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 $n = 10^4$:
  - RMM $= 10^4(2 \times 12 + 4 \times 1) = 280000$
- How heavy is a piece of string?
  - Weight-per-unit-length×Actual-length

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3 Relative Molecular Mass: RMM

3.1 Significance of RMM

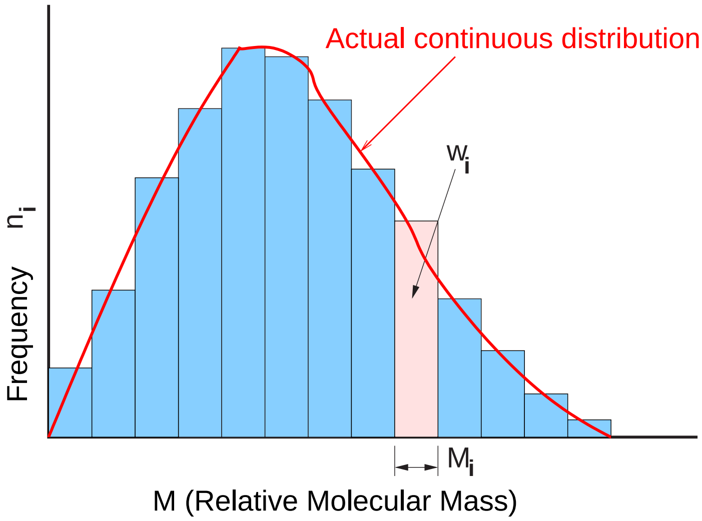
- RMM is a measure of mechanical strength
- As a general rule… longer molecules (higher RMM) have higher strength

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)?

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
  - $M_i = \text{RMM}_i \times$ 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

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

8 Relative Molecular Mass: RMM

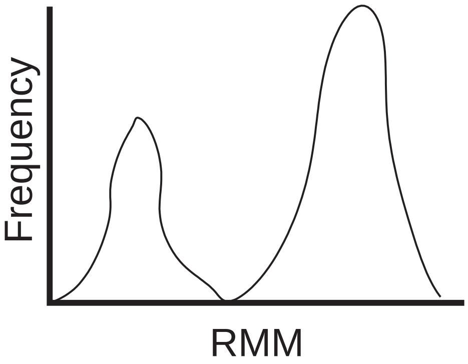
8.1 Significance of RMM

- 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

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

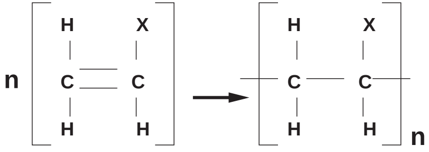
10.1 Crystalline

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

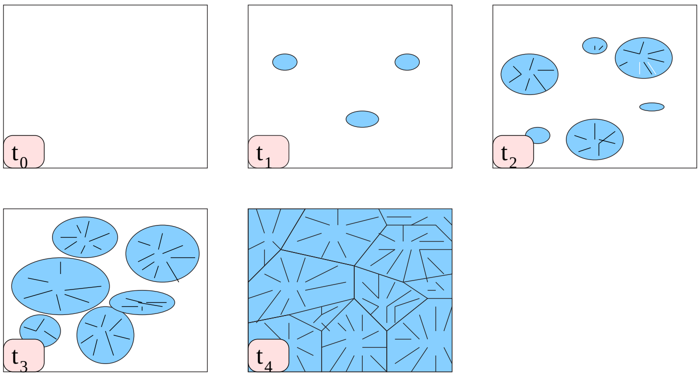
11.1 Crystallization and Melting

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



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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

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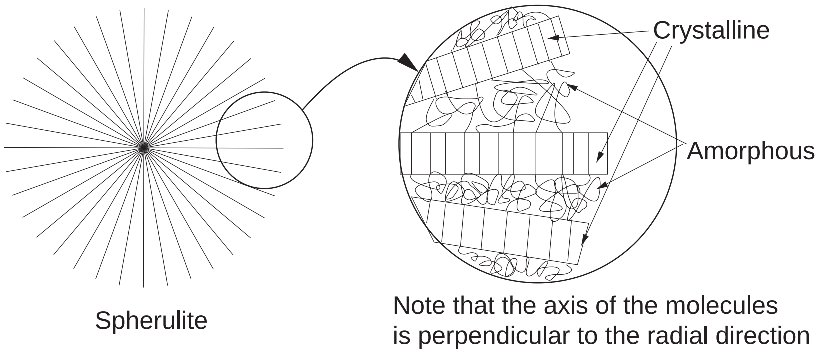
14 Structure of Polymeric Solids

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