to low temperatures</td>
</tr>
<tr>
<td></td>
<td>High Tensile Strength</td>
<td>Highest Tensile Strength</td>
</tr>
<tr>
<td></td>
<td>High Impact Resistance</td>
<td>Low elongation</td>
</tr>
<tr>
<td></td>
<td>Better ESCR</td>
<td>Opaque</td>
</tr>
<tr>
<td></td>
<td>Better Strength to low temp.</td>
<td>Won’t block</td>
</tr>
<tr>
<td></td>
<td>Less Warp</td>
<td>Lowest resistance to ESCR</td>
</tr>
<tr>
<td></td>
<td>Lower thickness</td>
<td></td>
</tr>
</tbody>
</table>

ESCR = Environmental Stress Crack Resistance
PE Product Range

The diagram illustrates the relationship between density (Kg/m³) and melt index (g/10 Min) for various PE product ranges and their corresponding molding processes. The product ranges include:

- **Homopolymer**
  - HD Film, Pipe & Blow Molding
  - MD Film, Pipe & Blow Molding
  - Ultra Strength Film
- **Flexomers**
- **Geo-membrane**
- Roto-Molding
- LD Injection Molding
- HD Injection Molding

The density ranges from 900 to 970 Kg/m³, and the melt index ranges from 0.01 to 1000 g/10 Min.
PE Additives Basics
What is an Additive?

• Polyethylene additives are selected to enhance and improve the properties inherent to the base polymer.

• Additives generally make up between 0.05% and 0.5% of a commercial resin by weight, but their contribution to resin performance is much greater.

In addition to doing their intended function, PE additives should not:

• Affect odor and taste properties of the plastic
• Plate out on processing equipment
• Affect polymer color or appearance (except where desired)
• Affect the environmental or food-contact status of polyethylene
• Adversely affect the performance of other additives
Laws and Regulation

Additives must meet regulations for food contact, drug packaging applications (etc.)

- Canada: Food and Drugs Act, Health Canada Food and Drug Regulations (HPFB)
- USA: Federal Food, Drugs and Cosmetic Act, FDA regulations
- EU: Food contact Directives, Regulations

**The end-use application of a resin puts a constraint on the type of additive package and usage levels that can be employed.**
Additives Types

- **Stabilizers**
  - Antioxidants
  - UV Stabilizers
  - Acid Neutralizers

- **Modifiers**
  - Slip Agents
  - Antiblock Agents
  - Antistatic Agents
  - Cling Agents
  - Fillers

- **Processing Aids**
  - Melt Fracture Suppressants
  - Lubricants
  - Mold Release Agents
STABILIZERS
Polyethylene Degradation - Oxidation

Organic materials such as polyethylene are susceptible to degradation reactions, particularly oxidation.

Degradation reactions and processes which proceed uninhibited can lead to organoleptic issues, a general deterioration in physical properties, and ultimately, to premature product failure.

Initiators:

- **PHYSICAL**
  - thermal energy
  - mechanical stress
  - electromagnetic radiation (hv)
    - solar
    - artificial (gamma irradiation)

- **CHEMICAL**
  - catalyst residues
  - oxygen, including its active forms (• O, O2, O3, and • OH)
  - atmospheric pollutants (NOx, SOx)
  - stress cracking agents (e.g., chlorine)
  - biological enzymes
Polyethylene Degradation - Oxidation

- The first step in polyethylene degradation is radical formation which is induced by one or more initiators.
- Once an alkyl radical is created in an aerobic atmosphere, it will quickly react with oxygen. (The Autoxidation Process)

![Diagram of Polyethylene Degradation](Image)

- Polymer
- RH or RR
- R· + H· or R· + R· (Chain Scission)
- Energy or Catalyst Residues
- RO· + ·OH
- ROH + H₂O
- +O₂
- Oxygen
- RO·
- ROO·
- ROQH
- Polymer
- RH
Under the relatively harsh conditions of extrusion processing, polyethylene is susceptible to degradation, the extent of which is dependent upon the:

- extrusion processing parameters
- polyethylene resin architecture (e.g., unsaturation content)
- type and level of additive package used
Antioxidants

- Antioxidants are used in polyethylene as sacrificial agents to protect the polymer from the various degradation mechanisms which occur during extrusion processing as well as throughout the life-cycle of the manufactured article.
  - Durable articles (pressure gas pipe, rotational molded articles) require robust antioxidant packages
  - Non-durable articles (general purpose film) require less stabilization

- Historically, there have been two different types of antioxidants:
  - **Primary Antioxidants**
    - chain terminating mechanism
    - “long-term” stabilization
  - **Secondary Antioxidants**
    - Hydroperoxide decomposing mechanism
    - “processing” stabilization

- Synergistic effects
- More recently, new classes have also been developed:
  - carbon centered radical scavengers
  - Hydroxylamines
Antioxidants

Primary antioxidants:
- secondary aromatic amines
- sterically hindered phenols

These antioxidants function by donating their reactive hydrogen atom(s) (i.e., OH, NH groups) to peroxy radicals.

Secondary antioxidants:
- phosphites
- thioethers (esters)

These antioxidants function by reducing hydroperoxides to alcohols.
- phosphites are oxidized to phosphates
- thioethers are oxidized to sulfoxides
Problems with Antioxidants

- Resin discoloration resulting from:
  - Formation of colored species
  - Gas-fading

- Corrosion and black speck formation resulting from:
  - Phosphite hydrolysis
Polyethylene Degradation – Photo-Oxidative

• High energy of short wavelength light
  – UV-region: 300 - 400nm
  – 95 kcal at 300nm to 57 kcal at 500nm

• Light must be absorbed to initiate photochemical reactions; chromophores in the UV region
  – Polymer
  – Functional groups (such as: double bonds, carbonyl groups, and hydroperoxides)
  – Impurities
Classes of UV Stabilizers

A. UV Screeners
B. UV Absorbers
C. Sterically Hindered Amine Light Stabilizers (HALS)
   • Decompose Hydroperoxides and scavenge free radicals
UV Screeners

- Fillers (TiO$_2$ and CaCO$_3$)
- Carbon Black
- Pigments
- Metal based pigments may catalyze the generation of free radicals
- Some fillers may absorb or react with stabilizers
- Reflected light may actually concentrate UV energy at polymer surface
UV Absorbers

A light stable chemical structure that will competitively absorb harmful UV radiation and dissipate it through non-destructive pathways (heat, fluorescence, phosphorescence).

- Absorption of harmful UV radiation and dissipation as heat
- Certain absorption depth necessary for protection (Lambert-Beer; sample thickness)
Hindered Amine Light Stabilizer (HALS)

- A multi-functional chemical that will efficiently trap radicals, decompose alkyl hydroperoxides, and quench excited states at in-use temperatures
- Re-generable
- Action independent of sample thickness
- Effective at low levels as hydroperoxide decomposers and free radical scavengers
MODIFIERS
Hindered Amine Light Stabilizer (HALS)

- A multi-functional chemical that will efficiently trap radicals, decompose alkyl hydroperoxides, and quench excited states at in-use temperatures
- Re-generable
- Action independent of sample thickness
- Effective at low levels as hydroperoxide decomposers and free radical scavengers
Slip Agents

- A material which acts at the surface of the film/object to reduce the friction between it and another surface
- Usually organic compounds which function by migration to the surface of the polymer

**WHY?**

- Polyethylene films have a high coefficient of friction (CoF), which leads to their tendency to adhere to themselves and to metal surfaces
  - common processing problems with blown film extrusion include sticking and pulling in the nip rolls and collapsing frame, resulting in wrinkling
- In order to be easily converted into bags or used on form/fill/seal equipment, PE film needs to have a CoF ≤ 0.2
Fatty Amide Slip Migration

The concentration of a fatty amide slip additive that develops on a PE film surface (i.e., CoF) is dependent upon:

- the initial slip concentration in the resin
- the thickness of the film
- the molecular architecture of the resin
- the presence of interfering additives
Fatty Amide Slip Migration

CoF

Time after extrusion

Graph showing the change in CoF over time after extrusion.
Anti Block Agent

- Anti block is an additive used for easier film separation (perpendicular motion/separation)
- The adhesion between two adjacent film layers is called blocking
- Blocking is a form of “mild” heat seal caused by:
  - Low molecular weight species
  - Re-crystallization, “squeezed”
  - Polymer or other additives
- Blocking force can be regular or induced…
  - Regular = no additional temperature or pressure
  - Induced = with the addition of heat and pressure (wind up roll, hot climate, etc.)
Anti Block Agent

• Anti blocking can be achieved by altering the film surface
  • Reducing film to film contact area
  • Roughen the film surface, “little bumps”
• Anti block additives can be inorganic or organic
• Common types include: Diatomaceous Earth (DE), Talc

VS.
PROCESSING AIDS
Dynamar PPA

- Elimination of Melt Fracture
- Reduction in Operating Pressure
- Alleviation of Die Build Up
- Reduction in Gel Formation
- Faster Color Changeover

LLDPE w/o PPA  LLDPE with PPA
PPA Benefits

• Increase throughput
• Improve processing of lower MI resins
• Reduce or eliminate LDPE Blending
• Allow extrusion through narrower die gaps
  • better balance of properties
• Improve gloss and surface smoothness
• Reduce production downtime
• Reduce chance of degradation by operating at lower process temperatures
• Energy Savings
Origin of Sharkskin

One of the proposed mechanisms:
Upon die exit, the outer layer of the melt is stretched by the elastic recovery of the flow profile.
When the die is coated, there is slip at the die wall, giving a blunt flow profile.
Potential Interference

- Abrasion
- Adsorption
- Chemical Reaction
- Competition for the metal die wall
Non Interfering Additives

- Primary Antioxidants
- Secondary Antioxidants
- Slips
- Antistats (low temperatures)
- Polyethylene oxides
- Carbon Blacks
Potentially Interfering Additives

- HALS
- UV Stabilizers
- Antistats (Higher Temperatures)
- Stearates
- Hydrotalcite
- Antiblocks
- Pigments (Inorganic)
Minimize Additive Interactions

- Increase ratio of PPA/additive
- Decrease processing temperature
- Select less “interfering” additives
- Minimize degree of contact (Add via separate concentrates)
- Select optimum PPA