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# 1 3rd Year Engineering Materials

## Polymers – Lecture 3

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### 2 Relative Molecular Mass: RMM

#### 2.1 Definitions

- The RMM of a molecule is the ratio of the mass of the molecule to 1/12 of the mass of a Carbon-12 atom
- RMM of a Carbon atom is 12
- RMM of a Hydrogen atom is 1

#### 2.2 Polymers

- RMM of a polymer is related to the degree of polymerization
  - For Polyethylene (PE), with  $n = 10^4$ :
    - $\text{RMM} = 10^4(2 \times 12 + 4 \times 1) = 280000$
  - How heavy is a piece of string?
    - $\text{Weight-per-unit-length} \times \text{Actual-length}$
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### 3 Relative Molecular Mass: RMM

#### 3.1 Significance of RMM

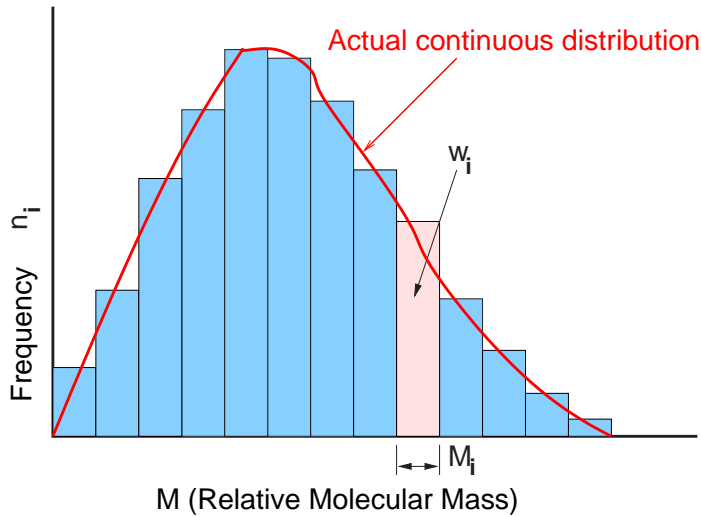
- RMM is a measure of mechanical strength
- As a general rule... longer molecules (higher RMM) have higher strength

#### 3.2 Distribution of RMM

- The polymerization process results in chains of varying length
  - This means molecules with different RMM are present
  - Characterising the Distribution of RMM is a statistical exercise
    - What is the mean?
    - What shape does the distribution have?
    - What size of spread is present (Standard Deviation)?
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## 4 Relative Molecular Mass: RMM

### 4.1 Distribution of RMM



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## 5 Average RMM

### 5.1 Definitions

- $W$  is total mass of a specimen
- $w_i$  is the share of the mass made up by a fraction  $i$
- $n_i$  is number of moles of fraction  $i$  present
- $M_i$  is the molar mass of the molecules in fraction  $i$ 
  - $M_i = \text{RMM}_i \times \text{mass of a mole of carbon}/12$
- Therefore  $w_i = n_i M_i$ 
  - i.e. Number-of-moles times Mass-per-mole

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## 6 Average RMM

### 6.1 Number Average

- i.e. Total mass divided by the number of molecules

$$\bar{M}_n = \frac{\sum n_i M_i}{\sum n_i} = \frac{\sum w_i}{\sum n_i} = \frac{W}{\sum n_i}$$

### 6.2 Weight Average

- i.e. Total mass divided by the number of molecules

$$\bar{M}_w = \frac{\sum w_i M_i}{\sum w_i} = \frac{\sum w_i M_i}{W} = \frac{\sum n_i M_i^2}{\sum n_i M_i}$$

## 6.3 Range

- The ratio

$$\bar{M}_w / \bar{M}_n$$

gives a measure of the range of molecular sizes in the specimen

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## 7 Relative Molecular Mass: RMM

### 7.1 Significance of RMM

- Higher RMM gives better tensile strength
    - Longer molecules become more entangled than shorter molecules
    - Greater level of entanglement means more energy required to cause sliding
    - Tensile strength higher
  - Higher RMM gives higher melting point
    - Again, due to level entanglement
    - Longer molecules require more energy (heat) before they can slide relative to one another
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## 8 Relative Molecular Mass: RMM

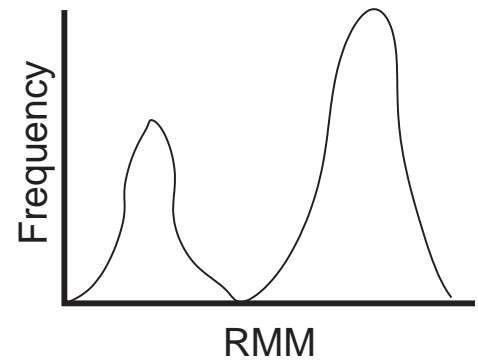
### 8.1 Significance of RMM

- Spread in the RMM of the polymer produces a spread in the melting point
    - Shorter molecules disentangle at low temperature
    - Material begins to soften
    - Softening continues progressively as temperature increases and longer and longer molecules disentangle
  - Sharp melting point useful for injection moulding
    - Rapid freeze is desirable
  - Broad melting temperature is useful for extrusion
    - Improves melt strength
    - Polymer can hold a form even when largely melted due to remaining longer molecules still being entangled
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## 9 Relative Molecular Mass: RMM

### 9.1 UHMWPE

- Extremely long polymer chains
  - ⇒ Good strength & impact toughness, high melting point
- Typically, RMM-Distribution is very narrow
  - ⇒ Not so good for extrusion
- Blending with lower RMM PE gives bimodal RMM-distribution
- The low RMM material acts as a low-melting point lubricant



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## 10 Structure of Polymeric Solids

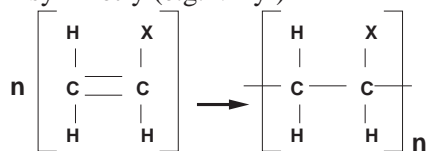
### 10.1 Crystalline

Molecular chains packed to produce an ordered atomic array

### 10.2 Amorphous

Non-crystalline: irregular molecular structure prevents crystallinity. For example...

- Random side branches (e.g. PE)
- Asymmetry (e.g. Vinyl)



### 10.3 Semi-Crystalline Plastics

Most materials have both crystalline and amorphous regions in their structure

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## 11 Structure of Polymeric Solids

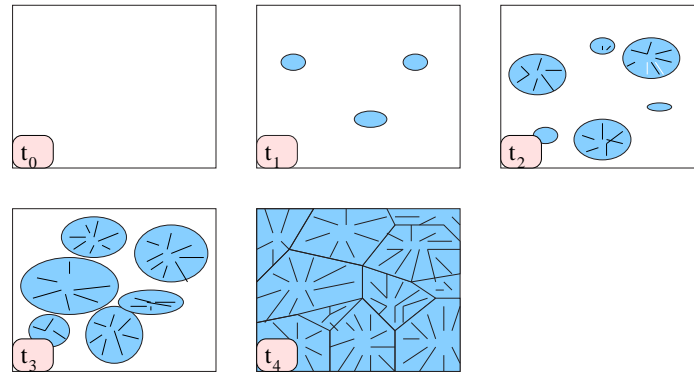
### 11.1 Crystallization and Melting

Two Stages

1. Molecule assumes its lowest-energy conformation
  - Planar zig-zag for PE
  - Helix for molecules with bulkier side-groups
    - PTFE
    - Vinyls
  - This change can result in volume change and geometric distortion of a component (e.g. PTFE at 10°C, polybutane at room temperature).
2. Molecules pack together like parallel rods

## 12 Structure of Polymeric Solids

### 12.1 Crystallization and Melting

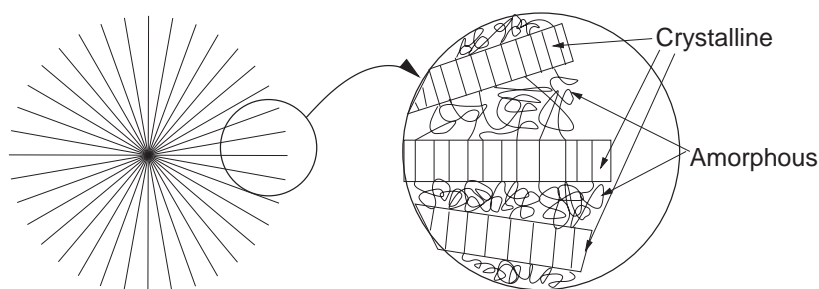


## 13 Structure of Polymeric Solids

- Initial crystallization forms Spherulites (shown in preceding figure).
- Spherulite is composed of crystals
- Crystals are very thin twisted lamellae/layers
  - In PE, crystal lamellae are about 10nm thick
  - Lamellae are separated by thin (approx 10nm) lamellae of amorphous material
- Crystal size affects subsequent melting temperatures
- High degree of crystallinity increases strength/stiffness of a polymeric material
- Highly crystalline materials have lower impact toughness

## 14 Structure of Polymeric Solids

### 14.1 Spherulite and Crystal Structure



Note that the axis of the molecules is perpendicular to the radial direction the molecule passes through both amorphous and crystalline regions

## 15 Structure of Polymeric Solids

### 15.1 Crystallinity and Material Properties

- Polymer crystals are highly anisotropic
  - ⇔ Material properties depend on direction/orientation
- Along molecule we have covalent chemical bonds
  - Carbon-to-Carbon
- In transverse direction we have far weaker secondary forces:
  - van der Waals
  - Dipole
  - Hydrogen bonds
- In direction of molecule modulus is 100GPa to 400GPa
- In transverse direction, modulus is 100 times lower
- In polymeric fibres, molecules are engineered to align along fibre direction

## 16 Structure of Polymeric Solids

### 16.1 Thermal Transitions – Thermoplastics

- If highly crystalline, material will have a crystalline melt temp.  $T_m$ 
  - At this (fairly constant) temperature, inter-molecule crystal bonds break down and material becomes liquid
- If amorphous: Glass Transition Temperature  $T_g$ 
  - At low temperatures, molecules are immobile in a disorganised tangle
  - As temperature increases, around  $T_g$  molecules begin to become more mobile
  - After transition, molecules are still tangled, but can move somewhat freely (stiffness decreases profoundly: 1/1000)
- Most materials have crystalline and amorphous regions
  - $T_g/T_m \approx 0.6$
  - Excellent **toughness** in this region

