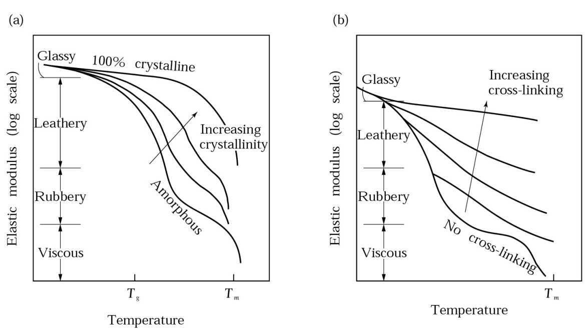
Thermoplastics and Thermosettings

- Polymers are basically divided into:
  1. Thermoplastics
     - Solids at room temperature that are melted or softened by heating, placed into a mould and then cooled to give the desired shape
     - Can be reshaped at any time by heating the part (recycled)
  2. Thermosets
     - Can be either liquids or solids at room temperature that are place into a mould and then heated to cure (set) or harden, thus giving the desired shape and solid properties
     - Thermosets cannot be reshaped by heating

Thermoplastics and Thermosettings

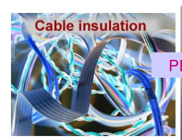
- This basic difference between thermoplastics and thermosets lead to two basic different behaviours:
- In thermoplastics the atoms are bonded by covalent bonds
- Thermosets have (in addition to covalent bonds that join the atoms), covalent bonds which join the chains one to another (cross-links)
- Cross-links are normally formed by heating the polymer (curing)

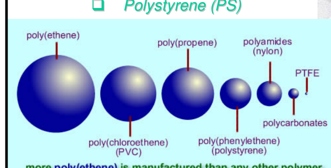
Mechanical Behaviour: effect of cross-linking and crystallinity



Thermoplastic materials

- Thermoplastic materials include:
  - Commodity plastics: used in high-volume and in widely recognised applications
    - *Polyethylene (PE)*
    - *Polypropylene (PP)*
    - *Polyvinyl chloride (PVC)*
    - *Polystyrene (PS)*





Thermoplastic materials

- Engineering plastics: have ability to replace metallic parts in applications such as automotive, appliances and housewares. They also possess the following:
- High strength and stiffness (comparable to metals when in terms of specific properties)
- Retention of mechanical properties over a wide range of temperatures
- Toughness, Dimensional stability, ability to withstand environmental factors such as water, solvents and other chemicals

- Engineering plastics include
  - *Polyamides or Nylons*
  - *Acetals or polyoxymethylenes (POM)*
  - *Polycarbonates (PC)*
  - *Acrylics (PAN, PMMA)*
  - *Fluoropolymers (PTFE, FEP, PFA)*

Thermoset materials

- Thermoset parts are made from polymer resins that are capable of forming chemical crosslinks.

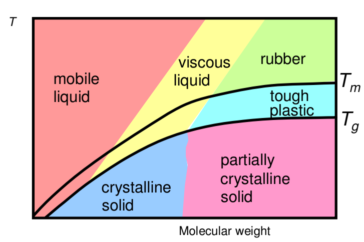
- As the number of crosslinks increases, the stiffness of the material also increases. Thus, many thermosets are typically stiffer and more brittle that thermoplastics

- The impact toughness can be increases by adding fillers or reinforcements (also increase strength)

- Thermosets include:
  - *Phenolics (PF)*
  - *Amino plastics (UF and MF)*
  - *Polyester thermosets (TS)*
  - *Epoxies (EP)*
  - *Thermoset polyamides*

Thermoplastics vs. Thermosets

- Thermoplastics:
  -- little crosslinking
  -- ductile
  -- soften w/heating
  -- polyethylene
  polypropylene
  polycarbonate
  polystyrene



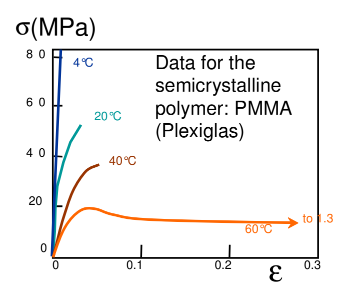
Adapted from Fig. 15.19, *Callister 7e.* (Fig. 15.19 is from F.W. Billmeyer, Jr., *Textbook of Polymer Science*, 3rd ed., John Wiley and Sons, Inc., 1984.)

- Thermosets:
  -- large crosslinking
  (10 to 50% of mers)
  -- hard and brittle
  -- do NOT soften w/heating
  -- vulcanized rubber, epoxies,
  polyester resin, phenolic resin

T and Strain Rate: Thermoplastics

- Decreasing *T*...
  -- increases *E*
  -- increases *TS*
  -- decreases %*EL*

- Increasing strain rate...
  -- same effects as decreasing *T*.



Adapted from Fig. 15.3, *Callister 7e.* (Fig. 15.3 is from T.S. Carswell and J.K. Nason, 'Effect of Environmental Conditions on the Mechanical Properties of Organic Plastics", *Symposium on Plastics*, American Society for Testing and Materials, Philadelphia, PA, 1944.)

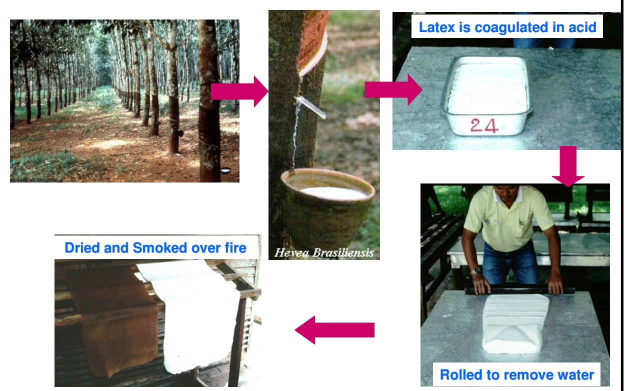
Polymer types:
Elastomeric (Rubber) Material

- Elastomers are a group of polymers that have very large elastic elongation
- Elastomers are materials that can be repeatedly stretched to over twice their length and then immediately return to their original length when released.
- Elastomers can be either thermoplastics or thermosets

- Elastomers can also be natural or synthetic

Natural Rubber:

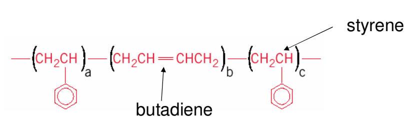
- This is obtained by a suspension of a non-soluble component in water called, *latex*.



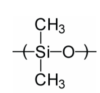
- Natural rubber has the tendency to soften and creep at elevated temperatures
- However, this problem was solved by *Goodyear* when he accidentally discovered that cooking natural rubber with sulfur would increase high temperature stability of the material.
- The use of heat and sulfur (S) led to the name of the process, *vulcanisation*. This process is used to cross-link or cure elastomeric materials.
- Useful rubber, sulfur content (1-5)%. If to much sulfur, reduce its extensibility.

- Synthetic rubber and thermoplastic elastomers

SBR- styrene-butadiene rubber



– Silicone rubber

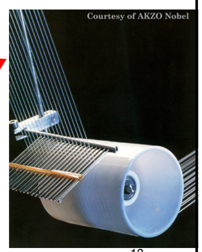


Polymer Types: Fibers

fiber, is a class of materials that are continuous filaments or are in discrete elongated pieces, similar to lengths of thread. Polymer fibers are a subset of man-made fibers, which are based on synthetic chemicals (often from petrochemical sources) rather than arising from natural materials by a purely physical process.

Fibers – ratio length : diameter >100

- Textiles are main use
  - Must have high tensile strength
  - Usually highly crystalline & highly polar
- Formed by spinning
  - ex: extrude polymer through a spinnerette
    - Pt plate with 1000's of holes for nylon
    - ex: rayon – dissolved in solvent then pumped through die head to make fibers
  - the fibers are drawn
  - leads to highly aligned chains- fibrillar structure



Polymer Types

- Coatings – thin film on surface – i.e. paint, varnish
  - To protect item
  - Improve appearance
  - Electrical insulation
- Adhesives – produce bond between two adherents
  - Usually bonded by:
    1. Secondary bonds
    2. Mechanical bonding

    Natural adhesive: animal glue, starch, rosin

    Synthetic adhesive: polysiloaxanes, epoxies, polyimides, acrylics
- Films – blown film extrusion – bags for packaging foods, textiles products
- Foams – gas bubbles in plastic – cushions in automobile, furniture, packaging, thermal insulation

Advanced Polymers

- Ultrahigh molecular weight polyethylene (UHMWPE)
  - Molecular weight ca. 4×10^6 g/mol
  - Excellent properties for variety of applications
    - bullet-proof vest, golf ball covers, hip joints, etc.

Artificial total hip replacement . These components are (from left to right) as follows: femoral stem, ball, acetabular cup insert, and acetabular cup. (Photograph courtesy of Zimmer, Inc., Warsaw, IN, USA.)

Adapted from chapter-opening photograph, Chapter 22, *Callister 7e.*

Polymer Additives

Improve mechanical properties, processability, durability, etc.

- Fillers
  - Added to improve tensile strength & abrasion resistance, toughness & decrease cost
  - ex: carbon black, silica gel, wood flour, glass, limestone, talc, etc.

- Plasticizers
  - **Plasticizers** are additives that increase the plasticity or fluidity of the material to which they are added
  - Added to reduce the glass transition temperature T_g
  - commonly added to PVC - otherwise it is brittle

e.g. phthalates add to PVC

Ester plasticizers serve as plasticizers, softeners, extenders, and lubricants, esters play a significant role in rubber manufacturing.

Other plasticizers
Benzoates
Epoxidized vegetable oils
Sulfonamides

- Stabilizers

Stabilizers for polymers are used directly or by combinations to prevent the various effects such as oxidation, chain scission and uncontrolled recombinations and cross-linking reactions that are caused by photo-oxidation of polymers.

- Antioxidants
- UV protectants

The effectiveness of the stabilizers against weathering depends on solubility, ability to stabilize in different polymer matrix, the distribution in matrix, evaporation loss during processing and use.

- Lubricants
  - Added to allow easier processing
  - "slides" through dies easier – ex: Na stearate

- Colorants
  - Dyes or pigments

- Flame Retardants

Flame retardants are materials that inhibit or resist the spread of fire.
  - Cl/F & B

Processing of Polymers

- Several processing methods are used to fabricate polymer parts.

- Method use depends on:

1. Type of polymer materials used, thermoplastic or thermoset.
2. If thermoplastics: the temperature which it softens (Thermoplastics can be recycled)
   - Above T_g for amorphous
   - Above melting temperature for semicrystalline
3. The atmospheric stability of the material being formed
4. Geometry and size of the finish product.

Molding is the most common method for forming plastic polymer
e.g. compression-, transfer-, blow-, injection-, extrusion- molding

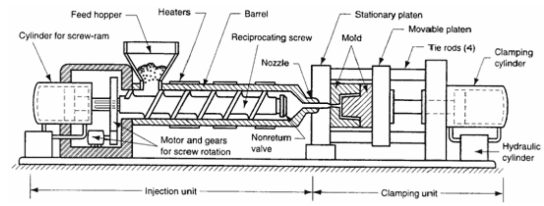
Thermoplastic Processing Methods:

- Injection Moulding
- Extrusion Process
- Blow Moulding : extrusion and injection blow moulding
- Thermoforming processes
- Rotational Moulding

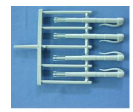
Thermoset Processing Methods:

- Compression Moulding
- Reaction injection moulding

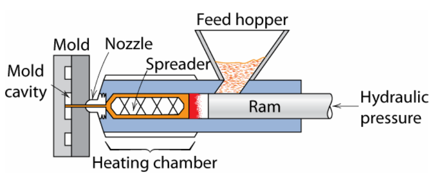
Injection Moulding



Mobile Phone



Rubber Pen

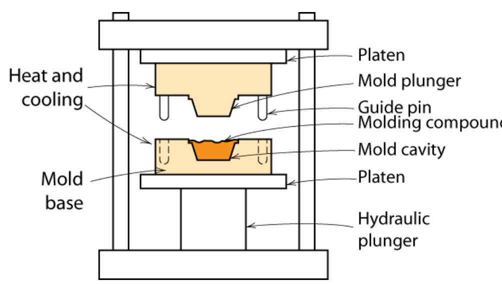


Injection Moulding

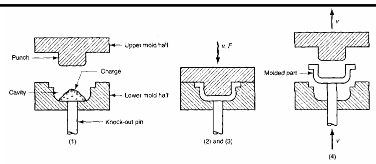
- A common process for forming plastics and involves four steps:
  1. Powder or pelletized polymer is heated to the liquid state.
  2. Under pressure, the liquid polymer is forced into a mould through an opening, called a sprue. Gates control the flow of material.
  3. The pressurized material is held in the mould until it solidifies.
  4. The mould is opened and the part removed by ejector pins.
- Advantages of injection molding include rapid processing, little waste, and easy automation. Molded parts include combs, toothbrush bases, pails, pipe fittings, and model airplane parts.

Compression and transfer Moulding

- thermoplastic or thermoset



Compression Moulding



- This process was the first to be used to form plastics. It involves four steps:

1. Pre-formed blanks, powders or pellets are placed in the bottom section of a heated mould or die.
2. The other half of the mould is lowered and is pressure applied.
3. The material softens under heat and pressure, flowing to fill the mould. Excess is squeezed from the mould. If a thermoset, cross-linking occurs in the mould.
4. The mould is opened and the part is removed.

- When thermoplastics are used, the mould is cooled before removal so the part will not lose its shape.

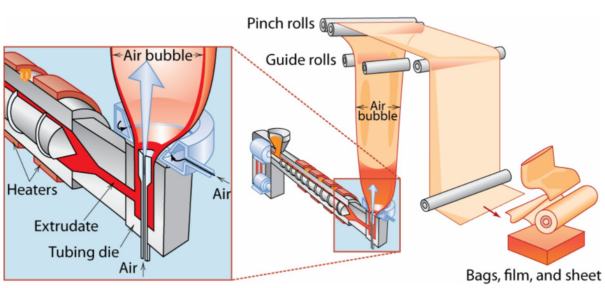
- When thermosets are used, they may be ejected while they are hot and after curing is complete. This process is slow, but the material moves only a short distance to the mold, and does not flow through gates or runners. Only one part is made from each mold.

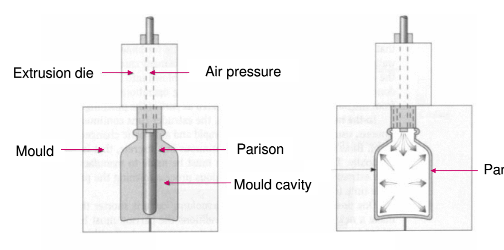
Blow Moulding

- Blow molding produces bottles, globe light fixtures, tubs, automobile gasoline tanks, and drums. It involves:

1. A softened plastic tube is extruded
2. The tube is clamped at one end and inflated to fill a mould.
3. Solid shell plastics are removed from the mould.

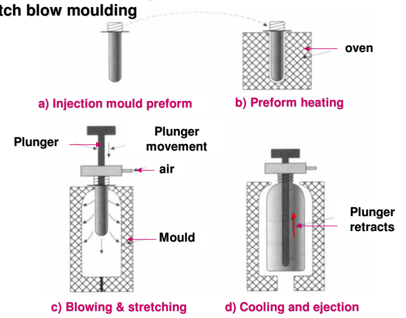
- This process is rapid and relatively cheap.



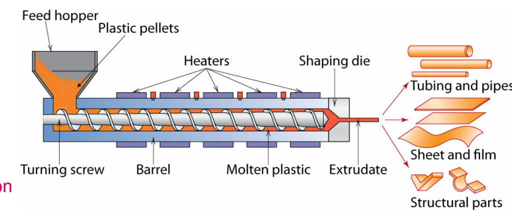


Extrusion blow molding process steps

- Blow moulding includes:
  1. **Injection blow moulding**
  2. **Extrusion blow moulding**
  3. **Stretch blow moulding**



Injection blow molding process steps



Extrusion

- This process makes parts of constant cross section like pipes and rods. liquid polymer goes through a die to produce a final shape. It involves four steps:

  1. Pellets of the polymer are mixed with colouring and additives.
  2. The material is heated to its proper plasticity.
  3. The material is forced through a die.
  4. The material is cooled.

- An extruder has a hopper to feed the polymer and additives, a barrel with a continuous feed screw, a heating element, and a die holder. An adapter at the end of an extruder blowing air through an orifice into the hot polymer extruded through a ring die produces plastic bags and films.

PROCESS	TP or TS	Advantages	Disadvantages
INJECTION MOULDING	TS, TP	Most precise control of shape and dimensions. Highly automatic process and has fast cycle time. Widest choice of materials.	High capital cost and is only good for large batch size. Has large pressures in mould (20,000 psi).
COMPRESSION MOULDING	TS	Has lower mould pressures (1000 psi). Does minimum damage to reinforcing fibers (in composites), and large parts are possible.	Requires more labour, longer cycle than injection moulding. Has less shape flexibility than injection moulding, and each charge is loaded by hand.
BLOW MOULDING	TP	Can make hollow parts (especially bottles). Stretching action improves mechanical properties. Has a fast cycle, and is low labour.	Has no direct control over wall thickness. Cannot mould small details with high precision, and requires a polymer with high melt strength.
EXTRUSION	TP	Used for films, wraps, or long continuous parts (e.g; pipes).	Must be cooled below its glass transition temperature to maintain stability.

TP: thermoplastic, TS: thermoset

Summary

- General drawbacks to polymers:
  -- E, σ_y, K_c, $T_{application}$ are generally small.
  -- Deformation is often T and time dependent.
  -- Result: polymers benefit from composite reinforcement.
- Thermoplastics (PE, PS, PP, PC):
  -- Smaller E, σ_y, $T_{application}$
  -- Larger K_c
  -- Easier to form and recycle
- Elastomers (rubber):
  -- Large reversible strains!
- Thermosets (epoxies, polyesters):
  -- Larger E, σ_y, $T_{application}$
  -- Smaller K_c

Table 15.3 *Callister 7e*:

Good overview of applications and trade names of polymers.