Introducing Polyolefins
Content

- Importance of polyolefins
- Global consumption
- Domestic production and consumption
- Application
- Polyolefins family
- PE classification
- PP structures
- Key properties
- Additivation
Polyolefins: the most important synthetic polymers

- Global plastics production in 2013 approximately 300 Million tons
- Polyolefins represent 45%

Polyolefins 45%

PVC 14%

Others 20%

PVC 14%

Others 20%
Global polyolefins consumption
Global consumption by types
Per capita consumption

The chart shows the per capita consumption of two products, PE and PP, across different regions. The x-axis represents various regions: North America, South America, Western Europe, Central Europe, Africa, Asia, and Global. The y-axis represents the kg per capita consumption.

North America has the highest consumption, followed by Western Europe and Central Europe. Africa shows the lowest consumption for both products. The global consumption is also relatively high, indicating a widespread use of these products globally.
Domestic Production and Consumption

![Bar chart showing domestic production and consumption for PE and PP from 2001 to 2015.](chart.png)
Consumption by application
Examples for application 1
Examples for application 2
The Polyolefins Family

Polyolefins

Polyethylenes
- LDPE
- HDPE, LLDPE

Polypropylenes
- Copolymers
- Homopolymers
  - Block copolymers
  - Random copolymers
The main building blocks: ethylene and propylene
Comonomers: $\alpha$-olefins
butene-1, hexene-1, octene-1
Polyethylenes (PE)

- HDPE and LLDPE: linear structure with short chain branches (SCB)
  - SCB formation: copolymerization with alpha-olefins
  - HDPE: 0-5 SCB/1000 C; 0.926-0.970 kg/dm³
  - LLDPE: 6-21 SCB/1000 C; 0.915-0.926 kg/dm³

- LDPE: branched structure with short and long chain branches (LCB)
  - 6-20 SCB/1000 C – formed by intramolecular chain transfer
  - 1-3 LCB/1000 C – formed by intermolecular chain transfer
  - 0.915-0.935 kg/dm³
# PE Classification by Density

## PE grades by density

<table>
<thead>
<tr>
<th>DENSITY</th>
<th>COMONOMER</th>
<th>PE GRADE</th>
</tr>
</thead>
<tbody>
<tr>
<td>0,926-0,970</td>
<td>–/alfa-Olefins</td>
<td>HDPE</td>
</tr>
<tr>
<td>0,926-0,940</td>
<td>alfa-Olefins</td>
<td>MDPE</td>
</tr>
<tr>
<td>0,915-0,935</td>
<td>–/Acrylates/VA</td>
<td>LDPE</td>
</tr>
<tr>
<td>0,915-0,926</td>
<td>alfa-Olefins</td>
<td>LLDPE</td>
</tr>
</tbody>
</table>

![Schematic representation of various PE structures](image-url)
HDPE chain segments
LLDPE chain segment
LDPE chain segment
Polypropylenes (PP)

Homopolymers
- Isotactic PP – stereoregular, crystalline
- Syndiotactic PP – stereoregular, crystalline
- Atactic PP – amorf structure

Copolymers
- Random copolymers – with maximum 5% ethylene content
- Block (heterophasic, impact) copolymers – with 5-20% ethylene content
PP Structures

Isotactic homopolymer

Atactic homopolymer

Syndiotactic homopolymer

Block copolymer

Random copolymer
Isotactic PP chain segment
Syndiotactic PP chain segment
Atactic PP chain segment
PP homopolymer and random copolymer chain segments
PP block copolymer chain segments
Properties
Key properties

- Molecular weight and molecular weight distribution
- Melt index
- Density (comonomer content in PE)
- Mechanicals
- ESCR
- Opticals
Connection between properties

Primary properties
- molecular weight
- molecular weight distribution
- comonomer content
- stereoregularity (PP)

Secondary or end use properties
- melt index
- mechanicals
- opticals
- ESCR
Molecular weight

- Number average

\[ M_n = \frac{\sum N_i M_i}{\sum N_i} = \frac{\sum w_i}{\sum w_i/ M_i} \]

- Weight average

\[ M_w = \frac{\sum N_i M_i^2}{\sum N_i M_i} = \frac{\sum w_i M_i}{\sum w_i} \]

- Polydispersity – measure of molecular weight distribution

\[ P = M_w / M_n \]
Molecular weight and molecular weight distribution

- **Number average molecular weight** ($M_n$)
- **Weight average molecular weight** ($M_w$)

Number of molecules vs. molecular weight
Bimodal product properties

Low Mw homopolymer:
- increased crystallinity → higher stiffness
- good processability

High Mw copolymer:
- tie chains between crystals
- elastic properties
- high mechanical strength
- high toughness
- excellent ESCR

Comonomer built into high Mw molecules:
- impact strength
- ESCR
Structure and properties

Crystalline layers: stiffness
Tie molecules: ESCR, impact strength
Comonomer and density

- **Strong influence on important PE properties**
  - Impact strength
  - ESCR

- **Density depends on comonomer content**
  - (SCB=short chain branching) more SCB = lower D
  - Longer comonomer chain = lower D

- **Comonomers tend to incorporate into lower**
  - $M_w$ molecules deteriorating organoleptic properties
Melt index

- **Melt index** – measure of ease of flow
  - Instead of determination of molecular weight
  - Fast standard method to
    - control quality
    - compare products

- **Melt index and molecular weight**
  - High melt index = low viscosity = low molecular weight
  - Low melt index = high viscosity = high molecular weight

- **Non Newtonian behaviour**
  - Melt index (viscosity) depends on load
  - Melt indices measured at different loads give indication on molecular weight distribution
Principle of melt indexer
Mechanical properties

- **Tensile strength (TS)**
  - Higher crystallinity results in higher TS
  - $TS_{PP} > TS_{HDPE} > TS_{LDPE}$

- **Impact strength (IS)**
  - Ability to withstand shock loading
  - Higher $M_w$ = higher IS
  - Lower $D$ = higher IS

- **Flexural modulus (FM)**
  - Measure of stiffness – higher FM means higher stiffness
  - Higher $D$ = higher FM
  - $FM_{PPHOMO} > FM_{PPHECO} > FM_{PPRACO}$
Measuring tensile strength
Measuring impact strength
Measuring flexural modulus
ESCR – environmental stress cracking resistance

- Ability to withstand cracking under load in chemicals
- Mainly used for PE - very important for blow moulding and pipe grades
- Lower D = higher ESCR
- Higher $M_W$ = higher ESCR
- Role of comonomer distribution – comonomers built into high $M_W$ molecules give very good ESCR
Optical properties - Haze

- Diffusely scattered light compared to total light transmitted (reduction in clarity)
  
  \[H_{PPRACO} < H_{PPHOMO} < H_{PPHECO}\]
  
  \[H_{LDPE} < H_{LLDPE} < H_{HDPE}\]
Optical properties - Gloss

- The ratio of reflected to incident light for the specimen, compared to the ratio for the gloss standard.
Additivation

Polyolefins mainly PP and HDPE need different additives to meet end use requirements. Typical concentration: some hundreds through some thousands ppm (1 ppm=1 g/t)

Typical polyolefins additives

- Stabilizers – to protect polymer from oxidative degradation during
  - Processing – melt stabilization (high temperature, short time + oxygen)
  - Long term use
    - thermal stabilization (low temperature, long time + oxygen)
    - UV stabilization – (low temperature, long time, UV light + oxygen)

- Processing aids and property modifiers
  - Slip agents – to reduce friction during processing
  - Antistatic agent – to prevent build up of electrostatic charging
  - Antiblocking agent – to avoid sticking of film layers
  - Nucleating agents – to improve stiffness
  - Clarifying agents – to increase product transparency