TOPIC 7. Polymeric materials

1. Introduction
   - Definition
   - General characteristics
   - Historic introduction
   - Polymers: Examples

2. Classification

3. Properties: Structural aspects

4. Solid state
   - Crystallinity
   - Thermal transitions
   - Mechanical behaviour
1. INTRODUCTION: DEFINITION

POLYMER

“Organic compound, natural or synthetic, with high molecular weight made of repetitive structural units”

Large size chains formed from the covalent union of various monomer units (macromolecule)

PLASTIC

1. Polymer whose fundamental property is plasticity (thermoplastic). It is deformed plastically under the action of pressure and/or heat.

2. Mixture (of a polymer with additives) that can be transformed by flowing or moulding in liquid or molten state.
1. INTRODUCTION: GENERAL CHARACTERISTICS

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<th>Applications</th>
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<td>$T_f$</td>
<td>Easy processing</td>
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<tr>
<td>$\varepsilon$</td>
<td>Products of elevated consumption</td>
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<tr>
<td>$\rho$</td>
<td>High ductility</td>
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<td>$\sigma_t$</td>
<td>Neumatics. Plastics for packaging</td>
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<td>$R_{\text{chemic.}}$</td>
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<td>Tubes, bins, boxes, Coatings</td>
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1. INTRODUCTION: HISTORIC INTRODUCTION

Polymers: synthetic and natural materials:

Cellulose, starch, proteins, leather, wool, cotton, synthetic fibres of polyesters and polyamides, plastics, rubbers, adhesives etc

Production 1995: 110 millions of tons (Spain: 2,6)
2000: 180 millions of tons (Spain: 2,7)

HISTORIC BACKGROUND

Origins of Humanity ⇒ natural products: leather, wool, cellulose....

1838: Vulcanizing of natural rubber
1846 Cellulose nitrate
1870 Celluloid
1907 Bakelite
1920 Macromolecular Hypothesis (Staudinger)
1926 Polyvinyl chloride (PVC)
1933 Polyethylene (PE)
1938-39 Nylon (fibers) y Polystyrene (PS)
1954 Polypropylene (PP)
1960 Applications of Epoxy Resins
198- Polymers of high specifications
1. INTRODUCTION: EXAMPLES

Poly ethylene PE: Most popular plastic

Polypropylene PP: used as plastic and as fibre

Polystyrene PS: economic and resistant. Styrofoam™: foam of PS

Polyvinylidene fluoride PVDF: high electric and fire resistance

Polymethyl methacrylate PMMA: transparent plastic. Substitute of crystal

Nylon (polyamides): most common polymers used as fibers

Nylon 66

Nylon 6
2. CLASSIFICATION

According to origin
- Natural, synthetic ...

According to polymerization mechanism
- Addition, condensation

According to chemical composition
- Acrylics, vinyls...

According to structure
- Semicrystalline and amorphous

According to applications
- Elastomers, plastics, fibres, adhesives...

According to their behaviour with temperature
- Thermoplastic
- Thermosetting
2. CLASSIFICATION

According to applications

**Elastomers.** Are materials with very low modulus of elasticity and high extensibility

**Plastics.** Are the polymers in which, when a sufficiently intense force is applied, they irreversibly deform

**Fibres** Present a high modulus of elasticity and low extensibility

**Coatings.** Are substances, normally liquid, that adhere to the surface of other materials

**Adhesives.** Are substances that combine a high adhesion and a high cohesion,

According to their behaviour with temperature

**Thermoplastic.** Flow on heating and they become hard on cooling. Their molecular structure presents few (or none) crosslinks.

**Thermosetting.** They chemically decompose when heated, instead of flowing. This behaviour is due to a crosslinked structure
2. CLASSIFICATION

POLYMERS OF GENERAL USE (Commodity)

Polymers of high consumption: polyolefins, polyacrylates and methacrylates, polystyrene, PVC, resins, phenols, urea and melamines, polyesters, polyurethanes, epoxy resins and diverse elastomers

TECHNICAL AND ENGINEERING POLYMERS

Good properties between 0-100 ºC: polyamides, polycarbonates, polyphenylene oxide (PPO), polysulfones, polyphenylene sulpphide (PPS), aliphatic-aromatic polyesters, Polyether ether ketone (PEEK)

SPECIAL POLYMERS

High price polymers with outstanding characteristics, liquid crystals of high modulus and advanced composite materials

Factors that determine their use: plastic, fibres or as rubber:
Flexibility in the chain, intermolecular interactions and grade of regularity in the polymer
3. PROPERTIES

The properties of polymers depend on multiple factors:

- Molecular Weight & its distribution
- Structural aspects
- Crystallinity

- Monomeric nature (families of polymers)
- Number of monomeric units (molecular weight) and its distribution
- Monomeric functionality (branches and crosslinking)
- Relative positions of the groups (tacticity and changes in shape)
- Ordering of the units (sequences)
- Ordering the positions of the chain branches (crystallinity)
The factors that determine the application of the polymer
3. PROPERTIES: MOLECULAR WEIGHT

MOLECULAR WEIGHT

Macromolecular molecular weight: \( M_n = M_0 X_n \)

where:
- \( M_n \) = number-average molecular weight
- \( M_0 \) = monomer molecular weight
- \( X_n \) = degree of polymerization (average number of monomer units in a chain)

For a polymer \( \Rightarrow \) distribution of chain longitude or molecular weights:

Mean Molecular Weight \( \Rightarrow \) Definition of the various molecular weights:

- \( M_n = \sum M_i x_i \)  
- \( M_w = \sum M_i w_i \)

Index of polydispersion:

\[
I = \frac{M_w}{M_n}
\]

- \( M_n \) = number-average molecular weight
- \( M_w \) = weight-average molecular weight
- \( M_i \) = mean molecular weight in size range \( i \)
- \( x_i \) = fraction in number of molecules in range \( i \)
- \( w_i \) = fraction in weight of molecules in range \( i \)
3. PROPERTIES: STRUCTURAL ASPECTS

CONFIGURATION STATES

Polymeric molecular chains are NOT strictly straight:

Schematic representation of a molecular chain of a simple polymer with various fringes produced from bond rotation:

This behaviour provokes the entanglement between chains ⇒ high elasticity

\(<r>: \text{distance between the extremes of the chain}\)

\(<s^2>: \text{mean radius of rotation}\)
3. PROPERTIES: STRUCTURAL ASPECTS

MOLECULAR STRUCTURE

- Linear
- Branched
- Crosslinked
3. PROPERTIES: STRUCTURAL ASPECTS

TACTICITY
The best example is polypropylene

PP isostatic

isotactic polypropylene, has excellent mechanical properties

PP syndiotactic

PP atactic

atactic polypropylene is a wax type material, with very bad mechanical properties
3. PROPERTIES: STRUCTURAL ASPECTS

ISOTACTIC

SYNDIOTACTIC

ATACTIC
3. PROPERTIES: STRUCTURAL ASPECTS

COPOLYMERS IN SEQUENCE

- Copolymer with random units
- Copolymer with alternating units
- Copolymer with block units
- Graft copolymers

**Example of Copolymerization**

\[
\begin{align*}
\text{Polyethylene} & \quad + \quad \text{Poly vinyl acetate} \\
\left[ \begin{array}{c} 
H \\
C \\
H \\
H \end{array} \right]_n & \quad + \quad \left[ \begin{array}{c} 
H_3C \\
O=O \\
C \\
C \end{array} \right]_m \\
\rightarrow & \quad \text{Ethylene vinyl acetate (EVA) copolymer}
\end{align*}
\]
3. PROPERTIES: CRYSTALLINITY

CRYSTALLINITY OF POLYMERS

Packing macromolecular chains in order to produce an atomic arrangement with periodic order.

Properties = depend on the amount of crystallinity

Crystallization $\Rightarrow$ ↑ amount of packing
density (crystalline polymer) $>$ density (amorphous polymer)
4. SOLID STATE: CRYSTALLINITY

Morphology of the polymeric crystals

✓ Polymeric monocystals

⇒ Different type of bundles:

Chain-folded model

Structure of a chain-folded lamina

http://commons.wikimedia.org/wiki/File:Lamellenbildung_bei_der_Kristallisation_von_PolymerenEN.svg

Fringed-micelle model:

http://commons.wikimedia.org/wiki/File:Polymer_Lamellae_2D.png
4. SOLID STATE: CRYSTALLINITY

The majority of polymers that crystallize from liquids form:

SPHERULITES

\[ \% \text{crystallinity} = \frac{\rho_c(\rho_s - \rho_a)}{\rho_s(\rho_c - \rho_a)} \times 100 \]

- \(\rho_s\) = actual density of the polymer
- \(\rho_c\) = density of totally crystalline polymer
- \(\rho_a\) = density of totally amorphous polymer

Interlaminar connections condition the properties of the polymer

Transmitted polarized light photomicrograph of PE

4. SOLID STATE: CRYSTALLINITY

FACTORS THAT AFFECT CRYSTALLINITY

1. KINETIC FACTORS

   Conditions for Crystallinity:
   The number and size of crystals formed = depend on
   \[ \Delta T = T_{\text{melting}} - T_{\text{crystallization}} \]
   \( \Rightarrow \) Increasing \( \Delta T \) the size of the crystal decreases and the
   number of crystals increases

The FLEXIBILITY of the chains depends on the structure:

- Linear polymers have a greater amount of crystallinity
  compared to branched polymers
- Complex monomeric structures \( \Rightarrow \) decreases the amount of
  crystallinity

In order for a polymer to crystallize, its molecules must have sufficient elasticity in order to be able to move and be accurately placed.
4. SOLID STATE: CRYSTALLINITY

2. STRUCTURAL FACTORS THAT AFFECT CRYSTALLINITY

Greater crystallinity $\Rightarrow$ greater $T_m$

- Symmetry
- Tacticity:
  - Atactic $\Rightarrow$ amorphous
  - Isotactic, syndiotactic $\Rightarrow$ crystalline
- Branched
- Configuration CIS against TRANS
- Nº of C pairs in between heteroatoms
- Molecular weight
- Copolymerization
- Plasticisers
- Polarity: favours ordering
Cooling curves for thermoplastic polymers

Non crystalline thermoplastics cool throughout the line ABCD

Partially crystalline thermoplastics cool throughout the line ABEF

A= liquid, B= liquid of high viscosity, C= undercooled liquid (rubbery), D = glassy solid
E = solid crystalline regions in matrix of supercooled liquid, F = solid crystalline regions in glassy matrix

Temperature

Specific volume

Gradient change

Non crystalline thermoplastic

Partially crystalline thermoplastic

$T_g$ = Glass transition temperature

$T_m$ = Melting temperature
Cooling curves for thermoplastic polymers

Specific volume versus temperature upon cooling from the liquid melt for polymers with different structure
Thermal transitions: $T_m$ and $T_g$

$T_m$: Melting temperature $\rightarrow$ crystalline regions

$T_g$: Glass transition temperature $\rightarrow$ amorphous regions

Glass transition $\rightarrow$ changes in the specific heat and the dilatation coefficient
FACORS THAT INFLUENCE IN THE T\textsubscript{g}

**MOLECULAR WEIGHT**
Increasing the molecular weight we decrease the mobility of the chains ⇒ \( \uparrow \) T\textsubscript{g}

**INTERMOLECULAR INTERACTIONS**
Increasing the interactions ⇒ \( \uparrow \) Kinetic Energy ⇒ \( \uparrow \) T\textsubscript{g}

**CHAIN FLEXIBILITY**
Greater mobility ⇒ Decreases the rotational energy and increases the entropy and decreases T\textsubscript{g}

**SYMMETRY**
Symmetric Molecules present a low dipolar moment and therefore low T\textsubscript{g}

\[
\begin{array}{|c|c|}
\hline
\text{[-CH}_2\text{-CHX-]}_n \text{ with X} & T_g (^\circ C) \\
\hline
-H \text{ (PE)} & -110 \\
-\text{CH}_3 \text{ (PP)} & -20 \\
-\text{Cl} \text{ (PVC)} & 81 \\
-\text{C}≡\text{N} \text{ (AN)} & 97 \\
-\text{C}_6\text{H}_5 \text{ (PS)} & 100 \\
\hline
\end{array}
\]
# 4. SOLID STATE: THERMAL TRANSITIONS

## Melting and Glass Transition Temperatures for Some of the More Common Polymeric Materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Glass transition temperature (°C)</th>
<th>Melting temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene (low density)</td>
<td>-110</td>
<td>115</td>
</tr>
<tr>
<td>Polytetrafluoroethylene</td>
<td>-97</td>
<td>327</td>
</tr>
<tr>
<td>Polyethylene (high density)</td>
<td>-90</td>
<td>137</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>-18</td>
<td>175</td>
</tr>
<tr>
<td>Nylon 6,6</td>
<td>57</td>
<td>265</td>
</tr>
<tr>
<td>Polyester (PET)</td>
<td>69</td>
<td>265</td>
</tr>
<tr>
<td>Poly(vinyl chloride)</td>
<td>87</td>
<td>212</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>100</td>
<td>240</td>
</tr>
<tr>
<td>Polycarbonate</td>
<td>150</td>
<td>265</td>
</tr>
</tbody>
</table>
4. SOLID STATE: THERMAL TRANSITIONS

Influence of Molecular Weight

![Graph showing the relationship between temperature and molecular weight, with regions for mobile liquid, viscous liquid, rubber, tough plastic, crystalline solid, and partially crystalline plastic, marked with Tm and Tg.]
4. SOLID STATE: MECHANICAL BEHAVIOUR

MECHANICAL BEHAVIOUR: Thermoplastic polymers

Behaviour of thermo amorphous, crystalline and 50%50 amorphous/crystalline
4. SOLID STATE: MECHANICAL BEHAVIOUR

MECHANICAL BEHAVIOUR: Thermoplastic polymers

Effect of the crystallinity in the modulus of elasticity: