ME5005/ME4002
DESIGN FOR MANUFACTURE
PRODUCTION ENGINEERING

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Lecture 6: Polymer materials

Polymer materials

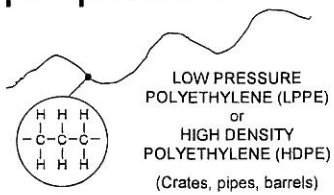
- Polymer:
  - Poly = Many
  - Meros = Part
- Polymer molecules consist of many small units (*monomers*) joined end to end
  - e.g.: polyethylene (PE)

$$\phi_1\text{-}[CH_2\text{-}CH_2]_n\text{-}\phi_2$$

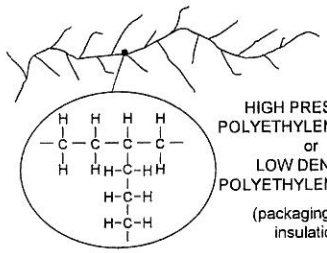
- The number of monomers *n* generally varies from 10^3 to 10^6
- The *end groups* ϕ_1 and ϕ_2 occur in very small quantities and may usually be neglected
  - may influence chemical stability

Mechanical properties

- Mechanical properties determined by:
  - molecule length, i.e. the value of n, and hence the molecular size or *RELATIVE MOLECULAR MASS* (RMM)
  - molecule shape, i.e. the number of side branches on the long main molecule
- e.g.: polyethylene may be linear or side-branched



LOW PRESSURE POLYETHYLENE (LPPE)
or
HIGH DENSITY POLYETHYLENE (HDPE)
(Crates, pipes, barrels)

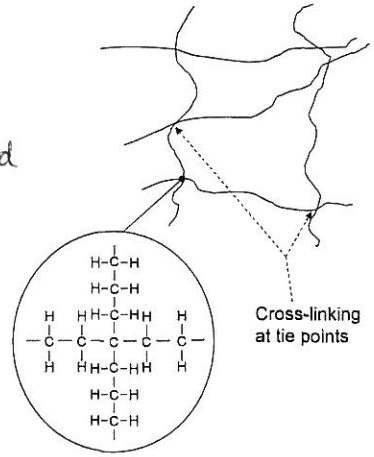


HIGH PRESSURE POLYETHYLENE (HPPE)
or
LOW DENSITY POLYETHYLENE (LDPE)
(packaging, film, insulation)

Classification of polymers

- Polymers may be classified according to their physical properties as:

1. *THERMOPLASTIC*
   - May be repeatedly remelted into a liquid, reshaped and cooled to solidify
2. *THERMOSETTING*
   - polymer chains are *cross-linked* by chemical bonds at tie points
   - Cross links are permanent and produced by chemical reactions triggered by heating
   - Polymer will NOT remelt and flow

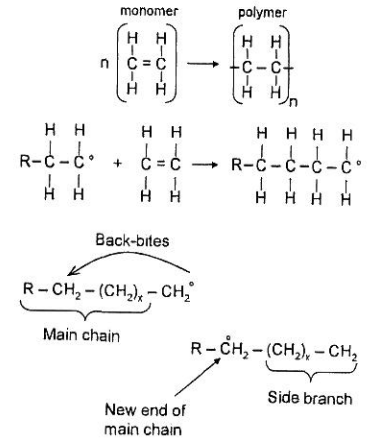


Polymerisation method

- Polymers may also be classified by their method of production (*polymerisation*)
  - Addition polymers
    - Formed by the simple addition of unsaturated monomers to the end of the growing chain, e.g. polyethylene (PE), polyvinylchloride (PVC)
  - Condensation polymers
    - Formed by joining two different molecules together, during which a smaller molecule (usually water) is split off
- Either method may produce thermoplastic or thermosetting polymers

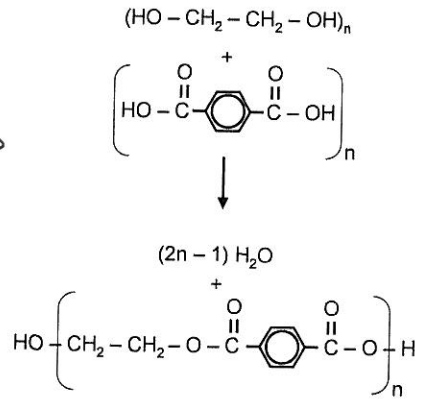
Addition polymers

- The 'growing' end of the molecule has an unpaired electron (*free radical*) that captures and opens the double bond of an approaching monomer
- The monomer is added to the molecule and the unpaired electron is transferred to the end of the chain
- Side-branches form when the chain 'back-bites'
  - Free radical removes a hydrogen atom from a group further back along the main chain
  - Occurs at high temperatures (≈200°C) when the long chains are more mobile
  - Catalysts are used to synthesize polymers with no side branches



Condensation polymers

- Condensation polymers are usually of the form:
  –A–B–A–B–A–B–
  - extremely regular in structure
  - Tend to form crystals easily when cooled from a liquid
- e.g.: the reaction of ethylene glycol and terephthalic acid produces poly(ethyleneterephthalate) plus water
  - more commonly known as PET or Mylar®
  - Carbonated drinks bottles

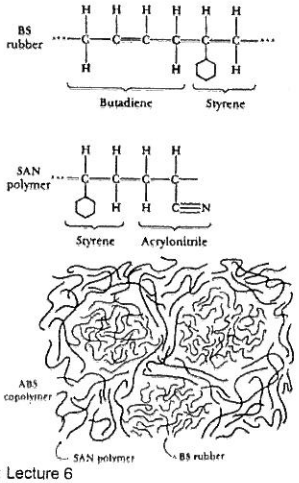


Common polymers

- Thermoplastics
  - Polyethylene PE
  - Polyvinyl chloride PVC
  - Polypropylene PP
  - Polystyrene PS
  - Polymethylmethacrylate PMMA ('Perspex')
  - Polyvinylidene chloride PVDC
  - Polytetrafluoroethylene PTFE
  - Polyamide PA ('Nylon')
  - Polycarbonate PC
  - Polyimide PI
  - Polybutylene terephthalate PBT
- Thermosets
  - Polyphenylene oxide PPO
    - Phenolic resins
  - Amines ('Melamine')
  - Polyesters
  - Expoxy resins ('Araldite')
  - Polyurethane PUR
  - Silicone
- Elastomers (rubber)
  - Polybutadiene PBD
  - Polychloroprene ('Neoprene')
  - Butadiene-styrene BS
  - Silicone

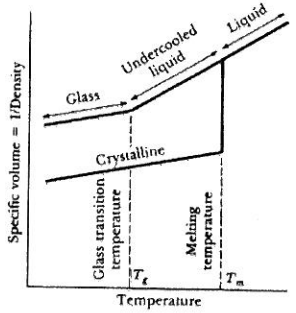
Copolymers

- Many useful polymer materials are produced from a mixture of two different polymers
  - Copolymers
- The structure of the two polymers may be:
  - Alternating copolymers
    -A-B-A-B-A-B-A-B-A-B-
  - Random copolymers
    -A-B-A-A-B-A-B-B-B-A-
  - Block copolymers
    -A-A-A-B-B-B-A-A-A-B-
  - Grafted copolymers
    - side chains different polymer to main chain
- e.g.: ABS copolymer formed from BS and SAN polymers

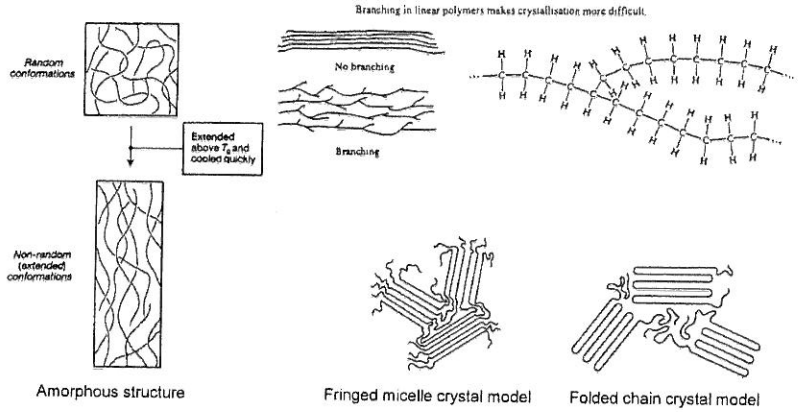


Polymer cooling rates

- As with metals, the microstructure of polymers depends on the cooling rate:
  - Slow cooling leads to a *crystalline* polymer
    - Molecules have time to order themselves into a dense regular structure
  - Fast cooling leads to *amorphous* or *glassy* polymer
    - Long molecules are semi-randomly orientated and tangled
    - Molecules tend to align in the forming direction and are trapped when cooled
    - Lower density than crystalline



Polymer microstructures



Amorphous structure

Fringed micelle crystal model

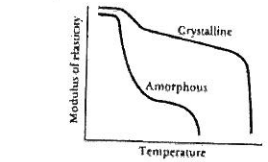
Folded chain crystal model

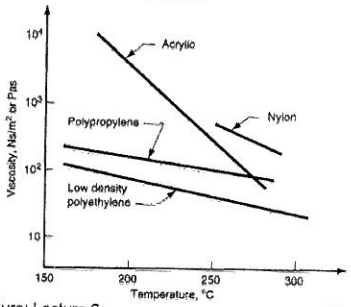
Polymer additives

- Fillers
  - Particles or fibres to alter mechanical properties (usually strengthen), reduce material cost, improve dimensional and thermal stability (reduce shrinkage)
- Plasticisers
  - Chemical additive to reduce T_g and make polymer softer and more flexible during forming, e.g.: PVC may be rigid or flexible
- Colorants
  - Powdered pigments distributed throughout the polymer
  - Soluble liquid dyes used to colour transparent polymers
- Lubricants
  - Improve melt flow and component release
- Flame retardants, cross-linking agents, UV absorbers, antioxidants

Polymer properties

- The first polymer molecules to touch the cooled die walls are rapidly cooled
  - Thin amorphous skin
  - Little or no contraction
  - Layer is weak and ductile
- This first amorphous layer *thermally insulates* the remaining molten polymer from the cooled die
  - Bulk cools at slower rate
  - Crystalline microstructure
  - Large drop in specific volume
  - Stronger material
  - Amorphous layer *deforms* as the bulk shrinks
- Viscosity also varies with temperature





Thermoplastic extruder

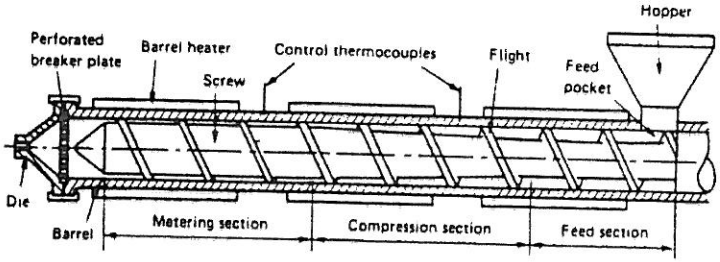


Illustration of a single-screw plasticating extruder (after Fenner)

(Thermoplastic barrel L:D ratio is typically _____)

Extruder barrel types

A. 3-zone
   - Feed
   - Compression
   - Metering

B. Vented
   - To remove gases dissolved in the melt

C. 'PVC-type'
   - For amorphous polymers that gradually soften through the glass transition

D. 'Nylon-type'
   - For crystalline polymers with a sharp melting point

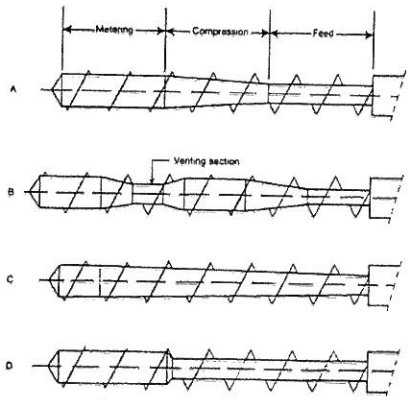
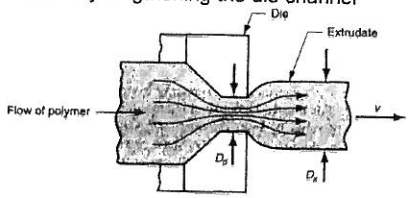


Illustration of the four important types of extruder screw

Viscoelastic die swell

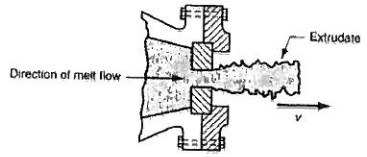
- Polymer melt is forced under pressure into the narrow constrained _____
  - extruded polymer expands after exiting as the constraint is removed
- Elastic recovery from compressive stresses acting on the polymer before it flowed into the die restriction cause the extrudate to swell
  - 'remembers' previous cross section in the _____
  - characterise by the *swell ratio*, r_s
  - reduced by lengthening the die channel



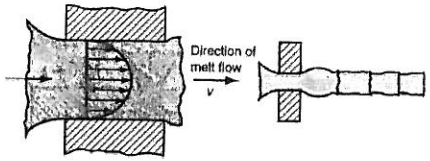
$$r_s = \frac{D_x}{D_d}$$

Extrusion defects

- Streamlined dies required to ensure smooth laminar flow
  - _____ in sharp dies breaks up the melt producing a *melt fracture*
  - Excessive _____ in the die produces a velocity profile in the melt
  - The surface is stretched and ruptures, producing a *sharkskin* effect or *bambooing*

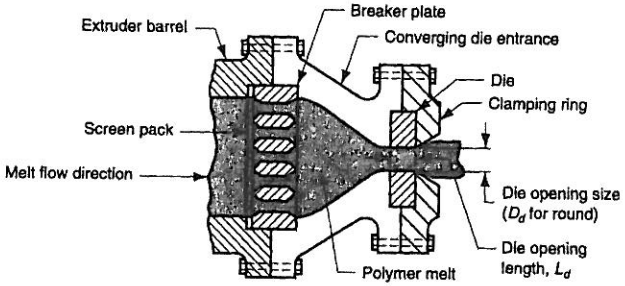


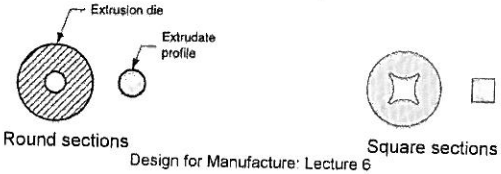
melt fracture



bambooing

Nozzles and extrusion dies

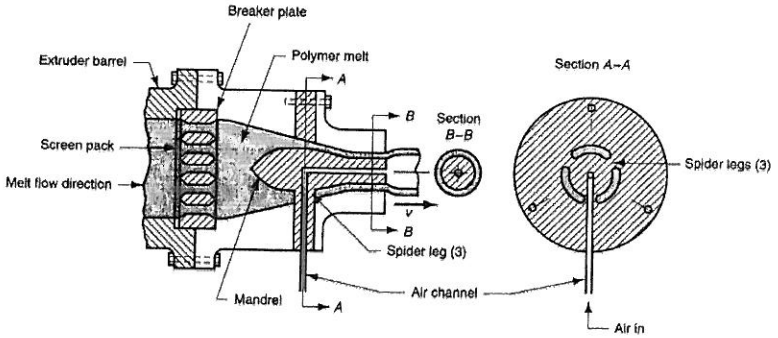




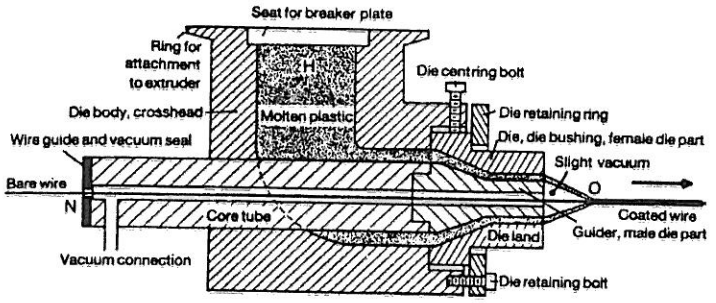
Round sections

Square sections

Extruded hollow sections



Wire insulation



Wire coating tubing die (after Richardson).