Polymer Materials Science
BMEGEPT9107, 2+0+0, 3 Credits

2. Morphological Structure of Polymers

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Polymer Materials Science

Books, textbooks, lecture notes, guides

- L.M. Vas: Lecture notes, ppt slides, [http://pt.bme.hu/~vas](http://pt.bme.hu/~vas)
Polymer Materials Science
Recapitulation

■ Structure of Polymers (microscale levels)
  • Atomic structure
  • Molecular structure
  • Morphological or fine structure

■ Properties of Polymers (macroscale levels)
  • Mechanical properties
  • Effect of temperature
  • Effect of humidity
  • Other properties

Content of Polymer Materials Science
Recapitulation

■ Polymer materials, typical material classes, molecular and morphological structure of polymers, polymer blends and alloys
■ Testing methods of polymer structures
■ Mechanical behavior of polymer materials
■ Behavior of polymers under changing temperature, humidity and other environmental factors
■ Strength and fracture-mechanical properties of polymers
■ Phenomenological modeling of the mechanical behaviors of solid polymers
■ Statistical-mechanical modeling of polymers
Classification of Polymers
Recapitulation

Classification respect of structure

- **Linear polymers** (linear, chain molecular structure)
  - Semi-crystalline polymers (e.g. PE, PP, PA, PAN, PET)
  - Amorphous polymers (PVC, PS, PMMA, PC)
- **Crosslinked polymers** (network structure – amorphous polymers.)
  - Elastomers (weakly cross-linked, e.g. rubbers: NR, BR, PUR)
  - Duromers (strongly cross-linked; resins: e.g. UP, EP, VE)

Classification in respect of thermal and mechanical behavior

- **Thermoplastics** (they can be molten reversibly ⇒ linear polymers; e.g. PE, PP, PA, PET, PVC, PS, PMMA, PC)
- **Non-thermoplastics - thermosets**
  - Linear polymers (Kevlar, PAN, cellulose, chitin, protein)
  - Crosslinked polymers (elastomers, duromers)
  - Semi-crosslinked & semi-crystalline polymers (wool fiber, XPE)

Structural Levels of Polymers
Recapitulation

<table>
<thead>
<tr>
<th>Structural graph</th>
<th>Structural levels of PE:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Crystal-cell</td>
</tr>
<tr>
<td></td>
<td>Crystallite</td>
</tr>
<tr>
<td></td>
<td>Levels 20 to 80 nm</td>
</tr>
<tr>
<td></td>
<td>Fibril</td>
</tr>
<tr>
<td></td>
<td>Crystal lamella</td>
</tr>
<tr>
<td></td>
<td>Spherulite</td>
</tr>
<tr>
<td></td>
<td>Sizes 30 to 300 μm</td>
</tr>
<tr>
<td></td>
<td>Polymer part</td>
</tr>
<tr>
<td></td>
<td>Polymer component</td>
</tr>
</tbody>
</table>

Graph-point:
structural level

Graph-line:
transition between structural levels
( Along the line: ordering and uniting operations)
Micro- and macrostructural levels of polymers

Recapitulation

Properties measurable on macro-level are the resultant of the microscale ones.
- Density
- Mechanical properties
- Thermal properties
- Moisture take up
- Others

Morphological structure 1.

- Differences between the materials of small and large molecules
  - Long term elasticity
  - Differences in the crystallinity
    Crystalline parts – primary transition ($T_c < T_m$)
    Amorphous parts – secondary transition ($T_g$)

<table>
<thead>
<tr>
<th></th>
<th>Crystallinity</th>
<th>Melting</th>
<th>Hysteresis</th>
<th>Character of transition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Materials of small</td>
<td>Total</td>
<td>Sharp melting point</td>
<td>No</td>
<td>Through equilibrium states</td>
</tr>
<tr>
<td>molecules</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Materials of large</td>
<td>Partial</td>
<td>Melting interval</td>
<td>Exists</td>
<td>Far from equilibrium state</td>
</tr>
<tr>
<td>molecules</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Morphological structure 2.

- **Transitions of 1st and 2nd order**
  - **First order transition** ($T_m$): the free enthalpy ($G$) is continuous, the volume ($V$) is discontinuous
  - **Second order transition** ($T_g$): $G$, $V$ are continuous, the thermal expansion coefficient ($\alpha$) is discontinuous

\[
V = \left( \frac{\partial G}{\partial F} \right)_T
\]

\[
\alpha = \left( \frac{\partial V}{\partial T} \right)_p
\]

Small molecule material

Polymer material

Morphological structure 3.

- **Revelation of crystallinity by X-ray diffraction**

Diffractograms of small and large molecule materials

Small molecule crystalline material

Salt (NaCl)

Amorphous polymer (PS)

Semicrystalline polymer (PET)

Basic condition of crystallinity: stereoregular molecule chains
Morphological structure 2.

- Polymer crystal cells (extended, spiral chain forms)

<table>
<thead>
<tr>
<th>PE crystal cell</th>
<th>PP crystal</th>
<th>PA6.6 crystal cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chain form: extended</td>
<td>Chain form: spiral</td>
<td>Chain form: extended</td>
</tr>
<tr>
<td>(a = 0.736) nm</td>
<td>(a = 0.492) nm</td>
<td>(a = 0.254) nm</td>
</tr>
<tr>
<td>(b = 0.492) nm</td>
<td>(b = 0.492) nm</td>
<td>(b = 0.254) nm</td>
</tr>
<tr>
<td>(c = 0.254) nm</td>
<td>(c = 0.254) nm</td>
<td>(c = 0.254) nm</td>
</tr>
</tbody>
</table>

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Morphological structure 5.

- Crystallization process of polymers
  - Nucleus-formation and growing

\[
\begin{align*}
\text{Avrami equation:} & \quad m_L(t) = m_0 e^{-\alpha t^n} \\
\text{Nucleus-size:} & \quad \text{growth constant} \\
\text{Temperature:} & \quad T = 110^\circ C, n=2 \\
\text{Temperature:} & \quad T = 236^\circ C, n=4 \\
\text{Temperature:} & \quad T = 240^\circ C, n=4
\end{align*}
\]

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Morphological structure 6.

- Crystallization process of polymers – Nucleus-formation and growing

Nucleation and the types of nuclei

- Morphological units – ordered parts

**Crystallite**: The smallest ordered part in the polymer
- Its internal order: 3D
- Not a single crystal! Because it is not bounded by planes.

Names on the basis of size ratios of the envelope/hull brick:
Morphological structure 7.a.

- Polymers and morphological structure types
  
  - Unoriented homopolymers
    - Fringed micellar structure
    - Paracrystalline structure
    - Spherulite structure
    - Other special structures
  
  - Oriented homopolymers
    - Transcrystalline structure (local)
    - Shish-kebab structure
    - Fibrillar structure (global)
  
  - Core-sheath structure of injection molded homopolymer
  
  - Co-polymers, polymer blends
  
  - Filled polymers, fiber reinforced composites

Morphological structure 4.

- Fringed micellar structure

  - Molecular chains pass through several crystalline and amorphous zones.

  - In case of small crystallinity
Morphological structure 5.

- Paracrystalline structure (Large crystallinity is possible.)

Ideal lattice and light-diffraction image  
1st order lattice distortion and light-diff. image

2nd order lattice distortion and light-diff. image

Hosemann (1950)

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Morphological structure 6.

- Paracrystalline structure (Large crystallinity is possible.)

Ideal lattice  
Paracrystal-lattice (Paracr.)  
Amorphous  
Cluster

Abb. 2.13. Verschiedene Gittertypen nach Hosemann: a kristallin, b ideal parakristallin, c parakristallin, d amorph, e Clusterbildung

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Morphological structure 7.

- Spherulite structure

<table>
<thead>
<tr>
<th>Spherulite:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spherical, birefringent formation</td>
</tr>
</tbody>
</table>

PEO – Ø0.2 mm

HDPE fast crystallization, 100x

HDPE spherulites embedded into granular structure, 100x

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Morphological structure 8.

- Spherulite structure

RefRACTive index: \( n \)

Polymer chain: \( n_2 < n_1 < n_1 || \)

Stages of formation by Bernauer

PP spherulite

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Morphological structure 9.

- Schematic summary of the spherulite structure

In general spherulites are formed if there is/are no strong flow gradient or/and shearing effect.

Ordered (crystalline) and amorphous parts in the spherulite

Interdefect areas or crystallites. If it spans over the total fibrillar diameter it can be isolated.

Defects in the fibres resulting in line broadening of X-ray scattering lines contributing to the amorphous content.

Single crystalline nucleus. If the density of nuclei is high normally just this unit develops.

Spherulite with fibrillar branching. Chains are perpendicular to the long axis.

Interfibrillar material. This is the main amorphous component. It is left out between the growing fibrils.

Fig. 4.33. A schematic summary of polymer structure. Appearance of various morphological units within the spherulites. Amorphous zones are formed at the interfaces of spherulites. (After Sharples 1966.)

Morphological structure 12.

- Oriented, fibrillar structures - Shish-kebab structures

In general, instead of spherulites, oriented structures are formed in presence of strong flow gradient or/and shearing effect.
Morphological structure 10.

- Transformation of spherulite into fibrillar structure during uniaxial drawing of PA6.6 foil

Morphological structure 11.

- Ordered structures and amorphous parts in oriented polymers
Morphological structure 13.

- Strongly oriented, fibrillar structures

**Transcrystalline structure**
- Around carbon fiber in PP

**Fibrils**
- PA6.10 – 15000x
- Cellulose – 15000x

Many crystal nuclei – Hindered spherulite growth

Fig. 4.38. Parallel ordering of fibrils, on transcrystalline. Growth process starts from surface nuclei. (After Sherwin, 1986).

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Morphological structure 14.

- Strongly oriented, fibrillar structures - Fibers

**Oriented polyester (PET) fiber**

100% paracrystalline HPPE (SK60)

Liquid crystalline Kevlar (100% paracrystalline)

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Morphological structure 16.

- Other structural formations - Single crystals

PA6 single crystal

PE single crystal

Thickening of PE single crystal by heat treating

Lamellae and chain folding

Morphological structure 17.

- Other structural formations

Hedrite (PE)

Dendrite (PE)

PTFCE

Extended chain lamellae (crystallized under high pressure)
Morphological structure 18.

- Complex structure of extruded and injection moulded polymer parts

![Image of complex structure](image)

Figure 3.22. Schematic Representation of Polymer Morphology in a Rapidly Quenched Crystalline Polymer-Injection Moulded Apical (ROA): T_{cool} = 300°C, T_{melt} = 370°C. A: Skin Region. B: Nematic Core. C: Smectic Core. D: Sample Cross-Section (3D).

Morphological structure 15.

- Anisotropic liquid – liquid crystalline or mesophase structures

  - Nematic
  - Smectic
  - Cholesteric

![Image of mesophase structures](image)

Fig. VII A-1
Liquid crystalline mesophases in polymers containing rod-like sections.
Morphological structure 21.

- Multiphase combined structures - Copolymers

Amorphous copolymer structure composed of incompatible polymer components

Figure 3.11: Schematic of an AB-type block copolymer. Homopolymers A and B are incompatible, and form separate domains or microphases of randomly coiled chains. (A.E. Woodward, 1989)


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Morphological structure 19.

- Multiphase, combined structures

High impact PS – rubbery additive

High impact PVC – chlorinated PE

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Morphological structure 22.

- Multiphase, combined structures – Copolymer, blend

Lamellar crystal structure in PS/PEO diblock-copolymer

Two phase structure of 5% PS/95% large molecule mass PMMA blend


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Morphological structure 23.

- Multiphase, combined structures – TPE, TPR

**Thermoplastic elastomer** (TPE): linear block-copolymer, physical crosslinked structure (meltable binding segments)

Place of TPR between traditional elastomers (cauchous) and plastomers

Hard segment at ambient temperature:
- Amorphous glassy state
- Crystalline state (crystallite)


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Morphological structure 24.

- Multiphase, combined structures - TPE

![Phase morphology types of two component systems]

- TPE range

![Molar mass of the elastomer blocks]

- Mass ratios of the soft and hard segments


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Morphological structure 25.

- Comparison of main polymer material classes

<table>
<thead>
<tr>
<th></th>
<th>Plastomers</th>
<th>Rubbers</th>
<th>Thermoplastic elastomers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical structure</td>
<td>Linear or branched macromolecules</td>
<td>Dense network</td>
<td>Segments (blocks) of different properties</td>
</tr>
<tr>
<td>Transition temperature</td>
<td>(T_g)(&lt;25^\circ\ C) (T_m)(&gt;25^\circ\ C)</td>
<td>--</td>
<td>(T_g)&lt;(25^\circ\ C) (T_m)(&gt;25^\circ\ C)</td>
</tr>
<tr>
<td>Characteristic behavior</td>
<td>Solid at room temp. Hard, rough or hard, rigid</td>
<td>Soft, elastic</td>
<td>Soft, elastic</td>
</tr>
<tr>
<td></td>
<td>Solid until (T_g)</td>
<td>Elastic up to (T_m)</td>
<td>Viscous flow</td>
</tr>
</tbody>
</table>

\(T_g\) – Glassy temperature, \(T_m\) – Melting temperature, \(T_d\) – Decomposition temperature

temp – temperature, Am. – amorphous, Crys. – crystalline


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Morphological structure 26.

- Fiber reinforced polymer composites

- Filament carbon/epoxy
- Filament/continuous fiber composite
- Filament glass/UP
- Short glass fiber reinforced unsaturated polyester (UP)
- Chopped/short fiber composite

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Morphological structure 21.

- Multiphase, combined structures

- Short glass fiber reinforced liquid crystal polyester

Fig IX B-1

Properties of morphological structures 1.

- **Crystallinity**  
  Measurement: DSC, WAXS, Density measurement

- **Crystal particle size**  
  Measurement: WAXS, DSC

- **Orientation** – characterized by chain segments
  - Crystalline  – Measurement: WAXS
  - Amorphous  – Measurement: WAXS, by calculation
  - Average  – Measurement: Birefringence, sonic speed measurement (ultra-sound)

Properties of morphological structures 2.

- **Chain orientation and its significance**  
  Production of fibers, oriented foils

- **Isotropic**, **Uniaxial**, **Biaxial (planar)**

- **Drawing cellulose fibers**

- **Cold drawing and neck formation (+20-30°C)**

- **Orientation during necking**